

KINETIC AND MECHANISTIC STUDIES ON THE BIOLOGICAL
AND CHEMICAL LEACHING OF NICKEL FROM SULPHIDE ORES.

A Thesis submitted in partial fulfillment of the requirements for
the Degree of Doctor of Philosophy in the Department of Chemical
Engineering in the University of Natal.

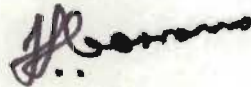
by



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PREFACE.

This work was carried out in 1971, 1972 and 1973 under the supervision of the Department of Chemical Engineering, University of Natal, Durban. The laboratory facilities at the Johannesburg Consolidated Investment Company Minerals Processing Research Laboratories were used for the experimental work. The material incorporated in this thesis is original, except where indicated, and has not been submitted for a higher degree in any other university or institution.



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ATTACHMENTS.

1. CORRANS, I.J., HARRIS, B., RALPH, B.J., "Bacterial Leaching : An Introduction to its Application and Theory and a Study on its Mechanism of Operation," Jour. S.A.I.M.M. 72 (8) March, 1972. 219
2. CORRANS, I.J., "Improvements in Hydrometallurgy," S.A. Application No.73/4851, July, 1973. 230

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I would like to thank my supervisors, Dr. M.T. Scholtz of the University of Natal and Dr. A. Kistner of the C.S.I.R. for their

encouragement/...

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ABSTRACT.

The aim of this investigation was to extend the knowledge of the bacterial leaching of copper and zinc sulphides into the area of nickel sulphide leaching.

By far the major portion of both theoretical and practical expertise which is available in the field of bacterial leaching is based on the treatment of copper and zinc sulphides. As yet there is little information available on the bacterial leaching of nickel sulphides to meet the growing interest in this field both in South Africa and elsewhere.

To a large degree, it was necessary to start from basic principles in this novel extension of bacterial leaching technology so that the work covers a fairly wide field in general rather than one particular aspect in detail.

A strain of 'nickel adapted' Thiobacillus ferrooxidans was isolated from the tailings dam of a disused nickel mine. The growth characteristics of this strain were studied in some detail on sulphur using both batch and continuous techniques. This was done as it was considered that growth on sulphur would provide useful information which could be correlated with the mineral leaching results.

The mineral pentlandite (NiFeS_2) was chosen as the one with which to work because of its economic importance. This was prepared in a highly purified form from a concentrate of the Rhodesian

Shangani/.....

Shangani deposit.

Bacterial leaching tests in both batch and continuous operation were then carried out in order to define the effects of various physico-chemical parameters on the leaching of nickel from this mineral. As a preliminary to these tests, a detailed chemical kinetic study in the absence of bacteria of the leaching of nickel was carried out using similar physico-chemical conditions. The results of the bacterial and chemical leaching tests were then compared and used to postulate a mechanism and model for the process.

It was found that the rate of leaching of nickel from pentlandite in acid ferric sulphate solutions was directly proportional to the concentration of ferric ions and speed of agitation of the stirrer and to the square root of the oxygen concentration. The form of the rate expression was interpreted in terms of a mixed diffusive and chemical rate controlling mechanism.

Bacterial growth rates on flowers of sulphur were found to be controlled by the rate of dissolution of oxygen from the gas bubbles into the bulk solution. When this latter condition was made non-rate limiting, it was found that growth rates were still dependent on the rate of agitation, implying mass transport control by another mechanism.

The batch bacterial leaching results showed a linear pattern of nickel leaching and bacterial growth, with a marked dependence on oxygen concentration and rate of agitation. A mechanism in

accordance with the batch data was postulated, which proposed that the rate of bacterial leaching was proportional to the concentration of bacteria attached at the mineral surface and to the square of the oxygen concentration. The rates of bacterial leaching were computed by taking the difference between the overall measured leach rate and the chemical leach rate based on the chemical kinetic data.

The leach rates in continuous bacterial leaching were higher than those predicted from the batch data. This effect was interpreted in terms of higher specific growth rates being achieved in continuous operation.

An economic assessment was made of the process based on the optimum leach rates obtained in continuous leaching and found to show some promise.

NOMENCLATURE.

$^{\circ}\text{C}$	degrees centigrade,
cal.	calorie,
d	diameter,
D	dilution rate,
e	electron,
E	per cent extraction,
$[\text{Fe}^{+++}]$	concentration of ferric ions.
g	gram,
hr	hour,
$H, \Delta H$	activation energy,
$[\text{H}^+]$	concentration of hydrogen ions.
i_c	cathodic limiting current,
i_e	exchange current,
I	diffusive flux,
K, K_1, K_2 etc.	reaction rate constants,
K_a, K_v	area and volume constants for solids; e.g. area, $= K_a d^2$.
l	litre,
mg	milligrams,
ml	millilitre,
m	mass,
M	molar concentration,
M_a, M_c	activation overpotentials,
[N]	concentration of bacterial nitrogen.
pH	$-\log [\text{H}^+]$,

ppm	parts per million, i.e. mg per litre.
P	production rate of hydrogen ions.
pO_2	partial pressure of oxygen, as a per cent.
R	gas constant.
R_1, R_2 etc.	reaction rates.
S	concentration of sulphur.
S_a	specific surface area.
T	absolute temperature.
w	weight.
W	stirrer speed, revolutions per minute.
X_A	concentration of attached bacteria.
X_u	concentration of unattached bacteria.
\bar{X}_A	saturation concentration of attached bacteria.
Y	yield constant.

Greek Symbols.

ρ	density.
μ	specific growth rate.
μm	micrometer, 10^{-6} of meter.
$\mu g, \mu M$ etc	10^{-6} of respective quantity.
π	circumference/diameter, 3,14159.....

1. INTRODUCTION.

The role of microbes in causing disease and their use in fermentation processes have been known since the time of Pasteur. They are generally associated with purely organic mileaux and even today it is not generally known that microbes can exist and multiply in totally inorganic environments under relatively harsh physico-chemical conditions. Indeed micro-organisms are known to inhabit virtually every ecological niche in the biosphere.

Microbes exist and grow at great depths in the lithosphere and tolerate extremes of temperature and pressure (1). They may be resistant to high concentrations of metal ions in solution and to a range of pH values. The scale of the geological action brought about by microbial activity can be appreciated by considering the extent of the fossil fuel deposits, the chert and kieselguhr beds and coral formations. Not as obvious, however, is the action of microbes in the slow weathering of rocks or in the secondary enrichment and oxidation of sulphide deposits.

The phenomenon of natural leaching or oxidation of sulphides has been known for many years. Pliny (2) discusses the "vitriolus quasi vitrum" formed on rocks, while at Rio Tinto in Spain 17th century records speak of acid copper-bearing ground waters (3). This natural leaching of minerals, commonly called bacterial leaching, is thus but one aspect of weathering processes in which microbes are involved. Bacterial leaching is caused by the action of microbes on iron sulphide ores which may be intermixed with the sulphides/.....

sulphides of other metals such as copper. The bacteria are known to catalyse the oxidation of both iron and sulphur, yielding acid ferric sulphate solutions, often bearing other associated metals in solution. These bacteria, known as various species of Thiobacilli, utilise the energy released from the oxidation reactions to fix carbon and nutrients from dissolved inorganic materials. In this way they grow and multiply in a similar manner to that which a yeast cell or a cell of human tissue utilises the energy released in the catalytic (enzymatic) oxidation of carbohydrates.

In recent times man has learnt to exploit the phenomenon of natural leaching to help win metal from low grade or waste ores (4). Since the study of Colmer and Hinkle in 1947, (5) in which it was conclusively shown that bacteria were indeed playing a fundamental role in the leaching process, many studies have been carried out with the aim of improving the rates of metal leaching (6, 7.)

Copper sulphides and uranium oxide (mixed with iron sulphides) are the only two ores being biologically leached on a significant commercial scale at present. The ore being leached is usually in the form of a large dump of waste material. (See Figure 1a). Leach solutions are allowed to percolate down through the rock where the bacterial activity occurs. A large number of studies have been devoted to improving the technology of this dump leaching process (8,9,10). Rates of extraction are slow, but because the material is waste and overheads and operating costs are low, the operation is profitable over periods of up to five years or more.

A similar/.....

Figure 1a. Dump Leaching

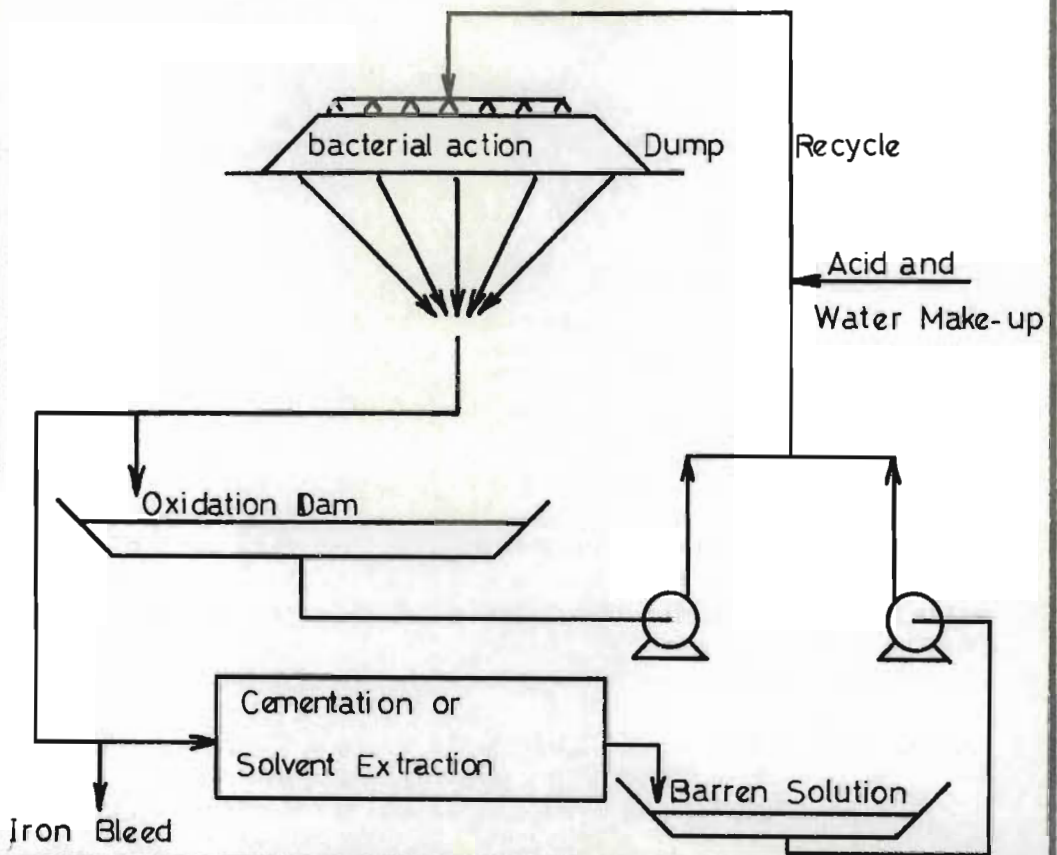
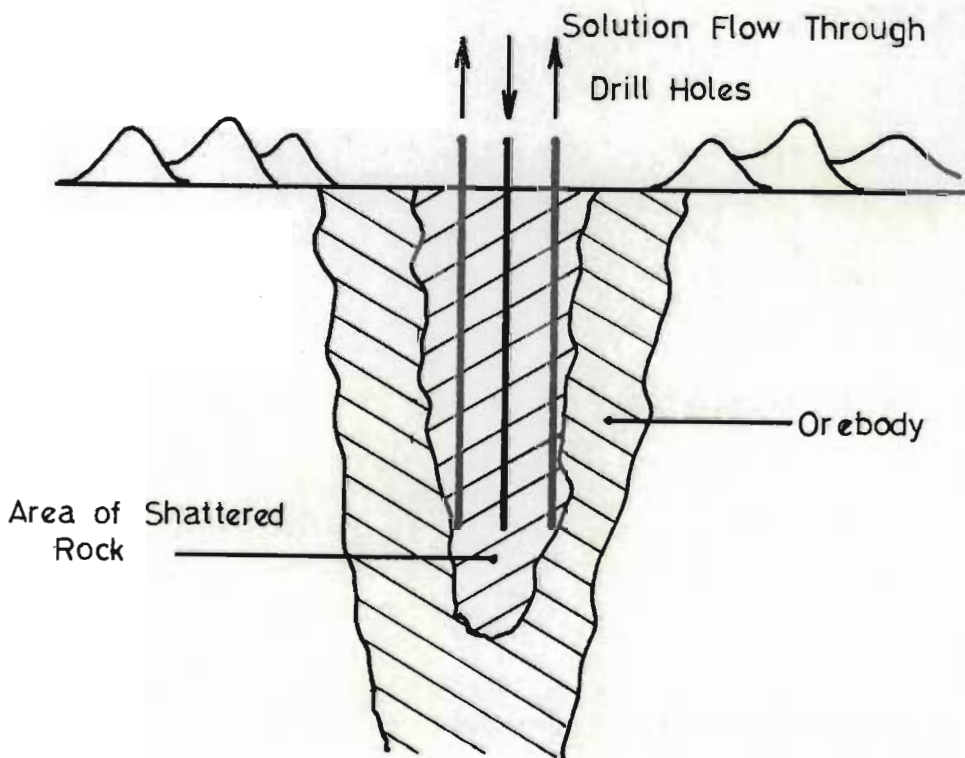


Figure 1b. In-situ Leaching



A similar procedure is used in the technique of in-situ leaching. The ore, which is usually of a low grade, is treated by allowing leach solution to percolate from the ground level or by pumping leach solution through injection drill-holes. (See Figure 1b.) Solution is then recovered from tunnels undermining the orebody or from adjacent drill holes. A pre-requisite of applying this technique is sufficient porosity in the orebody. This can often be improved by explosive shattering and tests of this nature with nuclear explosives have recently been carried out in the U.S.A. (11) The technique of in-situ leaching has found particular application in the porphyry type copper deposits in North America and holds great promise for the recovery of valuable metals from ores which were formerly considered uneconomical to treat by conventional mining-extraction methods.(12)

The extension of bacterial leaching to more sophisticated processes such as stirred tank leaching is yet in the developmental stage. Workers at the British Columbia Research Council have been particularly active in this field and have developed methods of biologically leaching copper and zinc concentrates in stirred reactors which are claimed to compete economically with existing extraction methods. (13, 14) The sulphides of various other metals, e.g. nickel, arsenic, molybdenum, antimony have been shown in laboratory investigations to be amenable to bacterial leaching treatment. (15, 16)

An undesirable aspect of natural bacterial oxidation of sulphides

is the/.....

is the acid mine drainage water which results from such leaching. A new area of sophisticated technology to deal with this problem is evolving in the U.S.A. (52.)

Greater use of bioleaching may come about with changing economic patterns and further understanding of, and improvements in bacterial leaching technology. The aim of the present investigation is to study the bacterial leaching of nickel sulphide so as to obtain information on the mechanism of the process and to utilise the data in assessing the commercial feasibility of the process as a means of nickel winning. These aims are discussed more fully in the final section of the literature review where they are better appreciated in the light of current literature.

2. LITERATURE REVIEW.

2.1. Development of Bacterial Leaching Technology.

Since the early work of Taylor and Whelan (1943) (3) and Colmer and Hinkle (1947) (5), numerous studies have been carried out on various aspects of bacterial leaching. Many of these are laboratory studies with little real contribution to the knowledge of bacterial leaching; they often merely report that leaching a specific sulphide ore with bacteria yields rates higher than those obtained in sterile controls (17.) Several others have made significant contribution to the subject. (6, 7, 18, 19.)

More practical investigations deal with the technology of dump and in-situ leaching operations (20, 21) or leaching of concentrates in stirred tanks. (12)

As early as 1887, S. Winogradsky (22) had described a group of bacteria able to oxidise elemental sulphur to sulphuric acid. Many reviewers claim that Colmer and Hinkle were first to demonstrate the role of bacteria in metal sulphide leaching, but as early as 1922 in their paper "Oxidation of Zinc Sulphide by Microorganisms," Rudolph and Hellbronner (23) came to the following interesting conclusions:-

"1/....."

- 1) Microorganisms are able to transform zinc sulphide to zinc sulphate.
- 2) The growth of these organisms is not inhibited by the resulting soluble zinc.
- 3) The addition of elementary sulphur to impure cultures increases the rate of solubility of zinc blende.
- 4) The "Lipman" sulphur-oxidising organisms produce sufficient H_2SO_4 from elementary sulphur to render zinc carbonate and zinc silicate soluble.
- 5) A possible biological method can be worked out for economical utilization of low-grade zinc sulphide ores."

In 1933 Carpenter and Herndon (24) were unsuccessful in showing that microbes were at least in part responsible for the acid-sulphate content of some mine waters. Colmer and Hinkle were however able to show this in 1947 when, with the use of antiseptics and biological filters they were able to inhibit the oxidation of iron. This led to the interesting discovery

that/.....

that in addition to the ability to oxidise sulphur to sulphuric acid, the organism was able to oxidise ferrous iron to the ferric state. This, in turn, gave rise to the name Thiobacillus ferrooxidans. A period of isolation and classification testing followed.

In 1957 Vishniac and Santer (25) published a comprehensive review of the Thiobacilli which helped rationalise classification within the genus. Further study of the physiology of the Thiobacilli was facilitated by the development of an improved growth medium and cell harvesting technique by Silverman and Lundgren. (26)

It has been conclusively shown that under the appropriate growth conditions, certain Thiobacilli can greatly increase the rate of metal leaching from a wide range of metal sulphides. Most of the work, however, has concentrated on the sulphides of copper and iron because of the economic importance of the former and of the relevance of the latter in acid mine drainage and in uranium leaching. Two techniques are used in bacterial leaching studies, the air lift percolator and the ecological shake flask. (See Figure 2.) The former has the advantage of simulating to a certain degree the operation of a dump leach, but often rates are limited by

oxygen/.....

Figure 2a. Ecological Shake Flask

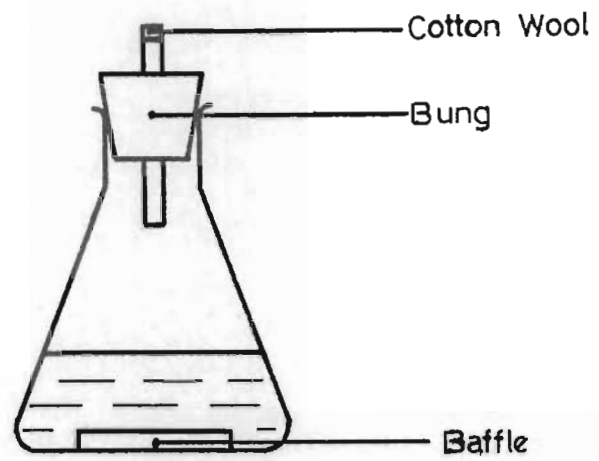
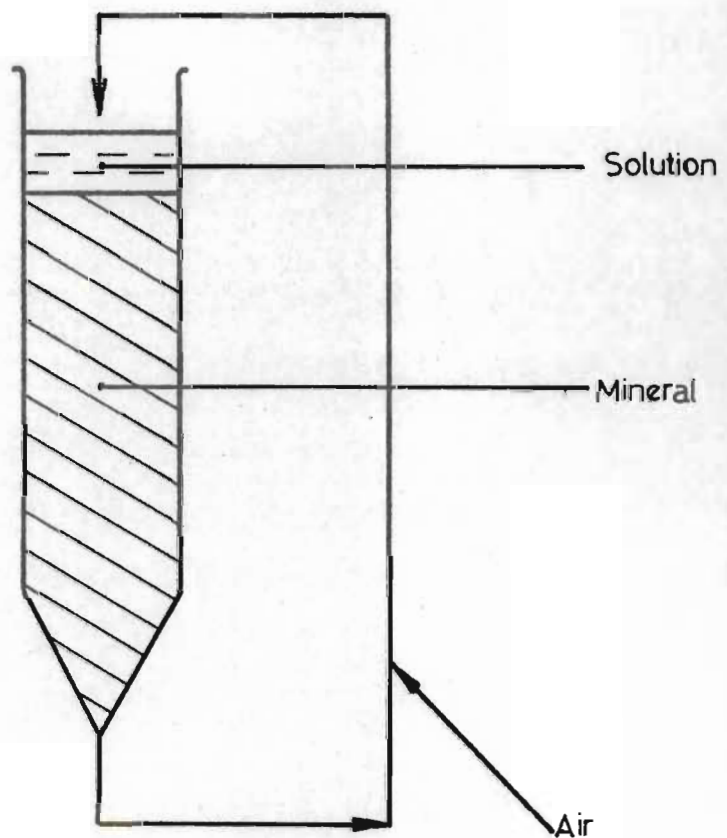


Figure 2b. Percolation Column



oxygen availability. The latter method provides a rapid and reliable means of assessing the importance of a number of parameters such as temperature, pH, nutrient strengths etc, and has been extensively used and developed by the workers of the British Columbia Research Council. (12, 13) The 9K medium of Silverman and Lundgren (26) is generally used in bacterial leaching work as it provides an adequate supply of inorganic nutrients.

Generally it may be said that in order to ensure rapid leaching, the following are necessary:-

- 1) A good supply of oxygen; (enhanced by adequate agitation).
- 2) A supply of carbon dioxide; usually concentrations found in air are adequate, but increasing the level up to about 2 per cent may be beneficial.
- 3) A pH value between 2 and 3.
- 4) A temperature range of 30°C to 40°C.

Usually the exact optimum conditions for leaching are specific for a single ore-type because of the effect of the mineralogical structure on the leach rate. Ferric ion is known to be a good oxidant of, and hence leachant of, sulphide ores. This effect has given rise to two schools of thought on the mechanism of bacterial leaching, with two mechanisms having been postulated, the direct and the indirect. (27)

In the direct mechanism, it is considered that bacteria oxidise
the/.....

the reduced sulphur species and in so doing facilitate the solubilisation of the associated metal. The mere production of acid is not of primary importance because most sulphides leach comparatively slowly in acid. The acid would help in maintaining the metal cation in a stable soluble form, but it seems that the chief role played by the bacteria in this direct mechanism is a catalytic action at the mineral-solution interface. The exact nature of this catalysis is, as yet, unknown, although the previous work of Correns, Harris and Ralph (28) suggests that it is related to cathodic depolarisation. There is strong evidence that during leaching the bacteria are firmly associated with the mineral surfaces, but the first steps in the metabolism of sulphur are as yet not clear. Roy and Trudinger (29) have suggested that most evidence points to a reaction between sulphur and a cellular component at the surface of the bacterial cell. This contact mechanism is supported by the fact that wetting agents can facilitate sulphur oxidation by bacteria.

The indirect mechanism of bacterial leaching involves ferric ion as the primary leaching agent with the function of the bacteria being the reoxidation of the ferrous ions to the ferric state. Iron sulphides are virtually always found associated with other metal sulphide ores in nature so that soluble iron will report in leach solutions. It is this very fact which has probably given rise through evolution to the ability of Thiobacillus ferrooxidans to derive energy for

growth/.....

growth from both the oxidation of sulphur (or sulphide) and ferrous ions,

In practice, both mechanisms probably function simultaneously. The relative importance of each will be decided by the ore-type and the physico-chemical conditions of the leaching environment. The study of Corrans, Harris and Ralph (28) in which synthetic, iron-free, copper sulphides were leached using bacteria, helped to clarify the nature of these two mechanisms.

Dump or heap leaching technology has been developed largely in the mid-Western U.S.A. The low grade waste rock is dumped to form a heap 10 to 20 metres high and leach solution allowed to percolate through the rock. The economics of these processes have been reviewed by Shoemaker (30).

Important parameters to be considered include:

- 1) The rate of percolation.
- 2) Rock size, i.e. exposed surface area.
- 3) Porosity of the rock.

Bacteria will normally grow spontaneously in the dump, provided sulphide mineral surfaces and sufficient dissolved oxygen are available to them. Nutrients such as nitrogen and phosphorus are usually available in sufficient quantity from the gangue material of the rock. Acid consumption of the gangue is important in determining the economics of the

operation/.....

operation. Harris (31) and others have shown that mass transport of dissolved oxygen is the rate limiting step in heap leaching. By treating the heap as a pseudo-particle, Harris has developed a useful chemical engineering approach to leaching. At British Columbia Research Council (73) and at Kennecott Research (74) in Salt Lake City extensive studies are being carried out with a view to modelling the dump leaching operation.

2.2. Studies of the Physiology and Morphology of the Bacteria.

Colmer and Hinkle (5) were first to classify the bacteria responsible for acid mine draining as Thiobacillus ferrooxidans, because of the observed ability to oxidise both sulphur and ferrous iron. Later workers doubted the ability of the organism to oxidise sulphur so that a separate genus Ferrobacillus, was proposed. (32). The validity of this genus has since been questioned as it has been found that the sulphur oxidising capacity may be latent in the organism, needing only a time of adaption to manifest itself.

The most useful work on classification of the Thiobacilli in general and T.ferrooxidans in particular was carried out by Hutchinson and co-workers, (33) using a statistical approach to the problem. A wide range of metabolic properties was tested and organisms classified according to the results of these numerous tests. This is a far more logical method of classification than choosing one property as a criterion for specification/....

specification. There is no sharp distinction in properties, but a gradual change in degree of activity. Organisms with a large number of similar properties are then classified as a single 'strain.' A new method of classification based on the fatty acid composition of the cells has recently been developed.(34)

T. ferrooxidans is widespread in nature and is usually found wherever natural or artificial leaching produces acid-sulphate waters.

T. Thiooxidans is a similar organism which is often associated with T. ferrooxidans. It lacks the ability to oxidise iron, but can oxidise a wider range of sulphur compounds, including thiosulphate which appears to be a variable property in T. ferrooxidans. These properties are summarised in Table 1. T. Concretivorus operates at a higher pH than T. ferrooxidans. Other species include T. Thioparus, T. Novellus and several others described by Trudinger (35) in a recent review of the Thiobacilli. A thermophilic organism has recently been isolated by Williams. (40)

Thiobacilli are small gram negative rods, about 1-2 μm long and 0,5 - 0,8 μm diameter. Two or more cells are often joined end to end, especially during active growth. The cell wall and fine structure appear to be fairly typical of gram negative organisms. Motility may occur at certain stages during growth,

but/.....

Members of this genus are gram negative rods measuring $0,5 \mu\text{m} \times 1 - 3 \mu\text{m}$. All are capable of autotrophic growth and oxidise sulphide, sulphur or thiosulphate to sulphate.

Organism	Habitat	General Characteristics
<i>T. ferrooxidans</i>	Acid mine and soil waters containing H_2S .	Strict aerobe, pH range 1,5 - 5,8. Also oxidises Fe^{++} .
<i>T. thiooxidans</i>	Soil	Strict aerobe, pH range around 2, withstand 5% H_2SO_4
<i>T. concretivorus</i>	Corroding concrete structures	Similar to <i>T. thiooxidans</i> .
<i>T. thioparus</i>	Canal water, mud, soil	Generally aerobic, pH range 4,5 - 7,8. Anaerobic in presence of NO_3 .
<i>T. neapolitanus</i> (<i>Thiobacillus X</i>)	Sea water, corroding concrete.	Strict aerobe, similar to <i>T. thioparus</i> .
<i>T. denitrificans</i>	Canal, river water, salt water, peat, composts, mud	pH range near neutrality. Utilises NO_3 in absence of air.
<i>T. novellus</i>	Soils	Facultative autotroph, pH range near neutrality.
<i>T. intermedius</i>	Fresh water mud	Facultative autotroph, pH range 2 - 7.
<i>T. thiocyanoxidans</i>	Gas works liquor, sewage effluent	Similar to <i>T. thioparus</i> , can oxidise thiocyanate.
<i>T. perometabolis</i>	Soil	Needs yeast extract or casein hydrolysate for growth.

TABLE 1 ; THE THIOBACILLI.

but the presence of flagella has not been conclusively shown.

Thiobacilli are grouped with organisms called autotrophs. (Autotrophs derive all their requirements for growth from inorganic materials.) They are known as chemolithic autotrophs, indicating that they derive energy by chemical oxidation as opposed to photosynthetic organisms, such as the algae, which utilise the energy of sunlight. It is known that certain species of Thiobacilli can derive energy from oxidation of organic materials and thus exhibit heterotrophic characteristics. Whether this is true of I. ferrooxidans is not yet clear as conflicting reports appear in the literature. Silver and co-workers (36) demonstrated the inhibitory effects of organic compounds on the oxidising ability of I. ferrooxidans and this has recently been supported by the work of Tuovinen (37) and co-workers in Finland. This latter work concludes that it would be impossible to utilise organic wastes, like sewage, to supply nutrients for the growth of I. ferrooxidans. This finding, however, has been contradicted by Shafia (38) who has studied the transition of what he classifies as a Ferrobacillus species from chemolithotrophy to organotrophy.

The metabolism of these organisms is being studied by a large number of workers at present, judging by recent reports appearing in the literature, (39, 40, 41) and has been well reported in recent reviews. (42, 35, 29, 43, 37). The major

unsolved metabolic problem is the path whereby solid sulphur or sulphide is taken up by the cells. Roy and Trudinger (29) infer that the uptake mechanism probably involves direct contact at the cell wall. The majority of the work certainly supports this postulation. A recent study by Moriarty (44) at the University of Adelaide has shown that an early intermediate in the pathway of sulphide oxidation is bound to the membrane and contains a linear polymerised form of sulphur rather than the stable S_8 ring.

Carbon dioxide uptake by Thiobacilli is via the Calvin cycle, as occurs in green plants. Two recent studies have shown that the enzyme, carbonic anhydrase, is involved in the assimilation of carbon dioxide. (45, 46)

The pH requirement of T. ferrooxidans is known to be in the range 2 - 3. Other species can oxidise sulphur compounds at higher pH values, e.g. T. thioopares. (See Table 1.)

T. thiooxidans has also been shown to oxidise sulphur at a pH as high as 7, but loses its ability to fix carbon dioxide at the high pH level. In nature, acid ferric sulphate solutions are well buffered at pH 2,5 so that T. ferrooxidans has evolved in this pH region.

The electron transport system of Thiobacilli appears to be by a typical cytochrome system. Moriarty (51) has shown that T. concretivorus (similar to T. Thiooxidans) contains

cytochromes/....

cytochromes of the types b, c, a, and d, and suggests that flavine and ubiquinone may also be components of the electron transfer chain. The Glycolytic pathway operates in Thiobacilli and most of the enzymes involved have been identified in these organisms.(48)

An important practical aspect of the growth of T. ferrooxidans is its ability to tolerate and grow in high concentrations of cations which are normally toxic to other organisms. This is no doubt also an evolutionary consequence. Using bacteria, Duncan and co-workers (12) have leached copper and zinc concentrates yielding solutions containing up to 25 g/l copper and 120 g/l zinc. In general it can be said that high levels of the cations Cu^{++} , Zn^{++} , Ni^{++} , Fe^{++} , Co^{++} , Mn^{++} and Al^{+++} may be tolerated. Cations of silver, molybdenum and mercury are toxic in fairly low concentrations as are anions of tellurium, arsenic and selenium.(49) The exact levels of tolerance depend on the strain of Thiobacillus and the period of adaption of the culture. Light has also been reported to inhibit growth, (50) although this has not been observed for all species.

The growth requirements of T. ferrooxidans were first investigated in depth by Silverman and Lundgren (26) who developed the 9K medium. (See Table 2.) This medium was found to yield high growth rates and cell concentrations. A more recent study of nutrients was carried out by Tuovinen (37) and co-workers, who concluded that sulphate ion was essential

TABLE 2 : 9K MINERAL SALTS MEDIUM.

Salt	Amount
$(\text{NH}_4)_2 \text{SO}_4$	3g
K_2HPO_4	0,5g
KCl	0,1g
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0,5g
$\text{Ca}(\text{NO}_3)_2$	0,01g
H_2SO_4	to give desired pH
Water	up to 1 litre

and that nitrate and chloride ions were inhibitory at certain levels.

2.3. Studies of Nickel Leaching.

Nickel sulphides are leached on a commercial scale in a large number of localities. The Sherrit-Gordon process involves leaching a concentrate of nickel and cobalt sulphides in ammoniacal solution.(53) Other processes for leaching mixed sulphides of nickel in acid solution use high temperature-pressure (autoclave) conditions. These processes are discussed in most texts on hydrometallurgy. (54, 55)

The bacterial leaching of nickel sulphides would appear from an examination of the literature to have received virtually no attention. This is probably due to the lack of low grade or waste nickel sulphide rock in areas where heap leaching could be suitably carried out; in regions of Canada for example, it would be too cold for adequate bacterial growth. Recently there has been a growing interest in the possibility of heap leaching nickel sulphides in areas such as Australia and Southern Africa, where large tonnages of waste are anticipated from the developing nickel mines. At the University of New South Wales, Ralph (82) has reported a growing interest by Mining Corporations in Western Australia in the recovery of nickel from pyrrhotite wastes. A similar interest is being displayed by the Johannesburg Consolidated Investment Company in view of the anticipated open pit mining

operations/.....

operations at the Shangani nickel deposit.

The chemical reactions whereby pentlandite dissolves in acid ferric sulphate solutions are complex. Little work on this subject has been reported in the literature. Klets et al (70) have shown that during the leaching of a pentlandite-pyrrhotite mixture with ferric chloride solutions, elemental sulphur was formed in the surface layers. Phases such as millerite (NiS) beyrichite (NiS) and troilite (FeS) were also formed and jarosite ($KFe_3(SO_4)_2(OH)_6$) was precipitated from solution at low acid concentrations. Shneerson et al (71) studied the autoclave leaching of pentlandite under oxygen pressure. The activation energy was found to be 14 k cal/mole and the order with respect to oxygen pressure was $\frac{1}{2}$. Millerite was formed as an intermediate phase. The interpretation of these results is complicated by the fact that the stoichiometry of the pentlandite was not known or is not given.

2.4. Aims of the Present Investigation.

The aims of the present study are:-

- (1) To carry out an experimental investigation of the bacterial leaching of nickel from the nickel sulphide, pentlandite.
- (ii) To obtain new information on the mechanism whereby nickel is leached from pentlandite.
- (iii) To evaluate the feasibility of using bacterial leaching for the recovery of nickel from pentlandite.

:It/.....

It was hoped to enhance the practical relevance of this work by using a pentlandite of current interest from the Shangani orebody in Rhodesia.

In this investigation care has been taken to accurately define the organisms, the mineral substrate and the experimental procedures, so allowing a thorough interpretation of the results. The organism used was a strain of Thiobacillus ferrooxidans, carefully isolated from a pentlandite leaching environment and maintained as a stock culture using standard microbiological techniques. Its growth on a variety of substrates was tested. The mineral used was purified and accurately defined both analytically and mineralogically. Experimental techniques were carefully chosen and controlled and use was made of methods, such as polarisation and electron probe analysis, in order to gain deeper insight into the process.

3. EXPERIMENTAL.

3.1. Materials and Methods.

3.1.1. Apparatus.

Shake Flasks.

The ecological shake flask, shown in Figure 2a provides a quick and accurate means of carrying out growth tests and initially assessing the effect of a wide range of parameters on bacterial leaching. The growth medium and substrate were placed in the conical flask and inoculated with bacteria. The neck of the flask was sealed with a rubber bung, having a small orifice plugged with cotton wool to allow oxygen into the flask. The flasks were agitated on a shaker with an orbital motion. Temperature was controlled using a thermostated space heater. A disadvantage of this method is the difficulty of continuously measuring pH or oxygen tension in a large number of flasks.

Instrumented Reactors.

The most accurate methods of studying bacterial leaching on a laboratory scale are by the use of instrumented reactors. In this investigation two reactor sizes were used, 0,25 litre and 5,5 litre, the instrumentation being the same in each case. A typical system is shown in Figure 3 and illustrated in Plate 1.

Temperature was controlled by a custom-made transistorised proportional controller. Sensing was by means of a thermistor

and/.....

Figure 3. Instrumented Reactor

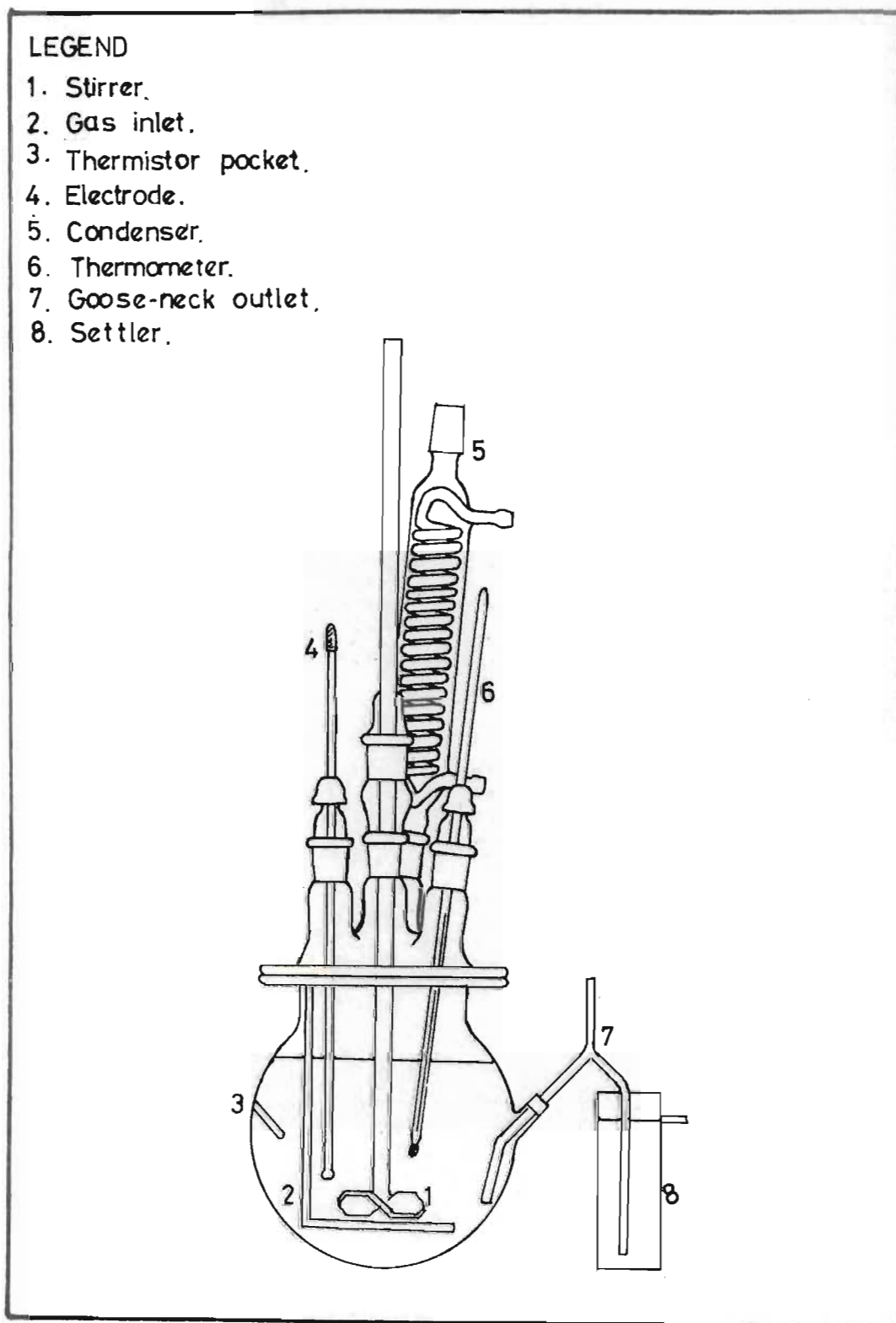
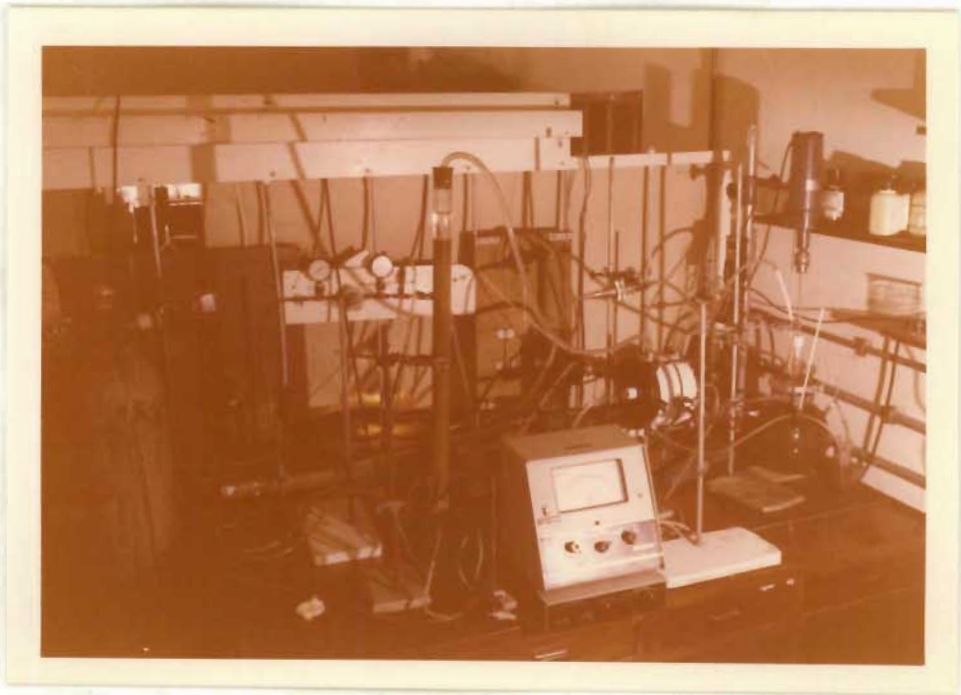
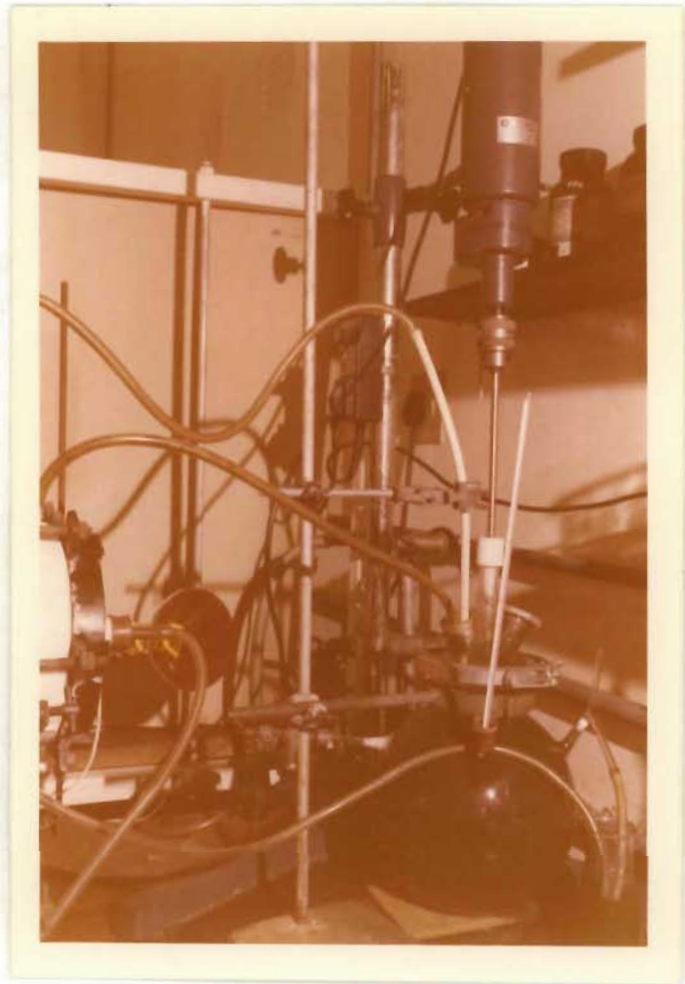


PLATE NO. 1

5,5 LITRE INSTRUMENTED REACTOR.



and heating by infra-red lamps. pH was monitored and controlled using a Radiometer model 26c pH meter coupled to a Radiometer automatic titrator model TTT11b. Agitation was carried out using a Heidolf continuously variable stirrer through a Quickfit stirrer gland number ST4. Dissolved oxygen was measured using a Radiometer Makereth-type electrode. During continuous operation, medium was added using a Sigmamotor peristaltic pump No.T8. Air, oxygen and carbon dioxide were sterile filtered through a 0,22 μ m membrane and metered to the reactors using rotameters. A ground glass fitted lid carried the various sensors and a reflux condenser through which the exit gas was passed to minimise evaporation losses.

Stirred Flasks.

Conical flasks of 250 ml capacity were specially adapted to allow the entrance of gas and the taking of samples. (See Figure 4.) The temperature was controlled by immersing the flasks in a water bath. Agitation was by means of Heidolf continuously variable stirrers via a Quickfit gland number ST4. The gas exit from each flask was connected to a reflux condenser in order to maintain a constant volume of solution during the tests.

3.1.2. Materials.

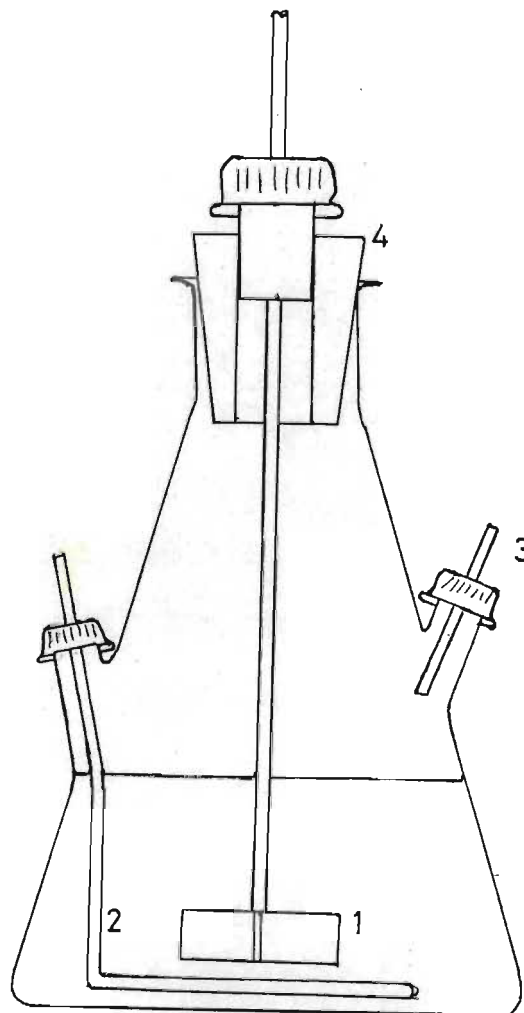
Growth Medium.

The 9K growth medium developed by Silverman and Lundgren was used in the present study (26). The composition of this material is shown in Table 2. Essential trace elements were supplied as impurities
in the/.....

Figure 4. Stirred Flasks used in Kinetics and Leaching.

LEGEND.

1. Paddle stirrer.
2. Gas inlet.
3. Gas outlet.
4. Bung.



in the make-up tap water and as impurities in the chemicals used.

One of the following substrates was added to this basal medium:-

- (i) 2% - 5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at a pH of 2,5.
- or (ii) 5% - 20% elemental sulphur.
- or (iii) Metal sulphides, e.g. pentlandite.
- or (iv) 2% Sodium Thiosulphate.

The ferrous sulphate medium was sterilised by filtration through a 0,2 μm membrane filter using aseptic technique. The sulphur medium was sterilised by steaming for 1 hour on three successive days; autoclaving cannot be used because of the low melting point of sulphur. The thiosulphate medium was sterilised by autoclaving at 120°C for 30 minutes as was the sulphide mineral. The mineral was then added to the sterile growth medium when cold.

Solid medium was prepared by adding 1 per cent ion agar to 5 per cent sodium thiosulphate in 9K medium or 5 per cent ferrous sulphate in 9K medium at pH 4,5. This medium was sterilised by autoclaving at 120°C for thirty minutes.

Standard texts on microbiological methods were used as references for this preparation work (56, 57)

Preparation of Sulphide Minerals.

A high purity pentlandite was prepared from Shangani flotation concentrates the composition of which is shown in Table 3a. The concentrates were first passed over a laboratory-size gravity

concentration/....

TABLE 3 : DETAILS OF PENTLANDITE CONCENTRATES.

A. Low Grade Concentrate.

Chemical Assay:

	Ni	Fe	Cu	S
Total per cent	18,27	37,03	1,5	33,7

Mineralogical (X-ray diffractometric analysis.)

	Pentlandite	Pyrrhotite	Pyrite	Talc	Dolomite	Chlorite
Approx %	60	20	10	5	trace	trace

Calculated mineralogical composition.

	Pentlandite	Pyrrhotite	Pyrite	Chalcopyrite	Gangue
%	55,5	19,8	11,6	4,4	8,7

B. High Grade Concentrate.

Chemical Assay.

	Fe	Ni	Cu	S
Total per cent	32,3	30,6	0,5	34,3

Mineralogical (X-ray diffractometric analysis.)

Pentlandite	Pyrite	Chalcopyrite	Talc
Major	Minor	Trace	Trace

Calculated Mineralogical Composition.

	Pentlandite	Pyrite	Chalcopyrite	Gangue
%	90,0	6,1	1,5	2,4

Screen Analysis. (Mesh size)

	+35	-35+48	-48+65	-65+100	-100+150	-150+200	-200+325	-325
%	0	0	0,1	2,7	8,3	19,1	32,4	37,4

concentration table (Wilfley table) to remove most of the residual gangue and obtain a sulphide-rich fraction. This fraction was then passed through a wet magnetic separator (Sala laboratory model) to remove the magnetic pyrrhotite (FeS) fraction. Finally, a flotation at pH5 was carried out to remove some of the residual pyrite (FeS_2). The composition of the final pentlandite concentrate is shown in Table 3b. This material was found to be about 90 per cent pentlandite ($\text{NiFeS}_{1,8}$) with about 6,1 per cent pyrite (FeS_2).

3.1.3. Procedures.

Isolation of Nickel Leaching Strain of Thiobacillus Ferrooxidans.

A sample was taken using aseptic technique from the acid drainage water leaving the tailings dam of the Pilansberg Nickel Mine near Rustenburg. The sulphide content of the tailings contained pyrrhotite and pentlandite, similar to the Shangani ore-type. The drainage water was found to contain 170 ppm nickel and 23 500 ppm iron and had a pH of 2,4. Microscopic examination at a magnification of X800 using phase contrast optics showed the presence of a number of short rod-shaped bacteria resembling Thiobacilli.

A 2ml sample of this water was inoculated into 50 ml of sterile 9K medium at pH 2,5 containing 5 per cent pentlandite concentrate. This was incubated for three weeks at 30°C during which time the oxidation of iron was evident and about 500 ppm nickel was leached into solution. The pH rose to 3. The bacterial population was also observed to increase considerably during this period. This

inoculation/.....

inoculation-incubation procedure was repeated four times at two-weekly intervals and then serial dilutions of the culture were plated out on ferrous sulphate solid medium. After five days, brown colonies about 0,5 cm diameter had formed. A plate was then chosen which displayed relatively few discrete colonies and a single colony selected to re-inoculate a ferrous sulphate medium. This was chosen as the stock culture of the nickel leaching strain of Thiobacillus ferrooxidans and used in the investigation. The culture was maintained on slopes of ferrous sulphate solid medium which were re-inoculated from a mixed ferrous sulphate-pentlandite medium every three months.

The growth of the strain was then tested on chalcopyrite (Cu,FeS_2) and pyrrhotite and found to be positive in each case after a short period of adaption. Growth was also positive on elemental sulphur and this was later investigated in some detail. (See section 4.1)

Electron Probe and Optical Microscopy.

Sintered discs of pentlandite concentrates and mounted polished specimens of the mineral were examined after leaching using both optical techniques and a JEOL model JXA 3SM electron probe analyser. Useful information on mineralogical and chemical transformations during leaching were obtained using these techniques.

Bacterial Assays.

A micro Kjeldahl method was used to determine bacterial nitrogen. This method was based on work described by Davis et al (58) and

standard/.....

standard micro Kjeldahl techniques. Samples of 1 ml were centrifuged to crop the bacterial cells which were digested in sulphuric acid. Nitrogen was then determined spectrophotometrically.

A direct Bacterial counting technique was also used, employing a Petroff-Hausser bacterial counting chamber. When solid substrates, like sulphur were being used, the sample was agitated vigorously for five minutes with 2 or 3 drops of i-propanol to detach the bacteria from the sulphur. The solids were allowed to settle for five minutes and counting done on supernatant liquid. With practice, one could distinguish fairly accurately between bacteria and fine sulphur particles under the phase contrast microscope.

Chemical Assays.

Leach solutions were assayed on a routine basis using a Techtron model AA5 atomic absorption analyser. At other times, use was made of the analytical services at the J.C.I. Minerals Processing Research Laboratories, which included classical wet methods and instrumental techniques.

Mineralogical Assays.

The services of the Mineralogical section of the J.C.I. Minerals Processing Research Laboratory were employed. These facilities included classical optical methods, X-ray diffractometric analysis and electron probe analysis.

Experimental Methods in Chemical Kinetic Studies.

Leaching was carried out by mixing the crushed pentlandite concentrate as a 10 per cent slurry in the leach solution. The mineral used was the high grade Pentlandite, prepared as described in section 3.1.2.

The prepared pentlandite was screened to minus 200 plus 325 mesh and was washed in 1 M H_2SO_4 for 5 minutes and dried with acetone just prior to use, to remove the surface oxide layer. (This procedure was found to give a more reliable leach curve by eliminating the initial rapid release of surface nickel oxide into solution.) Leaching was carried out in 250 ml stirred conical flasks containing 150 ml of the appropriate leach solution and 15 g of the mineral. Samples of 1 ml were taken from the flasks at regular time intervals. These were filtered and the nickel concentration measured using atomic absorption spectrophotometry. Usually five samples were taken over four hours, but for those tests where leach rates were very low, sampling was carried out over a period of twenty hours. The concentration-time curves obtained were linear (within limits of experimental errors) and the slopes of these lines, representing initial leaching rates of nickel were computed using a linear regression programme based on least squares fit. Each test was done in triplicate and, if more than 20 per cent variance was obtained between between two of the calculated rates, the test was repeated.

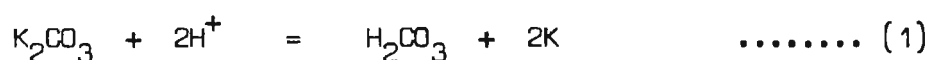
Experimental Methods used in Bacterial Growth and Leaching Studies.

The desired quantity of sulphur or pentlandite was added to the

leach/.....

leach solution, which was normally the 9K medium. After mixing for a few minutes the bacteria were added as a washed cell suspension prepared from the stock culture. Strict aseptic technique was not followed in these tests because of the highly selective nature of the growth medium.

In the growth tests on sulphur the pH was automatically controlled by adding a standard solution of K_2CO_3 . The rate of hydrogen ion production was then computed according to the relationship:-



This relationship was checked by carrying out a blank titration in 9K medium to assess the possible effects of pH buffers in the medium. The results are shown in Figure 5 from which it is seen that:-



Experimental Methods Used In Polarisation Experiments.

Sintered discs of pentlandite concentrates were prepared by pressing the mineral in a 25 mm diameter die under a pressure of 500 bars. The "green" disc was sintered under an atmosphere of hydrogen sulphide for 12 hours at 800°C. After this treatment the disc was firm and could be readily handled. The disc was attached to a holder as shown in Figure 6a. The disc was then immersed in the

leach/.....

Figure 5. Titration Curve (H_2SO_4 in 9K medium / K_2CO_3 .
pH 3 30°C)

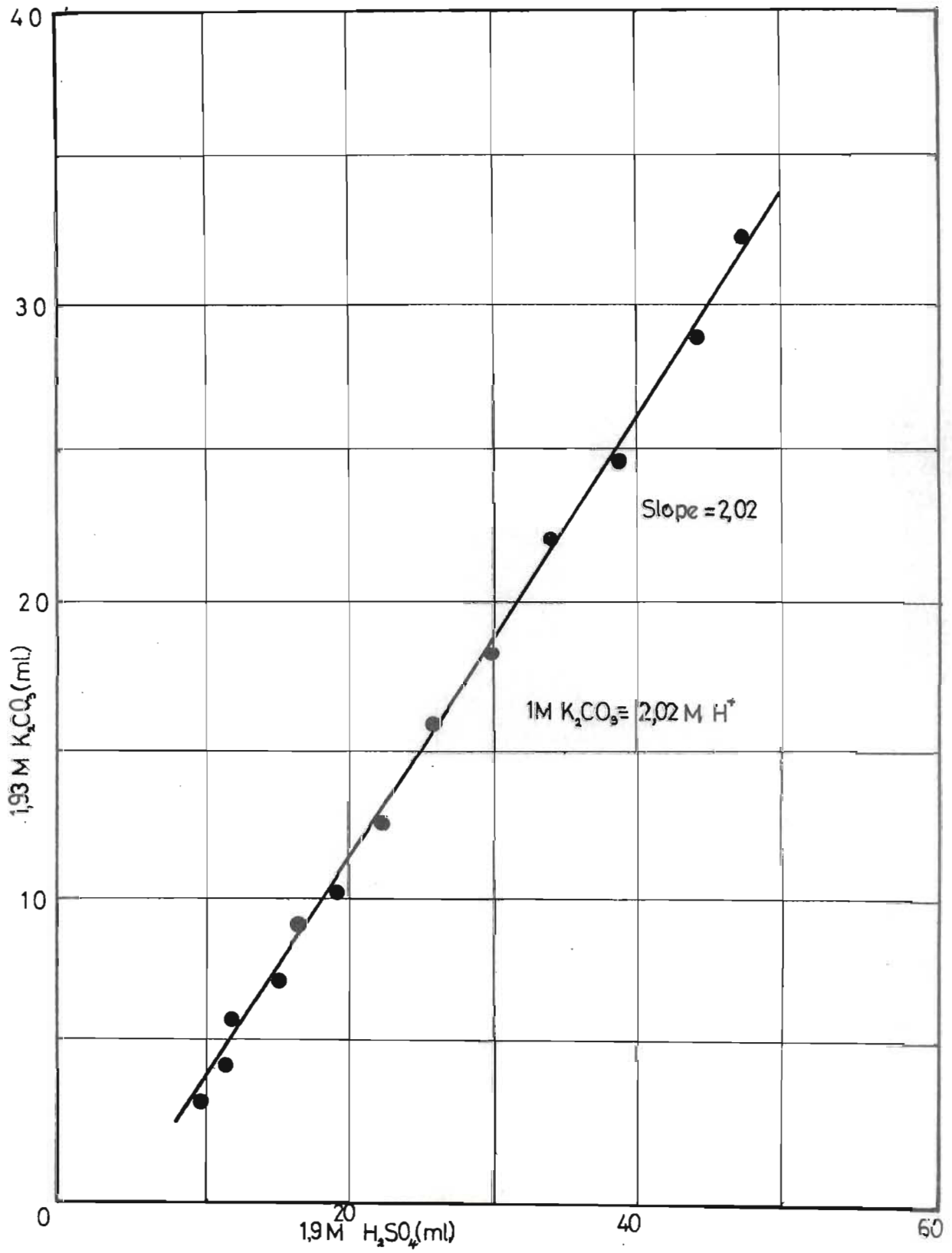
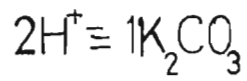
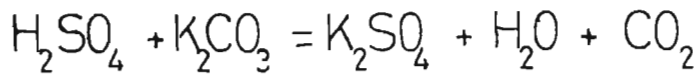


Figure 6a. Mounting for Sintered Discs

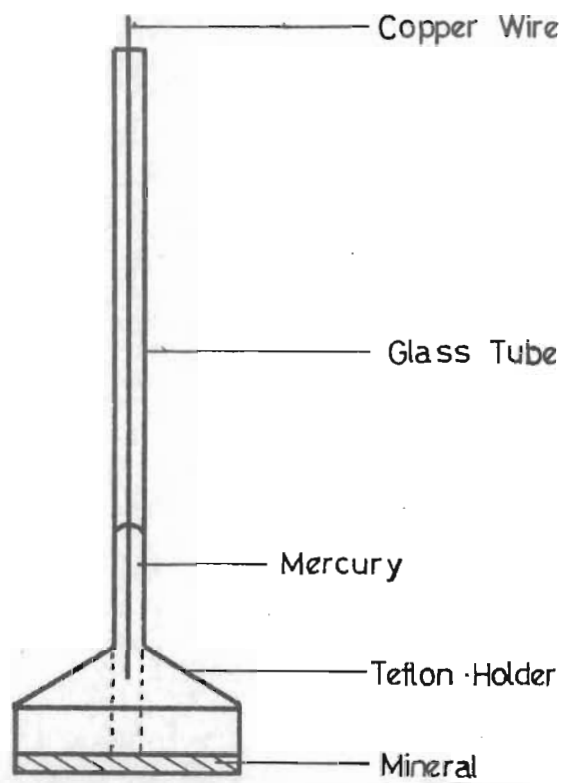
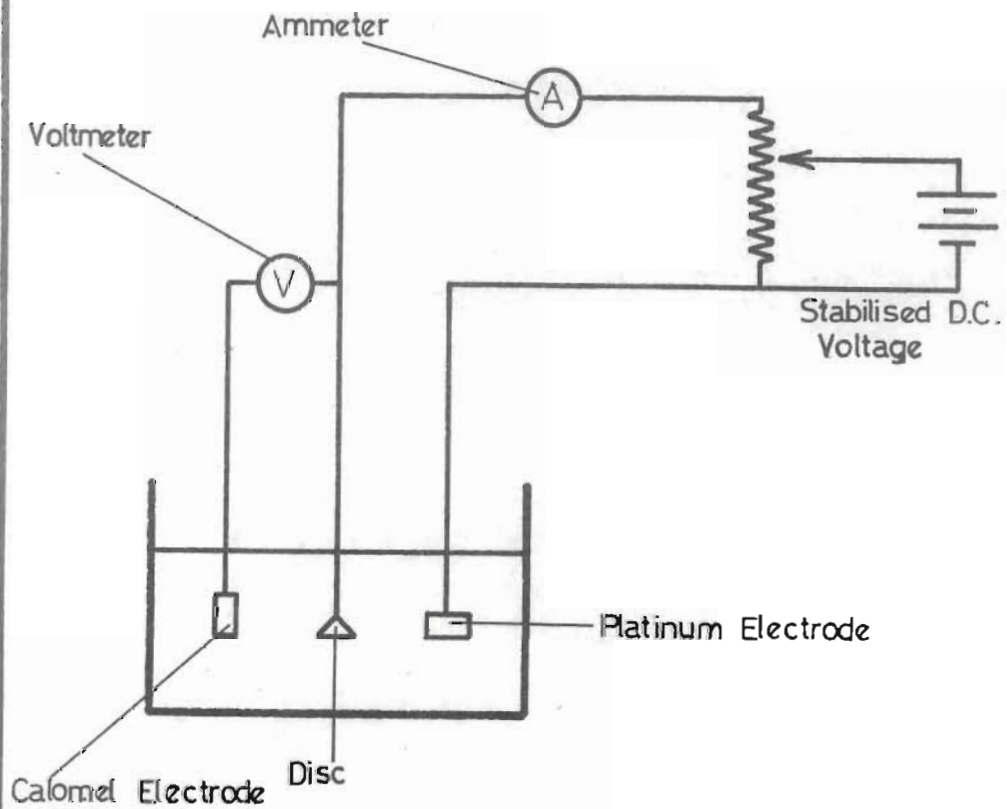


Figure 6b. Polarisation Circuit



leach solution in a flask as shown in Figure 4. The back of the disc was electrically connected to a polarisation circuit for the purpose of measuring the current-voltage characteristics of the pentlandite disc-electrode under different conditions (75, 76.) The reason for using a disc of mineral which can be rotated, is because the hydrodynamic equations relating to mass transfer at the surface may be readily solved, as described by Levich (72.)

4. RESULTS AND DISCUSSION.

4.1. Preliminary Experiments.

4.1.1. Chemical Kinetic Studies on the Leaching of Pentlandite in Acid Ferric Sulphate Solutions.

The most important physico-chemical parameters involved in the chemistry of heap leaching are considered to be: (66, 67, 68.)

- i) Ferric ion concentration, $[Fe^{+++}]$ - molar
- ii) Oxygen concentration, pO_2 - per cent partial pressure.
- iii) Temperature. $^{\circ}C$
- iv) Hydrogen ion concentration, $[H^+]$ - molar
- v) Mass transport, i.e. rate of stirrer rotation, W - r.p.m.

These are not all easily controllable in a heap leaching operation, but information on their effect on leach rate contributes to the overall picture of the process. There are other factors involved, but these are outside the scope of this initial investigation, which was aimed at providing a background to the bacterial leaching studies.

A 2^5 factorial experiment was carried out to investigate the effects and interactions of the above five factors on the leaching of nickel from the mineral pentlandite in acid ferric sulphate solutions. This was followed by a conventional kinetic investigation of the leaching of pentlandite in acid ferric sulphate solutions.

Factorial Experiment/.....

Factorial Experiment.

The values chosen for each factor are shown in Table 4, and the complete factorial design of the 2^5 experiment, together with the results, is shown in Table 5. The detailed experimental leach data are given in Appendix 1.

The measured rates of nickel leaching (shown in Table 5) were processed according to the method described by Mendelowitz (69) to find the average effect for each factor and combination of factors. The details of this method together with an example of the calculations are given in Appendix 2.

The results of the factorial experiment may be summed up as follows:-

- 1) Temperature increase between 30°C and 80°C has the greatest average positive effect on leach rate. The average increase in the leach rate due to increasing the temperature from 30°C to 80°C was 113,88 ppm Ni^{++}/hr .
- 2) The average effect in increasing the ferric ion concentration from 0,01 M to 0,25 M was an increase of 85,98 ppm Ni^{++}/hr . This is approximately the same as the average effect of the combination ferric ion-temperature; viz. 84,42 ppm Ni^{++}/hr .
- 3) Other factors and combinations showing lesser significant average effects are
 - i) pO_2
 - ii) W

iii)/.....

TABLE 4 : VALUES OF FACTORS TESTED.

Factor	Level	
	0	1
Fe ⁺⁺⁺	0,01M	0,25M
pO ₂	1%	100%
Temperature	30°C	80°C
H ⁺	2 × 10 ⁻⁴ M	2,0M
Agitation rate	0 r.p.m.	400 r.p.m.

TABLE 5: DESIGN AND RESULTS OF FACTORIAL EXPERIMENT.

Test No	1	2	3	4	5	Leach Rate ppm/hr	1	2	3	4	5	Effect
1	0	0	0	0	0	0	0,80	9,89	355 25	675 19	2 067 77	129,24
2	1	0	0	0	0	0,80	9,09	345,36	319 94	1 392 58	1 375 61	85,98
3	0	1	0	0	0	2,77	130,04	19,72	837 06	559 75	896 85	56,05
4	1	1	0	0	0	6,32	215,32	300,22	555 52	815 86	409 45	25,59
5	0	0	1	0	0	0	7,42	46,92	333 13	86 37	1 822 45	113,88
6	1	0	1	0	0	130,04	12,30	790,14	226 62	810 48	1 350 77	84,42
7	0	1	1	0	0	8,29	156,15	46,13	556 62	101 61	718 41	44,90
8	1	1	1	0	0	207,03	144,07	509,39	259 24	307 84	401 97	21,12
9	0	0	0	1	0	4,25	1,19	4,35	93 57	615 97	-316 85	-19,80
10	1	0	0	1	0	3,17	45,73	328,78	-7 20	1 206 48	-403 89	-25,24
11	0	1	0	1	0	8,20	135,95	5,18	562 78	540 69	-415 85	-25,99
12	1	1	0	1	0	4,10	654,19	221,44	247 70	810 08	-298 13	-18,63
13	0	0	1	1	0	29,50	7,31	0,34	71 45	60 03	-334 93	-20,93
14	1	0	1	1	0	126,65	38,82	556,28	30 16	658 38	-409 97	-25,62
15	0	1	1	1	0	9,89	146,60	2,55	282 34	90 07	-382 97	-23,94
16	1	1	1	1	0	134,18	362,79	256,69	25 50	311 90	-302 77	-18,92
17	0	0	0	0	1	0	0,80	8,29	335 47	-35 31	717 39	44,84
18	1	0	0	0	1	1,19	3,55	85,28	280 50	-281 54	256 11	16,01
19	0	1	0	0	1	23,29	130,04	4,88	743 22	-106 51	724 11	45,26
20	1	1	0	0	1	22,44	198,74	-12,08	463 26	-297 38	206 23	12,89
21	0	0	1	0	1	0	1,08	44,54	324 43	-100 77	590 51	36,91
22	1	0	1	0	1	135,95	4,10	518,24	216 26	-315 08	269 39	16,84
23	0	1	1	0	1	116,93	97,15	31,51	555 94	-41 29	598 35	37,40
24	1	1	1	0	1	537,26	124,29	216,19	254 14	-256 84	221 83	13,86
25	0	0	0	1	1	3,02	1,19	2,75	76 99	-54 97	-246 23	-15,39
26	1	0	0	1	1	4,29	0,85	68,70	-16 96	-279 96	-190 87	-11,93
27	0	1	0	1	1	18,77	135,95	3,02	473 70	-108 17	-214 31	-13,39
28	1	1	0	1	1	20,05	420,33	27,14	184 68	-301 80	-215 55	-13,47
29	0	0	1	1	1	15,50	1,27	-2,04	65 95	-93 95	-224 99	-14,06
30	1	0	1	1	1	131,10	1,28	284,38	24 12	-289 02	-193 63	-12,10
31	0	1	1	1	1	110,85	115,60	0,01	286 42	-41 83	-195 07	-12,19
32	1	1	1	1	1	251,94	141,09	25,49	25 48	-260 94	-219 11	-13,69

See Appendix 2 for further details of the calculations of the "effect".

iii) pO_2 - W

iv) pO_2 - Temperature

4) A surprising result is the negative average effect of $[H^+]$ in the range tested.

5) The leach rate is optimised under the conditions of test 24, i.e. high levels of all factors excepting $[H^+]$. The relative importance of factors is as follows:-

- | | | |
|------------------|---|----------|
| i) temperature | - | positive |
| ii) $[Fe^{+++}]$ | - | positive |
| iii) pO_2 | - | positive |
| iv) W | - | positive |
| v) $[H^+]$ | - | negative |

6) All combinations with $[H^+]$ have negative average effects. All other combinations have positive average effects.

Kinetic Experiment.

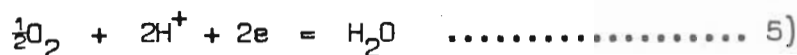
It is well established that the rates of leaching of most sulphides in acid ferric sulphate solutions are controlled by the cathodic reactions of the electro-chemical couples.(77) This appears to be true in the case of pentlandite as well, especially considering the dramatic increases in leach rate obtained when using ozone as described later in this section. Two electron acceptors are available in the present leaching experiments, viz oxygen and ferric ions, so that the overall rate is probably composed of two separate rates:-

$R_{Overall}/\dots\dots$

$$R_{\text{overall}} = R_1 + R_2 \quad \dots\dots\dots 3)$$

R_1 = rate due to cathodic ferric reduction

R_2 = rate due to cathodic oxygen reduction; i.e.



Ingraham and co-workers have studied the kinetics of leaching of a variety of copper sulphides under similar conditions to those used in the present experiments. For covellite (CuS) these investigators found the activation energy of leaching to be 22 k cal/mole, indicating strong rate control by chemical processes.(66) On the other hand for chalcocite (Cu_2S) they found the activation energy of leaching to be 5 k cal/mole and the rate controlling step to be diffusion of reactants through boundary layers into the solid-liquid interface.(67) The mineral chalcopyrite was found to have an activation energy of leaching of 14 k cal/mole, a value lying between those for chemical and mass transport as rate control.(68) These workers postulated that in the leaching of chalcopyrite, the mechanism involves the diffusion of reactants through a film of surface sulphur. This sulphur is formed as a result of the leaching and its thickness increases continually. This explained the parabolic nature of the kinetics observed. The rate limiting step is diffusion of ferric sulphate through the layer of sulphur. At high concentrations of ferric sulphate, the reverse diffusion of ferrous sulphate is rate limiting. Agitation was found to

have no effect on leach rate. In many respects the process resembles pore diffusion in catalyst particles.

In the present investigation the observed activation energy of nickel leaching was 14 k cal/mole, (See Figure 11) the same magnitude as Ingraham and co-workers observed in the case of the leaching of chalcopyrite. It is not likely however that the mechanisms are the same. In the leaching of pentlandite, it was found that the sulphur did not accumulate on the mineral surface, but readily detached and became suspended in the leach solution. The observed kinetics were also linear. The value of the activation energy, would then seem to indicate a 'mixed' mechanism in which both chemical processes and mass transport phenomena are rate controlling.

This is consistent with the postulate that the overall rate is comprised of two separate rates, since it is most likely that the ferric reaction is mass transport controlled, while the cathodic oxygen reduction is chemical rate controlled. The former reaction is known to be kinetically and thermodynamically more favourable than the oxygen reduction reaction in sulphide leaching. (This is also consistent with the results of the factorial experiment where it is shown that ferric ion concentration has a greater positive effect on leach rate than oxygen concentration.) In the rate expression, ferric concentration and agitation would be grouped together as would oxygen and hydrogen ion concentration. Thus the following rate expression is proposed:-

$$R_{\text{overall}}/\dots$$

$$R_{\text{overall}} = K_1 [\text{Fe}^{+++}]^a W^b + K_2 p\text{O}_2^c [\text{H}^+]^d \dots\dots\dots 6)$$

where K_1 and K_2 are rate constants.

Effects of Ferric Ion Concentration on Leach Rate:

When the effect of ferric ion on leach rate was measured, keeping other parameters constant, the rate expression could be reduced to the form;

$$R_{\text{overall}} = K_3 \cdot [\text{Fe}^{+++}]^a + K_4$$

$$\text{Where } K_3 = K_1 \cdot W^b, \quad W = 200 \text{ r.p.m.}$$

$$K_4 = K_2 \cdot p\text{O}_2^c \cdot [\text{H}^+]^d$$

$$p\text{O}_2 = 50\%, \quad [\text{H}^+] = 2 \times 10^{-2} \text{ M.}$$

A plot of $\log (R_{\text{overall}} - K_4)$ versus $\log [\text{Fe}^{+++}]$ would have a slope of 'a' and an intercept equivalent to K_3 . This is shown in Figure 7a, where K_4 was obtained by extrapolation to zero concentration on the plot of R_{overall} versus $[\text{Fe}^{+++}]$ shown in Figure 7b.

K_4 was found to be equal to 23 ppm/hr. This represents the rate of leaching when $[\text{Fe}^{+++}] = 0$, $p\text{O}_2 = 50\%$ and $[\text{H}^+] = 2 \times 10^{-2} \text{ M.}$

In Figure 7a the data are compared with a line of slope 1,0

and/.....

Figure 7a. $\log R_1$ vs $\log[Fe^{+++}]$

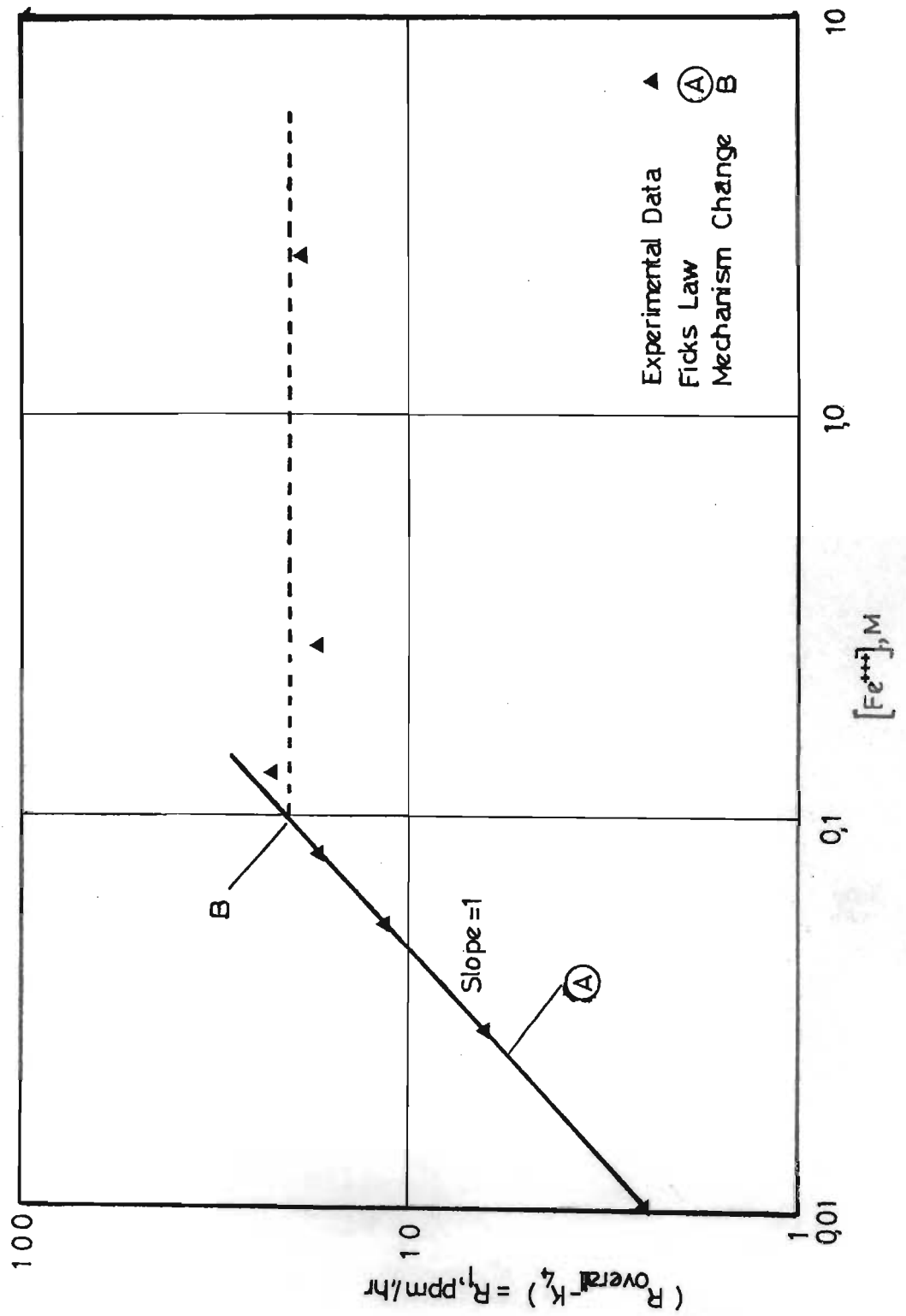
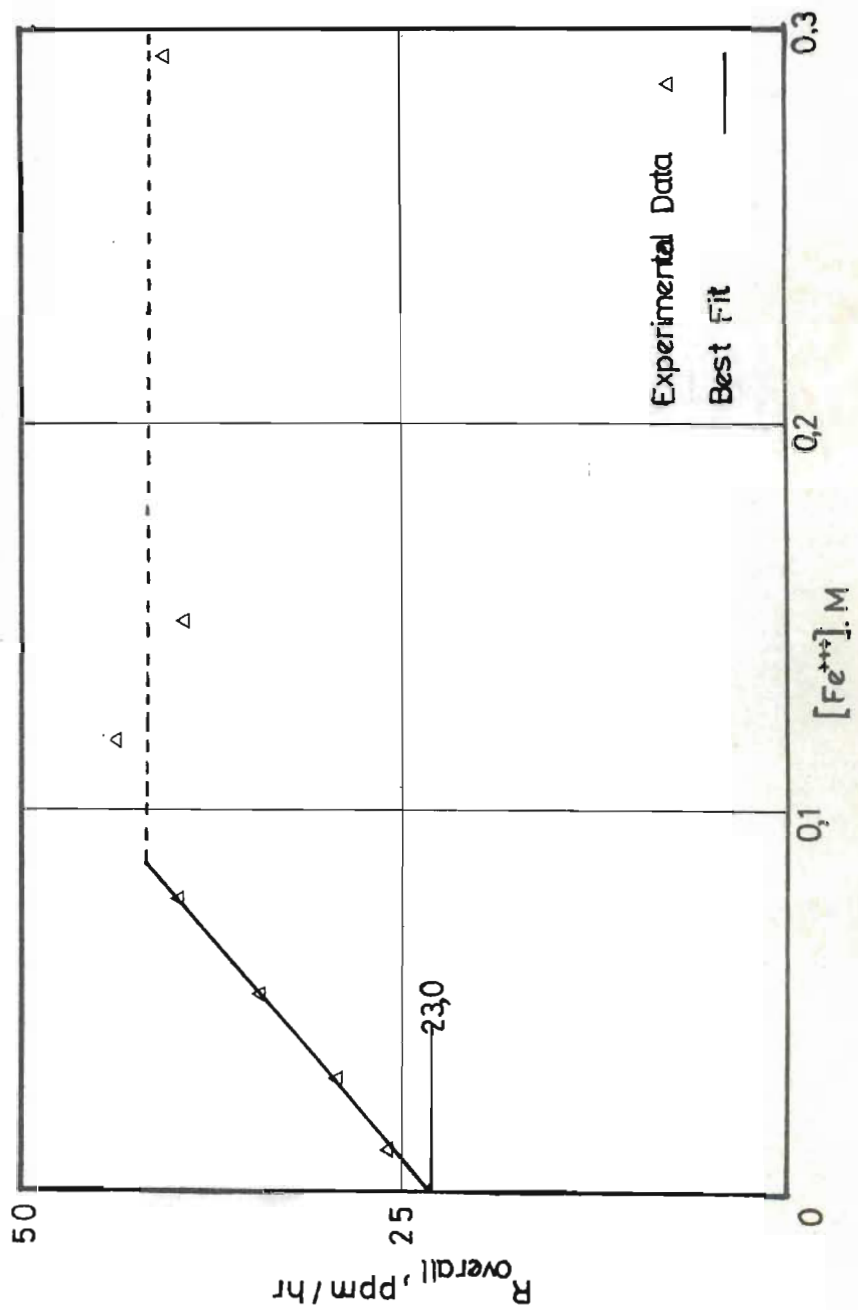


Figure 7b. R_{overall} vs. $[\text{Fe}^{++}]$



and are consistent with this line up to about 0,1 M Fe^{+++} , after which the rate would appear to be independent of $[\text{Fe}^{+++}]$. (At this point the reaction is probably controlled by the diffusion of some other reactant or product.) These data are further discussed later in this section.

Effect of Agitation on Leach Rate.

Figure 8a shows a plot of $\log (R_{\text{overall}} - K_4)$ versus $\log W$, where K_4 was taken to be 23 ppm/hr from Figure 7b. Again a line of slope 0,833 has been drawn through the data for purposes of the discussion later in this section. The data are reasonably consistent with this line. K_4 was also estimated from these data by means of a linear plot of R_{overall} versus W . (See Figure 8b.) K_4 was found in this case to be 23 ppm/hr, in good agreement with the previously measured value.

Effect of Oxygen Concentration on Leach Rate.

In this case the rate expression was reduced to:-

$$R_{\text{overall}} = K_6 + K_7 \cdot p\text{O}_2^c$$

where $K_6 = K_1 \cdot [\text{Fe}^{+++}]^a \cdot W^b$, equivalent to the rate of leaching when $p\text{O}_2 = 0$, $[\text{Fe}^{+++}] = 0,125\text{M}$ and $W = 200 \text{ r.p.m.}$

$$K_7 = K_2 [\text{H}^+]^d.$$

A plot of $\log (R_{\text{overall}} - K_6)$ versus $\log p\text{O}_2$ would have a slope of 'c'. This is shown in Figure 9a. K_6 was obtained

from/.....

Figure 8a. $\log R_1$ vs $\log W$

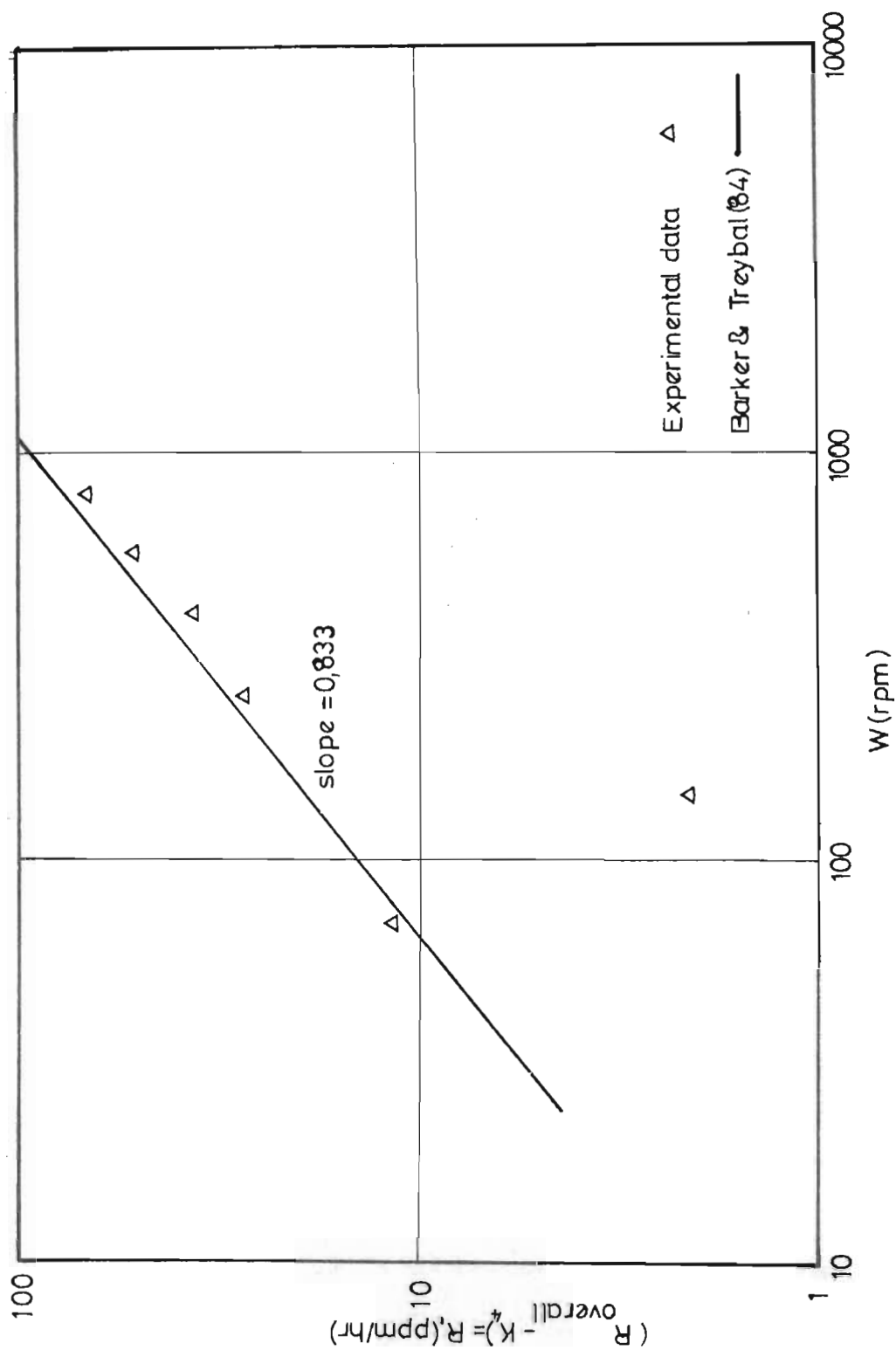


Figure 8b R_{overall} vs W
(Extrapolated to $W=0$)

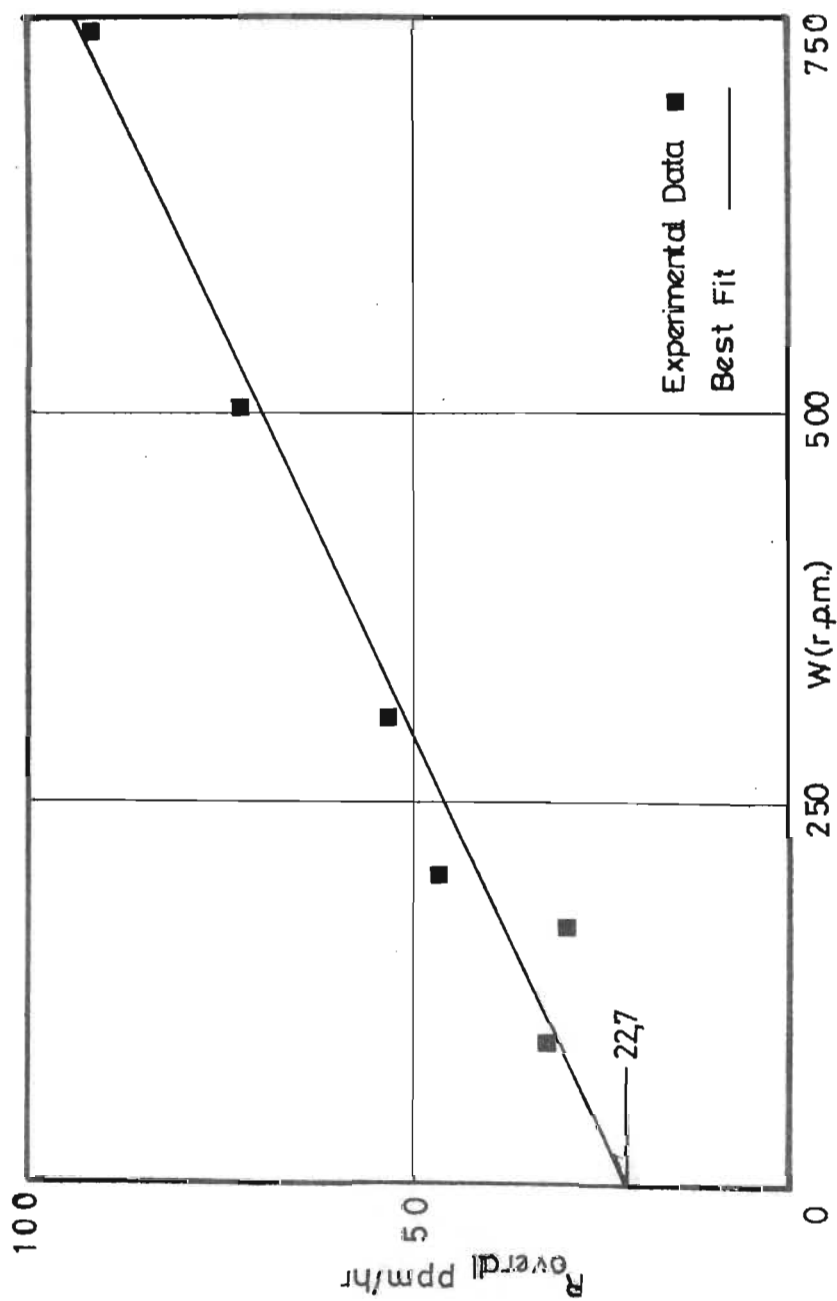


Figure 9a. $\log R_3$ vs $\log PO_2$

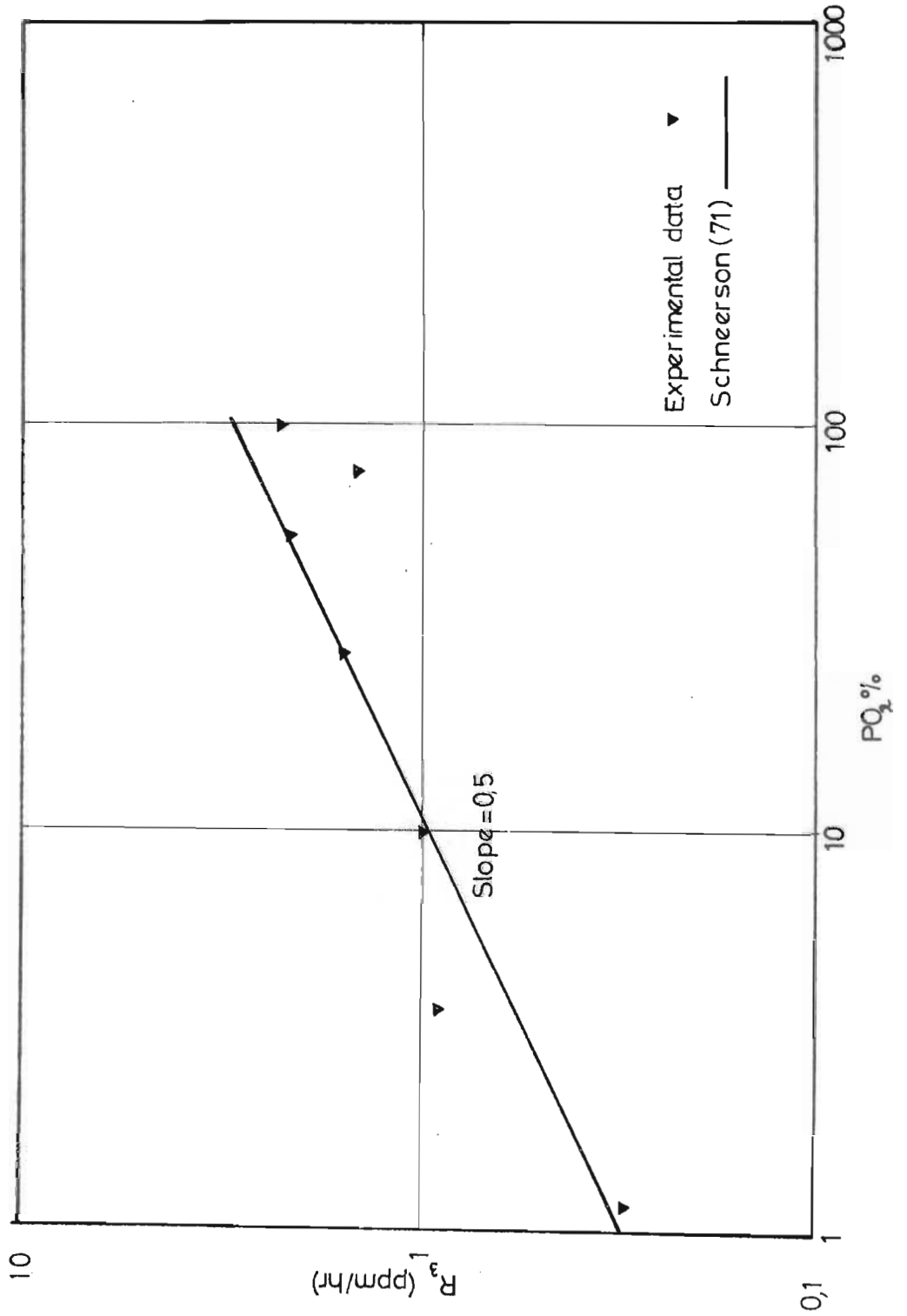
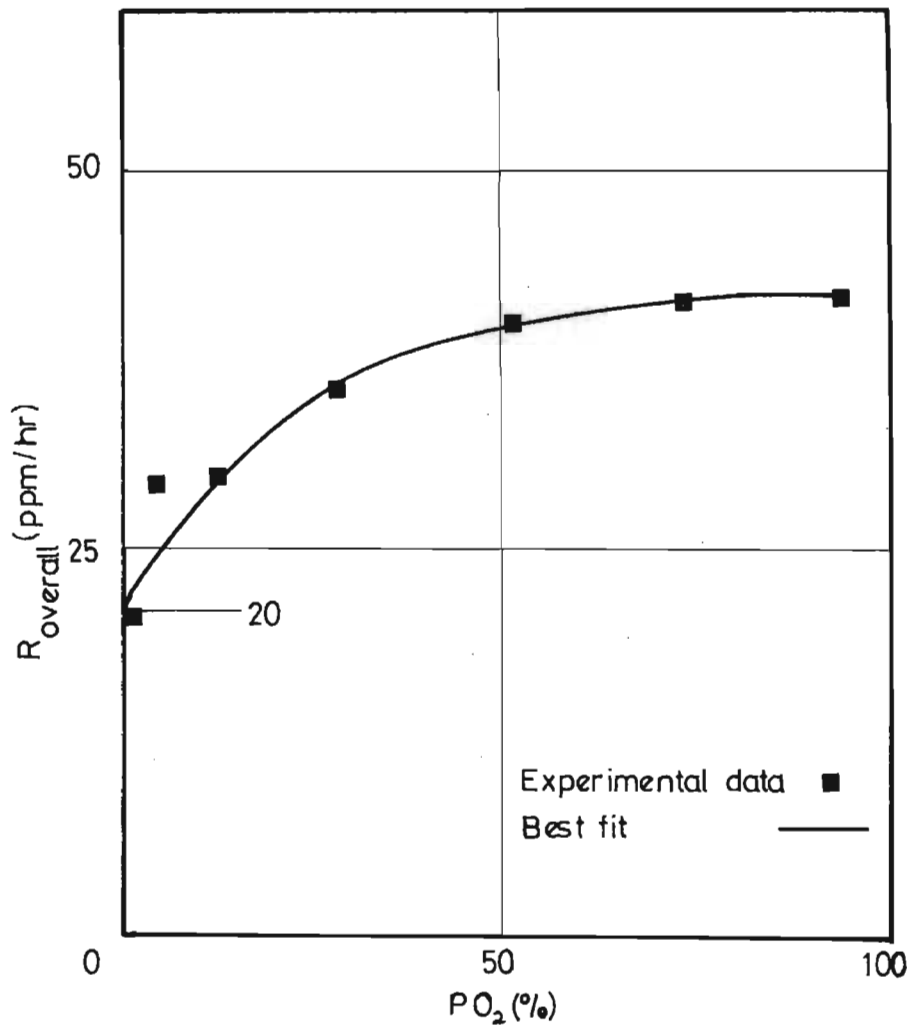


Figure 9b. R_{overall} vs PO_2

(Extrapolation to $PO_2=0$)



from the intercept of the plot of R_{overall} versus pO_2 shown in Figure 9b; K_6 is estimated to be 20 ppm/hr from this plot.

The data in Figure 9a are compared with a line of slope 0,5.

Effect of $[H^+]$ on Leach Rate.

In this case a plot of $\log (R_{\text{overall}} - K_6)$ versus $[H^+]$ would have a slope equal to 'd'. The value of K_6 measured previously was used since in practice $[H^+]$ cannot be zero.

Figure 10 gives the value of 'd' = 0,1 for pH 4 to pH 0,75

and 'd' = -1,0 for pH 0,75 to pH -0,75.

Effect of Temperature.

The Arrhenius plot for the leaching of pentlandite in acid ferric sulphate solutions is shown in Figure 11. From the slope of this graph, the activation energy was calculated to be 14 k cal/mole. (See Appendix 3.)

Detailed experiment data for these kinetic tests are given in Appendix 4.

Leaching with Ozone.

A series of empirical tests were carried out to test the effects on leaching of a wide range of chemical compounds. The aim of this exercise was purely of a practical nature to see whether some reasonably cheap additive could be found which would enhance leach rates in practical situations,

such/.....

Figure 10. $\text{Log}R_2$ vs $\text{log} [\text{H}^+]$

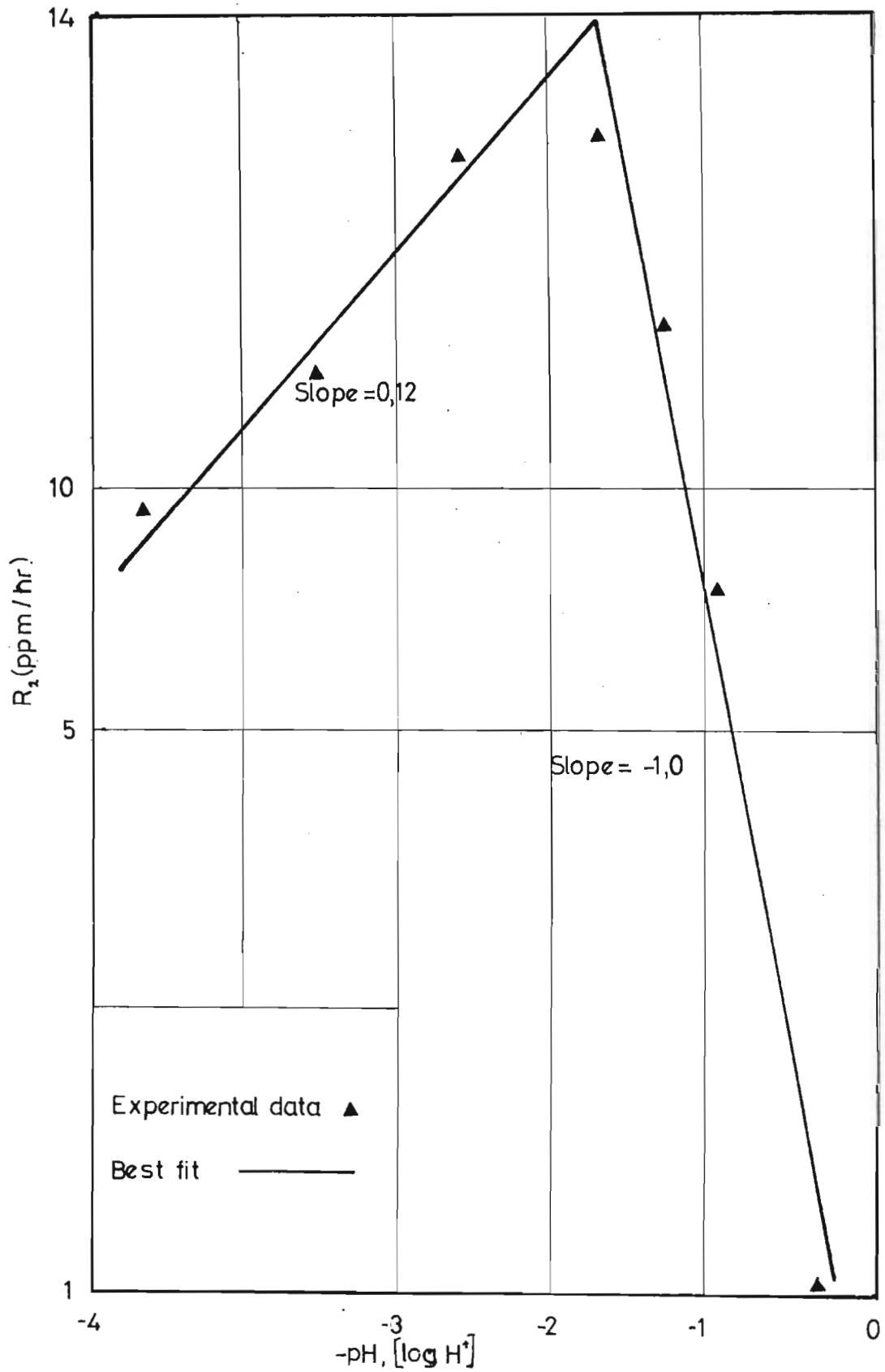
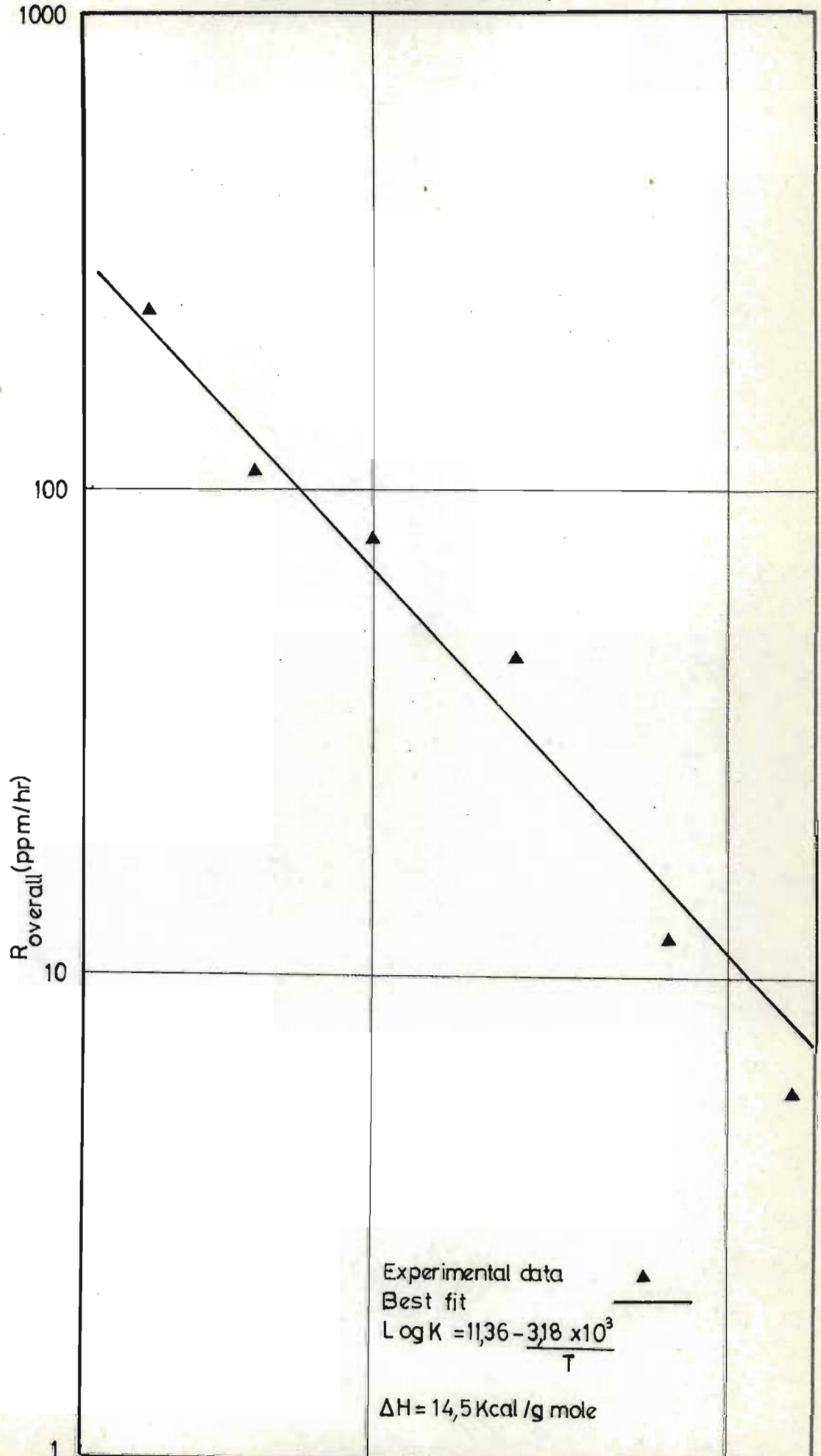


Figure 11. Effect of Temperature on Chemical Leach Rate (Arrhenius Plot)



such as dump leaching.

The experimental conditions were similar to those used in the chemical kinetic studies with air being bubbled into the solution. The various materials added were:-

- 1) 1g MnO_2 .
- 2) 1g Activated Carbon.
- 3) 1.65g finely divided platinum.
- 4) 10 ml NaOCl solution.
- 5) 1g $KClO_3$.
- 6) 1 ml 30 per cent H_2O_2 .
- 7) 1g E.D.T.A.
- 8) 1g NaCl.
- 9) 1g Na_2CO_3 .
- 10) Ozonised oxygen bubbled into leach solution during leaching.

A control test was also carried out.

All the tests except numbers 2 and 10 gave results equivalent to or less than the control leach. In the case of test 2 (activated carbon), the leach rate was about 25 per cent higher than the control. With the use of ozonised oxygen in test 10, the leach rate showed a dramatic increase; about ten times greater than the control. These data are given in Appendix 5.

This discovery was followed up and a patent has been applied for, entitled "Improvements in Hydrometallurgy,

using/...

using Ozone." (83). This improvement in leach rate due to the use of ozone was in fact found to hold for a wide range of sulphide minerals.

The action of ozone supports the postulate that cathodic reactions are rate limiting in sulphide leaching. It is probable that the ozone is readily providing powerful electron acceptors in the form of atomic oxygen at cathodic sites on the mineral surface. This is discussed more fully in Section 3.2.2. in conjunction with the postulated mechanism of oxygen reduction on the surface of the mineral pentlandite.

Activated carbon, being a powerful adsorbent of gas, probably helps provide atomic oxygen at the mineral surface. It would be expected that H_2O_2 would also show some positive effect on leach rate because of the evolution of atomic oxygen. The relatively long periods of leaching, up to 72 hours or more, would probably negate any effect which may be due to the rapid release of oxygen from this compound.

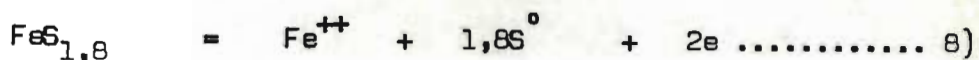
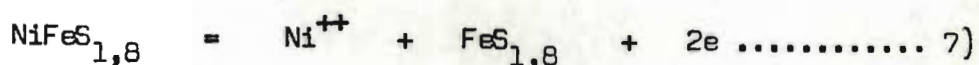
Mechanism of Chemical Leaching.

Examinations of leach residues from the present experiments using optical microscopy, X-ray diffraction and electron probe analysis have shown that two intermediate phases, pyrrhotite (in small amounts) and elemental sulphur (in stoichiometric amounts,) are formed. Jarosite is precipitated from solution at pH values above 4,5. The unleached pentlandite

was/.....

was covered with a thin, loosely bound layer containing pyrrhotite and sulphur. The leached surface was cracked and pitted showing that dissolution occurred preferentially at regions of crystal imperfections and grain boundaries. When a sintered disc of pentlandite was electrolysed in sulphuric acid solution at pH3 for 24 hours by maintaining a voltage of +5v on the disc with respect to a platinum electrode, the molar ratio of nickel to iron dissolved was 1,05:1. The disc was found to be covered with a loose layer of pyrrhotite and a small amount of sulphur. Most of the sulphur detached from the specimen and reported as an amorphous suspension in the solution.

Considered together, these results suggest that pentlandite dissolves in acid solutions by an electrochemical mechanism with the following sequence of anodic reactions: (taking the stoichiometry of the pentlandite to be as shown.)



Discussion of Chemical Kinetic Studies.

It was proposed earlier in this section that the rate of nickel leaching from pentlandite follows a rate equation which has the form:-

$$R_{\text{overall}} = R_1 + R_2 \dots\dots\dots 3)$$

In/.....

In this model R_1 was considered to represent the rate of leaching due to the cathodic reduction of ferric ions at the mineral surface and was represented by the term;

$$K_1 \cdot [\text{Fe}^{+++}]^a \cdot W^b$$

It was postulated that the rate of ferric leaching was mass transport controlled.

R_2 was considered to represent the rate of leaching due to the cathodic reduction of oxygen at the mineral surface and was represented by;

$$K_2 \cdot p\text{O}_2^c \cdot [\text{H}^+]^d$$

In general terms Fick's Law of diffusion may be written;

$$V \cdot \frac{dC}{dt} = k \cdot A \cdot (C - C_i) \quad \dots\dots\dots 9)$$

where V is the volume of solution

A is the interfacial area

C is the bulk liquid concentration of diffusing species

C_i is the interfacial concentration of diffusing species.

k is the mass transfer coefficient.

When applied to ferric ions, $C_i = 0$ and C may be assumed constant, equal to $[\text{Fe}^{+++}]$, since the leaching was followed for a relatively short time only.

$$\therefore V \frac{dC}{dt} = k A [\text{Fe}^{+++}] \quad \dots\dots\dots 10)$$

$$\text{i.e. } R_1 \propto k A [\text{Fe}^{+++}] \quad \dots\dots\dots 11)$$

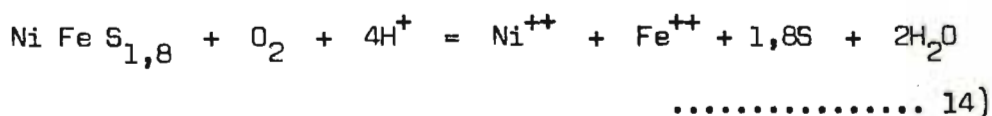
Barker and Treybal (84) have shown that mass transfer coefficients for suspended solids dissolving in agitated liquids vary as the speed of stirrer rotation to the power 0,833.

$$\text{i.e. } k \propto W^{0,833} \dots\dots\dots 12)$$

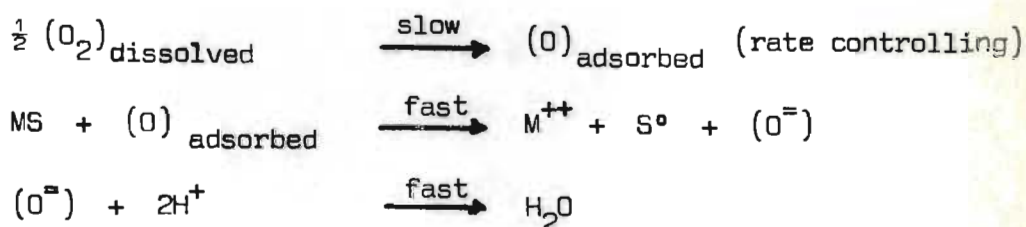
$$\therefore R_1 \propto [Fe^{+++}] W^{0,833} \dots\dots\dots 13)$$

Schneerson (71) in a study on the autoclave leaching of pentlandite, has shown that the rate of leaching is proportional to $pO_2^{\frac{1}{2}}$.

The leaching of nickel from pentlandite takes place according to the following overall reaction when oxygen is the terminal electron acceptor:-



The following mechanism is proposed as representing the individual steps in this scheme:- (For the sake of simplicity pentlandite is represented as MS where M represents the total metallic portion. This is valid, as nickel and iron were leached in equivalent amounts.)

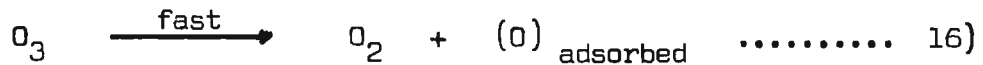


therefore/...

therefore:

$$\begin{aligned} \frac{d [M^{++}]}{dt} &= \frac{2d [Ni^{++}]}{dt} = \frac{d [O]}{dt} \text{ adsorbed} \\ &\propto [O_2]^{\frac{1}{2}} \text{ dissolved} \\ \text{i.e. } R_2 &\propto pO_2^{\frac{1}{2}} \dots\dots\dots 15) \end{aligned}$$

The mechanism of oxygen adsorption is supported by the fact that when ozone was used in place of oxygen (as discussed previously in this section) dramatic increases in leach rates were obtained. It is probable that the atomic oxygen derived from ozone is more rapidly adsorbed onto the mineral surface; i.e.



Thus the proposed model is:-

$$R_{\text{overall}} = K_1 [Fe^{+++}] W^{0,833} + K_2 pO_2^{\frac{1}{2}} [H^+]^0 \dots\dots\dots 17)$$

This model has been compared with the experimental data in Figures 7a, 8a, 9a and 10 by superimposing lines of the appropriate slope on the experimental points. It is considered that the model is consistent with the experimental data.

A comparison between experimental data and calculated data based on the model is given in Figure 12. Good agreement between the model and the experimental data was found.

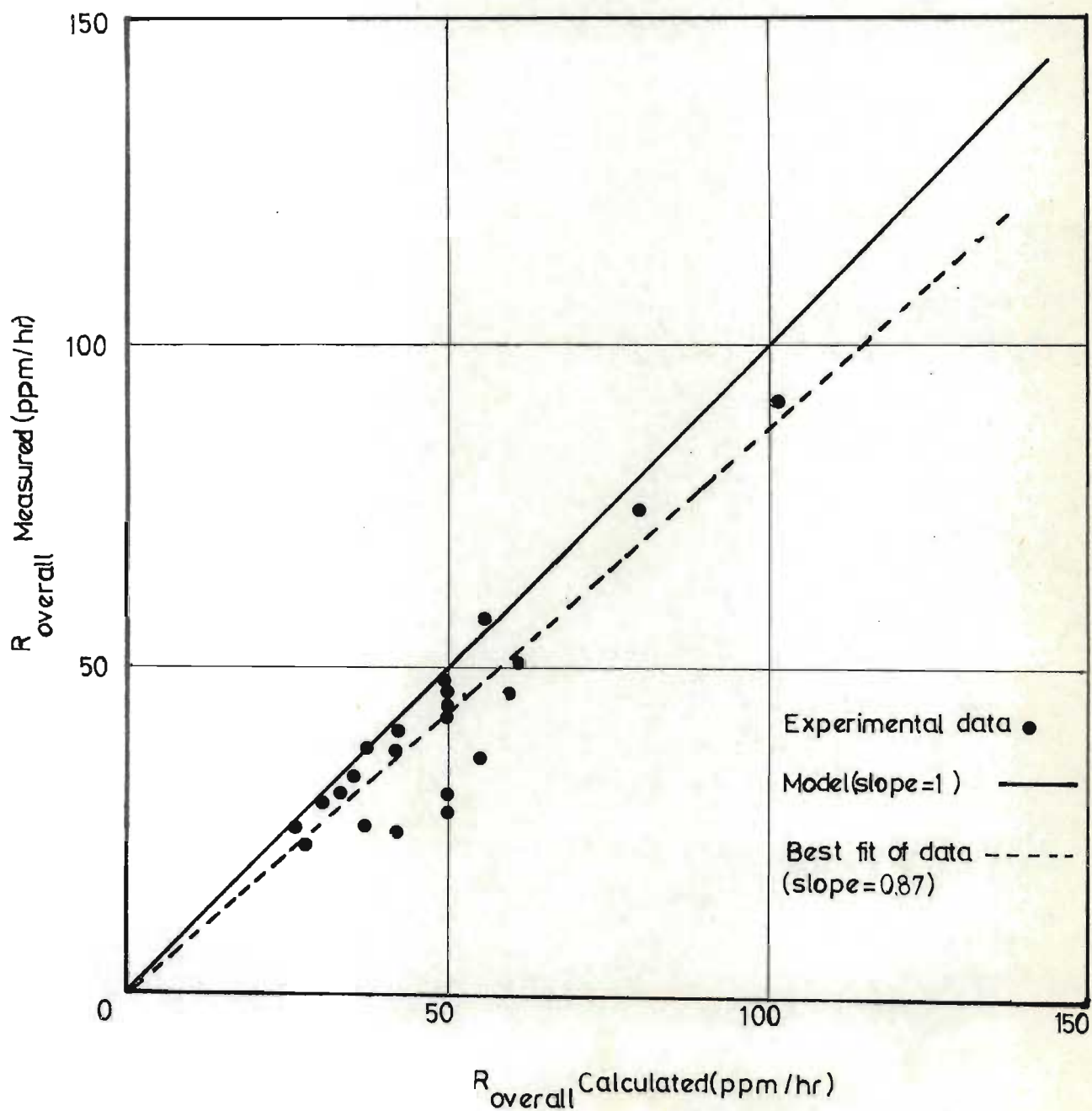
K_1 and K_2 were calculated from the experimental results, as shown in Appendix 15, and found to be

$$K_1 = 3,2 \text{ mg/hr - mole - r.p.m.}^{0,833} \dots\dots\dots 18)$$

$$K_2 = 3,3 \text{ mg/hr - } pO_2^{\frac{1}{2}} - \ell \dots\dots\dots 19)$$

These/.....

Figure 12. Comparison of Experimental Data and Proposed Model.



These are not absolute constants but apply to the conditions of mineral particle size, pulp density, temperature, etc. used in these particular experiments.

The specific surface of the sample used was estimated from the size distribution curve and using the shape factor for crushed quartz. (See Appendix 6.) This was calculated as 300 m²/g. The units of R_{overall} are ppm/hr, i.e. mg/l-hr. This may be converted to absolute units:-

$$R_{\text{absolute}} = R_{\text{overall}} \times \frac{1}{S_a} \times \frac{1}{M}$$

S_a = specific surface
 = 300 m²/g

M = mass of mineral per litre
 = 100 at 10% pulp density.

$$\therefore R_{\text{absolute}} = \frac{R_{\text{overall}}}{30 \times 10^3} \text{ mg/m}^2\text{-hr}$$

Thus in absolute terms the individual rate constants at 50°C are:-

$$K_1 = 10,67 \times 10^{-5} \text{ mg-l/m}^2\text{-hr-mole-r.p.m.}^{0,833} \dots\dots\dots 20)$$

$$K_2 = 0,11 \times 10^{-3} \text{ mg-l/m}^2\text{-hr-pO}_2^{\frac{1}{2}} \dots\dots\dots 21)$$

These may be corrected for different temperatures from the activation energy data on Figure 18, i.e.

$$\log K = 11,36 - \frac{3,18 \times 10^3}{T} \dots\dots\dots 22)$$

4.1.2. Polarisation Studies.

When an electrode is in equilibrium with ions in solution, the partial current of anodic dissolution is equal and opposite to the cathodic current. The exchange current density, i_0 , is defined by the magnitude of the currents and the electrode area. The current density is determined by the concentration of metal ions and the activation energy of dissolution. A low activation energy will generally mean a high exchange current.

If the potential drop across the double layer associated with the electrode is altered by superimposing an external E.M.F., then the electrode is said to be polarised. If the potential is made more positive, then an increase of electrical energy of ions in the electrode will result and the anodic current will rise. The activation energy is correspondingly decreased. Similarly the cathodic current will decrease and there will be a net anodic current. The Tafel (75) equations relate the change in potential across the double layer to the current density:-

$$M_a = A_a + b_a \log i \dots\dots\dots 23)$$

$$M_c = A_c + b_c \log i \dots\dots\dots 24)$$

where M_a is the anodic activation over-potential; M_c is the cathodic activation overpotential.

i is the current density.

A_a, b_a, A_c, b_c are constants.

A plot/.....

A plot of potential (equilibrium potential + M) versus log current density should thus be a straight line. (See Figure 13.) Departures from linearity occur at high current densities because of concentration overpotentials where mass transport effects (e.g. diffusion) become rate limiting.

Metal sulphides are generally good electrical conductors so that polarisation curves may be obtained for these in solutions containing the corresponding metal ions (76). The idea behind a polarisation study of bacterial leaching was to compare the values of the exchange current density for oxidation of pentlandite in the presence of bacteria to the values obtained in control leaches. This would indicate what effect, if any, the bacteria were having on the activation energy of the oxidation reaction. Changes in limiting current values would show an effect on mass transport.

Polarisation During Chemical Leaching.

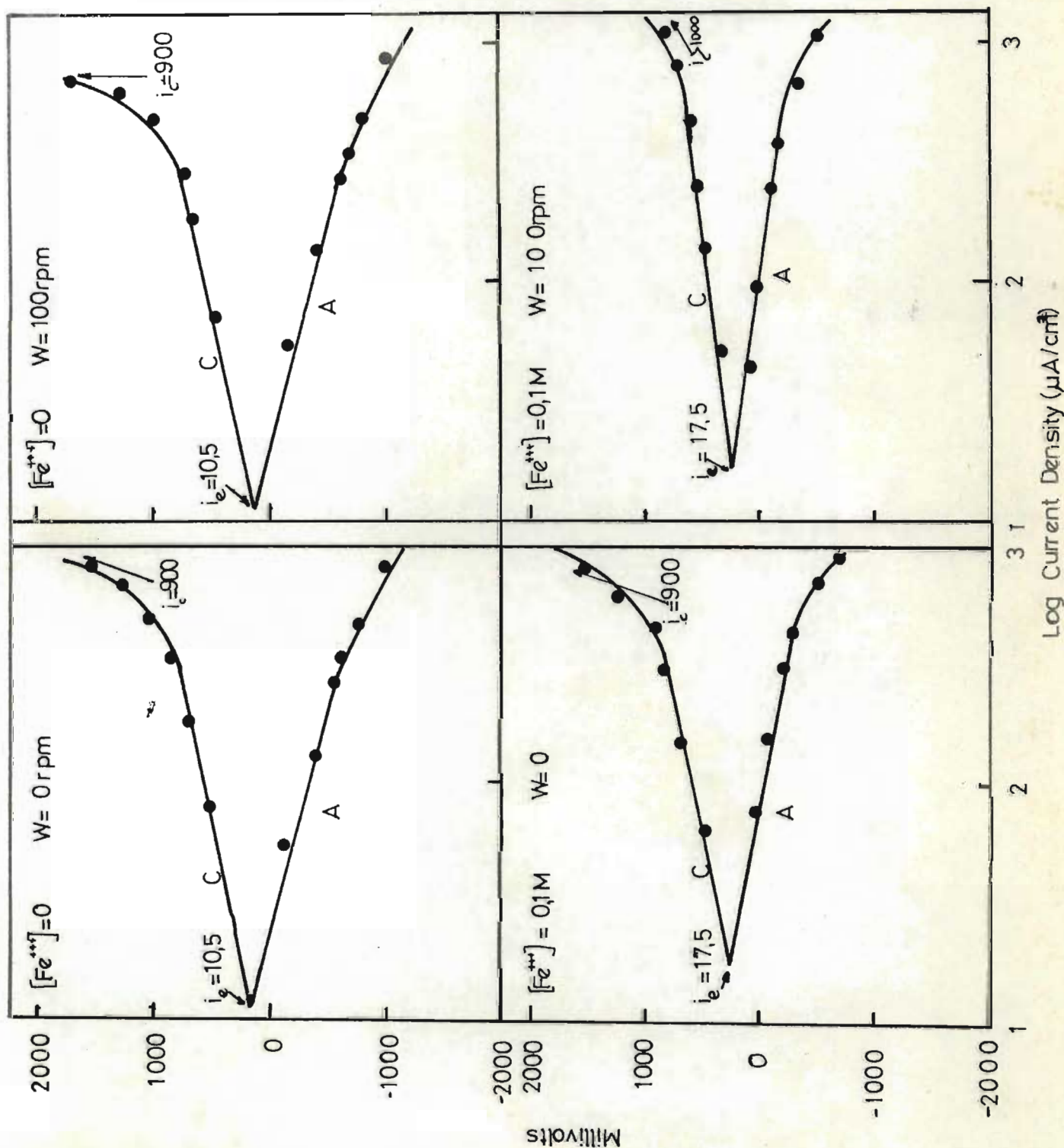
A series of polarisation tests were carried out using discs of sintered pentlandite. The discs were immersed in acid ferric sulphate leach solutions and the experimental conditions were such that concentration of ionic species were virtually unchanged over the test period; i.e. up to four weeks. The typical current voltage relationships obtained are shown in Figure 13 and the detailed experimental data are given in

Figure 13. Polarisation (Current-Voltage) Curves - Chemical Leaching.

9K solution
 pH 2,5
 Gas -Air
 30°C
 $[Ni^{2+}] = 0,1M$
 $[Fe^{2+}]$ and agitation as indicated

i_e = Exchange current
 i_c = Limiting cathodic current
 C = Cathodic curve
 A = Anodic curve

Experimental data on day 10 of leach •



Appendix 12. No significant changes in the shape of the curves could be detected during the test period, although examination of the surface showed that leaching had, in fact, taken place. The limiting cathodic current was found to be greatly affected by disc rotation speed in the presence of ferric ions.

Polarisation During Bacterial Leaching.

These tests proved to be completely negative. Current-voltage curves similar to those measured in chemical leaching were obtained and no significant difference could be detected due to bacterial growth. A typical current voltage curve is shown in Figure 14 and the experimental data are given in Appendix 12.

CONCLUSION.

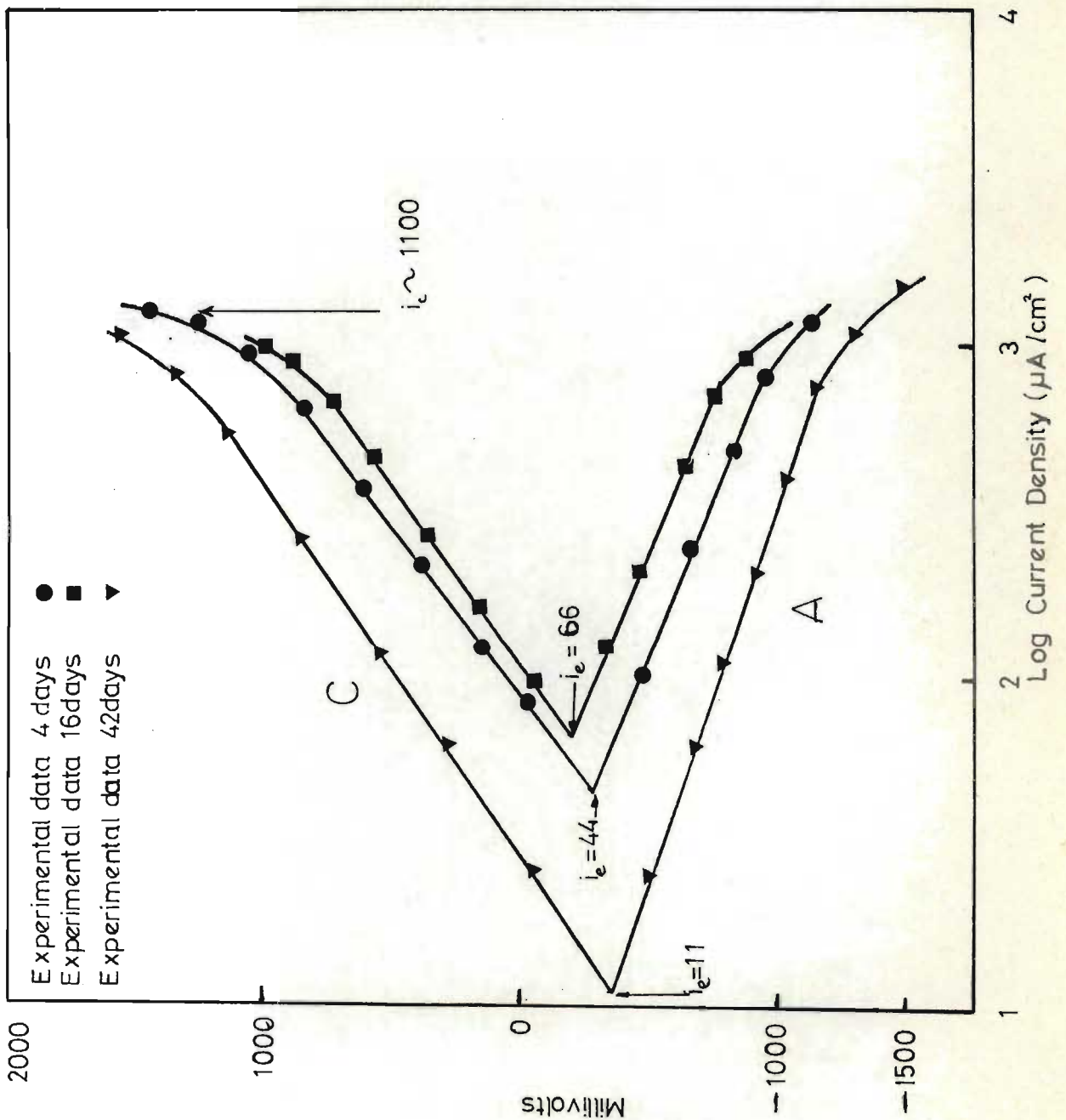
It may be that the sintered disc is unsuitable for carrying out this type of electro-chemical study and that it is necessary to use large single crystals of mineral as described by Wright (76). As this work was an adjunct to the main theme of the present investigation, the problem was not pursued further.

One useful observation was the increase in limiting cathodic current obtained when the disc rotation speed was increased, providing Fe^{+++} was present. This finding supports the postulate made in the previous section that ferric ion is rate controlling by a mass transport mechanism.

Figure 14. Polarisation (Current-Voltage) Curves -
Bacterial Leaching.

9K solution
pH 2,5
Gas -Air
30°C
[Ni²⁺] 0,1M
Agitation 100rpm

i_e = exchange current
 i_c = limiting cathodic current
C = cathodic curves
A = anodic curves



4.1.3 BACTERIAL GROWTH ON SULPHUR.

It is probable that bacterial growth on elemental sulphur resembles in many ways growth on metal sulphides. Sulphur is often produced during the leaching of metal sulphides so that in the micro-environment of the bacterial cell, it may well be that even during growth on a metal sulphide the bacterial cell is in contact with S^0 species only. This proposed mechanism may not apply in all cases of sulphide leaching, but certainly suggests that some detailed study of the growth of bacteria on elemental sulphur is warranted, if only from a comparative point of view. (It was felt that a similar detailed approach to the growth on ferrous sulphate was not justified although the bacterial oxidation of ferrous to ferric ion plays an important role in biological leaching. The subject of ferrous oxidation has been well studied recently (59, 60.) It was considered that a repetition of this work was not warranted as, unlike growth on sulphur, use could be made of the available information.)

Initially the batch growth characteristics of the strain of T. ferrooxidans were studied, followed by continuous growth experiments.

Batch Test No.1.

This initial test was carried out to measure the rate of acid production by the bacteria growing on sulphur. The results are given in Appendix 7 and are shown graphically in Figure 15.

The/.....

Figure 15. Batch Growth Test 1 on Sulphur.

250 ml. 9K solution

2% w/v S

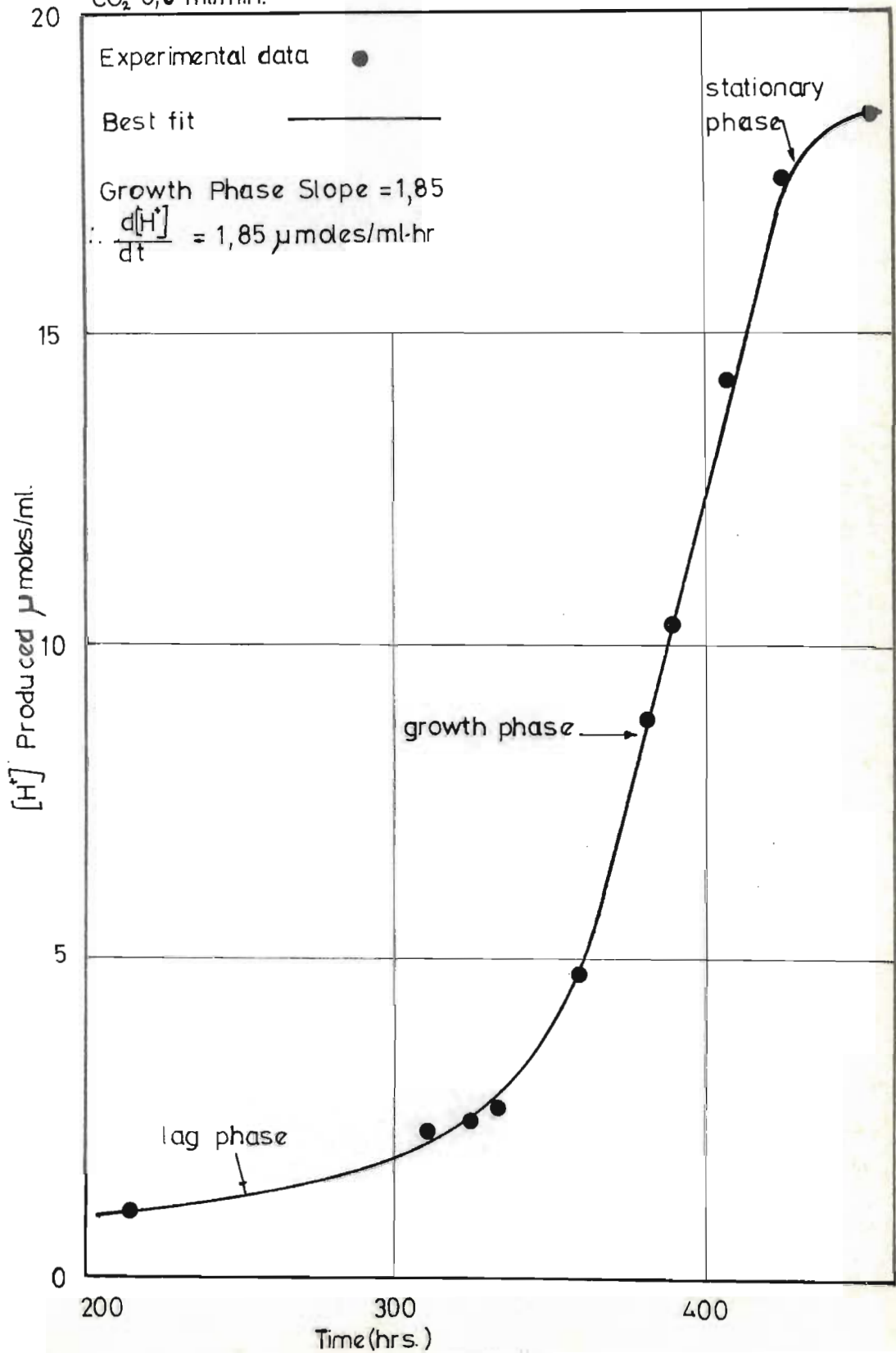
30°C

Agitation 150rpm

pH 3,0

Air 40 ml/min.

CO₂ 0,8 ml/min.



The form of the curve is typical of batch growth of microorganisms, showing a lag phase, a growth phase and finally a stationary phase. One major difference is apparent i.e. the linear portion during the growth phase. This feature is discussed in conjunction with further data in Section 4.2.

Batch Test No.2.

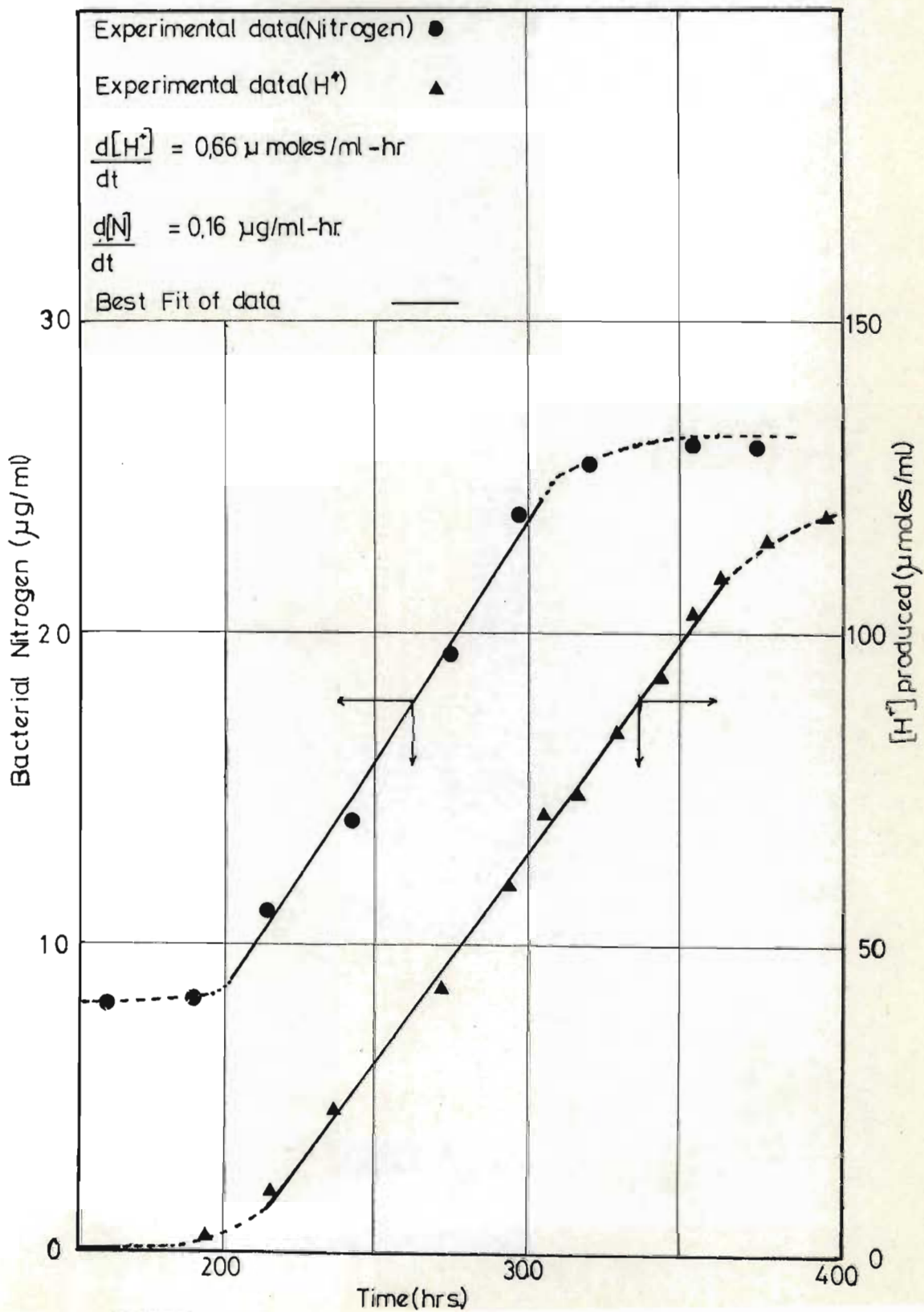
A second batch growth experiment was conducted to test the relationship between acid production and bacterial growth in 9K medium. The growth was carried out in the larger reactor, to reduce the effects of sampling. Flowers of sulphur (2% w/v) and Tween 20 (a surfactant) were added at a rate of 0,1 ml per 50g of sulphur to help 'wet' the sulphur and reduce the flotation of sulphur caused by the air bubbles. Tween 20 was tested and was found to have no inhibitory effects on the growth, unlike other surfactants which markedly reduced the growth rate. (See Appendix 8. Tween 20 has also been found to assist in the bacterial leaching of copper. (61))

The results of this test are given in Appendix 7 and are shown graphically in Figure 16.

An interesting feature displayed in Figure 14 is the apparent linear production rate of hydrogen ions and bacterial nitrogen which was also noted in test 1. (c.f. Figure 13.) The maximum rate of hydrogen ion production in this case is 0,66 μ moles/ml-hr.

Figure 16. Batch Growth Test '2' on Sulphur.

5.5l. 9K soln.
 2%wt/vol. S
 30°C
 Agitation 500 r.p.m.
 pH 3.0
 Air 200 ml/min
 CO₂ 4.0 ml/min



A best fit of the results for nitrogen production gives a maximum production rate of:-

$$\frac{d[N]}{dt} = 0,16 \mu\text{g/ml-hr} \dots\dots\dots 25)$$

Thus:

$$\frac{d[N]}{dt} = Y \times \frac{d[H]}{dt} \dots\dots\dots 26)$$

where Y = 0,24g nitrogen/mole H^+ (yield constant) $\dots\dots\dots 27)$

This yield constant is used in the analysis of data for leaching of pentlandite in Section 4.2.3.

The nitrogen production rate does not appear to be quite as linear as the hydrogen ion production rate, but when considered in the light of the estimated accuracy (10 per cent) of the Micro-Kjeldahl method, this observation is not significant. (See Figure 14.)

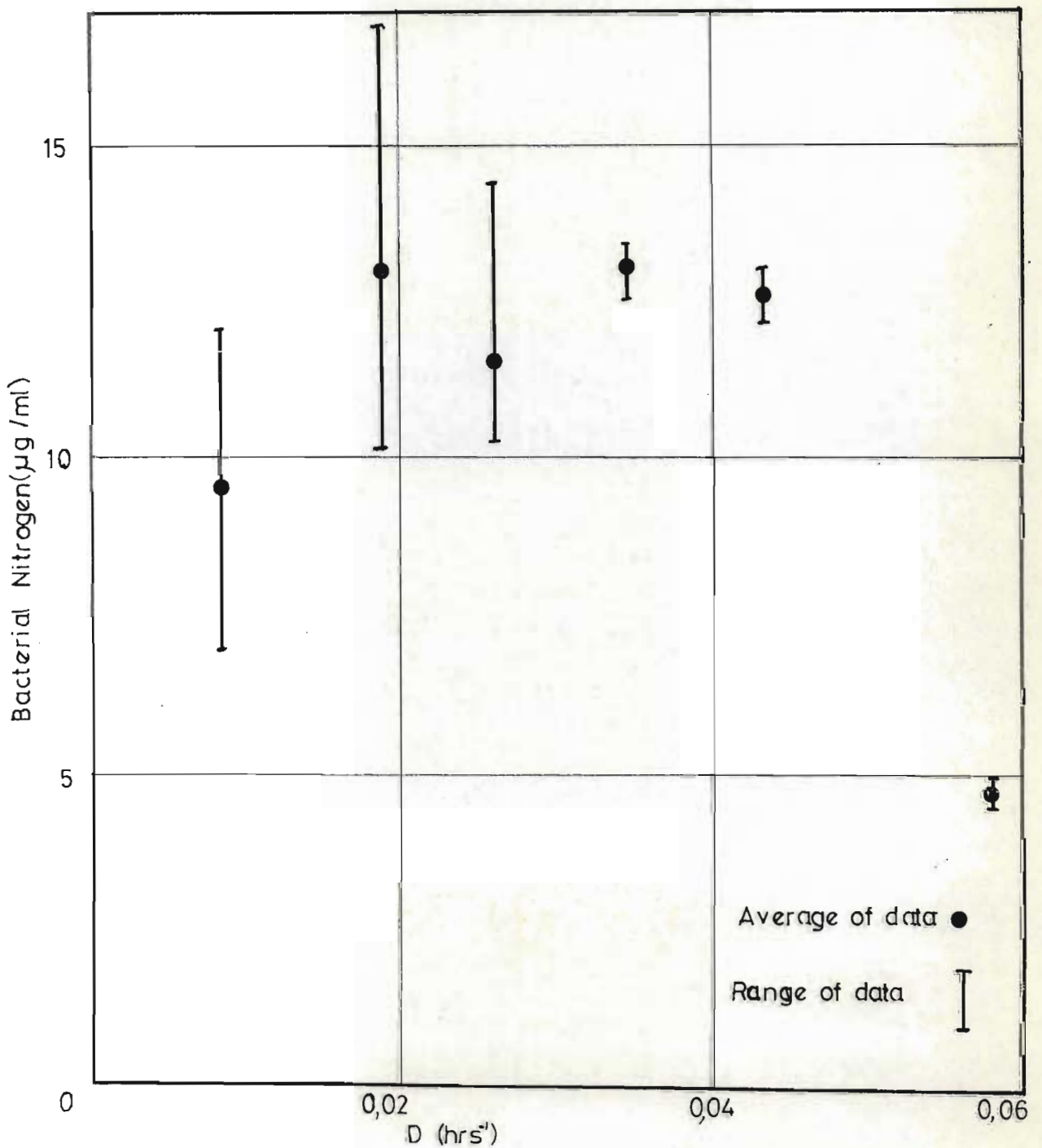
Continuous Growth on Flowers of Sulphur.

The batch growth described above was used to start a constant volume continuous culture, run as a chemostat, the results of which are given in Appendix 7 and are shown graphically in Figure 17. After two reactor volumes of feed had passed into the vessel, steady state condition had been obtained as evidenced by the measured rate of acid production and data were taken after this period. Extreme difficulty was experienced in continuously adding 2 per cent flowers of

sulphur...

Figure 17. Continuous Culture on Flowers of Sulphur

5,5l 9K solution
2% w/v S
30°C
Agitation 500 rpm
pH 3,0
Air 200 ml/min.
CO₂ 4,0 ml/min.



sulphur in the feed. The sulphur blocked the tubing of the peristaltic pump and attempts at adding the sulphur separately also failed. Instead it was decided to add a bulk quantity of sulphur and surfactant every 24 hours directly into the reactor. The amount of sulphur to be added was calculated from the formula $(S_0 - S)V$, where S is the calculated present concentration of sulphur, S_0 is the calculated level to which the sulphur concentration is to be raised to yield a mean value of 2 per cent over the next 24 hours and V is the reactor volume. The derivation of this formula is given in Appendix 9.

Relationship Between Bacterial Nitrogen and Cell Count.

The measurement of bacterial nitrogen is a tedious procedure so that a test was carried out to see if this could be replaced with direct counting. Twelve samples were taken at different stages of the continuous culture operation and analysed for bacterial nitrogen. The same samples were also used to carry out a direct bacterial count using the Petroff-Hausser bacterial counting chamber and the following relationship established:-

$$1,27 \times 10^7 \text{ cells} \equiv 1 \mu\text{g} \pm 0,15 \text{ nitrogen} \dots\dots\dots 28)$$

The twelve sets of results shown in Appendix 10 did not differ by more than 15 per cent from this average value.

Continuous Growth on Sulphur Prills.

It was noted during these growth tests on sulphur that the

oxygen/...

oxygen concentration in solution was generally well below the air saturation level. This would seem to indicate that the rate of growth was being limited by the transfer of oxygen from the air bubbles into the liquid phase and would explain the linear nature of the growth curves in Figures 13 and 14. It was decided to carry out a growth test in which the rate limiting feature was not the transfer of oxygen from gas bubbles.

If the available surface area of sulphur is extremely high, as is the case with finely powdered flowers of sulphur, then the oxygen demand is very high and one has to use extremely vigorous rates of agitation before mass transport can be rendered non-rate-limiting. Such conditions can for example, be achieved using sonic energy or high frequency vibromixing. Several workers have pointed out that under such conditions the bacterial growth may be affected because of the prevention of the necessary close contact between bacteria and solid substrate. (61, 62). One way to overcome this dilemma is thus to decrease the sulphur surface area so that mass transport from gas bubbles may become non-rate-limiting at a lower input of mechanical energy per unit volume of solution.

To decrease the surface area, molten sulphur was poured into cold water to form uniform spherical prills. The prills were screened to -4 +8 mesh. The prilled sulphur was subjected to X-ray diffractometric analysis in order to check that the

crystalline/.....

crystalline structure had not been altered by this treatment and thus introduce an unknown parameter. The structure was found to be completely orthorhombic, the same structure as the original flowers of sulphur.

To further ensure that the availability of some nutrient in the 9K medium was not rate-limiting, it was decided to carry out the growth test in a continuous pH-stat operation rather than run the reactor as a chemostat. In chemostat operation, medium is added to the reactor at a fixed dilution rate and the culture is allowed to select its own growth rate. (63) It is possible in this system that at low dilution rates when the bacterial population is high, some nutrient may become rate-limiting. With the pH-stat system the dilution rate is automatically selected according to the rate of production of hydrogen ions. The automatic titrator was used to control the system at pH 3. Fresh medium was added at a pH of 7,26. As hydrogen ions were produced in the reactor as a result of bacterial growth on the sulphur prills, so the automatic titrator would add fresh medium at the higher pH to compensate for the drop in pH in the reactor. Thus an equilibrium dilution rate was selected by the culture according to the rate of production of hydrogen ions which is directly related to the rate of bacterial growth.

The conditions of the experiment were as in the case of batch test 2. Five hundred grams of sulphur prills were added to 9K

medium/.....

medium in the 5,5 ℓ reactor. The prills displaced 300 ml so that the effective solution volume was 5,2 ℓ. The stirring rate was varied from 1 to 1 000 r.p.m. At least two volume equivalents were allowed to enter the reactor before the equilibrium dilution rate was measured at each rate of agitation. The effect of agitation on dilution rate, i.e. growth rate, is shown graphically in Figure 18 and the data are tabulated in Appendix 7. The results show that under the conditions of the experiment, agitation has a marked effect on the dilution rate. Dissolved oxygen was metered at all levels of agitation and found to correspond to the saturation value in each case.

The rate of production of hydrogen ions and hence bacterial growth rate may be calculated from the dilution rate by carrying out a mass balance on hydrogen ions. (See Appendix 11.)

This gives the relationship:-

$$P = D \times 5,3 \times 10^{-3} \text{ moles/ℓ-hr} \dots\dots\dots 29)$$

P = rate production of hydrogen ions

D = dilution rate.

The relationship in Figure 18 between dilution rate and rate of agitation may be written as:-

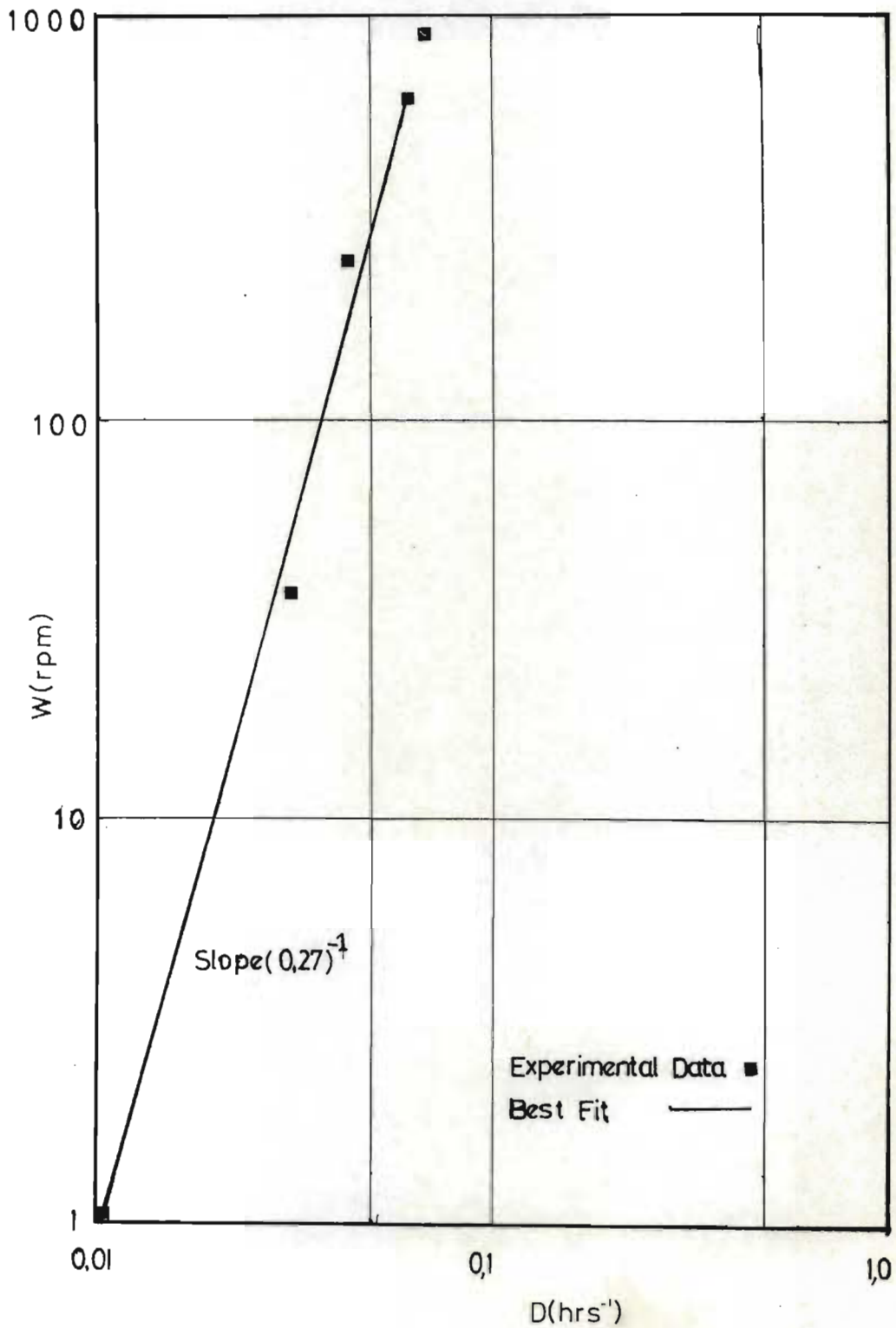
$$D = k \cdot W^{0,27} \dots\dots\dots 30)$$

where k is a constant

and W is the angular velocity of the stirrer.

Figure 18. Dilution Rate vs. Agitation Rate
(Continuous Culture, run as pH Stat)

5,2 l 9K soln.
500g S prills
30°C
pH 3
Air 200 ml/min
CO₂ 4,0 ml/min



From equation 27,

$$\frac{d [H^+]}{dt} = P = (5,3 \times 10^{-3}) \cdot k \cdot W^{0,27} \text{ moles/l-hr...31}$$

From equation 24,

$$\frac{d [N]}{dt} = (5,3 \times 10^{-3}) \cdot 0,24 \cdot k \cdot W^{0,27} \mu\text{g/l-hr.... 32}$$

The exponent on W is 0,27 compared to 0,833 found for chemical leaching pentlandite. However under the agitation conditions of this experiment complete suspension of the sulphur prills was not achieved, unlike the total suspension attained with the -200 mesh pentlandite.

Discussion of Growth Tests on Sulphur.

An apparent linear growth pattern was found in these growth studies; 'apparent' because the intrinsic mechanism must still be exponential in that one cell divides to form two cells. The linear characteristics mean that the doubling time is determined by the rate of dissolution of oxygen from the gas phase into the growth solution. It was found when using sulphur prills as the growth substrate that although mass transfer of oxygen from the gas bubbles into the bulk of the solution was non-rate-limiting, agitation still had an effect on growth rate. This implies that mass transport by another mechanism was now the rate limiting step. This mechanism is probably the transfer of some nutrient, possibly oxygen, to the growth sites on the surface of the sulphur prills.

It was/.....

It was clear during these growth tests on sulphur that some of the bacteria were attached to sulphur surfaces while other cells were freely suspended in the liquid. To investigate this effect an experiment was carried out using ordinary flowers of sulphur in batch growth. The concentration of unattached bacteria was measured at different rates of agitation up to 1400 r.p.m. with a propellor stirrer. The concentration of unattached bacteria remained constant up to this rate of agitation, but when a vibromixer was used for vigorous agitation, the concentration of unattached bacteria increased.

It would seem that only when extremely violent agitation is used, are the bacteria prevented from attaching to the sulphur.

In the classical model developed by Monod (65) and others (63) for the operation of a continuous culture, it is assumed that the bacterial population as a whole is in statistical equilibrium. When dealing with growth on a solid substrate, this model may not be valid, especially when one considers that a certain fraction of the bacterial population is attached to the sulphur surface and one can envisage an equilibrium between cells actively growing on sulphur surfaces and others detached from sulphur surfaces. The equilibrium condition is probably a complex function of agitation, surface,

tension/.....

tension, bacterial numbers, surface area of substrate and other factors. To test the above hypothesis the classical Monod relationships were applied to the results of the continuous growth test.

The culture was kept growing at equilibrium (on sulphur prills) for 1 week, running as a pH-stat with $D = 0,013 \text{ hr}^{-1}$. The rate of production of hydrogen ions, P , was calculated to be $0,065 \times 10^{-3} \text{ moles/ml-hr}$. A $25 \mu\text{m}$ membrane filter was attached to the outlet of the vessel. This allowed bacteria and solution to leave as overflow, but retained sulphur in the vessel. The equilibrium bacterial count in the overflow was, (i.e. concentration of unattached bacteria) $X_u = 1,6 \times 10^7 \text{ cells/ml}$, equivalent to a rate of cell production;

$$\left(\frac{dx}{dt}\right)_{\text{measured}} = 20,8 \times 10^7 \text{ cells/l-hr} \dots\dots\dots 33)$$

Using equations 26 and 28 the rate of bacterial cell production can be calculated from P :- (The assumption was made that the batch yield constant applies.)

$$\begin{aligned} \left(\frac{dx}{dt}\right)_{\text{calculated}} &= (0,065 \times 10^{-3}) \times 0,24 \times \frac{14 \times 10^7}{11 \times 10^6} \\ &= 19,75 \times 10^7 \text{ cells/l-hr} \dots\dots\dots 34) \end{aligned}$$

This value exhibits a reasonable agreement with the measured rate of cell production.

At the end of the run when equilibrium conditions still applied, the contents were stirred vigorously for 1 hour with a vibromixer/.....

a vibromixer and a representative sample taken for a bacterial count as described in section 3.1.3. The total number of bacteria was found to be $8,1 \times 10^7$ cells/ml; assuming that all attached bacteria are displaced by the vibromixer, the number of attached bacteria, X_A is:-

$$\begin{aligned} &= (8,1 - 1,6) \times 10^7 \\ &= 6,5 \times 10^7 \text{ cells/ml} \quad \dots\dots\dots 35) \end{aligned}$$

A mass balance on bacteria at steady state gives:-

Rate of growth of bacteria = Rate of washout of bacteria

i.e. $\mu X_A = DX_u$, since growth is controlled by X_A

where μ = specific growth rate of bacteria.

$$\therefore \mu = 0,013 \times 1,6 \times 10^7 = 0,0032 \text{ hr}^{-1} \quad \dots\dots\dots 36)$$

This value of μ does not correspond with the measured value of $D = 0,013 \text{ hr}^{-1}$. It appears then that the classical Monod model (65) which gives $\mu = D$ at steady state does not hold for growth on solid sulphur. (The Monod model is based on Chemostat operation and although this test was operated as a pH stat, once equilibrium is established, it is in effect a chemostat.) A more complex situation exists where an equilibrium is established between cells attached to the surface and cells freely suspended in the medium.

Obviously more detailed work could be carried out to study the growth of the bacteria on sulphur, both in batch and continuous operation. The main aim of the present investigation however,

was/.....

was to study the bacterial leaching of nickel sulphide (pentlandite) and the growth tests on sulphur were terminated at this stage.

4.2. Bacterial Leaching of Pentlandite Concentrates.

4.2.1. Batch Leaching.

A wide range of parameters was initially tested using batch culture in order to establish the relative importance of these in the bacterial leaching of nickel from pentlandite concentrates. The higher grade concentrate, assaying 30 per cent nickel, was used in these tests so that unknown factors arising from the presence of gangue materials could be minimised. Conical flasks of 250 ml capacity similar to those employed in the chemical kinetic tests were used in these batch leach experiments. The concept of the tests in the bacterial leaching work was, however, entirely different to that in the chemical kinetic studies. In the latter, the leach rates were measured over a very short period of time as the interest was solely in the initial rate of leaching. In the case of the bacterial leaching tests, the period of leaching was extended because growth conditions were necessary for the bacteria to function.

The use of bacterial concentrates under non-growth conditions in the kinetic experiments was in fact carried out. It was found that no significant effects were obtained under these conditions and it was concluded that bacterial leaching could only be studied under conditions in which the cells were growing.

A typical batch growth curve for bacteria is shown in Figure 19. The curve is characterised by:-

- 1) An initial lag phase in which the bacterial cells are preparing for growth.
- 2) A growth phase in which the cells multiply. In this phase the cell numbers continuously double after a fixed period of time, called the generation time. This is the average time between cell divisions. The shape of the growth curve is usually exponential during this phase.
- 3) A stationary phase in which some nutrient in the growth medium is exhausted.

From the previous discussion it would appear that bacterial leaching of nickel is growth-associated so that one would expect the batch leach curves to have a similar shape to a typical batch growth curve. A typical experimental leach curve is shown in Figure 22. It is seen that in this curve and the subsequent experimental leach curves (Shown in Figures 23-25) the various phases discussed previously are not clearly defined. It is not possible to tell whether the 'growth' phase is exponential or linear. The curves generally show a 'kink' near the beginning of the leach period, after which the nickel concentration increases steadily until a stationary phase is reached. The significance of this stationary phase is discussed later on in this section.

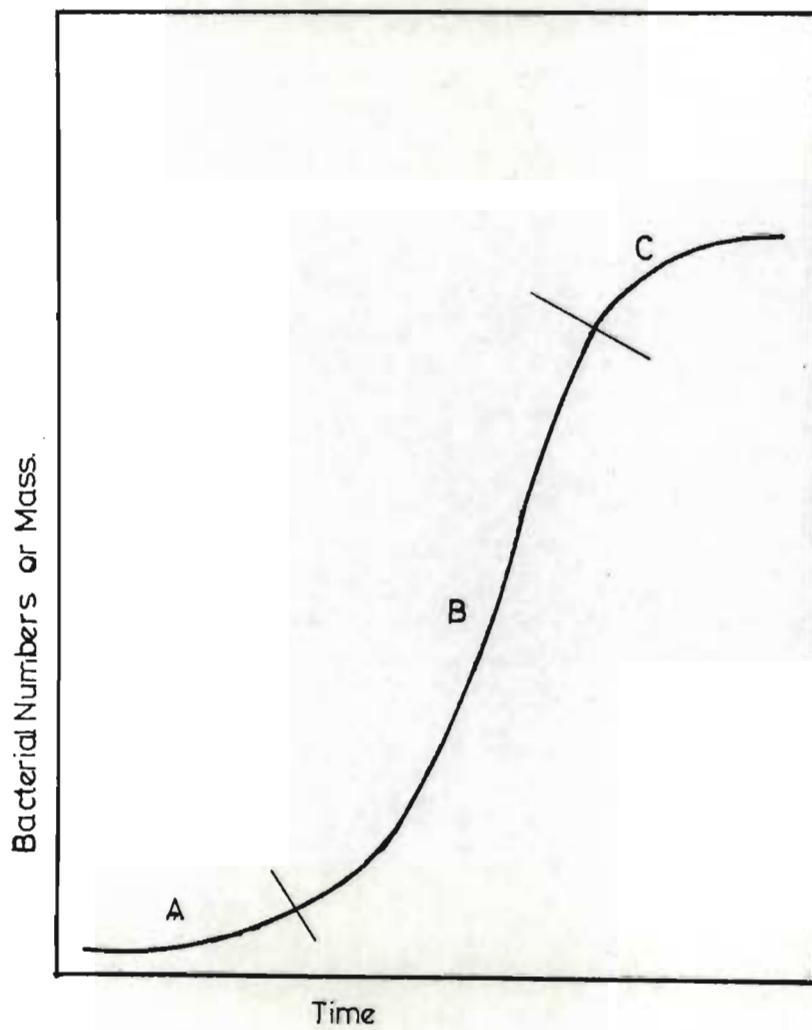
Exponential/....

Figure 19. Typical Batch Bacterial Growth Curve.

A = Lag Phase.

B = Growth Phase (exponential).

C = Stationary Phase.



Exponential type growth is obtained if the growth rate is controlled by the number of bacteria. The growth pattern is linear if growth is limited by the availability of some nutrient at the surface of the bacteria. From the experimental data in Figures 22-25 one cannot say if the growth, or leaching, is of a linear or exponential nature. The leach rate is seen to drop when the nickel concentration reaches about 20 g/l Ni^{++} ; (unless the extraction approaches 100% prior to this.) It is considered that this ceiling value of 20 g/l may be due to a toxicity effect of the Ni^{++} ions. If this ceiling value could be removed it may be possible to obtain more data points and hence determine with more confidence whether the leach pattern is exponential or linear.

An experiment was therefore designed to remove soluble nickel and iron from the leach solution so that the form of the leach curve may be resolved. This was accomplished using dialysis as described below.

Leaching - Coupled with Dialysis of the Nickel.

This experiment was carried out to establish whether or not the nickel cations were having any inhibitory effects on the growth of the bacteria prior to the toxic limit of approximately 20 g/l. To do this the nickel which was leached was continuously removed by dialysis through a

0,22 μm pore-size Millipore membrane and collected on Dowex-50 ion-exchange resin.

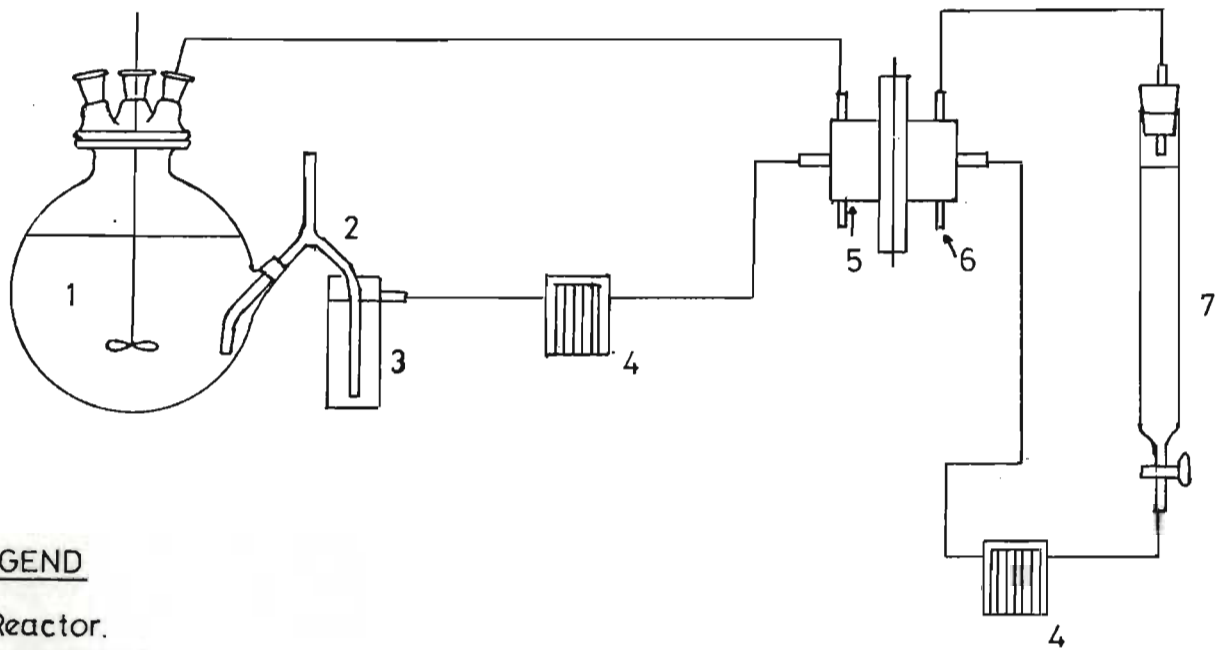
The batch growth was carried out in the 5,5 l reactor and solution was circulated continuously using a peristaltic pump to the dialysis chamber (see Figure 20.) The membrane was held in position in a teflon holder, made in two halves and clamped together. A closed loop containing 9K solution at the same pH (2,5 approximately) as that in the reactor was circulated on the ion exchange side of the membrane. The ion exchange columns were packed with 500g of resin and stripped with 15% w/w sulphuric acid every 2 or 3 days. After stripping the columns were re-loaded with a 9K solution, so that no 9K salts were removed from the leaching system.

Prior to this procedure, a 1,0 μm pore-size membrane was used. The bacteria were found to enter the ion exchange circuit and were adsorbed onto the resin. This problem was overcome using the smaller pore-size membrane.

Pentlandite concentrates were leached at a pulp density of 5 per cent, at 30°C and at a pH of 2,0 to 2,5. Agitation was at 200 r.p.m. using a propellor-type stirrer and air was added to the reactor at a rate of 500 ml/min. The oxygen concentration in solution was metered and found to be at air saturation throughout the

experiment/.....

Figure 20. Apparatus used for Dialysis Experiment

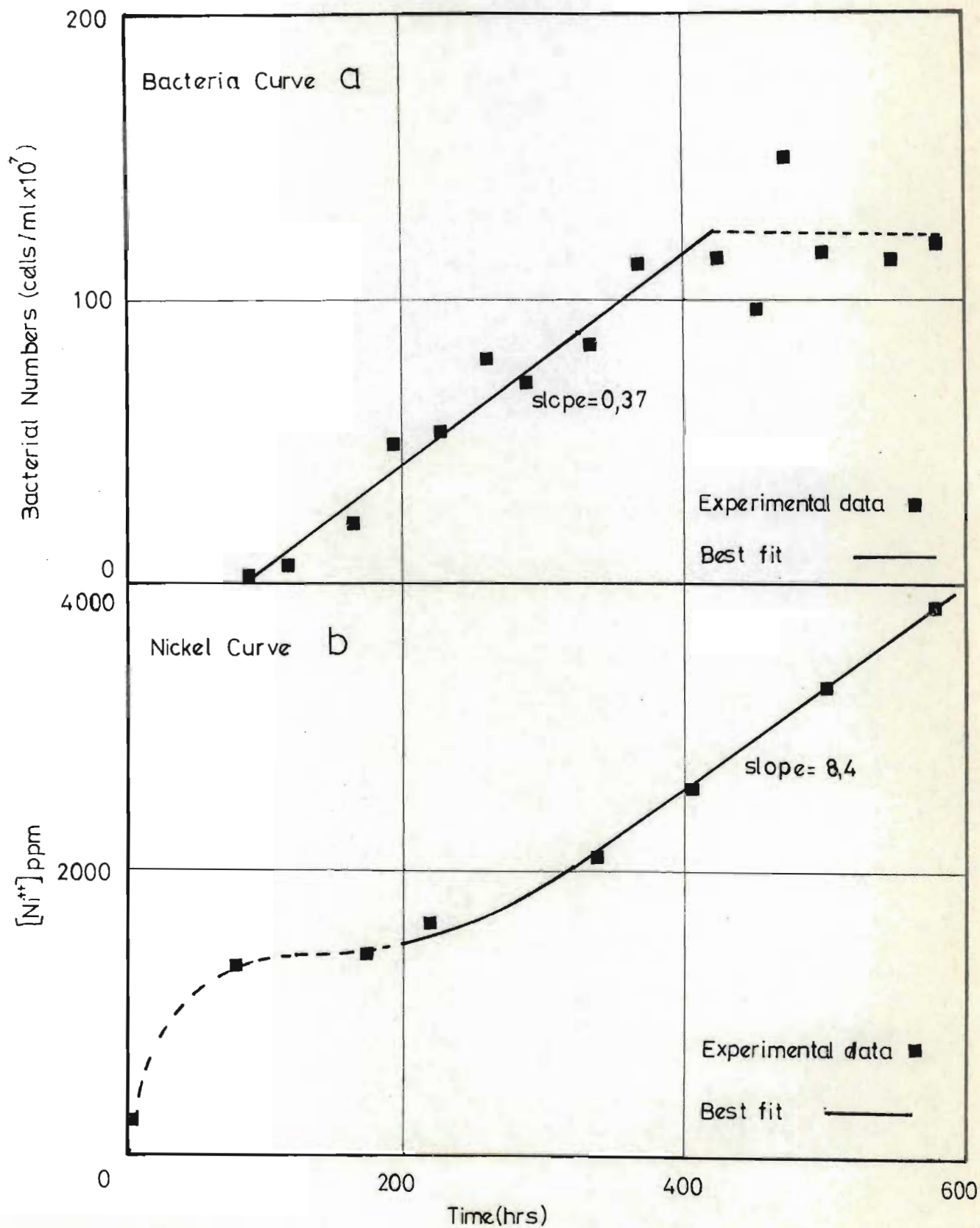


LEGEND

1. Reactor.
2. Goose-neck.
3. Settler.
4. Peristaltic (finger) pumps.
5. Membrane holder.
6. Drain.
7. Ion-exchange column.

Figure 21. Bacterial Leaching- Dialysis of Ni^{++}

9K
 pH 2,0-2,5
 W 200rpm
 Gas-Air
 5 % w/v Pentlandite



experiment. The solution was inoculated with bacterial concentrates prepared from an active culture growing on pentlandite. Bacterial numbers were counted daily while the total amount of nickel leached was calculated from the quantity of nickel collected on the ion-exchange columns. The theoretical concentration of nickel (i.e. the concentration of nickel in the reactor had the nickel not been removed by ion-exchange) was calculated and used to plot a leach curve. The results are shown graphically in Figures 21a and 21b and the detailed experimental data are given in Appendix 13.

It may be seen that after a lag of about 100 hours the bacterial numbers started to increase. Up to 400 hours there was a general linear increase in bacterial numbers up to about 130×10^7 cells per ml. Thereafter there was a noticeable levelling-out of the rate of increase of bacteria.

The calculated nickel concentration initially rose rapidly to about 1 500 mg/l (due to the leaching of oxidised nickel at the surface,) and then increased slowly for 200 hours. After this the rate of nickel leaching increased and reached a constant value (linear kinetics) of about 8,5 ppm/hr which was maintained up to 600 hours. The nickel leaching appeared to lag slightly behind the bacterial growth. Iron leaching followed a pattern similar to that of

the/.....

the nickel. The actual nickel and iron concentrations in the leach solutions remained at 400 mg/l \pm 50 mg/l during the experiment.

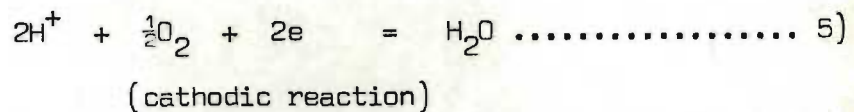
The removal of nickel (and iron) had no significant effect on the bacterial leaching pattern. The kinetics were linear and the rate of leaching was equivalent to that expected in similar conditions (See Figures 22-25) had the nickel not been continually removed from the leach solution.

In view of the results of the dialysis experiment, the linear portion of the leach curves, after the initial kink, in all the subsequent batch experiments were taken as a unique description of the leach rate.

Effect of Pulp Density.

Pentlandite concentrates were leached in 9K solution at pH 3.0. Air was bubbled into the solution which was agitated with a paddle stirrer at 200 r.p.m. The temperature was controlled at 30°C. The pulp density was varied from 5 per cent to 20 per cent solids w/v. The leach solutions were inoculated with bacterial concentrates prepared from an active culture growing on pentlandite. Inoculum was added to give an initial cell count of 10^7 cells/ml in each case. Sterile control leaches were also carried out.

The leach curves are shown in Figures 22-25 while detailed experimental data are given in Appendix 14. In the case of the controls, the pH rose steadily because of the consumption of hydrogen ions in the leaching process by a reaction of the following type:-



Eventually the leach rate dropped off at the higher pH levels.

In the case of the bacterial leaching tests, bacterial production of sulphuric acid maintained a fairly constant pH in the solutions and the nickel leach rates were higher than in the sterile controls either until extraction of nickel was virtually complete (5 per cent pulp density) or until approximately 20 g/l nickel concentration was leached.

The leach rate at each pulp density was estimated from the linear portion of the leach curve. Figure 26 shows the linear relationship obtained between leach rate and pulp density. A high (95 per cent) extraction was obtained using 5 per cent solids when the concentration of nickel in solution reached 14 000 ppm. The final percentage extraction was progressively lower as the pulp density was increased, since the maximum amount of

nickel/.....

Figure 22. Batch Bacterial Leaching of Pentlandite Concentrates (5% pulp density)

9K Solution
pH 3,0
30°C
W 200 rpm
Gas Air

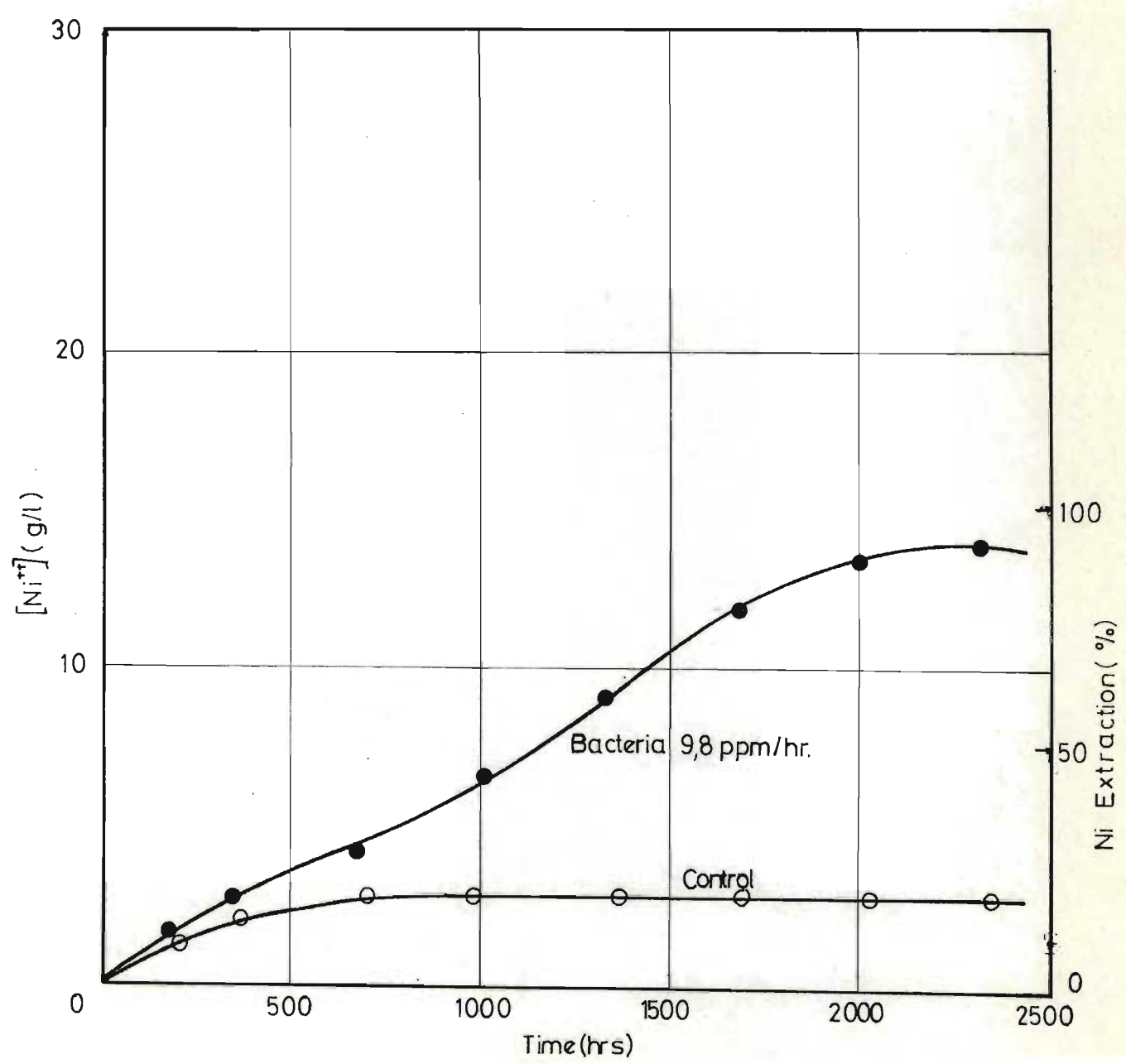


Figure 23. Batch Bacterial Leaching of Pentlandite Concentrates (10% pulp density)

9K Solution
pH 3,0
30°C
W 200rpm
Gas Air

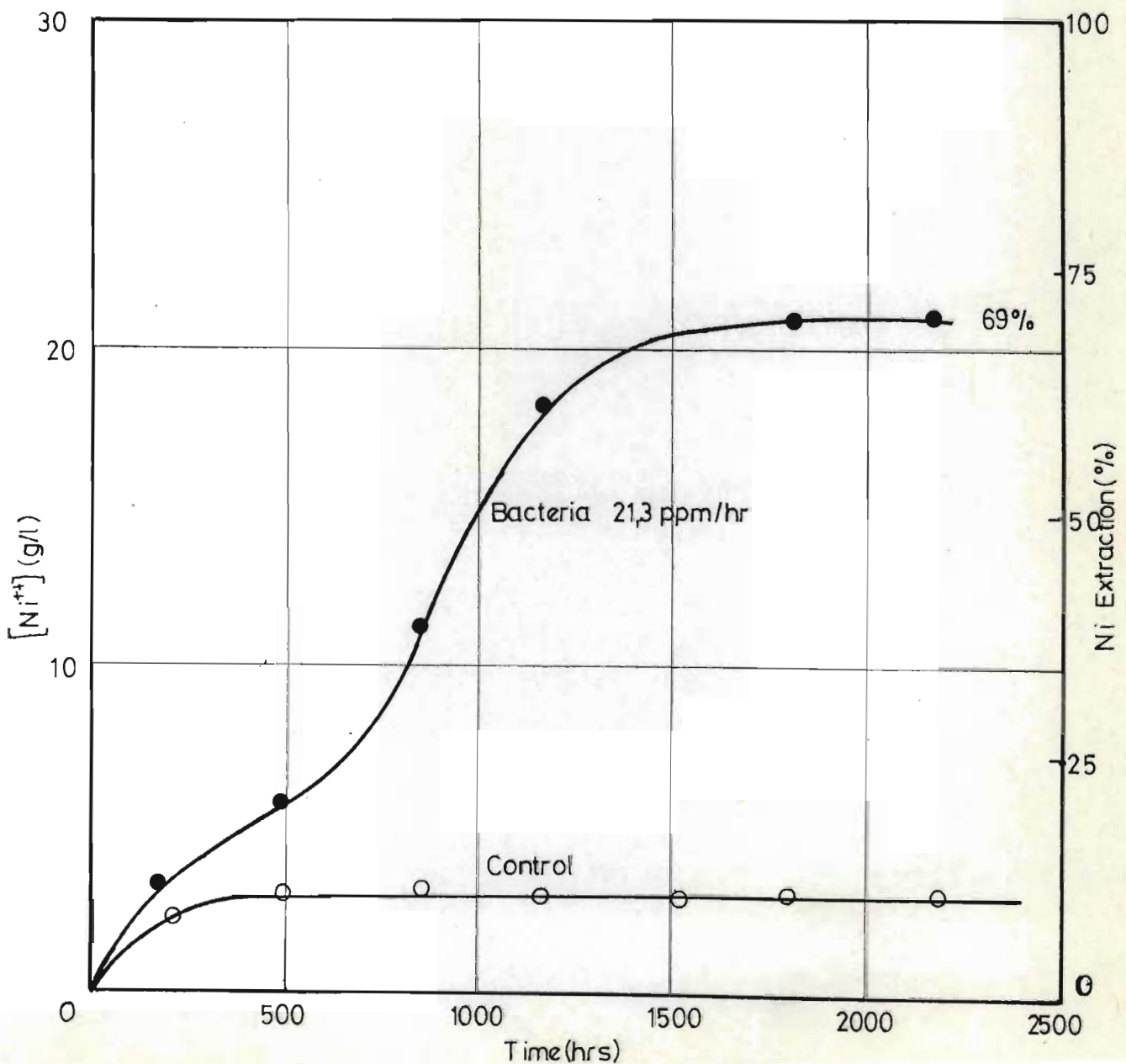


Figure 24. Batch Bacterial Leaching of Pentlandite Concentrates (15% pulp density)

9K Solution
pH 3,0
30°C
W 200rpm
Gas Air

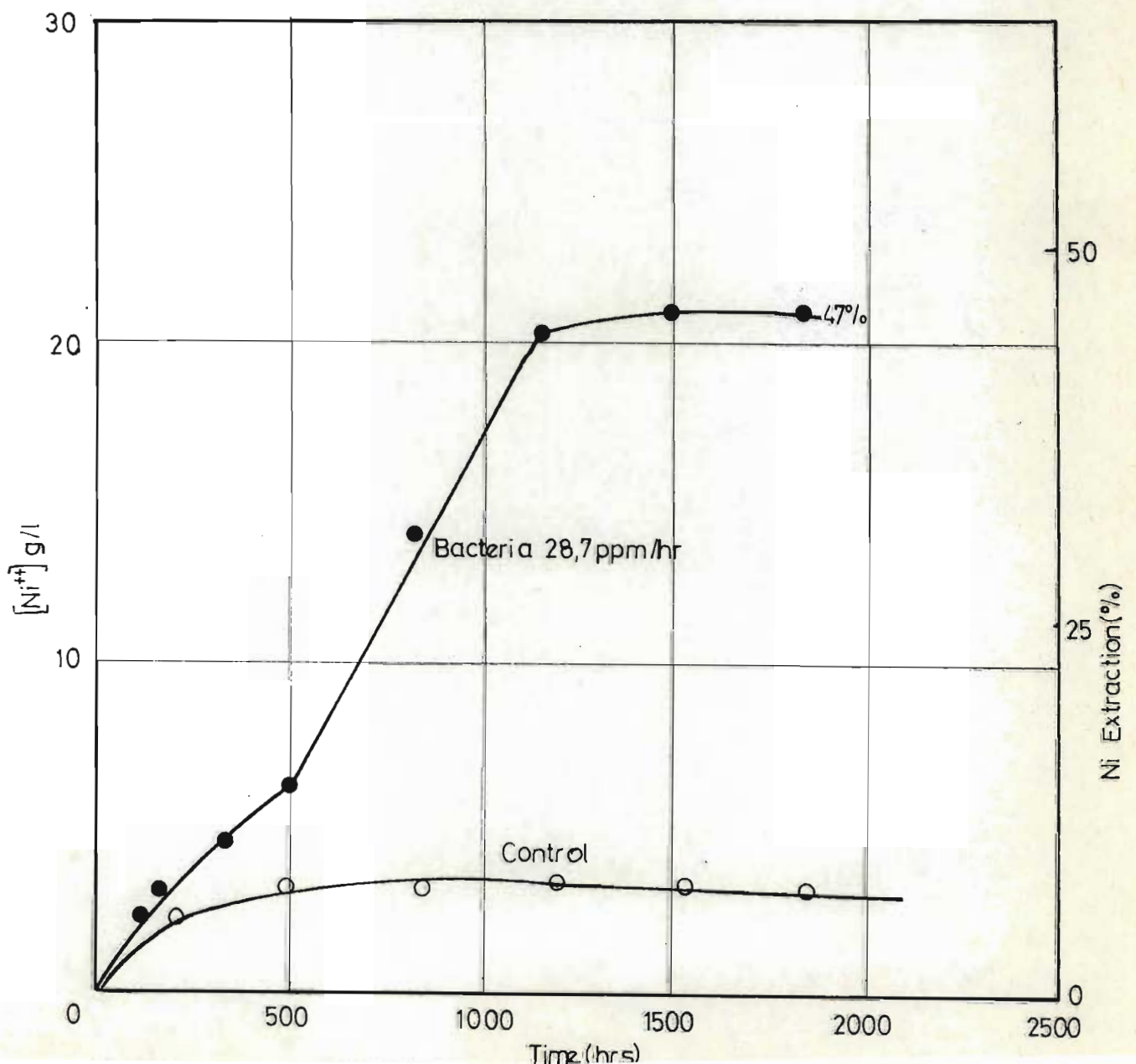


Figure 25. Batch Bacterial Leaching of Pentlandite Concentrates(20%pulp density)

9K Solution
pH 3,0
30°C
W 200 rpm
Gas Air

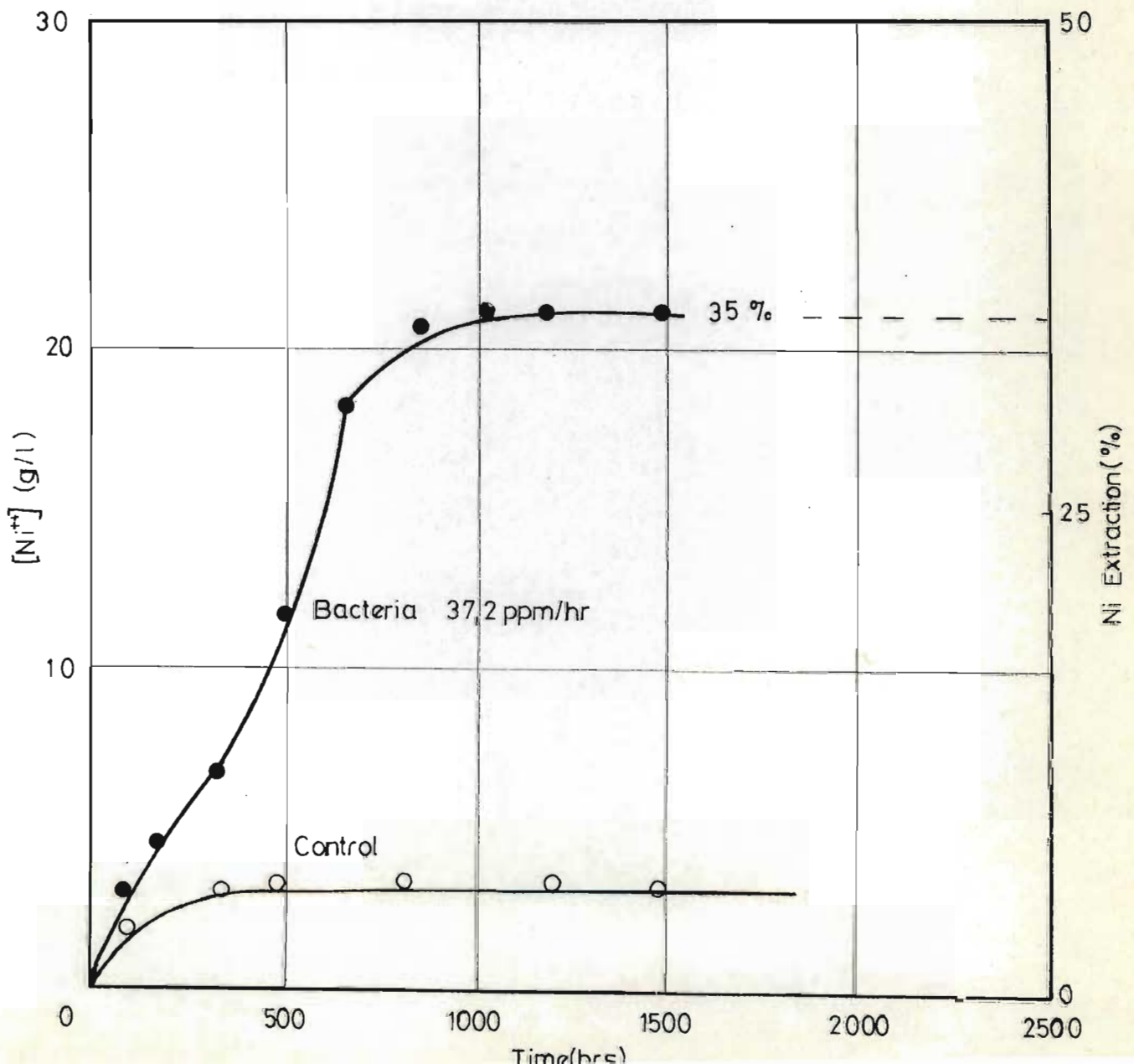
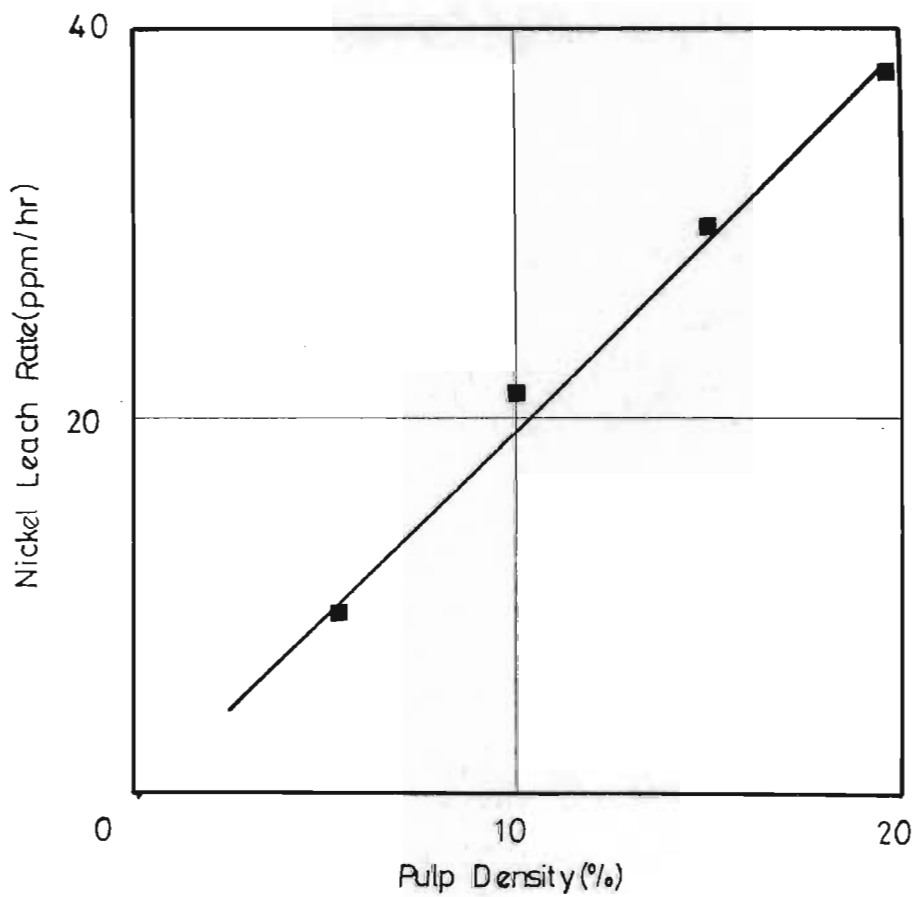


Figure 26. Batch Bacterial Leaching Rate
as a Function of Pulp Density.

9K Solution
pH 3.0
30°C
W 200 rpm
Gas Air



nickel that could be leached in all cases was about 21 000 ppm. This is probably due to nickel becoming toxic to the bacteria above this concentration.

Effect of pH.

Pentlandite concentrates were leached as a 20 per cent slurry under the conditions described in the pulp density tests. The pH of the leach solutions was varied from 1,5 to 5,0.

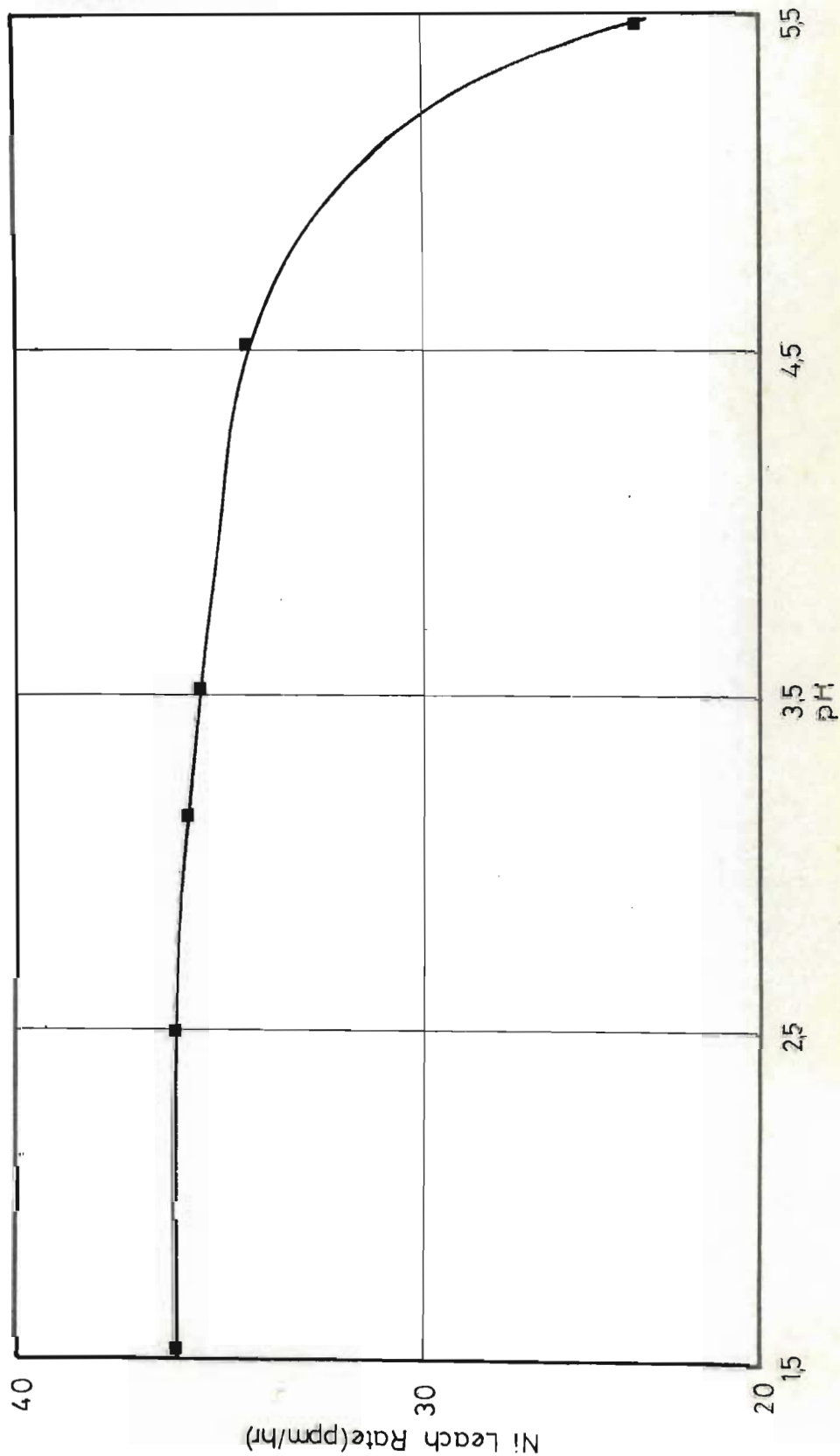
The leaching patterns of the tests and controls were similar to those in the pulp density tests, with the pH rising in the sterile controls while staying fairly constant in the presence of active bacteria. (The detailed experimental data are given in Appendix 14.) The leach rates were measured from the leach curves and Figure 27 shows that these are virtually independent of pH in the range 1,5 to 4,5. Above pH 4,5 there was a sudden decrease in the rate of nickel extraction.

In the case of these tests, the iron leach pattern was also investigated. Below pH 4,0 the iron was leached in approximately equal stoichiometric amounts to the nickel. Above pH 4,0 however, the leach rate of iron was lower than the leach rate of nickel due to the precipitation of iron as a reddish brown insoluble substance identified mineralogically by X-ray diffraction analysis to be ammonium jarosite. Thus, as expected, the

leaching/....

Figure 27 Batch Bacterial Leaching
Rate as Function of pH.

9K Solution
30°C
W 200 rpm
20% w/v pentlandite
Gas Air



leaching of iron is greatly dependent on pH in the range 1,5 to 5,0 because of the instability of soluble ferric species above pH 4,0.

In a situation like dump leaching it is normal to get a drop in pH of the leach liquors from near neutrality to pH 2,5. Usually an excess of sulphur exists in the form of pyrite so that if the gangue rock does not consume an excessive amount of acid, the pH will drop. In these present tests, a high purity pentlandite was used and the acid production was balanced by the usage of acid in the leach reactions so that the pH remained static.

Effect of Agitation.

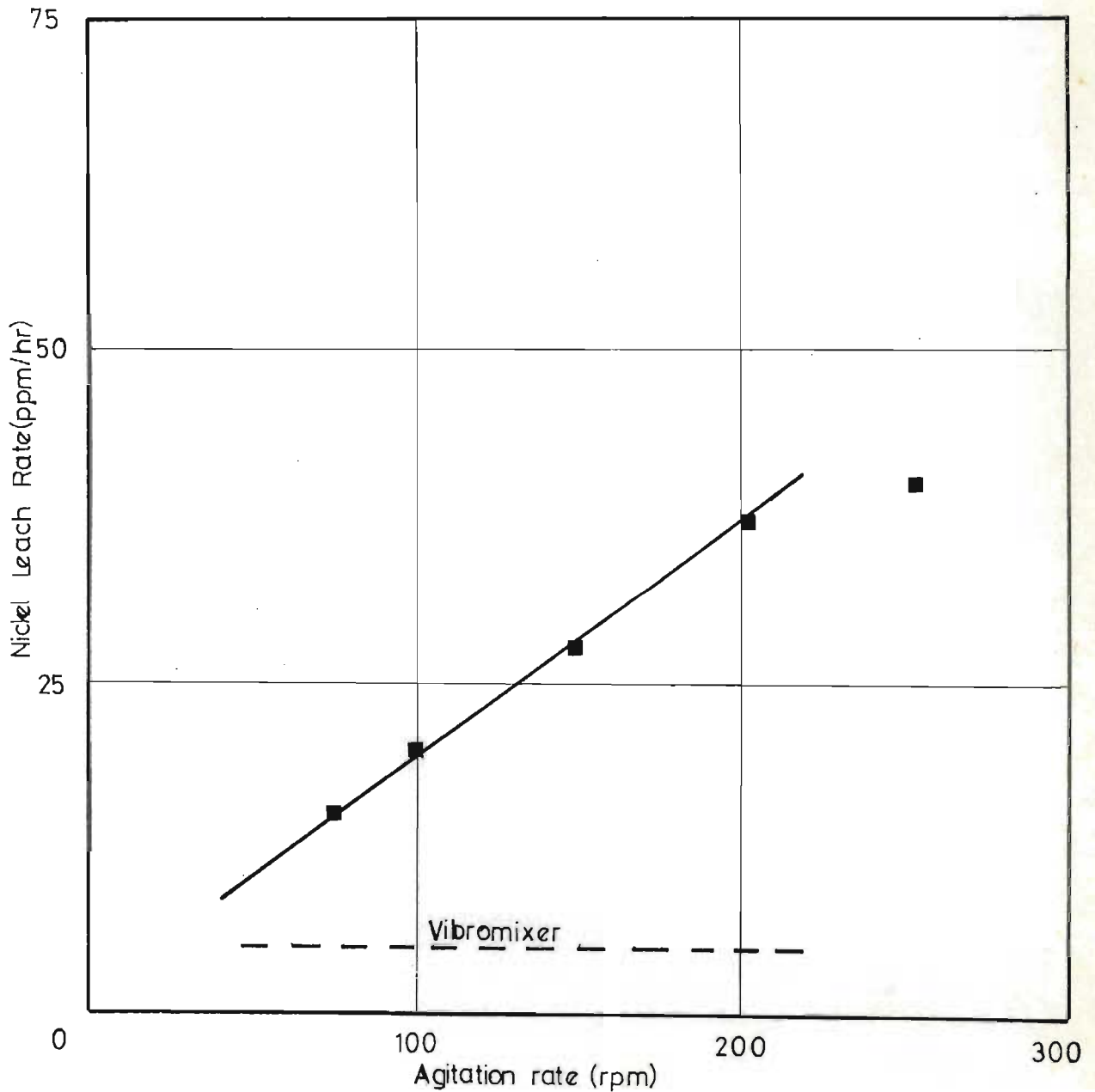
Pentlandite concentrates were leached as a 20 per cent slurry with air under the conditions described previously. The agitation rate was varied from 75 to 250 r.p.m. (The detailed experimental data are given in Appendix 14.) The maximum leach rate was obtained from the leach curves and Figure 28 shows the relationship between the maximum rate of nickel leaching and agitation rate.

A further test was carried out to investigate the effect of highly vigorous agitation. The paddle-type stirrer was replaced with a vibromixer, type Chemap E1. This

gives/.....

Figure 28 Batch Bacterial Leaching Rate as a Function of Agitation Rate (w)

9K Solution
30°C
pH 3.0
20% w/v pentlandite
Gas Air



gives an extremely vigorous turbulence in the leach solution. The leach curve under these conditions is shown in Figure 29 while experimental data is given in Appendix 14. It is seen that bacterial leaching is inhibited to some extent under conditions of violent agitation. This inhibition is similar to the agitation effect on the growth of bacteria on sulphur discussed in Section 4.1.2. Increasing agitation would appear to be beneficial in bacterial leaching, up to an optimum value, after which the bacterial growth is impeded by excessive turbulence.

The rate of leaching measured at 250 r.p.m. does not fit the linear relationship of the other data. In light of the results on sulphur where agitation was carried out at higher levels without causing a decrease in leach rates, no significance has been attached to this odd data point in Figure 28.

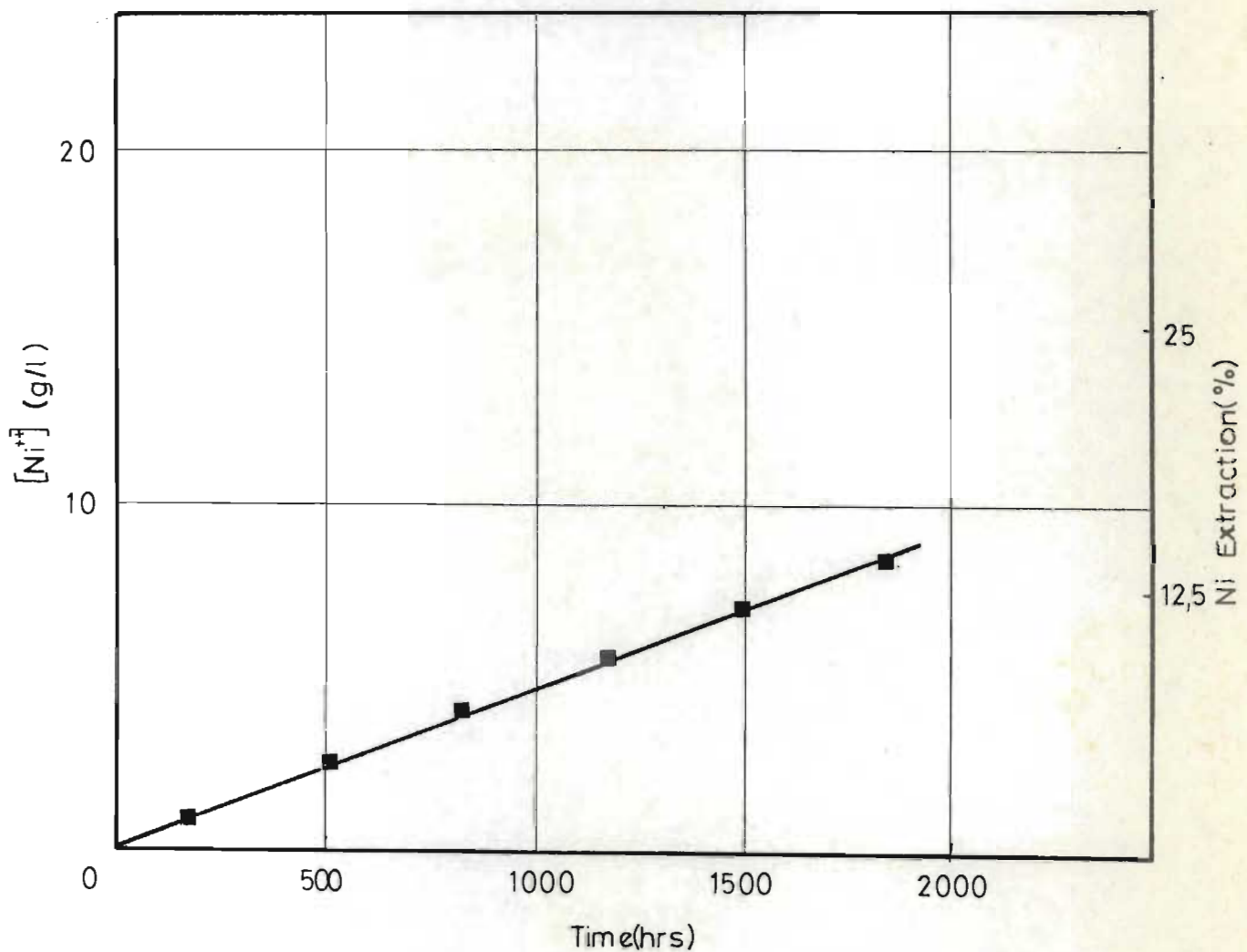
Effect of Particle Size.

Six size fractions of the pentlandite concentrate, corresponding to those given in Table 3 (Section 3.1.2.) were leached at a pulp density of 5 per cent. The conditions were similar to those previously described. A pulp density of 5 per cent was used so that high levels of extraction could be obtained without the nickel concentration reaching a toxic level. The leaching

characteristics/.....

Figure 29 Batch Bacterial Leaching of Pentlandite Concentrates at 20% Pulp Density.
(Vibromixer Agitation)

9 K Solution
30°C
pH 3,0
20 % w/v pentlandite
Gas Air



characteristics were followed for 1 000 hours. After this period it was found that the -325 mesh fraction was virtually completely leached while the larger screen fractions showed correspondingly decreasing extraction percentages. The relationship between percentage extraction and average particle dimension, based on Tyler Standard screen sizes, is shown in Figure 30. Superimposed on this figure is the size distribution curve for the pentlandite concentrate, taken from Table 3. The theoretical cumulative extraction is also shown. This was calculated:-

$$\text{cumulative extraction} = \sum_{i=1}^6 (W_i \times E_i)$$

W = wt per cent of fraction

E = extraction per cent of fraction

It is seen that extraction efficiency is extremely low for particle sizes above 100 microns, i.e. 150 mesh.

Figure 31 is a logarithmic plot of rate of nickel leaching versus surface area of size fraction. The surface area of each size fraction was calculated according to the method given in Appendix 6. These data are consistent with the line of slope 1,0 drawn on the graph indicating a direct relationship between surface area and leach rate of nickel. This area dependence is typical/.....

Figure 30 Nickel Extraction as a Function of Particle Size (batch bacterial leaching)

9K Solution
 30°C
 pH 3,0
 20% w/v pentlandite
 w 200rpm
 Gas Air

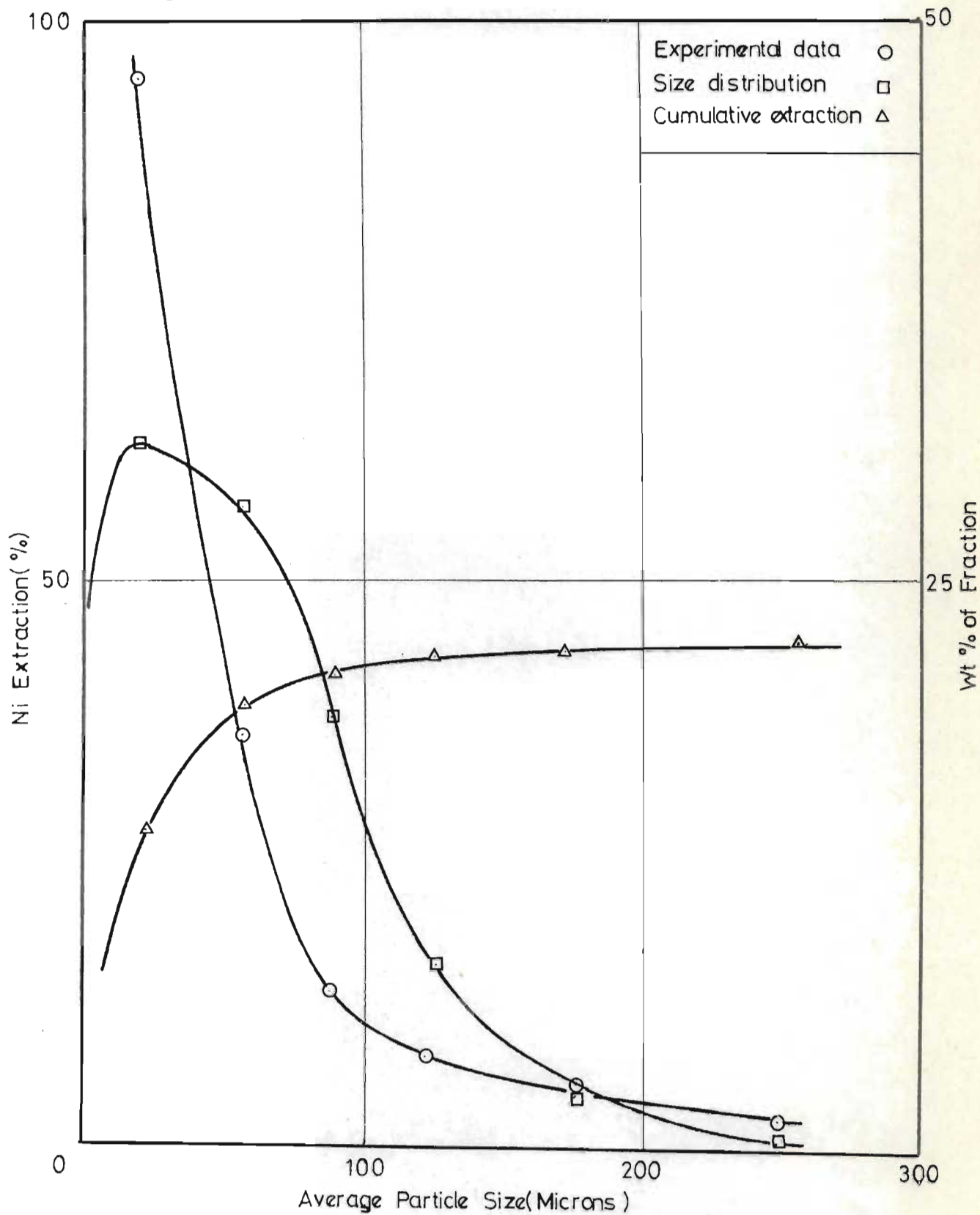
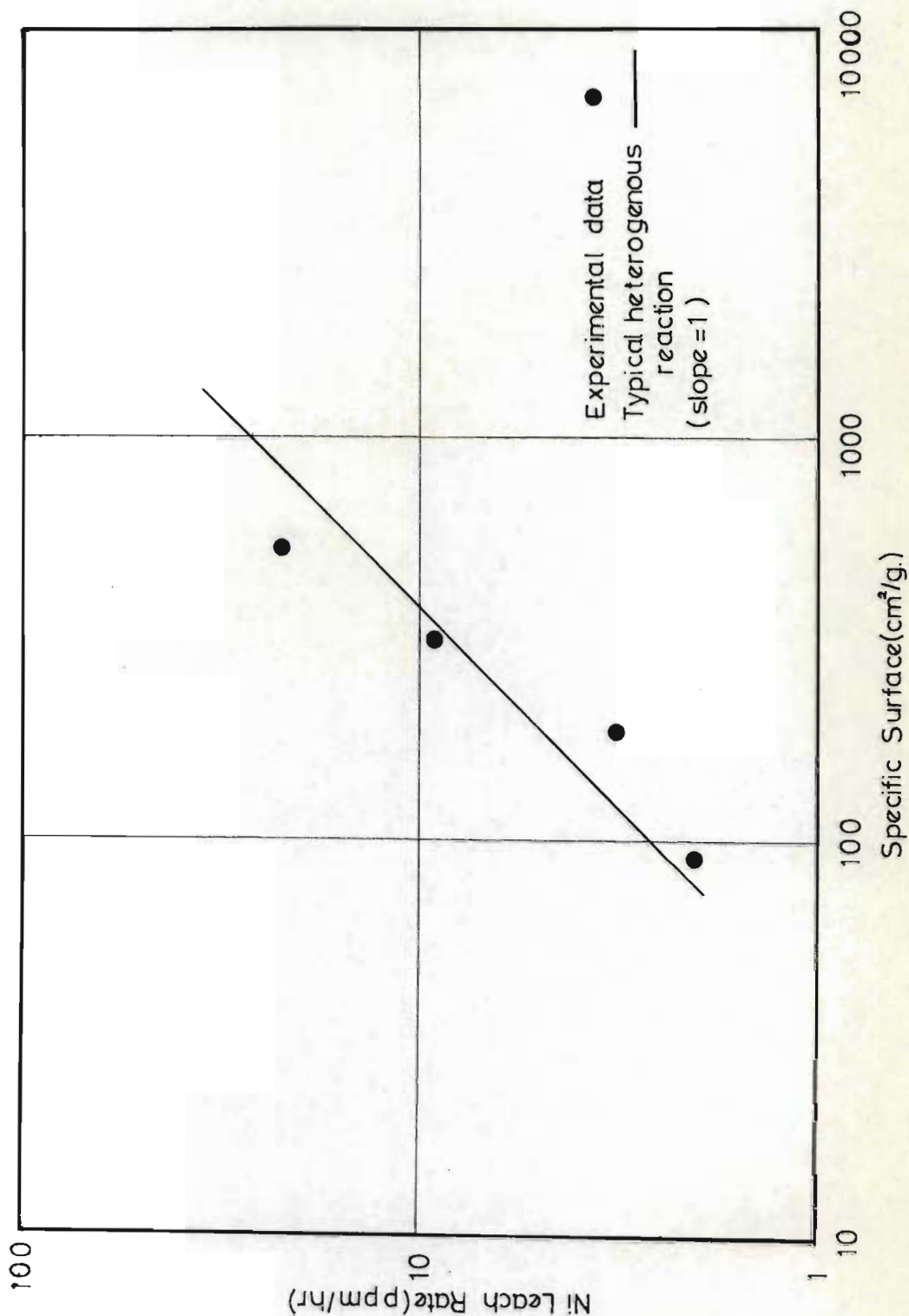


Figure 31. Batch Bacterial Leaching Rate as a Function of Specific Surface Area of Mineral.

9K Solution
30°C
pH 3.0
w 200 rpm

Gas Air
5%w/v pentlandite



typical of a heterogeneous reaction.

Effect of Nutrients.

Pentlandite concentrates were leached at a pulp density of 20 per cent using similar conditions to those described previously. The composition of the nutrient growth medium was altered and leaching carried out using the following compositions:-

- 1) Tap water.
- 2) $(\text{NH}_4)_2 \text{SO}_4 + \text{K}_2 \text{HPO}_4$ in tap water.
- 3) $1/10 (\text{NH}_4)_2 \text{SO}_4 + \text{K}_2 \text{HPO}_4$ in tap water.
- 4) $(\text{NH}_4)_2 \text{SO}_4 + 1/10 \text{K}_2 \text{HPO}_4$ in tap water.
- 5) $1/10 (\text{NH}_4)_2 \text{SO}_4 + 1/10 \text{K}_2 \text{HPO}_4$ in tap water.

Concentrations in the above media are as used in 9K medium or (as indicated by the 1/10 prefix) 1/10 that in 9K.

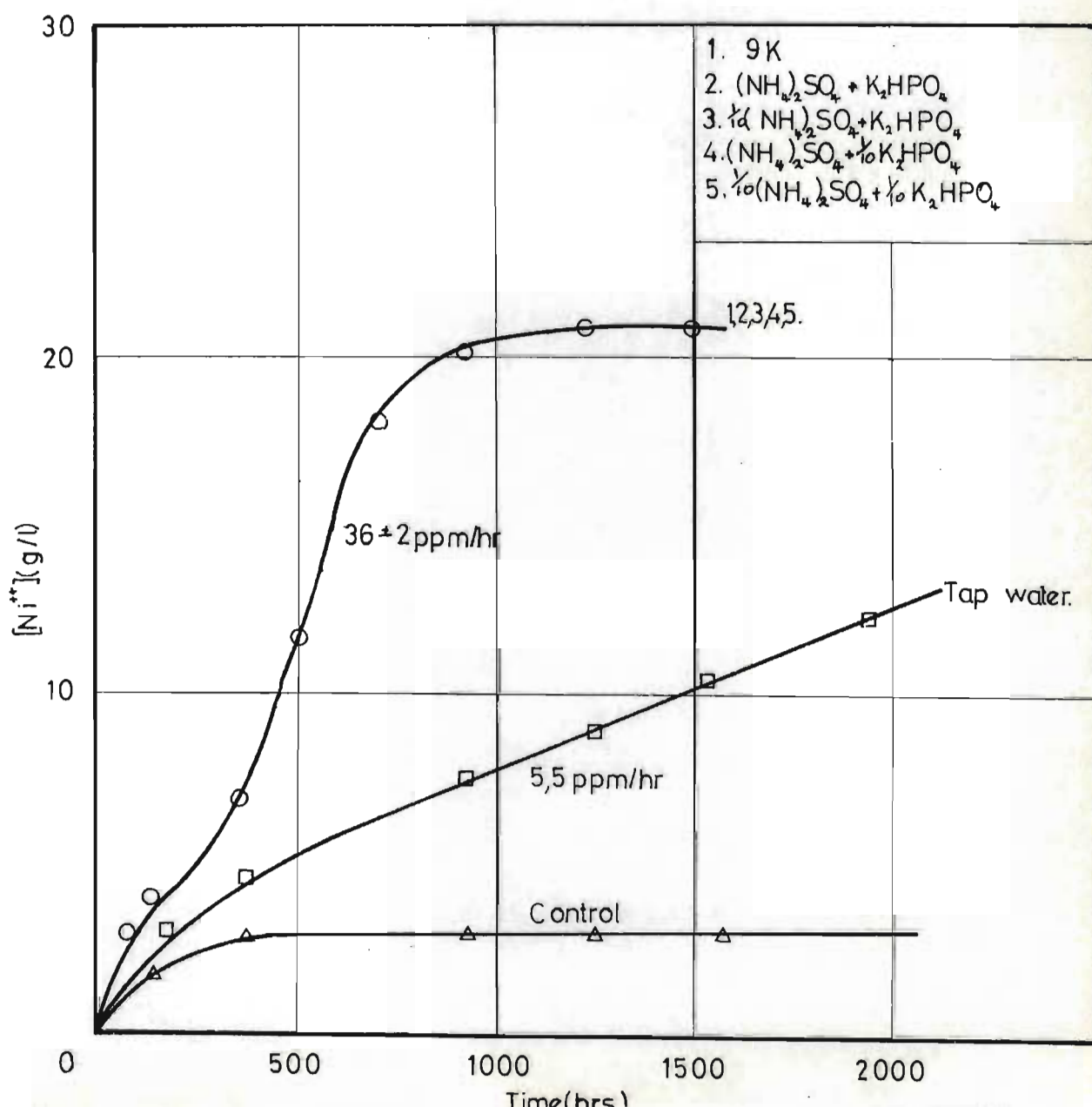
Leaching was carried out for 2 months and the Leach rate of nickel measured over this time period. The results of these tests, together with the results of leaching in 9K medium from the pulp density tests are shown in Figure 32. (The detailed experimental data are given in Appendix 14.)

It is seen that leaving out the trace elements and reducing the nitrogen and phosphorous levels to 1/10 the level of 9K medium has no effect on leach rate. Below

this/.....

Figure 32. Effect of Nutrients on Bacterial Leaching Rate of Nickel.

30°C
 Gas Air
 pH 3,0
 w 200 rpm
 5% w/v pentlandite



this level, leaching is impaired.

Effect of Oxygen Concentration.

Pentlandite concentrates were leached at a pulp density of 20 per cent using similar conditions to those described previously. The concentration of oxygen in the gas bubbled into the solutions was varied from 20 per cent to 80 per cent. The leach rates were measured from the leach curves. Detailed experimental data are given in Appendix 14. Figure 33 shows the relationship between oxygen concentration and leaching rate for batch bacterial leaching of pentlandite concentrates. It is seen that the leach rate increases with increasing oxygen concentration up to about 70 per cent v/v; above this level the leach rate is approximately constant. It is later shown (Section 4.2.2.) that pure oxygen is toxic and an optimum oxygen concentration is therefore implied at approximately 70 per cent.

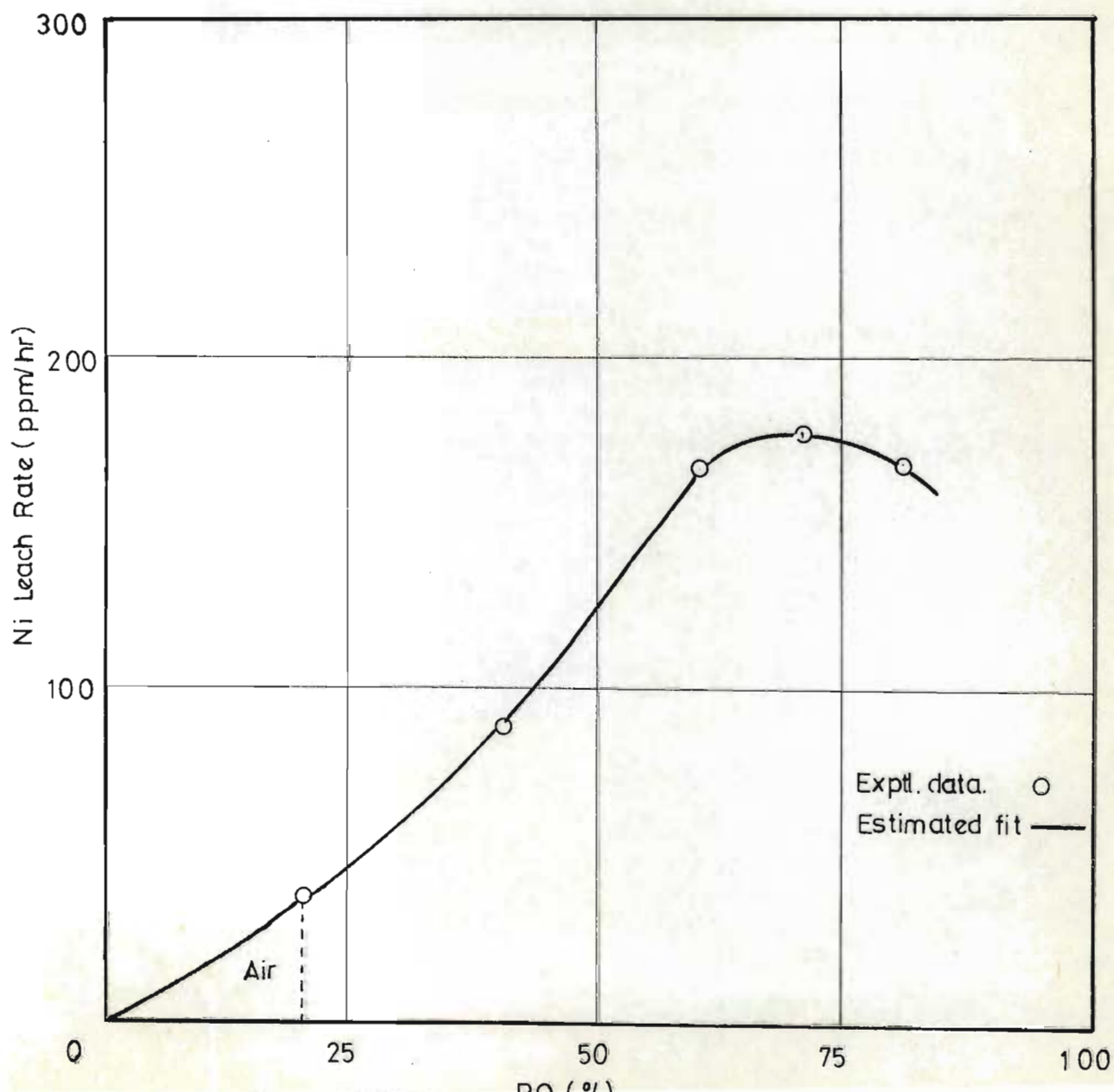
Effect of Carbon Dioxide Concentration.

Pentlandite concentrates were leached at a pulp density of 20 per cent, as described previously. Air was bubbled into the solution and a series of tests carried out by enriching the air with carbon dioxide up to a level of 2 per cent v/v. The leaching rates of nickel were measured from the leach curves. (Detailed

experimental/.....

Figure 33. Batch Bacterial Leaching Rate as a Function of Oxygen Partial Pressure,

9 K Solution
30°C
pH 3,0
W 200 rpm
20% w/v pentlandite



experimental data are given in Appendix 14.) Figure 34 shows the relationship between concentration of carbon dioxide and leach rates of nickel. It is seen that the leach rate is increased by increasing the carbon dioxide level up to 1 per cent v/v. Little increase in leach rate is obtained by further increasing the proportion of carbon dioxide up to 2%.

Effect of Temperature.

Pentlandite concentrates were leached at a pulp density of 20 per cent with air bubbled through the solution as described previously. Tests were carried out by varying the temperature between 25°C and 40°C. The leach rates of nickel were measured from the leach curves at each temperature. Detailed experimental data are given in Appendix 14. Figure 35 shows the relationship between temperature and leach rate of nickel. It may be observed that leach rate increases with temperature.

Discussion of Batch Leach Tests.

It has been shown in these tests that bacteria may be used to leach pentlandite concentrates at fairly high rates and up to reasonably high percentage extractions when the optimum physico-chemical conditions are used. To achieve maximum leach rates a fine grind (-150 mesh), and fairly vigorous agitation are necessary. Air, enriched in oxygen up to 70 per cent v/v should be

supplied/.....

Figure 34 Batch Bacterial Leaching Rate as a Function of Carbon Dioxide Concentration in the Gas Feed.

9K Solution
30°C
pH 3.0
W 200rpm.
Gas Air
20% w/v pentlandite

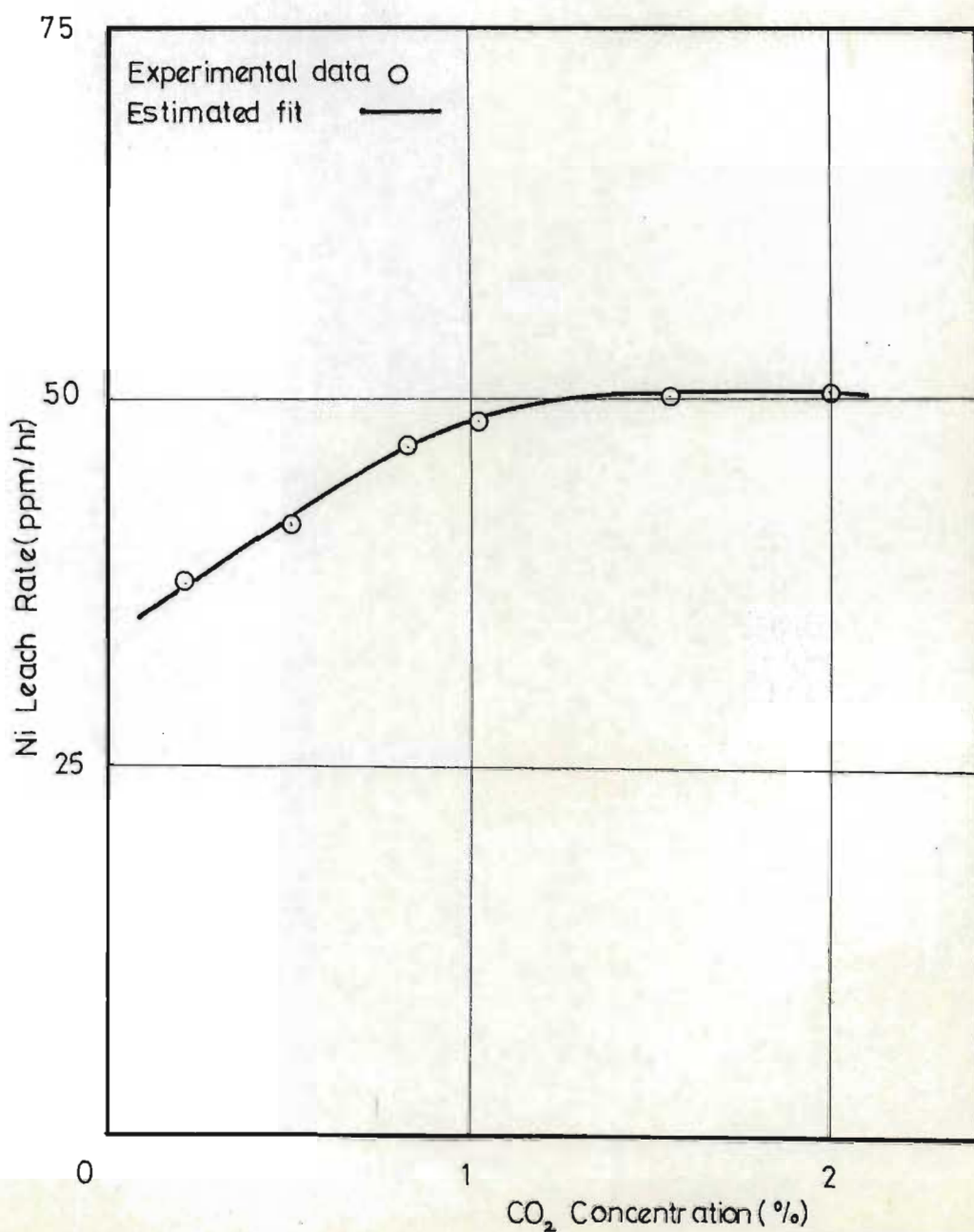
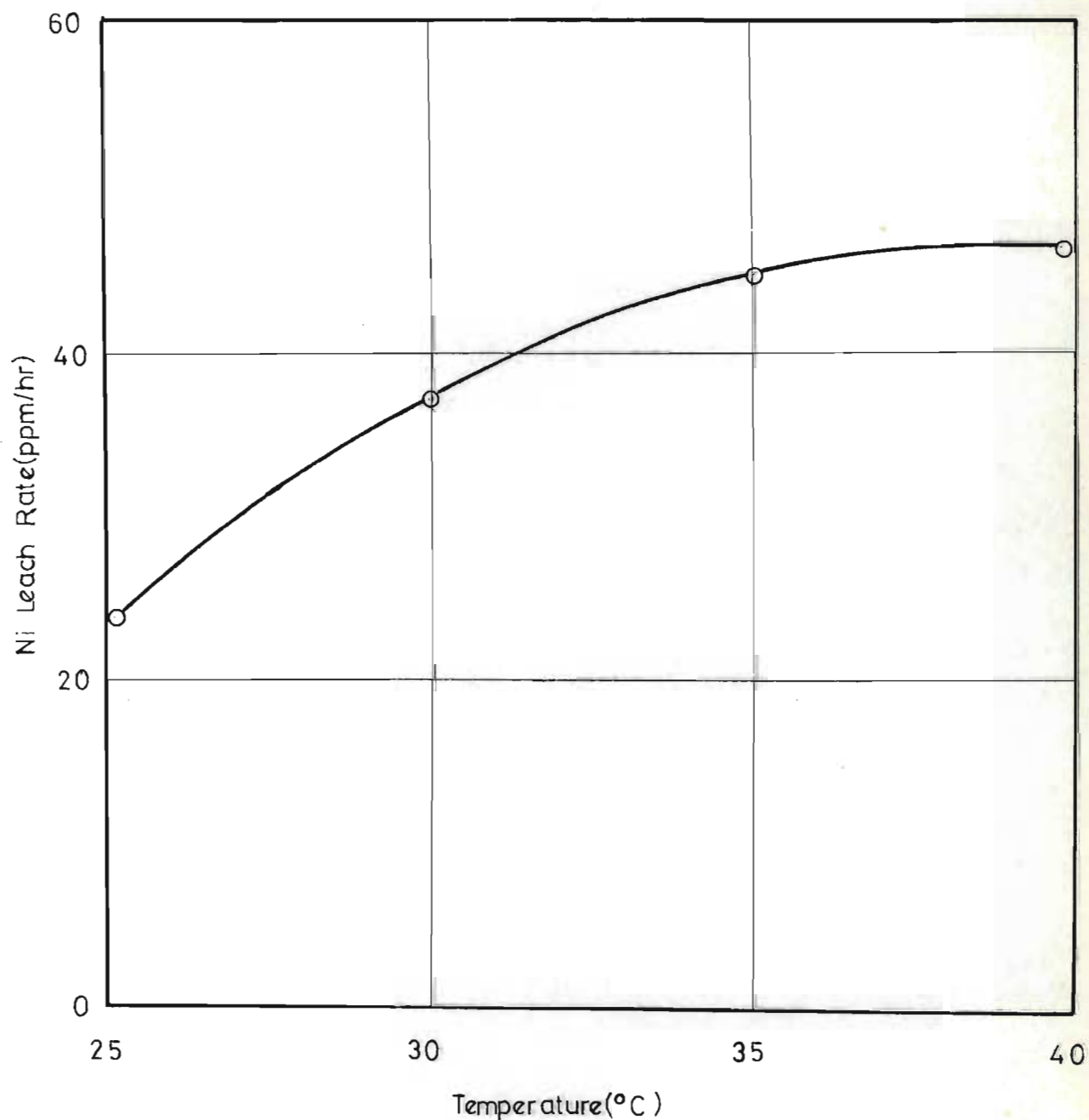


Figure 35. Batch Bacterial Leaching Rate as a Function of Temperature

9 K Solution
pH 3,0
W 200rpm
Gas Air
20 %w/v pentlandite



supplied to the reactor and the temperature should be maintained in the range 30° - 35°C. pH was found to have little effect on the leach rate of nickel in the range 2,5 - 4,5. The pH remained fairly constant at the initial values, decreasing slightly in a few tests. In the control tests, the pH would rise rapidly unless acid was added continuously and eventually would approach neutrality where leach rates would progressively decrease. Carbon dioxide was found to have a very slight beneficial effect on leach rates; a certain amount of CO₂ was probably generated by the action of acid on the small amount of carbonate in the gangue. Leaving out the trace elements and lowering the phosphate and nitrogen levels to 1/10 of the normal 9K level was found to have no effect on rate or nickel recovery. It is therefore unlikely that availability of any of the 9K constituents becomes rate limiting during leaching.

Under optimum conditions, the pentlandite concentrate could be leached at high rates to give good extractions in about 8 - 9 days.

There appear to be at least three possible roles which the bacteria can play in the leaching of pentlandite.

- i) They may oxidise ferrous ions to ferric ions more rapidly than the chemical process.

- ii) They may oxidise sulphur (S^0) to sulphuric acid
 iii) They may oxidise sulphide (S^{2-}) to sulphuric acid.

Item i) represents the so-called indirect mechanism of bacterial leaching and in effect would be covered in the term R_1 (diffusion controlled rate) discussed previously. The action of the bacteria would be solely to increase the ferric ion concentration which, in turn, has a direct effect on the leach rate of nickel up to approximately $0,1M Fe^{+++}$.

The production of acid from S^0 species as in item ii) above should have little effect on the leach rate per se because the chemical kinetic studies have shown that nickel leaching is only slightly dependent on hydrogen ion concentration. The production of acid does, however, provide a means of stabilising the leached nickel cations in solution, and maintaining the pH level in the optimum range.

Item iii) may be thought of as representing a true bacterial leaching action in that an alternative electron accepting reaction is provided at the mineral surface.

The overall rate of nickel leaching can thus be represented:-

$$R_{\text{overall}} = R_1 + R_2 + R_3 \dots\dots\dots 36)$$

where/.....

where R_1 and R_2 are rates due to the previously discussed chemical cathodic reactions and R_3 is a rate due to direct bacterial action.

The work of Corrans, Harris and Ralph (28) has shown that direct bacterial action on sulphides as represented by R_3 in the rate expressions does in fact occur. It is thought that this mechanism involves depolarisation or stimulation of cathodic reactions at the mineral surface. The exact pathways of electrons at the surface during this action remains a matter of conjecture as insufficient is known about the exact means of sulphur uptake by Thiobacilli (29).

It became clear during the batch tests that the rates of bacterial leaching were higher than those expected from a purely chemical leach so that some biological rate function, as represented by R_3 , clearly exists.

It was also evident that the bacterial population consists of two distinct fractions; one attached to the mineral surface and one freely suspended in the medium. As discussed in Section 3.2.1. it seems that only the attached portion was controlling the growth rate. The bacterial leaching results were compared with the calculated values of R_1 and R_2 using the rate equation derived in the chemical kinetic studies.

Correction/.....

Correction for Chemical Leaching.

R_3 was calculated by subtracting the sum of R_1 and R_2 from the overall rate. (Details of these calculations are given in Appendix 15.) The values of R_3 under the different conditions are shown in Figures 36 - 41.

From the batch results it is seen:-

- i) R_3 depends linearly on pulp density.
- ii) R_3 depends only slightly on pH in the range 1,5 - 4,0.
- iii) R_3 depends to a large extent on the oxygen concentration and rate of agitation.
- iv) R_3 increases with CO_2 content of the gas up to about 2 per cent.
- v) R_3 decreases markedly above 35°C .

It was observed that the leaching characteristics were linear (except possibly in the initial stages of the leach) (See page 71) and the exponential curves generally associated with bacterial growth were not obtained. This was also found in the experiment where the soluble nickel was continually removed by dialysis and ion exchange so that it was clear that the linearity is not a result of some inhibitory effect of the nickel cations on the bacterial growth.

The most significant observations in the batch leaching tests are considered to be the large dependence of the

bacterial/.....

Figure 36. Corrected Batch Bacterial Leach Rate as a Function of Pulp Density.

9K Solution
30°C
pH 3.0
W 200rpm
Gas Air

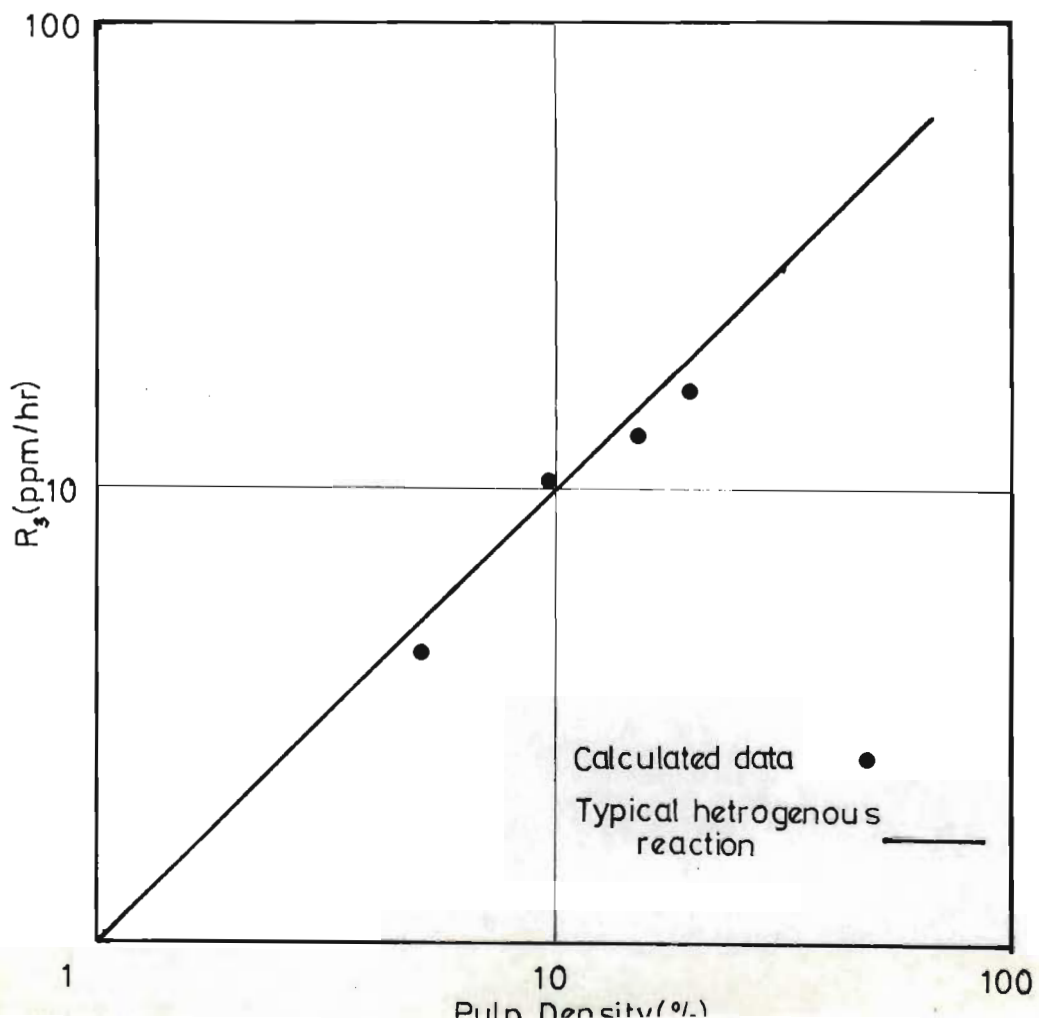


Figure 37. Corrected Batch Bacterial Leach Rate as a Function of pH.

9K Solution
30°C
W 200 rpm
Gas Air
20% w/v pentlandite

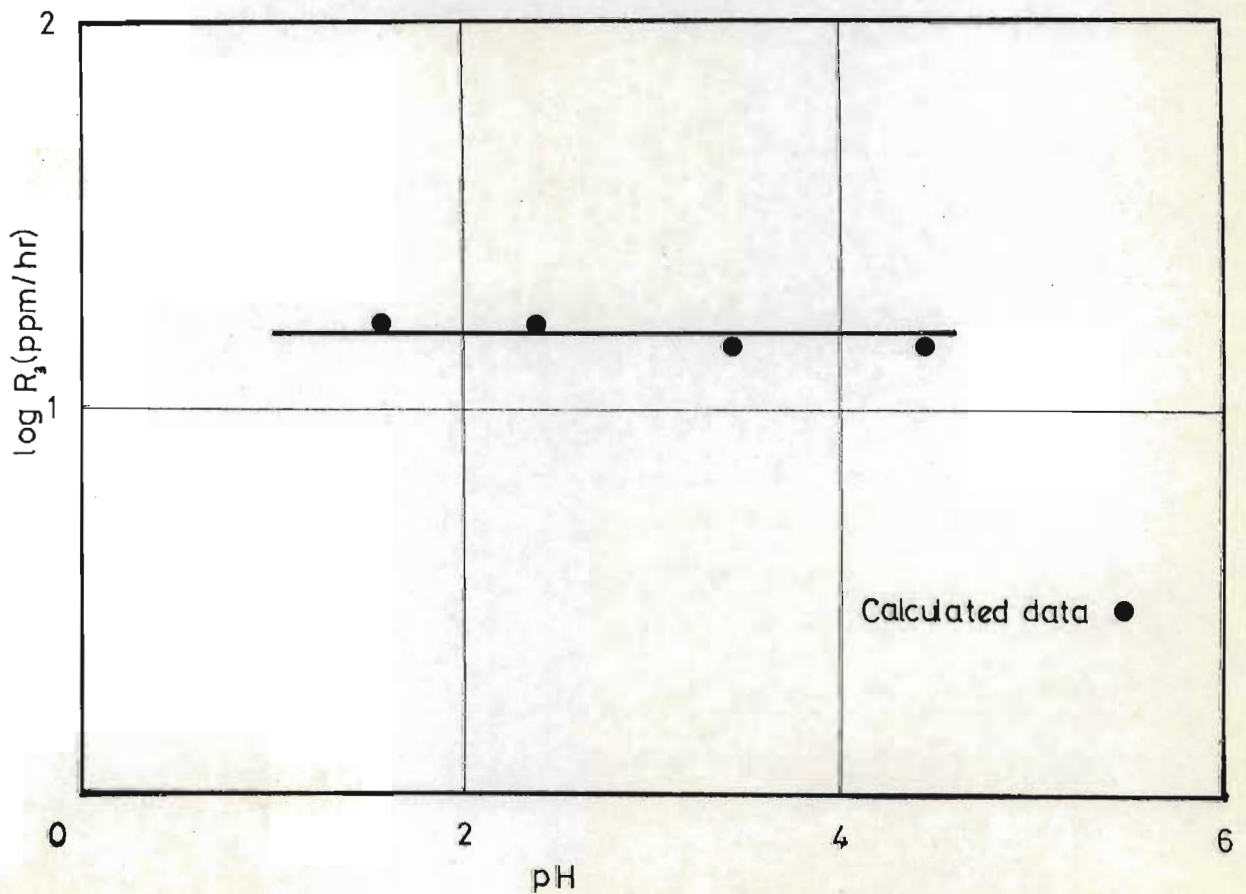


Figure 38. Corrected Batch Bacterial Leaching as a Function of Agitation Rate.

9K Solution
30°C
pH 3,0
Gas Air
20% w/v pentlandite

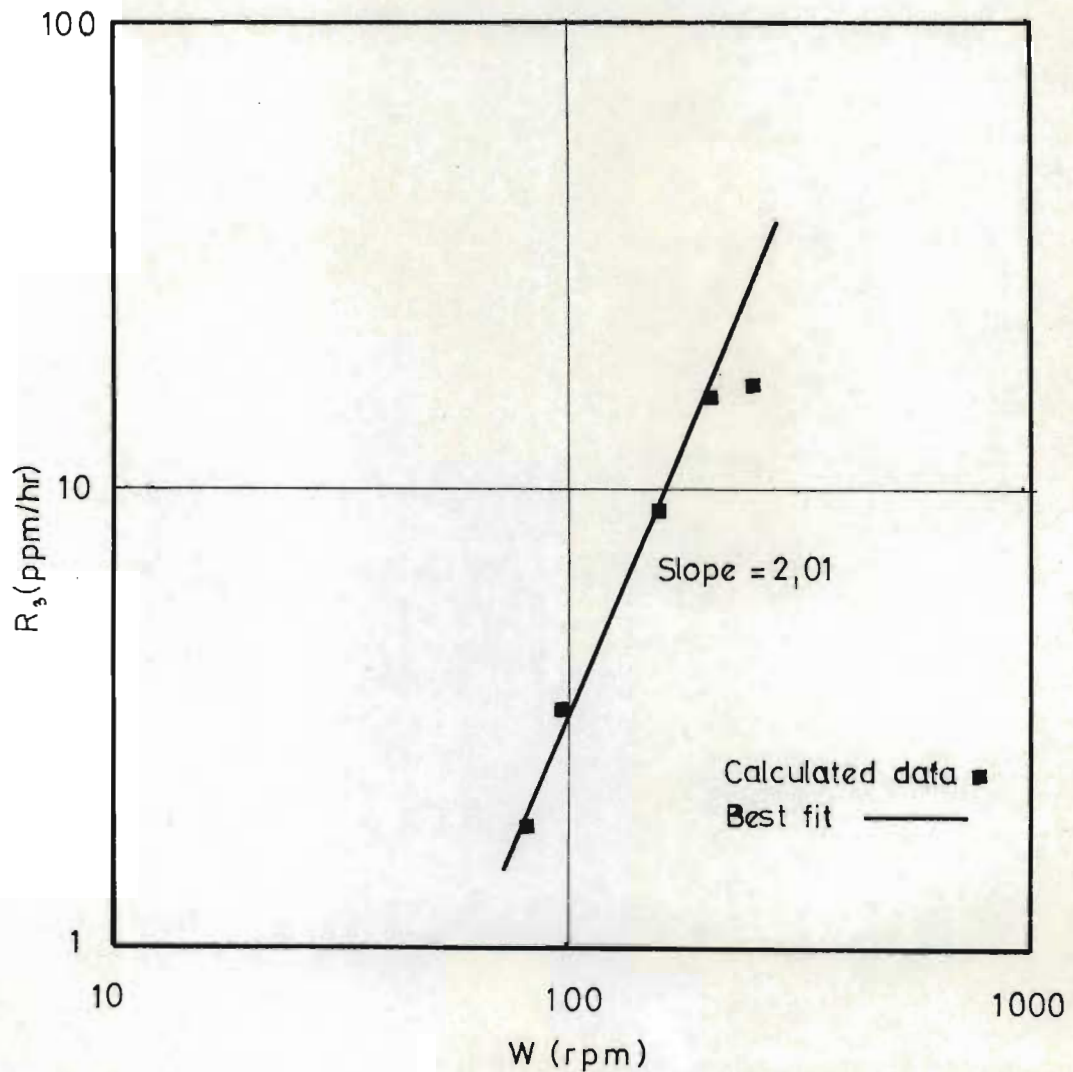


Figure 39. Corrected Batch Bacterial Leach Rate as a Function of Oxygen Concentration.

9K Solution
 30°C
 pH 3,0
 W 200 rpm
 20% w/v pentlandite

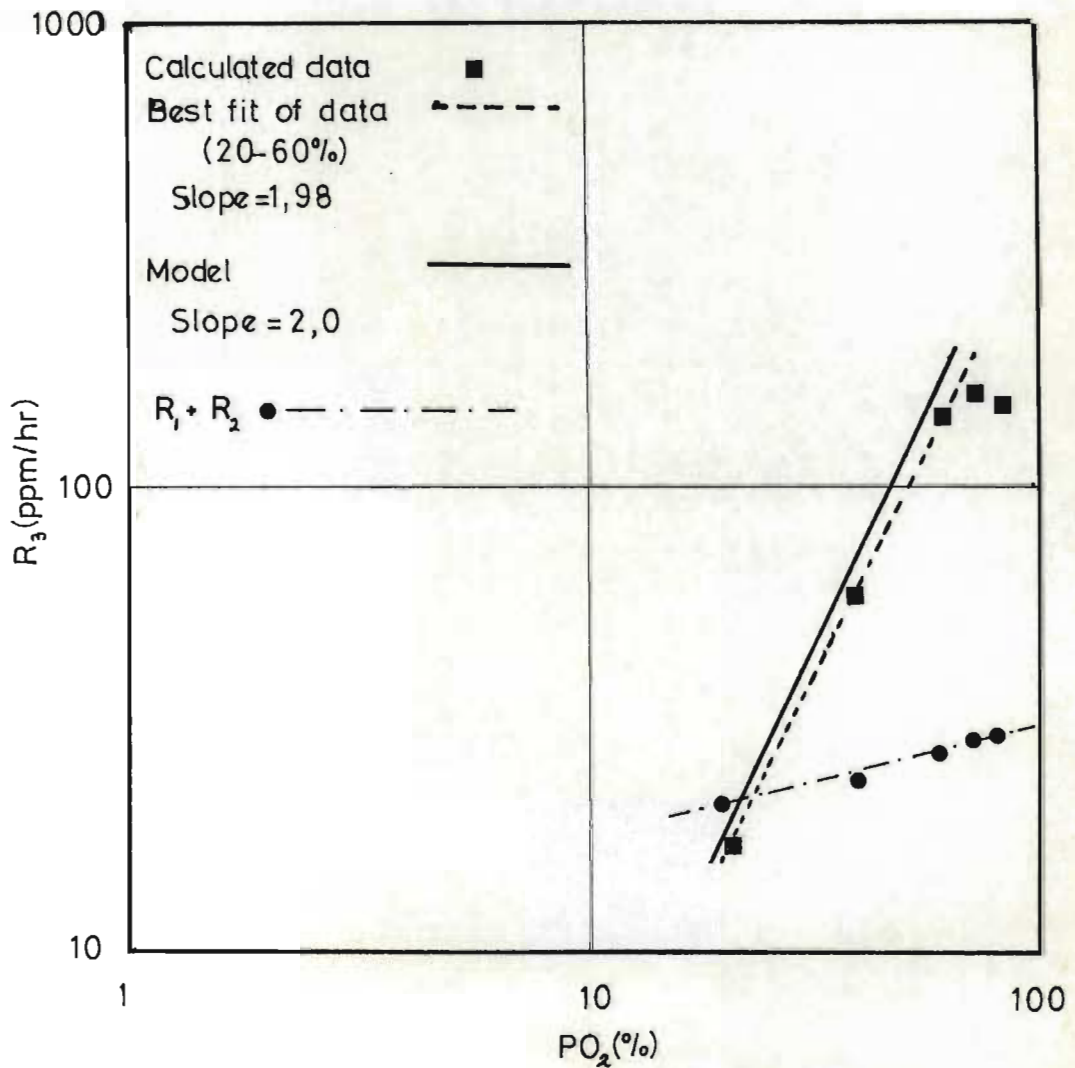


Figure 40. Corrected Bacterial Leach Rate as a Function of Carbon Dioxide Concentration.

9K Solution
30°C
pH 3,0
Gas Air
20%w/v pentlandite

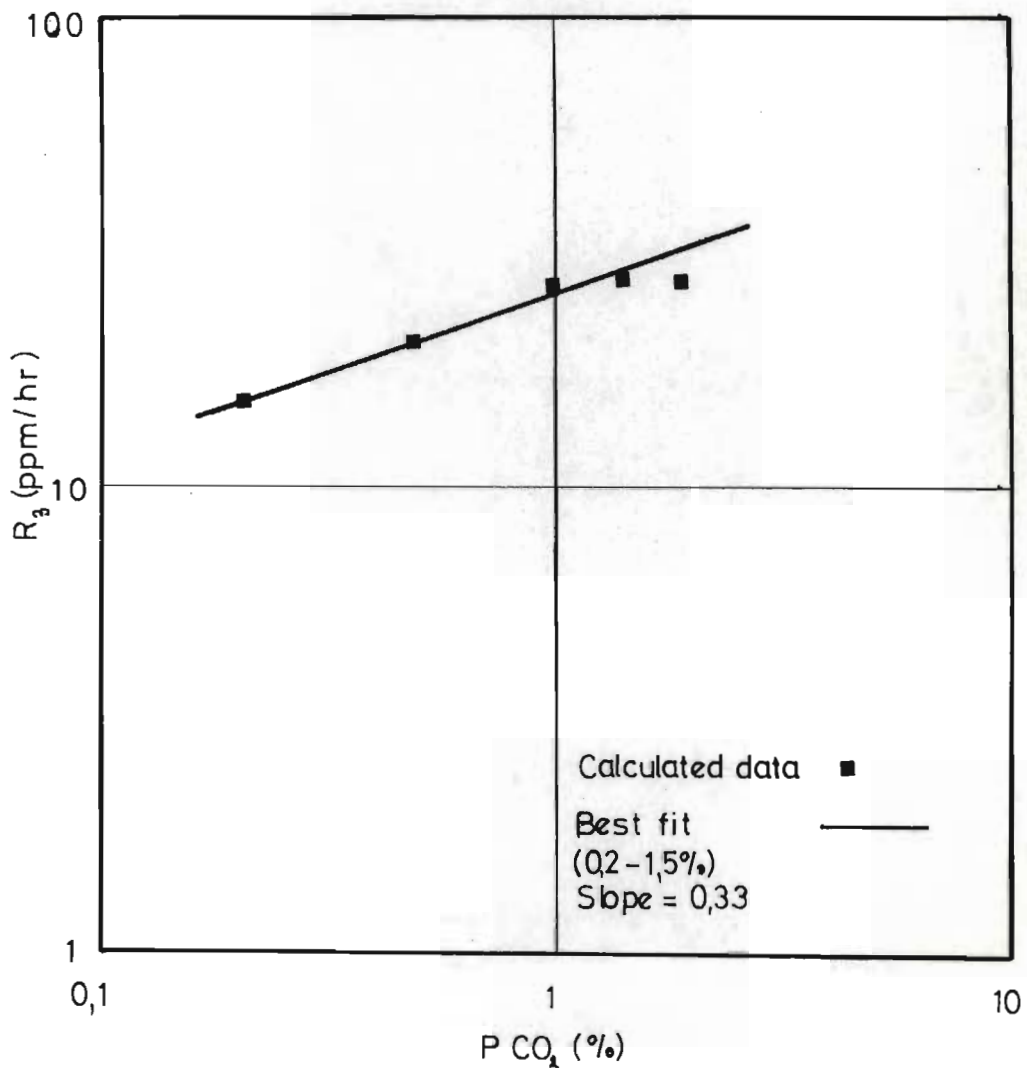
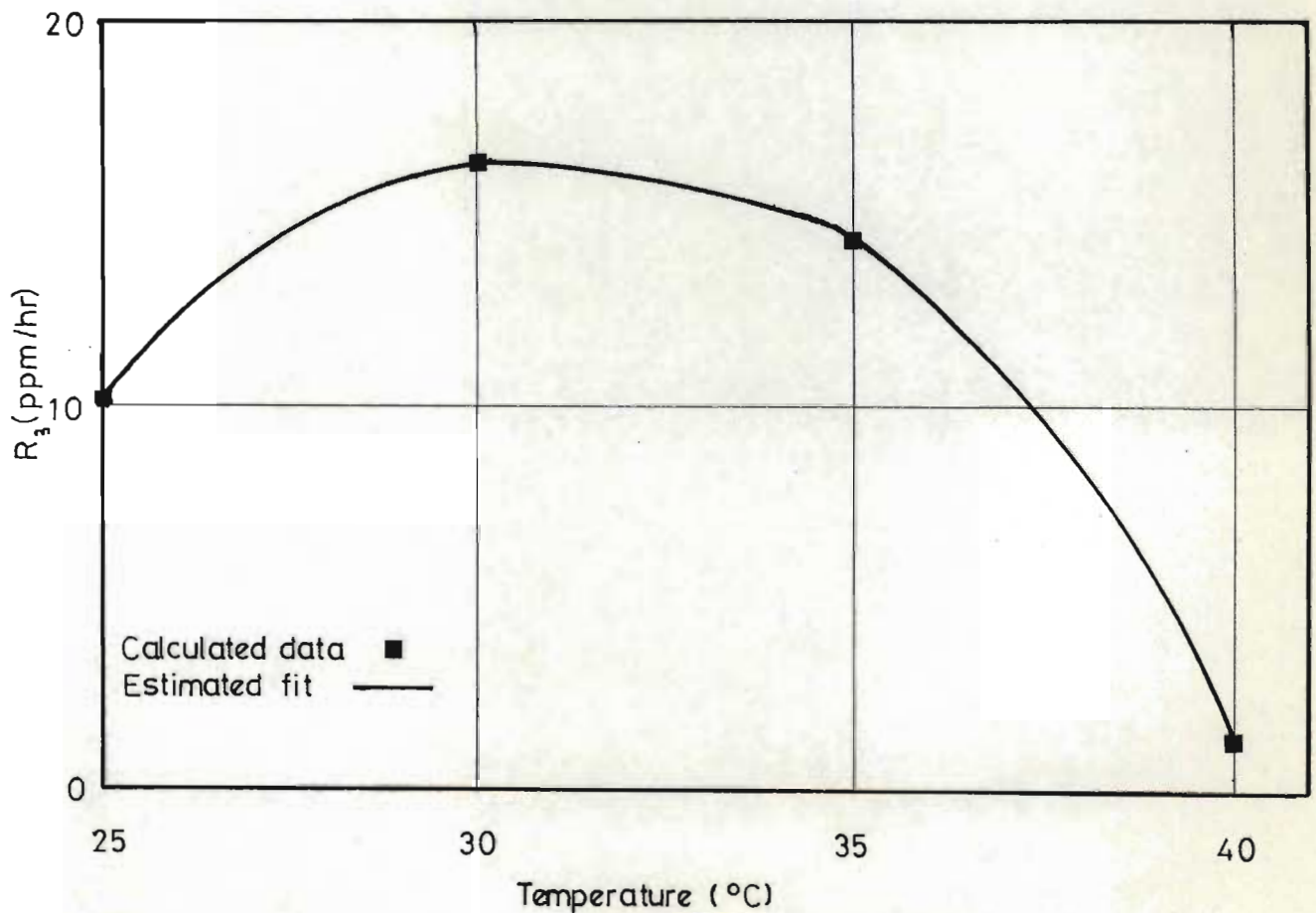


Figure 41. Corrected Batch Bacterial Leach Rate as a Function of Temperature.

9K Solution
w 200 rpm
pH 3.0
Gas Air
20% w/v pentlandite



bacterial leach rate (R_3) on oxygen concentration and agitation. At 70 per cent oxygen concentration, the value of R_3 is increased by a factor of over five times above the value of the chemical rate. This implies rate control by a mass transport process. From Figures 38 and 39 it may be seen that the data for agitation and oxygen concentration are consistent with lines of slope 2 drawn through the data. Clearly mass transfer of oxygen by diffusion across boundary layers cannot then be rate controlling. If this were so one would expect a linear relationship according to Ficks' Law.

$$\text{i.e. } I = k [pO_2 - pO_2^S] \dots\dots\dots 37)$$

where I = diffusive flux of oxygen
g moles/unit area-unit time.

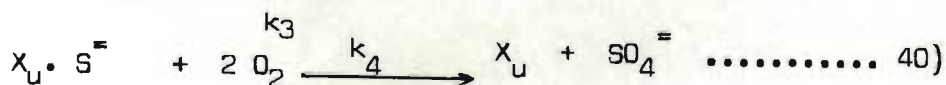
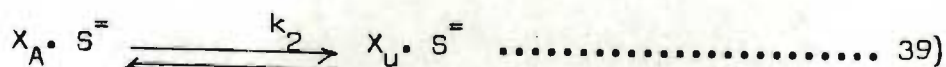
k is a constant, dependent on various physico-chemical parameters.

pO_2 = concentration of oxygen in the bulk solution

pO_2^S = concentration of oxygen at the (mineral) surface.

Bacterial Leaching Model.

If a mechanism is considered whereby the bacterial cells, carrying the enzymes which catalyse the oxidation reactions, are first adsorbed onto the mineral surface, than a rate expression of the following form may be derived:-



$S^=$ represents/.....

S^- represents the negatively charged sulphide ions produced at the mineral surface by a reaction of the form:-



The leach rate has been found to be limited by the cathodic reactions and the surface to be cathode polarised (28) so that it is probable that bacteria from the bulk solution attach at the mineral surface and take up sulphide. The next step in the scheme (equation 39) represents an equilibrium between bacteria (containing sulphide) at the mineral surface and in the bulk solution.

- i.e. $[X_u]$ = concentration of unattached bacteria, cells/unit volume
- $[X_A \cdot S^-]$ = concentration of attached cells -sulphide at the mineral surface.
- $[X_u \cdot S^-]$ = concentration of unattached cells -sulphide in the solution.

The final step in the scheme, (equation 40) represents the uptake of oxygen by the unattached cells - sulphide to produce sulphate ions.

$$\frac{d [SO_4^{=}] }{dt} = k_4 [O_2]^2 \cdot [X_u \cdot S^-] \dots\dots\dots 42)$$

$$= 2 R_3$$

$$\frac{d [X_u \cdot S^-] }{dt} = k_2 [X_A \cdot S^-] - k_3 [X_u \cdot S^-] - k_4 [O_2]^2 [X_u \cdot S^-]$$

$$= 0 \text{ at steady state } \dots\dots\dots 43)$$

$[X_u \cdot S^-] / \dots\dots\dots$

$$\therefore [X_u \cdot S^=] = \frac{k_2}{k_3 - k_4 [O_2]^2} \cdot [X_A \cdot S^=] \dots\dots\dots 44)$$

substituting equation 44 in equation 42;

$$R_3 = \frac{1}{2} \frac{k_2 \cdot k_4}{k_3 - k_4 \cdot [O_2]^2} \cdot [X_A \cdot S^=] \cdot [O_2]^2 \dots\dots\dots 45)$$

If $k_3 \gg k_4$, i.e. if it is assumed that the rate of reaction of oxygen with the unattached cells - sulphide is much slower than the rate of detachment of bacteria from the mineral surface, then the above expression for R_3 may be simplified :- (This assumption is probably valid in view of the relatively low rates of reaction which were obtained.)

$$R_3 = \frac{k_2 \cdot k_4}{2k_3} \cdot [X_A \cdot S^=] \cdot [O_2]^2 \dots\dots\dots 46)$$

Now $[X_A \cdot S^=]$ is proportional to the numbers of bacteria and the available surface area of mineral. If the bacterial numbers are relatively large compared to the available surface area, $[X_A \cdot S^=]$ will tend to reach a maximum value determined by the surface area of mineral.

$$\text{i.e. } [X_A \cdot S^=] = k \cdot M \cdot S_A \dots\dots\dots 47)$$

k is a constant

M = mass of mineral.

S_A = specific surface of mineral, area/unit mass.

Substituting equation (47) in equation (46);

$$R_3 = \frac{k_2 \cdot k_4}{2k_3} k \cdot M \cdot S_A \cdot [O_2]^2 \dots\dots\dots 48)$$

Assuming/.....

Assuming Henry's Law applies:-

(i.e. $[O_2]_{\text{dissolved}} \propto pO_2$)

$$R_3 = K \cdot (pO_2)^2 \dots\dots\dots 49)$$

The effect of agitation on leach rate is incorporated in the constant, K , since $\frac{k_2}{k_3}$ is a function of W, the rate

of agitation. The rate constant k_4 in equation 42 would be dependent on the specific growth rate of the bacteria.

This model explains the linear nature of the leach curves; this is due to the 'saturation' of the mineral surface with bacteria, once the bacterial numbers become excessive. At this point, surface area of mineral substrate becomes rate controlling. Torma (86) has also recorded linear rates of leaching and although he has empirically fitted a Monod-type model to the results using surface area of mineral as the substrate term, he makes no attempt to explain the linear kinetics. Torma has found that in sulphide leaching:-

$$\text{Rate} \propto \frac{A}{K + A} \dots\dots\dots 50)$$

where A is the surface area of the mineral.

When bacterial growth takes place on a solid substrate the effective concentration or area of substrate is considerably lower than when a soluble substrate is used.

This is why it is considered that the saturation effect of the bacterial-enzyme system is more relevant with solid

substrates/...

substrates than with soluble substrate. (i.e. the surface becomes saturated at relatively low concentrations of bacteria.) In the initial stages of growth on a solid substrate the kinetics would tend to display exponential characteristics, but specially designed experiments would be necessary to detect this effect; e.g. highly accurate means of determining biomass in low concentration would be necessary to detect initial growth patterns.

4.2.2. Continuous Leaching.

In order to further test the model of the bacterial leaching of pentlandite, a series of leach tests were carried out using the continuous culture technique. The aims of this continuous bacterial leaching work were:-

- 1) To further check the postulated mechanism of the attached-unattached bacteria.
- 2) To test whether the batch model could be used to predict the operation of a continuous leach.
- 3) To further investigate the economic possibilities of leaching pentlandite concentrates using bacteria.

The leaching was carried out on a flotation concentrate prepared from the Shangani ore. This concentrate was prepared on a large pilot plant and was considered to be typical of future production concentrates, (see Section 3.1.2.). The concentrate was leached as a 5 per cent slurry and used without any further grinding.

Leaching was carried out in the same instrumented reactor as was used in the continuous growth tests on sulphur. The overflow from the reactor was arranged in such a manner that unleached pentlandite was retained in the vessel. This was done using a goose neck arrangement; the relatively dense pentlandite particles settled back into the reactor due to the very low linear velocity of fluid through the exit goose neck (See Figure 3.) A small amount of gangue, jarosite and other relatively low density material also left the reactor. Sludge was occasionally withdrawn from the reactor through a drain situated about 2,5 cm above the bottom. Before draining, the agitation would be stopped for one hour and the gas feed closed. The pentlandite would quickly settle and the sludge could then be drawn off above this. Fresh concentrates were added about twice a week, depending on the magnitude of the leach rate. The additions were calculated from the extraction percentage to maintain the pentlandite concentration at 5 per cent in the reactor.

The same method of intermittent addition of solid was used as for the continuous culture work on sulphur. With high extraction rates the concentration decreased from approximately 7,5 per cent after addition to approximately 2,5 per cent just prior to new addition. The average was maintained at 5 per cent as described in Appendix 16. At lower leach rates the variation was not as great being

from/.....

from 6 per cent decreasing to 4 per cent before addition.

The equilibrium conditions were measured when at least two reactor volumes of feed had been added at each dilution rate. Leach medium was made up as follows:-

$(\text{NH}_4)_2 \text{SO}_4$	3,0g
$\text{K}_2 \text{HPO}_4$	0,1g
H_2SO_4	to give pH 3,0
Tap water	1 litre

This solution contained the same amounts of $(\text{NH}_4)_2 \text{SO}_4$ and K_2PO_4 as the 9K growth medium. Omitting the other 9K salts was found from the batch leach tests to have little or no effect on the rate of extraction or per cent recovery of nickel, as requirements were supplied in sufficient quantity as impurities in the tap water and from the gangue materials in the concentrates.

Agitation was carried out by means of a propellor-type stirrer rotating at 200 r.p.m. Gas was added to the reactor via a circular sparge ring at a total flowrate of 500 ml per minute. This arrangement of sparge ring and stirrer gave a vigorous aeration effect.

The continuous leach was inoculated from a batch culture growing on pentlandite and run as a batch leach for one

week/.....

week before fresh medium was added continuously.

Continuous Leaching Using Normal Air..

Air was fed to the reactor and the equilibrium nickel concentration measured at several dilution rates. These results are shown in Figure 42 and the detailed experimental data are given in Appendix 17. The critical dilution rate was found to be about $0,016 \text{ hr}^{-1}$. (The critical dilution rate is that at which wash out of the organisms occurs in a continuous culture. In this instance it refers to that dilution rate where the nickel concentration tends to approach zero.) The optimum dilution rate, where leach rate was maximised, occurred at $D = 0,015 \text{ hr}^{-1}$, the maximum rate being $13,4 \text{ ppm Ni}^{++}$ per hour. During this series of tests the pH was self stabilised at $2,5 \pm 0,2$. The iron leaching followed a similar pattern to the nickel regarding both rates and concentration.

Continuous Leaching Using Air Enriched With CO_2 .

The use of air enriched with CO_2 at 2 per cent v/v was found to give slightly improved leaching rates of nickel. These results are shown in Figure 43 and the detailed experimental data are given in Appendix 17. The critical dilution rate in this case was $0,017 \text{ hr}^{-1}$ with the maximum leach rate being $19,5 \text{ ppm Ni}^{++}$ per hr at $D = 0,015 \text{ hr}^{-1}$. The pH was self stabilised in the range $2,5 \pm 0,2$ and the iron leach pattern was similar to that

for/.....

Figure 42. Continuous Leaching - Air.

30 °C
pH 3.0 (feed)
W 200 rpm
5 % w/v pentlandite

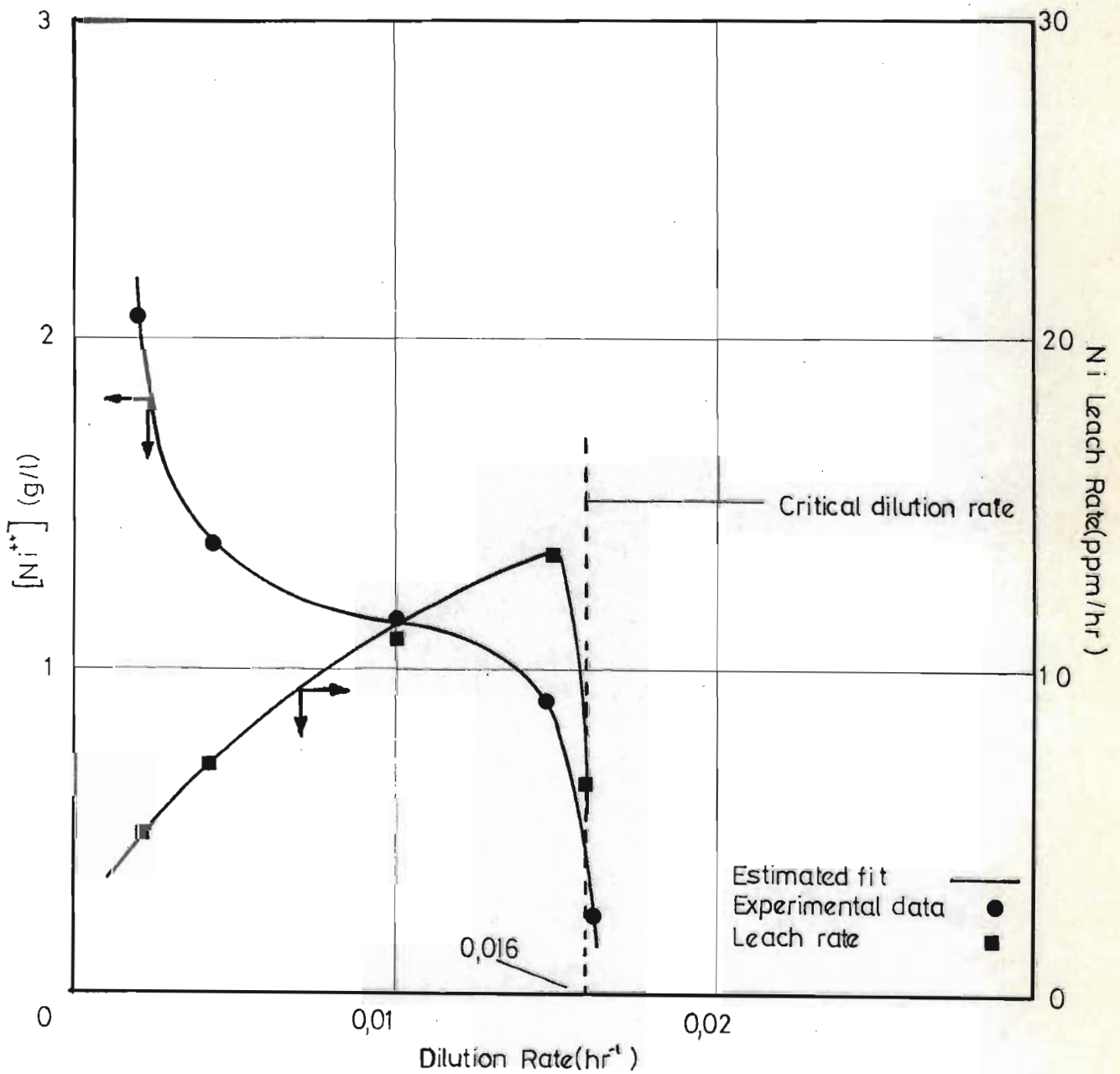
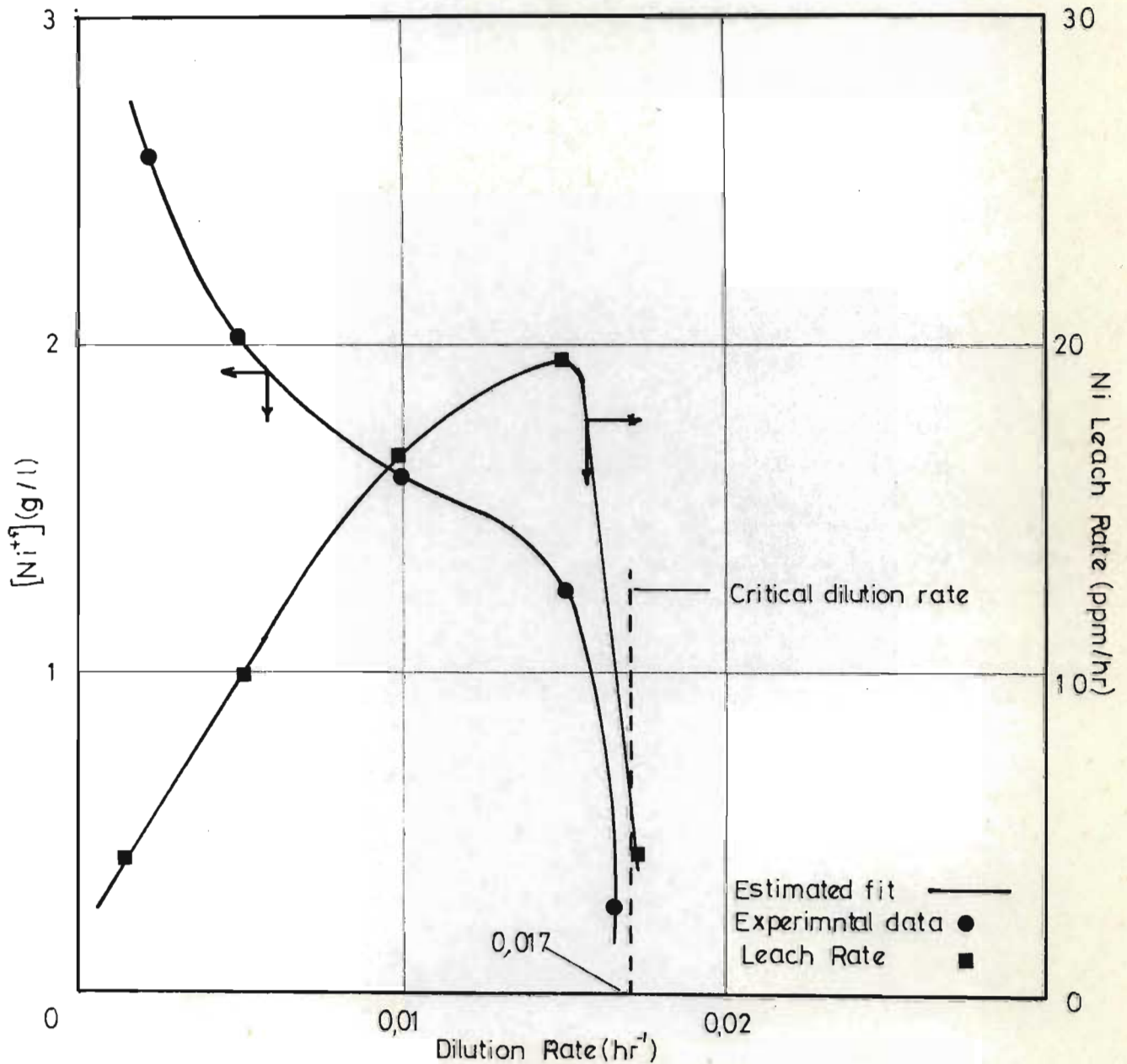


Figure. 43. Continuous Leaching-Air+2% CO₂

30°C
 pH 3,0 (feed)
 W 200rpm
 5% w/v pentlandite



for nickel leaching.

Continuous Leaching Using Air Enriched with Oxygen.

Three degrees of oxygen enrichment were used in these tests, 40 per cent, 60 per cent and 70 per cent O_2 v/v. Above 70 per cent, the oxygen appeared to become toxic and leach rates decreased. This dependence on oxygen concentration is similar to that found in the batch leach tests. The results of these tests are shown in Figure 44 and the detailed experimental data are given in Appendix 17. The maximum leach rate of 95,5 ppm Ni^{++} /hr was achieved with 70 per cent O_2 v/v at a dilution rate of $0,014 \text{ hr}^{-1}$.

Effect of Temperature in Continuous Leaching.

Leaching was carried out at a dilution rate of $0,01 \text{ hr}^{-1}$ and air added to the solution. The temperature was varied in steps from 25°C to 40°C and the equilibrium nickel concentration measured in each case. These results are shown in Figure 45 and the detailed experimental data are given in Appendix 17. The results correspond to those of the batch leach tests with the optimum temperature for bacterial leaching being $30^\circ - 35^\circ\text{C}$.

Effect of Changing the pH of the Feed Medium in Continuous Leaching.

The pH of the feed medium was increased from pH 3,0 up to pH 5,5, the latter pH representing no addition of acid.

It was/....

Figure. 44. Continuous leaching, air and oxygen

30°C
 pH 3.0 (feed)
 W 200 rpm
 5% w/v pentlandite

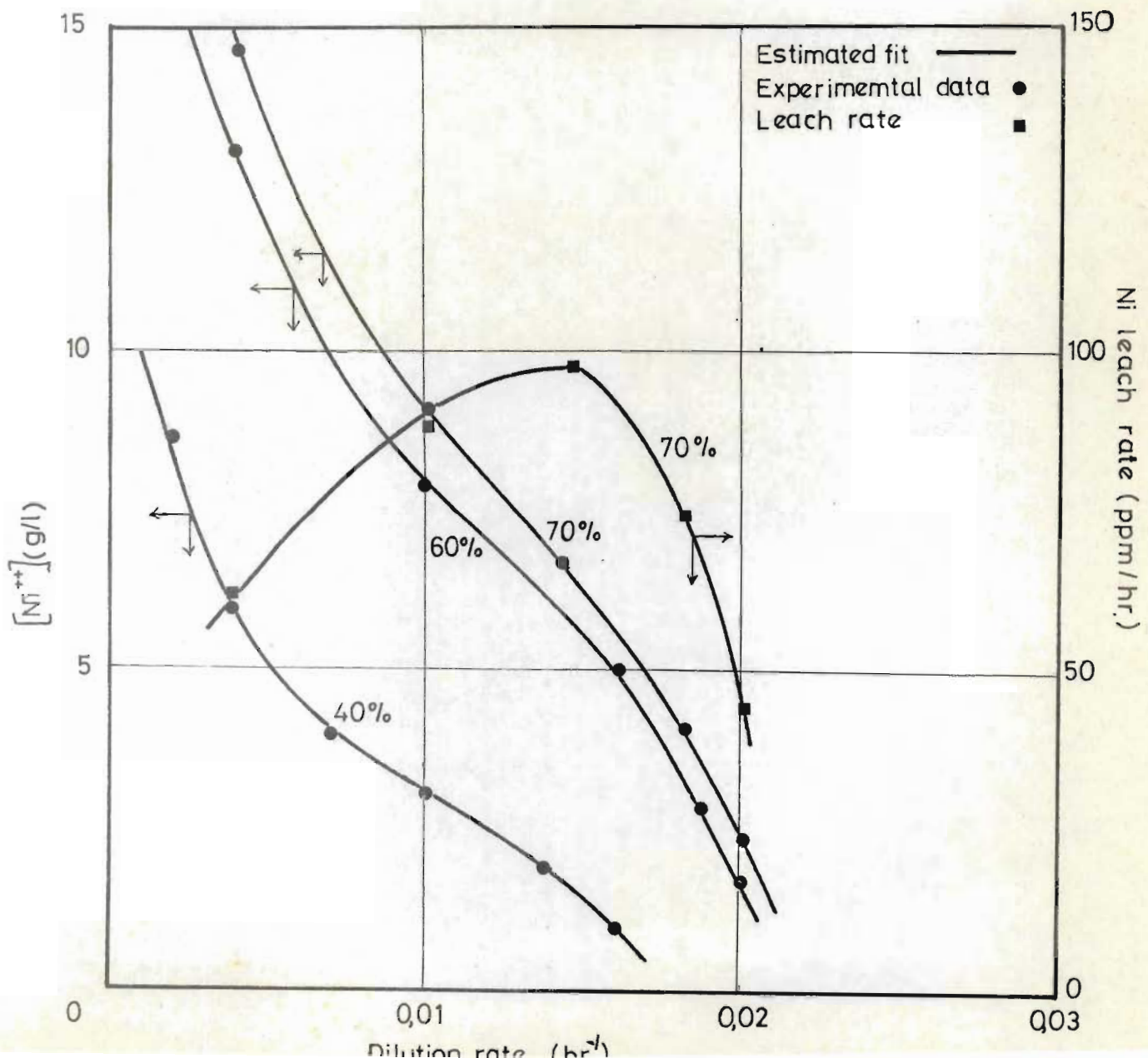
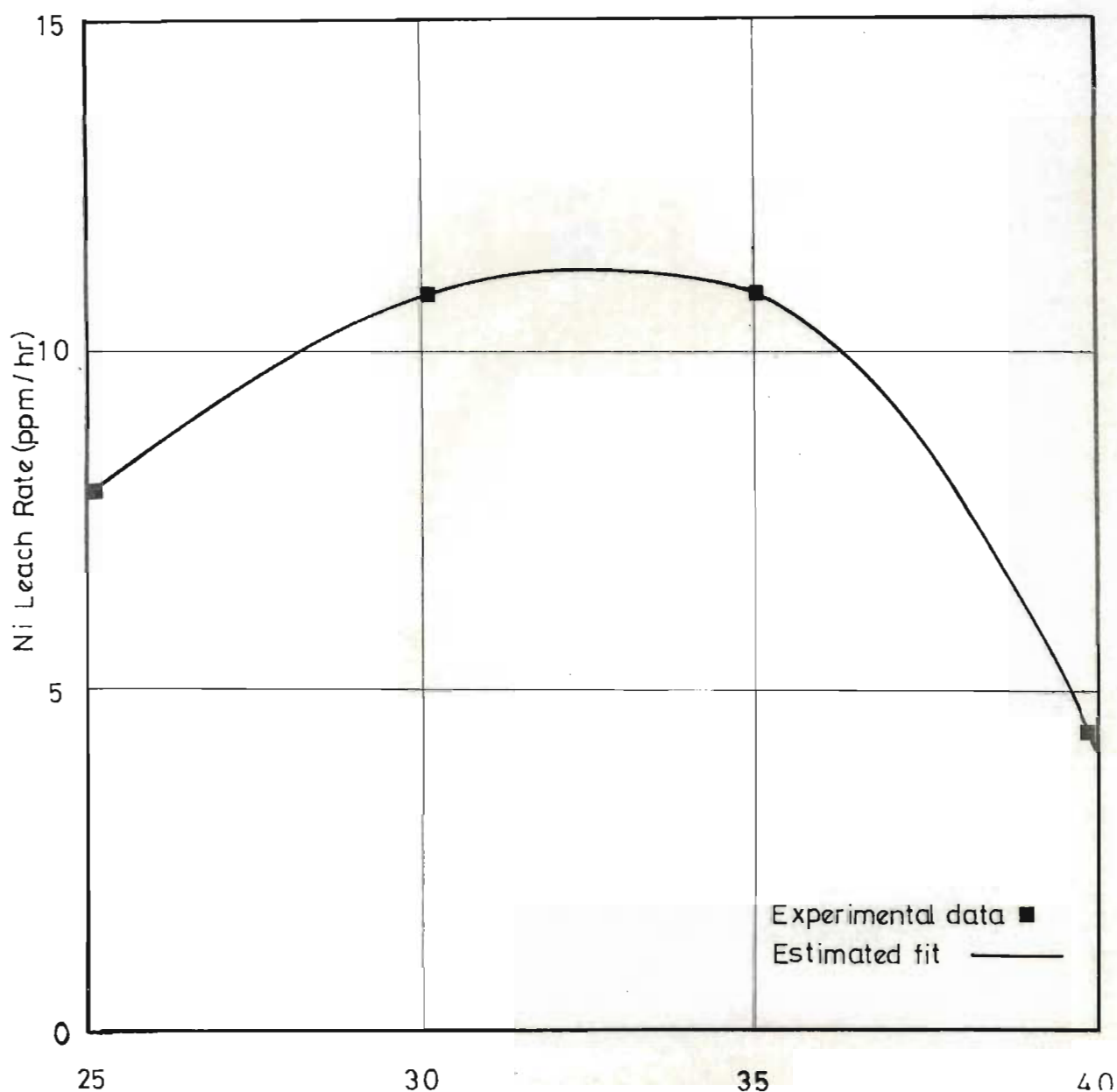


Figure 45. Continuous Bacterial Leach Rate as a Function of Temperature.

Dilution rate 0,01 hr⁻¹
pH 3,0 (feed)
W 200 rpm
Gas Air
5% w/v pentlandite



It was found that this had virtually no effect on the pH in the reactor, which remained in the range pH 2,5 - 2,8. Thus it would appear that for the particular ore-type being used, the acid production by bacterial growth was sufficient to keep the pH constantly in the optimum range in spite of acid-consuming gangue materials being present and the pH of the feed being higher. This change in pH was discussed in section 4.2.1. In the batch tests a high purity pentlandite was used and the pH was self-stabilised during bacterial growth. With the use of a lower grade concentrate, containing pyrite and pyrrhotite, excess acid can be produced to lower the pH.

Detailed experimental data for this set of tests is given in Appendix 17.

Continuous Leaching - Sterile Conditions.

At the end of continuous leach tests, two checks were carried out to see whether the leach rates being obtained were in fact higher due to bacterial growth than the purely chemical leach rates. The bacterial population was 'killed' by adding 0,1 per cent formaldehyde in the feed solution. The leach rate decreased and approached a value predicted by the chemical kinetic model.

This finding was further checked by re-inoculating the

leach/.....

leach vessel and allowing equilibrium growth conditions to be attained. Pure oxygen, which is toxic to the bacteria, was fed to the reactor. A similar decrease in leach rate was obtained which approached the predicted value for chemical leaching.

These data are given in Table 6, from which it is clear that a higher rate of leaching, as represented by R_3 , is being obtained due to the bacterial growth on the mineral.

Correction for Chemical Leaching.

R_3 , the rate of bacterial leaching, for the continuous leach tests, was calculated by subtracting the chemical leach rates, R_1 and R_2 , from the overall leach rate. Details of these calculations are given in Appendix 18. The values of R_3 under the different conditions are shown graphically in Figures 46 -50. It may be seen from the graphs of R_3 versus dilution rate, that the variation of R_3 follows a similar pattern to the variation of R_{overall} , displaying a fairly constant critical dilution rate.

The effect of scale-up on the kinetic data from the 250 ml batch flasks to the larger 5.5 l reactor is discussed in Appendix 18.

YIELD CONSTANTS/.....

TABLE 6:

CONTINUOUS LEACHING. STERILE CONDITIONS.

$$D = 0,01 \text{ hr}^{-1}$$

CONDITIONS	R_{overall} measured	$R_1 + R_2$ calculated
Air	11,5	1,9
Air + Formaldehyde	1,9	1,9
70% O ₂	88	4,8
100% O ₂	5,3	5,3

Figure 46. Corrected Continuous Leach Rate as a Function of Dilution Rate.

30°C
pH 3.0
W 200 rpm
Gas Air
5%w/v pentlandite

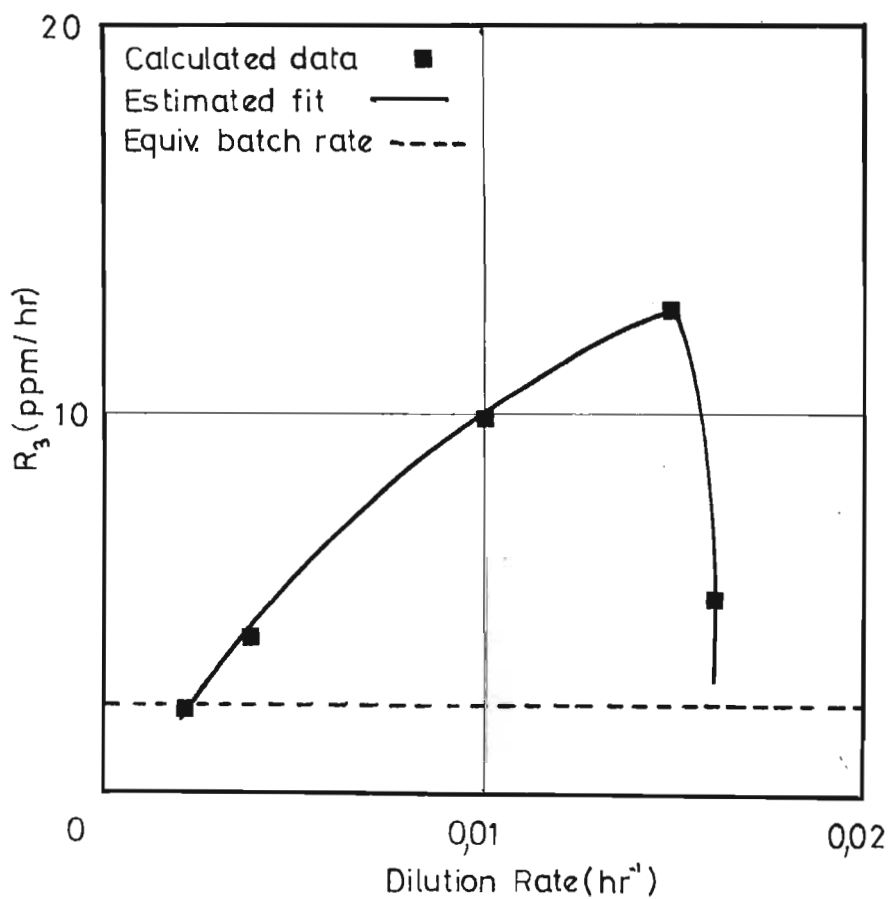


Figure 47 Corrected Continuous Leach Rate as a Function of Dilution Rate.

30°C
pH 3,0
W 200 rpm
Gas Air+2%CO₂
5% w/v pentlandite

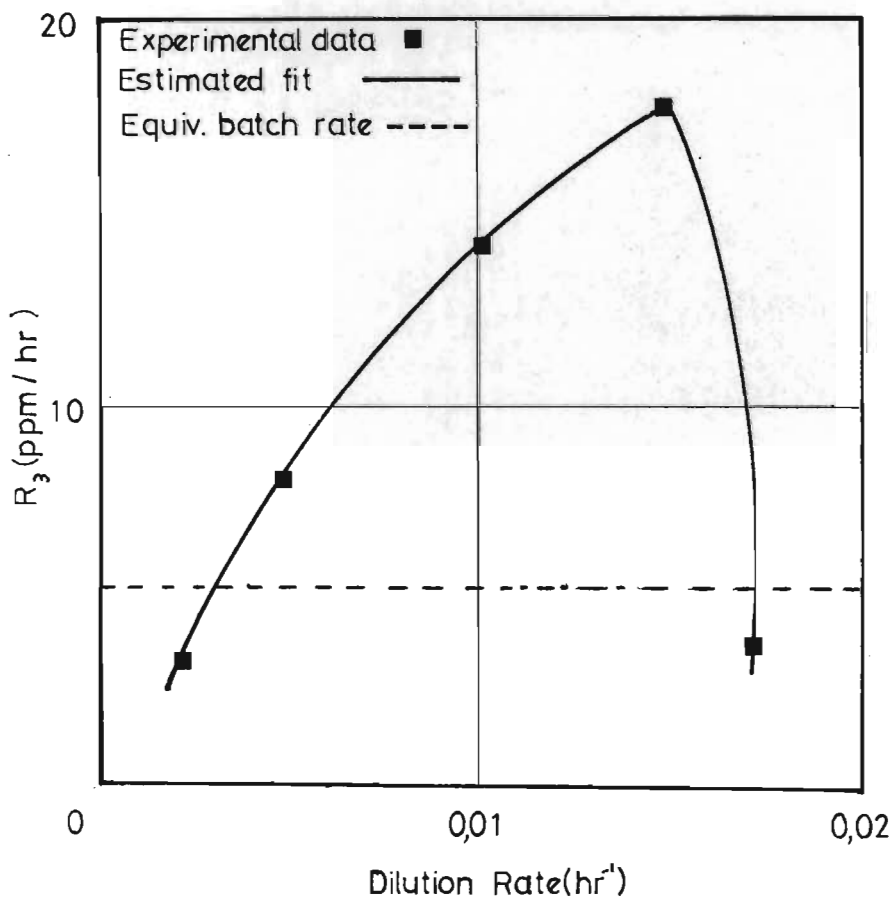


Figure. 48 Corrected Continuous Leach Rate as a Function of Dilution Rate.

30°C
pH 3.0
W 200 rpm
5% w/v pentlandite
Gas 40% oxygen

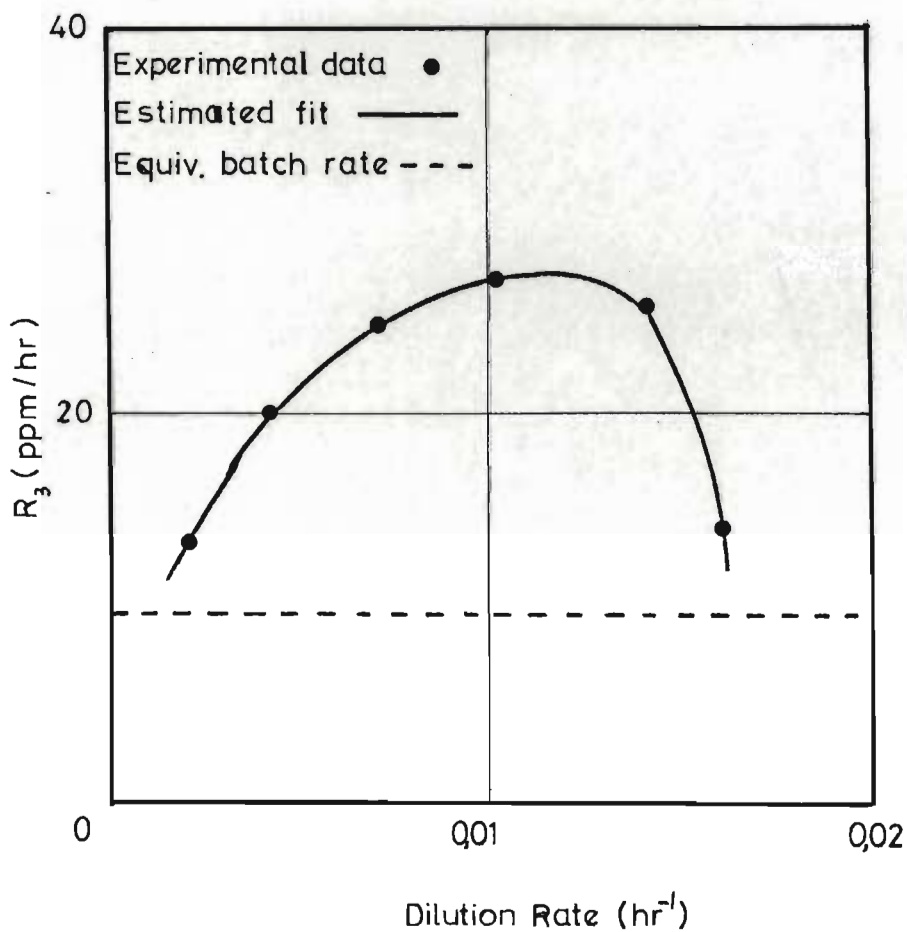


Figure 49. Corrected Continuous Leach Rate as a Function of Dilution Rate.

30°C
pH 3,0
W 200 rpm
Gas 40% N₂ + 60% Oxygen
5% w/v pentlandite

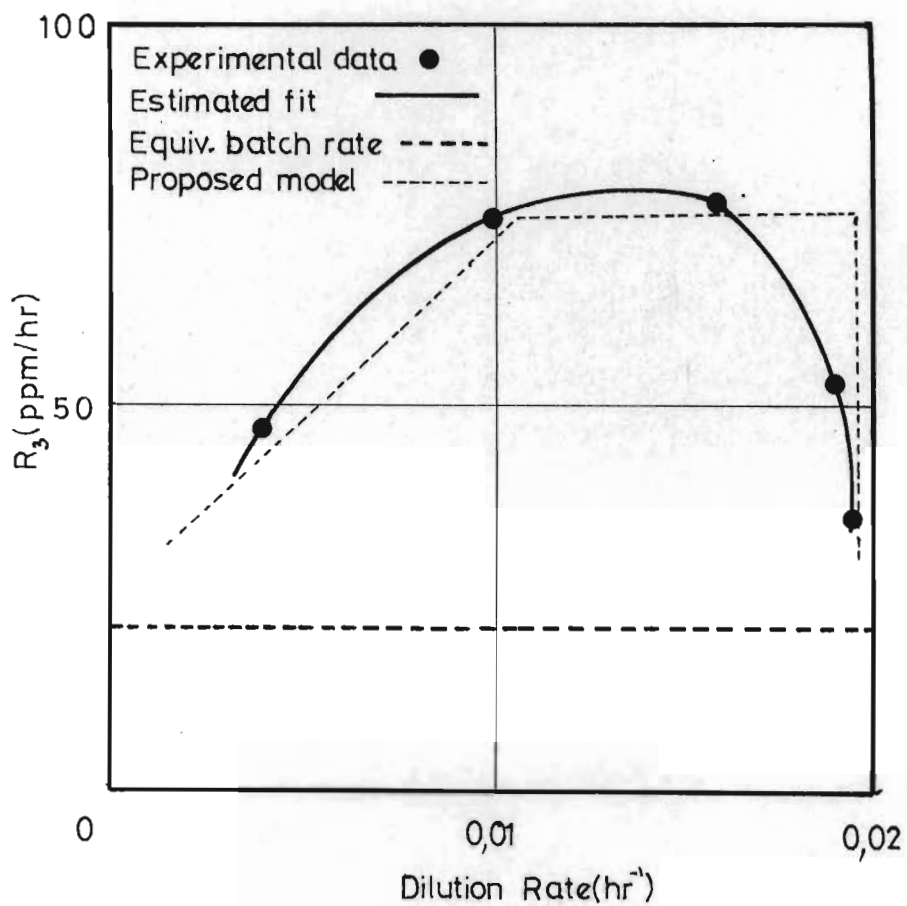
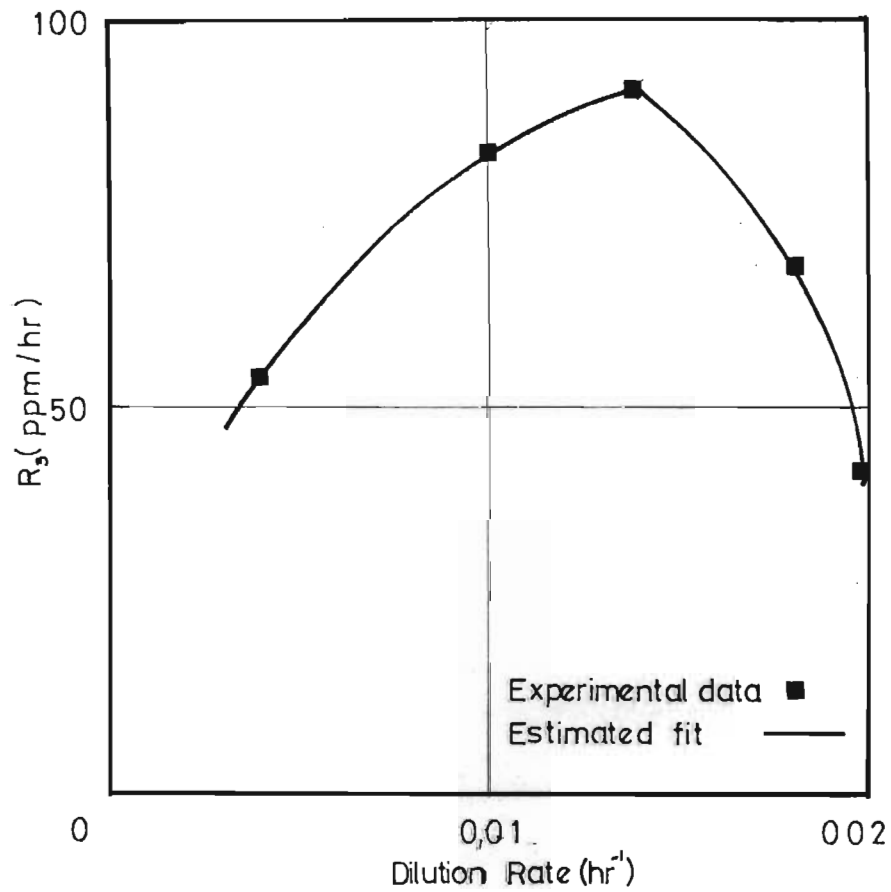


Figure 50. Corrected Continuous Leach Rate as a Function of Dilution Rate.

30°C
pH 3,0
W 200 rpm
Gas 30% N₂ + 70% Oxygen
5 %w/v pentlandite



Yield Constants.

The value of the yield constant was calculated from the growth data on sulphur and from the leach data in the dialysis experiment. Good agreement was found between these two calculated values, the average being $1,3 \times 10^{13}$ cells/mole Ni^{++} . The details of these calculations for the yield constant are given in Appendix 19. The yield constant was used to compare measured and calculated values of R_3 .

Appendix 20 shows good agreement between these values.

APPLICATION/.....

APPLICATION OF THE BACTERIAL LEACHING MODEL TO CONTINUOUS LEACHING.

The values of R_3 which would be expected in batch experiments under the same conditions as used in the continuous leaching were calculated (see Appendix 18) and are shown on Figures 46 - 50. It may be seen that the continuous leaching rates are much higher than those calculated in the equivalent batch conditions.

The batch model proposed that:-

$$R_3 = K (pO_2)^2 \quad \dots\dots\dots 49)$$

Incorporated in K was the rate constant k_4 (equation 40) which was postulated as being dependent on the specific growth rate of the bacteria. (Since the rate of metabolism of S^m must be related to the specific growth rate.)

$$\text{i.e. } R_3 = K^1 k_4 (pO_2)^2 \quad \dots\dots\dots 51)$$

$$\text{and } k_4 \propto \mu \quad \dots\dots\dots 52)$$

$$\mu = \text{specific growth rate, hr}^{-1}$$

Now μ is dependent on the concentration of some element or nutrient in the leach medium. This nutrient is probably not nitrogen or phosphorus, in light of the results of the batch tests in which these nutrients were reduced in the 9K medium without affecting the rates of leaching.

If/.....

If T is the concentration of limiting nutrient, then;

$$\mu = f(T)$$

Assuming the Monod (65) model to hold;

$$\mu = \mu_m \left(\frac{T}{K_m + T} \right) \dots\dots\dots 53)$$

$$\mu_m = \text{maximum specific growth rate, hr}^{-1}$$

K_m is a constant.

In continuous operation, the following mass balance may be carried out on the limiting nutrient:-

Rate of change of concentration = rate of entry - rate of washout - rate of utilisation.

$$\text{i.e. } \frac{dT}{dt} = D T_F - D T - \frac{\mu X_A}{y} \dots\dots\dots 54)$$

X_A = concentration of bacteria at the mineral surface.

T_F = concentration in feed.

y = yield constant for limiting nutrient.

At steady state, $\frac{dT}{dt} = 0$;

$$\therefore D T_F - D \bar{T} - \frac{\mu X_A}{y} = 0 \dots\dots\dots 55)$$

\bar{T} = equilibrium concentration.

Substituting equation (53) in equation (55) gives:-

$$\mu = \frac{\mu_m}{K} \left(T_F - \frac{\mu X_A}{D \cdot y} \right) \dots\dots\dots 56)$$

(The

(The Monod relation in equation (53) was simplified by assuming $\bar{T} \ll K_m$. This is valid since \bar{T} will approach zero if it is limiting.

The above equation may be solved for μ :-

$$\mu = \frac{D \cdot \mu_m \cdot T_F \cdot y}{\mu_m \cdot X_A + K_D y} \dots\dots\dots 57)$$

If D is small,

$$\mu = \frac{D \cdot T_F \cdot y}{X_A} \dots\dots\dots 58)$$

If D is large;

$$\mu = \frac{\mu_m \cdot T_F}{K} \dots\dots\dots 59)$$

Substituting equations (58 and 59) in equation (51) gives:-

(a)

$$R_3 = K'' \cdot \frac{D}{X_A} \cdot (pO_2)^2, \text{ for small values of D.}$$

where $K'' = f(D, T_F, y, \text{etc.})$

When D is small X_A tends to a constant value, representing the saturation of the mineral surface with bacteria, so that;

$$R_3 \propto D(pO_2)^2 \dots\dots\dots 60)$$

when D is small,

and;

(b)

$$R_3 \propto (pO_2)^2 \dots\dots\dots 61)$$

when D is large.

Insufficient microbiological data is available to evaluate the equality constants for the above equations (60) and (61). (The values of μ_m , y , X_A , T_F , k_2 and k_3 etc., would be required to evaluate these constants.) An arbitrary curve of the relationship between R_3 and D in continuous culture, of the form predicted by the model, has been superimposed on Figure 49. It would appear that the experimental data are consistent, at least in form, with the model predictions.

In continuous culture the following mass balance on bacteria is applicable:-

$$\text{Rate of growth} = \text{rate of increase} + \text{rate of washout} \dots \dots \dots 62)$$

Now if it is assumed that the rate of growth is determined by the concentration of bacteria attached to the mineral surface, then:-

$$\text{Rate of growth} = \mu \cdot X_A \cdot A$$

$$\mu = \text{specific growth rate of bacteria, hr}^{-1}$$

$$X_A = \text{concentration of bacteria attached at the mineral surface, cells/unit area.}$$

$$A = \text{total surface area of mineral.}$$

(This assumption is supported by the batch data where the rate of bacterial nickel leaching was determined by the surface area of mineral. There is a direct relationship between the rate of nickel leaching and rate of bacterial growth, as seen in the dialysis experiment, so it is likely that rate of bacterial growth is determined by the concentration of surface bacteria.)

Rate/.....

$$\text{Rate of Washout} = D \cdot X_u \cdot V \dots\dots\dots 63)$$

(since only unattached bacteria will washout)

D = dilution rate, hr^{-1}

X_u = concentration of unattached bacteria,
cells/unit volume.

V = volume of growth solution.

At steady state;

(rate of increase of cells = 0).

Thus,

$$\mu \cdot X_A \cdot A = D \cdot X_u \cdot V \dots\dots\dots 64)$$

It is then obvious why $\mu \neq D$ as in a homogenous system (soluble substrate system.) When D is small, X_u reaches a high equilibrium concentration so that X_A reaches the maximum saturation concentration of attached bacteria.

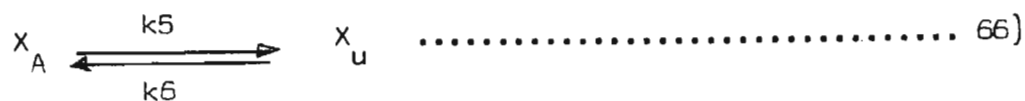
As D increases, X_u will decrease until eventually the surface concentration of bacteria falls below the saturation level. As D is increased still further and X_A decreases, eventually the specific growth rate will reach a maximum level and wash-out of bacterial cells from the reactor will occur. The value of D at which wash-out occurs is called the critical dilution rate and is represented as D_c .

$$\therefore \mu_m \cdot X_A \cdot A = D_c \cdot X_u \cdot V \dots\dots\dots 65)$$

μ_m is the maximum specific growth rate of bacteria, hr^{-1} .

In/.....

In terms of attached-unattached bacteria equations 38, 39 and 40 may be simplified:-



$$\therefore \frac{dX_U}{dt} = k_5 \cdot X_A \cdot \frac{A}{V} - k_6 \cdot X_U - DX_U \dots\dots\dots 67)$$

(mass balance)

= 0 at steady state.

$$\therefore X_U = \frac{k_5 \cdot X_A \cdot A}{(k_6 + D) V} \dots\dots\dots 68)$$

i.e. the batch equilibrium is $X_U = KX_A$.

(Except when X_U is large, when X_A tends to a constant saturation level.)

Substituting equation 68 in equation 65 we obtain:-

$$D_c = \frac{\mu_m \cdot k_6}{k_5 - \mu_m} \dots\dots\dots 69)$$

The model predicts that in continuous culture, the rate of bacterial leaching of nickel from pentlandite (R_3) will depend on the dilution rate as given by equations 58 and 59, up to a value of the critical dilution rate which is determined only by the maximum specific growth rate of the bacteria and the equilibrium constant between attached and unattached bacterial concentrations. The critical dilution rate should be independent of other parameters like oxygen concentration.

It was noted in section 4.2.3. when the leaching was carried out

under/.....

under near optimum conditions using higher rates of agitation (500 r.p.m. compared to 200 r.p.m.) that the critical dilution rate increased from the value of approximately $0,019 \text{ hr}^{-1}$ measured in these tests to approximately $0,025 \text{ hr}^{-1}$ (See Figure 51.) This is due to the effect of agitation on the equilibrium constants between attached and unattached bacteria as predicted by equation 66 above.

The approximately constant values of the measured critical dilution rate may be appreciated by considering the table below.

DETAILS OF TEST	D_c, hr^{-1}
Air	0,016
Air + 2% CO_2	0,017
40% O_2	0,017
60% O_2	0,019
70% O_2	0,020

4.2.3. Economics of Continuous Leaching.

Pentlandite concentrates can be leached in continuous operation and equilibrium conditions are readily obtained. The pattern of leaching observed in batch tests with regard to various parameters was closely followed in the continuous leaching. A critical dilution rate was observed which was usually in the region $0,018 - 0,02 \text{ hr}^{-1}$.

The continuous leaching was operated for over 10 000 hours during which it was unnecessary to reinoculate the vessel. At no time during this run were any problems experienced from a point of infection so that in practice one need only apply strict aseptic technique in the stock culture maintenance stage of an operation.

A series of tests were carried out in which pentlandite

concentrates/.....

concentrates were leached under conditions approaching what would constitute near-optimum practical conditions.

The concentrates were leached as a 20 per cent slurry at 30°C. Oxygen enriched air at 70 per cent O₂ v/v was fed to the reactor. The dilution rate was varied in increments from 0,005 to 0,025 hr⁻¹. The feed solution was tap water containing 0,3 g/l (NH₄)₂ SO₄ and 0,05 g/l K₂HPO₄; (i.e. 1/10th of the concentration of the 9K solution.) No other nutrients were added. The agitation rate was 500 r.p.m. giving a vigorous stirring action. Above 500 r.p.m. cavitation in the vicinity of the propellor was observed, so that efficiency of the stirring dropped off. In practice more efficient stirring systems could be used.

No further comminution was carried out on the concentrates fed to the reactor as it is felt that, if possible, further grinding should be avoided in practice.

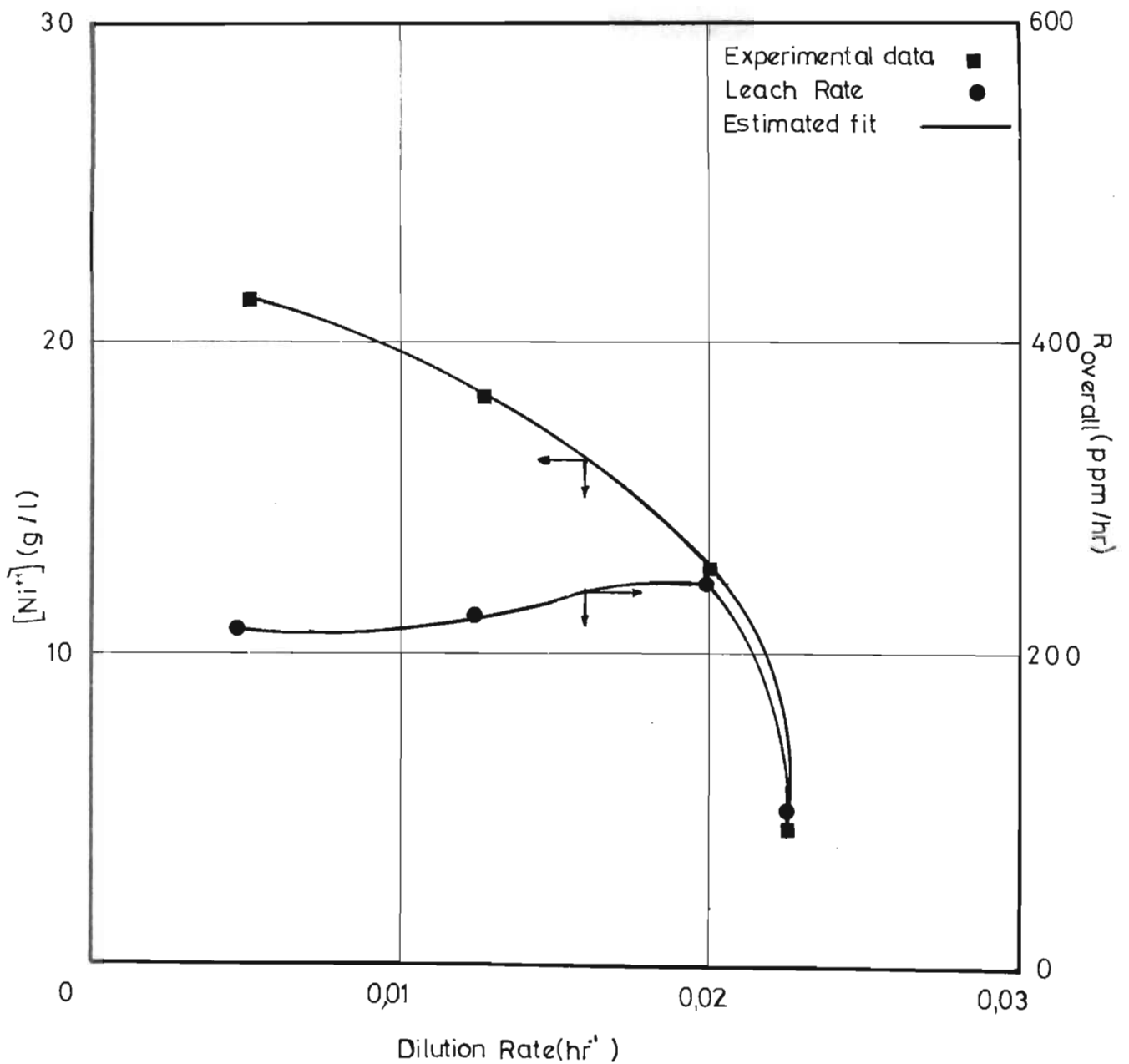
The results of this test are shown graphically in Figure 51 and the detailed experimental data are given in Appendix 21. It may be seen that the dilution rate where the overall leach rate is at a maximum is 0,02 hr⁻¹. At this dilution rate the equilibrium nickel concentration was 12,5 g/l with an overall leach rate of 250 ppm/hr.

This latter rate of leaching is somewhat lower than those

which/.....

Figure 51. Continuous Leaching - Optimum Conditions.

30°C
W 500rpm
pH 3.0
Gas 30% N₂ + 70% Oxygen
20% w/v pentlandite



which Duncan (14) has obtained when leaching sphalerite (ZnS) and chalcopyrite (CuFeS_2) concentrates with bacteria. The difference probably lies in the fact that in Duncan's work the material is ground to minus 400 mesh and agitation is far more vigorous than in the present investigation. In practice the mesh of grind, agitation rate and leach rate will be balanced to give an economic optimum operating point.

The maximum leach rate of 250 ppm Ni^{++} /hr was used in the preliminary economic assessment of a process to treat a pentlandite concentrate by bacterial leaching. This assessment is given in Appendix 22. When applied to the proposed concentrates at the Shangani mine in Rhodesia, the method of bacterial leaching appears to show some attraction, both from an economic and technical point of view.

5. SUMMARY AND CONCLUSIONS.

A study on the leaching of the nickel mineral, pentlandite, ($\text{Ni Fe S}_{1,8}$) has been carried out. Leaching was achieved using both biological and chemical methods and comparisons were made between the two systems. The chief aim of the investigation was to obtain leach data which could be used to clarify both the biological and chemical mechanisms of pentlandite leaching in dilute sulphuric acid solutions. Models of the leach process, based on the data, have been proposed and a brief economic assessment of a biological leaching process carried out. It is considered that the results are sufficiently encouraging to warrant further investigation of the heap leaching of pentlandite in waste rock. (The dump sites at the new Shangani mine are being suitably laid out for leaching at some future date).

The chemical leaching of pentlandite in acid ferric sulphate solutions was studied. It is proposed that the overall chemical leach rate may be represented by two separate rates, one mass transport controlled and the other chemical rate controlled. The mass transport mechanism is consistent with the data of Treybal (84) when ferric ions are the diffusing reactant. The chemical mechanism is consistent with the work of Shneerson (71) and may be explained in terms of oxygen adsorption onto the mineral surface.

A linear/.....

The 'true' rate of bacterial leaching was calculated by subtracting the chemical leach rates from the overall measured leach rates. The chemical rates were calculated from the chemical kinetic data. This correction allowed a more thorough interpretation to be made of the bacterial leaching results. Under optimum conditions the biological leach rate was over five times greater than the combined chemical leach rates.

A model is proposed (based on the batch data) in which it is envisaged that bacteria attach at the mineral surface and take up negatively charged sulphur. Detachment then occurs followed by metabolism and oxygen up-take. The attachment-detachment equilibrium is considered to be dependent on agitation. The linear nature of the leach curves may be explained in terms of the growth being controlled by the available surface area of substrate. (i.e. mineral.) Alternatively the process may be thought of as rapidly reaching what is called the stationary phase in normal growth curves; the mineral surface becomes saturated with attached bacteria and the growth and leaching patterns are linear. This dependence of the leach rate on surface area is consistent with the recent work of Torma. (86)

Continuous leaching/.....

A linear growth pattern was observed for the particular strain of Thiobacillus ferrooxidans on sulphur. This linear growth pattern is considered to be due to either the rate of dissolution of oxygen or the rate of diffusion of some nutrient at the sulphur surface being growth limiting.

Sintered discs of pentlandite were found to be unsuitable for studying bacterial leaching by electro-chemical (e.g. polarisation) techniques. Examination of mineral surfaces after both chemical and biological leaching using optical and electron microscopy showed that small amounts of pyrrhotite (FeS) are formed as an intermediate in the leaching reaction. Sulphur was found to detach readily from the mineral surface.

A series of batch bacterial leach tests were carried out to test the effect on leaching of the following parameters:-

1) Pulp density.

A linear relationship exists.

2) pH.

In the range pH 1,5 to pH 4,5 the leach rates are virtually constant.

3) Agitation.

This parameter markedly affects leach rate.

4) Particle size/.....

4) Particle size. (Mesh of Grind)

A linear relationship exists with respect to surface area.

5) Nutrients.

Reducing the nitrogen and phosphorous levels to 1/10th the normal 9 k level has no effect.

6) Oxygen Concentration.

A marked increase in leach rate is obtained up to 70 per cent (v/v) oxygen.

7) Carbon Dioxide.

A slight increase is obtained up to approximately 1 per cent (v/v).

8) Temperature.

The optimum temperature is in the range 30° - 35°C.

The pattern of the leach curves are rather ill-defined and seem to be approximately linear. A ceiling of about 21 000 ppm Ni⁺⁺ in solution was found and is considered to be due to toxicity of soluble nickel.

A test was carried out in which the soluble nickel was continually removed by dialysis. The linear nature of the nickel leaching and bacterial growth is more clearly defined in this test.

Continuous leaching was carried out over a period of 10 000 hours. The effects of a number of parameters on the leach rates were measured, the results being largely as expected from the batch data. The growth rates (i.e. leach rates) in continuous leaching were higher than those of the equivalent batch leaches; at low dilution rates the equivalent batch rates were approached. This finding is considered to imply that the specific growth rate of the bacteria is being controlled by the concentration of some nutrient in the leach medium.

The biological leach rate is thus mainly a function of the surface area of mineral, oxygen concentration, agitation and specific growth rate of the bacteria.

In conclusion it was found that:-

1. During the chemical leaching of nickel from pentlandite in acid ferric sulphate solutions, the leach rate shows a marked dependence on oxygen concentration.

2/.....

2. The rate of chemical leaching may be represented by a kinetic equation as follows:-

$$R_{\text{overall}} = R_1 + R_2, \text{ where}$$

$$R_1 = K_1 \cdot [\text{Fe}^{+++}] \cdot W^{0,833} \text{ and}$$

$$R_2 = K_2 \cdot pO_2^{\frac{1}{2}}$$

Good agreement was found between experimental data and data calculated using the above model.

3. The use of ozonised oxygen gives large increases in the leach rate of nickel. This fact supports the hypothesis that the rate is limited by the rate or rates of cathodic reactions at the mineral surface.
4. Inconclusive results were obtained when polarisation studies were carried out on the bacterial leaching of nickel from sintered discs of pentlandite.

5. The bacterial growth on sulphur is characterised by linear growth patterns. A yield constant of 0,24 g cell nitrogen/mole H^+ produced was measured. A relationship of $1,27 \times 10^7$ bacterial cells per $1 \mu g$ of cell nitrogen was established from experimental data. The linear characteristics of growth in these initial tests are considered to be due to rate of oxygen transfer from the gas bubbles being rate limiting.
6. In continuous culture on sulphur, equilibrium conditions may be obtained and washout occurs at a dilution rate of approximately $0,06 \text{ hr}^{-1}$. Continuous culture was carried out on sulphur prills (as opposed to fine powdered sulphur) where the transfer of oxygen from the gas bubbles was rendered non rate limiting. In this latter case the growth rate of bacteria was still found to be dependent on the rate of agitation; mass transfer by another mechanism was now rate limiting. It was found that the Monod-type relationship which gives $\mu = D$ at steady state does not apply in these experiments.
7. If soluble nickel is continually removed from the leach solution during a batch bacterial leach experiment, the rates of nickel leaching and bacterial growth are distinctly linear and the rate of leaching is the same as that obtained if the soluble nickel had not been removed. The nickel cations appear to become toxic to the bacteria at concentrations above approximately 21 g/l Ni^{++} . The yield constant calculated from the dialysis experimental data is close to the value measured from the

growth/.....

growth data on sulphur.

8. The batch bacterial leach rates of nickel were measured over a wide range of physico-chemical conditions. The chemical leach rates were calculated using the chemical kinetic model and subtracted from the measured batch rates to give what may be considered a "true" batch bacterial leach rate (This was represented as R_3 ; i.e. $R_{\text{overall}} = R_1 + R_2 + R_3$.)

9. It was found that:-

- a) R_3 depends linearly on pulp density and surface area of mineral.
- b) R_3 depends only slightly on pH in the range 1,5 to 4,0.
- c) R_3 is greatly increased by increasing the oxygen concentration with the maximum rate occurring at approximately 70 per cent oxygen.
- d) R_3 increases with increasing agitation up to 250 r.p.m. Excessive agitation (vibromixing) causes a decrease in R_3 .
- e) R_3 increases with carbon dioxide concentration up to 2 per cent.
- f) R_3 shows an optimum value at 30°C to 35°C.
- g) Reducing the main 9K medium constituents to 1/10th of their usual level has no effect on R_3 .

10/.....

10. A model for the bacterial leaching of nickel from pentlandite is proposed, based on the batch data. It is envisaged that unattached bacteria in the leach solution are first adsorbed onto the mineral surface where negatively charged sulphur is taken up. The bacteria containing the negatively charged sulphur then desorb from the mineral surface and take up oxygen in order to metabolise the sulphur. In this way the bacteria function as effective cathodic depolarising agents (electron acceptors). This postulate is supported by the previous work of Corrans. (28) The effect of agitation is to increase the rate of transfer of cells to and from the mineral surface. The rate of bacterial leaching R_3 may be represented as follows:-

$$R_3 = K \cdot S_a \cdot pO_2^2.$$

The effect of agitation is incorporated in the constant K. The rate is independent of bacterial numbers once the surface has become saturated with bacteria, which occurs fairly rapidly as witnessed by the linear leach and growth rates. There are, of course, maximum limits to the various rate determining parameters.

Insufficient experimental data is available to evaluate K so that a more rigorous test of the model could not be made.

11. Equilibrium conditions were obtained in continuous bacterial leaching experiments and a reactor was operated as a chemostat for nearly two years. The effects of a number of physico-chemical parameters during the operation of the continuous bacterial leach were/.....

were investigated. Critical dilution rates in the region of 0,016 to 0,02 hr⁻¹ were measured. At the end of the continuous experiment a sterile leach was carried out and a decrease in leach rate was measured. The bacteria thus clearly have a positive effect on the overall leach rate.

12. The results of the continuous leaching tests were corrected for chemical leaching as described in paragraph 8 for the batch data. The effects of the physico-chemical parameters are similar to those noted in the batch tests.
13. The batch bacterial leaching model predicts that R_3 will be independent of dilution rate D , up to a critical value when the surface concentration of bacteria drops below the saturation level. The continuous leach data show marked deviations from this model at low dilution rates implying that some constituent of the feed medium becomes rate limiting.
14. It is proposed that the critical dilution rate is related to the maximum specific growth rate of the bacteria as follows:

$$D_c = \frac{\mu_m \cdot k_6}{k_6 - \mu_m}$$

15. Using the yield constant measured during the growth on sulphur, good agreement between measured and calculated values of R_3 was found.

16. A brief economic assessment was made of a process to continuously leach nickel from Shangani concentrates using bacteria. The process is based on the results of the present investigation and is found to be economically attractive.

17. As an extension of the present investigation more work could be conducted in the area of continuous culture both on sulphur and pentlandite concentrates to further test the proposed models.

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APPENDIX 1.DETAILED EXPERIMENTAL DATA FOR FACTORIAL EXPERIMENT.

These data are shown in the accompanying Table 7. The leach rates were calculated using a method of least squares fit on the data. Some tests were carried out more than once when the leach rates of the original duplicate test showed more than approximately 15 per cent variance. The average leach rates used in the calculation of the 'effect' are given in Table 5, (Section 4.1.1.) in the main text.

In spite of the precautions taken to eliminate the initial rapid release of nickel into solution, (by acid washing the sample) some tests, especially where the acid strength was high, showed a distinct departure from linear leaching near the beginning. In these tests the linear regression was carried out by ignoring the first one or two data points.

TABLE 7. DETAILED ASSAY RESULTS FOR INDIVIDUAL TESTS. (FACTORIAL EXPERIMENT).

TEST NO.	TIME HOURS.	Ni ppm		Fe ppm		Leach Rate ppm/hr
1	0	<0,5	<0,5	<2	<2	0,17 0,20
	1	7,5	5	24,5	54	
	3,5	3,5	4			
	5,5	3	4,2			
	25,25	7,5	7,5	47	52,5	
2	0	<0,5	<0,5	12 400	12 400	1,04 0,53
	1	5	6,5			
	3,5	7	5,2			
	5,5	6	5			
	25,25	22,5	23	14 300	15 100	
70,5	105	68	15 500	16 300		
3	0	<5	<5	<2	<2	4,41 5,70
	3	112	44	50	12	
	21,5	133	133	72	36	
3	0	<0,5	<0,5	<0,5	<0,5	3,36 3,22
	1	2	3			
	2	5	6			
	4	9	11			
	21,25	50	68	70	<0,5	
4	0	<5	<5	14 600	14 600	6,68 3,00
	3	16	23	14 300	15 400	
	21,5	142	70	15 900	16 400	
4	0	2	2	10 618	10 618	5,36 6,834
	1	6	6			
	2	9	10			
	4	17	20			
	21,25	116	144	12 870	13 191	
5	0	<0,5	<0,5	<0,5	<0,5	0,22 0,18
	1	3	3			
	2,25	2	2			
	4	2	<0,5	<0,5	<0,5	
6	0	1	1	13 500	13 500	124,1 136,0
	0,5	51	72			
	1	123	146			
	2,25	294	321			
	4	488	544	13 500	14 120	

TEST NO.	TIME HOURS.	Ni ppm		Fe ppm		Leach Rate ppm/hr
7	0	<2	<2	<2	<2	5,05
	3	24	34			6,21
	21	110	137	16	<2	
7	0	<0,5	<0,5	<0,5	<0,5	9,49
	1	26	26			7,09
	2	37	37			
	4	57	57	291	215	
8	0	<2	<2	14 000	14 000	43,57
	3	610	538			42,95
	21	1 100	1 060	10 000		
8	0	<0,5	<0,5	13 290	13 290	187,74
	1	203	222			217,19
	2	405	445			
	4	752	868	12 356	12 931	
9	0	<2	<2	<2	<2	5,07
	1,5	131	68	271	82	6,30
	3	195	75	488	94	
	5	128	162	350	700	
	21	190	172	750	700	
9	0	<1	<1			4,8
	3	136	129			3,7
	21,5	221	196			
10	0	<2	<2	13 750	13 750	5,38
	1,5	77	80	15 400	15 600	5,27
	3	172	106	17 000	16 200	
	5	94	160	15 200	16 700	
	21	172	152	16 200	16 200	
10	0	<1	<1			3,11
	3	114	104			3,21
	21,5	193	189			
11	0	<1	<1	<5	<5	8,23
	0,5	<1	<1	<5	<5	8,17
	0,5	7	8			
	1	13	13			
	2,5	27	27			
	4,5	42	42			

TEST NO.	TIME HOURS.	Ni ppm		Fe ppm		Leach Rate ppm/hr
12	0	<2	<2	13 800	13 800	4,12 4,08
	0,5	5	6			
	1	9	10			
	2,5	17	19			
	4,5	26	23			
13	20,5	97	83	14 400	14 400	29,50 29,50
	0	<3	<3	<10	<10	
	1	213	194			
	2	238	225			
	3	281	250	1 463	694	
	4	306	275	1 463	638	
14	0	<3	<3	13 200	13 200	123,80 129,50
	1	289	256			
	2	418	381			
	3	538	544			
	4	650	644	1 505	7 200	
15	0	<5	<5	<10	<10	16,74 14,76
	1	195	175			
	2	215	210			
	3	240	220			
	19	435	390	1 535	1 324	
15	0	<3	<3	<10	<10	10,01 9,77
	0,5	72	66			
	1	90	87			
	2	102	99			
	4	114	111	720	540	
16	0	<5	<5	13 625	13 625	199,98 191,39
	1	350	345			
	2	410	380			
	3	505	485			
	19	3 831	3 667	16 490	15 775	
16	0	<3	<3	8 600	8 600	134,21 134,15
	0,5	81	99			
	1	144	156			
	2	222	233			
	4	357	384	15 600	15 800	

TEST NO.	TIME HOURS.	Ni ppm		Fe ppm		Leach Rate ppm/hr
17	0	0	0	1	1	0,20 0,17
	1	7	7	380	44	
	2	6	7	242	36	
	5	7	8	154	63	
	21,75	8	8	276	60	
18	0	0	0	11 300	11 300	1,47 0,91
	1	13,5	13,5			
	2	16	16			
	5	21	18	11 600	11 450	
	21,75	44	33	11 300	11 300	
19	0	<5	<5	<2	<2	13,14 13,04
	3	162	157	109	34	
	21,5	330	326	27	34	
19	0	<0,5	<0,5	<0,5	<0,5	24,90 21,68
	1	8	8			
	2	20	18			
	4	51	45			
	21,25	512	453	<0,5	<0,5	
20	0	<#	<5	13 800	13 800	13,67 36,15
	3	147	167	14 100	15 400	
	21,5	335	800	14 300	14 600	
20	0	2	2	10 618	10 618	22,24 22,64
	1	13	13			
	2	25	23			
	4	51	45			
	21,25	462	476	11 261	11 904	
21	0	<0,5	<0,5	<0,5	<0,5	0,83 0,56
	0,5	4	4			
	1	2	3			
	2,25	3	<0,5			
	4	<0,5	<0,5	2	<0,5	
22	0	1	1	13 500	13 500	140,6 131,3
	0,5	103	107			
	1	208	190			
	2,25	394	361			
	4	570	538	12 251	11 836	

TEST NO.	TIME HOURS.	Ni ppm		Fe ppm		Leach Rate ppm/hr
23	0	<2	<2	<2	<2	33,91 25,58
	3	252	240			
	21	770	600	26	62	
23	0	<0,5	<0,5	<0,5	<0,5	110,60 123,26
	0,5	45	46			
	1	73	81			
	2	230	246			
	4	429	469	404	352	
23	0	<5	<5	<5	<5	84,35 140,70
	0,5	29	28			
	1	70	89			
	2	150	229			
	4	333	546	28	43	
24	0	<2	<2	14 000	14 000	83,33 118,60
	3	900	900			
	21	2 000	2 700	9 000	9 000	
24	0	<0,5	13 290	<0,5	13 290	188,05 355,28
	0,5	213	469			
	1	357	868			
	2	576	1 656			
	4	816	1 511	10 417	10 058	
24	0	<5	<5	13 788	13 788	557,34 517,18
	0,5	240	202			
	1	485	403			
	2	1 166	972			
	4	1 798	1 652	10 571	10 571	
25	0	<2	<2	49	49	3,03 3,01
	1,5	115	118	314	238	
	3	142	140	293	260	
	5	147	142	550	293	
	21	190	190	775	350	
26	0	<2	<2	12 200	12 200	5,21 3,37
	1,5	82	84	15 600	15 850	
	3	113	113	15 600	16 000	
	5	119	114	17 200	16 000	
	21	179	173	16 700	16 700	

TEST NO.	TIME HOURS.	Ni ppm		Fe ppm		Leach Rate ppm/hr
27	0	<1	<5	<1	<5	17,92 19,65
	0,5	15	15			
	1	21	20			
	2,5	46	44			
	4,5	84	81			
	20,5	370	404	500	432	
28	0	<2	<2	13 800	13 800	20,05 12,66
	0,5	15	16			
	1	24	22			
	2,5	52	44			
	4,5	92	71			
	20,5	414	267	13 800	14 600	
29	0	<3	<3	<10	<10	15,0 15,0
	1	175	181			
	2	231	213			
	3	238	238			
	4	250	256	631	625	
30	0	<3	<3	12 200	12 200	134,70 127,50
	1	344	388			
	2	481	506			
	3	631	656			
	4	731	775	14 500	15 050	
31	0	<5	<5	12	12	74,00 98,81
	1	210	245			
	3	315	390			
	19	1 475	1 950	1 535	1 888	
31	0	<3	<3	<10	<10	94,69 117,45
	0,5	114	138			
	1	147	193			
	2	216	281			
	4	411	508	320	900	
31	0	<5	<5	<5	<5	117,20 104,50
	0,5	144	162	610	600	
	1	219	242	878	860	
	2	367	406	1 120	1 040	
	4	658	724	1 700	1 600	

APPENDIX 2.CALCULATION OF THE AVERAGE EFFECTS FOR THE FACTORS AND
COMBINATIONS OF FACTORS: MENDELOWITZ (69).

The figures in column six of Table 5 represent the average effects for the factors or combinations of factors in the corresponding row, e.g. row 7 (corresponding to test 7) shows an average effect on the nickel leach rate by using pure oxygen gas at 30°C and 80°C of 44,9 ppm/hr. The same is true for single factors and for the third, fourth and fifth order combinations of factors. The larger the "effect", the more important the factor or combination in determining the leach rate of nickel.

In order to determine more precisely which effects and interactions are significant, some estimate of the experimental error is needed. The "t" test was applied to the 4 and 5 factor average effects to give a standard error of contrast of 14,2 ppm/hr. The "t" values for 16 degrees of freedom and corresponding probabilities obtained from tables are shown in the accompanying Table 8.

Any value in column 6 which exceeds the product ("t" x standard error) is significant at the corresponding probability. For example, at a probability of 0,995, temperature (Test 5) has a marked effect on the leach rate of nickel. At lower probabilities, other factors and combinations have lesser effects.

TABLE 8.'t' VALUES AND PROBABILITIES.

't'	Probability	't' x Standard Error
3,25	0,995	48,6
2,92	0,99	43,9
2,12	0,95	31,8
1,75	0,90	26,2

Column 1 was calculated by adding the leach rate results in pairs and then subtracting the leach rate results in pairs. Column 2 was drawn up by carrying out the same operation on Column 1. This was done until the number of columns was equal to the number of factors, five in this case. The average effect was then found by dividing the figures in column 5 by 16 since there are 16 pairs of tests for each factor or combination. The first figure in column 5 is the sum total of all the leach rates.

The standard error of contrast was calculated:-

$$\sqrt{\frac{(-18,92)^2 + (13,86)^2 + (-13,47)^2 + (-12,10)^2 + (-12,19)^2 + (-13,69)^2}{6}}$$

$$= 14,2 \text{ ppm/hr.}$$

APPENDIX 3.CALCULATION OF ACTIVATION ENERGY. (85).

Arrhenius' Law states that:

$$k = k_0 e^{-\Delta H/RT}$$

k is the reaction rate constant

k_0 is the frequency factor

ΔH is the activation energy.

$$\therefore \ln k = \ln k_0 - \frac{\Delta H}{R} \cdot \frac{1}{T}$$

A graph of $\ln k$ vs $\frac{1}{T}$ should therefore be a straight line with a slope of $-\frac{\Delta H}{R}$. Figure 11 shows good agreement between the

experimental data and Arrhenius' Law, the slope of the line of best fit being $-3,18 \times 10^3$ °K

$$\therefore -\frac{\Delta H}{R} = -3,18 \times 10^3 \times 2,3$$

(The factor 2,3 converts the log value of the slope to the natural logarithm.)

$$R = 1,98 \text{ cal/deg-mole}$$

$$\therefore \Delta H = 14,5 \text{ cal/g-mole.}$$

APPENDIX 4.

DETAILED EXPERIMENTAL DATA FOR KINETIC TESTS.1. TABLE 9: Effect of $[Fe^{+++}]$ on leach rates.

pO_2	=	50%
Temperature	=	50°C
$[H^+]$	=	2×10^{-2} M
W	=	200 r.p.m.

Time Hours	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	$[Fe^{+++}] = 0,01M$	
0,5	19	17	23		
1	26	26	33		
2	45	49	48		
3,5	72	93	94		
				Average	Calculated
$R_{overall}$ ppm/hr	22,6	26,0	27,8	25,5	25,9

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	[Fe ⁺⁺⁺] = 0,025 M	
0,5	18	15	37		
1,0	27	25	70		
2,0	46	42	140		
3,5	80	73	205		
5,0	98	98	330		
R _{overall} , ppm/hr	19,5	19,2	63,3	Average	Calculated
				-	29,8
0	0	0	0	[Fe ⁺⁺⁺] = 0,025	
0,5	18	27	17		
1,0	32	47	29		
2,0	57	97	50		
3,5	107	150	85		
5,0	146	180	120		
R _{overall} , ppm/hr	29,2	36,7	23,4	Average	Calculated
				29,8	29,8
0	0	0	0	[Fe ⁺⁺⁺] = 0,05 M	
0,5	17	20	24		
1,0	29	36	46		
2,0	53	68	83		
3,5	125	143	155		
5,0	136	172	190		
R _{overall} , ppm/hr	29,2	36,0	39,0	Average	Calculated
				37,5	36,4
0	0	0	0	[Fe ⁺⁺⁺] = 0,075M	
0,5	26	30	23		
1,0	50	52	45		
2,0	92	105	77		
3,5	150	160	126		
5,0	210	220	173		
R _{overall} , ppm/hr	41,4	43,4	34,0	Average	Calculated
				42,4	43,0

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	[Fe ⁺⁺⁺] = 0,125 M	
0,5	37	26	24		
1,0	58	42	40		
2,0	119	93	82		
3,75	205	163	149		
5,0	262	219	203	Average	Calculated
R _{overall} , ppm/hr	53,0	44,0	41,0	46	56,0 *
0	0	0	0	[Fe ⁺⁺⁺] = 0,15 M	
0,5	25	26	27		
1,0	38	49	51		
2,0	73	91	97		
3,75	127	147	152		
5,0	180	200	200	Average	Calculated
R _{overall} , ppm/hr	35,4	39,6	40,0	38,3	62,6 *
0	0	0	0	[Fe ⁺⁺⁺] = 0,3M	
0,5	32	28	24		
1,0	50	47	40		
2,0	96	91	80		
3,75	150	150	128		
5,0	204	210	230	Average	Calculated
R _{overall} , ppm/hr	40,0	41,4	43,6	41,7	101,9 *

* Out of range of model; [Fe⁺⁺⁺] > 0,1 M

TABLE 10:

2. Effect of W on leach rates.

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pO_2 = 50%
 Temperature = 50°C
 $[H^+]$ = 2×10^{-2} M
 $[Fe^{+++}]$ = 0,125 M

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	W = 75 r.p.m.	
0,5	22	24	28		
1,0	38	39	41		
2,0	64	65	72		
3,5	117	114	130		
5,0	159	163	193		
$R_{overall}$, ppm/hr	31,4	31,6	37,4	Average	Calculated
				33,5	34,8
0	0	0	0	W = 125 r.p.m.	
0,5	21	18	19		
1,0	33	26	29		
2,0	62	47	49		
3,5	120	80	83		
5,0	150	110	115		
$R_{overall}$, ppm/hr	30,6	21,5	22,3	Average	Calculated
				25,0	41,3
0	0	0	0	W = 200 r.p.m.	
0,5	37	26	24		
1,0	58	42	40		
2,0	119	93	82		
3,5	205	163	149		
5,0	262	219	203		
$R_{overall}$, ppm/hr	52,3	44,4	41,0	Average	Calculated
				46,6	49,6

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	W = 300 r.p.m.	
0,5	24	32	29		
1,0	50	70	63		
2,0	82	148	130		
3,5	156	232	205		
5,0	205	294	267		
R _{overall} , ppm/hr	442	60,1	54,2	51,8	60,1
0	0	0	0	W = 500 r.p.m.	
0,5	44	41	46		
1,0	83	75	84		
2,0	178	166	188		
3,5	292	270	308		
5,0	362	342	386		
R _{overall} , ppm/hr	74,3	70,0	79,3	74,5	80,3
0	0	0	0	W = 750 r.p.m.	
0,5	50	63	49		
1,0	92	104	96		
2,0	210	225	220		
3,5	380	358	347		
5,0	425	450	455		
R _{overall} , ppm/hr	90,7	92,1	92,8	91,9	102,3

TABLE 11:

3. Effect of pO_2 on leach rates.

Temperature = 30°C

$[H^+]$ = $2,0 \times 10^{-2}$ M

W = 200 r.p.m.

$[Fe^{+++}]$ = 0,125 M

TIME HOURS	Ni ⁺⁺ - ppm.				
	1	2	3		
0	0	0	0	pO ₂ = 1%	
0,5	23	35	15		
1,0	33	57	27		
2,0	54	107	47		
3,5	93	180	80		
5,0	133	256	122		
				Average	Calculated
R _{overall} , ppm/hr	25,5	50,2	23,6	-	27,3
0	0	0	0	pO ₂ = 1%	
0,5	16	14	18		
1,0	25	22	28		
2,0	42	40	49		
3,5	60	70	82		
5,0	100	109	122		
				Average	Calculated
R _{overall} , ppm/hr	18,4	21,0	23,5	22,4	27,3
0	0	0	0	pO ₂ = 3,6%	
0,5	15	14	14		
1,0	28	27	26		
2,0	54	53	52		
3,5	96	100	100		
5,0	150	150	155		
				Average	Calculated
R _{overall} , ppm/hr	29,4	29,8	30,7	30,0	32,6

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	pO ₂ = 10%	
0,5	17	26	18		
1,0	31	45	32		
2,0	65	90	58		
3,5	116	150	104		
5,0	174	214	155	Average	Calculated
R _{overall} , ppm/hr	34,6	42,3	30,4	-	36,7
0	0	0	0	pO ₂ = 10%	
0,5	18	11	16		
1,0	28	18	25		
2,0	54	36	49		
3,5	131	65	84		
5,0	154	106	128	Average	Calculated
R _{overall} , ppm/hr	32,6	20,6	24,9	26,0	36,7
0	0	0	0	pO ₂ = 25%	
0,5	17	15	15		
1,0	35	29	29		
2,0	75	65	65		
3,5	125	105	95		
5,0	170	135	130	Average	Calculated
R _{overall} , ppm/hr	34,4	27,6	26,0	-	42,8
0	0	0	0	pO ₂ = 25%	
0,5	21	21	28		
1,0	36	35	50		
2,0	61	66	108		
3,5	97	110	182		
5,0	156	170	280	Average	Calculated
R _{overall} , ppm/hr	29,3	32,7	55,0	39,0	42,8

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	pO ₂ = 50%	
0,5	37	26	24		
1,0	58	42	40		
2,0	119	93	82		
3,5	205	163	149		
5,0	262	219	203	Average	Calculated
R _{overall} , ppm/hr	53,0	44,4	41,0	46,0	49,7
0	0	0	0	pO ₂ = 75%	
0,5	24	29	20		
1,0	38	46	32		
2,0	71	97	62		
3,5	128	150	108		
5,0	168	192	150	Average	Calculated
R _{overall} , ppm/hr	36,6	38,5	29,7	-	54,9
0	0	0	0	pO ₂ = 75%	
0,5	25	21	17		
1,0	47	35	32		
2,0	93	71	61		
3,5	160	120	111		
5,0	240	180	164	Average	Calculated
R _{overall} , ppm/hr	47,3	35,3	32,5	36,6	54,9
0	0	0	0	pO ₂ = 100%	
0,5	18	38	15		
1,0	33	82	33		
2,0	72	175	76		
3,5	140	310	143		
5,0	200	420	204	Average	Calculated
R _{overall} , ppm/hr	40,5	85,7	41,7	56	59,3

TABLE 12:

4. Effect of $[H^+]$ on leach rates.

pO_2 = 50%
 $[Fe^{+++}]$ = 0,135 M
 W = 200 r.p.m.
 Temperature = 30°C

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	$[H^+] = 2 \times 10^{-4} M$	
0,5	18	17	15		
1,0	32	28	27		
2,0	65	53	53		
3,5	118	93	93		
5,0	185	128	131	Average	Calculated
$R_{overall}, ppm/hr$	36,4	25,4	26,1	29,3	49,6
0	0	0	0	$[H^+] = 2 \times 10^{-3} M$	
0,5	25	28	21		
1,0	43	51	37		
2,0	70	86	62		
3,5	118	143	105		
5,0	155	193	148	Average	Calculated
$R_{overall}, ppm/hr$	30,4	37,8	28,8	32,3	49,6
0	0	0	0	$[H^+] = 2 \times 10^{-2} M$	
0,5	37	26	24		
1,0	58	42	40		
2,0	119	93	82		
3,5	205	163	149		
5,0	262	219	203	Average	Calculated
$R_{overall}, ppm/hr$	53,0	44,3	41,0	46,1	49,6

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	[H ⁺] = 2 × 10 ⁻¹ M	
0,5	32	30	44		
1,0	41	48	78		
2,0	71	88	144		
3,5	115	138	212		
				Average	Calculated
R _{overall} , ppm/hr	34,4	43,1	63,0	46,8	49,6
0	0	0	0	[H ⁺] = 5 × 10 ⁻¹ M	
0,5	35	35	30		
1,0	53	56	46		
2,0	93	99	70		
3,5	146	157	109		
5,0	200	200	156		
R _{overall} , ppm/hr	38,6	29,3	29,2		
0	0	0	0	[H ⁺] = 1 M	
0,5	27	27	26		
1,0	39	41	38		
2,0	66	67	62		
3,5	100	110	100		
5,0	139	147	140		
R _{overall} , ppm/hr	26,4	28,4	26,7		
0	0	0	0	[H ⁺] = 2 M	
0,5	28	25	25		
1,0	40	39	36		
2,0	69	63	54		
3,5	110	100	85		
5,0	164	150	124		
R _{overall} , ppm/hr	31,1	28,3	23,0		

TABLE 13:

5. Effect of temperature on leach rates.

pO_2 = 50%
 $[Fe^{+++}]$ = 0,125 M
 W = 200 r.p.m.
 $[H^+]$ = 2×10^{-2} M

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	T = 30°C	
0,5	7	9	8		
1,0	9	13	12		
2,0	15	20	19		
3,5	22	28	28		
5,0	27	35	35	Average	Calculated
R _{overall} , ppm/hr	5,1	6,5	6,7	6,1	9,4
0	0	0	0	T = 40°C	
0,5	16	16	13		
1,0	18	24	21		
2,0	29	40	32		
3,5	45	66	50		
5,0	61	87	69	Average	Calculated
R _{overall} , ppm/hr	11,3	16,7	13,1	13,7	19,5
0	0	0	0	T = 50°C	
0,5	37	26	24		
1,0	58	42	40		
2,0	119	93	82		
3,5	205	163	149		
5,0	262	219	203	Average	Calculated
R _{overall} , ppm/hr	53,0	44,4	41,0	46,1	40,7

TIME HOURS	Ni ⁺⁺ - ppm				
	1	2	3		
0	0	0	0	T = 60°C	
0,5	40	54	35		
1,0	70	96	64		
2,0	131	185	123		
3,5	230	325	235		
5,0	365	475	429	Average	Calculated
R _{overall} , ppm/hr	71,0	93,8	69,4	78,1	85,0
0	0	0	0	T = 70°C	
0,5	80	80	80		
1,0	130	150	160		
2,0	260	280	310		
3,5	440	430	460		
5,0	550	540	560	Average	Calculated
R _{overall} , ppm/hr	124,1	122,0	132,0	126,0	152,0
0	0	0	0	T = 80°C	
0,5	125	125	137		
1,0	270	277	295		
2,0	462	500	500		
3,5	625	670	645		
5,0	720	805	760	Average	Calculated
R _{overall} , ppm/hr	* 231,6	* 251,5	* 250,5	244,4	293,0

* (0 - 2 hours)

APPENDIX 5.DETAILED EXPERIMENTAL DATA FOR THE LEACHING OF PENTLANDITE IN THE PRESENCE OF OZONE.1. TABLE 14: TEST WITH OZONE.

Volume : 200 ml water
 Agitation : vibromix (vigorous.)
 Gas : ozonised oxygen (2 - 3 % O₃)
 pH : (initial) : 5,0
 Temperature : 30°C
 Solids : 20% acid washed lower grade pentlandite concentrates.

Time Hours	Ni ⁺⁺ ppm	Fe ppm	pH	Extraction of Nickel, %
0	0	0	5,0	0
16,5	12 600	660	1,7	35
43,5	23 250	18 600	1,3	64
65	29 000	17 800	-	81

2. TABLE 15: CHEMICAL CONTROL.

Volume : 200 ml water
 Agitation : vibromix (vigorous.)
 Gas : oxygen
 pH : (initial) : 5,3
 Temperature : 30°C
 Solids : 20% acid washed low grade pentlandite concentrates.

Time Hours	Ni ⁺⁺ ppm	Fe ppm	pH	Extraction of nickel, %
0	0	0	5,3	0
23	1 080	2	5,8	3,0
17	1 700	4	5,55	4,7
71	2 500	40	5,5	6,9
95	3 500	-	5,45	9,7

APPENDIX 6.CALCULATION OF SPECIFIC SURFACE OF MINERAL.

The mineral used was screened as -200 mesh + 325 mesh; i.e. 74 μ m to 44 μ m. An 'average' particle dimension was thus taken as 59 μ m, i.e. 59×10^{-4} cm; i.e. $\frac{(74 + 44)}{2} \mu$ m

For particles of various geometric shapes;

$$\text{Area} = K_a d^2$$

$$\text{Volume} = K_v d^3$$

Where K_a and K_v are constants and D is a typical dimension.

For spheres, $K_a = \pi$ and $K_v = \pi/6$ and d is the diameter.

For crushed quartz $K_a = 2,5$ and $K_v = 0,27$. (64)

The specific surface area of a material (i.e. the surface area per unit mass) may be calculated:-

$$S_a \text{ (specific surface)} = \frac{K_a}{K_v} \cdot \frac{1}{\rho d_m}$$

where ρ = density

d_m = typical dimension.

If it is assumed that crushed pentlandite is geometrically similar to crushed quartz and that 59 μ m represents a typical dimension, then:- ($\rho = 5,0$ for pentlandite.)

$$S_a = \frac{2,5}{0,27} \times \frac{1}{5,0 \times 59 \times 10^{-4}} \approx 300 \text{ cm}^2/\text{g}$$

The specific surface for the different size fractions used in the batch bacterial leaching may be calculated from the above formula to give the following results:-

Mesh size,	Average Dimension, μm .	Specific Surface cm^2/g .
-325	20	925
-200 +325	59	300
-150 +200	90	205
-100 +150	125	148
-65 +100	180	103
-48 +65	250	74

APPENDIX 7.EXPERIMENTAL DATA FOR BACTERIAL GROWTH ON SULPHUR.1. TABLE 16: BATCH GROWTH TEST 1.

Substrate : 2% w/v Flowers of Sulphur in 250 ml 9K medium
 Temperature : 30°C
 Agitation: : 150 r.p.m.
 pH : 3,0
 Gas : Air, 40 ml/min
 CO₂ 0,8 ml/min

Time Hours	H ⁺ produced μ moles/ml
105	0,8
220	0,9
313	2,3
330	2,5
342	2,8
360	4,6
380	8,4
390	10,3
409	13,8
430	17,4
458	18,5

TABLE 17: Batch Growth Test 2.

Substrate	:	2 per cent w/v. Flowers of Sulphur in 5l 9K medium.
Temperature	:	30°C
Agitation	:	500 r.p.m.
pH	:	3,0
Gas	:	Air 200 ml/min
	:	CO ₂ 4 ml/min

Time, hrs	H ⁺ produced μ moles/ml
194	1,0
216	9,0
234	19,0
272	42,5
294	58,5
306	71,0
318	74,5
331	83,0
343	93,0
353	104,0
363	110,0
381	106,0
396	119,0

Time, hrs	Bacterial Nitrogen, μg/ml		
23	11,7	7,8	7,8
191	7,1	8,0	8,7
212		10,6	
244	12,0	15,6	
271	19,2	19,7	
293	24,0	24,6	
332		26,0	
356	24,0	28,5	
380	26,4	25,7	

TABLE 18: Continuous Culture on Flowers of Sulphur.

Substrate	:	2 per cent Flowers of Sulphur in 9 K medium.
Temperature	:	30°C
Agitation	:	500 r.p.m.
pH	:	3,0
Gas	:	Air 200 ml/min. CO ₂ 4 ml/min.

Dilution Rate D, hr ⁻¹	Equilibrium Bacterial Nitrogen, µg/ml			
0,008	7,0	12,2		
0,018	17,5	12,0	12,2	10,0
0,024	14,5	11,2	11,0	10,2
0,034	12,4	13,2	13,0	13,4
0,042	11,7	12,2	13,0	

TABLE 19: Continuous Culture on Sulphur Prills (pH - stat).

Substrate : 10 per cent sulphur prills in
9K medium.

Temperature : 30°C

pH : 3,0

Gas : Air 200ml/min.
CO₂ 4 ml/min.

Agitation Rate, r.p.m.	Measured Dilution Rate, hr ⁻¹
1	0,01
50	0,03
250	0,04
750	0,06
1 000	0,06

APPENDIX 8.THE EFFECT OF SURFACTANTS ON THE GROWTH RATE OF THE BACTERIA
ON SULPHUR.

The tests were carried out in 250 ml 9K solution containing 2 per cent flowers of sulphur. The solutions were agitated at 200 r.p.m. in 500 ml conical flasks on an orbital shaker. The pH was adjusted to 3,0 at the beginning of each test and temperature was controlled at 30°C.

Details of tests:-

Flask 1: Control.

Flask 2: 0,01 ml "Tween 20."

Flask 3: 0,01 ml "Teepol."

Flask 4: 0,01 ml "R.B.S. 25." (Chemical Concentrates, London.)

The results of these tests are given in the accompanying Table 20.

Table 20/.....

TABLE 20: RESULTS OF SURFACTANT TESTS.

Time Hours	Bacterial cells/ml			
	1	2	3	4
0	5×10^7	5×10^7	5×10^7	5×10^7
48	$5,3 \times 10^7$	$5,1 \times 10^7$	5×10^7	$4,9 \times 10^7$
96	$6,8 \times 10^7$	$7,0 \times 10^7$	$4,7 \times 10^7$	$4,8 \times 10^7$
144	$9,6 \times 10^7$	$9,5 \times 10^7$	$4,5 \times 10^7$	$4,6 \times 10^7$
192	$14,0 \times 10^7$	$13,8 \times 10^7$	-	-
240	$14,9 \times 10^7$	$15,5 \times 10^7$	$4,3 \times 10^7$	$4,5 \times 10^7$

It was concluded that Tween 20 does not inhibit the growth of the bacteria on sulphur, while Teepol and R.B.S. 25 have a marked inhibitory effect.

APPENDIX 9.CALCULATION OF THE AMOUNT OF SULPHUR TO BE ADDED AT INTERVALS TO THE CONTINUOUS CULTURE.

The assumption was made that the amount of sulphur consumed as a result of bacterial growth is small, compared to the amount being washed out of the reactor. This may be checked:-

Amount of sulphur consumed by bacterial growth at a growth rate equivalent to 1μ mole H^+ produced per ml - hour, (see section 4.1.3)

$$= 1 \times 0,5 = 0,5 \mu \text{ moles/ml-hr}$$

Amount of sulphur being washed out of reactor

$$= S \times D$$

Where S = concentration of sulphur, μ moles/ml

D = dilution rate, hr^{-1}

If $D = 0,05 \text{ hr}^{-1}$

amount = $\frac{2 \times 10^{-2}}{32} \times 10^6 \times 0,05$ (based on $S = 2\%$)

= 30μ moles/ml-hr

Now, the amount of sulphur in the reactor at time t is given by:

$$S = S_0 e^{-Dt} \text{ ----- (a)}$$

S = conc. of sulphur at time t

S_0 = initial conc. of sulphur, $t = 0$

t = time

If 2 per cent sulphur was fed continuously, then over 24 hours,

$S \times t / \dots\dots\dots$

$S \times t = 2 \times 24 = 48$. If instead, sulphur is added once every 24 hours, the average sulphur concentration is still maintained at 2 per cent by ensuring that:-

$$\int_0^{24} S dt \text{ is equal to } 48$$

$$\text{i.e. } \int_0^{24} S_0 e^{-Dt} dt = 48$$

$$48 = \frac{S_0}{D} (1 - e^{-24D})$$

$$S_0 = \frac{48D}{1 - e^{-24D}}$$

For a particular dilution rate, S_0 is found using this equation and S calculated from equation 'a,' with $t = 24$. The amount of sulphur is calculated as $V(S_0 - S)$, where V is the volume of the reactor.

APPENDIX 10.RELATIONSHIP BETWEEN CELL NUMBERS AND BACTERIAL NITROGEN.

The accuracy of the direct cell counting method, using a Petroff-Hausser counting chamber, was checked against the direct determination of bacterial nitrogen using a micro Kjeldahl method. The latter method is long and tedious so it was hoped that the quicker direct counting method could be used. Good agreement (within 15 per cent) was found between the two methods, so that normally direct counting was used to determine bacterial concentration.

Twelve samples were taken during the continuous culture of the bacteria on sulphur. These were analysed for bacterial nitrogen and cell numbers were counted. The results of these tests are shown in the accompanying Table 21.

TABLE 21; COMPARISON OF BACTERIAL NITROGEN AND CELL COUNTS.

Bacterial Nitrogen $\mu\text{g/ml}$	Cell No. cells/ml	Cells/ μg
11,7	$16,3 \times 10^7$	$1,39 \times 10^7$
8,0	$11,7 \times 10^7$	$1,46 \times 10^7$
10,6	$12,1 \times 10^7$	$1,14 \times 10^7$
12,0	$14,5 \times 10^7$	$1,21 \times 10^7$
15,6	$16,8 \times 10^7$	$1,08 \times 10^7$
19,2	$24,4 \times 10^7$	$1,27 \times 10^7$
24,0	$32,0 \times 10^7$	$1,33 \times 10^7$
24,6	$35,6 \times 10^7$	$1,45 \times 10^7$
26,0	$29,7 \times 10^7$	$1,14 \times 10^7$
28,5	$39,8 \times 10^7$	$1,40 \times 10^7$
26,4	$34,4 \times 10^7$	$1,30 \times 10^7$
25,7	$26,1 \times 10^7$	$1,01 \times 10^7$

Average cells/ μg = $1,27 \times 10^7$

APPENDIX 11.CALCULATION OF RATE OF PRODUCTION OF HYDROGEN IONS IN pH-STAT
CONTINUOUS CULTURE. (P).

Mass balance on hydrogen ions:-

Rate of change of $[H^+]$ = Rate of entry + Rate of production
-(Rate of washout + Rate of consumption)

$$\frac{d[H^+]}{dt} = D [H^+]_f + P - D[H^+] - R$$

$$= 0 \text{ at steady state}$$

where D = dilution rate, hr^{-1}

$[H^+]_f$ = concentration of H^+ in feed

$[H^+]$ = concentration of H^+ in reactor

R = rate of consumption of H^+ ions due to the buffering
action of the 9K medium

$$\therefore D ([H^+] - [H^+]_f) = P - R \text{ ----- (a)}$$

$$\text{pH of feed} = 7,26$$

$$\therefore [H^+]_f = 5,5 \times 10^{-8} \text{ moles/l}$$

$$\text{pH in reactor} = 3,0$$

$$\therefore [H^+] = 10^{-3} \text{ moles/l}$$

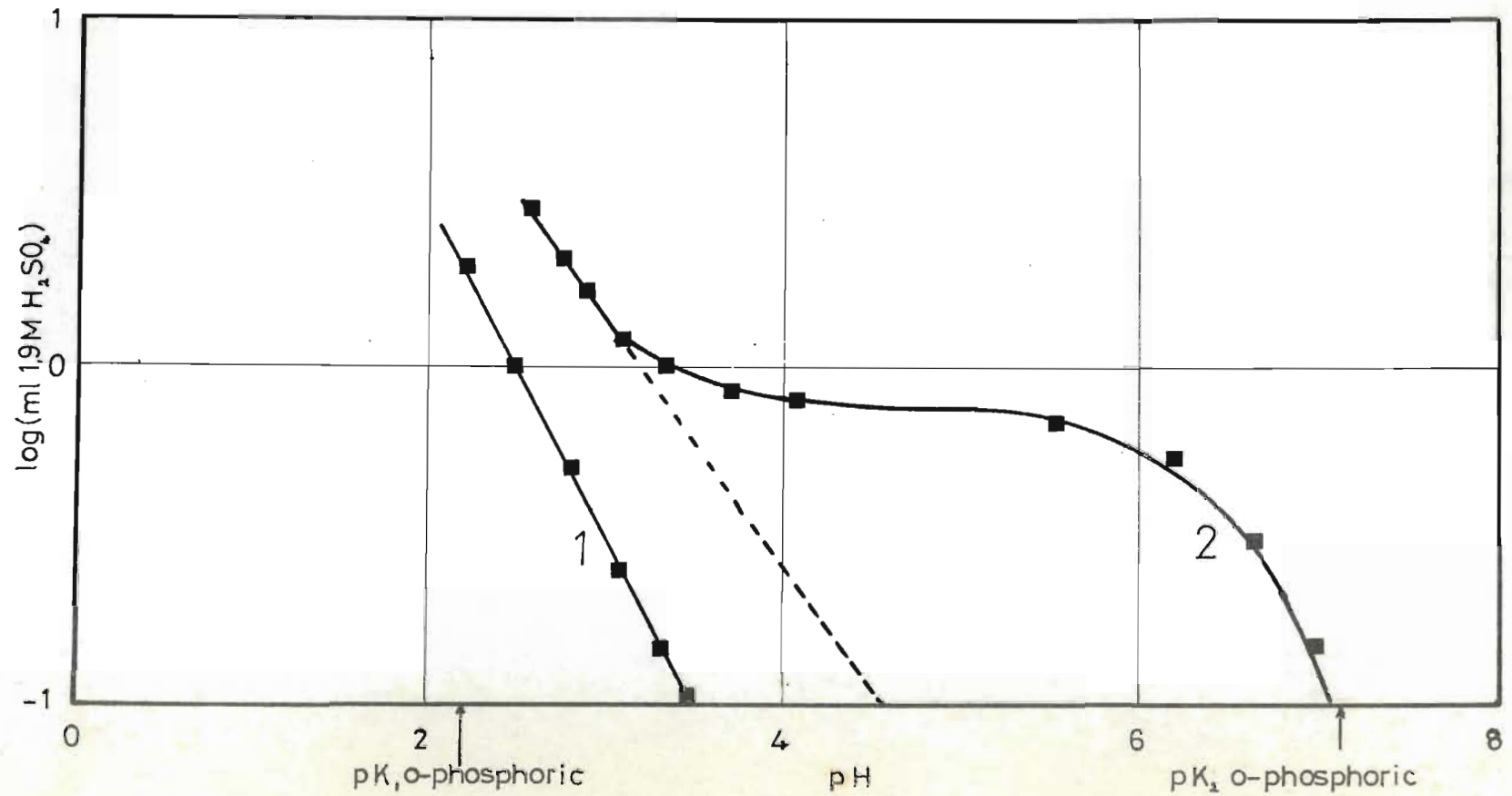
To find R, the rate of consumption of hydrogen ions, it was necessary to draw up a titration curve for 9K media. This is shown in the accompanying Figure 52. Sulphuric acid was slowly added to 9K medium and the change in pH was noted. R was found by the difference between the actual quantity of acid (H^+ ions) required

to lower/....

Figure 52. Titration Curve for 9K-Medium at 30°C.

Slope of 1 = -1, $\text{pH} = -\log(\text{H}^+)$, Theoretical.

Slope of 2 = -1,53



to lower the pH of 9K medium and the theoretical amount required. This was measured from the curve and found to be $4,3 \times 10^{-3}$ moles H^+ per litre at pH 3. This figure represents the consumption of H^+ by lowering the pH of the incoming feed from 7,26 to 3,0.

$$\therefore R = 4,3 \times 10^{-3} \times D$$

Substituting R in equation 'a'

$$D (10^{-3} - 5,5 \times 10^{-8}) = P - 4,3 \times 10^{-3} D$$

$$\therefore P = D \times 5,3 \times 10^{-3} \text{ moles/l-hr}$$

Using the above equation, P the rate of production of hydrogen ions can be calculated from the measured dilution rate.

In order to further check this conversion factor, the following test was carried out

0,19 M H_2SO_4 was added to the reactor at a fixed rate and the pH controlled at 3,0 by adding 9K medium (pH 7,26) with an automatic titrator. Table 22 below gives the results obtained.

TABLE 22/.....

TABLE 22: BLANK TITRATION OF 9K MEDIUM IN CONTINUOUS OPERATION.

D hr ⁻¹ (measured)	P moles/l-hr H ⁺ added	P/D x 10 ³	T hours over which D was measured	T x P/D x 10 ⁻³
0,08	0,52 x 10 ⁻³	6,5	3,5	22,75
0,08	0,36 x 10 ⁻³	4,5	18,0	81,00
0,09	0,455 x 10 ⁻³	5,1	17,0	86,70
0,08	0,431 x 10 ⁻³	5,4	4,0	21,60

$$\begin{aligned}
 P/D &= \frac{\sum T \times P/D}{\sum T} \\
 &= 5,0 \times 10^{-3}
 \end{aligned}$$

This checks with the previous calculated conversion factor.

APPENDIX 12.DETAILED EXPERIMENTAL DATA FOR POLARISATION TESTS.

Sintered discs of pentlandite, 25 mm diameter, were leached in 9K solutions under different conditions. The discs were electrically connected to a polarising circuit so that cathodic and anodic voltages could be externally applied to the discs. The voltage was varied in increments and measured with a sensitive millivoltmeter; the corresponding current flowing in the circuit was calculated from the voltage drop (measured with a potentiometer) across a standard resistor.

These current voltage excursions were carried out at periods of between 3 and 7 days approximately. A typical record of the current-voltage data is shown in the accompanying Table 23.

The current density was calculated from the measured voltage drop (mv) across the standard 10Ω resistor according to Ohm's law and taking the disc surface area to be 5 cm^2 .

$$\begin{aligned} \text{e.g. mv} &= 2,6 \\ \therefore \text{current density} &= \frac{2,6 \times 10^3}{5 \times 10} = 52 \mu\text{A}/\text{cm}^2 \end{aligned}$$

The applied voltage was measured against the saturated calomel electrode (mv S.C.E.) and converted to the hydrogen scale, mv (H_2), by correcting the reading for the shunt resistance (a factor of 1,5

in/.....

in this case) and subtracting the voltage from the standard S.C.E. voltage, 241 mv.

$$\begin{aligned} \text{e.g. mv S.C.E.} &= 300 \\ \text{mv (H}_2\text{)} &= 241 - (300 \times 1,5) \\ &= -209 \text{ mv} \end{aligned}$$

These current-voltage data were used to draw up polarisation curves as shown in Figure 17 in the main text. From these graphs the exchange current density, i_e , and the limiting cathodic and anodic current densities, i_c and i_a , were measured. The values of these current densities for the chemical and bacterial leaching tests are given in the accompanying Tables 24 and 25.

TABLE 23: TYPICAL RECORD OF CURRENT-VOLTAGE DATA.

(Polarisation for chemical leaching, day 1.)

Experiment No: P4

Date : 13/9/1972

Time : 15,40 hrs

Solution : 9K

pH : 2,5

Temp. : 30°C

Agitation : 100 r.p.m.

Gas : Air

General : $[Fe^{+++}] = 0$, $[Ni^{++}] = 0,1 M$

Polarity at disc. +

Standard Ω	mV	$\mu A/cm^2$	mV S.C.E.	mV (H ₂)
10	0	0	+40	181
10	2,6	52	+300	-209
10	7,4	148	+450	-434
10	13,0	260	+530	-554
10	18,3	366	+585	-636
10	26,6	532	+650	-734
10	41,2	824	+750	-884

Polarity at disc. -

Standard Ω	mV	$\mu A/cm^2$	mV S.C.E.	mV (H ₂)
10	3,7	74	-165	489
10	8,6	172	-250	616
10	15,4	308	-340	751
10	22,4	448	-530	1 036
10	31,0	620	-670	1 246
10	40,2	804	-815	1 463

TABLE 24: POLARISATION DATA FOR CHEMICAL LEACHING.

9K solution; pH 2,5; gas air; 30°C; $[\text{Ni}^{++}] = 0,1 \text{ M}$

i_e = exchange current density, $\mu\text{A}/\text{cm}^2$

i_c = cathodic limiting current density, $\mu\text{A}/\text{cm}^2$

i_a = anodic limiting current density, $\mu\text{A}/\text{cm}^2$

$[\text{Fe}^{+++}] = 0$

Day No.	W = 0 r.p.m.			W = 100 r.p.m.		
	i_e	i_c	i_a	i_e	i_c	i_a
0	60	900	1 000	35	850	900
1	55	950	1 000	10,5	850	950
6	47	900	1 000	75	900	1 000
10	10,5	900	1 100	10,5	900	1 100
14	26	900	1 100	23	900	1 100
20	22	850	950	23	900	1 000
24	24	950	1 000	8	950	1 000

$[\text{Fe}^{+++}] = 0,1 \text{ M}$

Day No.	W = 0 r.p.m.			W = 100 r.p.m.		
	i_e	i_c	i_a	i_e	i_c	i_a
0	50	900	1 000	38	1 100	950
1	43	950	1 100	41	1 100	1 000
6	27	900	1 100	25	1 100	1 000
10	17,5	900	1 100	17,5	1 100	1 100
14	19	900	1 100	32	1 100	1 100
20	37	900	1 000	51	1 100	1 000
24	41	950	1 000	43	1 100	1 100

TABLE 25: POLARISATION DATA FOR BACTERIAL LEACHING.

9K solution; pH 2,5; gas air; 30°C; $[Ni^{++}] = 0,1 M$;
 $[Fe^{+++}] = 0,1 M$; W = 100 r.p.m.

i_e = exchange current density, $\mu A/cm^2$

i_c = limiting cathodic current density, $\mu A/cm^2$

i_a = limiting anodic current density, $\mu A/cm^2$

Day No.	i_e	i_c	i_a
0	39	1 000	1 100
4	44	1 100	1 000
10	41	1 000	1 100
16	66	1 000	1 000
23	53	1 100	1 100
35	27	1 000	1 000
42	11	1 100	1 100

APPENDIX 13.DETAILED EXPERIMENTAL DATA FOR DIALYSIS EXPERIMENT.

These data are shown in the accompanying Table 26. The nickel concentration is the theoretical level which would have been reached in the reactor had not the nickel been continually removed by dialysis and ion exchange. Bacterial numbers were determined by direct counting.

TABLE 26:

DETAILED EXPERIMENTAL DATA FOR THE DIALYSIS EXPERIMENT.

9K solution; pH 2,0 - 2,5; W 200 r.p.m; Gas air;

5 per cent w/v pentlandite.

Time Hours	Ni ⁺⁺ ppm
0	167
66	1 336
162	1 436
234	1 670
330	2 104
404	2 672
498	3 307
570	3 874

Time Hours	Bacteria cells/ml x 10 ⁷
90	0,8
115	4,7
162	22,0
195	50,1
234	56,8
258	79,3
282	71,8
330	84,2
364	115,5
426	116,2
450	96,9
474	151,0
498	113,6
548	111,9
570	120,2

APPENDIX 14.

DETAILED EXPERIMENTAL DATA FOR BATCH BACTERIAL LEACHING.1. TABLE 27: EFFECT OF PULP DENSITY.

9K solution, pH 3,0; 30°C, W 200 r.p.m.; gas air.

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		Pulp Density
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l	
0	0	0	0	0	5%
168	1,81	2,32	1,05	1,55	
336	2,75	2,67	2,05	2,27	
672	4,23	4,15	2,62	2,81	
1 008	6,42	7,30	2,67	2,85	
1 344	9,02	9,51	2,80	3,01	
1 680	11,63	12,27	3,00	3,10	
2 016	13,68	13,91	2,95	3,05	
2 352	13,97	14,18	2,95	3,10	
0	0	0	0	0	10%
168	3,21	4,01	2,21	2,71	
504	5,87	5,97	2,86	2,95	
840	11,34	12,48	2,92	3,24	
1 176	18,05	17,43	3,05	3,28	
1 512	20,42	19,75	3,05	3,32	
1 848	20,81	20,20	3,00	3,37	
2 184	20,79	19,93	3,00	3,35	

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		Pulp Density
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l	
0	0	0	0	0	15%
84	2,41	3,76	-	-	
168	3,12	2,94	2,21	2,57	
336	4,67	4,78	-	-	
504	6,50	6,97	3,15	3,92	
840	14,20	15,30	3,20	3,95	
1 176	20,63	20,27	3,31	3,81	
1 512	21,07	21,54	3,25	3,87	
1 848	21,05	22,76	3,29	3,90	
0	0	0	0	0	20%
84	2,85	3,07	2,00	2,76	
168	4,76	4,93	-	-	
336	6,73	7,15	2,83	3,04	
504	11,69	12,80	3,06	3,27	
672	18,32	19,76	-	-	
840	20,67	22,54	3,17	3,78	
1 176	20,98	23,01	3,25	3,54	
1 512	21,34	23,05	3,19	3,19	

TABLE 28: EFFECT OF pH.

9K solution; 30°C; W 200 r.p.m; gas air; 20% w/v pentlandite.

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		pH
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l	
0	0	0	0	0	1,5
84	2,35	2,76	-	-	
168	4,76	5,14	2,15	1,05	
336	6,15	7,68	-	-	
504	11,27	12,17	3,72	1,76	
672	19,81	18,76	-	-	
840	20,32	19,45	3,89	2,95	
1 176	20,67	20,17	-	-	
1 512	20,98	22,32	3,64	3,28	
0	0	0	0	0	2,5
84	2,19	1,95	-	-	
168	4,74	3,76	2,49	1,97	
336	6,32	5,84	-	-	
504	11,18	10,98	2,97	1,56	
672	18,27	19,26	-	-	
840	20,71	21,34	2,95	2,57	
1 176	20,35	20,76	-	-	
1 512	20,28	21,28	3,01	3,18	
0	0	0	0	0	3,0
84	2,05	2,17	-	-	
168	4,37	4,28	2,56	2,34	
336	6,15	6,18	-	-	
504	10,86	11,56	3,14	3,28	
672	18,03	17,34	-	-	
840	20,02	19,68	3,72	3,37	
1 176	20,76	21,26	-	-	
1 512	20,53	19,74	3,79	3,25	

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		pH
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l	
0	0	0	0	0	3,5
84	2,12	2,32	-	-	
168	4,25	3,97	3,71	2,12	
336	5,98	6,43	-	-	
504	10,21	13,86	3,48	2,03	
672	16,83	19,72	-	-	
840	18,97	21,37	3,56	1,85	
1 176	20,18	22,48	-	-	
1 512	20,84	22,76	3,29	1,76	
0	0	0	0	0	
84	2,23	2,19	-	-	
168	4,17	3,06	1,38	1,61	
336	5,25	4,71	-	-	
504	9,76	8,26	1,35	1,52	
672	15,19	13,19	-	-	
840	17,87	14,27	1,27	0,76	
1 176	19,36	16,39	-	-	
1 512	20,48	19,04	1,56	0,53	
0	0	0	0	0	5,5
89	2,37	1,03	-	-	
168	3,07	1,29	1,27	0,31	
336	4,39	1,38	-	-	
504	6,14	1,27	1,29	0,35	
672	9,27	1,36	-	-	
840	13,92	1,57	1,38	0,29	
1 176	20,19	3,19	-	-	
1 512	20,92	3,94	2,05	0,23	

3. TABLE 29: EFFECT OF AGITATION RATE.

9K solution; 30°C; gas air; pH 3,0;
20% w/v pentlandite.

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		Agitation W, r.p.m.
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l	
0	0	0	0	0	75
168	4,12	5,28	-	-	
336	5,53	6,19	3,95	2,18	
672	10,03	11,26	-	-	
1 008	15,27	14,32	4,28	3,92	
1 344	19,98	19,78	-	-	
1 680	20,85	22,56	4,37	4,16	
2 016	20,76	21,79	-	-	
2 352	21,03	22,08	4,25	4,19	
0	0	0	0	0	
168	4,52	4,97	-	-	
336	6,27	6,32	5,13	2,18	
672	12,68	13,28	-	-	
1 008	19,20	18,15	4,97	2,56	
1 334	20,85	22,18	-	-	
1 680	20,97	21,76	3,95	3,18	
0	0	0	0	0	150
168	4,17	5,23	-	-	
336	6,05	6,29	5,02	4,95	
672	15,27	16,15	-	-	
1 008	21,28	20,15	4,96	4,82	
1 344	20,75	21,69	-	-	
1 680	21,37	22,82	3,87	3,96	

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		pH
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l	
0	0	0	0	0	200
84	2,85	3,07	2,00	2,76	
168	4,76	4,93	-	-	
336	6,73	7,15	2,83	3,04	
504	11,69	12,80	3,06	3,27	
672	18,32	19,76	-	-	
840	20,67	22,54	3,17	3,78	
1 176	20,98	23,01	3,25	3,54	
1 512	21,34	23,05	3,19	3,19	
0	0	0	0	0	
84	3,05	4,51	-	-	
168	4,12	5,72	3,15	2,18	
336	6,38	6,94	-	-	
504	12,65	12,58	2,87	3,27	
672	19,76	18,72	-	-	
890	21,03	20,19	2,76	2,46	
1 176	21,36	21,27	-	-	
1 512	20,75	20,83	2,54	3,05	
0	0	0	-	-	Vibromixer
168	0,91	1,54	-	-	
504	2,28	3,17	-	-	
840	3,65	3,76	-	-	
1 176	5,58	4,27	-	-	
1 512	7,03	3,89	-	-	
1 848	8,21	4,95	-	-	

4. TABLE 30: EFFECT OF PARTICLE SIZE.

9K solution; 30°C; gas air; pH 3,0; W 200 r.p.m.

5% w/v pentlandite.

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		Screen size & (Sa) cm ² /g	
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l		
0	0	0	0	0	-325 (531)	
84	1,61	1,79	-	-		
168	2,43	3,25	2,18	1,95		
336	4,25	5,67	-	-		
504	7,85	9,76	2,65	2,54		
672	11,48	12,85	-	-		
840	14,67	15,12	2,34	3,08		
1 008	14,85	15,89	-	-		
0	0	0	0	0		-200 +325 (300)
168	1,81	2,32	1,05	1,55		
336	2,75	2,67	2,05	2,27		
672	4,23	4,15	2,62	2,81		
1 008	6,42	7,30	2,67	2,85		
1 344	9,02	9,51	2,80	3,01		
0	0	0	0	0	-150 +200 (192)	
168	0,80	0,71	-	-		
336	0,82	0,83	0,37	0,21		
504	0,84	0,86	-	-		
672	1,21	1,27	0,45	0,32		
840	1,72	1,83	-	-		
1 008	2,21	2,31	0,35	0,31		
1 344	3,27	3,35	-	-		

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		Screen Size & (Sa)cm ² /g
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l	
0	0	0	0	0	-100 +150 (91)
168	0,71	0,78	-	-	
336	0,65	0,79	0,15	0,13	
504	0,46	0,81	-	-	
672	0,61	0,85	0,19	0,17	
840	0,82	0,88	-	-	
1 008	1,23	1,43	0,18	0,19	
1 344	1,75	1,82	-	-	
0	0	0	0	0	-65 +100
168	0,12	0,09	-	-	
336	0,14	0,10	0,01	0,01	
504	0,13	0,14	-	-	
672	0,38	0,36	0,01	0,01	
840	0,61	0,70	-	-	
1 008	0,82	0,75	0,02	0,02	
1 344	1,05	0,97	-	-	
0	0	0	0	0	-48 +65
168	0,09	0,07	-	-	
336	0,09	0,08	0,01	0,01	
504	0,21	0,19	-	-	
672	0,24	0,25	0,01	0,01	
840	0,31	0,32	-	-	
1 008	0,39	0,38	0,02	0,02	
1 344	0,50	0,47	-	-	

5. TABLE 31: EFFECT OF NUTRIENTS.

30°C; gas air; pH 3,0; W 200 r.p.m; 20% w/v pentlandite.

The concentration of the salts are as used in the 9K medium or (as indicated by 1/10 prefix) 1/10 that in 9K.

Time hours	Ni ⁺⁺ g/l	Fe g/l	Medium (Nutrient)
0	0	0	
168	3,15	2,98	
336	4,22	3,87	
840	7,19	8,23	Tap Water
1 176	8,87	9,17	
1 512	10,06	11,54	
1 848	11,87	12,57	
0	0	0	
84	2,76	3,15	
168	4,81	4,76	(NH ₄) ₂ SO ₄
336	6,42	6,28	+
504	11,58	10,97	K ₂ HPO ₄
672	17,92	16,95	+
840	20,03	20,08	Tap Water
1 176	20,87	21,76	
1 512	20,95	21,83	

Time hours	Ni ⁺⁺ g/l	Fe g/l	Medium (Nutrient)
0	0	0	
84	2,72	3,01	
168	4,95	4,87	
336	6,62	6,95	1/10 (NH ₄) ₂ SO ₄
504	11,76	12,73	+
672	18,05	19,18	K ₂ HPO ₄
840	20,97	21,24	+
1 176	21,04	21,78	Tap Water
1 512	21,12	21,83	
0	0	0	
84	2,56	3,21	(NH ₄) ₂ SO ₄
168	4,87	5,35	
336	6,75	6,87	+
504	11,54	12,42	1/10 K ₂ HPO ₄
672	18,17	19,19	
840	21,02	21,70	+
1 176	20,93	21,75	Tap Water
1 512	20,87	21,69	
0	0	0	
84	2,68	3,15	
168	4,87	3,97	1/10 (NH ₄) ₂ SO ₄
336	6,94	6,82	+
504	12,15	13,78	1/10 K ₂ HPO ₄
672	18,27	19,83	
840	21,07	21,56	+
1 176	21,15	22,78	Tap Water
1 512	21,13	22,93	

Data for 9K medium and control were taken from Table 27,
20% solids.

6. TABLE 32: EFFECT OF OXYGEN CONCENTRATION.

9K solution; pH 3,0; 30°C; W 200 r.p.m; 20% w/v pentlandite.

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		pO ₂ %
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l	
0	0	0	0	0	40
24	3,42	2,79	-	-	
48	4,22	5,35	3,76	2,19	
72	6,35	8,15	-	-	
120	10,51	12,74	4,21	3,86	
168	14,82	15,29	-	-	
216	19,25	20,70	5,83	4,27	
240	20,83	21,58	-	-	
264	21,15	22,07	6,72	5,08	
0	0	0	0	0	
24	4,98	4,15	-	-	
48	8,10	9,70	3,85	2,19	
72	11,95	12,32	-	-	
120	19,97	21,54	4,72	5,28	
144	20,90	21,67	-	-	
0	0	0	0	0	70
24	5,35	6,27	-	-	
48	8,25	9,17	3,90	2,76	
72	12,36	13,82	-	-	
120	20,87	21,29	4,65	3,89	
144	21,03	21,25	-	-	
0	0	0	0	0	80
24	4,87	3,95	-	-	
48	8,32	9,62	3,27	2,19	
72	12,01	13,17	-	-	
120	19,85	21,68	4,15	5,76	
144	21,10	21,75	-	-	

The data for air (20% oxygen) were taken from Table 27
20% pulp density.

7. TABLE 33: EFFECT OF CARBON DIOXIDE CONCENTRATION.

9K solution; pH 3,0; 30°C; W 200 r.p.m;

20% w/v pentlandite; gas air.

Time hours	Ni ⁺⁺ g/l	Fe g/l	CO ₂ % v/v
0	0	0	
84	3,42	3,72	
168	6,65	7,15	
336	13,51	14,97	0,5
504	20,82	21,28	
840	21,03	21,37	
0	0	0	
84	4,21	5,15	
168	6,92	7,03	
336	15,00	14,18	
504	21,29	20,27	
840	20,98	21,93	
0	0	0	
84	4,85	4,97	
168	8,27	9,16	1,0
336	16,15	17,28	
504	21,03	20,07	
840	21,05	21,09	
0	0	0	
84	4,92	4,53	
168	8,42	9,16	1,55
336	16,03	17,28	
504	21,28	20,25	
840	21,08	21,92	

Table 33 continued.

Time hours	Ni ⁺⁺ g/l	Fe g/l	CO ₂ % v/v
0	0	0	
84	4,97	5,60	
168	8,51	9,72	2,0
336	16,20	17,15	
504	21,30	21,84	
840	21,09	21,79	

The data for air(0,2% CO₂) were taken from Table 27

20% pulp density.

8. TABLE 34: EFFECT OF TEMPERATURE.

9K solution; pH 3,0; W 200 r.p.m; 20% w/v pentlandite; gas air.

Time Hours	TEST (BACTERIA)		CONTROL (STERILE)		Temperature °C
	Ni ⁺⁺ g/l	Fe g/l	Ni ⁺⁺ g/l	Fe g/l	
0	0	0	0	0	25
84	2,51	3,27	-	-	
168	4,28	4,38	2,15	2,02	
336	7,75	8,18	-	-	
504	11,82	12,19	3,08	2,85	
840	20,07	21,28	-	-	
1 008	21,12	21,32	2,97	2,82	
0	0	0	0	0	35
84	4,21	5,16	-	-	
168	7,82	8,23	4,19	2,18	
336	14,58	15,19	-	-	
504	21,26	22,18	5,28	6,27	
840	21,31	22,27	-	-	
1 008	21,87	23,54	5,47	6,38	
0	0	0	0	0	40
84	4,28	5,22	-	-	
168	7,97	8,17	6,19	6,25	
336	15,12	16,07	-	-	
504	21,39	22,13	7,28	8,25	
840	21,48	22,15	-	-	
1 008	21,72	22,38	8,15	8,47	

The data for 30°C were taken from Table 27, 20% pulp density.

APPENDIX 15.CORRECTION FOR CHEMICAL LEACHING. (BATCH RESULTS.)

The corrected rate of bacterial leaching, R_3 , was calculated by subtracting the chemical leach rates R_1 and R_2 (due to ferric ions and oxygen respectively) from the measured overall leach rates in the batch bacterial leaching experiments.

The chemical rate constants K_1 and K_2 were calculated from the data in Appendix 4:-

According to the proposed model;

$$R_1 = K_1 \cdot [\text{Fe}^{+++}] \cdot W^{0,833}$$

$$\therefore K_1 = R_1 / [\text{Fe}^{+++}] \cdot W^{0,833}$$

The accompanying Table 35 gives several values of K_1 calculated according to the above relationship. The data were taken from Tables 9 and 10 in Appendix 4. (R_1 was found by subtracting 23 ppm/hr from R_{overall} ; cf page 45).

In a similar manner K_2 was calculated from the data in Table 11 (Appendix 4) since according to the proposed model;

$$K_2 = R_2 / pO_2^{1/2}$$

The accompanying Table 36 shows several values of K_2 .

The values/.....

The values of K_1 and K_2 were corrected, using the activation energy data, from 50°C (the average temperature used in the chemical kinetic studies) to 30°C, the temperature used in batch bacterial leaching experiments. (Although the activation energy was calculated for the overall chemical rate, an effective correction can be made by using the activation energy data on the individual rate constants K_1 and K_2 .)

At 50°C and 10% pulp density;

$$K_1 = 3,2 \text{ mg/hr - mole - r.p.m.}^{0,833}$$

$$K_2 = 3,3 \text{ mg/hr - l - } pO_2^{\frac{1}{2}}$$

From the activation energy data;

$$\log K = 11,36 - \frac{3,18 \times 10^3}{T}$$

$$\log K' - \log K'' = 3,18 \times 10^3 \left(\frac{1}{T''} - \frac{1}{T'} \right)$$

Applying this formula;

$$K_1 = 0,8 \text{ mg/hr - mole - r.p.m.}^{0,833}$$

$$K_2 = 0,9 \text{ mg/hr - l - } pO_2^{\frac{1}{2}}$$

at 10% pulp density and 30°C.

The values of K_1 and K_2 at the other pulp densities were calculated by multiplying by 0,5, 1,5 and 2 for 5 per cent, 15 per cent and 20 per cent respectively.

Using/.....

Using the above values of K_1 and K_2 , R_1 and R_2 were calculated according to equation 17 in section 4.1.1. :-

$$\text{i.e. } R_1 = K_1 \cdot [\text{Fe}^{+++}]^{0,833}$$

$$\text{and } R_2 = K_2 \cdot p\text{O}_2^{\frac{1}{2}}$$

Then;

$$R_3 = R_{\text{overall}} - (R_1 + R_2)$$

R_{overall} values taken from the data given in Appendix 14 and shown graphically in Figures 22 - 35 were used to calculate the values for R_3 shown in Tables 37 - 42. (The ferric ion concentration was taken as 0,1M, i.e. 5,6 g/l, in these calculations. From the data in Tables 27 - 34 Appendix 14, it may be seen that the iron concentration rapidly exceeds 0,1M. Bacterial oxidation reactions were found to maintain the bulk of this iron in the Fe^{+++} oxidation state.)

TABLE 35:

CALCULATED VALUES OF K_1 .

$[Fe^{+++}]$ M	W r.p.m.	$W^{0,833}$	$R_{overall}$ ppm/hr	R_1 ppm/hr	K_1
0,01	200	82	25,5	2,5	3,1
0,025	200	82	29,8	6,8	3,4
0,05	200	82	37,5	14,5	3,6
0,075	200	82	42,4	19,4	3,2
0,01	75	36	33,5	13,5	3,8
0,01	125	56	25	2	0,3*
0,01	200	82	46,6	23,6	3,0
0,01	300	115	51,8	28,8	2,5
0,01	500	178	74,5	51,5	3,0
0,01	750	246	91,9	68,9	2,8
Average					3,2

$$K_1 = \frac{R_1}{[Fe^{+++}] \cdot W^{0,833}}$$

$$R_1 = R_{overall} - 23$$

*This point was ignored because of inferred experimental error.

$$K_1 = 3,2 \text{ mg/hr - mole - r.p.m.}^{0,833} \text{ at } 50^\circ\text{C,}$$

10% pulp density.

TABLE 36:

CALCULATED VALUES OF K_2

pO_2 %	$pO_2^{\frac{1}{2}}$	R overall ppm/hr	R_2 ppm/hr	K_2
1,0	1	22,4	2,4	2,5
3,6	1,9	30	10	5,2
10,0	3,16	26	6	2,0
25,0	5	39	19	3,9
50,0	7,06	46	26	3,8
75,0	8,65	36,6	16,6	2,0
100,0	10	56	36	3,6
Average				3,3

$$K_2 = R_2 / pO_2^{\frac{1}{2}}$$

$$R_2 = R_{\text{overall}} - 20$$

$$K_2 = 3,3 \text{ mg/hr} - \ell - pO_2^{\frac{1}{2}} \text{ at } 50^\circ\text{C},$$

10% pulp density.

TABLE 37:

CORRECTED BATCH BACTERIAL LEACHING AS A FUNCTION OF PULP DENSITY.

% Solids	LEACH RATES - ppm/hr			
	R _{overall}	R ₁	R ₂	R ₃
5	9,8	3,2	2,1	4,5
10	21,3	6,5	4,1	10,7
15	28,7	9,7	6,2	12,8
20	37,2	13,0	8,2	16,0

TABLE 38:

CORRECTED BATCH BACTERIAL LEACHING AS A FUNCTION OF pH.

pH	LEACH RATES - ppm/hr			
	R _{overall}	R ₁	R ₂	R ₃
1,5	37,5	13,0	8,2	16,3
2,5	37,5	13,0	8,2	16,3
3,5	36,5	13,0	8,2	15,3
4,5	35,5	13,0	8,2	14,3

TABLE 39:

CORRECTED BATCH BACTERIAL LEACHING AS A FUNCTION OF AGITATION RATE.

RPM (w)	LEACH RATES - ppm/hr			
	R _{overall}	R ₁	R ₂	R ₃
75	15,6	5,7	8,2	1,7
100	19	7,4	8,2	3,4
150	27,5	10,2	8,2	9,1
200	37,5	13,0	8,2	16,3
250	39	15,5	8,2	15,3

TABLE 40:

CORRECTED BATCH BACTERIAL LEACHING AS A FUNCTION OF OXYGEN CONCENTRATION.

pO ₂ %	LEACH RATES - ppm/hr			
	R _{overall}	R ₁	R ₂	R ₃
20	37,2	13,0	8,2	16,0
40	86,4	13,0	11,4	62,0
60	168,0	13,0	13,9	141,1
70	178,4	13,0	15,0	150,4
80	169,7	13,0	16,1	140,6

TABLE 41:

CORRECTED BATCH BACTERIAL LEACHING AS A FUNCTION OF CARBON DIOXIDE CONCENTRATION.

%CO ₂	LEACH RATES - ppm/hr			
	R _{overall}	R ₁	R ₂	R ₃
0,2	37,2	13,0	8,2	16,0
0,5	42,2	13,0	8,2	21,0
1	48,5	13,0	8,2	27,3
1,5	50,3	13,0	8,2	29,1
2	50,5	13,0	8,2	29,3

TABLE 42:

CORRECTED BATCH BACTERIAL LEACHING AS A FUNCTION OF TEMPERATURE.

°C	LEACH RATES - ppm/hr		
	R _{overall}	R ₁ + R ₂	R ₃
25	23,0	12,7	10,3
30	37,2	21,2	16,2
35	45,0	30,5	14,5
40	46,5	45,0	1,5

APPENDIX 16.METHOD OF CALCULATING PENTLANDITE ADDITIONS IN CONTINUOUS LEACHING.

A mass balance was carried out on nickel as follows:-

Rate of nickel addition to reactor = Rate of nickel leaving reactor.

$$M \times C = F \times C^1 \times T$$

M = mass of pentlandite added

C = per cent nickel in pentlandite

F = flowrate out of reactor

T = time period since last addition of pentlandite

C¹ = concentration of nickel in reactor (i.e. in exit stream)

C = 18 per cent, for the lower grade pentlandite concentrate

$$\therefore M = \frac{F \times C^1 \times T}{18}$$

The above formula was used to calculate the amount of pentlandite to be added for time periods of 2 - 3 days. After extended periods, e.g. 1 month, a further check was carried out by taking a representative sample from the reactor and measuring, by gravimetric means, the pulp density. The per cent pentlandite was then adjusted to 5 as required.

APPENDIX 17:DETAILED EXPERIMENTAL DATA FOR CONTINUOUS BACTERIAL LEACHING.TABLE 43: Continuous Leaching - Air.

9K solution, 30°C; pH 3,0, W 200 r.p.m.;
5% w/v pentlandite.

D hr ⁻¹	Ni ⁺⁺ g/l	R _{overall} ppm/hr
0,002	2,20	4,2
0,004	1,40	5,6
0,01	1,15	11,5
0,015	0,95	14,3
0,016	0,40	6,4

TABLE 44: Continuous Leaching - Air + 2% Carbon Dioxide.

D hr ⁻¹	Ni ⁺⁺ g/l	R _{overall} ppm/hr
0,002	2,70	5,4
0,005	2,00	10,0
0,01	1,60	16,00
0,015	1,30	19,5
0,016	0,32	5,1

TABLE 45: CONTINUOUS LEACHING - AIR AND OXYGEN.

D hr ⁻¹	Ni ⁺⁺ g/l	R _{overall} ppm/hr	% Oxygen v/v
0,002	8,60	17,2	40
0,004	6,00	24,0	
0,007	4,00	28,0	
0,01	3,00	30,0	
0,014	2,00	28,0	
0,016	1,00	16,0	
0,004	13,00	52,0	60
0,01	8,00	80,0	
0,016	5,00	80,0	
0,019	3,00	57,0	
0,02	1,70	34,0	
0,004	14,60	58,4	70
0,01	8,80	88,0	
0,014	6,78	95,0	
0,018	4,00	72,0	
0,02	2,10	42,0	

TABLE 46/.....

TABLE 46: CONTINUOUS LEACHING - EFFECT OF TEMPERATURE CHANGE.

Dilution rate held constant at $0,01 \text{ hr}^{-1}$; 9K solution; pH 3,0;
 W 200 r.p.m; 5% w/v pentlandite; gas air.

Temperature	Equilibrium Ni ⁺⁺ g/l	R _{overall} ppm/hr
25	0,84	8,4
30	1,10	11,0
35	1,10	11,0
40	0,44	4,4

TABLE 47: CONTINUOUS LEACHING - EFFECT OF CHANGE IN THE pH OF THE FEED.

Dilution rate held constant at $0,01 \text{ hr}^{-1}$; 9K solution; W 200 r.p.m.;
 5% w/v pentlandite; gas air.

pH Feed	pH Reactor	R _{overall} ppm/hr
3,0	2,5	11,2
4,0	2,5	11,2
4,5	2,6	11,15
5,0	2,7	11,15
5,5	2,8	11,2

APPENDIX 18.CORRECTION FOR CHEMICAL LEACHING (CONTINUOUS RESULTS.)Calculation of R_1 and R_2 .

As discussed in Appendix 15, the true rate of bacterial leaching was calculated by subtracting the chemical leach rates from the measured overall leach rate. The chemical leach rate constants, K_1 and K_2 were corrected for temperature and pulp density (See Appendix 15) and found to be:-

$$K_1 = 0,4 \text{ mg/hr - mole - r.p.m.}^{0,833}$$

$$K_2 = 0,45 \text{ mg/hr - l - } \rho O_2^{\frac{1}{2}}$$

at 5% pulp density and 30°C.

These constants were measured for the higher grade pentlandite concentrate (30% nickel.) A linear correction was made in applying these constants to the lower grade concentrate (18% nickel) which was used in the continuous leaching experiments; i.e. the above rate constants were multiplied by a factor 18/30 to give:-

$$K_1 = 0,24 \text{ mg/hr - mole - r.p.m.}^{0,833}$$

$$K_2 = 0,27 \text{ mg/hr - l - } \rho O_2^{\frac{1}{2}}$$

The values of R_{overall} were taken from the data given in Appendix 17. R_3 , the corrected rate of bacterial leaching, was calculated from the equation:-

$$R_3 = R_{\text{overall}} - (R_1 + R_2)$$

In the calculation of R_1 (where $R_1 = K_1 [Fe^{+++}] W^{0,833}$), the value of $[Fe^{+++}]$ was taken as the value measured for total nickel concentration, since it was found that the iron was completely in the ferric oxidation state and that nickel and iron were leached in equivalent amounts. When the nickel concentration was above 0,1 M (5,6 g/l) the iron concentration used in the calculation of R_1 was taken as 0,1 M.

The accompanying Tables 48 - 53 give the calculated values of R_3 under the different experimental conditions.

Example:

Continuous leaching - air; $D = 0,01$;

R_{overall} was measured as 11,5 ppm/hr.

$$\begin{aligned} R_1 &= K_1 [Fe^{+++}] W^{0,833} \\ &= 0,24 \times 0,02 \times 200^{0,833}, [Fe^{+++}] = 1,15 \text{ g/l} \\ &\quad (0,02M) \text{ from Table 44.} \end{aligned}$$

$$\therefore R_1 = 0,4 \text{ ppm/hr}$$

$$R_2 = K_2 pO_2^{\frac{1}{2}}$$

$$= 0,27 \times (20)^{\frac{1}{2}}, pO_2 \text{ for air} = 20\% \text{ approximately}$$

$$\therefore R_2 = 1,2 \text{ ppm/hr}$$

Calculation of R_3 : (From Batch Data.)

The batch model of the corrected bacterial leach rate proposed that;

$$R_3 = K(pO_2)^2$$

$$\therefore K = R_3 / (pO_2)^2$$

From Table 40 (Appendix 15) the following data may be used to calculate K:

R_3 ppm/hr	pO_2 %	$(pO_2)^2$	$R_3/(pO_2)^2$
16	20	400	0,040
62	40	1 600	0,038
141	60	3 600	0,039
Average			0,039

In addition a least squares fit on the three data points for R_3 and $(pO_2)^2$ gives:-

$$R_3 = 0,01 + 0,039 (pO_2)^2$$

It is thus proposed that for the corrected batch leaching rate;

$$R_3 = 0,039 (pO_2)^2.$$

This applies for the higher grade pentlandite concentrate (30% nickel), for pO_2 between 0 per cent and 60 per cent and at a carbon dioxide concentration of 0,2 per cent (i.e. CO_2 as measured in normal air.) At higher carbon dioxide concentration, a correction may be made according to the data shown on Figure 40;

$$\text{i.e. } R_3 \propto (pCO_2)^{0,33}$$

Two further corrections are necessary when applying the K value to the continuous leaching; one for the lower grade concentrate, 18/30, and one for the lower pulp density used, 5/20.

∴ K/.....

$$\begin{aligned} \therefore K (\text{continuous}) &= 0,039 \times 18/30 \times \frac{5}{20} \\ &= 0,006 \end{aligned}$$

Thus R_3 , based on the batch data may be calculated:-

$$R_3 = 0,006 \times (pO_2)^2 \quad \text{ppm/hr}$$

The values of R_3 calculated using the above formula are given in the accompanying Tables 48-51. These values of R_3 are the batch rates which would be expected under the same conditions as used in the continuous leaching tests.

The constant K_4 used in the calculation of R_4 incorporates a mass transfer (agitation) effect and will be dependent on scale and geometric factors (e.g. size of vessel, stirrer diameter, etc.) This effect is apparently small in the scale-up from the 250 ml batch conical flasks to the larger 5,5 l continuous reactor as good agreement was found between measured and calculated chemical leach rates in continuous operation. (c.f. Table 6 in section 4.2.2.)

The size of stirrer used was chosen so as to keep the ratio of diameter of vessel : diameter of stirrer constant and thus minimise scale effects.

TABLE 48: CONTINUOUS LEACHING; AIR.

D, hr ⁻¹	Leach Rates - ppm/hr				
	R _{overall}	R ₁	R ₂	R ₃	R ₃ (Batch)
0,002	4,2	0,7	1,2	2,3	2,4
0,004	5,6	0,5	1,2	3,9	
0,01	11,5	0,4	1,2	9,9	
0,015	14,3	0,3	1,2	12,8	
0,016	6,4	0,1	1,2	5,1	

TABLE 49: CONTINUOUS LEACHING; AIR + 2% CO₂.

D, hr ⁻¹	Leach Rates - ppm/hr				
	R _{overall}	R ₁	R ₂	R ₃	R ₃ (Batch)
0,002	5,4	0,9	1,2	3,3	5,0
0,005	10,0	0,7	1,2	8,1	
0,01	16,0	0,5	1,2	14,3	
0,015	19,5	0,4	1,2	17,9	
0,017	5,1	0,1	1,2	3,8	

TABLE 50: CONTINUOUS LEACHING; 40% O₂.

D	Leach Rates - ppm/hr				
	R _{overall}	R ₁	R ₂	R ₃	R ₃ (Batch)
0,002	17,2	2,0	1,7	13,5	9,6
0,004	24,0	2,0	1,7	20,3	
0,007	26,0	1,3	1,7	25,0	
0,01	30,0	1,0	1,7	27,3	
0,014	28,0	0,7	1,7	25,6	
0,016	16,0	0,3	1,7	14,0	

TABLE 51: CONTINUOUS LEACHING; 60% O₂.

D	LEACH RATES - ppm/hr				
	R _{overall}	R ₁	R ₂	R ₃	R ₃ (Batch)
0,004	52,0	2,0	2,1	47,9	21,6
0,01	80,0	2,0	2,1	75,9	
0,016	80,0	1,7	2,1	76,2	
0,019	57,0	1,0	2,1	53,9	
0,02	34,0	0,6	2,1	31,3	

TABLE 52: CONTINUOUS LEACHING; 70% O₂.

D	LEACH RATES - ppm/hr				
	R _{overall}	R ₁	R ₂	R ₃	
0,004	58,4	2,0	2,3	54,1	
0,01	88	2,0	2,3	83,7	
0,014	95	2,0	2,3	90,7	
0,018	72	1,3	2,3	68,4	
0,02	42	0,7	2,3	39,0	

TABLE 53: CONTINUOUS LEACHING AT DIFFERENT TEMPERATURES;

$$D = 0,01 \text{ hr}^{-1}.$$

°C	LEACH RATES - ppm/hr			
	R _{overall}	R ₁ + R ₂	R ₃	
25	8,4	1,5	6,9	
30	11,0	1,6	9,4	
35	11,0	1,7	9,3	
40	4,4	1,7	2,7	

APPENDIX 19: CALCULATION OF BACTERIAL YIELD CONSTANT BASED
ON NICKEL.

The yield constant measured for the rate of production of hydrogen ions in Section 4.1.2 was ;

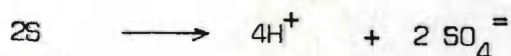
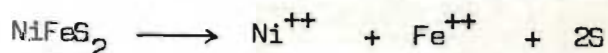
$$Y = 0,24 \text{ g bacterial nitrogen/mole H}^+$$

In addition the experimental data in this section showed;

$$1 \mu\text{g Nitrogen} \equiv 1,27 \times 10^7 \text{ bacterial cells.}$$

$$\begin{aligned} \therefore Y &= 0,24 \times 10^6 \times 1,27 \times 10^7 \\ &= 0,3048 \times 10^{13} \text{ cells/mole H}^+ \end{aligned}$$

The stoichiometry of the nickel leaching reactions may be represented:-



$$\therefore 1 \text{ mole Ni}^{++} \equiv 4 \text{ mole H}^+$$

$$\text{or } 1/4 \text{ mole Ni}^{++} \equiv 1 \text{ mole H}^+$$

$$\begin{aligned} \therefore Y &= 0,3048 \times 10^{13} \times 4 \\ &= 1,2 \times 10^{13} \text{ cells/mole Ni}^{++} \end{aligned}$$

This value of Y may be checked using the data from the dialysis experiment:-

$$\text{Number of bacteria produced during leach} = 130 \times 10^7 \text{ cells/ml.}$$

Amount/.....

Amount of nickel produced during experiment = 113×10^{-3} moles/l.

The amount of nickel leached due to chemical leaching during the experiment may be estimated:-

$$R_1 = K_1 [Fe^{+++}]_w^{0,833}$$

$$= 0,4 \times 0,007 \times 82$$

$$= 0,2 \text{ ppm/hr}$$

$$R_2 = K_2 pO_2^{\frac{1}{2}}$$

$$= 0,45 \times 4,5$$

$$= 2$$

\therefore Rate of chemical leaching = 2,2 ppm/hr.

Over 600 hours this represents 0,02 moles of Ni^{++} .

\therefore Amount of nickel leached due to bacterial leaching during

$$\text{experiment} = (113 - 20) \times 10^{-3}$$

$$= 93 \times 10^{-3} \text{ moles/l}$$

$$\therefore Y = \frac{130 \times 10^7}{93 \times 10^{-3}}$$

$$= 1,4 \times 10^{13} \text{ cells/mole } Ni^{++}$$

This value agrees with the value based on the sulphur growth data.

APPENDIX 20: COMPARISON OF CALCULATED VALUES OF R_3 WITH
MEASURED VALUES OF R_3 , CONTINUOUS LEACHING.

The value of Y was taken as the mean of the two calculated values, i.e. $1,3 \times 10^{13}$ cells/mole Ni^{++} . This value of Y was then used to calculate values of R_3 , the corrected rate of bacterial leaching, from the continuous leach data. The following relationship was used:-

$$R_3 = \frac{D \cdot X_u}{Y}$$

The calculated values of R_3 for the different measured values of X_u at the various dilution rates are given in the accompanying Table 54.

Example. (Air.)

$$\begin{aligned} D &= 0,002 \text{ hr}^{-1} \\ X_u &= 2,4 \times 10^8 \text{ cells/ml} \\ R_3 &= \frac{0,002 \times 2,4 \times 10^8}{1,3 \times 10^{13}} \times 58,7 \times 10^6 \text{ ppm/hr} \\ &\quad (\text{M.W. Ni} = 58,7) \\ &= 2,2 \text{ ppm/hr} \end{aligned}$$

TABLE 54: MEASURED VALUES OF R_3 COMPARED TO VALUES CALCULATEDFROM x_u .

Air

D hr^{-1}	R_3 , measured ppm/hr	x_u , measured, cells/ml	R_3 , calculated ppm/hr
0,002	1,9	$2,4 \times 10^8$	2,2
0,004	3,6	$1,6 \times 10^8$	3,3
0,01	9,6	$1,8 \times 10^8$	9,0
0,015	12,5	$1,6 \times 10^8$	11,0
0,016	4,8	$0,47 \times 10^8$	3,5

60% O_2

D hr^{-1}	R_3 , measured ppm/hr	x_u , measured, cells/ml	R_3 , calculated ppm/hr
0,004	47,4	$22,5 \times 10^8$	42,1
0,01	75,4	$16,8 \times 10^8$	78,3
0,016	75,6	10×10^8	76,1
0,019	53,4	$5,7 \times 10^8$	50,5
0,02	30,8	$3,5 \times 10^8$	32,5

APPENDIX 21.TABLE 55:EXPERIMENTAL DATA FOR CONTINUOUS LEACHING - OPTIMUM CONDITIONS.

Solution: Tap water; 0,3 g/l $(\text{NH}_4)_2 \text{SO}_4$; 0,05 g/l K_2HPO_4 ;
 (1/10th concentration of these salts in normal 9K
 solution.)

Other Conditions: 30°C, W=500 r.p.m.; 70% oxygen v/v;
 20% w/v pentlandite. (Lower grade.)
 PH 3,0.

D hour ⁻¹	Ni^{++} g/l	Leach Rate ($D \times [\text{Ni}^{++}]$) (ppm/hr)
0,005	21,25	106
0,0125	18,00	225
0,02	12,50	250
0,0225	5,65	127

APPENDIX 22.DETAILS OF THE ECONOMIC ASSESSMENT OF THE CONTINUOUS BACTERIAL LEACHING PROCESS.

The economic assessment is based on the proposed concentrates to be produced at the new Shangani mine in Rhodesia. Chittenden (78) has recently carried out a survey on the production costs of concentrates based on a milling rate of 900 000 tonnes p.a. at 0,9% Ni. The total cost to produce a 12% concentrate from this will be R4-30 per tonne; including operating costs and amortisation of capital over 15 years.

For the purposes of this survey it has been assumed that a leach rate of 250 ppm/hr can be used. This is based on the maximum leach rate obtained at 70% oxygen with 20% solids in the previously described continuous leaching.

It is also assumed that recycle will be used, both to separate unreacted sulphide particles in the outlet from the leach vessels and to build the nickel concentration up to 20 g/l. (This concentration appeared to be the maximum level at which bacterial growth would operate.) At a dilution rate of $0,02 \text{ hr}^{-1}$ the leaching volume required is:-

$$V = \frac{0,9 \times 10^9}{250} = 3,6 \times 10^6 \text{ litres,}$$

since 0,9 tonnes per hour of nickel are extracted.

$\therefore F = 72\ 000$ litres per hour,
since $D = F/V$

If leach tanks of 50 000 litre capacity are used, the number required will be 80, plus 3 or 4 spare. These will be mild steel construction with rubber lining, fitted with lids and turbine agitators.

The proposed process is shown in the accompanying Figure 53. The outflow from the leach vessels is passed to a hydro-cyclone where a split is made at 200 mesh. This will recycle the bulk of the unreacted sulphide back to the reactors. The cyclone overflow is then passed to a thickener where the solids are removed at 50% water w/w. These are then filtered and washed on rotary, rubber-lined, vacuum filters. The tailings are discarded while the filtrate is added to the thickener overflow. Washings are recycled to the reactors. The solutions are then polish filtered prior to nickel recovery.

The process for nickel recovery must at this stage remain purely speculative for a number of reasons:-

- 1) No suitable solvent exists for preferentially extracting nickel from sulphate solution at pH 2,5 - 3,5. At least one manufacturer has, however, indicated that such solvents will be commercially available in the very near future.
- 2) Direct electrowinning of nickel is usually carried out at concentrations of 50 - 80 g/l. The economics of the process at

KEY TO FIGURE 53.

- | | |
|--------------------|--------------------|
| a) Leaching Tanks. | e) Thickener. |
| b) Mixer. | f) Rotary filters. |
| c) Compressors. | g) Electrowinning. |
| d) Cyclones. | |

- 1) Concentrates; 8 t.p.h. 0,9 t.p.h. Ni.
- 2) Overflow from leach tanks; 2,44 t.p.h. Ni @ 20 g/l.
- 3) Cyclone underflow; 2 t.p.h. sulphides, 50 000 l.p.h.
- 4) Cyclone overflow; 4 t.p.h. solids, 1,44 t.p.h. Ni, 72 000 l.p.h.
- 5) Thickener overflow; 1,4 t.p.h. Ni, 70 000 l.p.h.
- 6) Thickener underflow; 50% solids, 2 000 l.p.h., 0,04 t.p.h. Ni.
- 7) Filtrate; 0,02 t.p.h. Ni, 1 000 l.p.h.
- 8) Wash water; 2 000 l.p.h.
- 9) Tailings; 4 t.p.h. solids, 25% water.
- 10) Washings; 0,02 t.p.h. Ni, 2 000 l.p.h.
- 11) Solution to Ni Recovery; 1,42 t.p.h. Ni.
- 12) Copper recovered.
- 13) Solution ex Ni Recovery; 0,52 t.p.h. Ni, 50 000 l.p.h.
- 14) Make-up water; 21 000 l.p.h.
- 15) Gas to leach tanks; 60% O₂ v/v., 17,4 t.p.h. gas.
- 16) Oxygen make-up; 4 t.p.h.
- 17) Oxygen evolved.

TABLE 56:

Estimated Capital Costs for Bacterial Leaching Plant
to Produce 0,9 tonne per hour of Soluble Nickel.

ITEM	DESCRIPTION	COST-RAND
Leach Tanks	83 @ R4 500 with 100 kw agitators	375 000
Compressors	1 + stand by, complete	10 000
Cyclone	15 - 30 cm	1 200
Thickener	100 m ²	26 000
Thickener Pumps	1 + stand by	5 000
Filter	10 m ² , Rotary vacuum and accessories	16 000
Polish Filter	e.g. 'FUNDA'	50 000
Piping, Pumps	Plastic or Rubber lined	10 000
Buildings	to house filter only	10 000
Civils	foundations etc	5 000
Site preparation		5 000
Electrics		10 000
Mixer		10 000
Conveyor		1 000
Feed Bin		2 000
Instrumentation		10 000
Erection Costs	10% of Capital Expenditure	60 000
Spares	4% " " "	25 000
Contingencies	20% " " "	100 000
	TOTAL	750 000

Figure 53. Proposed Process for Bacterial Leaching of Nickel Concentrates.

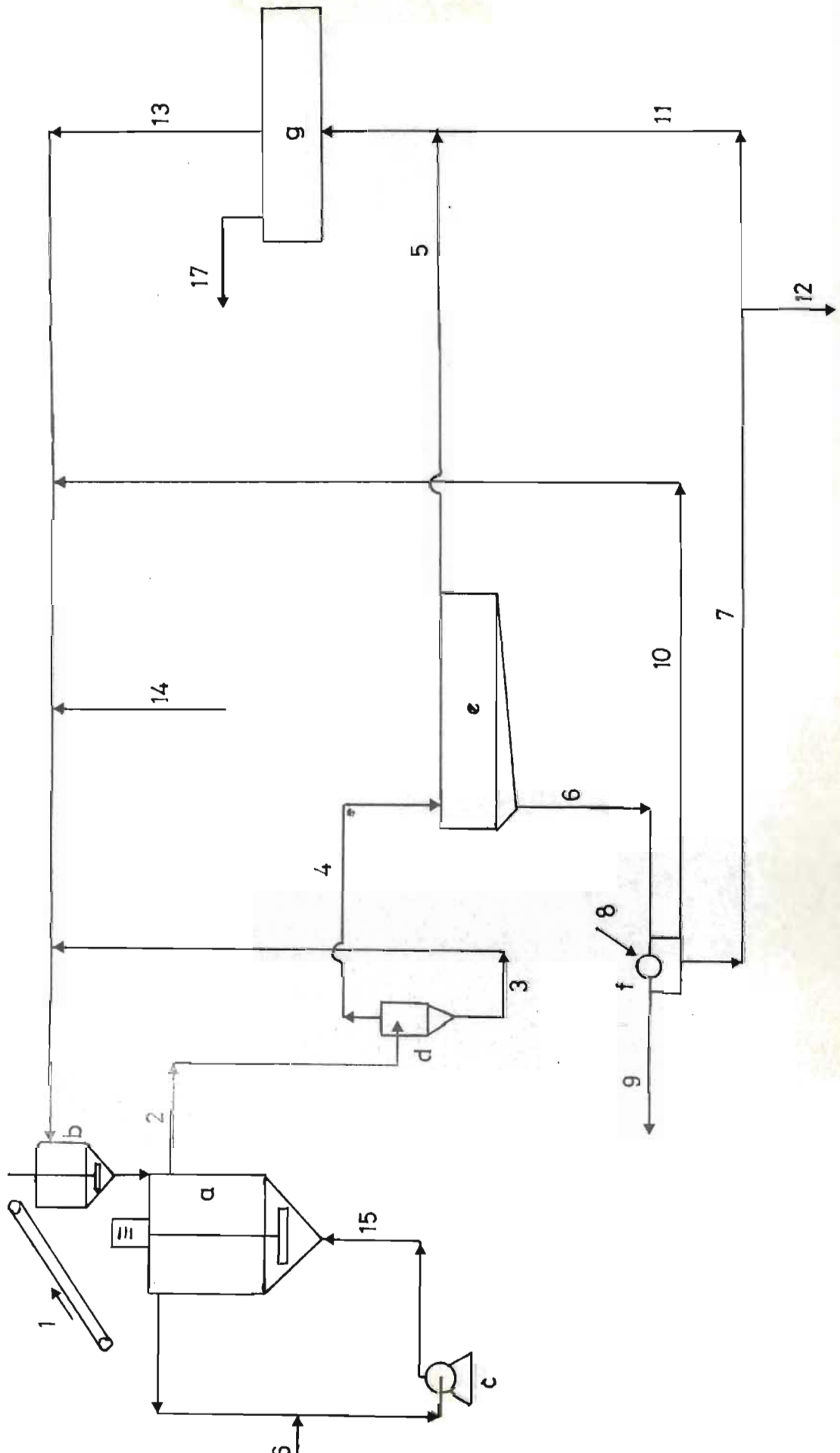


TABLE 57:

Estimated Operating Costs for Bacterial Leaching Plant
to Produce 0,9 tonne per hour of Soluble Nickel.

ITEM	DESCRIPTION	COST R/HOUR
Oxygen	4 t.p.h. @ R8-00 p.t.	32-00
Water	40 kl/hr @ 7c/kl	3-00
Nutrients	fertiliser, 1kg/tonne @ R40-00/tonne	0-10
Electricity	(83 x 100 kw) + 10% @ 0,5c/kwh	50-00
Labour	4 supervisors, 24 unskilled	12-00
Maintenance	$\frac{1}{2}$ fitter, $\frac{1}{2}$ electrician, materials	10-00
Indirect costs	overheads, managerial, clerical etc.	2-00
Concentrates	R4-50 per tonne	35-00
	TOTAL	R144-10

Total Operating Cost per tonne Ni

$$= \frac{144}{0,9} = R160-00$$

20 g/l will not be as attractive, but coupled to the low cost of nickel solubilisation by bacterial leaching, the overall process may prove suitable.

- 3) Cementation of nickel can be done on iron, providing the solution is hot. It is not known whether this is being used in practice. In any case the availability of large quantities of cheap scrap iron at Shangani is doubtful while a suitable outlet for cement-nickel may be hard to find.

For the purposes of this exercise we have assumed that nickel is recovered by direct electrowinning. In this process the acid strength is increased and some oxygen will be available for recycle to the leach reactors. Copper will be removed prior to nickel recovery, either by solvent extraction or cementation. It was assumed that in this, the costs would balance any revenue obtained by the sale of cement-copper.

The sizes of the cyclone, thickener and filters were based on data available from tests carried out by the Metallurgical Section of the J.C.I. Minerals Processing Research Laboratory.

The estimated capital and operating costs are shown in Tables 56 and 57. Capital and Operating costs were estimated from a number of available publications. (79, 80, 81.)

The total estimated operating costs amount to R160-00 per tonne

of/.....

of nickel and the total capital cost estimate amounts to R750 000. Amortising over 15 years this amounts to R7-00 per tonne of nickel. The total cost of producing a solution containing 20 g/l Ni is thus approximately R170-00 per tonne of nickel. The current price of nickel is about R2 200 per tonne so that allowing for extraction, refining, shipping etc., there is certainly some attraction to bacterial leaching of nickel concentrates.

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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.

SINOPSIS

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 bakterieë as katalisatore van logingsprosesse 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 ₂ 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 ₃ Sb ₂ S ₇	Tetrahedrite

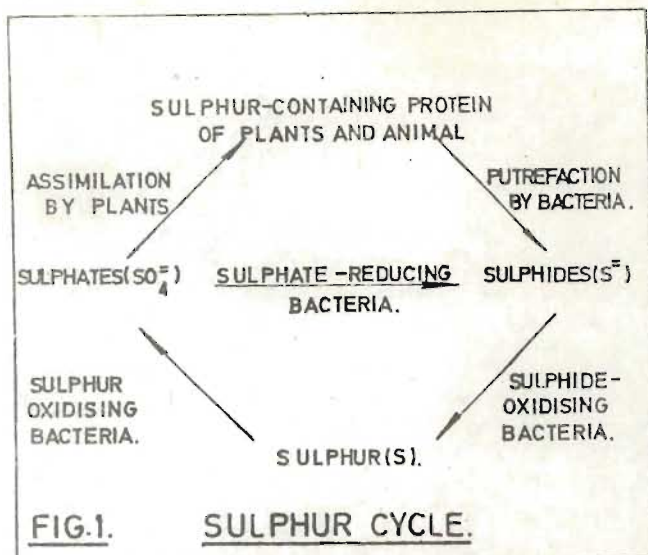


Fig. 1—Sulphur cycle

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. sulphoxidans* 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:

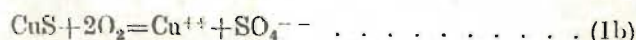
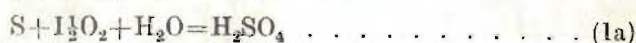


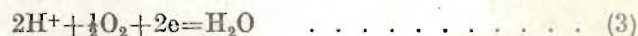
TABLE II

PRINCIPAL CHARACTERISTICS OF SOME MINE WATER BACTERIA

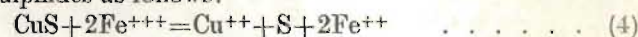
Bacteria	Nitrogen source	Oxidation of		
		Sulphur	Thio-sulphate	Ferrous ion
T. Thiooxidans	NH ₄ ⁺	yes	yes	no
T. Ferrooxidans	NH ₄ ⁺	yes	variable	yes

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.

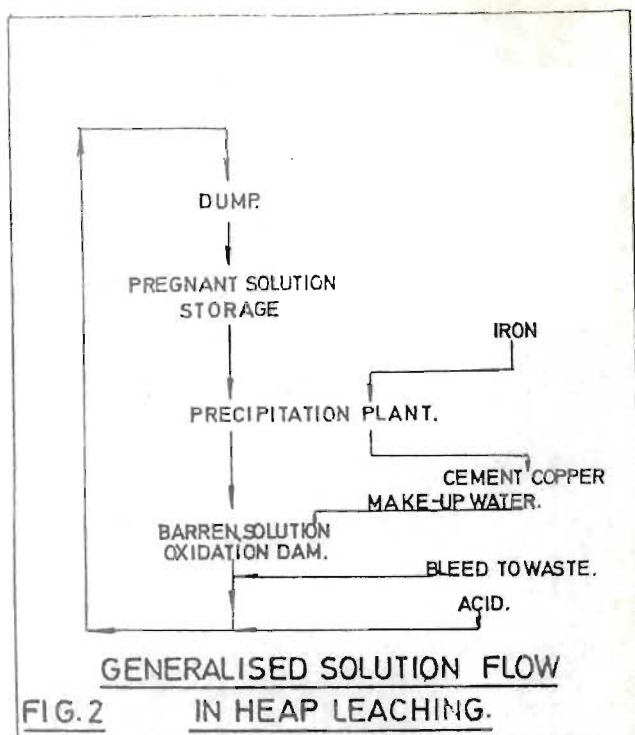


Fig. 2—Generalised solution flow in heap leaching

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 Minerã do 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 Junglo	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

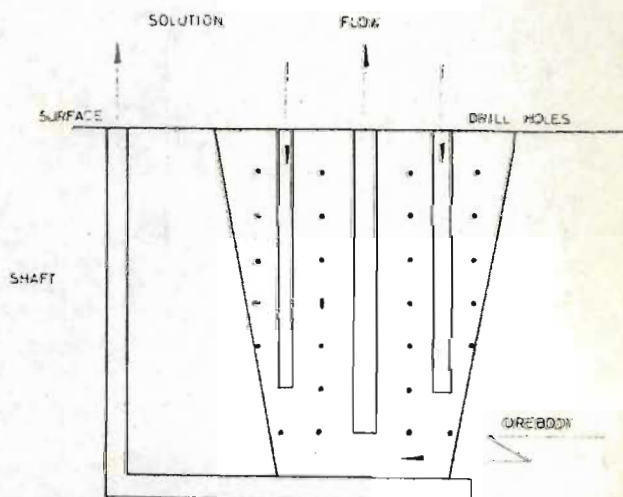


Fig 3 In Situ Leaching

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 obtained'¹⁸. 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.

A STUDY ON THE MECHANISM OF BACTERIAL LEACHING

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

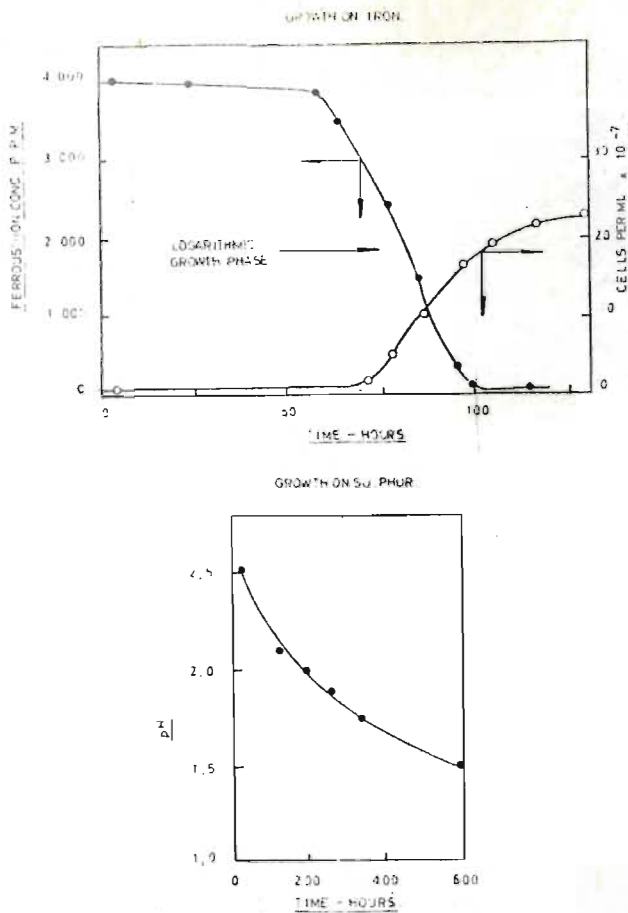


Fig 4 Growth rate of *T. ferrooxidans*

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.

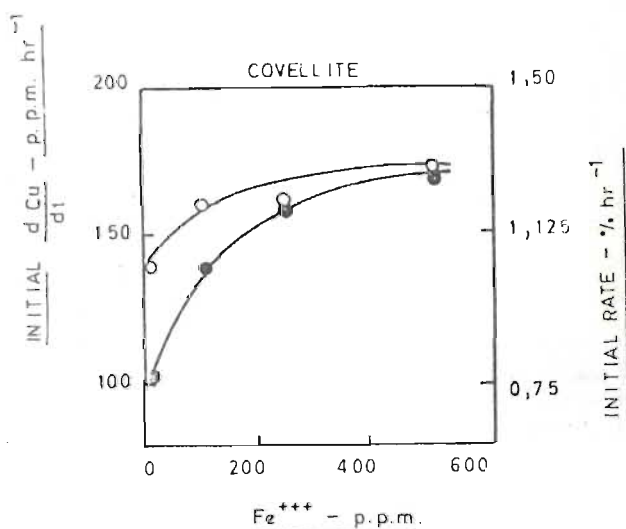
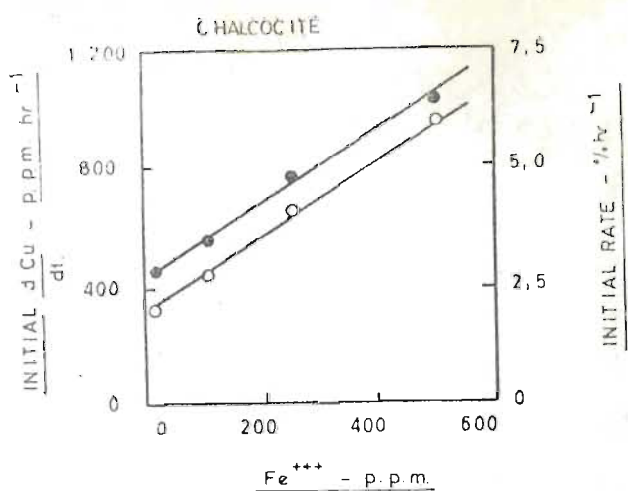
RESULTS

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 ion 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 Ingraham²¹ 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 ²⁺ ppm	Bacteria cells/ml
1	2	2,5	500	10 ⁵
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.

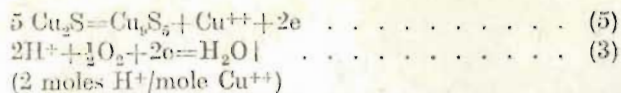
In the other three tests with chalcocite, there was an initial release of copper (1 per cent in 4 days) and an increase of the pH to 4,0. After this no further leaching was observed.

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.

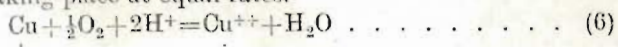
Long term leaching under growth conditions

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 electrochemical mechanisms are assumed.



A large difference 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.

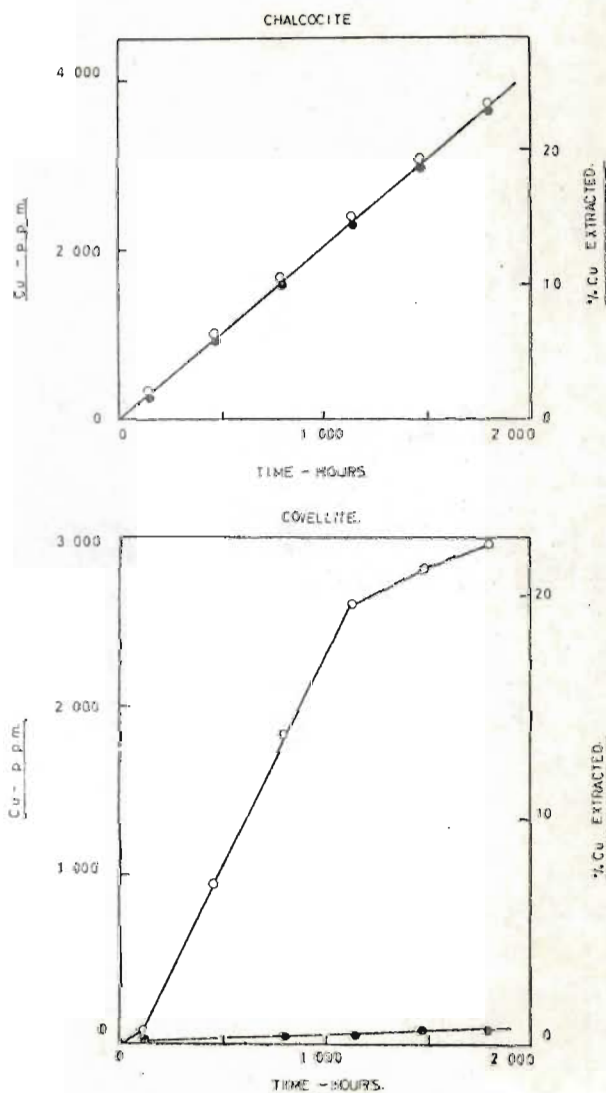


Fig 6 Long term leaching data

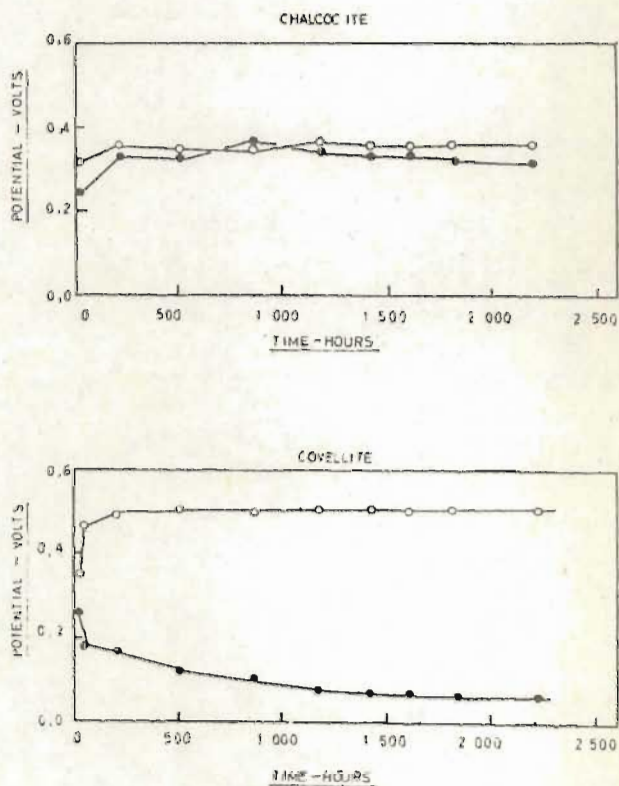


Fig 7 Rest potential measurements

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.

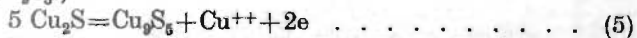
The surface of the specimen leached in the absence of bacteria displayed only slight optical activity and was pitted and slightly cracked at grain boundaries. Certain regions showed no effects of corrosion, but sulphur-rich areas were observed in the surface pits and cracks. The rest of the surface differed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

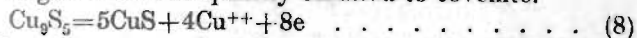
DISCUSSION

It has been shown that the leaching of metal sulphides is an electrochemical oxidation process^{26, 27, 29} 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

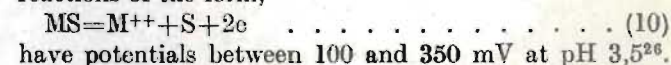
other than the removal of sulphur may be attributed to bacterial action.

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

extensive and precise information on the intimate mechanisms involved, both insofar as the changes occurring in the mineral substrate are concerned and the events occurring at the micro-organism-mineral surface interface.

In the investigations described, some further information on the mechanisms of microbial leaching of the copper minerals chalcocite and covellite has been obtained, by the use of synthetic specimens as model substrates and a range of physico-chemical techniques. In brief, it has been shown that in the bacterial leaching of synthetic chalcocite, the indirect mechanism of ferric leaching is paramount, while in the leaching of synthetic covellite the direct mechanism is important. The direct mechanism operates by preventing the accumulation of a protective layer of sulphur and by the depolarisation of the cathodic reaction.

ACKNOWLEDGEMENTS

The investigations described were carried out during a period of secondment of one of the authors (I.J.C.) from J.C.I. Co. Ltd., to the University of New South Wales, Sydney, Australia. The authors thank J.C.I. Co. Ltd., for their support and their continuing interest in this work.

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Name of Inventor: IAN JAMES CORRANS

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PROVISIONAL SPECIFICATION

APPLICATION No.:

TITLE OF INVENTION: "IMPROVEMENTS IN HYDROMETALLURGY"

NAME OF APPLICANT: JOHANNESBURG CONSOLIDATED INVESTMENT
COMPANY LIMITED

ADDRESS: Consolidated Buildings,
cnr. Fox and Harrison Streets,
Johannesburg.

X I/WE DO HEREBY DECLARE THIS INVENTION TO BE DESCRIBED IN THE FOLLOWING STATEMENT:

THIS invention relates to hydrometallurgy and more particularly to the leaching of metals values from metal ores, concentrates, mattes or other metal bearing materials.

5 Conventional metal sulphide ores, e.g. copper and nickel sulphide ores, are leached using acid leach solutions which may contain ferric ions or oxygen to accelerate the leaching process or using bacterial leaching processes. Acid leaching in the presence of ferric ions or oxygen accelerators has the disadvantage that high temperatures and/or oxygen
10 pressures are required to produce effective leaching conditions. Similarly in bacterial leaching special biological growth additives have to be employed in order to obtain high rates of metal dissolution.

15 It is an object of the present invention to provide a method of leaching which is believed to be an improvement over these prior art methods.

20 According to the invention, a method of solubilising metal values from a metal containing material includes the step of contacting the material with ozonised oxygen in the presence of water or an aqueous solution.

Preferably the ozonised gas comprises oxygen containing up to about five percent ozone in equilibrium with the oxygen. It may be made by methods known in the art. An example of a method of producing ozone is as follows:

Refrigerated, dehydrated air is passed into a vertical tubular ozonator. This operates by a glow discharge in the annular space between the metal tubes and coaxial dielectric material. Typically the air leaving the machine would contain 1,25% O_3 (w/w), with a power consumption of 7,3 kwh/lb O_3 ("Ozone, Practical aspects of its Generation and Use" . Diaper, E.W.J. Part I Chemtech, June 1972, p. 368.

Part II Chemtech, August 1972 p. 498.) If oxygen is used in place of air, the quantity and concentration of ozone may be increased two or three times and the power consumption cut by about half.

The metal containing material may be a metal sulphide ore, concentrate, matte or other metal sulphide bearing material. Preferably, the material is slurried with the water and the slurry contacted with the ozonised oxygen.

5 If desired, the water used in the method may contain some acid. The use of ozonised oxygen has been found to reduce the acid requirements by autogenously producing acid in the leach.

10 It has been found that the rate of solubilisation when using the method of the invention is higher than the rate using the prior art methods discussed above.

15 According to another aspect of the invention, ferrous ions resulting from the leaching of metal-containing material with acid in the presence of ferric ions are oxidised to ferric ions using ozonised oxygen. Thus, the ferric leach solution is regenerated and may be recycled to the leaching stage.

20 The following examples are used to illustrate the use of ozonised oxygen in the present invention. Some of the examples relate to the leaching of metal values from ores and others to the oxidation of ferrous ions and sulphur.

Example 1.

25 A nickel-iron sulphide (pentlandite) concentrate was leached as a 20% slurry in water using a propeller-type agitator at 200 r.p.m. Ozonised oxygen was bubbled into the solution and the temperature was controlled at 30°C. After 165 hours the nickel concentration was 13,8 g/l and the iron concentration 0,5 g/l, representing 35% nickel extraction. During the test the pH dropped from 5,1 to 2,8 without the addition

of acid. A control experiment using oxygen only leached 4% of the nickel during the same period of time.

5 A series of bacterial leach tests were carried out on the pentlandite concentrates under similar conditions, using a strain of *Thiobacillus ferrooxidans* bacteria adapted to growth on nickel sulphides. The pentlandite was leached as a 20% slurry in an inorganic growth medium. The slurry was stirred with a propellor-type agitator, aerated, and the temperature controlled at 30°C. The highest rate of nickel leaching, obtained in the pH range 2,5-4,5, was 40 mg/l/hr representing 17% nickel extraction in 165 hours.

Example II.

15 In a test using the same conditions as in example I, the propellor-type stirrer was replaced by a vibratory type agitator. In this case, 75% of the nickel was leached in 70 hours. During the test the pH dropped from 5,1 to 1,3 without the addition of acid. Iron started reporting in solution at a pH of approximately 4,5. In a control experimental using oxygen only, 7% of the nickel was leached in the same period of time. In this case the pH remained constant at 5,1.

Example III.

25 Tests were carried out using the same conditions as in example II except that the leaching was carried out at 45°C and 60°C. At 45°C, 38% of the nickel was leached in 70 hours and at 60°C 37% of the nickel was leached in the same period; c.f. 75% extraction obtained in example II.

Example IV.

30 A copper-iron sulphide (chalcopyrite) concentrate was leached as a 20% slurry in acidified water using a vibratory type

agitator. Ozonised oxygen was bubbled into the solution and the temperature was controlled at 30°C. After 165 hours 92% of the copper was leached giving 46 g/l copper in solution. During this time the pH of the solution dropped from 3,0 to 2,0 without the addition of acid. In a control experiment using oxygen only, less than 1% of the copper was leached during the same period of time.

Example V.

A zinc sulphide (sphalerite) concentrate was leached as a 20% slurry in acidified water using a vibratory-type agitator. Ozonised oxygen was bubbled through the solution and the temperature was controlled at 30°C. After 26 hours, 25 percent of the zinc was leached giving 36 g/l zinc in solution. The pH was controlled at 3,0, with a sulphuric acid consumption of 1 g H₂SO₄ per 6g of zinc leached. In a control experiment using oxygen only, less than 0,5% of the zinc was leached in the same period of time.

Example VI.

A solution containing 10 g/l ferrous ion in a sulphate solution was oxidised by bubbling ozonised oxygen through the solution and agitating with a vibratory type agitator. The temperature was uncontrolled at 20°C ± 5°C. Ninety percent of the ferrous ions were oxidised to the ferric state in two hours. During this time the pH of the solution dropped from 2,5 to 2,0 without the addition of acid. In a control experiment using oxygen only, 5% of the ferrous ions were oxidised to the ferric state in one hour.

A solution containing 4 g/l ferrous ion in a sulphate growth medium was oxidised using a specially adapted strain of Thiobacillus ferrooxidans bacteria. Temperature was controlled at 30°C, pH at 2,5 and air was bubbled into the

agitated solution. During the growth phase of 40 hours, 90% of the ferrous ions were oxidised to the ferric state.

Example VII.

5 A solution containing 10 g/l ferrous ion in a chloride solution was oxidised using the same conditions as in example VI; 99,5% of the ferrous ions were oxidised to the ferric state after 1,1 hours. During this time, the pH of the solution dropped from 2,5 to 1,55 without the addition of acid. In a similar test using a propellor-type agitator, 10 instead of the vibratory type, more than 99,5% of the ferrous ions were oxidised to the ferric state after 1,5 hours. During this time the pH of the solution dropped from 2,5 to 1,75 without the addition of acid.

15 In a control experiment with oxygen only, using a vibratory type of agitator, 3% of the ferrous ions were oxidised to the ferric state after 1,1 hours.

Example VIII.

20 A nickel-copper matte containing 45% nickel and 27% copper was leached as a 15% slurry using a vibratory type agitator. Sulphuric acid was added at 80g per litre. Ozonised oxygen was bubbled through the solution. After 30 hours 75% of both the nickel and copper had been dissolved, the solution containing 45 g/l Ni and 27 g/l Cu. During this period of time the pH of the solution rose from zero to 3,6. No acid 25 was added during the leach. The temperature rose from 25⁰C to 40⁰C during the leach.

In two control experiments using both oxygen and air, 45% of the nickel and 25% of the copper were leached respectively during the same period of time.

Example IX.

5 A nickel-copper matte was leached using the same conditions as example VIII, except that the pH was controlled at 5,0 during the experiment. After 30 hours 41% of the nickel and 3% of the copper had been dissolved.

In a control experiment using oxygen, 8% of the nickel and less than 0,1% of the copper were dissolved.

Example X.

10 A 5% slurry of powdered sulphur and water was treated by bubbling ozonised oxygen through the solution agitated with a vibratory type agitator. The temperature was approximately 30°C, i.e. ambient. After 21 hours the pH dropped from 7,0 to 0,55 and 24,16 g/l H₂SO₄ was produced.

15 In a control experiment using oxygen no acid was produced in the same period of time.

20 Slurries of sulphur were oxidised with a specially adapted strain of Thiobacillus ferrooxidans bacteria in an inorganic growth medium. Temperature was controlled at 30°C, pH at 3,0 and air was bubbled into the agitated solution. The highest rate of acid production obtained was 0,15 g of H₂SO₄ per litre per hour, representing 3,15 g of acid produced per litre in 21 hours.

25 Ozone consumption was measured during the leaching experiments and was consistently found to be 2 to 2,5 moles ozone per mole of metal in solution : (i.e. per mole of Ni⁺⁺, Cu⁺⁺, Zn⁺⁺.)

DATED THIS 17th DAY OF JULY, 1973.

SPOOR AND FISHER

APPLICANT'S PATENT ATTORNEYS