AN ASSESSMENT OF OXYGEN AVAILABILITY, IRON BUILD-UP AND THE RELATIVE SIGNIFICANCE OF FREE AND ATTACHED BACTERIA, AS FACTORS AFFECTING BIO-OXIDATION OF REFRACTORY GOLD-BEARING SULPHIDES AT HIGH SOLIDS CONCENTRATIONS

by

ANDREW DOUGLAS BAILEY

BSc. (Chem. Eng.) UCT, MSc. (Chem. Eng.) UCT

University of Cape Town

Thesis Presented for the Degree of

DOCTOR OF PHILOSOPHY

in the Department of Chemical Engineering

UNIVERSITY OF CAPE TOWN

JUNE, 1993

The University of Cape Town has been given the right to reproduce this thesis in whole or in part. Copyright is held by the author.

The copyright of this thesis vests in the author. No quotation from it or information derived from it is to be published without full acknowledgement of the source. The thesis is to be used for private study or non-commercial research purposes only.

Published by the University of Cape Town (UCT) in terms of the non-exclusive license granted to UCT by the author.

University of Cape Town

ABSTRACT

Bacterial oxidation is currently finding significant application for the oxidative pretreatment of refractory gold-bearing sulphides. Plants processing sulphide concentrates have commonly been operated at solids concentrations of between 18 and 20 per cent (m/v) (i.e 180 and 200 $kg.m^{-3}$). At higher concentrations, a decline in the bio-oxidation rate has been observed. Other metallurgical processes, such as chemical leaching and cyanidation, are performed at higher solids concentrations of between 40 and 50 per cent (400 and 500 $kg.m^{-3}$), providing an incentive to increase the solids concentration at which bio-oxidation plants are operated.

A review of literature indicated the following factors to be potential causes of reduced bio-oxidation rates at high solids concentrations: oxygen and carbon dioxide mass transfer; a low bacteria-to-solids ratio; mechanical damage of the bacteria; and the build-up of inhibitory oxidation products. Interaction of these factors in the completely-mixed reactors that are commonly used for bio-oxidation, has confounded the interpretation of the effects of individual factors.

Analysis of literature data revealed a link between the sulphide grade of a particular material and the highest solids concentration at which the bacterial oxidation rate was maximal. The oxygen demand is directly proportional to the sulphide concentration in the reactor. Correlations were used to predict the oxygen transfer potential in the experimental reactors and it was found that as long as the oxygen transfer potential exceeded the oxygen demand, the bio-oxidation rate was proportional to the solids concentration for a specific material. When the oxygen demand equalled or exceeded the oxygen transfer potential, then the bacterial oxidation rate was limited by oxygen availability. The sulphide grade is characteristic of a particular ore or concentrate and from the data analysis oxygen availabiiity appeared to be the underlying reason why low grade materials could be oxidised at the maximum specific bio-oxidation rate at far higher solids concentrations than high-grade materials.

University of Cape Town

The experiments performed in this study were designed to further investigate the apparent relationship, identified by analysis of literature data, between sulphide grade and the solids concentration at which the bacterial oxidation rate was maximal. The effect of both solids concentration and sulphide grade on the bio-oxidation rate was investigated and related to the oxygen availability in the reactor.

Two, high grade pyrite concentrates (sulphur > 28%) and a low pyrite content ore (2% sulphur) were used for the testwork. Inert silica was mixed with the high-grade concentrate to simulate intermediate sulphide grades. A novel fluidised bed reactor as well as batch stirred tank reactors were used. The fluidised bed reactor (FBR) allowed the solids and liquid environments to be controlled independently, enabling specific factors, thought to limit the bio-oxidation rate, to be isolated for investigation. The FBR effectively circumvented the problem of interaction between the various factors that is encountered in completely-mixed reactors.

In the FBR it was possible to ensure the availability of sufficient oxygen, even at high bed solids concentrations. In contrast to observations in stirred tank reactors, the specific bio-oxidation rate of high sulphide content material in the FBR was constant up to 45 per cent solids (450 $kg.m^{-3}$), the maximum concentration tested. When the solids loading (and consequently the oxygen demand) was increased, however, it was found that the moment the oxygen demand exceeded the oxygen supply rate, the bio-oxidation rate was limited. This confirmed the hypothesis that had been proposed after analysis of the literature data. The FBR has emerged as a useful tool for determining the specific bio-oxidation rate under controlled conditions.

Batch stirred tank reactor (STR) studies further consolidated the relationship between the sulphide grade and the oxygen demand, as a key factor in determining the highest solids concentration at which a reactor can be operated at the maximum specific bio-oxidation rate. The bio-oxidation rate of the low-grade ore (1.24% S) was found to be proportional to the solids concentration up to 60 per cent solids (600 $kg.m^{-3}$), the highest solids concentration tested; considerably above the concentration at which the rate usually decreases when high sulphide content material is processed. This observation was due to the low

University of Cape Town

oxygen demand in the reactor even at 60 per cent solids. Furthermore, it was demonstrated that the addition of inert solid particles to 10 per cent (100 $kg.m^{-3}$) pyrite concentrate, up to a maximum total solids concentration of 30 per cent (300 $kg.m^{-3}$), did not affect the specific bio-oxidation rate in the STR. It was also apparent from the STR results that mechanical destruction, or trauma, of the bacteria was not a primary cause of low bio-oxidation rates at high solids concentrations.

The experimental results obtained from both the FBR and STR testwork confirmed that it is not the solids concentration *per se* that affects the bio-oxidation rate at high solids concentrations, but rather the magnitude of the oxygen demand in relation to the oxygen transfer potential of the system. The highest solids concentration at which bio-oxidation can be conducted at the maximum specific oxidation rate is limited by the oxygen transfer potential of the system.

The bacteria were shown, in FBR reactor tests, to be capable of oxidising all of the ferrous iron generated during the processing of high pyrite content solids at a concentration of 50 per cent (50 $kg.m^{-3}$). Ferric iron concentrations in excess of 30 $g.l^{-1}$, however, decreased the ferrous oxidation rate of the bacteria.

Results from FBR tests in which the free cells in the system were suddenly depleted, indicated that the attached bacterial population was more significant to bio-oxidation than the free bacterial population. If there was a sudden depletion of the free bacteria, then attached bacteria were found to leave the mineral surface to replenish the solution, maintaining both the redox potential and the bio-oxidation rate. The bio-oxidation rate was, however, adversely affected when the attached bacterial population was low.

University of Cape Town

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to the following people:

Professor G.S. Hansford, my PhD supervisor, for his guidance, training in research methodology and constructive criticism.

MINTEK, Randburg, South Africa for their financial support of the research. In particular, Dr A. Pinches and Dr W.A.M. Te Riele for their valuable input and interest in the project.

Staff of the electronic and main workshops in the Chemical Engineering Department: Mr. E.W. Randall; Mr. G. de la Cruz; Mr. A.M. Barker; Mr. R. Senekal; Mr J. Daniels; and Mr M. Williams, for building and maintaining much of the equipment used.

Laboratory Manager, Mrs. L. Harrower and Mrs. M. Josias for their tremendous help in analysing and processing the samples.

All my colleagues in the department, for their willing assistance whenever necessary and friendship. In particular, thanks to my bioleaching colleagues: Mr. P.J. Myburgh, Mrs B. Fenemore and Mrs P.F. Lockey.

Finally, my family and friends for their continuous support and interest throughout my studies, I have really appreciated it.

University of Cape Town

Dedicated to my parents
and the memory of M.S.E.

University of Cape Town

PUBLICATION DECLARATION

In terms of Rule GP 8 for PhD Theses, I give my permission for the inclusion in this thesis of material that has been published in the following papers:

1. Bailey, A.D. and Hansford, G.S., (1993), "A Fluidised Bed Reactor as a Tool for the Investigation of Oxygen Availability on the Bio-oxidation Rate of Sulphide Minerals at High Solids Concentrations", *Minerals Engineering*, **6,** (4), pp. 387-396.

2. Bailey, A.D. and Hansford, G.S., (1993), "Effect of Removal of Unattached Cells on the Bio-oxidation rate of Pyrite in a Fluidised Bed Reactor", *Biotechnology Letters*, **15**, (5), pp. 543-548.

3. Bailey, A.D. and Hansford, G.S., (1993), "Factors Affecting Bio-oxidation of Sulphide Minerals at High Concentrations of Solids: A Review", *Biotechnology and Bioengineering*, **42**, pp. 1181-1189.

4. Bailey, A.D. and Hansford, G.S., (1994), "Oxygen Mass Transfer Limitation of Batch Bio-oxidation at High Solids Concentration", *Minerals Engineering*, **7**, (2/3), pp. 293-304.

5. Hansford, G.S. and Bailey, A.D.,(1993), "Oxygen Transfer Limitation of Bio-oxidation at High Solids Concentration", *Biohydrometallurgical Technologies*, **1**, Eds. A.E. Torma, J.E. Wey and V.I. Lakshmanan, The Minerals, Metals and Materials Society, Pennsylvania, pp. 469-478.

University of Cape Town

.....

PROFESSOR G S HANSFORD
(PhD SUPERVISOR)

TABLE OF CONTENTS

University of Cape Town

University of Cape Town

University of Cape Town

University of Cape Town

University of Cape Town

LIST OF FIGURES

University of Cape Town

University of Cape Town

LIST OF TABLES

University of Cape Town

University of Cape Town

NOMENCLATURE AND GLOSSARY

a	mass of solids	g
C	liquor dissolved oxygen concentration	mg.l^{-1}
C^*	saturated dissolved oxygen concentration	mg.l^{-1}
C_c^*	saturated dissolved CO_2 concentration	mg.l^{-1}
C_{CRIT}	critical dissolved oxygen concentration	mg.l^{-1}
D_c	characteristic particle diameter	µm
D_i	average diameter in fraction i	µm
E	concentration of element	mg.l^{-1}
F_i	fraction of sample is size fraction i	
K_La	mass transfer coefficient	s^{-1}
L	limited solids concentration	%
M	concentration of solids in reactor	kg.m^{-3}
M_P	mass of particle	kg
M_T	total mass of sample	kg
P	pyrite oxidation rate	(kg pyrite)(m_2 pyrite)$^{-1}$ d^{-1}
(P/V)	power input per unit volume	kW.m^{-3}
Q	gas sparge rate	l.min^{-1}
R	oxygen utilisation rate	(kg O_2)(m_2 pyrite)$^{-1}$ d^{-1}
R_{PY}	pyrite oxygen demand)	(kg O_2)(m_2 pyrite)$^{-1}$ d^{-1}
R^2	regression coefficient	
S_{PY}	surface area fraction pyrite	
T_{SA}	total surface area	m^2
V_{PY}	volume fraction pyrite	
Y_{PY}	mass fraction pyrite	
μ_{rel}	relative slurry viscosity	
ρ	pyrite density	kg.m^{-3}
ρ_{sil}	silica density	kg.m^{-3}

University of Cape Town

Bed solids concentration	:	concentration of solids in the fluidised bed of particles in the reactor, expressed as a percentage (m/v). Defined in Figure 2.3.
Liquid hold-up	:	refers to the volume of liquid inbetween the solid particles in the fluidised bed.
Overall solids-to-liquid ratio:		concentration of solids in the entire fluidised bed reactor and surge tank system, expressed as a percentage (m/v). Defined in Figure 2.3.
Solids concentration	:	1 % solids 1 g solids / 100 ml pulp 10 kg solids / m^3 pulp It should be noted that a solids concentration that is quoted in "$kg.m^{-3}$" represents mass of solids per volume of pulp.
Superficial liquid velocity	:	the volumetric flowrate of liquid up through the fluidised bed reactor, divided by the cross-sectional area of the reactor, or zone of the reactor.

ABBREVIATIONS

CUR	carbon dioxide utilisation rate
FBR	fluidised bed reactor
OBD	Oguz-Brehm-Deckwer (correlation)
ORP	Redox potential
OTP	oxygen transfer potential
OTR	oxygen transfer rate
OUR	oxygen utilisation rate

University of Cape Town

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

During conventional cyanide extraction of gold from certain sulphide minerals it has been noticed that gold recoveries are low. This is caused by the "refractory" nature of these ores which can be attributed to causes ranging from the distribution of the gold as microcrystalline particles to the interference with the cyanidation process caused by carbon, base metals, or pyrrhotite in the ore (Miller, 1990; Komnitsas and Pooley, 1989).

To liberate the gold from the ore matrix and improve recovery, it is necessary to oxidise the ore prior to the cyanidation step. Historically, the most commonly used oxidative pretreatment process has been roasting (Stanley, 1987), but in recent years there has been a proliferation of new technologies. Fluo solids roasting, pressure oxidation and bacterial oxidation are generally recognised as holding the most promise (Carter, 1991). Roasting is still a commonly selected option, with six new roasting plants having been commissioned in Australia in the last five years and the 2.5 M mt/yr Newmont Gold Company's (USA) whole-ore roasting facilities due to be commissioned in 1994 (Engineering and Mining Journal, 1993). Roasting has the disadvantage of requiring expensive gas clean-up to prevent atmospheric pollution, particularly when arsenopyrite is present. Pressure oxidation is less commonly used as it requires both high temperatures and pressures (Stanley, 1987). Bio-oxidation has recently progressed to the stage where it has become a viable process option, particularly for the oxidation of refractory pyrite and arsenopyrite ores and concentrates (Dempsey *et al.*, 1990; Lawson and van Aswegen, 1992). For plants with a processing capacity of less than 1200 tpd concentrate, the process has been demonstrated to have significant economic advantages over the alternative processes (Carter, 1991).

University of Cape Town

Several full-scale and pilot bio-oxidation plants treating refractory gold-bearing sulphides have been operated, with the first industrial plant started at Fairview in South Africa in 1986, followed by plants in Brazil and Australia (Slabbert *et al.*, 1992). Newmont Mining (Nevada) is applying bio-oxidation to 600-tonne heaps of refractory ore at mining operations on Nevada's Carlin Trend deposit, the largest gold deposit outside South Africa (Gooding, 1991). In South Africa, Genmin (General Mining, Metals and Minerals Limited, South Africa) is involved in the operation of a 35 metric ton per day (tpd) bio-oxidation plant to treat arsenopyrite concentrate at its Fairview gold mine situated in the Eastern Transvaal (Booth *et al.*, 1991). Genmin is also involved in the operation of a 150 tpd bio-oxidation plant at Sao Bento in Brazil; a 40 tpd plant at Harbour Lights in Australia (Dew and Godfrey, 1991); and with the development of the 140 tpd Asarco Wiluna Mine plant, also in Australia. A 20 tpd plant has been operated at Vaal Reefs Gold Mine (Anglo American Corporation, South Africa), treating a refractory pyrite concentrate (Dempsey *et al.*, 1990). MINTEK (The Council for Mineral Technology, Randburg, South Africa) have used the same ore in their 1 tpd pilot plant operation (Neale *et al.*, 1991). The Ashanti Goldfields Corporation (Ghana) is currently developing a plant at Sansu that will be the largest of its type in the world, with a throughput of 760 tpd.

All of the South African plants have been reported to have been operated at between 18 and 20 per cent (180 and 200 $kg.m^{-3}$) solids. For a variety of high sulphide content ores, it has been found that the maximum oxidation rate is achieved at solids concentrations in the range at which the plants are operated (Torma *et al.*, 1970; Sakaguchi *et al.*, 1976; Hoffman *et al.*, 1991). At higher solids concentrations, the oxidation rate begins to decline and the optimal plant cost is closely associated with the solids concentration at which the oxidation rate is maximal (Huberts *et al.*, 1991).

Other hydrometallurgical processes such as the cyanide extraction of gold and the acid leaching of uranium are performed at higher solids concentrations. Between 40 and 60 per cent (400 and 600 $kg.m^{-3}$) solids being standard for most ores and concentrates (Woodcock, 1985; Stanley, 1987). So, there is an incentive to investigate those factors which restrict current operation of bio-oxidation plants to solids concentrations below 20 per cent.

University of Cape Town

Useful data on the effect that solids concentration has on the bio-oxidation rate has been published recently by researchers at the Council for Mineral Technology, Randburg, South Africa (Neale *et al.*, 1991; Pinches *et al.*, 1991; van Staden, 1991). The bio-oxidation rate was determined for three different sulphide minerals: a pyrite concentrate (28% S), an arsenopyrite-concentrate (6% S) as well as a low grade run-of-mine pyrite ore (1% S). The solids concentrations at which the tests were conducted extended up to approximately 850 kg.m $^{-3}$. The rate data quoted in the publications have been plotted together in Figure 1.1a.

The researchers showed that it was possible to oxidise a low sulphide content (1.1% sulphide-sulphur) run-of-mine ore at a solids concentration of 55 per cent (550 kg.m^{-3}) in a continuous process. Bio-oxidation of a low-sulphide arsenopyrite-pyrite concentrate (6.2% sulphide-sulphur) was also possible at a solids concentration of 42.9 per cent (429 kg.m^{-3}). The solids concentrations are considerably higher than those reported generally in the literature for higher sulphide content material. With a pyrite concentrate (28% sulphide-sulphur), however, the bio-oxidation rate was found to drop with increasing solids concentration. The decrease was subsequently shown to arise from an increasing concentration of leach products, primarily sulphuric acid. Agitation rates also had to be increased at high solids concentrations to prevent oxygen-limited conditions.

The fact that lower grade sulphide material could be oxidised at high solids concentrations, indicated that it was possible that the amount of sulphide material present limited the bio-oxidation rate and not the overall solids concentration *per se*. In order to investigate the effect of the sulphide content on the bio-oxidation rate, the rate data that were shown in Figure 1.1a have been replotted in Figure 1.1b against the sulphide-weighted surface area. The sulphide-weighted surface area was estimated from the product of the total surface area concentration and sulphide fractions that were quoted in the publications.

University of Cape Town

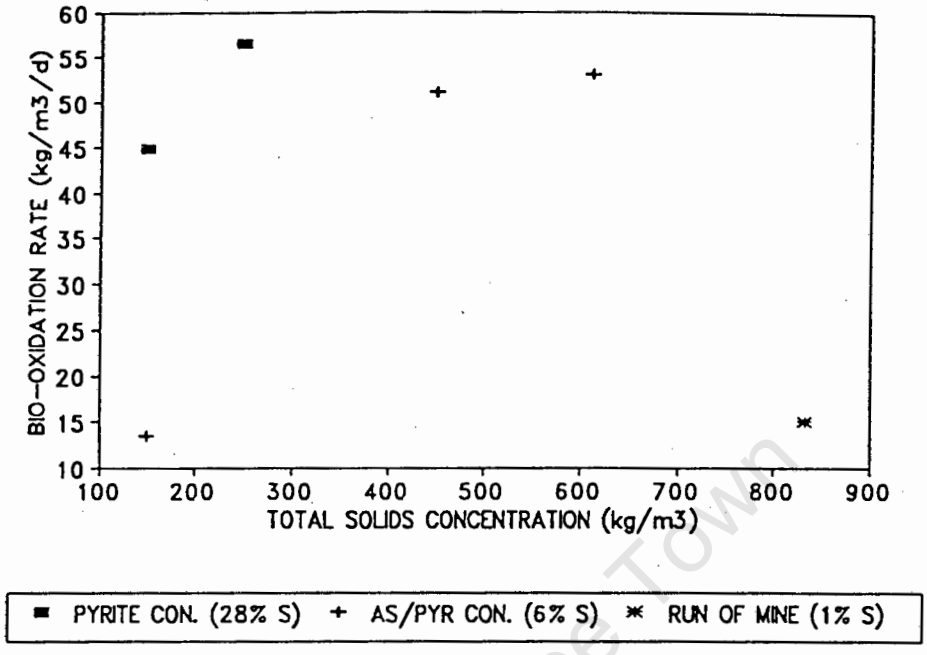


Figure 1.1a: Bio-oxidation Rate vs Solids Concentration (Data of: Pinches *et al.*, 1991; van Staden 1991).

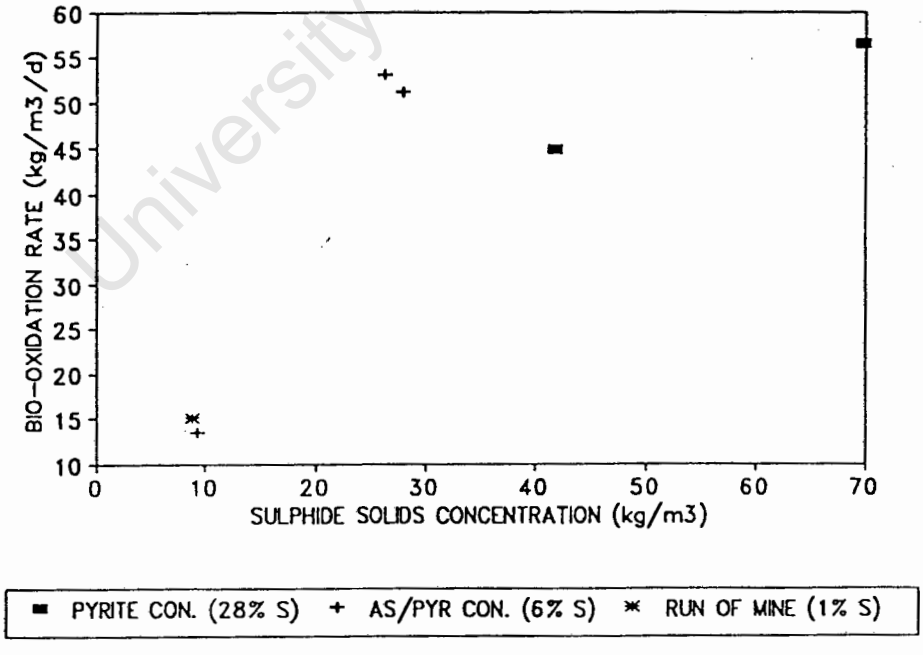


Figure 1.1b: Bio-oxidation Rate vs Sulphide-weighted Solids Concentration (Data of: Pinches *et al.*, 1991; van Staden, 1991)

University of Cape Town

Of particular note is the fact that the oxidation rates of the run-of-mine ore and the low sulphide arsenopyrite-pyrite concentrate were essentially the same at similar sulphide-weighted surface area concentrations. The overall solids loadings were, however, very different with the sulphide-rich test performed at 13 per cent (130 $kg.m^{-3}$) solids and the run-of-mine ore at 55 per cent (550 $kg.m^{-3}$). From these results it would appear that whatever factor(s) is limiting the bio-oxidation process at high solids concentrations is associated with the sulphide content of the material and not merely the total amount of solids present.

University of Cape Town

1.2 THESIS OBJECTIVES

The first objective of this thesis was to review research reported in the literature which has discussed the effect of solids concentration on bio-oxidation. The findings of this survey are presented in Chapter Three. Several reasons have been proposed in the literature as possible causes of the decline in oxidation rate that has been observed at high solids concentrations. These factors are also discussed in the literature review. The review highlighted the fact that the various factors tend to interact, complicating the interpretation of the results. A link between the sulphide grade of the material and the solids concentration at which the bio-oxidation rate is maximal is also evident.

Experimental methods as well as a description of the various reactors and materials used in this research project are given in Chapter Four.

To investigate the effect of oxygen limitation on the bio-oxidation rate, two sets of data from the literature were studied in Chapter Two. Correlations have been used to predict the maximum oxygen transfer potential of both systems. The oxygen demand was calculated as a function of solids concentration using the published rate data. The predicted oxygen demand and oxygen transfer potentials were then compared with the bio-oxidation rates that were measured experimentally.

Batch stirred tank reactor bio-oxidation tests were performed at a range of different sulphide and total solids concentrations, to further investigate the relationship between the sulphide concentration and the bio-oxidation rate. The results from this study are reported in Chapter Five.

An additional objective of the thesis was to develop a system that would enable the various factors influencing the bio-oxidation rate to be controlled independently, so that their individual effects might be studied. The applicability of a fluidised bed reactor for such a study is discussed at the end of this chapter. Oxygen transfer, in particular, has been investigated more rigorously using the fluidised bed reactor. The results, presented in Chapter Six, have also been compared with those obtained from the batch reactor tests.

The data collected from studies investigating the effect of oxygen transfer and availability on bacterial oxidation (i.e. work presented in Chapters Five and Six) have been summarised and discussed in Chapter Seven. The rate data have been expressed on bases that allow comparison of the results of tests performed on the different materials as well as in the fluidised bed reactor and stirred tank reactors.

The relative significance of the free and attached bacterial populations has been assessed by performing a series of free cell depletion studies, using the fluidised bed reactor. In the testwork, the free, unattached bacteria were suddenly removed from the system by solution replacement after different periods of normal batch operation. The results of these tests are discussed in Chapter Eight.

Ferric sulphate build-up in bio-oxidation reactors is common to bio-oxidation of all sulphides that contain iron. Its effect on the bio-oxidation rate has been investigated by the staged addition of ferrous sulphate to runs performed in the fluidised bed reactor operated at constant overall and bed solids concentrations. The findings are presented in Chapter Nine. The ability of the bacteria to oxidise ferrous ions was also assessed during this experimental work.

Finally, conclusions are drawn from all of the experimental work and presented in Chapter Ten.

University of Cape Town

1.3 CONTRIBUTION OF PRESENT THESIS

A number of different factors have been proposed by various researchers as causes of the decline in the bio-oxidation rate that has been commonly observed at high solids concentrations. Oxygen limitation, in particular, has been cited as a possible cause of limitation during operation at high solids concentration. Although this belief has been long-held, no rigorous study has been performed to demonstrate this, to the author's knowledge subsequent to a DIALOG literature survey of the Chemical Abstracts data base. Researchers such as Hackl *et al.* (1989) and Pinches *et al.* (1991) have observed that the bio-oxidation rate is sensitive to both the solids concentration as well as to the sulphide grade of the material. The researchers attributed these observations, however, to solution properties and low pH values and did not investigate the role of oxygen availability in the context of sulphide grade as has been done in this thesis.

In the stirred tank reactors that are commonly used for bio-oxidation, many of the factors thought to affect operation at high solids concentrations interact, or exist simultaneously, making it difficult to single out one particular factor as the more significant cause of rate limitation. The research presented in this thesis has made use of a fluidised bed reactor (FBR) for bio-oxidation as a novel research tool that has enabled the factors to be controlled independently and the individual effects of selected factors to be studied more rigorously.

Using the fluidised bed reactor, it has been shown that under conditions where: sufficient bacteria were available; the iron concentration in solution was low; and sufficient oxygen and carbon dioxide were available; that the specific bio-oxidation rate was essentially independent of the solids concentration in the fluidised bed. Batch testwork performed on a low sulphide grade material supported these findings, indicating that the specific bio-oxidation rate remained constant up to the highest solids concentration tested, of 60 per cent (600 $kg.m^3$). These results indicated that for the bacterial culture used, the speculation that it was mechanical interaction of the solids at high solids concentrations that was causing limitation (eg. by bacterial trauma) was invalid. The maximum solids concentration at which bio-oxidation can be performed has been shown, through

University of Cape Town

the observations made during the experimental work presented in this thesis, to rather be dependent on the sulphide grade of the material.

When oxygen availability was limiting, however, the bio-oxidation rate has been conclusively shown to be defined by the oxygen transfer potential of the system. To analyse literature data use was made of the correlation developed by Oguz, Brehm and Deckwer (1987) for $k_L a$ as a function of solids concentration to predict the oxygen transfer potential in bio-oxidation reactors at different solids concentrations. These predictions were compared to the oxygen demand in the reactors. The experimental results and the predictions based on the correlations were found to be in close agreement as to when oxygen-limited conditions would occur. The application of correlations for $k_L a$ that incorporate the effect of solids concentration has not been previously attempted in bacterial oxidation.

The actual role that the solid material plays at high solids concentration has also been clarified by this work: firstly the presence of solid material does lower the oxygen transfer potential (OTP) of the system, as indicated by the Oguz-Brehm-Deckwer (1987) correlation; it is the sulphide content of the solids that determines the oxygen demand and to prevent a decline in the specific oxidation rate it must be ensured that the oxygen transfer rate exceeds the rate of oxygen supply (OTP); finally due to the observations made during batch STR bio-oxidation of low-grade material, it would appear that the solids do not affect bio-oxidation purely by mechanical interaction, i.e. by causing bacterial trauma. The experimental work also indicated that bio-oxidation of low sulphur content material could successfully be performed at a solids concentration of 60 per cent (600 $kg.m^{-3}$) at the maximum specific bio-oxidation rate. This is a higher solids concentration than other high solids concentrations quoted in the literature.

University of Cape Town

1.4 THE FLUIDISED BED REACTOR FOR A STUDY OF FACTORS AFFECTING BIO-OXIDATION AT HIGH SOLIDS CONCENTRATIONS

As mentioned earlier, many of the factors thought to influence bio-oxidation at high solids concentrations, interact during oxidation in a stirred tank reactor. A fluidised bed reactor, however, meets the requirements for independent control of the various factors. A reasonably narrow size fraction of ore particles can be maintained in a fluidised bed by liquor that is continually recirculated from the top of the reactor back to the bottom. By changing the liquor flowrate, the bed expansion can be varied, and thereby the bed solids concentration, without altering the overall solid-to-liquid ratio. Alternatively, it is possible to vary the overall solid-to-liquid ratio by increasing, or decreasing, the amount of solids charged to the reactor. Although the overall solids loading is varied, it is, however, possible to still operate at the same bed solids concentration during the different tests. The terms "overall solid-to-liquid ratio" and "bed solids concentration" are defined in Figure 1.2. The dashed line enscribing the entire system depicts the overall solid-to-liquid ratio, whilst the ellipse drawn around region of the fluidised bed reactor containing the bed of solids, indicates the bed solids concentration.

University of Cape Town

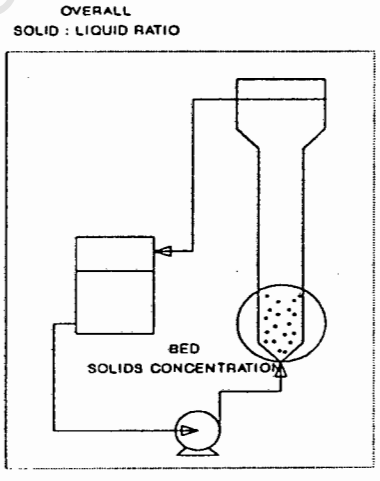


Figure 1.2 : Schematic Diagram of Fluidised Bed Reactor and Surge Tank, Defining Solids Concentration Terminology

An additional feature of the fluidised bed reactor/surge tank arrangement is that all aeration, temperature and pH control can be performed in the surge tank which is included in the recycle liquor loop. As the aeration is performed in the absence of solids, the effect that solids have on gas-to-liquid oxygen transfer is eliminated.

An important consideration is the effect of the superficial velocity on liquid-to-solid mass transfer in the fluidised bed as changes in the superficial velocity are necessary to achieve the different bed expansions. The effect has been studied by Burru and Briens (1991) in both two-phase (such as the system used in this thesis) and three-phase systems. It was found that changes in the fluidising velocity had no effect on the liquid-solid mass transfer coefficient. The correlations developed by the researchers, showed that the mass transfer coefficient was proportional to the square root of the superficial liquid velocity and inversely proportional to the liquid hold-up. This has the effect that as the superficial velocity is increased, its effect on the mass transfer coefficient is almost fully counterbalanced by the increase in the liquid hold-up. This was borne out in their experimental work as well as that of other workers who made similar observations (Arters and Fan, 1986; Nikov and Delmas, 1987; Fukuma *et al.*, 1988).

Therefore, in this work bio-oxidation tests have been performed in a fluidised bed reactor to study some of the factors affecting bio-oxidation at high solids concentrations more rigorously. Details of the reactor system used for this investigation are presented in Chapter Three. The results from experimental work using the fluidised bed reactor are discussed in Chapters Six, Seven, Eight and Nine.

University of Cape Town

CHAPTER TWO

ASSESSMENT OF OXYGEN TRANSFER AND DEMAND IN BIO-OXIDATION REACTORS

To investigate the effect of oxygen transfer limitation on bio-oxidation in stirred tank reactors from a theoretical point of view, literature correlations have been sought to enable both the oxygen transfer potential (OTP) and the oxygen demand for a particular system to be predicted. In Section 2.3, the oxygen demand and transfer potential predictions for two literature data sets have been compared with the quoted bio-oxidation rate data.

University of Cape Town

2.1 OXYGEN DEMAND

The bio-oxidation rate has been shown by Hansford and Drossou (1988) to be directly proportional to the surface area concentration. More specifically, the bio-oxidation rate is directly proportional to the sulphide surface area available for oxidation. This relationship holds until a solids concentration is reached where the bio-oxidation is limited by some factor, such as oxygen availability. The maximum surface area concentration studied by Drossou (1986) was 3832 $m^2.m^{-3}$, and no such limitation was encountered during oxidation under those conditions. The pyrite* bio-oxidation rate can be based on the pyrite surface area, as follows:

$$\text{Pyrite oxidation rate} = P \ (\text{kg pyrite})(m^2 \text{ pyrite})^{-1}d^{-1} \qquad [2.1]$$

Reaction stoichiometry (Equation 3.1) for pyrite oxidation, indicates that for every 1kg of pyrite oxidised, 1kg of oxygen is required. Using this information, a

---

* The argument would be similar for other sulphide minerals, as long as the appropriate reaction stoichiometry was substituted.

corresponding oxygen utilisation rate, R, may be determined from the pyrite bio-oxidation rate:

$$\text{Oxygen utilisation rate} = R \ (\text{kg } O_2)(\text{m}^2 \text{ pyrite})^{-1}\text{d}^{-1} \qquad [2.2]$$

The pyrite surface area is dependent on: the concentration of solids in the reactor; the particle size; and the ore grade (i.e. its pyrite content). If the pyrite surface area concentration in the reactor, A $(\text{m}^2 \text{ pyrite})(\text{m}^3 \text{ reactor})^{-1}$ is known, then the oxygen demand for a particular system can be calculated:

$$\text{Oxygen Demand} = R \times A \ (\text{kg}O_2)(\text{m})^{-3}\text{d}^{-1} \qquad [2.3]$$

For an ore of a particular particle size, the demand is linearly dependent on the solids concentration, as shown in Figure 2.1. The slope of the oxygen demand line is dependent on the sulphide content. A high sulphide content material (eg. 30 per cent sulphide sulphur) results in a steep slope. For a low grade material (eg. 1 per cent sulphide sulphur), the oxygen demand does not increase as much with increasing solids concentration, so the slope is not as steep.

University of Cape Town

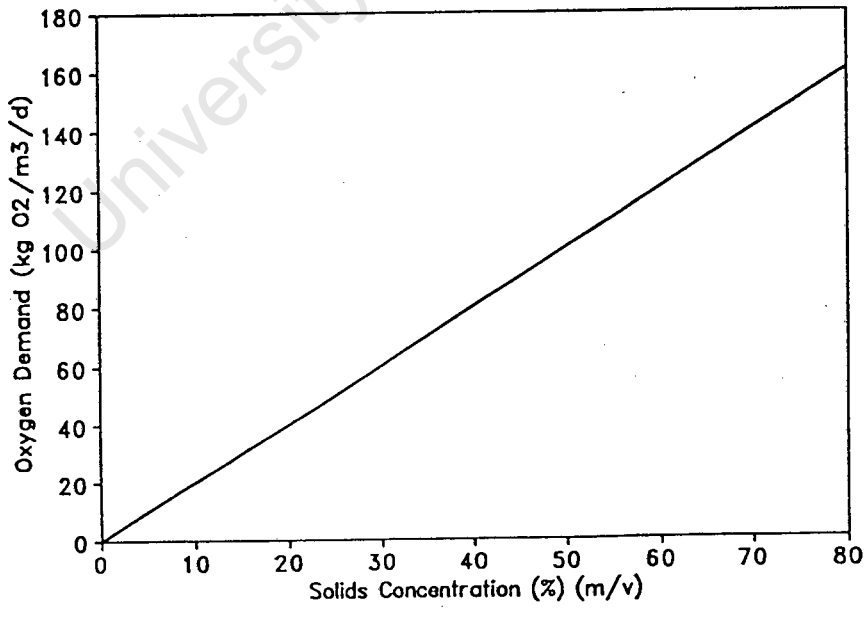


Figure 2.1 : Predicted Oxygen Demand for a Pyrite Flotation Concentrate Containing 65% Pyrite

2.2 OXYGEN TRANSFER POTENTIAL

The oxygen transfer rate (OTR) is given by the product of the mass transfer coefficient, $k_L a$ and the concentration driving force (Bailey and Ollis, 1987):

$$OTR = k_L a (C^* - C) \quad [2.4]$$

Where C^* is the saturated dissolved oxygen concentration and C is the liquor dissolved oxygen concentration. C^* depends on the oxygen concentration in the gas that is being used for sparging (i.e enriched or normal air) as well as the operating temperature and pressure in the reactor.

2.2.1 Maximum Driving Force

In bio-oxidation, there is a lower limit on C, namely the critical dissolved oxygen concentration, C_{CRIT} where the growth and metabolism of the bacteria are affected by the low dissolved oxygen concentrations. Liu *et al.* (1988) found that oxygen limitation began at a dissolved oxygen concentration of approximately 0.7 ppm. Growth of their bacteria ceased altogether when the concentration dropped to 0.28 ppm. The maximum possible driving force in a particular system would then be the difference between C^* and C_{CRIT}. This allows the definition of an oxygen transfer potential (OTP) for a particular system:

$$OTP = k_L a (C^* - C_{CRIT}) \quad [2.5]$$

2.2.2 Oxygen Mass Transfer Coefficient, $k_L a$

The oxygen mass transfer coefficient, $k_L a$ is dependent on: the power input per unit volume; the gas sparge rate; the liquor viscosity; and the liquid-phase diffusivity of oxygen (Bailey and Ollis, 1987). The power input per unit volume is affected by: the vessel geometry; type of impeller; and baffling used as well as the rate of agitation and aeration.

University of Cape Town

2.2.2.1 Effect of Liquor Viscosity on k_La

Correlations have been developed by a number of different researchers for the oxygen k_La in air-sparged, agitated tanks containing slurries of different materials (Mills *et al.*, 1987; Oguz *et al.* (1987); and Schumpe *et al.* (1987)). Of particular note is the correlation developed by Oguz, Brehm and Deckwer (1987), which will be referred to as the OBD correlation. The significant feature of the correlation is the incorporation of a relative slurry viscosity term μ_{rel}, as shown below:

$$k_La = 6.6 \times 10^{-4} (\mu_{rel})^{-0.39} (Q)^{0.5} (P/V)^{0.75} \quad [2.6]$$

where Q is the gas sparge rate (ℓ.min $^{-1}$) and (P/V) is the power input per unit volume (kW.m $^{-3}$). Relative viscosity if synonymous with apparent viscosity. It is defined as the slurry viscosity relative to that of water under the same physical conditions.

As will be discussed in Chapter 3, apparent viscosity data at a range of solids concentrations have been determined for a wide variety of mineral slurries. Typical data sets for silica and pyrite slurries in water, are shown in Figure 2.2. Initially the relative slurry viscosity is hardly affected by increasing solids concentration, but at some transition point, however, the relative viscosity increases more markedly with solids concentration. In the context of the OBD correlation, this increase in apparent viscosity would correspond to a decrease in k_La and a lowering of oxygen mass transfer. The relative viscosity of a mineral slurry is dependent on the volume fraction of solids (Hansford *et al.*, 1976), so the transition point occurs at a lower pulp density for silica (relative density = 2.6) than pyrite (relative density 5.0). This has important implications for the processing of low grade material (i.e. primarily silica), as the sharp decrease in k_La would be encountered at a lower solids concentration than with a high grade material (i.e. essentially pure pyrite). This point is shown in the analysis of literature data for a low and high grade material presented in Section 2.4.

To investigate the effect that the solids concentration has on k_La, pyrite apparent viscosity data of Rao (1966) were substituted into the OBD correlation. Other parameters in the OBD correlation were determined from data of van Staden

University of Cape Town

(1991) and are quoted in Section 2.3. The relationship between k_La and the solids concentration of pyrite given by the correlation is shown in Figure 2.3.

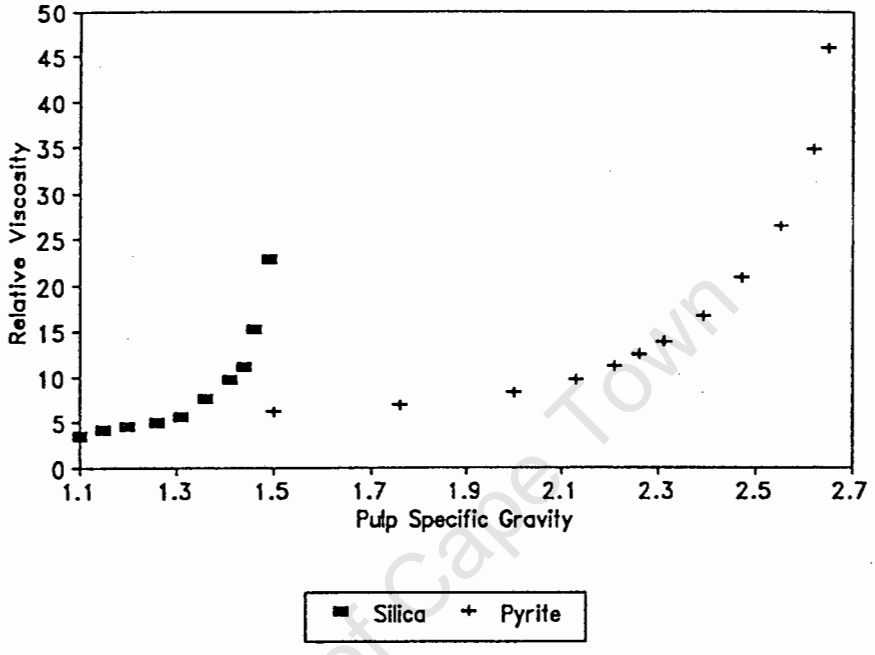


Figure 2.2: Apparent Slurry Viscosity versus Solids Concentration (Data of Rao, 1966)

2.2.2.2 Effect of Diffusivity on k_La

The diffusion coefficient will vary with ionic strength and with the concentration of solutes that are likely to change the liquid viscosity (Bailey and Ollis, 1987). The effect of sulphate ions on the diffusivity of ferric ions has been investigated by Madsen (1982). An empirical regression model, expressing the apparent ferric ion diffusion coefficient as a function of sulphate concentration, was developed from the experimental data gathered during tests in several different synthetic leach solutions. A plot of the model is shown in Figure 2.4. At a sulphate concentration 0.2 moles.l^{-1} there had been over a three-fold decrease in the diffusion coefficient from the pure-water case. At higher sulphate concentrations, however, the decrease in the diffusion coefficient with increasing sulphate concentration was not as marked.

University of Cape Town

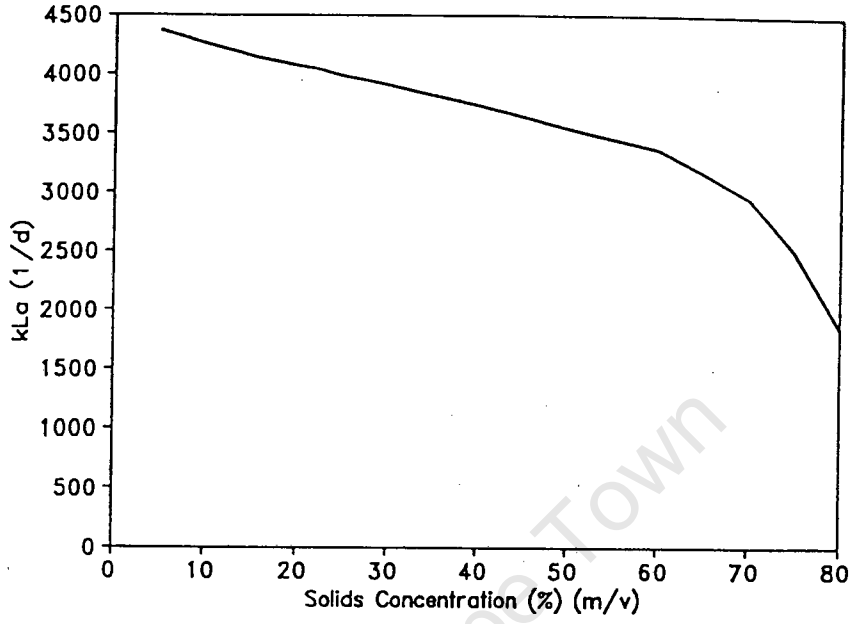


Figure 2.3: $k_L a$ versus Solids Concentration as Calculated from Oguz-Brehm-Deckwer Correlation, using the Rao (1966) Pyrite Apparent Viscosity Data and Experimental Parameters of van Staden (1991).

University of Cape Town

Sulphate is present in bio-oxidation at concentrations that are generally above 0.2 (mol. sulphate).l^{-1}. If the diffusivity of oxygen is affected in the same way as ferric ion diffusivity by the presence of sulphate ions, then the presence of ferrous or ferric sulphate in bio-oxidation systems is likely to affect oxygen transfer significantly.

In bio-oxidation systems operating effectively, essentially all of the iron present is in the ferric form. To assess the effect of ferric sulphate on oxygen mass transfer, the $k_L a$ for oxygen was determined experimentally in ferric sulphate solutions of different concentrations. The tests were performed in stirred tank reactors (Section 4.5.1) and the $k_L a$ was determined according to the method outlined in Appendix One. The pH was adjusted to pH 2 using sulphuric acid and the solution was maintained at 35°C. The air sparge rate was constant in all tests at 3 l.min^{-1} and the reactor working volume was 4 litres.

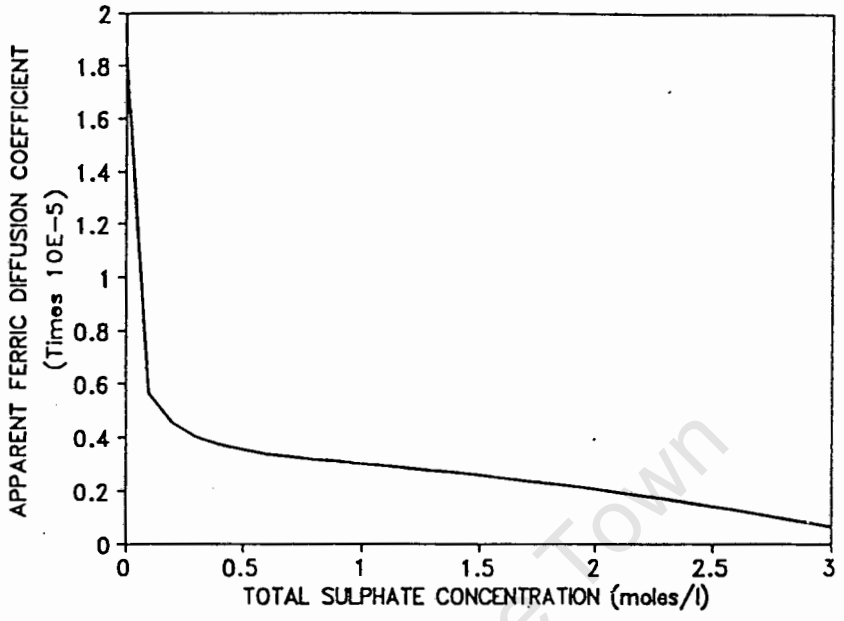


Figure 2.4: Relationship Between Apparent Ferric Diffusion Coefficient and the Total Sulphate Concentration From the Madsen (1982) Correlation.

University of Cape Town

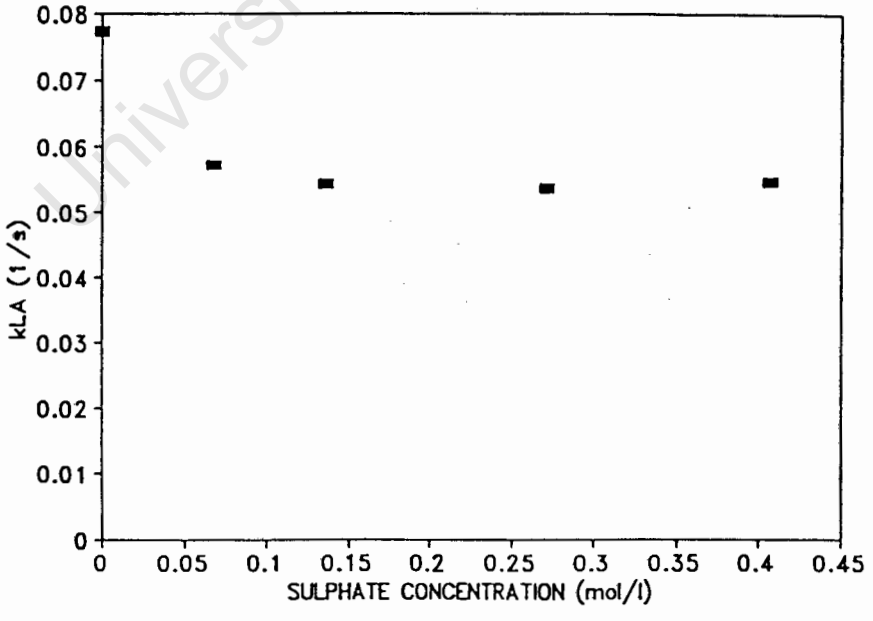


Figure 2.5 : $k_L a$ Measured at Different Ferric Sulphate Concentrations (pH = 2.0; Temperature = 35°C)

The results are presented in Figure 2.5 and show a similar trend to the diffusivity results of Madsen (1982) (Figure 2.4). Ferric sulphate at a concentration of 9.77 $g.l^{-1}$ (i.e. 3.8 g $Fe.l^{-1}$ and 0.10 (moles SO_4^{2-}).l^{-1}) effectively reduced the k_La, that had been measured in the distilled water slurry, by 26 per cent. At higher ferric sulphate concentrations there was little further reduction in the value of k_La.

2.3 OXYGEN TRANSFER POTENTIAL VERSUS DEMAND

The equations for the oxygen demand and oxygen transfer potential of a system developed in Sections 2.1 and 2.2 respectively, are shown schematically in Figure 2.6. As long as the oxygen demand is less than the oxygen transfer potential, the system will not be oxygen limited. From the point of intersection of the demand and transfer potential lines, and at higher solids concentrations (depicted by the shaded portion of the graph), the system will be oxygen limited. In this oxygen limited region the maximum oxidation rate is defined by the oxygen transfer potential.

University of Cape Town

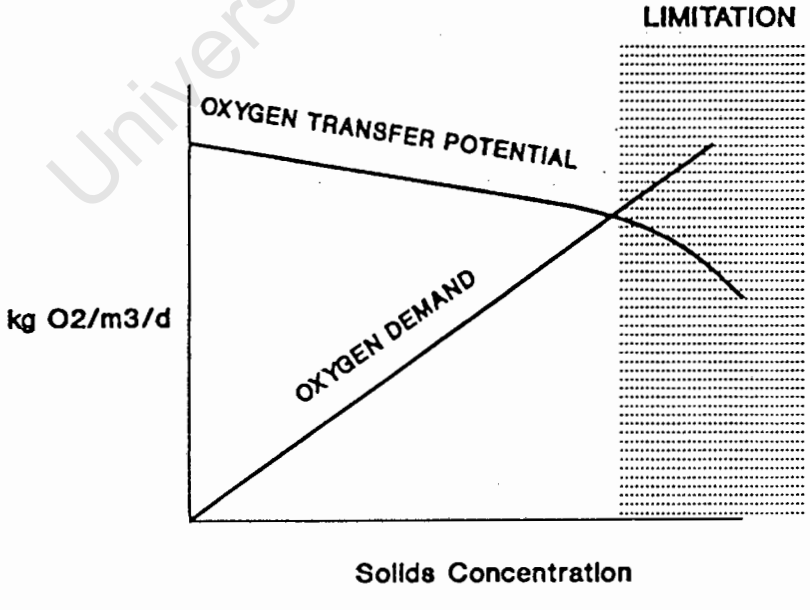


Figure 2.6: Schematic Diagram of Oxygen Transfer and Demand vs. Solids Concentration

2.4 ANALYSIS OF LITERATURE DATA

To compare the predicted oxygen transfer potential and oxygen demand with actual experimental data, use has been made of data from recent publications by Pinches *et al.* (1991) and van Staden (1991). It should be noted that both publications refer to the same experimental data that were generated by a research group lead by Dr. Pinches at Mintek (Randburg, South Africa). As the van Staden publication is a thesis it contains more detailed information than the paper. The paper was included so that the research group could be identified. The experimental data were obtained from continuous bio-oxidation tests in a 3-stage cascade system. For the purposes of this study only the first reactor is considered.

Bio-oxidation rate data for a low grade (1% S) run-of-mine ore and a pyrite concentrate (28% S) were available, as well as sufficient information to allow the OBD correlation (Section 2.2.2.1) to be used. Apparent viscosity data of Rao (1966) were used to estimate the apparent slurry viscosity for both sulphides at a range of solids concentrations. Detailed calculations are shown in Appendix 2. Unknown parameters in the OBD correlation were estimated using the measured k_La data reported by van Staden (1991). These parameters (volume of slurry, power input and gas flow rate) were held constant, resulting in an expression for k_La that depended solely on the relative slurry viscosity (which was a function of solids concentration). Typical values of these constants were: power input per unit volume = 0.89 $kW.m^{-3}$ and gas flowrate of 10.6 $\ell.min^{-1}$ (or 15.26 $m^3.d^{-1}$). The oxygen demand of 0.0049 (kg O_2)(m^2 pyrite)$^{-1}d^{-1}$ was calculated from the measured bio-oxidation rate of the pyrite concentrate (Appendix 2).

The oxygen transfer potential of the system, an estimated oxygen demand, as well as experimental bio-oxidation rate data are shown for both sulphide materials in Figures 2.8 and 2.9. The bio-oxidation rate data have been converted using reaction stoichiometry to allow them to be expressed in units of (kg O_2)$m^{-3}d^{-1}$, enabling direct comparison with the oxygen transfer potential and demand of the system.

University of Cape Town

For the high sulphide content pyrite concentrate, the oxygen demand at a solids concentration of 13.6 per cent (136 $kg.m^{-3}$) was equivalent to the oxygen transfer potential of the system. Experimental data of van Staden (1991) indicated that the dissolved oxygen concentration was approximately 0.8 ppm once steady-state conditions had been achieved. According to the findings of Liu *et al.* (1988), oxygen limited conditions commence below a solids concentration of 0.7 ppm, so conditions in the reactor were very close to being oxygen limited.

At the higher solids concentrations of 21.3 per cent (213 $kg.m^{-3}$), oxygen limited conditions would be expected to exist in the reactor. This prediction was in agreement with experimental observations (van Staden, 1991) as the bio-oxidation rate of 26.71 (kg O_2).m^{-3}.d^{-1}, measured at 21.3 per cent solids fell on the OTP line (as shown in Figure 2.7), indicating oxygen limitation. The actual calculated oxygen transfer potential at that solids concentration was 27.08 (kg O_2).d^{-1}.m^{-3}. The oxygen demand predicted for the system at 21.3 per cent solids was 44.05 (kg O_2).m^{-3}.d^{-1}. This was considerably higher than the oxygen transfer potential and characteristic of oxygen limited conditions.

Only one data set was available for the low sulphide content, run-of-mine ore. The bio-oxidation rate at 55 per cent (550 $kg.m^{-3}$) solids is shown in Figure 2.8. A predicted oxygen demand is also shown at a range of solids concentrations. The demand was based on the pyrite oxidation rate measured for the high sulphide content material (during non-oxygen limited conditions). Different inherent oxidation rates of the two materials may be the reason why the measured oxidation rate (8.28 (kg O_2).m^{-3}.d^{-1}) fell below the predicted value (9.26 (kg O_2).m^{-3}.d^{-1}). In the absence of rate data for the run-of-mine ore at other solids concentrations it cannot be established whether some other limiting factor had caused the experimental result to be lower than predicted.

University of Cape Town

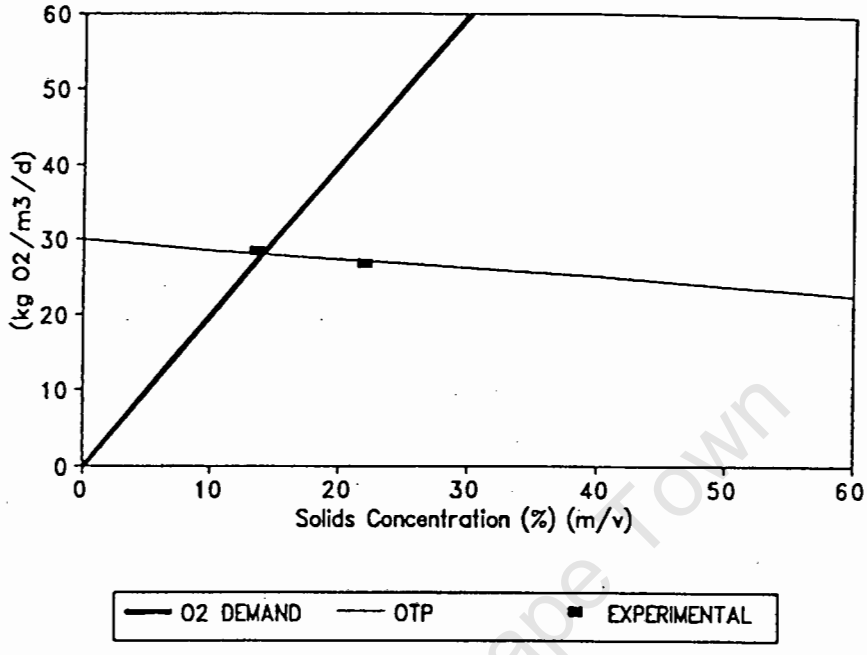


Figure 2.7: Oxygen Transfer Potential, Demand and Bio-oxidation Rate for High Sulphide Content Flotation Concentrate (28% Sulphur).

University of Cape Town

For the run-of-mine material, the decrease in the oxygen transfer potential of the system was far more marked at high solids concentrations than previously found with the sulphide concentrate. This was due to the lower specific gravity of the run-of-mine ore, which was essentially silica. The larger volume fraction of ore present at any particular solids concentration decreased the oxygen k_La more significantly (as discussed in Section 2.2.2.1). Both the measured and predicted oxygen demands fell well below the predicted oxygen transfer potential (17.63 (kg O_2).m^{-3}.d^{-1}.) of the system, as shown in Figure 2.8. Oxygen limited conditions would not be expected to exist. This was reflected in the experimental data as the dissolved oxygen concentration was approximately 3 ppm, well above the critical value.

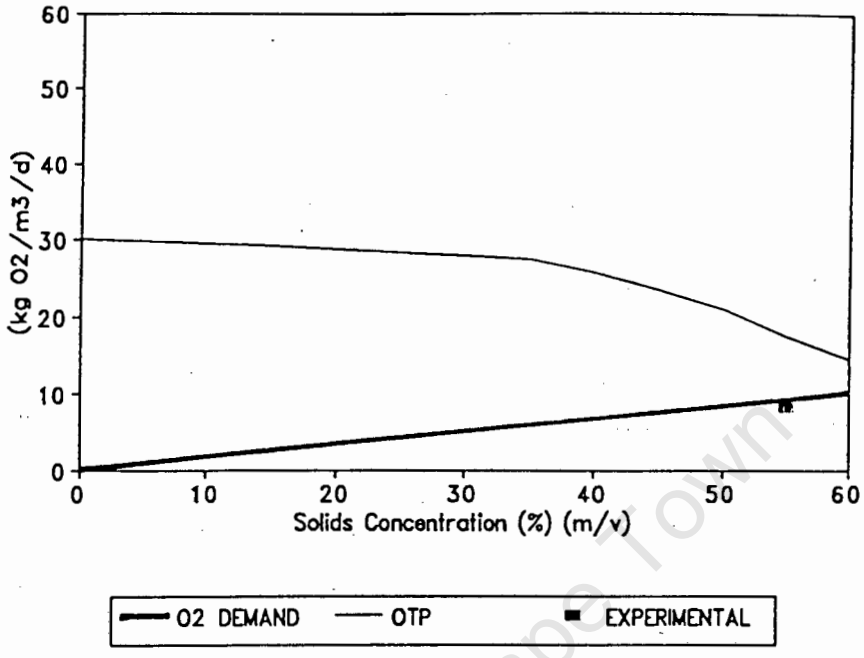


Figure 2.8: Oxygen Transfer Potential, Demand and Bio-oxidation Rate for Low Sulphide Content Run-of-Mine Ore (1% Sulphur).

University of Cape Town

2.5 CONCLUSIONS FROM THE OXYGEN TRANSFER AND DEMAND INVESTIGATION

In the context of the current maximum solids concentration of 20 per cent (200 $kg.m^{-3}$), which is commonly used for the bio-oxidation of high sulphide content materials, the presence of solid particles is likely to lower the oxygen transfer potential of a system by approximately 20 per cent, in comparison to a system operating without any solids.

It is possible to predict the oxygen demand of a system by expressing the bio-oxidation rate as a function of sulphide surface area and then using reaction stoichiometry to calculate a corresponding oxygen demand. The oxygen demand of the system is strongly dependent on the surface area and sulphide content of the ore. Correlations, such as the OBD correlation, for k_La can be used to estimate the oxygen transfer potential of a system. When the oxygen demand of

the system exceeds the oxygen transfer potential, oxygen limited conditions prevail, lowering the bio-oxidation rate. It has been shown that these predictions are in good agreement with experimental data, quoted in the literature, for both a low and high grade sulphide material at a range of solids concentrations.

The presence of sulphate ions in the oxidation medium (present primarily as ferric sulphate) have been found to lower k_La for oxygen. From the data of Madsen (1982) showing the effect that sulphate has on ferric ion diffusivity in a leach medium, it would appear that the sulphate ions present in the bio-oxidation medium have a similar effect on oxygen diffusivity, resulting in a lower k_La than determined in slurries made up in distilled water. (The presence of other ions in the bio-oxidation medium will also adversely affect the diffusivity of oxygen).

There is a need to perform batch reactor experiments to obtain additional bio-oxidation rate data at different solids concentrations and sulphide grades. This data will enable the relationship between the oxygen transfer potential and the bio-oxidation rate to be studied in more detail. Towards this end, several batch runs at different reactor sulphide concentrations have been conducted and are discussed in Chapter Five.

University of Cape Town

CHAPTER THREE

LITERATURE REVIEW

3.1 INTRODUCTION

It has been assumed that the reader of this literature review is familiar with the bacterial oxidation process. Bacterial oxidation has been reviewed in detail by Miller (1990), Drossou (1986), Lundgren and Malouf (1983), Brierley (1978), Karaivko *et al.* (1977) and Torma (1977). Features of the process of particular significance to this thesis are discussed briefly below.

The chemolithotrophic bacteria (eg. *Thiobacillus ferrooxidans, Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans)* involved in the bio-oxidation process are reliant on iron and (or) sulphur as their energy source (Schlegel, 1988). The mixed population of bacteria oxidise the sulphide ore matrix, breaking it down and releasing the entrapped gold. The greater proportion of the bacteria attach directly to the mineral surface where they perform "direct" oxidation of the sulphide. The remaining bacteria stay in the solution and oxidise ferrous iron (generated during the oxidation of the sulphide mineral) into the ferric form. The ferric iron generated is a strong oxidising agent and it further attacks and oxidises the ore. In this way, the free bacteria participate in "indirect" oxidation (Brierley, 1978).

The bacterial oxidation of pyrite occurs according to the following reaction:

$$4\ FeS_2 + 15\ O_2 + 2\ H_2O \ \text{----}> \ 2\ Fe_2(SO_4)_3 + 2\ H_2SO_4 \qquad [3.1]$$

The oxidation process requires oxygen and the bacteria rely on carbon dioxide as their carbon source (Schlegel, 1988). Other nutrients such as nitrogen, phosphate and potassium, can be supplemented, but are often available in

University of Cape Town

sufficient quantities as trace deposits in the ore. The *Thiobacillus*-type bacteria most commonly used in large-scale operations, are mesophiles and oxidation is optimal in the region of 35°C. The bacteria are acidophilic, existing in acidic conditions of around pH 2 (Torma, 1977).

The first part of this review examines research findings presented in the literature on the effect that solids concentration has on bio-oxidation and the reasons given for these effects. The various factors proposed as potential causes of decreased oxidation rates at high solids concentrations are discussed in more detail in the following sections. Finally, conclusions are drawn from the literature survey and the applicability of a fluidised bed reactor for the study of the effect of solids concentration on bio-oxidation is discussed.

3.2 EFFECT OF SOLIDS CONCENTRATION ON BIO-OXIDATION

A number of researchers have investigated the effect of increasing solids concentration on the bio-oxidation rate. One of the earliest studies was performed by Torma *et al.* (1970) who investigated the leaching of zinc from a zinc sulphide concentrate (33.23% sulphur) by *Thiobacillus ferrooxidans*. The oxidation rate as a function of solids concentration is plotted in Figure 2.1, showing the decrease in the oxidation rate at high solids concentrations.

It was found that at low solids concentrations (0 to *ca.* 14%) the zinc extraction rate was directly proportional to the solids concentration. Between 14 and 20 per cent (140 and 200 $kg.m^{-3}$) solids, the extraction rate appeared to be independent of the solids concentration. From 20 per cent up to the maximum experimental solids concentration of 26.6 per cent (266 $kg.m^{-3}$), there was a decrease in the rate of extraction. It was shown that neither phosphorus nor nitrogen was rate-limiting. Although an increase in the shaker speed did not alter the results significantly, it was postulated by the authors that the decrease in oxidation rate arose from solids interference with the mass transfer of oxygen or carbon dioxide to micro-organisms.

University of Cape Town

During the leaching of copper from a chalcopyrite concentrate (29.0% S) in 250 ml Erlenmeyer flasks, Sakaguchi *et al.* (1976) made similar observations. The air used for aeration was enriched with carbon dioxide to 0.2 per cent.

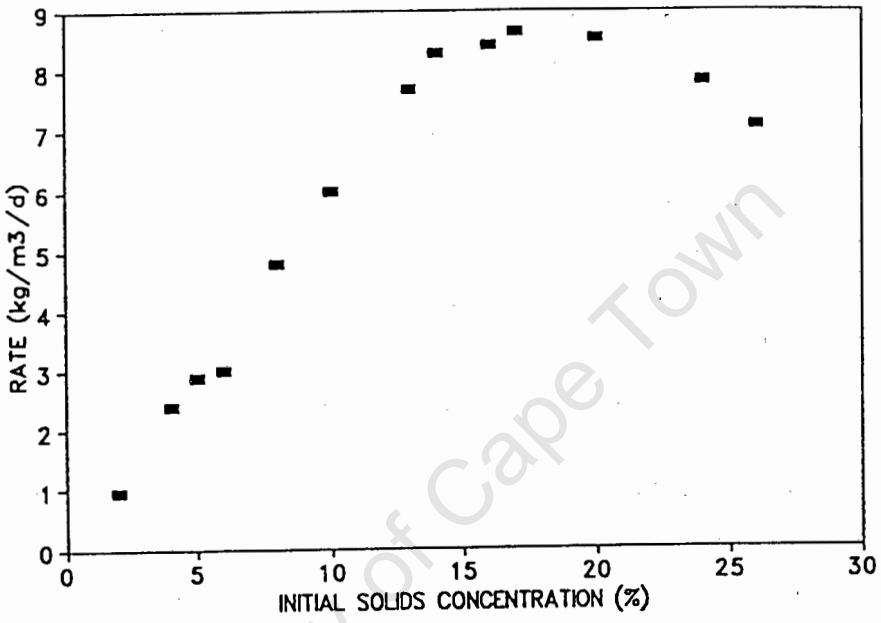


Figure 3.1: Bio-oxidation Rate vs Solids Concentration Data (Torma, 1970).

University of Cape Town

The effect of different particulate materials on the growth of *Thiobacillus ferrooxidans* on ferrous sulphate medium in shake flasks, was investigated by Dispirito *et al.* (1981). Pyrite, glass beads, sulphur and fluorapatite of similar size fractions were studied and it was found that depending on the concentration and material used, inhibitory effects ranged from extended lag times to decreased ferrous oxidation rates. When glass bead concentrations were increased above 4 per cent, no growth was detected. Below 4 per cent, the rate decreased linearly with increasing solids concentration, indicating mechanical damage to the bacteria. The pyrite sample was found to contain a soluble chemical that inhibited bacterial growth for up to five weeks even with a concentration of solids that was as low as 1 per cent. The presence of some residual flotation reagents and reagents used for uranium extraction, on solid materials has been observed to cause bacterial inhibition (Hackl *et al.*, 1989). Although the details of the

upstream processing of the pyrite are not given by Dispirito *et al.* (1981), it is possible that the "soluble toxin" was such an inhibitory reagent. Inhibition encountered with elemental sulphur under agitated conditions was significantly reduced in stationary flasks. Bacterial attachment is likely to have been enhanced under the more quiescent conditions. Increasing the pH was found to decrease the amount of inhibition. It was postulated that electrostatic interactions, related to the hydrogen ion concentration, could have affected bacterial attachment.

In shake flask tests performed by Roy and Mishra (1981), increasing solids concentration was found to lengthen the lag time as well as decrease the pyrite oxidation rate. The lengthened lag time was thought to have been caused by an inhibition of cell attachment, because addition of the surfactant, Tween-80, shortened the lag time.

Studies of the influence of solids concentration and bioreactor design on microbial coal desulphurisation were conducted by Beyer *et al.* (1986). Airlift reactors, a modified version of the airlift reactor and stirred tank reactors were used for the investigation. Batch oxidation rates in the airlift reactors were determined at concentrations of 2, 10 and 20 per cent (20, 100 and 200 $kg.m^{-3}$) solids. The highest oxidation rate was obtained with 10 per cent solids. Substrate limitation at 2 per cent caused the lower oxidation rate whilst at 20 per cent, it was proposed that the bacteria-to-solid ratio was rate limiting. By altering the airlift reactor's rounded bottom to a more conical shape, the growth and oxidation ability of the micro-organisms was found to be enhanced at 20 per cent solids. Oxidation was possible even at 30 per cent solids after the modification was made. The shape of the bottom of solid-suspended bubble columns was studied by Koide *et al.* (1983). It was found that the critical gas velocity required to fully suspend the solid particles decreased when a conical-bottomed reactor was used instead of a flat-bottomed one. These results imply that more energy is required for solids suspension in a rounded-bottomed (or flat-bottomed) reactor, increasing the amount of shear to which at least a portion of the particles was exposed. Better mixing in the conical-bottomed reactor, which would prevent oxygen limited regions (especially if the solids were not fully suspended in the rounded-bottomed reactor) may also have contributed to the improved micro-organism growth and bio-oxidation rate that Beyer *et al.* (1986) observed.

University of Cape Town

Further work by Beyer *et al.* (1986) was conducted at 20 per cent solids in a stirred tank reactor. The cell concentration was found to decrease rapidly with time. Strong agitation conditions in both the airlift and stirred tank reactors resulted in decreased micro-organism viability. The results point towards high shear levels (dependent on reactor geometry, agitation conditions and solids concentration) as an important cause of bacterial trauma resulting in decreased oxidation rates and growth rates. As the solids concentration increases, the shear effects are likely to become more predominant. Further complications arise because high shear conditions are desirable for good oxygen or carbon dioxide mass transfer, during operation at high solids concentrations.

During an investigation of the bio-oxidation of a refractory gold-bearing pyrite concentrate (85% pyrite), Hoffman *et al.* (1991) noted that the lag time increased with increasing concentration of solids in the reactor. Typically, the lag time increased from 12 days at 10 per cent solids to 42 days at 25 per cent solids. The volumetric batch pyrite oxidation rate passed through an optimum of 4.7 (kg pyrite)$m^{-3}d^{-1}$ at 20 per cent solids, although the rates at the other test concentrations were fairly close (3.7 (kg pyrite)$m^{-3}d^{-1}$). The *specific* pyrite oxidation rate, however, decreased with increasing solids concentration over the range tested. In continuous reactor experiments at solids concentrations between 7.5 and 20 per cent, the oxidation rates were three times higher than those in the batch mode. Although the volumetric oxidation rate rose, analysis of the data revealed that the increased rates were not proportional to the increments in solids concentration. The researchers ensured that nutrients were not limiting the process by enriching the sparge gas with carbon dioxide and maintaining a dissolved oxygen concentration in excess of 1 mg.l^{-1} oxygen and carbon dioxide requirements are discussed in more detail in Sections 3.3 and 3.4). This is reflected in the continuous data as the volumetric oxidation rate did increase with increasing solids concentration. The decrease observed in the specific oxidation rate was possibly the result of cell limitation as a constant inoculum of 10 per cent (v/v) of a mixed culture of pyrite-adapted organisms was used throughout the study. At high solids concentrations it is possible that the bacteria-to-solids concentration was low.

University of Cape Town

particular, arsenopyrite is more active than pyrite, so oxidation of arsenopyrite commences at a lower ORP than the more noble pyrite (Komnitsas and Pooley, 1991). Furthermore, where these two minerals are in direct contact, passivation of the pyrite will occur resulting in the preferential oxidation of arsenopyrite.

The study of arsenopyrite-pyrite bio-oxidation by Komnitsas and Pooley (1991) has shed considerable light on the effect of solids concentration on the relative bio-oxidation of the two mineral constituents. To examine their data more closely, Hansford and Bailey (1992) modelled the data using a logistic equation. Both the pyrite and the arsenopyrite bio-oxidation rate constants in the logistic equation were found to decrease with increasing solids concentration. The analysis also revealed that the time before significant oxidation of the pyrite phase occurred, increased with increasing solids concentration. The decrease in the ORP that had been observed with increasing solids concentration, was the likely cause of this effect, as a lower ORP would increase the preference for arsenopyrite oxidation.

In summary, high solids concentrations have been found to influence the lag time, bio-oxidation rate and the ultimate extent of oxidation. The factors proposed as potential causes of these phenomena include: oxygen and carbon dioxide availability and mass transfer; low bacteria-solids ratio; mechanical damage or inhibition of the bacteria; inhibition of bacterial attachment; and the build-up of toxic leach products, metabolites or the presence of other detrimental substances such as residual flotation reagents. These factors are summarised in Table 2.1.

The remainder of this chapter discusses the various factors in more detail.

University of Cape Town

Table 3.1: Summary of Factors Affecting Bio-oxidation at High Solids Concentrations.

FACTOR	LAG TIME	RATE	EXTENT
Inhibitory substances (Initial)	X	X	X
Inhibitory substances (Build-up)		X	X
Oxygen mass transfer/availability		X	X
Carbon dioxide mass transfer/ availability		X	X
Cell concentration	X	X	
Mechanical damage of cells	X	X	
Attachment	X		
Precipitation (Jarosite)			X

University of Cape Town

3.3 AVAILABILITY OF OXYGEN

The bacteria used in bio-oxidation require oxygen for the oxidation process (Brierley, 1978). For growth of *Thiobacillus ferrooxidans* on medium containing 9 $g.l^{-1}$ ferrous iron (Silverman and Lundgren, 1959) the critical dissolved oxygen concentration below which inhibition of the bacteria is observed has been established as 0.7 $mg.l^{-1}$ by Liu *et al.* (1988). Below 0.2 $mg.l^{-1}$ oxygen, oxidation was found to cease altogether. Oxygen enrichment of the process air has been successfully used to increase the rate of oxygen transfer to the reactor (Corrans, 1974).

Several researchers have cited the adverse effect of increasing solids concentration on oxygen mass transfer as the cause of low bio-oxidation rates at high solids concentrations (Marchant, 1986; Sakaguchi *et al.*, 1976; Torma *et al.*,

1972). Solids influence bacterial oxidation in two ways. Firstly the sulphide content of the particles determines the oxygen demand, so as the solids concentration increases, the oxygen demand increases. Solids also affect oxygen mass transfer by modifying the interfacial turbulence at low solids concentrations. At higher solids concentrations, the interfacial area is affected by an increase in the apparent viscosity and by altered bubble coalescence rates. Depending on the size of the particles, diffusion-blocking of oxygen transfer may also occur (Lee *et al.*, 1982). A decrease in gas hold-up at high solids concentrations was observed by Mills *et al.* (1987), which would also have contributed to a decrease in the oxygen transfer area.

The effect of solids concentration on the oxygen mass transfer coefficient, k_La has been investigated by a number of researchers (Oguz *et al.*, 1987; Mills *et al.*, 1987; Joosten *et al.*, 1977). Although correlations have been developed for k_La, there has, however, been little investigation that has taken variations in particle shapes, size distributions and densities into account. The solids concentration at which there is a more marked decrease in the k_La has been found to be dependent on the type of solid material (Mills *et al.*, 1987). Joosten *et al.* (1977) observed that the difference in density between the solid and liquid components of a slurry was an important parameter affecting k_La. Low density particles were found to cause the most marked decrease in the k_La at high solids concentrations. This is due to the correspondingly high volume fraction of low density solid material and the fact that the relative viscosity is dependent on the solids volume fraction (Hansford *et al.*, 1976).

A particularly useful correlation for k_La was developed by Oguz, Brehm and Deckwer (1987) using data collected from a range of mineral slurries in water. The important feature of the correlation was that it related k_La to the relative viscosity of the slurry. The relationship between the solids concentration and the relative viscosity of a range of mineral slurries has been studied by a number of workers (Neill, 1988; Hansford *et al.*, 1976; Rao, 1966; Marsden, 1962). This means that it is possible to relate k_La to the solids concentration via the apparent slurry viscosity.

Oxygen mass transfer also depends on the gas sparge rate and the power input per unit volume from agitation (Oguz *et al.*, 1987). The maximum gas sparge

University of Cape Town

rate and the extent of oxygen enrichment are largely determined by cost factors. The power input per unit volume is limited by the fact that high shear conditions are detrimental to the bacteria.

Only limited work has been reported in the literature of attempts that have been made to assess the effect of solids concentration on oxygen mass transfer in bacterial oxidation. Gormely (1990) studied k_La prediction for bio-oxidation reactors as an integral part of reactor design and scale-up. The effect of solids concentration on oxygen mass transfer was not, however, taken into account. The influence of the sulphide grade of the material on the oxygen demand and oxygen transfer requirements were also not discussed. In a subsequent paper (Gormely, 1992) the Mills *et al.* (1987) correlation, which relates the oxygen mass transfer coefficient to the solids concentration via the solids volume fraction, was cited, but not incorporated in the design procedure.

The oxygen transfer requirements for the growth of *Thiobacillus ferrooxidans* on pyrite were assessed by Myerson (1981). The tests were, however, only conducted at one particular solids concentration and were primarily aimed at determining critical oxygen concentrations. Oxygen transfer measurements in bacterial oxidation reactors were also made by Nagpal *et al.*, (1993). Data were collected from the continuous reactor system at solids concentrations of 6, 11 and 16 wt per cent. The k_La values were determined from gas-phase mass balances. The measurements were made to determine whether or not operation was in the mass-transfer limited regime. It was, however, ensured that oxygen was in excess throughout the testwork, so the rate was chemical reaction rate limited.

Several researchers have identified a link between the sulphide grade of the material and the solids concentration at which bacterial oxidation is maximal (Pinches *et al.*, 1991; Hackl, 1989; Lawrence, 1988). Bioleaching was found by Hackl (1989) to be sensitive to the pulp density as well as the slurry sulphide concentration. Although it was stated that high sulphide content concentrates were generally leached at lower solids concentrations than low sulphide content ores, no explanation was given for this operating rationale. Similar observations were made by Lawrence (1988) who indicated that 30 per cent solids was practical for ores, but 20 to 25 per cent was usually used for concentrates. The

University of Cape Town

reasons given for the difference in operating conditions were the build-up of metal ions and acid in the leachate and also to reduce the heat of oxidation. No other factors limiting the solids concentration were discussed. Pinches *et al.* (1991) also attributed the fact that processing of high sulphide content materials was limited to low solids concentrations to excessive acid build-up.

There is a need for further investigation of the outcome of the analysis of literature data that was discussed in Chapters One and Two, i.e. that oxygen transfer is a key factor in determining the solids concentration at which bio-oxidation is maximal. The application of correlations to better understand the effect of solids on oxygen mass transfer in bacterial oxidation systems is discussed in more detail in Chapter Two.

University of Cape Town

3.4 AVAILABILITY OF CARBON DIOXIDE

The micro-organisms commonly used for pyritic sulphur degradation, are autotrophs, using carbon dioxide as their carbon source. This requirement makes the adequate supply of carbon dioxide to the micro-organisms essential for cell growth (Schlegel, 1988).

Carbon dioxide enrichment of the process air has proved to be beneficial for increasing the oxidation rate at high solids concentration in a number of different cases ranging from nickel and zinc leaching to coal desulphurisation (Kargi, 1982; Corrans, 1974; Torma *et al.*, 1972). Generally an optimum carbon dioxide enrichment (*ca.* 1%) has been found, above which there is little further increase in the oxidation rate.

The relative rates of mass transfer of oxygen and carbon dioxide were related by Liu *et al.* (1988). In their study it was estimated that unless the process air was enriched with carbon dioxide, then carbon dioxide limitation would be encountered before oxygen limitation. The experimental findings of Mandl (1984) supported their argument for normal air sparging. In an investigation of the relative mass transfer rates of both oxygen and carbon dioxide Boon *et al.* (1992) found that carbon dioxide limitation occurred at a far lower solids concentration in

a pachuca tank than in a stirred tank reactor (i.e. at a solids volume fraction of 0.03 as opposed to 0.26). They concluded that both shake flasks and pachuca tanks were unsuitable for kinetic studies at high solids concentrations, the mass transfer of both carbon dioxide and oxygen being far superior in stirred tank reactors.

The effect of the carbon dioxide concentration in the liquor on the bio-oxidation of a pyrite-arsenopyrite concentrate has been studied by Nagpal *et al.* (1993). During tests conducted at 16 per cent solids, carbon dioxide concentrations in the liquor that were in excess of 10 mg.l^{-1} were found to be inhibitory to bacterial growth. The optimal aqueous-phase concentration was found to be approximately 5 mg.l^{-1}. Carbon dioxide concentrations below this level sharply reduced the bacterial growth rate. The researchers also observed that the mineral oxidation rates were not directly linked to bacterial growth. This was in agreement with findings of Mandl (1984), who found that the non-growing bacteria (i.e. cultured in the absence of carbon dioxide) were still capable of performing oxidation. As the cells were not growing, oxidation rates could not, however, be maintained for prolonged periods. Kelly and Jones (1978) reported that the ferrous oxidation rate could be maintained for up to 140 hours in the absence of carbon dioxide.

Research to date has shown that carbon dioxide enrichment of the process air is beneficial up to a certain point. The economic implications of carbon dioxide enrichment, however, need to be assessed as the cost of enrichment may not be a viable option. Similar research to that required on oxygen availability, is necessary to determine the effect that the nature and concentration of solids have on carbon dioxide availability in bio-oxidation.

University of Cape Town

3.5 THE ROLE THAT BACTERIA PLAY IN BIO-OXIDATION AT HIGH SOLIDS CONCENTRATIONS

There are basically four bacterial factors that are thought to cause lower oxidation rates at high solids concentrations. Firstly, the cell concentration on inoculation may be too low with respect to the amount of ore present.

Alternatively, although there may be sufficient bacteria on inoculation, trauma caused by turbulence may inhibit their oxidation ability and growth. If the shear conditions are severe, mechanical destruction of the organisms may occur. Finally, the build-up of inhibitory oxidation products, or the introduction of large amounts of inhibitory reagents, residual on the solids due to upstream processes, may lower the oxidation ability of the bacteria. These aspects are discussed in more detail in the following sections.

3.5.1 Cell-to-Solid Ratio

A low cell-to-solid ratio on inoculation has been found to substantially increase the lag time during batch pyrite oxidation (Roy and Mishra, 1981; Atkins, 1978) as well as in coal desulphurisation studies (Detz and Barvinchak, 1979). Variation in the initial cell concentration between 1.5 x 10^6 and 2.7 x 10^7 (cells)(cm^2 of oxidisable surface)$^{-1}$(ml)$^{-1}$ was found by Pinches (1972) to have little effect on bacterial growth rates and the oxidation rate of the arsenopyrite-pyrite concentrate used. Varying the initial cell concentration over a wider range, however, (6 x 10^5 to 6 x 10^9 cells.ml^{-1}), Atkins (1978) found that the lag time was affected during pyrite oxidation tests. Whilst desulphurising coal at slurry concentration of 6 per cent, Detz and Barvinchak (1979) noticed that cell concentrations below 10^8 cells.ml^{-1} caused undesirably slow desulphurisation. A rapid and significant, 5-fold change in rate occurred when the initial cell concentration was increased from 10^7 to 10^9 cells.ml^{-1}. Beyond 10^9 cells.ml^{-1} little further benefit was derived. In conventional leaching, to ensure that the lag time is minimised, Yunker and Radovich (1985) commented that an initial bacterial concentration of between 10^8 and 10^9 cells.ml^{-1} should be used for inoculation. Periodic re-inoculation of the batch reactors was necessary when Detz and Barvinchak (1979) attempted to maintain cell concentrations of 10^9 cells.ml^{-1} whilst operating at high solids concentrations. This probably arose from a combination of a high oxidisable surface area in the reactor and high shear conditions adversely affecting bacterial growth.

The rate of ferrous iron production will be dependent on the redox potential (Natarajan, 1988) as well as the sulphide surface area concentration in the reactor. Long lag times are likely to result when there are insufficient bacteria to

University of Cape Town

oxidise ferrous ions at the rate at which they are being generated. This leads to an accumulation of ferrous ions in solution and a low ORP. The ORP will only begin to rise as the bacterial population increases in size as time progresses.

Small bacterial populations have been cited as the cause of low oxidation rates by a number of researchers (Komnitsas and Pooley, 1991; Sakaguchi *et al.*, 1976). In their continuous oxidation system, Chang and Myerson (1982) found that the ORP dropped as the pyrite surface area was increased (i.e. a low cell-to-solid ratio was created) and this was most marked at high dilution rates. The ORP drop would be most marked at high dilution rates because the cell concentration decreases at high dilution rates, the extreme case being when the dilution rate exceeds the maximum growth rate and total cell washout occurs.

3.5.2 Cell Trauma

Initially as agitation rates are increased, the rate of bio-oxidation has been found to be enhanced due to an improvement in the mass transfer conditions. However, when the intensity of agitation was increased beyond a certain point, Corrans (1974) found that bacterial oxidation was severely inhibited, most likely due to bacterial trauma.

The effect of shear on the growth of a variety of micro-organisms, including bacteria, has been studied by Toma *et al.* (1991). Observations made during the course of their investigations are useful as a basis for predicting the possible effect that shear could have on the bacteria used in bio-oxidation. Excessive turbulence inhibited microbial growth and metabolism in each of the micro-organisms studied, even at shear levels that were too low to cause actual destruction of the bacteria. The researchers introduced the term *turbohypobiosis* to describe this inhibition. They also defined a stress factor that was dependent on the energy input and distribution in the reactor.

In bio-oxidation, Pinches *et al.* (1991) observed a reduction in bacterial growth rates as the solids concentration was increased during both batch and continuous studies with several different sulphide materials. In a typical batch test, when the pyrite-arsenopyrite solids concentration was increased from 15 to

University of Cape Town

30 per cent, the bacterial doubling time increased from 15.1 to 21.3 hours. The bacterial doubling time was decreased by a small, but significant amount (1.5 hours), when the fraction of particles below 38 μm was increased from 40 to 80 per cent. This could have been due to a reduction in the amount of stress to which the bacteria were subjected.

During the bio-oxidation of high sulphide content material at high solids concentration, the oxygen demand is high, necessitating the use of high agitation rates to improve mass transfer. As the solids concentration increases, the shear to which the bacteria are subjected also increases. Although there is some evidence that excessive shear adversely affects the bacteria, no rigorous, detailed study has been performed on the effect that shear has on the bacteria used in bio-oxidation.

University of Cape Town

3.5.3 Mechanical Damage of the Bacteria

Evidence of mechanical destruction of the bacteria has been noticed by several researchers, using a range of different equipment. Reactor design for minimum shear was beneficial to leach rates in the coal desulphurisation studies of Beyer *et al.* (1986), discussed earlier. During the pilot plant testwork conducted by Hackl *et al.* (1989) it was postulated that low leach rates were caused by excessive shear stress. Impeller tip speeds of 5.3 $m.s^{-1}$ were found to be detrimental and leaching was improved when the speed was reduced to 3.3 $m.s^{-1}$. A change from Rushton turbines to axial flow impellers improved the leach rates substantially. The power input per unit volume to achieve the same degree of mixing and mass transfer is lower with axial flow impellers than with Rushton turbines

High temperature bio-oxidation processes are of current interest due to potential improvements in reaction rates (Brierley, 1978). The effect of shear in this process is of importance due to the fact that thermophilic bacteria such as *Sulfolobus* do not have as rigid cell walls as *Thiobacillus*, increasing their susceptibility to shear. In a study of the growth of *Sulfolobus* by Pinches *et al.* (1991) oxidation was limited to below 15 per cent (150 $kg.m^{-3}$) solids.

Pertinent work is currently in progress on the culture of a range of differnt micro-organisms in the presence of solids, especially in animal cell culture (Papoutsakis, 1991; Croughan *et al.*, 1988). Although anchorage dependent animal cells are more sensitive to shear than the bacteria that are used in bio-oxidation, due to their more fragile cell membranes, many of the questions being dealt with are relevant to bio-oxidation. High microcarrier concentrations have been shown to be detrimental to cell growth. The cells are affected by both mechanical (such as bead-bead interactions) and hydrodynamic forces (Papoutsakis, 1991). The animal cells have been found to be damaged by high relative fluid velocities when microcarriers are not entrained by the liquid flow. These forces are far lower when the microcarriers are entrained by the eddies. These observation indicate that relative size of flow eddies and particles is an important parameter.

Although mechanical destruction of various types of bacteria used for bio-oxidation has been noticed under various operating conditions, the amount of shear at the onset of cell damage has not been quantified at this stage. The effect of both mechanical and hydrodynamic forces on free and attached bacteria in bio-oxidation requires investigation.

University of Cape Town

3.5.4 Bacterial Attachment

During bio-oxidation, in excess of 90 per cent of the bacteria attach directly to the mineral surface (Roy and Mishra, 1981; McGoran *et al.*, 1969). If iron is not initially present in solution, Pogliani *et al.* (1990) showed that intimate contact between the bacteria and ore was essential for bio-oxidation to commence. Furthermore, if the bacteria are unable to make direct contact with the mineral surface, a sulphur-rich layer builds up as oxidation proceeds, limiting further oxidation (le Roux *et al.*, 1978).

It was postulated by Sanmugasunderam (1981) that bacterial attachment in an agitated slurry was likely to be more difficult for the bacteria to accomplish, especially if the micro-organisms orientate themselves and attach to specific sites. Studies of the attachment of *Thiobacillus ferrooxidans* in stationary and shaken flasks, performed by Cook (1964) appear to support this argument.

Inhibition was only observed in shaken cultures. If the flasks were left stationary for three days prior to shaking, however, the inhibition was overcome. The addition of surfactants to aid bacterial attachment also overcame the adverse effects of shaking.

3.5.5 The Effect of the Build-up of Substances that are Inhibitory to the Bacteria

Substances that are inhibitory to the bacteria could arise from essentially three sources. Firstly, residual reagents used during the upstream processing of the ore (eg. flotation reagents and certain cyanide compounds) may be introduced into the reactor along with the solids charge. It is possible that certain metabolites produced by the bacteria may also become inhibitory once they reach certain levels. Other inhibitors may be produced as a result of the build-up of oxidation products, such as solubilised metals.

Many flotation reagents are similar in chemical nature to detergents. Detergents have been found to solubilise bacterial cell envelope constituents, destroying the cell integrity (Harrison, 1991). It is possible that the inhibition of bacterial growth that has been observed in the presence of certain flotation reagents (Hackl *et al.*, 1989) was caused in this manner.

A build-up of toxic oxidation products that progressively inhibit the bacteria would explain an observed decrease in the extent of oxidation, or extraction, with increasing solids concentration. The oxidation rate would initially be high, then decrease at a certain point once the inhibitory product had reached a certain level. In their shake-flask study Roy and Mishra (1981) found such a relationship. The bacterial activity was initially high, but at some point the bacterial activity began to decline and the ferrous iron concentration began to rise. The researchers attributed this to the inhibition of the bacteria by either increased acidity or toxicity of the metal ions.

In testwork by Tuovinen *et al.* (1971) on the tolerance of *Thiobacillus ferrooxidans* to some metals, it was found that the bacteria were capable of tolerating zinc, nickel, copper, cobalt, manganese and aluminium ion concentrations of 10 $g.l^{-1}$. The lag time was, however, found to increase in the presence of these ions. The researchers proposed that bacterial adaptation

University of Cape Town

occurred during this period as subsequent tests in which the adapted culture was used as the inoculum showed a reduction in lag time. Silver and anions of tellurium, arsenic and selenium were found to be inhibitory at concentrations between 0.05 and 0.10 g.l^{-1}, whilst molybdenum caused death at concentrations in excess of 0.005 g.l^{-1}. High ferric iron concentrations have been reported to inhibit the bacteria at concentrations ranging between 4.5 and 11 g.l^{-1}, depending on the tolerance of a particular strain (Brierley, 1978). Nikolov and Karamenev (1992), in a summary of their recent work, stated that they had found that ferric iron concentrations between 14 and 50 g.l^{-1} had no effect on the oxidation ability of *Thiobacillus ferrooxidans* when grown in a biofilm. The ferric iron tolerance was higher than that when the cells were freely suspended. The bacteria also appeared to be less sensitive to other environmental conditions such as temperature and pH when grown in biofilms.

Resuspension of sulphide material in fresh medium enabled Atkins (1978) to achieve very high extents of oxidation, that were otherwise unattainable. Rates were initially improved immediately after solution replacement. Recent work by Attia and Elzeky (1991) showed that by partial replacement of the leach liquor (25% v/v/d) an approximately ten-fold improvement in the bio-oxidation rate could be attained. At a solids concentration of 10 per cent, the leaching of sulphides was increased from 17 to 31.2 per cent. The researchers attributed this increase in bio-oxidation rate to the decreased concentrations of inhibitory metals and extracellular products.

Further research into the screening of flotation reagents is required, in order to develop alternative suites of reagents that are not inhibitory to the bacteria. Solution replacement techniques, as well as other methods of maintaining low concentrations of inhibitory oxidation products during the course of a run, need to be developed especially for operation at high solids concentrations where build-up will be most noticeable.

3.6 CONCLUSIONS

This literature review has shown that solids can affect bio-oxidation in essentially three ways: by lengthening the lag time; by affecting the bio-oxidation rate; and

University of Cape Town

by decreasing the ultimate extent of oxidation. The factors that have been observed to affect bio-oxidation include: oxygen and carbon dioxide availability; low bacteria-to-solids ratio; mechanical damage or inhibition of the bacteria; inhibition of bacteria attachment; and the build-up of inhibitory leach metabolites, or other detrimental substances (eg. certain flotation reagents) in the reactor.

Many of the proposed factors interact in bio-oxidation reactors, complicating the interpretation of results. Although there is evidence that the factors discussed in this review affect bio-oxidation, their relative significance is unknown. A study needs to be performed using a system that will enable each of the factors to be controlled and investigated independently.

Carbon dioxide and oxygen limitations have been fairly extensively investigated and enrichment of the process air has proved beneficial. There is still, however, a need for further study into the effect of solids concentration on mass transfer and the corresponding carbon dioxide utilisation rate and oxygen demand during the bio-oxidation of materials of different sulphide grades.

There is a dearth of information on the effect of hydrodynamic or mechanical stress on bacterial growth, oxidation ability and attachment. High mass transfer requirements, necessary for the provision of sufficient oxygen and carbon dioxide to a system, makes the use of high aeration and agitation rates desirable. Different impeller and reactor geometries or types may enable lower shear environments, whilst still achieving the necessary mass transfer rates.

The effect of toxic oxidation products needs to be assessed from a microbial point of view. The role of chemical solution equilibria and the precipitation of salts such as jarosite also needs to be addressed.

University of Cape Town

CHAPTER FOUR

MATERIALS AND METHODS

4.1 SULPHIDE MINERALS

Three different sulphide materials were used in this study; two flotation concentrates and a run-of-mine ore. Essentially all of the sulphide in the samples was present as pyrite (Personal communication, J.W. Neale, Mintek, Randburg, South Africa). The origins of the samples are described below, whilst the density, total iron and sulphur contents of the materials are tabulated in Table 4.1.

University of Cape Town

4.1.1 Low Sulphide Content, Vaal Reefs Run-of-Mine Ore

A low sulphide content run-of-mine ore (1.24% S) was obtained from Vaal Reefs Gold Mine (Anglo American Corporation, South Africa). The material had been mined, milled and crushed. A particle size analysis of the material is given in Appendix Three, Table A.3.

4.1.2 Vaal Reefs Pyrite Flotation Concentrate

A high-grade pyrite, flotation concentrate (30.5% S) was also obtained from Vaal Reefs Gold Mine (Anglo American Corporation, South Africa). On this mine, the ore is milled before passing through an acid (H_2SO_4) leach and solvent extraction process for the recovery of uranium. This process is followed by a cyanide leaching step for preliminary gold recovery. Flotation is used to recover the remaining gold-bearing pyrite from the material that is used as backfill. This refractory pyritic concentrate is oxidised in roasters prior to re-cyanidation for gold recovery (Dempsey *et al.* 1990). The flotation reagents used during the time that the concentrate used in this study was collected, included : Dowfroth 200; Aeropromotor 407; copper sulphate; Sanfroth 6010; and Cyanamid SA90. Size

analysis data are tabulated in Appendix 3, Table A1, and shown graphically in Figure 4.1. The preparation of a narrow size fraction of material from this bulk concentrate, for use in the fluidised bed reactor, is discussed later in this chapter.

4.1.3 High Sulphide Content, Prieska Pyrite Flotation Concentrate

The Prieska pyrite flotation concentrate had the highest sulphide content (47.8% S). The concentrate originated from the Prieska Copper Mine at Copperton in the North West of the Cape Province in South Africa and had been stockpiled at Haartebeesfontein Gold Mine (Anglo American Corporation, South Africa). This material had been mined, crushed and milled before being fed to the first of three flotation stages. Flotation was performed at a pH of 7.5 (no pyrite floats) in the presence of cyanide to recover copper-bearing ore. Copper sulphate was added to the tails from the first stage which were then processed in a second flotation step to recover zinc-bearing ore. Lime was added to the tails from this step prior to the final flotation stage which produced the pyrite concentrate that was used in this study. Size analysis data are presented in Appendix 3, Table A4.

University of Cape Town

4.1.4 Quartz

Quartz, with approximately the same size range as the Prieska concentrate, was obtained from Industrial Sands (Consol), South Africa. The silica acted as an inert material and could be mixed with different quantities of the Prieska pyrite concentrate, to approximate sulphide material of an intermediate grade. This enabled different total solids concentrations to be achieved in reactors, whilst the concentration of sulphide (i.e. amount of pyrite) could be maintained constant.

During initial fluidisation studies using the Vaal Reefs pyrite concentrate (Section 6.1), it was noticed that there was excessive elutriation of smaller particles from the fluidised bed at the fluidising velocities required to suspend the larger particles. To prepare material for use in the fluidised bed work, bulk concentrate was fluidised in a 94mm diameter Perspex column using water. The superficial water velocity in the column produced a bed of solids that had a concentration of 20 per cent (200 $kg.m^{-3}$). The top of the column was open, allowing the water

and entrained fines to run to waste. After the formation of a distinct, well-defined bed of solids, the particles were removed from the vessel. The sample was then sieved through a 100 mesh screen to remove any excessively large particles before use in the fluidised bed reactor testwork.

Size analyses have been performed on all of the sulphides, using a Malvern Particle Size Analyser (Malvern Instruments, Malvern, England). Detailed results are given in Appendix 3. An analysis of one of the specially prepared fluidised bed reactor fractions is also given. The size analyses of the bulk and prepared size fraction of Vaal Reefs pyrite concentrate are shown in Figures 4.1 and 4.2 respectively. The analysis of the prepared size fraction shows how the fine material, present in the bulk sample, has been removed.

The density of the materials was determined using a pycnometer (Accupyc 1330, Micromeritics Instrument Corporation, USA). The pycnometer used helium to determine the volume of a known mass of sample. The average results of three readings are tabulated in Table 4.1. The sulphur and iron contents of the materials were determined using the techniques outlined in Section 4.4.2 and are also presented in Table 4.1.

University of Cape Town

Mineral	Density ($kg.m^{-3}$)	Iron (% Fe)	Sulphur (% S)
Vaal Reefs Run-of Mine	2801	1.99	1.24
Vaal Reefs Concentrate	4592	25.44	30.5
Prieska Pyrite Concentrate	4386	38.97	47.8

Table 4.1: Density, Total Iron and Sulphur Content of As-Received Materials

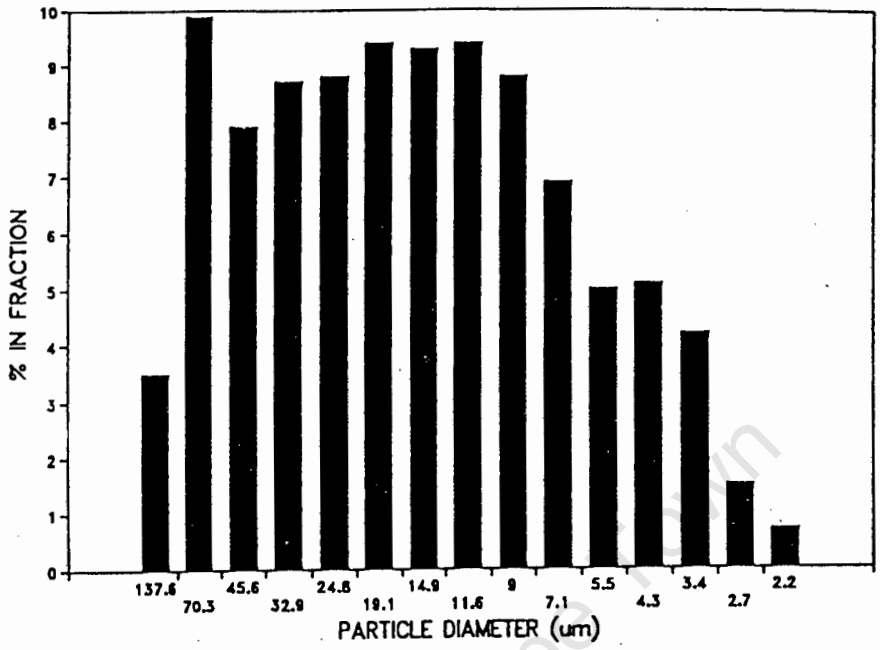


Figure 4.1 : Size Analysis of Bulk Vaal Reefs Pyrite Concentrate

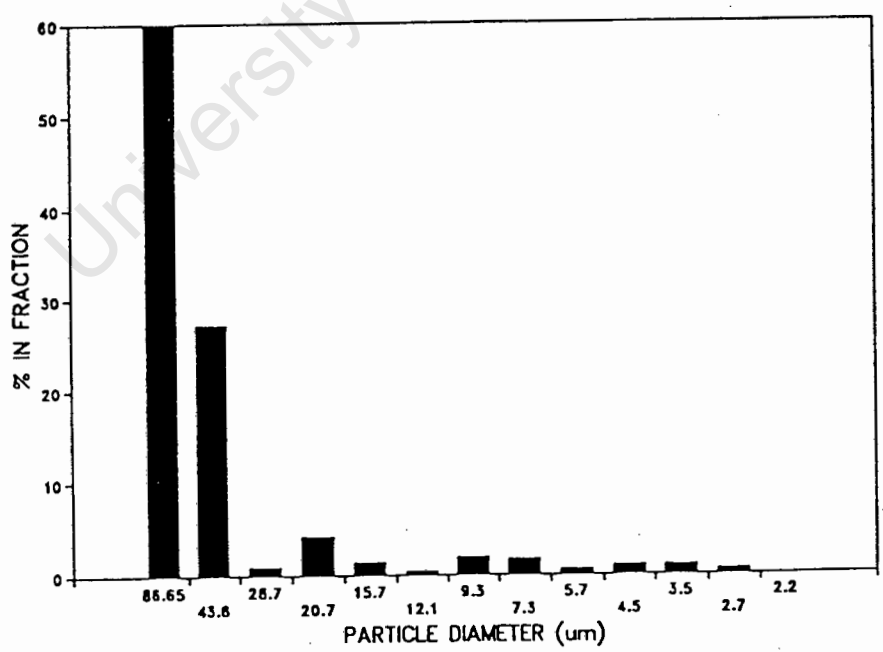


Figure 4.2 : Size Analysis of Prepared Fraction of Vaal Reefs pyrite for use in Fluidised Bed Reactor

University of Cape Town

4.2 CULTURE

The mixed culture of bacteria used in this experimental work was originally obtained from the Council for Mineral Technology, Mintek (Randburg, South Africa). The culture contained three main types of bacteria (Personal communication, R.M. Muhlbauer, Mintek, Randburg, South Africa), namely: *Thiobacillus ferrooxidans; Thiobacillus thiooxidans; and Leptospirillum ferrooxidans.* The culture obtained had been adapted to Vaal Reefs pyrite concentrate by successive subculturing. The bacteria were maintained in stirred tank reactors containing 10 per cent (100 $kg.m^{-3}$) solids and the iron-free medium of Silverman and Lundgren (1959). The bacteria, where possible, were adapted to the particular sulphide on which bio-oxidation tests were to be performed by successive subculturing (Torma, 1977).

Sufficient supernatant containing active bacteria was used to give an initial reactor concentration of 1 x 10^8 bacterial cells.ml^{-1} after inoculation. Typically the amount of inoculum used was approximately one third of the reactor working volume.

4.3 GROWTH MEDIUM

A Silverman and Lundgren (1959) nutrient medium, containing 4 g.l^{-1} ferrous iron was added to the ore and inoculum at the start of a fluidised bed reactor run. The composition of the medium is given in Table 4.2. For the batch reactor runs, nutrient salts were added directly to the solid material and inoculum in the reactor before the remaining volume was made up with a ferrous sulphate solution containing 4 g.l^{-1} ferrous iron. This ensured that there was a sufficiently high concentration of nutrients in the reactor.

The effect of the initial ferrous iron concentration has been investigated by Ehrlich (1986). During the leaching of silver from a mixed sulphide ore, 9.0, 0.9 and 0.0 g $Fe^{2+}.l^{-1}$ were added to the growth medium. It was found that 9 g.l^{-1} of ferrous iron enhanced the leach rate the greatest. During the oxidation of a molybdenite-pyrite ore, Bryner and Anderson (1957) also varied the initial ferrous

University of Cape Town

The samples removed from the batch stirred reactors were first centrifuged (Beckman TJ-6 Centrifuge) for 5 minutes at 4000 rpm (Relative Centrifugal Field = 2204^), to remove the suspended solids before analysis of the liquid sample.

4.4.1.2 Ferrous Iron

The ferrous iron concentration in the liquor was determined by titration with potassium dichromate, using sodium diphenylamine sulphonate as an indicator (Vogel, 1962). Solids present in the liquor samples taken from the batch reactors were once again removed by centrifugation prior to analysis.

4.4.1.3 Ferric Iron

The ferric iron concentration was calculated by subtracting the ferrous iron concentration from the total soluble iron concentration.

4.4.1.4 Total Iron Oxidised

Depending on the total dissolved iron concentration, solution redox potential (ORP), pH and the temperature, iron is precipitated to differing extents as jarosite and other basic sulphates. If arsenic is present in the mineral, other compounds such as ferric arsenate may also precipitate. The amount of iron precipitated as jarosite must be taken into account to determine the total amount of iron in the solid material that has been oxidised.

To redissolve the iron precipitates, sufficient hydrochloric acid is added to a known volume of pulp (i.e. liquor and suspended solids) to give a final HCl concentration of approximately 2.5 M. This procedure is given in detail in Appendix 1.

4.4.2 Solids Analysis

4.4.2.1 Iron

An acid digest was used to dissolve a pre-weighed solids sample. The method is given in Appendix 1. The resulting solution was appropriately diluted with distilled water and analysed for iron using atomic adsorption spectrophotometery.

---

^ Relative Centrifugal Field is the ratio of the centrifugal acceleration at a specified radius and speed, to the standard acceleration of gravity.

University of Cape Town

concentration between 0 and 6 g.l^{-1}. Their results indicated that there was an optimum iron concentration at 4 g.l^{-1}. A medium containing 4 g.l^{-1} was selected for use in this study to ensure that the initial iron concentration did not limit the oxidation rate. The iron concentration was also low enough to prevent inhibition of the bacteria (Brierley, 1978). Over 99 per cent of the iron in the inoculum was in the ferric form, so when the inoculum and the fresh medium were mixed, the resulting solution had a ferrous iron concentration that was below 4 g.l^{-1}. The total iron concentration was, however, approximately 4 g.l^{-1}.

CONSTITUENT	MASS (g)
$(NH_4)_2SO_4$	3.00
KCl	0.10
$MgSO_4.7H_2O$	0.50
K_2HPO_4	0.50
$Ca(NO_3)_2$	0.01
$FeSO_4.7H_2O$	19.91
Distilled Water*	up to 1l
H_2SO_4	to pH 1.8

* The distilled water should be acidified to approximately pH 1.8 prior to the addition of the salts.

University of Cape Town

Table 4.2: Constituents for Silverman and Lundgren (1959) 4K, (i.e. 4 g $Fe^{2+}.l^{-1}$) Medium

4.4 ANALYTICAL TECHNIQUES

4.4.1 Liquid Analysis

4.4.1.1 Total Soluble Iron

The total iron concentration in the liquor was determined by atomic adsorption spectrophotometery (Varian Spectra AA30 Spectrophotometer).

4.4.2.2 Sulphur

The sulphur content of the sulphide materials used in this research was determined using a Leco SC32 sulphur analyser. The furnace temperature was 1350°C. Three standards were used for calibration *viz.* 0.54% S, 1.14% S and 32.0% S.

4.4.3 Solution oxidation potential, ORP

The solution oxidation potential, ORP was measured using a platinum electrode (Radiometer, Denmark) and a standard silver/silver chloride reference electrode (Radiometer, Denmark). A Radiometer Copenhagen Model PHM82 meter was used.

4.4.4 pH

A Radiometer Copenhagen Model PHM82 pH meter (Radiometer A/S/ Copenhagen, Denmark) and an Ingold (Ingold Messtechnik, Germany) combined pH electrode were used to determine the pH. A Corning (United Kingdom) 250 meter and probe was also used for pH measurements. The meters were calibrated using buffers of pH 7 and pH 4. The calibration was checked against a buffer of pH 1.68, which was in the region of the operating pH.

University of Cape Town

4.4.5 Dissolved Oxygen Concentration

Dissolved oxygen concentration measurements were made using a YSI (Yellow Springs Instruments, United States of America), model 54A Oxygen meter and probe.

4.4.6 Bacterial Cell Concentration

An improved Neubauer counting chamber (Hawksley, England) was used to determine the bacterial concentration in solution. Magnification of 1000 times and oil immersion were used. The bacteria that were attached to the solid material were not enumerated.

4.5 REACTORS

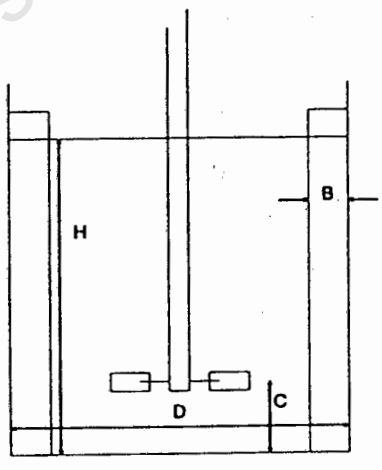
4.5.1 Batch Stirred Tanks

The batch stirred tank reactors used in this study were manufactured from PVC, with a height of 230mm and diameter of 190mm, giving a volume of 5 litres. The working volume was 3 litres. A schematic diagram of the reactors is shown in Figure 4.4.

4.5.1.1 Agitation

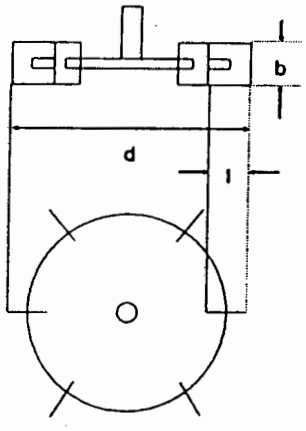
Four stainless steel baffles, 20mm wide and 210mm high, were put into the reactor to promote mixing. A six-bladed Rushton Turbine impeller was used and its dimensions are shown in Figure 4.4. The ratio of the tank to impeller diameter was 0.43 which was in the range quoted by Nagata (1975) as optimal for the suspension of solid particles in a flat-bottomed reactor. The reactor baffling and impeller were designed to conform to the specifications of a standard Rushton system (Nagata, 1975)

University of Cape Town



DIMENSIONS : B = 20 mm; C = 30 to 60 mm; D = 185 mm; H = 185 mm.

Figure 4.3: Schematic Diagram of Batch Reactor



DIMENSIONS : d = 80 mm; l = 20 mm; b = 16 mm

Figure 4.4: Rushton Turbine Impeller

Variable speed Heidolph RZR1 (Heidolph, Germany) stirrers were used in the batch reactors. A maximum rotation speed of 495 rpm was selected as this corresponded to a tip speed of 1.97 $m.s^{-1}$, which was well below 5.3 $m.s^{-1}$, which had been found by Hackl *et al.* (1989) to inhibit bacterial growth.

4.5.1.2 Aeration

Air was sparged into the reactor at 3 $l.min^{-1}$ which corresponded to 1 (litre air)(litre reactor)$^{-1}$(min)$^{-1}$, i.e. 1 VVM. During the oxidation of the Prieska ore, the flowrate was decreased to 1.5 $l.min^{-1}$, to enable the results to be compared to the work of van Staden (1991). The end of the 8 mm (internal diameter) stainless steel sparger was narrowed to a thin slit to aid air distribution. The outlet was positioned just below the centre of the impeller, to ensure that the bubbles leaving the sparger were broken up by the motion of the impeller.

4.5.1.3 Temperature Control

The batch stirred tank reactors were operated in a waterbath that was maintained at 35°C by a Labotec (South Africa) heater stirrer.

University of Cape Town

4.5.2 Fluidised Bed Reactor (FBR) Test Rig

A schematic diagram of the fluidised bed reactor (FBR) rig is shown in Figure 4.5. Two separate test rigs were built having total system working volumes of 4.47 and 4.15 litres respectively.

4.5.2.1 Fluidised Bed Reactor (FBR)

The fluidised bed reactor (FBR) was manufactured from clear Perspex, allowing the bed height to be observed during the course of a run. The straight section of the reactor had an internal diameter of 45mm and a length of 900mm. A conical section at the bottom of the reactor expanded gradually from the 8mm inlet nozzle to 45 mm, over a distance of 55 mm. This facilitated good liquid distribution in the reactor.

At the top of the reactor there was a conical disengaging zone to retain solid particles in the FBR. The internal diameter was increased from 45mm to 100mm over a length of 200mm. A 150mm straight section was added onto the top of the conical section and the outlet nozzle was situated 20mm above the start of this straight section. A Perspex lid could be fitted onto the top of the FBR to prevent evaporation.

4.5.2.2 Surge Tank, Aeration and Temperature Control

The surge tank was manufactured from Perspex, and enabled aeration, pH and temperature control to be performed outside the FBR. The liquor leaving the surge tank, through a nozzle at the bottom of the container, was saturated with oxygen and carbon dioxide and at the operating temperature of 35°C.

A flange on the top of the surge tank allowed a Gallenkamp Modular Fermenter (Gallenkamp, England) vessel lid to be clamped on. Various Gallenkamp controller probes (eg. temperature and pH) could be inserted through the ports in the lid. One of the ports was enlarged to allow for the insertion of the dissolved oxygen probe, liquor sample removal and the addition of make-up water.

Air was fed at 5 $l.min^{-1}$ through the hollow impeller shaft to an outlet just below the impeller. The impeller was magnetically driven by a Gallenkamp magnetic

University of Cape Town

stirrer unit. The rotation of the impeller reduced the size of the air bubbles and ensured that they were well distributed in the surge tank.

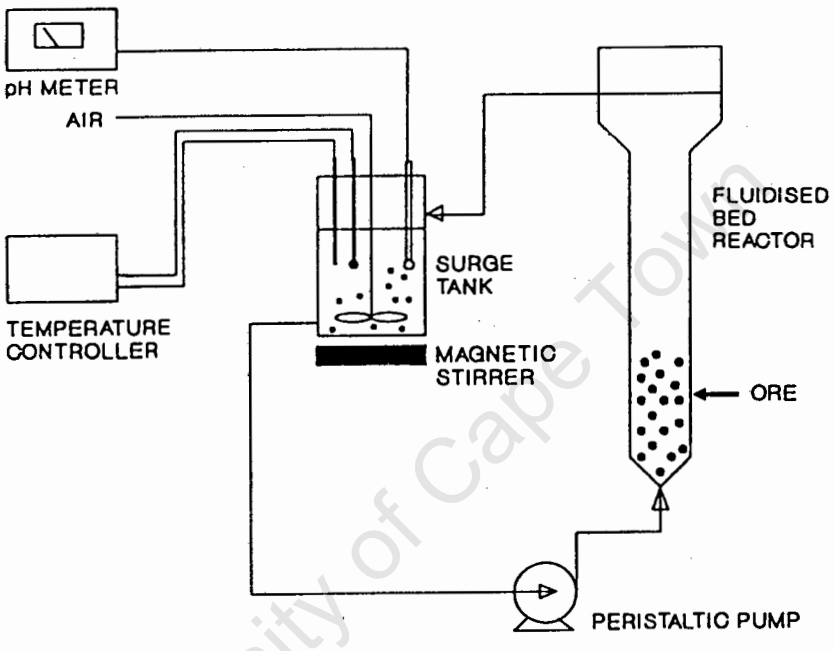


Figure 4.5: Schematic Diagram of Fluidised Bed Rig

University of Cape Town

4.5.2.3 Liquor Recirculation

A Watson Marlow (Watson Marlow, Cornwall, England) 503S peristaltic pump was used to pump liquor out of the surge tank into the bottom of the FBR. The liquor returning from the FBR flowed under gravity to the surge tank. The rotation of the peristaltic pump rollers was high enough to provide a reasonably smooth flow of liquid. Marprene tubing (8mm internal diameter, 1.5 mm wall thickness) was used in the peristaltic pump as it was found to be sufficiently durable to last the length of a run, without rupturing.

4.5.2.4 Liquid Flowrate

A valve on the liquor return line running between the FBR and the surge tank could be opened to divert the flow of liquid into a measuring cylinder. The time taken to collect a certain measured volume of liquid was noted, allowing the flowrate of liquid to be determined.

University of Cape Town

CHAPTER FIVE

BATCH STIRRED TANK REACTOR BIO-OXIDATION RATE DATA AT VARIOUS SOLIDS CONCENTRATIONS AND SULPHUR GRADES

University of Cape Town

The results of several batch stirred tank reactor (STR) studies that were performed at different solids concentrations as well as sulphide concentrations are reported in this chapter. Tests were conducted to further investigate the apparent relationship between the sulphide content of the mineral and the solids concentration at which bio-oxidation was maximal. Evidence of a possible link between the sulphide grade and the maximum solids concentration was found during the analysis of literature data, discussed in Chapters One and Two. The other objective of the work was to investigate the effect of solids on the bacterial oxidation rate of a low-grade material by generating a set of rate data, at solids concentrations both in, as well as above, the common operating range (*ca.* 20 to 30 per cent solids, i.e. 200 to 300 $kg.m^{-3}$). The motivation for this work is discussed in more detail in Section 5.1.

Two sulphide materials were used for the STR batch testwork, *viz.* Prieska pyrite concentrate with a high sulphide content (47.8% S) and Vaal Reefs run-of-mine pyrite ore, with a low sulphur content (1.24% S). Both of these sulphides have been described in detail in Chapter Four. Quartz was also used in some tests as an inert medium that could be mixed with the pyrite concentrate to decouple the total solids and sulphide concentrations in a reactor. This enabled intermediate sulphide concentrations in the reactor to be achieved.

5.1 BATCH BIO-OXIDATION OF LOW SULPHIDE CONTENT MATERIAL: VAAL REEFS RUN-OF-MINE ORE

In the data sets published by Pinches *et al.* (1991) and van Staden (1991), analysed in Chapter Two, the bio-oxidation rate of the low sulphur content, run-of-mine material was only determined at a solids concentration of 55 per cent (550 $kg.m^{-3}$). The fact that bio-oxidation could be performed successfully at the high solids concentration was, however, significant. The operating solids concentration was substantially higher than the concentrations at which plants have been commonly operated (Chapter One). In Chapter Two it was shown that the experimentally measured bio-oxidation rate was lower than the rate predicted using the specific pyrite bio-oxidation rate of the high sulphide content pyrite concentrate. As only the data point at 55 per cent solids was available no conclusion could be reached as to the cause of this discrepancy. The difference could have resulted from either: different intrinsic specific oxidation rates of the two pyritic materials; or, it could have been due to the fact that bacterial oxidation may have been limited in some way when operating at the high solids concentration. To reach a conclusion about the bio-oxidation of low sulphide content material at high concentrations of solids, rate data extending from the normal plant operating range (20 to 30 per cent solids) up to far higher solids concentrations need to be collected.

To investigate the effect of solids concentration on the bio-oxidation rate when processing low grade material, tests were performed using Vaal Reefs run-of-mine ore (1.24% S) at solids concentrations of 200, 400 and 600 $kg.m^{-3}$ (20, 40 and 60 per cent). Nutrient salts (Silverman and Lundgren, 1959) were added directly to the reactor, along with the ore and sufficient inoculum to give an initial reactor concentration of 10^8 cells.ml^{-1}. The additional volume was made up to the 3-litre working volume with an acidified 4 $g.l^{-1}$ ferrous iron solution. The reactors were maintained at a pH of 1.8.

University of Cape Town

5.1.1 Results from the Run-of-Mine Batch Tests

It was found, after initial pH adjustment using H_2SO_4, that the pH remained essentially unchanged throughout the runs. This was due to the small amount of pyritic material present in the reactors.

The change in the sulphur concentration of the solids was found to be the most accurate measure of the bio-oxidation rate. Solids removed from the reactor were washed with HCl (as discussed in Chapter Four) to remove precipitated jarosite prior to Leco sulphur analysis. The bio-oxidation rate based on the rate of appearance of iron in the solution was unreliable due to the small change in the iron concentration (*ca.* 1 $g.l^{-1}$) over 10 days. The analytical techniques (atomic absorption spectrophotometry involving dilution of the sample) used to determine the iron concentration solution could not discern the small daily increments with sufficient accuracy.

Two runs were performed at 200 $kg.m^{-3}$ (20 per cent solids). The experimental data are presented in Appendix 3, Tables B1 and B2. Results from the second run at 20 per cent solids showing the removal of sulphur from the solid material are plotted in Figure 5.1. The time-course redox potentials data are shown in Figure 5.2.

University of Cape Town

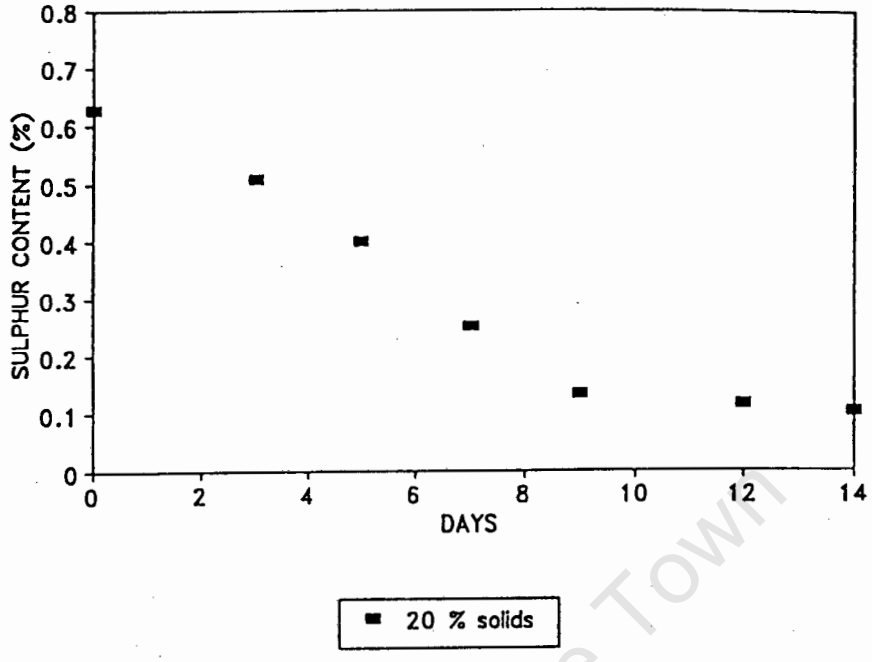


Figure 5.1 : Residual Sulphur Concentration (in solids) During a Run at 20 per cent (200 kg.m^{-3}) Solids Using Run-of-Mine Material (1.24% S)

University of Cape Town

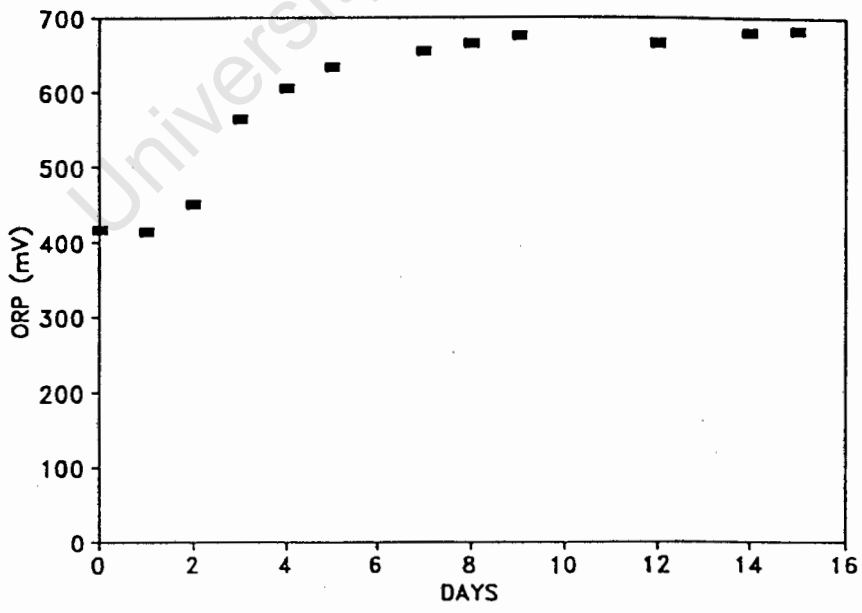


Figure 5.2 : Redox Potential Measurements During a Run at 20 per cent (200 kg.m^{-3}) Solids Using Run-of-Mine Material (1.24% S)

Within an hour of contact with the acidic growth medium approximately one third of the sulphur present in the feed material (i.e. the non-pyritic sulphur) was removed. A maximum sulphur removal rate was calculated for each test from regression of the data collected during the course of a run. Data collected during the initial lag period and measured after oxidation had begun to slow once essentially all of the sulphur had been removed from the ore were omitted from the calculation. The sulphur removal rate was converted into an equivalent pyrite oxidation rate using reaction stoichiometry. The rate data determined from the different tests are shown in Figure 5.3, along with a predicted bio-oxidation rate (Experimental data collected at 40 and 60 per cent solids are tabulated in Appendix 3, Tables B3 and B4). The prediction was based on the experimentally determined bio-oxidation rate at 200 kg.m^{-3} (20 per cent solids) and it was assumed that the rate was proportional to the increase in solids concentration.

University of Cape Town

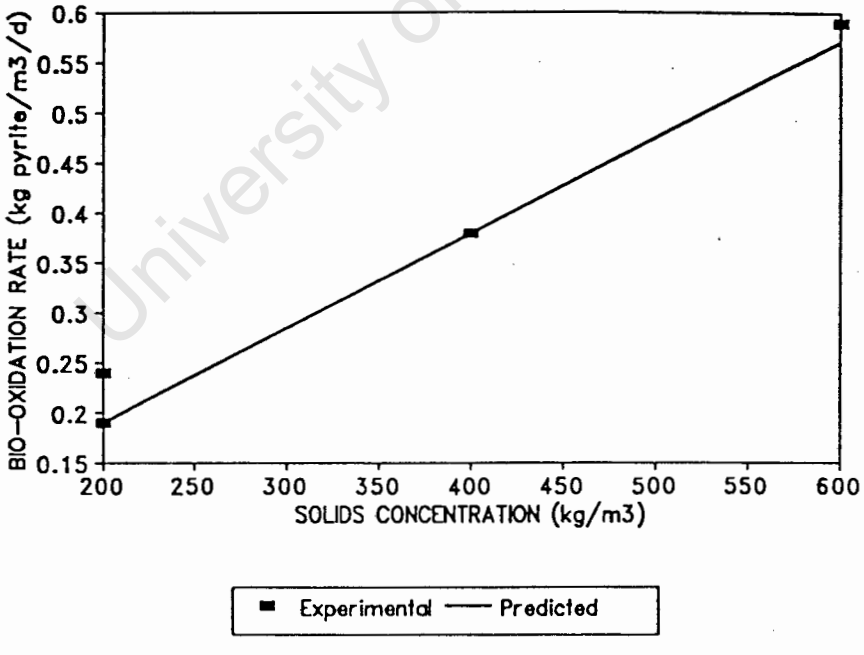


Figure 5.3 : Bio-oxidation Rate vs. Solids Concentration for Vaal Reefs Run-of-Mine Ore (1.24% S)

In Figure 5.3 it can be seen that the bio-oxidation rates measured were in good agreement with the predicted rates, i.e. the bio-oxidation rate was proportional to the solids concentration. Notably the proportionality still held at the highest solids concentration tested, i.e. 600 $kg.m^{-3}$. Two runs were performed at 20 per cent solids, bacteria generated during the first test being used to inoculate the repeat test. The pyrite bio-oxidation rate measured in the second test was higher than in the first test. Due to the small amount of material available for the testwork no pre-adaptation of the bacteria had been performed prior to the first run and it is possible that the higher rate in the second test was caused by a degree of bacterial adaptation. It is also possible that the culture used for inoculation was slightly more active, as the lag time in the first test was approximately six days, whilst the lag time in the second test was only two days. The rates observed at 40 and 60 per cent solids were compared with the first test at 20 per cent as these runs were performed simultaneously, and inoculated with bacteria from the same stock culture.

A specific bio-oxidation rate was determined by expressing the pyrite oxidation rate as the amount of pyrite oxidised per unit mass of pyrite, per day (i.e. (kg pyrite)(kg pyrite)$^{-1}d^{-1}$). The specific oxidation rates from the first test at 20 per cent and the tests at 40 and 60 per cent solids, were similar. The specific rate obtained from the second test at 20 per cent solids was higher than the other data due to the reasons that are discussed above. The specific rate data are shown in Figure 5.4.

During the testwork, the oxygen mass transfer coefficient was measured at each solids concentration, using the technique outlined in Appendix 1. The oxygen transfer potential (OTP) was calculated for each reactor by multiplying k_La by the concentration driving force ($C^* - C$) and fixing the value of C at 0.7 $mg.l^{-1}$, the lowest dissolved oxygen concentration permissible to ensure that sufficient oxygen was available in the reactor. For pyrite oxidation, stoichiometry indicates that for 1 kg of pyrite oxidised, 1 kg of oxygen is consumed. This allows the pyrite bio-oxidation rate ((kg pyrite)$m^{-3}d^{-1}$) to be compared directly with the OTP ((kg O_2)$m^{-3}d^{-1}$). The OTP values determined during the testwork are shown in Figure 5.5 along with the measured bio-oxidation rates, at the different concentrations of solids. It can be seen that the bacterial oxidation rate was substantially below the OTP indicating that a more than adequate supply of

University of Cape Town

oxygen should have been available under all of the operating conditions. This was borne out by the fact that the average dissolved oxygen measurement in the reactor at 600 kg.m^{-3} solids (i.e. the reactor in which the oxygen demand was the highest) was 7.4 mg.l^{-1}. This was little different from the C* of 7.6 mg.l^{-1} that was measured.

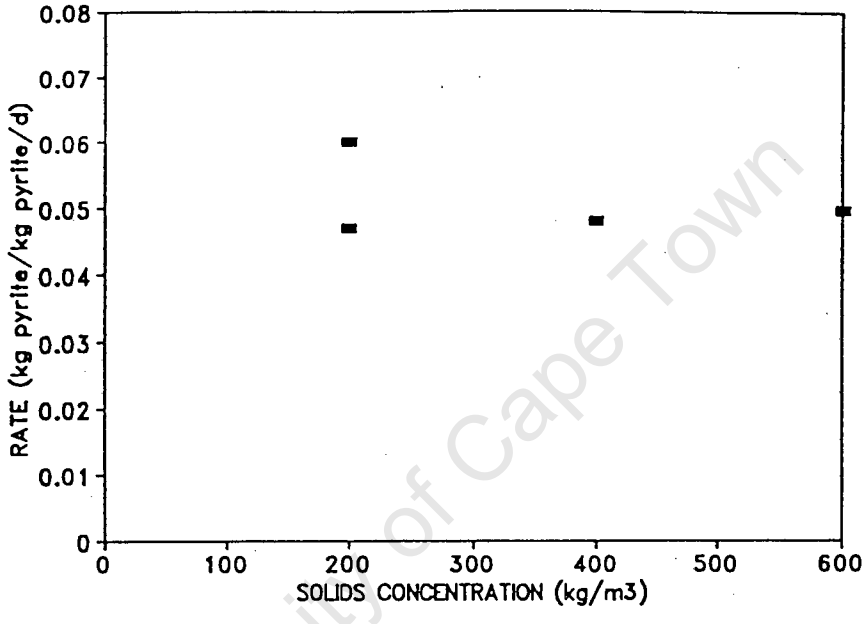


Figure 5.4 : Specific Bio-oxidation Rate vs. Solids Concentration for Vaal Reefs Run-of-Mine Ore (1.24% S)

University of Cape Town

The results of the testwork conducted on the run-of-mine material at different concentrations of solids confirmed the hypothesis that as long as sufficient oxygen was available, the biooxidation rate would be proportional to the solids concentration, even at high reactor solids concentrations. The maximum solids concentration of 60 per cent tested during this experimental work was three time higher than the solids concentration of 20 per cent where oxygen limitation is commonly encountered with high sulphide content materials (Chapter One).

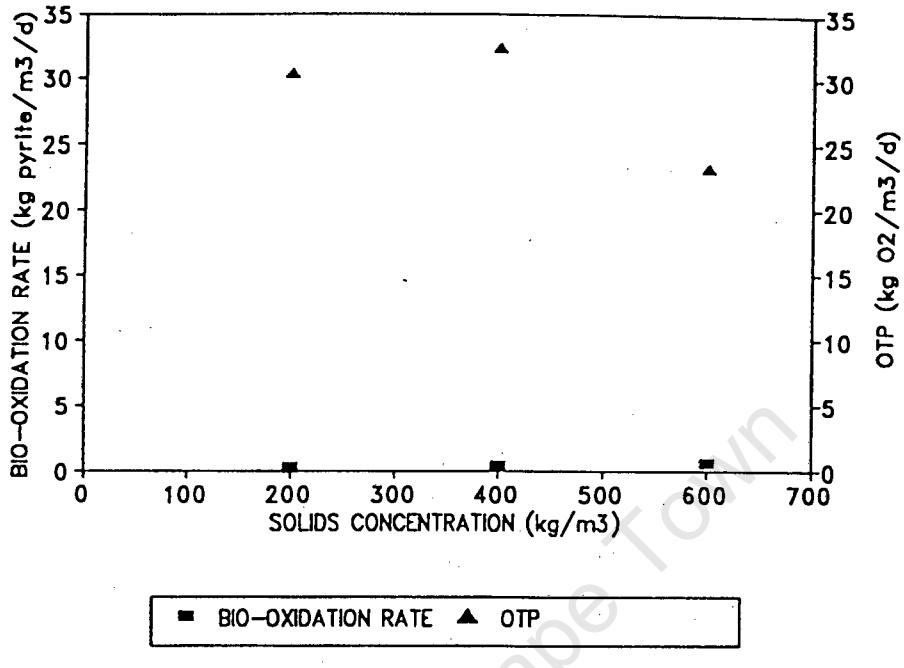


Figure 5.5 : Bio-oxidation Rate and Oxygen Transfer Potential (OTP) vs. Solids Concentration for
Vaal Reefs Run-of-Mine Ore (1.24% S)

University of Cape Town

5.2 BATCH BIO-OXIDATION OF HIGH SULPHIDE CONTENT MATERIAL: PRIESKA PYRITE CONCENTRATE TESTS AT 10 PER CENT SOLIDS

Two batch bio-oxidation tests were performed at 100 $kg.m^{-3}$ (10 per cent) Prieska pyrite concentrate in the stirred tank reactors. These tests acted as controls that enabled the rates determined in the FBR testwork to be compared with those determined in a more conventional type of bio-oxidation reactor. Due to the high pyrite content of the Prieska concentrate (47.8% S), a low solids concentration of 10 per cent was specifically chosen to ensure that oxygen could not limit the process.

The bio-oxidation rate was determined by monitoring the rate at which iron appeared in solution over the course of a run. Maximum rates were based on

HCl-washed iron concentration data (*vide* Section 4.4.1.4). A maximum bacterial oxidation rate was calculated by regressing the iron concentration data collected during the course of a run. Data collected during the lag period and after essentially all of the oxidation had occurred were omitted from the regression. The rate from the first test was found to be 0.0360 (kg pyrite)(kg solids)$^{-1}$.d^{-1} and in the second it was 0.0401 (kg pyrite)(kg solids)$^{-1}$.d^{-1}, the results obtained differing by 12.5 per cent. Bacteria generated during the first test were used for inoculation of the second test. This possibly caused the higher rate due to bacterial adaptation or an improvement in the activity of the culture. A similar observation was made during the repeat test conducted on the run-of-mine material discussed in Section 5.1.1. Time-course data, from one of the tests conducted at 10 per cent solids, showing the acid washed iron concentration, redox potential and dissolved oxygen concentration are presented in Figures 5.5, 5.6 and 5.7 respectively. Detailed experimental data are contained in Appendix 3, Tables C1 and C2.

The results of this testwork are discussed further in Section 5.3, in conjunction with the results of runs performed with mixtures of quartz and the Prieska concentrate. Quartz was added to the Prieska pyrite concentrate to increase the concentration of solids in the reactor without changing the concentration of sulphide material in the reactor.

University of Cape Town

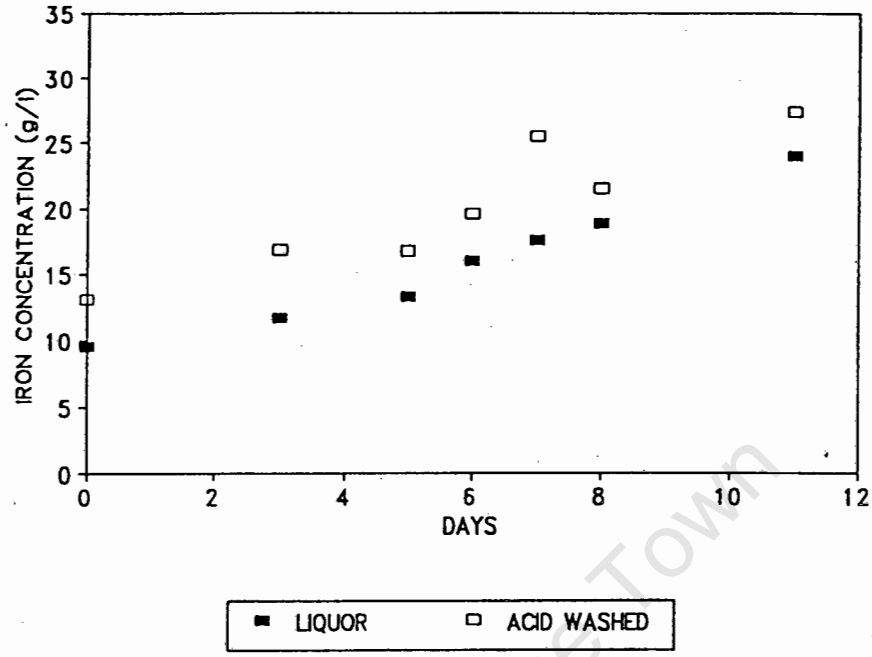


Figure 5.6 : Typical Total Iron Time-course Data for Bio-oxidation of High Sulphide Content, Prieska Concentrate (47.8% S)at 10 per cent (100 kg.m^{-3}) solids

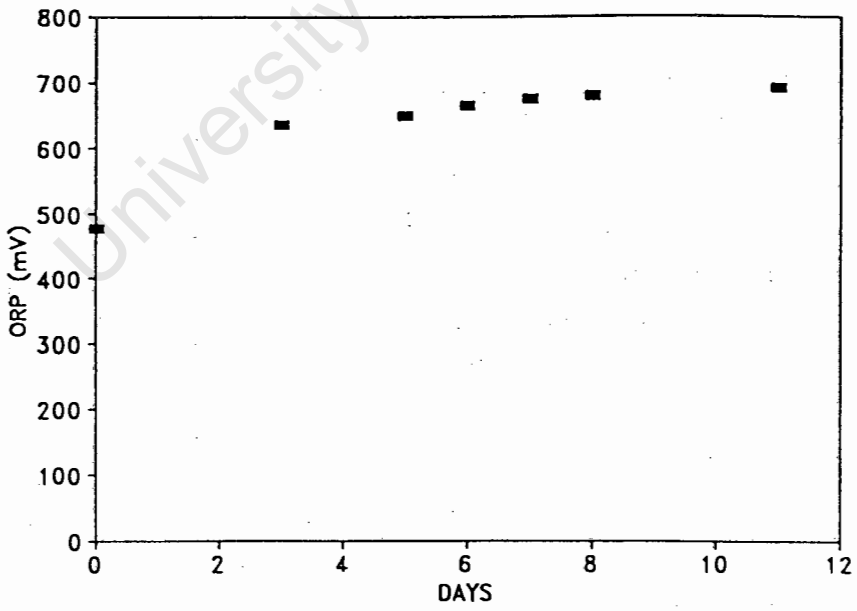


Figure 5.7 : Typical Redox Potential Measurements During Bio-oxidation of High Sulphide Content, Prieska Concentrate (47.8% S) at 10 per cent (100 kg.m^{-3}) solids

University of Cape Town

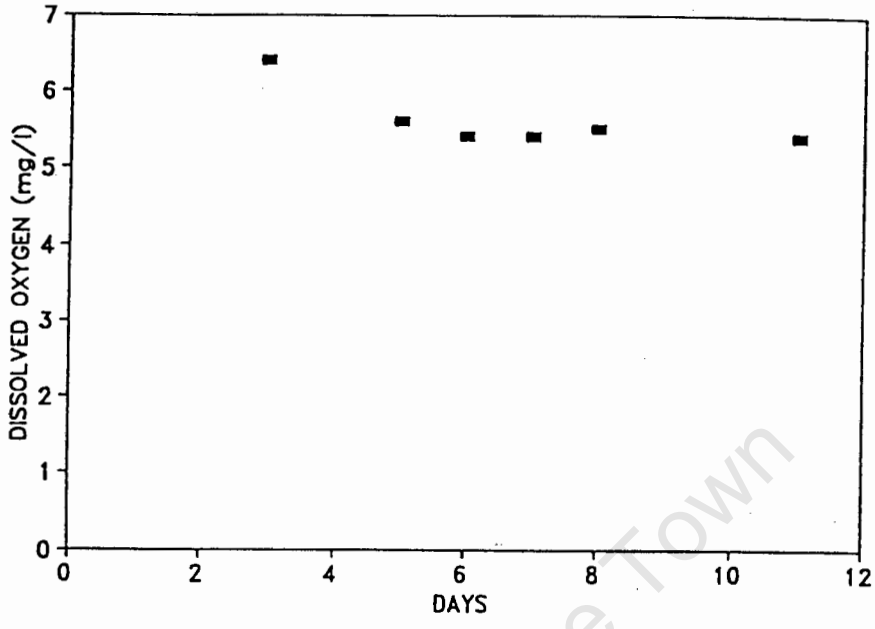


Figure 5.8 : Typical Dissolved Oxygen Concentration Measurements During Bio-oxidation of High Sulphide Content, Prieska Concentrate (47.8% S) at 10 per cent (100 kg.m^{-3}) solids

University of Cape Town

5.3 MIXTURES OF HIGH SULPHIDE CONTENT MATERIAL (PRIESKA PYRITE CONCENTRATE) AND QUARTZ

Testwork discussed in this section was performed to assess the relative effects of the total concentration of solids in a reactor and the concentration of sulphide material on the bacterial oxidation rate. These two factors could be investigated independently by adding different amounts of quartz to a fixed amount of Prieska pyrite concentrate. In this way, the total concentration of solids in a reactor could be altered, whilst the concentration of sulphide material could be held constant. The different ratios of pyrite to quartz in the reactors simulated material of lower sulphide grades than the pure Prieska pyrite concentrate. An additional feature of this testwork was the fact that the sulphide material present in all of the tests was the same. If different sulphide materials, i.e. from a range of sources, had been used to achieve intermediate sulphide grades for this testwork, different

intrinsic oxidation rates of the various sulphides may have confounded the results.

The batch reactors were operated in the same manner as those discussed in Sections 5.1 and 5.2. Three tests were performed, at total solids concentrations of 100, 200 and 300 $kg.m^{-3}$ (10, 20 and 30 per cent). All of the reactors contained 100 $kg.m^{-3}$ (10 per cent) pyrite. To achieve the total solids concentration of 200 $kg.m^{-3}$ a further 100 $kg.m^{-3}$ of quartz was added to the reactor. A breakdown of the solids loadings is tabulated in Table 5.1.

University of Cape Town

Table 5.1 : Solids Loadings in Pyrite/Quatrz Mixtures

TEST	TOTAL SOLIDS# ($kg.m^{-3}$)	PYRITE (%)	QUARTZ (%)
1	100	100	0
2	200	100	100
3	300	100	200

(# 1% solids = 10 $kg.m^{-3}$)

The bio-oxidation rates measured in the three reactors have been plotted against the total solids concentration in Figure 5.9. The oxygen transfer potentials, calculated from k_La measurements have been included in Figure 5.9. From the figure, it is clear that in all cases oxygen limitation would not have been expected because the oxygen transfer potential was substantially above the bacterial oxidation rate (during pyrite bio-oxidation one may compare the OTP directly with the bacterial oxidation rate because for every 1 kg of pyrite oxidised, 1 kg of oxygen is consumed).

Experimental data are presented in Appendix 3, Tables D1 and D2. The bio-oxidation rate at 100 kg.m^{-3} solids (i.e. only Prieska pyrite was present) was determined twice and the results have been discussed in Section 5.2. It was found that the specific pyrite bacterial oxidation rate remained essentially constant and was not influenced by the increase in the concentration of solids in the reactor by the addition of inert quartz. The cause of the higher rate that was observed during the repeat test at 100 kg.m^{-3} has been discussed in Section 5.2.

In order to interpret the results further, it is necessary to predict the concentration of solids at which oxygen limitation would occur if only Prieska pyrite concentrate was processed. Calculations were based on the measured pyrite bio-oxidation rate.

The oxygen demand during the second test performed at 10 per cent solids was 4.01 (kg O_2).m^{-3}.d^{-1}, based on the measured bio-oxidation rate of pyrite. The dissolved oxygen concentration was 4.7 mg.l^{-1} on average. Using the measured (immediately after inoculation) saturated dissolved oxygen concentration of 7.2 mg.l^{-1}, the oxygen mass transfer coefficient could be estimated as follows (note the oxygen demand has been expressed as (mg O_2).l^{-1}.s^{-1}):

$$\text{Oxygen Demand} = \text{OTR}$$
$$0.0464 \text{ (mg } O_2).l^{-1}.s^{-1} = k_La\,(C^* - C)$$
$$0.0464 \text{ (mg } O_2).l^{-1}.s^{-1} = k_La\,(7.2 - 4.7)$$
$$k_La = 0.0185 \text{ s}^{-1}$$

Using this k_La, the oxygen transfer potential (OTP) could be estimated:

$$\text{OTP} = k_La\,(C^* - C_{CRIT})$$
$$= 0.0185\,(7.2 - 0.7)$$
$$= 0.1206 \text{ (mg } O_2).l^{-1}.s^{-1}$$
$$= 10.42 \text{ (kg } O_2).m^{-3}.d^{-1}$$

University of Cape Town

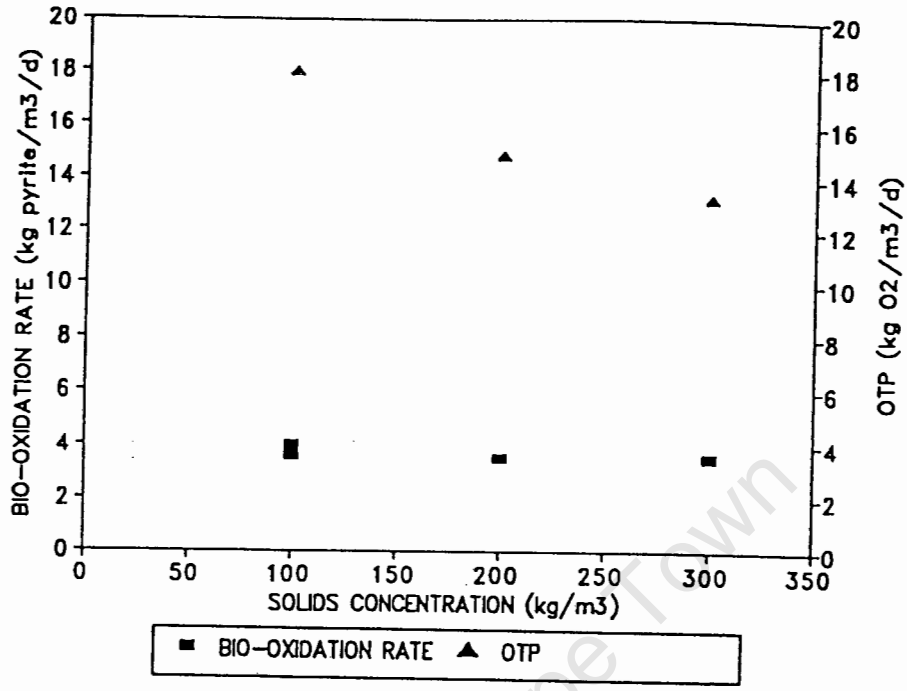


Figure 5.9 : Bio-oxidation Rate and Oxygen Transfer Potential (OTP) Measured in Various Mixtures of Pyrite Concentrate and Quartz.

The OTP could be used to estimate the solids concentration where oxygen-limited conditions would be encountered (i.e. oxygen demand = OTP). It was assumed that k_La remained constant as the solids concentration was increased. Let the solids concentration when the oxygen demand is equivalent to the OTP be L per cent, then:

At 10 per cent solids:

oxygen demand = 4.01 (kg O_2).m^{-3}.d^{-1}

At L per cent solids:

oxygen demand = 4.01 x L / 10

Under these conditions:

oxygen demand = OTP

4.01 x L / 10 = 10.42 (kg O_2).m^{-3}.d^{-1}

So, L = 26.0 per cent solids.

= 260 kg.m^{-3} solids

University of Cape Town

The calculations above predict that during the bio-oxidation of the high sulphide content Prieska pyrite concentrate, oxygen limitation would be expected to occur at approximately 260 $kg.m^{-3}$ (26 per cent) solids. The results of the pyrite/quartz mixture tests, however, showed that even at an overall solids concentration of 300 $kg.m^{-3}$, the specific pyrite oxidation rate was still the same as that measured at 10 per cent total solids. This was because in the pyrite/quartz mixture at 300 $kg.m^{-3}$ solids, the OTP still exceeded the oxygen demand and the dissolved oxygen concentration was 5.2 $mg.l^{-1}$ on average.

Further increases in the solids concentration, by the addition of inert quartz, would eventually affect the process. The solids would decrease the k_La to such an extent that the oxygen transfer potential would fall below the oxygen demand and oxygen-limited conditions would occur. It should be noted that the oxygen demand, which is based on the amount of sulphide material present, would have remained constant as it is not affected by the addition of the inert solid material.

The results confirm that it is not the solids concentration *per se* that affects the bio-oxidation rate at high solids concentrations, but rather the magnitude of the oxygen demand in relation to the oxygen transfer potential of the system.

The highest solids concentration at which bio-oxidation can be conducted at the maximum specific oxidation rate is limited by the oxygen availability in the system. The oxygen demand is proportional to the sulphide content of the material, so as shown in the results of this experimental work a low grade material may be bio-oxidised at a far high solids concentration than a higher grade material such as a flotation concentrate.

All of the data from this chapter have been compared, along with data generated using the fluidised bed reactor, in Chapter Seven.

The results of the testwork discussed in this chapter have important implications when the feed material for bio-oxidation is produced by flotation. In assessing the economics of a flotation plant followed by a bio-oxidation process, it may be advantageous to reduce the sulphide grade of the concentrate produced in the

University of Cape Town

flotation step. This should enable more gold to be recovered in the flotation step (i.e. less will be lost in flotation tailings). Although the total solids fed to the bio-oxidation plant would increase, the throughput of sulphide material would remain constant due to the lower sulphide grade of the material.

The experimental results from this chapter indicate that the bio-oxidation process is dependent on the sulphide solids concentration and is less sensitive to the total solids concentrations, within limits (if the sulphide solids concentration is held constant, an increase in the total solids concentration (eg. by the addition of inert quartz to the reactor) will only affect the process if it lowers the k_La to such an extent that the OTP can no longer meet the oxygen demand). This means that the bio-oxidation reactors could be operated at a higher solids concentration, without any loss in the sulphide oxidation capacity of the plant. The nett result should be an increase in total gold recovery from the combined processes.

University of Cape Town

CHAPTER SIX

FLUIDISED BED REACTOR (FBR) TESTWORK

A fluidised bed reactor (FBR) has been used for bio-oxidation testwork due to the fact that it enables the solids and liquid (or chemical) environment to be controlled independently of one another. The applicability of a fluidised bed reactor for bio-oxidation studies is discussed at the end of Chapter One. Whilst operating the reactor at a constant bed solids concentration (defined in Section 1.4), the overall solid-to-liquid ratio may be altered by adding different amounts of solid material to the system (i.e. by changing the overall solids loading of the system). Alternatively the reactor can be operated at a fixed overall solids concentration and by adjusting the flowrate of liquid up through the FBR, the bed expansion, and thereby the bed solids concentration, may be varied. These two modes of operation have enabled the oxygen availability, or oxygen transfer potential (OTP), to be varied, whilst other factors affecting the bio-oxidation rate could be controlled independently.

The results of tests investigating the effect of oxygen availability on the bio-oxidation rate of two different, high sulphide content, pyrite concentrates are presented in this chapter. Initial fluidisation studies to determine operating limits and reproducibility for this novel bio-oxidation reactor are also reported.

University of Cape Town

6.1 INITIAL FLUIDISATION STUDIES

6.1.1 Lower Limit to Bed Solids Concentration

The minimum velocity for fluidisation of the ore particles was estimated using the correlations published in Coulson and Richardson (1980) for a range of particle diameters. The calculated values are shown in Figure 6.1. A small change in particle diameter corresponded to a far larger change in fluidising velocity. The

fluidising velocity increased three-fold as the particle diameter was increased by a factor of 1.67.

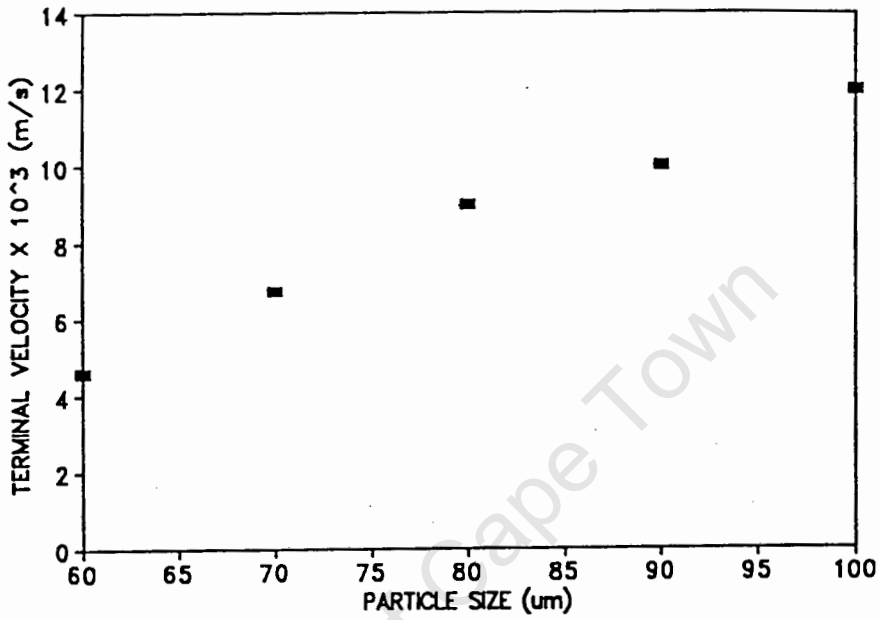


Figure 6.1 : Terminal Velocity vs. Particle Size

University of Cape Town

This relationship between the particle diameters and the terminal velocity results in bed segregation if the range of particle diameters is too great. Although particles of different diameters will tend to be thoroughly mixed during gas fluidisation, in liquid fluidisation there is a strong tendency towards bed segregation (Davidson and Harrison, 1971). Wen and Yu (1966) found that as long as the ratio of the minimum fluidisation velocities of the smallest and largest particles differ by less than a factor of approximately 2, then there is little bed segregation.

Severe bed segregation was found to occur during fluidisation tests using the bulk Vaal Reefs pyrite concentrate. To decrease the size range, the bulk concentrate was washed in a water-fluidised bed. The fine particles were elutriated from the bed and wasted with the water leaving the top of the open vessel. This procedure is discussed in more detail in Section 4.1. Gross, oversize material was removed by sieving the washed concentrate through a 100 mesh sieve. The resulting size fraction of ore was found to be sufficient to

prevent excessive bed segregation during the FBR testwork. A size analysis of this fraction and the bulk size distribution are presented in Section 4.1.

The tendency for bed segregation is higher at high bed expansions (Davidson and Harrison, 1971). This phenomenon was observed during the fluidisation tests on the Vaal Reefs pyrite concentrate, where it was found that the bed expansion was very sensitive to the fluidisation velocity at the upper range of velocities required to expand the bed sufficiently to give bed solids concentrations below 20 per cent (200 $kg.m^{-3}$). The relationship between bed expansion and fluidising velocity is shown in Figure 6.2. The data were compared with predictions derived from the correlation published in Coulson and Richardson (1980). Both theoretical predictions and experimental data are presented in Appendix 3, Table E. Below a bed solids concentration of 20 per cent solids, it was difficult to form a stable, well-defined bed, so 20 per cent solids was selected as the lowest bed solids concentration for use in the bio-oxidation tests. Bed solids concentrations of 20 per cent and above were acceptable for this study as this was the region where, as mentioned in Chapter One, the bio-oxidation rate has been found to decline during the processing of high sulphide content material.

University of Cape Town

6.1.2 Upper Limit to Overall Solids-to-Liquid Ratio

To achieve a particular bed solids concentration it is necessary to operate at a set fluidising velocity. This in turn determines the rate at which oxygen is supplied to the reactor.

The rate of oxygen transfer to the fluidised bed can be calculated from the fluidising liquid flowrate and the dissolved oxygen concentration of the liquid entering the reactor. The liquid entering is fully saturated with oxygen, having passed through the surge tank.

As the liquid passes up through the bed of particles, oxygen is consumed due to the oxidation process. The oxygen consumption, or demand, is a function of the amount of sulphide material present in the reactor. As the solids loading is increased there will be a particular loading where the oxygen demand will equal the oxygen supply. If the solids loading is increased further, oxygen-limited

conditions will exist. This sets the upper limit on the overall solids-to-liquid ratio at a particular fluidising velocity. To ensure that no oxygen limitation of the bacteria occurred, the minimum dissolved oxygen concentration was selected as 0.7mg.l^{-1} (Liu *et al.*, 1988). At higher fluidising velocities, the rate at which oxygen is supplied to the reactor increases, allowing a higher solids loading to be supported in the FBR before oxygen limitation occurs.

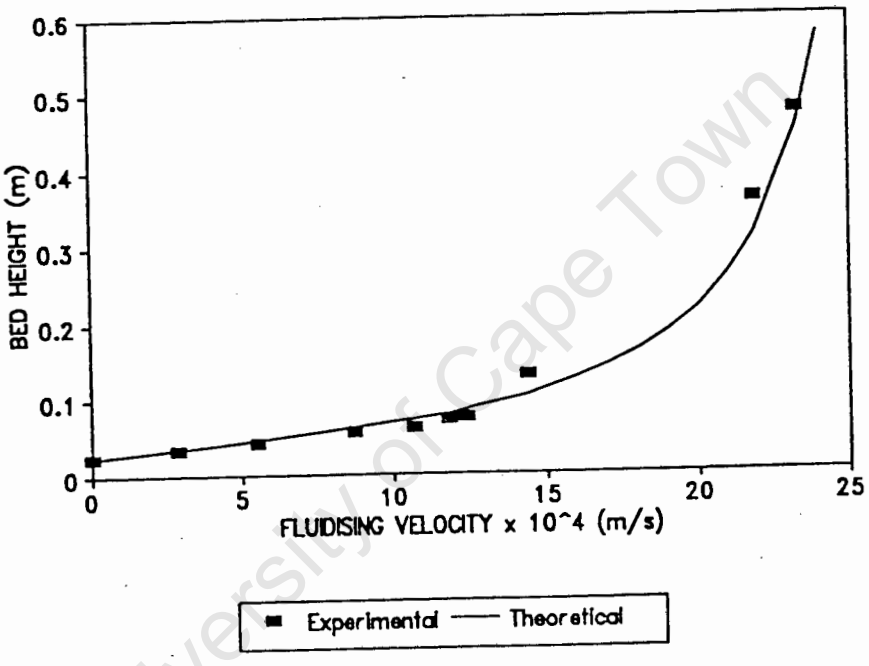


Figure 6.2 : Relationship Between the Bed Expansion and Fluidising Velocity

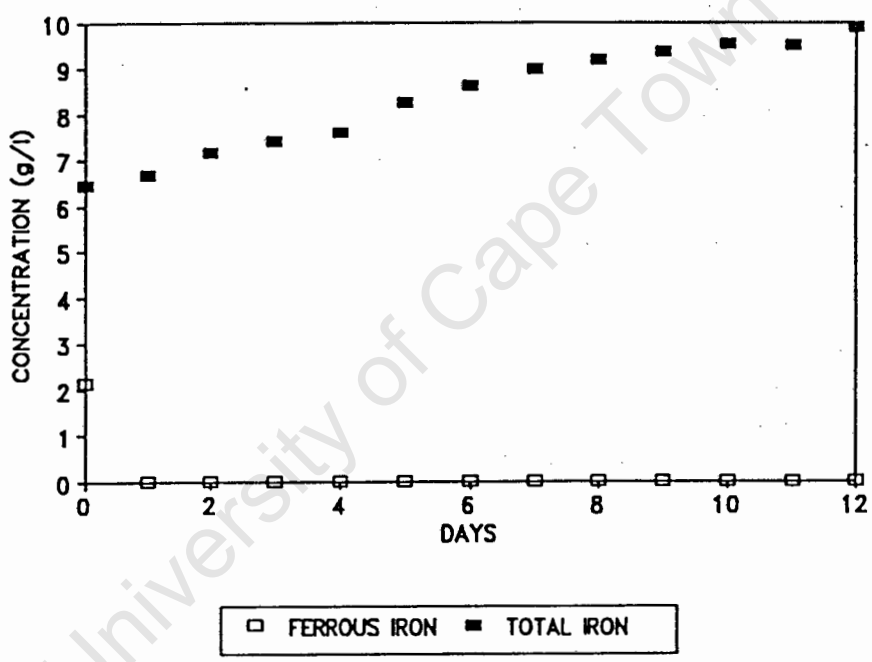
University of Cape Town

6.1.3 Typical Results of a FBR Run

The total and ferrous iron concentration data for a typical FBR run using Vaal Reefs pyrite concentrate are shown in Figure 6.3. The amount of ore charged to the reactor was 75g, representing an overall solids-to-liquid ratio of 1.7 per cent (17 kg.m^{-3}). The bed solids concentration was 20 per cent (200 kg.m^{-3}).

The free bacterial concentration was found to increase from approximately 2 x 10^7 to 4 x 10^8 cells.ml^{-1} within 10 days of batch operation. It should be noted that although the reactors were inoculated with sufficient inoculum to ensure that

the initial bacterial concentration in the reactor was 10^8 cells.ml^{-1}, attachment of the bacteria to the mineral resulted in an initial free bacterial population that was below 10^8 cells.ml^{-1}. The fact that the bacteria were able to establish themselves and increase their numbers within the test period indicates that significant mechanical damage of the bacteria was unlikely. During the course of a run, the redox potential generally rose from approximately 475 mV on inoculation to 750 mV. The active bacterial culture maintained essentially all of the iron (> 99 per cent) in the ferric form after the first 24 hours of batch culture.



University of Cape Town

Figure 6.3 : Typical Iron Concentrations Measured During the Course of an FBR Run

The bio-oxidation rate was calculated based on the build-up of iron in solution once pyrite oxidation had commenced. The best-fit line for the total iron concentration data set was determined using linear regression. The slope of this line represented the rate at which iron entered the solution. This rate was then converted, using reaction stoichiometry to the mass of pyrite oxidised per unit mass of solids charged to the reactor. Using this basis, the rates determined at

different overall solids-to-liquid ratios and bed solids concentrations could be readily compared.

6.1.4 Comparison of the Bio-oxidation Rate Based on the Oxygen Consumption and that Based on the Build-up of Iron in Solution.

The dissolved oxygen concentration was measured in the surge tank as well as at the top of the bed of mineral particles in the FBR. The flowrate of liquid up the reactor was measured and this enabled an oxygen utilisation rate in the bed to be determined. Using the reaction stoichiometry indicated in Equation 3.1, it was possible to calculate a corresponding iron oxidation rate from the oxygen utilisation rate. During pyrite oxidation, 1 kg of oxygen is required for every 1 kg of pyrite oxidised. The rates based on the oxygen utilisation rate and the solution iron concentration were in close agreement. Typical measurements made during the course of one particular run are shown in Table 6.1.

University of Cape Town

Table 6.1 : Comparison Between Oxidation Rates Based on Oxygen Consumption and on the Iron Concentration in Solution

BASIS:	Oxygen Utilisation Rate		Total Iron Concentration
DAY	RATE kg Pyrite/ kg solids/ d	PERIOD	RATE kg Pyrite/ kg solids/ d
4	0.036	Day 2	0.039
5	0.036	to Day 6	
6	0.034	Day 6	0.039
7	0.034	to Day 13	
9	0.041		

6.1.5 Reproducibility

The FBR experimental work was carried out in two similar sets of apparatus. The reproducibility of the results obtained from the two FBR systems as well as in successive runs was established by performing three runs at the same operating conditions. The first stage involved the simultaneous inoculation of the two rigs. A charge of 150g of Vaal Reefs pyrite concentrate was put into each reactor. The reactors were then inoculated with sufficient inoculum (approximately 1 litre) so that the initial bacterial concentration was 10^8 cells.ml^{-1}. The size of the inoculum was adjusted to compensate for the small difference in volume between the two rigs. The bed solids concentration was constant throughout the testwork at 20 per cent (200 kg.m^{-3}) solids. After completion of the two runs, a further run was conducted in one of the reactors.

The iron concentration in the liquor was monitored daily. Experimental data are shown in Appendix 3, Tables F1, F2 and F3. By regressing the data, the rate at which the iron concentration increased was determined. The rates determined during the three tests were found to vary by less than 7 per cent, indicating good reproducibility. The rate data as well as the regression coefficient, R^2 are tabulated in Table 6.2. The regression coefficient was generally high.

Table 6.2 : Results of Iron Build-up Rate in Reproducibility Tests

Run No.	Rate (g Fe).l^{-1}d^{-1}	R^2
1	0.439	0.991
2	0.442	0.985
3	0.431	0.955
Mean	0.437	-

University of Cape Town

6.1.6 Effect of Bio-oxidation on the Distribution of Solids in the FBR.

Typically as the run progressed, it was noticed that the bed became less well defined and a secondary bed of fine particles filled the zone above the original bed of particles. Most of the elutriated particles formed a second dense phase at the top of the reactor, below the disengaging zone. The secondary phase most probably resulted from elutriation of particles due to the reduction in their diameter as bio-oxidation progressed.

To determine a dissolved oxygen profile up the FBR, the dissolved oxygen concentration was measured at 15cm intervals from the bottom of the FBR to the top, just below the conical disengaging zone. The intervals gave six heights in all. The dissolved oxygen concentration measured in the surge tank was assumed to be the concentration at zero height, i.e. the bottom of the reactor. The dissolved oxygen profile was determined daily during one particular FBR run that was performed at a bed solids concentration of 20 per cent (200 $kg.m^{-3}$) and an overall solid-to-liquid ratio of 1.7 per cent (17 $kg.m^{-3}$) with Vaal Reefs pyrite concentrate. This bed solids concentration required the highest fluidising velocity used during this research, so the maximum observable elutriation would occur under these operating conditions. A plot of the dissolved oxygen concentration profiles is presented in Figure 6.4. Experimental data are shown in Appendix 3, Table G1.

By using the inlet and outlet dissolved oxygen concentrations for each segment of the FBR and knowing the flowrate of liquor up through the reactor, it was possible to calculate an average oxygen utilisation rate (OUR) for each zone. Some of the OUR profile data are shown in Figure 6.5. Experimental data are given in Appendix 3, Table G2.

University of Cape Town

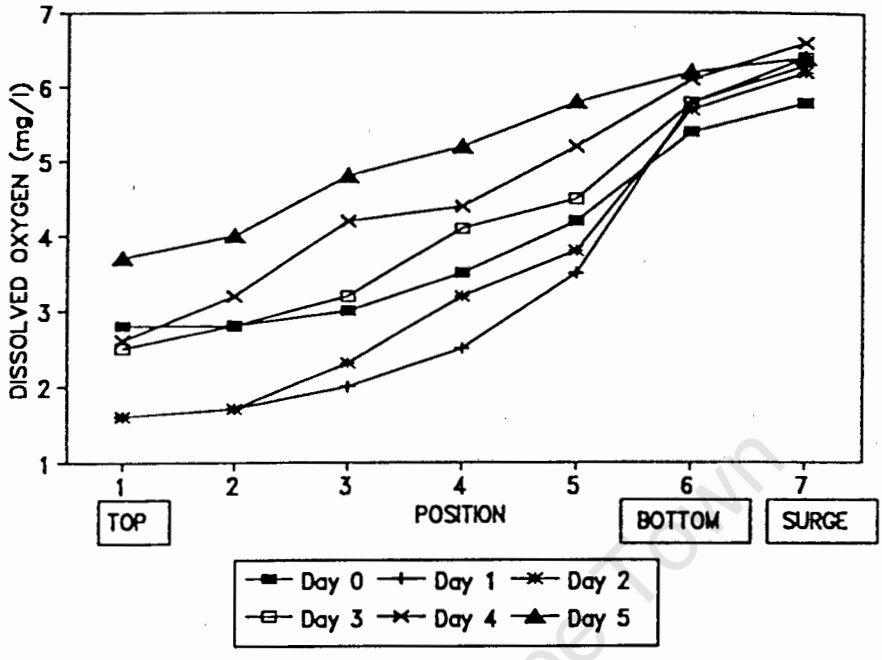


Figure 6.4 : Dissolved Oxygen Profiles in FBR

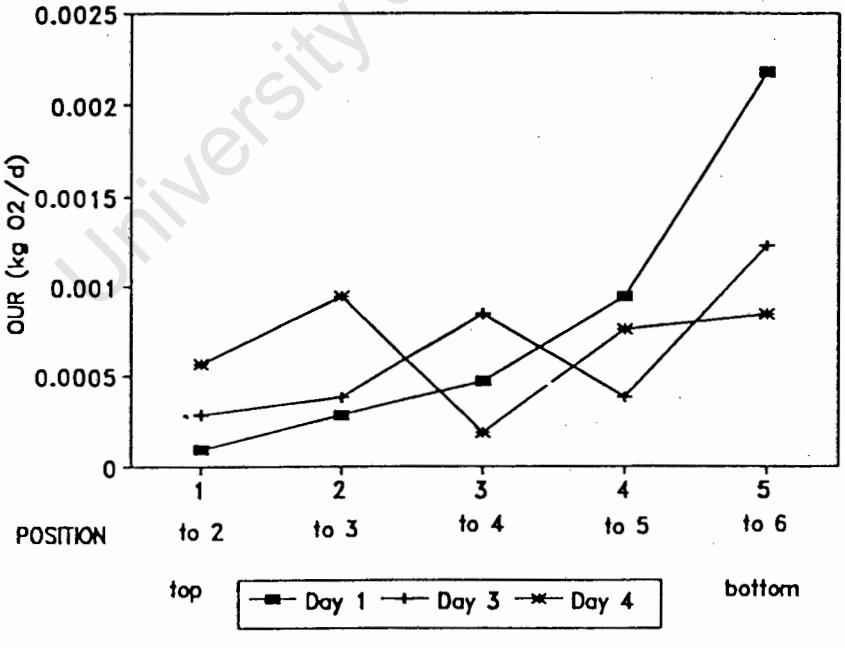


Figure 6.5 : Oxygen Utilisation Rate Profiles in FBR

University of Cape Town

For the first two days of operation, most of the oxygen utilisation occurred at the bottom of the column. Essentially all of the particles were contained in this bottom zone during this period. The profile on Day 3 indicated that the OUR in the bottom zone had decreased and a second peak occurred within the third segment from the bottom of the reactor. This corresponded to the initial entrainment of particles from the bed. By Day 5, the OUR was highest at the top of the column. As the oxidation process is dependent on surface area, even though the mass of small particles was low in comparison to those remaining in the bed, their collective surface area was high. Iron concentration data from only the first six days of operation were used in the calculation of the bio-oxidation rate, in an attempt to minimise the error in the bed solids concentration caused by the elutriation of particles as they decreased in size.

The test results also highlighted the close association between the presence of solids and oxygen consumption. This indicated that bacterial oxidation was occurring in close proximity to the solid material. During the period when data are collected to determine the bio-oxidation rate, the fluidised bed is well defined and may be considered to be the reaction zone, i.e. the site where bio-oxidation is primarily occurring. This finding is significant as it shows that the bacterial oxidation occurs under the conditions (e.g. bed solids concentration) prevalent in the fluidised bed of solids. Rate observations are then relevant to the operating conditions in the fluidised bed.

University of Cape Town

6.2 OPERATION AT VARIOUS OVERALL SOLIDS-TO-LIQUID RATIOS

To investigate the effect of oxygen availability on the bio-oxidation rate, runs were conducted with different overall solids-to-liquid ratios, whilst operating at a bed solids concentration of 20 per cent. The fluidisation velocity was kept constant for each sulphide material tested. This automatically fixed the rate at which oxygen was supplied to the FBR, i.e. the oxygen transfer potential (OTP) of the system.

The bio-oxidation rate was determined for the moderately high sulphide content Vaal Reefs pyrite concentrate (30.5% S) at overall system loadings of 17, 34 and 45 $kg.m^{-3}$ solids as well as for the high sulphide content (47.8% S) Prieska pyrite

concentrate at both 17 and 45 kg.m^{-3} solids. Further information on both sulphides is presented in Chapter Four. The dissolved oxygen concentration at the top of the reactor and in the surge tank was measured, allowing an oxygen utilisation rate to be calculated using the flowrate of liquor up through the bed. The build-up of iron in solution was also monitored on a daily basis so that it could also be used to determine the oxidation rate. The redox potential was measured at the top of the FBR as well as in the surge tank.

Bio-oxidation of the high sulphide content Prieska pyrite concentrate has been studied in both stirred tank and fluidised bed reactors, enabling the comparison of the bio-oxidation rates that were determined in the two different systems. Experimental results obtained from the stirred tank bio-oxidation testwork are presented in Chapter Five.

University of Cape Town

6.2.1 Vaal Reefs Pyrite Concentrate Results

The bio-oxidation rates that were observed during the batch FBR tests conducted on moderately high sulphide content (30.5% S) Vaal Reefs concentrate at the various overall system solids loadings, have been tabulated in Table 6.3. (Experimental data are presented in Appendix 3, Tables I1, I2, H2 and H3). All of the experiments were conducted at a bed solids concentration of 200 kg.m^{-3} (20 per cent solids)

The specific oxidation rate (i.e. (kg Pyrite)(kg solids)$^{-1}$d^{-1}) was found to decrease as the total solids loading in the reactor was increased. In the runs conducted at system solids concentrations of 34 and 45 kg.m^{-3} it was found that the dissolved oxygen concentration had dropped to 0.4 mg.l^{-1} at the top of the FBR. Dissolved oxygen concentrations in this range had been found by Liu *et al.* (1988) to limit bacterial oxidation. This indicated that oxygen limitation was the likely cause of the lower specific oxidation rates that had been obtained at the two higher solids loadings.

As pyrite is being oxidised, stoichiometry indicates that for every 1 kg of pyrite oxidised, 1 kg of oxygen is consumed. This means that for pyrite oxidation:

$$(\text{kg pyrite})m^{-3}.d^{-1} = (\text{kg } O_2)m^{-3}.d^{-1}.$$

In the test conducted at a system solids concentration of 17 kg.m^{-3}, the OTP was above the measured OUR and the pyrite oxidation rate. In the other two tests conducted under oxygen-limited conditions, however, the OTP limited the oxidation rate. The OUR is permitted to be slightly above the OTP because the OTP is based on a minimum dissolved oxygen concentration of 0.7 mg.l^{-1}, whereas the dissolved oxygen concentration had dropped below this critical value to 0.4 mg.l^{-1}. This increased the concentration driving force (C^* - C) and subsequently the amount of oxygen transferred The OTP relates to oxidation without oxygen limitation.

Table 6.3 : Vaal Reefs Concentrate Bio-oxidation Rate at Different Solids Concentrations

System Solids Conc.	Bed Solids Conc.	Oxygen Transfer Potential	Oxygen Utilisation Rate	Pyrite Oxidation Rate	Specific Pyrite Oxidation	Dissolved Oxygen Conc.
kg.m^{-3}	kg.m^{-3}	kg O_2.m^{-3}.d^{-1}	kg O_2.m^{-3}.d^{-1}	$\frac{\text{(kg Pyrite)}}{m^3.d}$	$\frac{\text{(kg Pyrite)}}{\text{(kg Pyrite).d}}$	mg.l^{-1}
17	200	13.59	11.06	8.28	0.0752	1.5
34	200	4.14	4.28	5.22	0.0475	0.4
45	200	3.46	3.58	3.34	0.0304	0.4

University of Cape Town

6.2.2 High Sulphide Content Prieska Pyrite Concentrate Results

Two FBR tests were conducted on the Prieska pyrite concentrate at overall system solids concentrations of 17 and 45 kg.m^{-3}. In both cases the bed solids concentration was 200 kg.m^{-3} (20 per cent solids). The experimental data have been summarised in Table 6.4. Detailed experimental data are presented in Tables H4 and H5 in Appendix 3.

At the overall solids concentration of 17 kg.m^{-3}, the dissolved oxygen concentration at the top of the FBR was 2.5 mg.l^{-1}. This indicated that oxygen was not limiting the process as the level was well above the critical concentration of 0.7 mg.l^{-1}. The specific pyrite bio-oxidation rate was 0.0401 (kg Pyrite)(kg Pyrite)$^{-1}$d^{-1}. This was in good agreement with the average specific oxidation rate of 0.0381 (kg Pyrite)(kg Pyrite)$^{-1}$d^{-1} measured during the batch stirred tank reactor tests on the Prieska concentrate at 100 kg.m^{-3}. The result from the FBR test and the second stirred tank reactor test were identical. The same inoculum culture had been used for both the FBR and STR in this case. The close agreement of the results obtained in the two different reactor systems (under non-oxygen-limited conditions) confirmed that the rates that were measured in the novel FBR system were representative of the rates obtained in more conventional bio-oxidation reactors.

The second FBR test that was conducted on the Prieska concentrate was performed at a system solids concentration of 45 kg.m^{-3} and a bed solids concentration of 200 kg.m^{-3}. The dissolved oxygen concentration at the top of the FBR fell to 0.3 mg.l^{-1} during the testwork, indicating oxygen-limited conditions (i.e. the dissolved oxygen concentration was below the critical value of 0.7 mg.l^{-1}). As a consequence of the oxygen-limited conditions, the specific oxidation rate of 0.0358 (kg Pyrite)(kg Pyrite)$^{-1}$d^{-1} was below that of 0.0401 (kg Pyrite)(kg Pyrite)$^{-1}$d^{-1} measured under conditions when sufficient oxygen was available.

University of Cape Town

Table 6.4 : Prieska Pyrite Concentrate Bio-oxidation Rate at Different Solids Concentrations

System Solids Conc.	Bed Solids Conc.	Oxygen Transfer Potential	Oxygen Utilisation Rate	Pyrite Oxidation Rate	Specific Pyrite Oxidation	Dissolved Oxygen Conc.
$kg.m^{-3}$	$kg.m^{-3}$	$kg\ O_2.m^{-3}.d^{-1}$	$kg\ O_2.m^{-3}.d^{-1}$	$\frac{(kg\ Pyrite)}{m^3.d}$	$\frac{(kg\ Pyrite)}{(kg\ Pyrite).d}$	$mg.l^{-1}$
17	200	13.82	9.60	8.02	0.0401	2.5
45	200	4.46	4.68	7.16	0.0358	0.2

University of Cape Town

The measured bio-oxidation rate in this test was higher than the OTP. The deviation was likley to have resulted from the observed carry-over of a substantial amount of fine material from the FBR into the surge tank, due to the failure of the solids disengaging zone at the top of the FBR under the heavily-loaded conditions in the bed. As the fine material passed through the surge tank on its way back to the FBR, bio-oxidation would have occurred in the aerobic conditions in the surge tank. The bio-oxidation occurring in the surge tank would have increased the rate at which iron appeared in solution, causing the anomalously high bio-oxidation rate that was observed.

The results from the fluidised bed testwork conducted on the high sulphide content Prieska concentrate indicated that the bio-oxidation rate was limited by the oxygen transfer in the system. This limit on the amount of oxygen that was available in the reactor defined the highest solids concentration at which operation was possible at the maximum specific bio-oxidation rate. The results

were in agreement with those obtained during the fluidised bed reactor study of the moderately high sulphide content Vaal Reefs concentrate.

6.3 OPERATION AT VARIOUS BED SOLIDS CONCENTRATIONS

In the FBR testwork discussed above in Section 6.2 and in stirred tank reactor batch studies, the solids loading was increased to increase the solids concentration. In the FBR it is, however, possible to increase the solids concentration in the reaction zone by lowering the bed expansion. The added advantage is that although the solids concentration in the reaction zone is increased, the other conditions, such as the iron concentration, cell-to-solids ratio and overall solids-to-liquid ratio are not affected. The main objective of this experimental work was to determine the oxidation rate of a high sulphide content material at high solids concentration, but in the presence of sufficient available oxygen to prevent oxygen limitation. Oxygen availability has been observed to be a rate limiting factor at high solids concentrations, both in this experimental work as well as in the literature (discussed in Chapters Two and Three).

The tests discussed in this section were all performed using Vaal Reefs pyrite concentrate at an overall system solids loading of 17 $kg.m^{-3}$ (i.e. a liquid-to-solid ratio of 1.7 per cent). The bio-oxidation rate was determined at bed solids concentrations of 200, 250, 300, 450 $kg.m^{-3}$ (20, 25, 30 and 45 per cent). Detailed experimental data are shown in Appendix 3, Tables I1 to I9. Higher bed solids concentrations could not be used because the oxygen demand at the overall system solids loading of 17 $kg.m^{-3}$ would exceed the oxygen supply rate (OTP) under those conditions. The primary objective of this testwork was to ensure an adequate supply of oxygen to prevent oxygen-limited conditions from occurring. Two tests were performed at each bed solids concentration (with the exception of the runs at 300 and 350 $kg.m^{-3}$). Two batches of ore, prepared according to the method described in Section 4.1, were used for the testwork.

During the initial testwork using the first batch of prepared sulphide it was noticed that the specific bio-oxidation rate data determined at a bed solids concentration of 200 $kg.m^{-3}$ were slightly higher than the other data. Insufficient material remained from the first batch of prepared sulphide to investigate this apparent

University of Cape Town

anomaly further, so a second batch of sulphide was prepared in the same manner as the first (i.e. using the method outlined in Section 4.1). The bio-oxidation rate was determined at both 200 and 250 $kg.m^{-3}$ solids using this second batch of material. In this case, the rate data at 200 and 250 $kg.m^{-3}$ solids were similar and furthermore both lay close to the average oxidation rate that had been obtained from the first set of experiments.

The specific bio-oxidation rate data, based on the iron concentration in solution are shown in Figure 6.6. Under the conditions used in this experimental work, the bio-oxidation rate remained essentially constant as the bed solids concentration was increased between 200 and 450 $kg.m^{-3}$ (i.e. ignoring the anomalously high initial data points at 200 $kg.m^{-3}$ solids and only considering the repeated data. The spread of the remaining data is under 15 per cent, representing a deviation of 7.5 per cent about the mean). The average specific bio-oxidation rate was 0.0433 (kg Pyrite)(kg solids)$^{-1}d^{-1}$. This rate agreed reasonably well with the value of 0.0557 (kg Pyrite)(kg solids)$^{-1}d^{-1}$ found by van Staden (1991) in a continuous bioreactor system using a pyrite concentrate of the same sulphide grade. The comparison showed once again (previously discussed in Section 6.2.2) that the rates determined in a FBR were representative of rates measured in conventional reactors.

Whilst operating the fluidised bed reactor at a high bed solids concentration, it is still possible to supply the requisite amount of oxygen for bio-oxidation, by selecting an appropriate overall solids-to-liquid ratio. Having ensured the availability of adequate oxygen to the bed of solids during the testwork discussed in this section, the results indicate that the concentration of solids *per se* does not cause a decrease in the bio-oxidation rate. In both this study and the studies of others (Komnitsas and Pooley, 1991; Pinches *et al.*, 1991; Sakaguchi *et al.*, 1976; and Torma *et al.*, 1970) it has been shown, however, that when adequate oxygen cannot be supplied to the reactor, then the bio-oxidation rate is limited by the availability of oxygen.

University of Cape Town

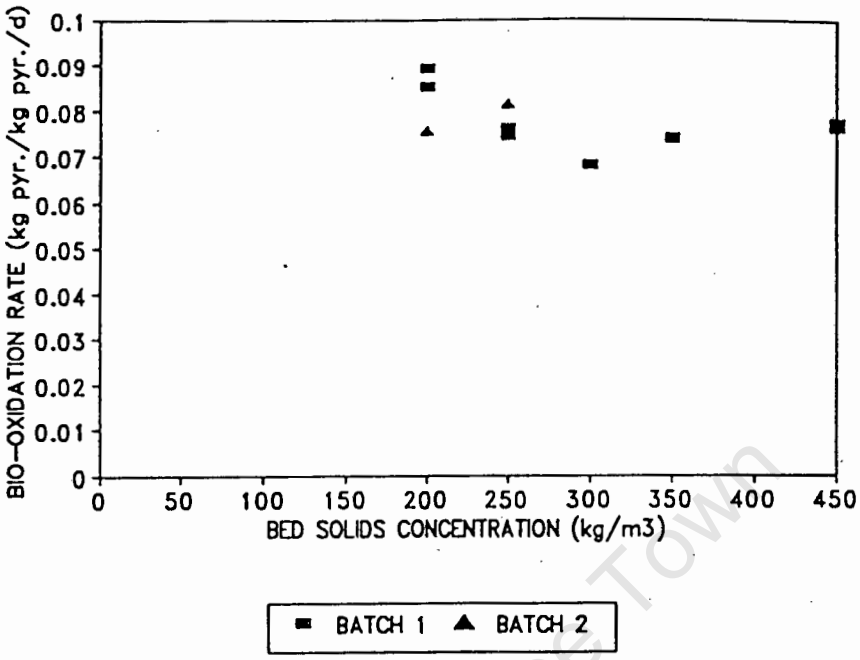


Figure 6.6 : Bio-oxidation Rate of Vaal Reefs Concentrate vs. Bed Solids Concentration at a Constant Overall Solid-to-liquid Ratio of 1.7 per cent, System Solids Concentration of 17 kg.m^{-3})

University of Cape Town

6.4 CARBON DIOXIDE AVAILABILITY IN THE FBR

The bacteria used in bio-oxidation utilise carbon dioxide as their carbon source, making the provision of adequate carbon dioxide in solution a prerequisite for cell growth (Schlegel, 1988). The rate of carbon dioxide mass transfer can be increased by raising the concentration of carbon dioxide in the sparge gas.

During the FBR tests, normal air (0.03% CO_2) was used for sparging. The following calculations were performed to determine whether or not adequate carbon dioxide was being supplied during tests that were conducted on both the Prieska and Vaal Reefs pyrite concentrate at solids loadings of 75g (i.e. conditions were oxygen availability was not limiting the process). This check was especially important for the testwork discussed in Section 6.3, where the bed solids concentration was varied at a constant overall solid-to-liquid ratio and it

was shown that, as long as sufficient oxygen was available, the specific bio-oxidation rate was independent of solids concentration.

The saturated carbon dioxide concentration, C_c^* in equilibrium with air containing 0.03% CO_2 was determined as 0.416 mg.l^{-1} using Henry's Law, with a Henry's Law constant of 0.797 $(mg.l^{-1})_{LIQUID}/(mg.l^{-1})_{GAS}$ (Nagpal *et al.*, 1993). The outlet carbon dioxide concentration was assumed to be zero in calculating the transfer potential of carbon dioxide in the FBR.

The yield of organic carbon was found by Liu *et al.* (1988) to be 0.0185 mg per mg of oxygen that was consumed. This information was used to convert measured oxygen utilisation rates (OUR) into carbon dioxide utilisation rates (CUR). As a detailed study of carbon dioxide utilisation was beyond the scope of this thesis, but acknowledging the importance of carbon dioxide availability, the Liu *et al.* (1988) yield coefficient was considered acceptable to provide a first approximation of the carbon dioxide utilisation rate. It should, however, be noted that the yield of organic carbon may vary according to the substrate and cell growth is also not always linked to substrate oxidation (Mandl, 1984). Ideally the yield should have been determined for each substrate used in this research.

University of Cape Town

6.4.1 Carbon Dioxide Availability During the Bio-oxidation of Prieska Pyrite Concentrate

For the oxidation of Prieska concentrate at a solids loading of 75g and bed solids concentration of 20 per cent:

Liquid flowrate through the FBR = 720 $l.d^{-1}$

So, the CO_2 Transfer Rate = 720 x (0.416 - 0.0)
= 300 (mg CO_2).d^{-1}
= 300 x 12/44 (mg C).d^{-1}
= 81.8 (mg C).d^{-1}

Measured OUR = 0.0036 (kg O_2).d^{-1}

Corresponding CUR = 0.0036 x 0.0185
= 66.6 (mg C).d^{-1}

The calculations indicate that under these conditions the carbon dioxide supply rate exceeded the carbon dioxide consumption rate, i.e. carbon dioxide was not rate limiting.

6.4.2 Carbon Dioxide Availability During the Bio-oxidation of Vaal Reefs Pyrite Concentrate

For the oxidation of Vaal Reefs concentrate at a solids loading of 75g and bed solids concentration of 20 per cent:

Liquid flowrate through the FBR = 584 $l.d^{-1}$

So, the CO_2 Transfer Rate = 584 x (0.416 - 0)
= 243 (mg CO_2).d^{-1}
= 243 x 12/44 (mg C).d^{-1}
= 66.3 (mg C).d^{-1}

Measured OUR = 0.0031 (kg O_2).d^{-1}
Corresponding CUR = 0.0031 x 0.0185
= 57.4 (mg C).d^{-1}

As the carbon dioxide transfer rate exceeds the demand, carbon dioxide does not limit the process under these conditions.

For the oxidation of Vaal Reefs concentrate at a solids loading of 75g and bed solids concentration of 45 per cent, i.e. the highest bed solids concentration in the Vaal Reefs study:

University of Cape Town

Liquid flowrate through the FBR = 514 $l.d^{-1}$

So, the CO_2 Transfer Rate = 514 x (0.416 - 0)
= 214 (mg CO_2).d^{-1}
= 214 x 12/44 (mg C).d^{-1}
= 58.3 (mg C).d^{-1}

Measured OUR = 0.0031 (kg O_2).d^{-1}
Corresponding CUR = 0.0031 x 0.0185
= 57.4 (mg C).d^{-1}

The carbon dioxide demand is below the transfer rate, so carbon dioxide limited conditions would not be expected. The two values are, however, very close indicating that a bed solids concentration of 45 per cent was a reasonable upper limit for the study. At higher bed solids concentrations, carbon dioxide limitation would be expected to occur.

In the FBR system, the free bacteria are continuously cycled between the fluidised bed and the surge tank. This means that even though carbon dioxide limited conditions could exist in the fluidised bed, the free bacteria would still be periodically exposed, in the surge tank, to conditions where carbon dioxide was readily available for cell growth. It has been shown by Mandl (1984) that the bacterial oxidation function is unaffected by carbon dioxide limitation as non-growing cells in the absence of carbon dioxide were still able to oxidise ferrous ions.

6.5 APPLICATIONS OF THE FBR SYSTEM

The fact that bio-oxidation rates determined in the FBR have been shown to be comparable to those determined in both a 0.003 m^{-3} batch lab-scale stirred tank reactor and in a 0.045 m^{-3} continuous stirred tank reactor (i.e. the reactor used by van Staden (1991)) demonstrates the applicability of the FBR for determining bio-

University of Cape Town

oxidation kinetics. The tests can be performed under controlled and well-defined conditions and only a small amount of sample is required (*ca.* 75g).

The oxygen demand per unit mass of ore can also be determined from an oxygen mass balance over the FBR. Accurate dissolved oxygen concentrations, independent of probe response, can be measured as little change in concentration will occur during the time required to take a measurement.

The critical dissolved oxygen concentration, at which the bio-oxidation rate is adversely affected due to oxygen limitation, can also be determined by performing runs at a constant bed solids concentration (i.e. constant OTP) and a range of overall system solids loadings (i.e. overall solid-to-liquid ratios).

6.6 CONCLUSIONS FROM THE FBR TESTWORK

The FBR testwork performed at a constant overall solids-to-liquid ratio (constant overall system solids loading) indicated that the bio-oxidation rate was independent of the solids concentration under conditions where sufficient oxygen was available. Carbon dioxide was also shown not to be limiting the process under the test conditions. The results have demonstrated that it is not the solids concentration *per se* that affects the bio-oxidation rate during operation at high solids concentration, but rather the oxygen availability in the reactor.

Oxygen limited conditions, at high solids loadings in the FBR have been shown to lower the bio-oxidation rate. The measured bio-oxidation rate at high solids loadings, that result in oxygen-limited conditions, is defined by the oxygen transfer potential (OTP) of the system.

The bio-oxidation rate measured in the FBR is comparable to rates determined in conventional stirred tank bio-reactors. The FBR has emerged as a useful tool for determining the specific oxidation rate of sulphides under controlled, well-defined conditions. Critical dissolved oxygen concentrations as well as oxygen utilisation rates can also be readily determined using a FBR.

University of Cape Town

The data generated in this chapter have been compared with the data generated in the batch reactors in Chapter Seven.

University of Cape Town

CHAPTER SEVEN

SUMMARY AND DISCUSSION OF TESTWORK CONDUCTED TO INVESTIGATE THE EFFECT OF OXYGEN AVAILABILITY ON BACTERIAL OXIDATION

University of Cape Town

Testwork has been conducted to investigate the effect of oxygen availability on the bacterial oxidation rate, with particular emphasis on operation at high concentrations of solids in the bioreactors. The studies have centered around the effect of solids concentration and more specifically, the influence of the sulphide solids concentration on the highest solids concentration at which a reactor can be operated at the maximum specific bacterial oxidation rate. This chapter has been included to summarise all of the experimental results from this work.

The testwork has involved the operation of batch stirred tank reactors (STR) at a range of solids concentrations, using materials of different sulphide grades. The results of the experiments have been discussed in Chapter Five. A fluidised bed reactor (FBR) was also used for similar testwork, although in this case the reactor enabled the solids and liquid environments to be controlled independently, giving greater control over the experimental conditions. The results of the FBR testwork have been presented in Chapter Six.

All of the experimental data have been collated and are shown in Table 7.1, allowing the comparison of the different tests on a common basis. Interpretation of the data should not be attempted in isolation from the discussions presented in Chapters Five and Six. Explanations of some apparent anomalies in the data have been dealt with in those chapters and are not repeated in this chapter. The solids concentration of the system has been shown in all cases and in the FBR testwork, the bed solids concentration is also

Table 7.1 : Summary of Fluidised Bed Reactor and Batch Stirred Tank Reactor Data

Appendix 3 Data Table	Material	Cs System kg/m3	Cs Bed $kg.m^{-3}$	Cpyr (kg Pyrite)/(kg solids)	OTP $(kg\ O_2)/m^3.d$	OUR $(kg\ O_2)/m^3.d$	Rpyr/ volume (kg Pyrite)/$m^3.d$	Rpyr/ Csolids (kg Pyrite)/(kg solids)·d	Rpyr/ Cpyrite (kg Pyrite)/(kg Pyrite)·d	DO $mg.l^{-1}$
FLUIDISED BED REACTOR TESTWORK										
I1	VRC	17	200	0.55	8.94	8.03	9.38	0.0469	0.0852	0.7
I2	VRC	17	200	0.55	11.31	5.55	9.82	0.0491	0.0892	3.4
I3	VRC B2	17	200	0.55	13.59	11.06	8.28	0.0414	0.0752	1.5
I4	VRC	17	250	0.55			10.23	0.0409	0.0744	
I5	VRC	17	250	0.55			10.45	0.0418	0.0760	
I6	VRC B2	17	250	0.55	17.73	12.03	11.20	0.0448	0.0814	1.6
I7	VRC	17	300	0.55	11.45	9.24	11.25	0.0375	0.0682	1.8
J1	VRC	17	350	0.55			14.25	0.0407	0.0740	1.4
I8	VRC	17	450	0.55			18.90	0.0420	0.0764	
I9	VRC	17	450	0.55	19.50	11.84	19.17	0.0426	0.0775	
H2	VRC	34	200	0.55	4.14	4.28	5.22	0.0261	0.0475	0.4
H3	VRC	45	200	0.55	3.46	3.58	3.34	0.0167	0.0304	0.4
H4	Prieska	17	200	0.84	13.82	9.60	8.02	0.0401	0.0477	2.5
H5	Prieska	45	200	0.84	4.46	4.68	7.16	0.0358	0.0426	0.2
BATCH STIRRED TANK REACTOR TESTWORK										
B1	ROM	200	-	0.02	30.34	0.00	0.19	0.0009	0.0470	7.6
B2	ROM	200	-	0.02	30.34	0.00	0.24	0.0012	0.0600	7.6
B3	ROM	400	-	0.02	32.37	0.94	0.38	0.0010	0.0480	7.4
B4	ROM	600	-	0.02	23.19	0.67	0.59	0.0010	0.0495	7.4
C1	Prieska	100	-	0.84	17.97	2.21	3.60	0.0360	0.0429	6.4
C2	Prieska	100	-	0.84	17.97	6.64	4.00	0.0400	0.0477	4.8
D1	Prieska/Q	200	-	0.42	14.77	4.32	3.52	0.0176	0.0420	5.3
D2	Prieska/Q	300	-	0.28	13.25	2.65	3.54	0.0118	0.0420	5.9

KEY

Cs	:	concentration of solids
Cpyr	:	concentration of pyrite
DO	:	dissolved oxygen concentration
Prieska	:	Prieska pyrite concentrate
Prieska/Q	:	Prieska pyrite concentrate/quartz mixture
ROM	:	Vaal Reefs Run-of-Mine ore
VRC	:	Vaal Reefs pyrite concentrate
VRC B2	:	Vaal Reefs pyrite concentrate, batch 2

University of Cape Town

shown. The concentration of pyrite has been expressed as a fraction of the total solid material in the reactors. The oxygen transfer potential (OTP), measured oxygen utilisation rate (OUR) and the dissolved oxygen concentration (DO) have also been included. The pyrite bio-oxidation rate has been expressed on three different bases: reactor volume; with respect to the total amount of solid material in the reactor; and with respect to the amount of pyrite material initially present in the reactor. For pyrite oxidation, stoichiometry indicates that for every 1 kg of pyrite oxidised, 1 kg of oxygen is consumed. Thus, the pyrite oxidation rate based on reactor volume can be compared directly with the oxygen utilisation rate.

It can be seen that the specific pyrite oxidation rate is essentially constant for a particular material, under conditions when sufficient oxygen was available. The specific oxidation rates of the run-of-mine ore and the Prieska pyrite concentrate were below the oxidation rate of the Vaal Reefs pyrite concentrate. This was most likely due to different levels of bacterial adaptation. The mixed bacterial culture used for this experimental work had been adapted to oxidation of Vaal Reefs concentrate over two years in the laboratory at the University of Cape Town. The culture had originally been obtained from Mintek (Randburg, South Africa) where it had also been grown on the concentrate for a number of years. In contrast, the bacteria had not been previously exposed to either the run-of-mine ore or the Prieska pyrite concentrate. In both cases when repeat tests were conducted on these two materials (i.e. test B2 and test C2) the specific oxidation rates measured were higher than those obtained on the first set. Longer-term adaptation of the bacteria to oxidation of the two materials would probably lead to higher oxidation rates, more in line with the Vaal Reefs oxidation rate.

The specific pyrite oxidation rates measured in the FBR tests conducted on the Prieska concentrate were in good agreement with corresponding rates measured in stirred tank reactor tests. In Chapter Six it was also noted that the oxidation rate of Vaal Reefs Concentrate was within 25 per cent of the value obtained by van Staden (1991) on a similar material in a continuous reactor system. The oxidation rate achieved in a continuous system is generally higher than that obtained in a batch reactor.

University of Cape Town

The adverse effect of oxygen limitation on the bacterial oxidation rate is evident in those FBR tests in which oxygen limitation occurred. Under oxygen-limited conditions during FBR tests H2 and H3, where the dissolved oxygen concentration had dropped to 0.4 mg.l^{-1}, the specific bio-oxidation rate was substantially lower than the rate obtained in tests when sufficient oxygen was available. In all tests where sufficient oxygen was available (i.e. the dissolved oxygen concentration exceeded 0.7 mg.l^{-1}) the oxygen transfer potential exceeded the oxygen utilisation rate. Oxygen limitation was also encountered during the bio-oxidation of the Prieska pyrite concentrate in the FBR at a system solids concentration of 45 kg.m^{-3}. Similar adverse effects on the oxidation rate were observed.

All of the stirred tank and FBR oxidation rate data have been plotted against the measured oxygen transfer potential under the various operating conditions, in Figure 7.1. The figure proves the hypothesis that oxygen transfer limits the bio-oxidation rate. All of the data (with the exception of two points) fall on or below the diagonal line. This indicates that the bio-oxidation rate does not exceed the oxygen transfer potential. For the hypothesis to be valid the bacterial oxidation rate cannot be greater than the oxygen transfer rate. The two data points that fall a little above the diagonal are due to the fact that the OTP is based on a dissolved oxygen concentration of 0.7 mg.l^{-1} as a minimum requirement for unlimited bacterial oxidation. Bacterial oxidation will, however, still occur at dissolved oxygen concentrations below this value, although the bacterial growth will be inhibited. A dissolved oxygen concentration that is below the critical concentration will result in a greater driving force (C^{*} - C) which allows the bio-oxidation rate to be a little above the oxygen transfer potential. The data falling above the diagonal line indicate operation under oxygen-limited conditions. The oxygen transfer potential of a system defines the highest concentration of solids at which bacterial oxidation may be performed at the maximum specific oxidation rate.

University of Cape Town

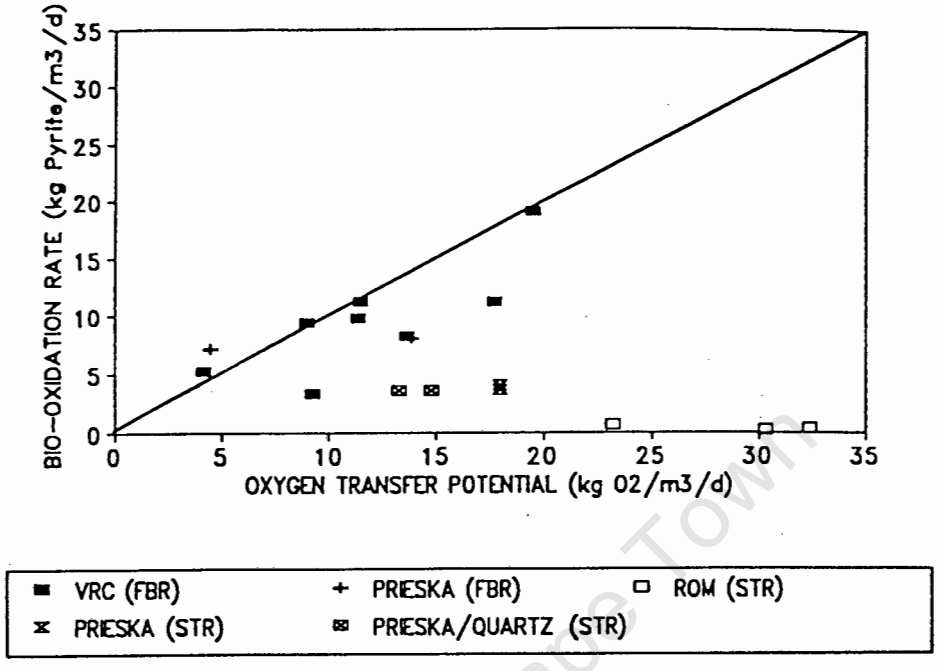


Figure 7.1 : Bio-oxidation Rate vs. Oxygen Transfer Potential Data from Batch Stirred Tank Reactor (STR) and Fluidised Bed Reactor (FBR) Tests. Legend key is given below Table 7.1.

University of Cape Town

CHAPTER EIGHT

EFFECT OF FREE CELL DEPLETION ON THE BIO-OXIDATION RATE OF PYRITE IN A FLUIDISED BED REACTOR

University of Cape Town

8.1 INTRODUCTION

During the bio-oxidation of sulphide minerals, approximately 90 per cent of the bacterial population have been found to attach directly to the mineral surface (McGoran *et al.*, 1969). The nature and selectivity of the bacterial attachment is not clearly understood (Murthy and Natarajan, 1992). These bacteria oxidise the iron and sulphur in the matrix and are said to participate in "direct oxidation" of the mineral (Roy and Mishra, 1981). The remaining unattached, or "free" bacteria, convert ferrous ions present in the solution, into the ferric form (Brierley, 1978). These bacteria participate "indirectly" in the oxidation process as the ferric ion that they generate is a strong oxidising agent which will attack and oxidise the mineral. Controversy exists as to which of the two oxidation mechanisms is the more significant (Murthy and Natarajan, 1992). The ability to oxidise ferrous iron is not restricted to the free bacteria because *Thiobacillus ferrooxidans* grown as a biofilm attached to an inert support medium has also been demonstrated to be capable of ferrous ion oxidation (Karamanev and Nikolov, 1988).

A model accounting for the continuous growth of *Thiobacillus ferrooxidans*, with respect to the role of the bacteria in solution, attached to the solid surface and the effect of soluble substrate concentration was developed by Chang and Myerson (1982). During the course of their experimental work the researchers found that the growth rate of the bacteria on the solids surface was a function of

the solid dilution rate and the total surface area concentration. They also proved their hypothesis that the number of bacteria attached to the solid surface was a function of the number of bacteria in solution and the surface area available for attachment. The researchers assumed a Langmuir-type absorption relationship that could describe the rate of bacterial absorption and desorption. Their equation showed that the concentration of bacteria attached to the solid surface was a first order function of the bacterial concentration in solution at low concentrations. The first order dependency decreases to zero order as the bacterial population is increased.

Whilst oxidising an arsenopyrite-pyrite concentrate, Komnitsas and Pooley (1991) noticed that as the solids concentration in their reactors was increased, the redox potential (ORP) dropped. This observation was attributed to the excessive attachment of bacteria to the mineral, lowering the number of free bacteria. The small population of free bacteria was thought to have been incapable of oxidising all of the ferrous iron that was generated during the oxidation process at high solids concentrations. In such a situation, an increase in the ferrous iron concentration in the reactor would cause the ferric-to-ferrous ratio to drop, resulting in a lowering of the ORP and in turn, a reduced oxidation rate. The literature review presented in Chapter Three, highlighted the fact that low total cell-to-solids concentrations have been found to cause lower bio-oxidation rates in a number of different studies (such as that of Detz and Barvinchak, 1979). The results, however, of an investigation on the effect that the free bacterial population, in particular, has on the bio-oxidation rate has not been reported.

During bio-oxidation at high solids concentrations, the free and attached bacterial populations are likely to be affected differently by hydrodynamic and mechanical stresses (Papoutsakis, 1991). It is important that the effect of a depletion in one or other population on the bacterial oxidation rate is known.

The objective of this study was to assess the relative significance of the attached and un-attached (i.e. free) bacteria in the bio-oxidation process. By suddenly replacing the liquid circulating through the FBR system, with bacteria-free liquid of the same composition, the free bacterial concentration could be artificially lowered by at least three orders of magnitude. The effect that the depletion of the free cell population had on the bio-oxidation rate could then be determined.

University of Cape Town

The replacement solution was matched to the conditions in the reactor just prior to free-cell depletion, so that the attached bacteria that would remain in the system throughout the procedure, would not be affected. The depletion technique is discussed in more detail below.

8.2 FREE CELL DEPLETION TECHNIQUE

Just prior to depletion, the total iron concentration, ORP and the pH of the liquor was determined. Fresh Silverman and Lundgren (1959) medium was prepared (Section 3.3) so as to contain the same total iron and nutrient salt concentrations and have the same ORP and pH, as the measured reactor conditions. Different amounts of ferrous or ferric sulphate were added to achieve the desired total iron concentration. Hydrogen peroxide was used to chemically oxidise excess ferrous iron, to raise the ORP to the same level as in the reactor. To avoid a temperature shock to the attached bacteria remaining in the FBR, the replacement medium was warmed to 35°C in an incubator. Ten litres of solution were used for the depletion procedure.

To start the depletion step, the return from the top of the FBR to the surge tank was temporarily broken and the liquor wasted. The surge tank was allowed to drain completely before replacement medium was poured into it. This further reduced the system volume, making the depletion of free cells far more effective. Once the ten litres of replacement solution had been added to the system, the return from the FBR was reconnected to the surge tank and batch operation continued as normal. The free cell removal could be completed within a matter of minutes. Throughout the removal, the flowrate of liquid to the fluidised bed was uninterrupted, ensuring that the attached bacteria were not affected by the procedure.

8.3 RESULTS OF THE FREE CELL DEPLETION TESTWORK

In all of the free cell depletion studies, a system solids concentration of 17 $kg.m^{-3}$ of Vaal Reefs pyrite concentrate was used and the FBR was operated at a bed solids concentration of 350 $kg.m^{-3}$ (35 per cent). Four free-cell depletion tests

University of Cape Town

were performed, with free cell removal occurring after 4 hours, 1 day, 3 days and 17 days of normal batch operation. Experimental data are given in Appendix 3, Tables J2, J3, J4 and J5 respectively. Cell attachment has been found to occur within 12 minutes (Sanmugasunderam, 1981), so removal of free cells 4 hours after inoculation was assumed to allow sufficient time for bacterial attachment. A further FBR run was performed at the same operating conditions, but operated as a usual batch test throughout, to act as a control (Experimental data for this run are shown in Appendix 3, Table J1). Free cells were enumerated on a daily basis, during the periods both before and after free cell removal. The ORP, pH, dissolved oxygen concentration and the total iron concentration were also determined daily.

After depletion, the free cell concentration was found to be reduced to well below 5×10^5 cells.ml^{-1}, representing a nearly 1000-fold reduction in the cell concentration on inoculation. The free cell concentrations measured in the different tests after the depletion step are shown in Figure 8.1.

To determine the rate at which the free cell concentration increased, the natural logarithms of the data were plotted in Figure 8.2. The bacterial growth rate was determined from the slope of the best-fit line through the data. The data collected during the control test have been included in this figure for comparison. As expected, the plot obtained from the control test was essentially a straight line, indicative of logarithmic bacterial growth. The free cell data after depletion were different, however, in that two "phases" of cell increase were apparent. During the first phase, there was a rapid, increase in the cell concentration, at rates approximately ten times the growth rate determined in the control test. After this rapid initial increase in concentration, the second "phase" was characterised by slower increase that was a similar magnitude as the control growth rate. The manner in which the free cell concentration rose during the first phase was unusual in that it was not logarithmic, as is normally expected for bacterial growth, the rate of cell increase being better described by a curve when plotted on semi-logarithmic axes, rather than the straight line that would be characteristic of logarithmic growth. The second "phase" did, however, show logarithmic increase. The free bacterial growth rate in the control case was calculated from the slope of the best-fit line through the data in Figure 8.2. For the depletion tests, the best-fit straight line was fitted to data selected as being

University of Cape Town

representative of each of the two separate phases. A rate of increase in the free cell concentration was estimated from the slope of the line during each phase. Rates determined from the various tests are tabulated in Table 8.1.

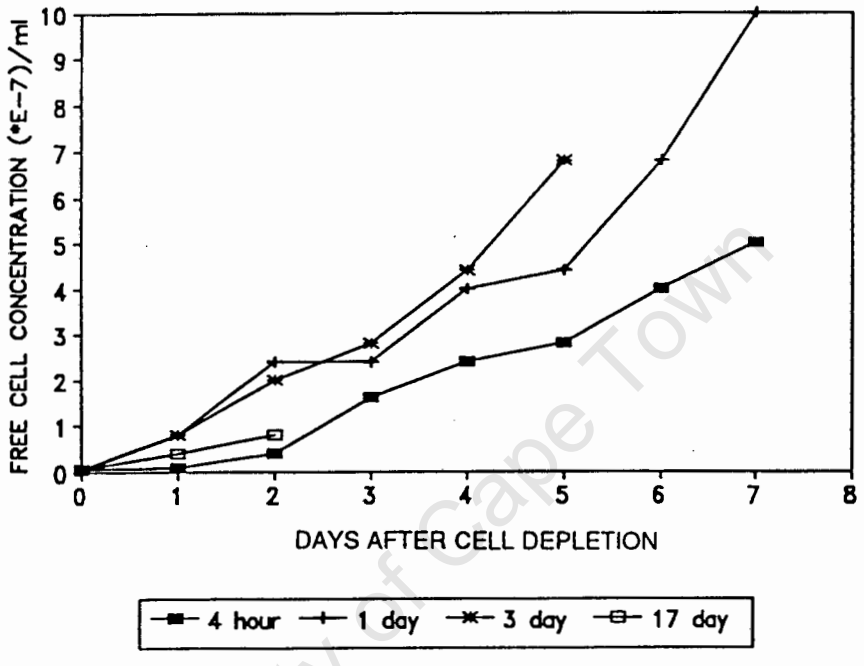


Figure 8.1 Free Cell Concentrations Measured After Depletion

University of Cape Town

After depletion, the rate of increase in the free cell concentration during both "phases" was found to be higher when the system was operated for a longer period under normal batch conditions before the free cell removal was performed. The fact that the rate of increase in the population immediately after the depletion was so much higher than the normal growth rate, indicated that bacteria must have detached from the solid particles to repopulate the solution. This meant that the increase in free cell numbers in the free cell depletion tests could not be solely attributed to growth. In his study of bacterial attachment and release from mineral surfaces, Sanmugasunderam (1981) found that the bacteria were produced on the mineral surface, and were capable of detaching easily. During normal batch operation, the numbers of bacteria present in both the solution and attached to the mineral surface increase with the culture age. The later that free cell depletion is performed, the greater the number of attached bacteria that are

retained on the mineral surface. This implies that cultures that are older when the free cells are removed have larger attached cell populations which are able to act as larger "reservoirs" for the rapid replenishment of the free bacteria population during the "recovery" period.

It is possible that depletion of the free bacteria may have had two effects on the system: firstly, it may upset the equilibrium between the bacteria in the solution and attached to the mineral surface, causing desorption of attached bacteria by a Langmuir-type relationship as proposed by Chang and Myerson (1982); secondly, the desorption of bacteria due to the low concentration of bacteria in the solution may have stimulated growth on the solid surface as the surface would no longer be saturated with bacteria.

The iron concentration data measured during the two phases of recovery were used to calculate an average bio-oxidation rate that would be characteristic of each period. The rate determined during the control test was taken as being representative of the bio-oxidation rate prior to free cell depletion for all of the tests. The rate data are presented in Table 8.1.

It was found that free cell depletion had little effect on the pyrite oxidation rate in both the 1- and 3-day tests. The rate was, however, almost halved when depletion was performed after only 4 hours. The ferrous oxidation rate, indicated by the change in ORP with time, was found to be below that in the other cases.

The ORP of 504mV measured in the 4-hour tests, immediately prior to depletion, was approximately 200 mV lower than in the cases when the free cell removal was performed after 1- and 3-days of normal batch operation (628 and 700mV respectively). To examine whether the low ORP immediately prior to cell depletion in the 4-hour test had adversely affected the bio-oxidation rate, the ORP of the fresh medium used for replacement after free cell removal in the 17-day test was deliberately chosen to be low, i.e. 332 mV. In the 17-day test, the rate at which the ORP rose was similar to the control case. Insufficient un-oxidised pyrite remained during the 17-day test to enable a pyrite oxidation rate to be determined, the ferrous sulphate having acted as the primary energy source for the bacteria. The results indicated that the low concentration of cells (attached) remaining in the system after free cell removal in the 4-hour test, was

University of Cape Town

responsible for the lower pyrite oxidation rate that was observed and not the low ORP. During the 4 hours of normal batch operation in this particular test, the total bacterial population would not have increased substantially over the concentration of 10^8 cells.ml^{-1} present at inoculation, so the residual population of attached bacteria after free cell depletion would, as a consequence, be small. Below a bacterial population of 10^8 cells.ml^{-1}, Detz and Barvinchak (1979) showed that the oxidation rate was strongly dependent on the cell concentration.

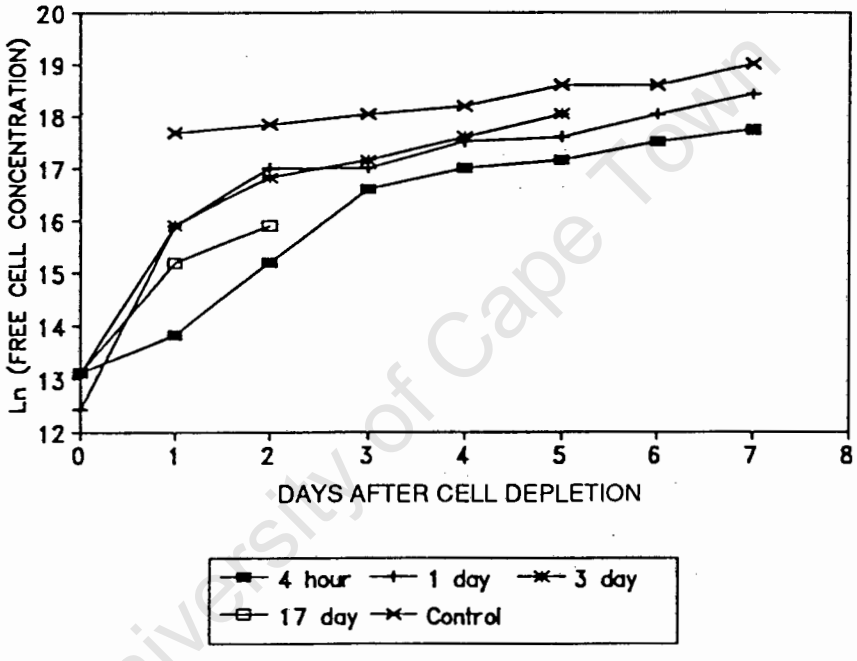


Figure 8.2: Natural Logarithm of Free Cell Concentration vs. Time after Free Cell Depletion

In light of the observations made in the 4-hour and 17-day tests, the low ORP values encountered by Komnitsas and Pooley (1991) during bio-oxidation at high solids concentrations are most likely to have been caused by a low overall population than merely a small free bacteria concentration. Detz and Barvinchak (1979) noted that a low cell-to-solid ratio caused low bio-oxidation rates.

University of Cape Town

DEPLETION STAGE:	PRE	POST		AVERAGE PYRITE RATE (POST DEPLETION)
		PHASE 1	PHASE 2	
	Growth day^{-1}	Recovery day^{-1}	Recovery day^{-1}	$(kg\ Pyrite)^{-1}(kg\ ore)^{-1}d^{-1}$
Control	0.216			0.0407
4-hour		1.178	0.278	0.0227
1-day		2.282	0.295	0.0392
3-day		2.770	0.506	0.0409
17-day		2.080	0.690	-

Table 8.1: Free Cell Recovery Rates After Free Cell Depletion and the Corresponding Pyrite Oxidation Rates During the Recovery Period.

University of Cape Town

8.4 CONCLUSIONS FROM THE FREE CELL DEPLETION STUDY

The free cell depletion studies indicated that the bio-oxidation rate was generally not affected by the sudden depletion of the free bacterial population. If, however, there was an insufficient number of attached bacteria remaining in the system after the removal of free bacteria, i.e. the coverage of the solid surface by the bacteria was low, then both the pyrite and ferrous oxidation rates were adversely affected. This was typically the case when there was only a short period of operation (in the region of four hours) prior to free cell depletion.

As the rate of increase in the free bacterial concentration in the post depletion period was between 5 and 10 times the normal bacterial growth rate, it was likely that attached bacteria desorbed from the mineral surface to replenish the solution, maintaining an equilibrium between the free and attached bacteria. The free bacterial concentration rose far more rapidly after free cell depletion, the longer the culture was operated in the normal batch mode prior to the depletion step. This trend was due to the increasing number of attached cells that were retained in the system after depletion, with increasing culture age. These

bacteria acted as a larger reservoir of bacteria making solution replenishment more rapid.

The testwork indicated that a low ORP results from a low total bacterial concentration. If sufficient attached bacteria are present in the system, they will detach to replenish the free bacterial population should the latter become depleted. This action maintains both the ferrous oxidation capacity and the ORP in the reactor.

The importance of the attached bacterial population in bio-oxidation was highlighted by the results of this study, as it is the depletion of this population that will ultimately lead to lower bio-oxidation rates. The low attached cell population could result from either a low total concentration of bacteria on inoculation, or alternatively from mechanical damage at high solids concentration. In investigations into the effect of shear on bio-oxidation, it will be important to accurately monitor the size of both the attached and free bacterial populations.

University of Cape Town

CHAPTER NINE

EFFECT OF FERRIC SULPHATE CONCENTRATION ON THE BIO-OXIDATION RATE AND THE FERROUS OXIDATION ABILITY OF THE BACTERIA

University of Cape Town

9.1 INTRODUCTION

Ferric iron is known to inhibit the growth of the bacteria that are used for bio-oxidation (Kumar and Gandhi, 1990). During the batch culture of *Thiobacillus ferrooxidans* on ferrous sulphate, Kelly and Jones (1978) found that the ferric iron competitively inhibited oxidation. The effect of ferric iron inhibition was shown empirically by Silver (1978) to be a parabolic function of the ferric iron concentration.

In their study, Kelly and Jones (1978) discovered that ferric sulphate did not affect the fixation of carbon dioxide, the bacteria's source of carbon for growth. So the inhibitory effect of ferric iron on the bacterial metabolism and growth was through its effect on the ferrous oxidation mechanism of the micro-organisms. The exact mechanism of ferric ion poisoning has not yet been established (Kumar and Gandhi, 1990).

Work conducted on the inhibition of *Thiobacillus ferrooxidans* by ferric iron was discussed by Brierley (1978) in a review of bacterial oxidation. Low ferric iron concentrations between 0.3 and 4.5 $g.l^{-1}$ were found by Kelly *et al.* (1977) to enhance bio-oxidation. Ferric concentrations above 11 $g.l^{-1}$ were, however, found to inhibit the bacteria and reduce the substrate oxidation rate. It should be noted that these were the concentrations at which an adverse effect on bacterial growth and oxidation were first detected. The bacteria were not completely inhibited and both growth and oxidation were still possible at those ferric ion

levels; complete inhibition of bacterial function would occur at higher ferric ion concentrations. With the culture used by Wong *et al.* (1973), inhibition was observed at a far lower ferric iron concentration of 0.14 g.l^{-1}. An extended lag phase was observed at 5g $Fe^{3+}l^{-1}$ by Kumar and Gandhi (1990) and both the growth and oxidation ability of their culture was impaired. Similar, though more severe observations were made at 10 g.l^{-1}. The culture was totally inhibited at 20 g.l^{-1}.

When grown in free culture, Karamanev and Nikolov (1988) found that the ferrous oxidation ability of *Thiobacillus ferrooxidans* was inhibited by ferric concentrations in excess of 6 g.l^{-1}. When grown as a biofilm, however, the bacteria were found to be uninhibited by ferric concentrations between 14 and 50 g.l^{-1} (Nikolov and Karamenev, 1988). The variation in the ferric iron concentration found to be inhibitory to the bacteria is likely to arise from differences in strains as well as adaptation of cultures. The relative tolerance of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* to both ferrous and ferric iron was studied by Collinet and Morin (1990). The researchers found that ferric iron was far more toxic to both bacteria than ferrous iron. *Thiobacillus thiooxidans* was also found to be more tolerant to ferrous ion than *Thiobacillus ferrooxidans*. Both types of bacteria started to be inhibited by ferric ions at 10 g.l^{-1}, and were completely inhibited at 20 g.l^{-1}. Evidence of bacterial adaptation to tolerate high metal ion concentrations has been noted by a number of researchers (Brierley, 1978; Torma, 1977; Zajic, 1969)

Researchers such as Komnitsas and Pooley (1991) have attributed low cell-to-solid ratios as the cause of low redox potentials during operation at high solids concentrations. The bacterial population was thought to be too small to oxidise ferrous ions at the rate necessary to maintain essentially all of the iron in the ferric form, i.e. maintain a high redox potential (ORP).

Based on the discussion above of reports in the literature of the inhibitory effect of ferric iron it is also possible that the concentration of ferric iron that are generated at high concentrations of solids may inhibit the ability of the bacteria to oxidise ferrous iron. The resulting build-up of ferrous iron would lead to a drop in the redox potential.

University of Cape Town

The objective of this study was to investigate the ability of the bacteria to oxidise amounts of ferrous iron equivalent to those generated during bio-oxidation at various solids concentrations and to assess the effect of ferric iron build-up on the ferrous oxidation by the bacteria.

Runs were conducted in the FBR system at a constant solid-to-liquid ratio and bed solids concentration. In conventional reactors, such as stirred tank reactors, the amount of ferrous iron generated increases with increasing solids concentration. In conjunction with increasing solids concentration, however, factors such as oxygen availability are also affected. In the FBR system, though, the only parameter that was varied was the amount of ferrous sulphate added. All other operating conditions could be maintained constant throughout. The reactor was inoculated with sufficient bacteria to ensure an initial reactor concentration of 10^8 cells.ml^{-1}, a concentration determined by both Detz and Barvinchak (1979) and Torma (1977) as adequate to prevent bacterial limitation of the bio-oxidation process.

Different amounts of ferrous sulphate were added to the FBR daily during the various runs, to simulate the amount of ferrous iron that could be generated in systems operating at particular solids concentrations. The second objective of this study was to investigate the effect of ferric sulphate build-up on the bio-oxidation rate. When the bio-oxidation system is operating efficiently, the bacteria maintain essentially all (in the FBR tests, typically above 99.8 per cent) of the iron in the ferric form. Research into the effect of ferric iron build-up on the bio-oxidation rate is particularly pertinent as it is a feature common to the oxidation of all sulphides containing iron - particularly pyrite and arsenopyrite, with which refractory gold is commonly associated.

University of Cape Town

9.2 FERROUS SULPHATE ADDITION TECHNIQUE

When the FBR is operated at the usual overall solids-to-liquid ratio of 1.7 per cent (17 kg.m^{-3}), very little ferrous iron enters the solution as the pyrite is oxidised, due to the low solids charge to the reactor. By adding ferrous sulphate to the reactor on a daily basis, it is possible to approximate the rate at which ferrous iron could enter the solution during the oxidation of a larger ore charge.

In the "indirect" method of bio-oxidation (Free, 1991) ferrous ions are oxidised into the ferric form by the bacteria. These ferric ions are strong oxidising agents and they attack the pyrite, hence the "indirect" participation by the free bacteria in the oxidation process. During the oxidation step the ferric ions are reduced into the ferrous form once more and the cycle continues. Additional ferrous ions are produced during the breakdown of iron-containing sulphide minerals such as pyrite (FeS_2), as one of the oxidation products. Oxidation also occurs via the "direct" method where the bacteria attach directly to the mineral surface and oxidise the pyrite. Free (1991) found that the both direct and indirect methods of oxidation were significant contributors to the overall oxidation rate during the oxidation of sulphides.

A standard ore charge of 1.7 per cent (17 $kg.m^{-3}$) was used for the FBR runs. For the simulation, an overall solids-to-liquid ratio in the FBR was selected, eg. 10 per cent (100 $kg.m^{-3}$), and the corresponding rate at which iron would enter the solution was calculated using a specific pyrite oxidation rate of 0.02 kg Fe/kg ore/d (this oxidation rate was determined during the FBR testwork discussed in Chapter 6). The actual rate at which iron would enter solution from the 1.7 per cent ore charge was taken into account when calculating the additional ferrous sulphate to be added on a daily basis. Sample calculations for the simulation of oxidation at an overall solids concentration of 10 per cent are shown below:

Pyrite Oxidation Rate	=	0.02 $(kg\ Fe)(kg\ ore)^{-1}d^{-1}$
Hypothetical overall solids concentration	=	10%
	=	100 $kg.m^{-3}$
Volume of FBR system	=	4.5 l
Iron Solubilisation Rate	=	4.5 * 100 * 0.02
	=	9.0 $(g\ Fe).d^{-1}$

The amount of iron entering solution from the actual ore charge:

University of Cape Town

Actual Solubilisation Rate = 75 * 0.02
= 1.5 (g Fe).d^{-1}

Calculate additional ferrous sulphate requirement:

Additional Iron = 9.0 - 1.5
= 7.5 (g Fe).d^{-1}

Additional $FeSO_4 .7H_2O$ = 7.5 * 4.975
= 37.2 (g $FeSO_4 .7H_2O$).d^{-1}

Sufficient bacteria were added in the inoculum to provide an initial reactor cell concentration of 10^8 cells.ml^{-1}. This gave a ratio of bacteria-to-solids of 6×10^{10} cells.g^{-1}.

University of Cape Town

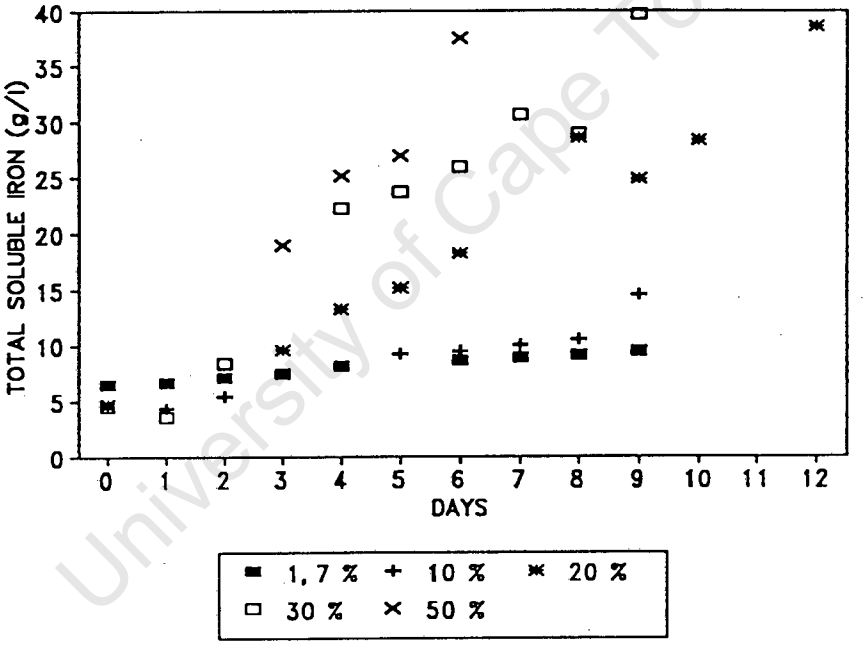
9.3 RESULTS FROM THE FERROUS SULPHATE ADDITION STUDY

The FBR was operated at a constant overall solids-to-liquid ratio of 17 kg.m^{-3} and at a constant bed solids concentration of 350 kg.m^{-3}. Amounts of ferrous sulphate were added during the FBR runs to simulate ferrous iron generation during the oxidation at overall solids-to-liquid ratios of 1.7; 10; 20; 30; and 50 per cent (17, 100, 200, 300 and 500 kg.m^{-3}) solids. Experimental data are shown in Appendix 3, Table K. The amounts of ferrous sulphate added in each case are tabulated with the experimental data which is presented in Appendix 3.

As the iron concentration built up, iron began to precipitate in the form of jarosite. This meant that the quantity of iron added to the system each day, was not directly reflected in the build-up of iron in solution. The soluble iron concentrations measured during the course of the runs are shown in Figure 9.1.

Immediately after the addition of ferrous sulphate to the reactor, the ORP was generally found to drop from 700mV to approximately 450mV. Over the following 24-hour period, the ferrous iron was oxidised into the ferric form by the bacteria, resulting in a high ORP, in the region of 700 mV.

The ORP level was used as an indicator of whether or not the bacteria were capable of oxidising essentially all the ferrous iron within a 24-hour period. The ORP values attained by the system 24 hours after the addition of ferrous sulphate, are shown in Figure 9.2 for each of the tests. In all cases, during the first part of a run, after the lag phase, the ORP was found to be above 700 mV by the end of the daily period. This indicated that the standard bacterial population of 10^8 cells.ml^{-1} on inoculation, was capable of oxidising essentially all (i.e.>99 per cent) of the ferrous iron added to the system, even in the case approximating ferrous generation during operation at 50 per cent solids.



University of Cape Town

Figure 9.1: Soluble Iron Concentration Data Measured Daily in the FBR During the Staged Ferrous Iron Addition Testwork (Reactor was sampled each day prior to addition of ferrous sulphate)

At some point, however, in runs simulating solids concentrations of 20 per cent and above, a stage was reached where the ORP, measured at the end of the 24 hours, began to drop. This indicated that the bacteria were no longer capable of oxidising the amount of ferrous iron necessary to maintain the high ORP, i.e. ferrous ions were accumulating in solution. As further amounts of ferrous iron

continued to be added on a daily basis the ORP to dropped even further. The soluble iron concentration was found to be approximately 30 g.l^{-1} in all cases when the ORP began to decline. 30 g.l^{-1} was the lowest iron concentration at which a drop in the ORP was encountered. Due to the staged addition of ferrous sulphate in different quantities, in certain runs the iron concentration was never measured to be exactly 30 g.l^{-1}.

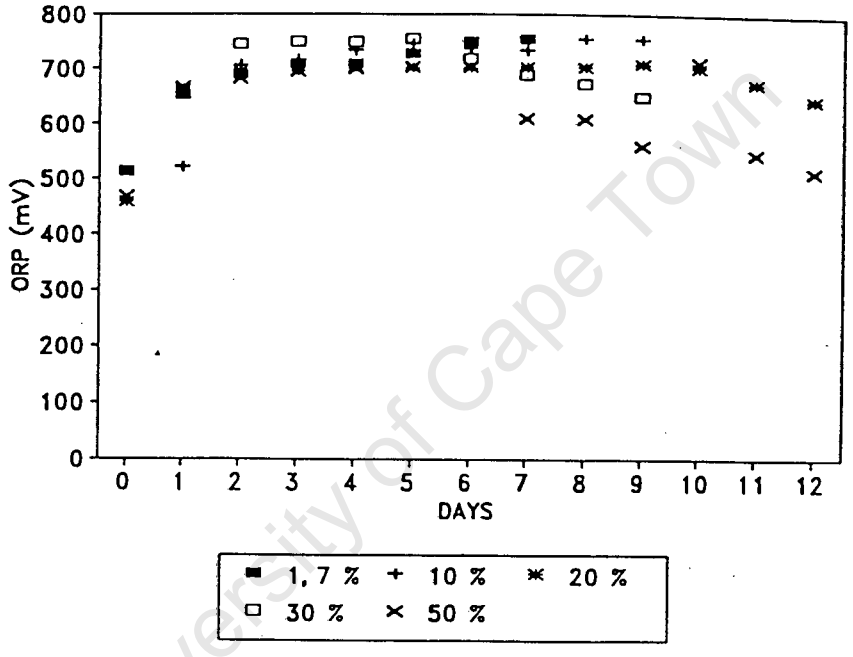


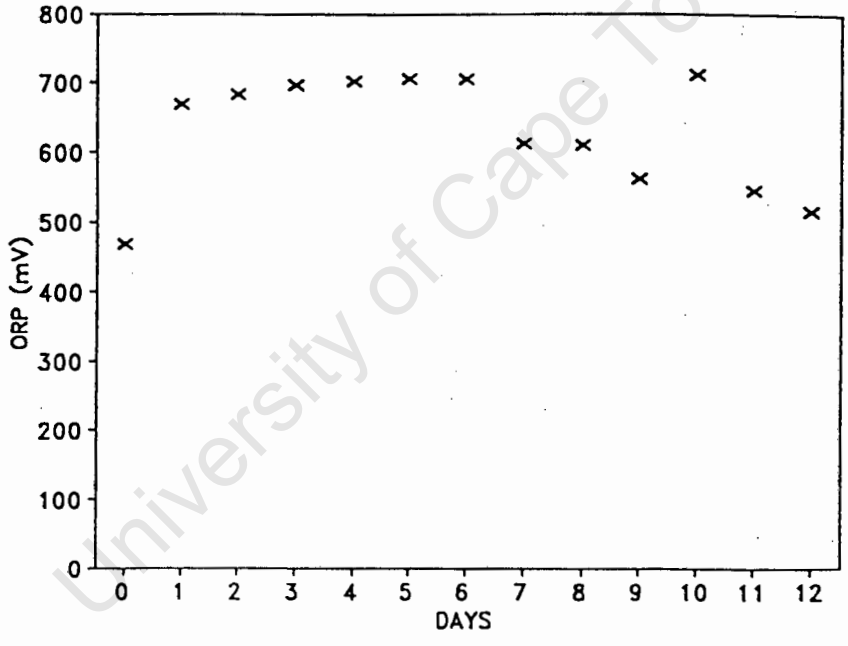
Figure 9.2 : Redox Potential (ORP) Measurements, 24 Hours After Ferrous Addition for Different Hypothetical Solids Concentrations.

University of Cape Town

The results of these tests are of consequence in batch operation, towards the end of a run where the iron concentration may have built up to this inhibitory level, as well as in the operation of continuous reactors where the steady-state iron concentration may be in excess of 30 g.l^{-1} during the oxidation of a high sulphide content material.

During the simulation of bio-oxidation at a solids concentration of 50 per cent, the iron concentration in the solution exceeded 30 g.l^{-1} by Day 6. Over the following three days the redox dropped from 704mV to 562mV. Redox data for this particular run are shown separately in Figure 9.3.

Ferrous sulphate was not added to the system on Day 9. By the end of the following 24-hour period, i.e. Day 10, the redox had risen to 713 mV. On Day 10, the daily addition of ferrous sulphate was recommenced and the ORP level at the end of the following 24 hours, was found to have decreased to 564mV. The results of this test indicated that the bacteria were still able to oxidise sufficient ferrous iron to achieve a redox potential that was in excess of 700 mV, but that a longer time was required to oxidise sufficient ferrous ions to attain this redox level. This was due to a lower bacterial ferrous oxidation rate that was most probably caused by the ferric iron inhibition.



University of Cape Town

Figure 9.3 : Redox Potential (ORP) Measurements, 24 hours after Ferrous Addition, for Test Approximating 50% Solids

As discussed by Brierley (1978) the exact ferric concentration at which the bacteria become inhibited is specific to a particular strain of bacteria. The mixed culture used in this study appeared to be more tolerant of ferric iron, than those used by Kelly *et al.* (1977), where inhibition was noted at a much lower concentration of approximately 11 g.l^{-1}.

Inoculum for this FBR study was obtained from a master culture in which the iron concentration never exceeded 10 g.l^{-1}. Bacteria have, however, been shown to be able to adapt to some particular environmental conditions over approximately 5 successive subcultures (Torma, 1977). No strain development was attempted during this study.

9.4 CONCLUSIONS FROM THE FERROUS SULPHATE ADDITION STUDIES

The results from the staged addition of ferrous sulphate to FBR runs indicated that an initial bacterial concentration of 10^8 cells.ml^{-1} (cell-to-solid ratio of 6 x 10^{10} cells.g^{-1}) was capable of oxidising 10 (g Fe^{2+}).l^{-1}.d^{-1} (i.e. as in the test approximating an overall solids concentration of 50 per cent). The results confirmed that the low ORP values observed by Komnitsas and Pooley (1991) during bio-oxidation at high solids concentration must have arisen due to a low bacteria-to-solids ratio. The adversely small bacterial population would have been incapable of oxidising ferrous ions at a rate sufficient to achieve a high ORP.

Soluble iron concentrations in excess of 30 g.l^{-1} are inhibitory to the ferrous oxidation process of the particular culture of bacteria used in this study, causing ferrous accumulation in solution and a lower ORP. This decrease in the ORP would cause a lower sulphide oxidation rate. The exact concentration at which the bacterial ferrous oxidation ability becomes inhibited may, however, be affected by strain tolerance and bacterial adaptation.

University of Cape Town

CHAPTER TEN

CONCLUSIONS

The objectives of this investigation were to:

1. Review reports in the literature of a decrease in the bio-oxidation rate of sulphide minerals at high solids concentrations.

2. Assess oxygen mass transfer in bio-oxidation reactors using literature data.

3. Perform batch bio-oxidation tests on pyrite ores and concentrates in a stirred tank reactor at different total solids concentrations.

4. Use a fluidised bed reactor (FBR) for bio-oxidation to investigate the effect of oxygen availability on bio-oxidation of pyrite. The FBR allows the liquid and solids environments to be controlled independently.

5. Assess the relative significance of the free and attached bacteria in bio-oxidation, by performing free cell depletion tests in the FBR system.

6. Investigate the effect of an increase in the ferric sulphate concentration on the rate of ferrous iron oxidation by pyrite-grown bacteria.

The main conclusions that have been drawn from this research are listed below.

1. Following the review of reports of rate limitation in bacterial oxidation in the literature, the following factors were established as potential causes of rate limitation during bacterial oxidation at high solids concentrations: oxygen

University of Cape Town

and carbon dioxide mass transfer; a low bacteria-to-solids ratio; mechanical damage of the bacteria; and the build-up of inhibitory oxidation products.

2. Analysis of bio-oxidation rate data reported in the literature formed the basis for the main hypothesis of this thesis. The analysis gave an indication that the bio-oxidation rate was proportional to the solids concentration in the reactor as long as the oxygen transfer potential exceeds the oxygen demand in the reactor. When the oxygen demand equals or exceeds the oxygen transfer rate, oxygen-limited conditions will prevail and the bio-oxidation rate is defined by the oxygen transfer rate. The experimental work conducted was designed to investigate this relationship further.

3. It has been shown that the concentration of solids affects bio-oxidation in two ways: firstly due to the influence of the sulphide content of the material on the oxygen demand; and secondly by affecting the oxygen mass transfer coefficient, k_La at high solids concentrations. The correlation developed by Oguz, Brehm and Deckwer (1987) was used to relate k_La to the solids concentration in bacterial oxidation. Less dense material (i.e. primarily silica) has a far more marked effect on k_La as the solids concentration is increased than denser material (such as pure pyrite). This is due to the fact that the relative viscosity of a slurry is a function of the solids volume fraction. A less dense material will have a correspondingly higher volume fraction at a particular solids concentration.

4. The results of both the FBR and batch stirred tank reactor tests confirmed the hypothesis that had been based on the analysis of literature data. It is the magnitude of the oxygen demand in relation to the oxygen transfer potential of the system that determines the highest solids concentration at which operation in possible at the maximum specific bio-oxidation rate.

   In the FBR where the solids and liquid environments could be controlled independently, when sufficient oxygen was available, the specific bio-oxidation rate of a high sulphide content material (28% S) was essentially constant at bed solids concentrations between 20 and 45 per cent (200 to

University of Cape Town

450 kg.m^{-3}). When solids loadings were increased so that oxygen limited conditions occurred, the bio-oxidation rate in the FBR was reduced, in agreement with the findings of other researchers that have been reported in the literature.

The batch stirred tank reactor bio-oxidation tests conducted on a low pyrite content run-of-mine material (1.2% S) indicated that the bio-oxidation rate was proportional to the solids concentration up to 60 per cent (600 kg.m^{-3}) solids, the maximum solids concentration tested. This solids concentration is approximately three times higher than the maximum solids concentration at which high grade material may be oxidised (20 per cent, 200 kg.m^{-3}).

Successful bio-oxidation could be achieved at the high solids concentration because the oxygen demand in a reactor is a function of the sulphide concentration (i.e. the sulphide grade of the material) and when processing the run-of-mine material, the oxygen demand is low compared to the oxygen transfer potential due to its low sulphide content. It may also be concluded that there is insignificant mechanical damage of bacteria at these high solids concentrations, ruling this out as the most important factor determining the maximum solids concentration at which bio-oxidation can be performed.

Rate data obtained from mixtures of pyrite and quartz confirmed that low sulphide content materials could be oxidised at substantially higher solids concentrations than high grade materials. The addition of inert silica to a reactor containing 10 per cent (100 kg.m^{-3}) pyrite did not affect the specific bio-oxidation rate up to a total solids concentration of 30 per cent (300 kg.m^{-3}), the highest concentration tested. A point will, however, be reached where the addition of silica will have reduced the oxygen transfer rate by such a great amount that it no longer exceeds the oxygen demand in the reactor and oxygen-limited conditions will prevail. Under these oxygen-limited conditions, the specific bio-oxidation rate would also reduce.

University of Cape Town

5. The rate data determined using the FBR showed good agreement with data obtained from both a 3-litre batch reactor and reported for a 45-litre continuous reactor. The FBR has emerged as a useful tool for obtaining kinetic data for the bio-oxidation of sulphides and for determining the critical dissolved oxygen concentration and oxygen utilisation rates. Only a small amount of material is required for the tests (*ca.* 75g).

6. Depletion of the free bacteria did not affect the bio-oxidation rate. The attached bacteria were found to be the more significant population. The attached bacteria were found to be capable of detaching from the mineral surface and replenishing the solution, maintaining both the redox potential and bio-oxidation rate. If, however, the attached bacterial population was low, then the bio-oxidation rate was reduced.

7. At ferric iron concentrations in excess of 30 $g.l^{-1}$, the ferrous oxidation ability of the bacteria was found to be inhibited. This resulted in a lower ORP which would lower the bio-oxidation rate. It was shown that the bacteria were capable of oxidising ferrous iron at an estimated rate of production of ferrous iron expected during the bio-oxidation of a high sulphide content material (28% S) at 50 per cent (500 $kg.m^{-3}$) solids.

University of Cape Town

REFERENCES

Ahonen, L. and Tuovinen, O.H., (1989), 'Effect of Temperature on the Microbiological Leaching of Sulfide Ore Material in Percolators Containing Chalcopyrite, Pentlandite, Sphalerite and Pyrrhotite as Main Minerals', *Biotechnology Letters*, **11**. (5), pp. 331-336.

Arters, D.C. and Fan, L.S., (1986), 'Solid-liquid mass transfer in a Gas-Liquid-Solid Fluidised Bed', *Chemical Engineering Science*, **41,** (1), pp 107-115.

Atkins, A.S., (1978), 'Studies on the Oxidation of Sulphide Minerals (Pyrite) in the Presence of Bacteria', *Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena*. Eds. Murr, L.E., Torma, A.E., and Brierley, J.A. Academic Press, New York, pp. 403-428.

Attia, Y.A. and Elzeky, M., (1991), 'Effect of Bacterial Adaptation and Solution Replacement on Bioleaching of Sulphidic Gold Ores', *Minerals and Metallurgical Processing*, **8**, (3), pp. 122-127.

Bailey, J.E. and Ollis, D.F., (1987), *Biochemical Engineering Fundamentals*, McGraw-Hill, Singapore, pp.488-494.

Beyer, M., Ebner, H.G. and Klein, J., (1986), 'Influence of Pulp Density and Bioreactor Design on Microbial Desulphurisation of Coal', *Applied Microbiology and Biotechnology,* **24**, pp. 342-346.

Boon, M., Meeder, T.A., Heojnen, J.J. and Luyben, K.Ch.A.M., (1992),'Influence of Oxygen Adsorption on the Dynamic $k_L a$ Measurement in Three-Phase Slurry Reactors', *Biotechnology and Bioengineering*, **40**, 1097-1106.

Booth, A., Smith, G.R. and van Aswegen, P.C., (1991). 'BIOX Plant Expansion at Fairview Mine', *South African Institute of Mining and Metallurgy Bacterial Oxidation Colloquium*, Johannesburg, South Africa, June 1991.

University of Cape Town

Brierley, C.L., (1978), 'Bacterial Leaching', *CRC Critical Reviews in Microbiology*, **6**, (3), pp. 207-262.

Bryner, L.C., and Anderson, R. (1957), 'Microorganisms in Leaching Sulfide Minerals', *Industrial and Engineering Chemistry*, **49**,(10), pp. 1721-1724.

Burru, I.G. and Briens, C.L., (1991), 'Particle-liquid Mass Transfer in Three-phase Fluidised Beds. Part 1: Newtonian Liquids', *Powder Technology*, **68**, pp. 243-353.

Carter, A.J., (1991), 'Economic Comparison of the Alternative Methods for the Recovery of Gold from Refractory Gold Ores', *South African Institute of Mining and Metallurgy Bacterial Oxidation Colloquium*, Johannesburg, South Africa, June (1991).

Chang, Y.C. and Myerson, A.S., (1982), 'Growth Models of the Continuous Bacterial Leaching of Iron Pyrite by *Thiobacillus ferrooxidans*', *Biotechnology and Bioengineering*, **24**, pp. 889-902.

Collinet, M-N, Morin, D., (1990), 'Characterization of Arsenic Oxidising *Thiobacillus*. Tolerance to Arsenite, Arsenate, Ferrous and Ferric Iron.', *Antonie van Leeuwenhoek*, **57**, pp. 237-244.

Cook, T.M., (1964), 'Growth of *Thiobacillus thiooxidans* in Shaken Culture', *Journal of Bacteriology*, **88**, (3), pp. 620-623.

Corrans I.J., (1974), 'Kinetic and Mechanistic Studies on the Biological and Chemical Leaching of Nickel from Sulphide ores', PhD. Thesis, Department of Chemical Engineering, University of Natal, South Africa.

Coulson, J.M. and Richardson, J.F. (1980), *Chemical Engineering. Volume 2: Unit Operations*, 3rd Edn., Pergamon Press, UK.

University of Cape Town

Croughan, M.S., Hamel, J-F.P. and Wang, D.I.C., (1988), 'Effects of Microcarrier Concentration in Animal Cell Culture', *Biotechnology and Bioengineering*, **32**, pp 975-982.

Davidson, J.F. and Harrison, D., (1971), *Fluidisation*, Academic Press, New York.

Dempsey, P., Human, P., Pinches, A. and Neale, J.W., (1990), 'Bacterial Oxidation at Vaal Reefs', *International Deep Mining Conference: Inovations in Metallurgical Plant*, South African Institute of Mining and Metallurgy, Johannesburg, South Africa.

Detz, C.M. and Barvinchak, G. (1979), 'Microbial Desulphurisation of Coal', *American Mining Congress Journal*, **65**, (7), pp. 75-82.

Dew, D.W. and Godfrey, M.W., (1991), 'Sao Bento BIOX Reactor', *South African Institute of Mining and Metallurgy Bacterial Oxidation Colloquium*, Johannesburg, South Africa, June 1991.

Dispirito, A.A. Duncan, P.R. and Tuovinen, O., (1981), 'Inhibitory Effects of Particulate Materials in Growing Cultures of *Thiobacillus ferrooxidans*', *Biotechnology and Bioengineering*, **23**, pp. 2761-2769.

Drossou. M., (1986), 'The Kinetics of the Bioleaching of a Refractory Gold-Bearing Pyrite Concentrate', M.Sc. Thesis, Department of Chemical Engineering, University of Cape Town, South Africa.

Engineering and Mining Journal, (1993), June, pp.20-25.

Ehrlich, H.L., (1986), 'Bacterial Leaching of SIlver from a Silver-containing Mixed Sulphide Ore by a Continuous Process', pp 77-88, In: *Fundamentals of and Applied Biohydrometallurgy*, Eds. Lawrence, R.W., Branion, R.M.R. and Ebner, H.G., Elsevier, Amsterdam.

Free, M.L., (1991), 'Bioleaching of Sulfide Ores - Distinguishing Between Indirect and Direct Mechanisms', In: *Minerals Bioprocessing*, Eds. Smith, R.W.

University of Cape Town

and Misra, M., The Minerals, Metals and Materials Society, USA, pp. 485-495.

Fukuma, M., Sato, K., Muroyama, K. and Yasunishi, A., (1988), 'Particle-to-liquid Mass Transfer in Gas-Liquid-Solid Fluidisation', *Journal of Chemical Engineering*, **21**, (3), pp. 231-237.

Gooding, K., (1991), 'Bacteria Give Gold Miners Germ of an Idea' *Financial Times* (London), Wednesday, October 30.

Gormely, L.S., (1990), 'Mathematical Modelling of Oxygen Transfer in a Stirred Tank Bioreactor', pp. 217-223, In: Eds. Fuerstenau, M.C. and Hendrix, J.L., *Advances in Gold and Silver Processing*, Society Min. Metall. Explor., Littleton, Colorado.

Gormely, L.S., (1992), 'Mechanical Agitation and Aeration in Hydrometallurgical Reactors', *Hydrometallurgy*, **29**, pp. 217-230.

Guay, R. and Silver, M., (1980), 'Uranium Biohydrometallurgy', *Process Biochemistry*, Dec./Jan., pp 8-11.

Hackl, R.P. Wright, F.R. and Gormely, L.S., (1989), 'Bioleaching of Refractory Gold Ores - Out of the Lab into the Plant' pp. 533-550. In: Salley, J., McCready, R.G.L. and Wichlacz. P.L. (eds.), *Biohydrometallurgy 1989*, International Symposium Procedings, Jackson Hole, Wyoming. Canadian Centre for Mining and Energy Technology, Canada.

Hansford, G.S. and Bailey, A.D., (1992), 'The Logistic Equation for Modelling Bacterial Oxidation Kinetics', *Minerals Engineering*, **5**, (10-12), pp. 1355-1354.

Hansford, G.S. and Drossou, M., (1988), 'A Propogating Pore Model for the Batch Bioleach Kinetics of Refractory Gold-bearing Pyrite', *Biohydrometallurgy Proc. Int. Symp, 1987,* Ed. Norris, P.R. and Kelly, D.P., pp. 345-358.

University of Cape Town

Hansford, G.S., Levy, C.D. and De Kock, J.W., (1976), Rheological Measurements on Pulps from South African Gold Mines', *Journal of South African Institute of Mining and Metallurgy*, **76**, (8), pp. 363-369.

Harrison, S.T.L. (1991), 'Bacterial Cell Disruption: A Key Unit Operation in the Recovery of Intracellular Products', *Biotechnology Advances*, **9**, pp. 217-240.

Hoffmann, W., Katsikaros, N. and Davis, G., (1991), 'Design of a Reactor Bioleach Process for Refractory Gold Treatment', Paper presented at *Biohydrometallurgy '91*, Troia, Portugal, September 9-13.

Huberts, R., Chilcott, A.J. and Pinches, A., (1991), 'Techno-economic Aspects of Bacterial Oxidation' *South African Institute of Mining and Metallurgy Bacterial Oxidation Colloquium*, Johannesburg, South Africa, June 1991.

Huheey, J.E., (1978), *Inorganic Chemistry Principles of Structure and Reactivity*, 2nd Edn.,Harper and Row, New York, p. 311.

Joosten, G.E.H., Schilder, J.G.M. and Janssen, J.J., (1977), 'The Influence of Suspended Solid Material on the Gas-Liquid Mass Transfer in Stirred Gas-Liquid Contactors', *Chemical Engineering Science,* **32**, pp. 563-566.

Karamenev, D.G. and Nikolov, L.N., (1988), 'Influence of Some Physicochemical Parameters on Bacterial Activity of Biofilm: Ferrous Iron Oxidation by *Thiobacillus ferrooxidans*', *Biotechnology and Bioengineering*, **31**, pp. 295-299.

Karaivko, G.I., Kuznetsov, S.I. and Colonizik, A.I., (1977), *The Bacterial Leaching of Metals and Ores*, Technicopy Limited, Stonehouse, England.

Kargi, F., (1982), 'Enhancement of Microbial Removal of Pyritic Sulphur from Coal Using Concentrated Cell Suspension of *Thiobacillus ferrooxidans* and an External Carbon Dioxide Supply', *Biotechnology and Bioengineering*, **24**, pp. 749-752.

University of Cape Town

Kelly, D.P., C.A. and Green, J.S., (1977), 'Factors Affecting Metabolism and Ferrous Iron Oxidation in Suspensions and Batch Cultures of *Thiobacillus ferrooxidans*', paper presented at *International Symposium on Metallurgical Application of Bacterial Leaching and Related Microbiological Phenomena*, Socorro, N.M., August 3 to 5, 1977.

Kelly, D.P. and Jones, C.A., (1978), 'Factors Affecting Metabolism and Ferrous Iron Oxidation in Suspensions and Batch Cultures of *Thiobacillus ferrooxidans*: Relevance to Ferric Iron Leach Solution Regeneration, pp. 19-44, In: L.E. Murr, A.E. Torma and J.A. Brierley, (Eds.) *Metallurgical Applications of Bacterial Leaching and Related Microbial Phenomina*, Academic Press, New York.

Koide, K., Yasuda, T., Iwamoto, S. and Fukuda, E., (1983), 'Critical Gas Velocity Required for Complete Suspension of Solid Particles in Solid-Suspended Bubble Columns', *Journal of Chemical Engineering of Japan,* **16**, (1), pp. 7-12.

Komnitsas, C. and Pooley, F.D., (1989), 'Mineralogical Characteristics and Treatment of Refractory Gold Ores', *Minerals Engineering*, **2**, (4), pp. 449-457.

Komnitsas, C. and Pooley, F.D., (1990), 'Bacterial Oxidation of an Arsenical Gold Sulphide Concentrate from Olympias, Greece', *Minerals Engineering*, **3**, (3/4), pp. 295-306.

Komnitsas, C. and Pooley, F.D., (1991), 'Optimisation of the Bacterial Oxidation of an Arsenical Gold Sulphide Concentrate from Olympias, Greece', *Minerals Engineering*, **4**, (12), pp. 1297-1303.

Kumar, S.R. and Gandhi, K.S., (1990), 'Modelling of Fe^{2+} Oxidation by *Thiobacillus ferrooxidans*', *Applied Microbiology and Biotechnology*, **33**, pp. 524-528.

Lawrence, R.W., (1988), 'The Potential of Thermophilic Bacteria in the Pretreatment of Refractory Ores', pp. 75-101, In: *BIOMINET*, 4th Annual,

University of Cape Town

Ed. McCready, R.G.L., Canadian Government Publishing Centre Supply and Services, Ottawa, Canada.

Lawson, E.N. and van Aswegen, P.C., (1992), 'The Beneficiation of Refractory Gold Ores Using Bacteria', pp. 150-152, In: A. Sharkey, (Ed.), *Mining and Quarrying Technology International*, Sterling Publishers, London, UK.

Lee, J.C., Ali, S.S. and Tasakorn, P., (1982), 'Influence of Suspended Solids on Gas-Liquid Mass Transfer in an Agitated Tank', *Proceedings of the 4th European Conference on Mixing*, Noordwijkerhout, The Netherlands, Paper H4, pp. 399-415.

Le Roux, N.W., Wakerley, D.S. and Perry, V.F., (1978), 'Leaching of Minerals Using Bacteria Other than *Thiobacilli*', pp. 167-191, In: Murr, L.E., Torma, A.E. and Brierley, J.A. (Eds.), *Metallurgical Applications of Bacterial Leaching and Related Microbial Phenomena*, Academic Press, New York.

Liu, M.S., Branion, R.M.R. and Duncan, D.W., (1988), 'The Effects of Ferrous Iron, Dissolved Oxygen and Inert Solids Concentrations on the Growth of *Thiobacillus ferrooxidans*', *Canadian Journal of Chemical Engineering*, **66**, (3), pp. 445-451.

Lundgren, D.G. and Malouf, E.E., (1983), 'Microbial Extraction and Concentration of Metals', *Advances in Biotechnological Processes*, **1**, pp. 223-249.

Madsen, B.W., (1982), 'Determination of Ferric Ion Diffusion and Activity Coefficients From Chronopotentiometric Data', Bureau of Mines Report R.I. 8617, USA.

Mandl, M., (1984), 'Growth and Respiration Kinetics of *Thiobacillus ferrooxidans* Limited by CO_2 and O_2', *Niologia (Bratislava)*, **39**: (4) 429-434.

Marchant, P.B., (1986), 'Commercial Piloting and the Economic Feasibility of PLant Scale Continuous Biological Tank Leaching at Equity Silver Mines Limited', pp. 53-57, In: *Fundamentals of and Applied Biohydrometallurgy,*

University of Cape Town

Eds. Lawrence, R.W., Branion, R.M.R. and Ebner, H.G., Elsevier, Amsterdam.

Marsden, D.D., (1962), 'The Effect of pH Value, Temperature and Density on the Kinematic Viscosity of Some South African Gold Mine Slurries', *Journal of South African Mining and Metallurgy*, pp. 391-398.

McGoran, C.J.M., Duncan, D.W. and Walden, C.C., (1969), 'Growth of *Thiobacillus ferrooxidans* on Various Substrates', *Canadian Journal of Microbiology*, **15**, pp. 135-138.

Miller, D.M., (1990), 'Bio-oxidation of a Gold-bearing Arseno/pyrite Concentrate', M.Sc. Thesis, Department of Chemical Engineering, University of Cape Town, South Africa.

Mills, D.B., Bar, R. and Kirwan, D.J., (1987), 'Effect of Solids on Oxygen Transfer in Agitated Three-Phase Systems', *American Institute of Chemical Engineers' Journal*, **33**, (9), pp. 1542-1549.

Murthy, K.S.N. and Natarajan, K.A., (1992), 'The role of Surface Attachment of *Thiobacillus ferrooxidans* on the Biooxidation of Pyrite', *Minerals and Metallurgical Processing*, **9**, (1), pp. 20-24.

Myerson, A.S., (1981), 'Oxygen Mass Transfer Requirements During the Growth of *Thiobacillus ferrooxidans* on Iron Pyrite' *Biotechnology and Bioengineering*, **23**, pp. 1413-1416.

Nagata, S., (1975), *Mixing: Principles and Applications*, Kodansha Ltd., Halstead Press, Japan.

Nagpal, S., Dahlstrom, D. and Oolman, T., (1993), 'Effect of Carbon Dioxide Concentration on the Bioleaching of a Pyrite-Arsenopyrite Ore Concentrate', *Biotechnology Bioengineering*, **41**, 459-464.

Natarajan, K.A., (1988), 'Electrochemical Aspects of Bioleaching Multisulphide Minerals', *Minerals and Metallurgical Processing*. **5**, (2), pp. 61-65.

University of Cape Town

Neale, J.W., Pinches, A., Muller, H.H., Hannweg, N.H. and Dempsey, P., (1991), 'Long-term Bacterial Oxidation Pilot Plant Operation at Mintek and Vaal Reefs', *South African Institute of Mining and Metallurgy Bacterial Oxidation Colloquium*, Johannesburg, South Africa, June, 1991.

Neill, R.I.G., (1988), 'The Rheology and Flow Behaviour of High Concentration Mineral Slurries', M.Sc. Thesis, Department of Civil Engineering, University of Cape Town, South Africa.

Nikolov, L.N. and Karamenev, D.G., (1992), 'Kinetics of the Ferrous Iron Oxidation by Resuspended Cells of *Thiobacillus ferrooxidans*', *Biotechnology Progress*, **8**, pp. 252-255.

Nikov, I. and Delmas, H., (1987), 'Solid-liquid Mass Transfer in Three-phase Fixed and Fluidised Beds', *Chemical Engineering Science*, **42**, (5), pp. 1089-1093.

Oguz, H., Brehm, A., and Deckwer, W-D., (1987), 'Gas/Liquid Mass Transfer in Sparged Agitated Slurries', *Chemical Engineering Science,* **42**, (7), pp. 1815-1822.

Papoutsakis, E.T., (1991), 'Fluid-mechanical Damage of Animal Cells in Bioreactors', *Trends in Biotechnology*, **9**, (12), pp.427-437.

Pinches, A., (1972), 'The Use of Micro organisms for the Recovery of Metals from Mineral Materials', PhD. Thesis, Department of Mineral Exploitation, University College, Cardiff, Wales.

Pinches, A., Huberts, R., van Staden, M. and Muhlbauer, R.M., (1991), 'Process Options and Parameters in the Development and Optimisation of Bacterial Oxidation Processes for the preoxidation of Refractory Sulphide Gold Ores', *South African Institute of Mining and Metallurgy Colloquium on Bacterial Oxidation*, Johannesburg, South Africa, June, 1991.

University of Cape Town

Pogliani, C., Curutchet, G., Donati, E. and Tedesco, P.H., (1990), 'A Need for Direct Contact with Particle Surfaces in the Bacterial Oxidation of Covellite in the Absence of a Chemical Lixiviant', *Biotechnology Letters*, **12**, (7), pp. 515-518.

Rao, T.C. (1966), p. 98. In: Lynch, A.J. (ed.) *Mineral Crushing and Grinding Circuits*. Elsevier, Amsterdam, (1977).

Roy, P and Mishra, A.K., (1981), 'Factors Affecting Oxidation of Pyrite by *Thiobacillus ferrooxidans*', *Indian Journal of Experimental Biology,* **19**, pp. 728-732.

Sakaguchi, H., Silver, M. and Torma, A.E., (1976), 'Microbiological Leaching of a Chalcopyrite Concentrate by *Thiobacillus ferrooxidans*', *Biotechnology and Bioengineering*, **18**, pp. 1091-1101.

Sanmugasunderam, V., (1981), 'Kinetic Studies on the Biological Leaching of a Zinc Sulphide Concentrate in Two Stage Continuous Stirred Tank Reactors', PhD. Thesis, Department of Chemical Engineering, University of British Columbia.

Schlegel, H.G., (1988). *General Microbiology*, 6th Edn., University Press, Cambridge, UK.

Schumpe, A., Saxena, A.K. and Fang, L.K., (1987), 'Gas/Liquid Mass Transfer in a Slurry Bubble Column', *Chemical Engineering Science,* **42**, (7), pp. 1787-1796.

Silver, M., (1978), 'Mechanisms of Iron Oxidising *Thiobacillus*', pp. 3-14, In: Murr, L.E., Torma, A.E.and Brierley, J.A. (Eds.), *Metallurgical Applications of Bacterial Leaching and Related Microbial Phenomena*, Academic Press, New York.

Silverman, M.P. and Lundgren, D.G., (1959), 'Studies on the Chemoautotrophic Iron Bacteria *Ferrobacillus ferrooxidans*. I. An Improved Medium and a

University of Cape Town

Harvesting Procedure for Securing High Cell Yields', *Journal of Bacteriology*, **77**, pp. 642-646.

Slabbert, W., Dew, D.W., Godfrey, M.W., Miller, D.M., van Aswegen, P.C., (1992), 'Commissioning of a BIOX Module at Sao Bento Mineracao', In *Randol Gold Forum Vancouver*, Randol International Limited, Golden, CO, pp. 447-452.

Stanley, G.G., (1987), 'The Extraction Metallurgy of Gold in South Africa', *South African Institute of Mining and Metallurgy Monograph Series, M7,* Johannesburg, **1,** p 307.

Toma, M.K., Ruklisha, M.P., Vanags, J.J., Zeltina, M.O., Letie, M.P., Galinina, N.I., Viesturs, U.E. and Tnegerdy, R.P., (1991), 'Inhibition of Microbial Growth and Metabolism by Excess Turbulence', *Biotechnology and Bioengineering,* **38**, pp. 552-556.

Torma, A.E., (1977), 'The Role of *Thiobacillus ferrooxidans* in Hydrometallurgical Processes', *Advances in Biochemical Engineering*, **6**, pp. 1-37.

Torma, A.E., Walden, C.C., Duncan, D.W. and Branion, R.M.R, (1972), 'The Effect of Carbon Dioxide and Particle Surface Area on the Microbiological Leaching of a Zinc Sulphide Concentrate', *Biotechnology and Bioengineering*, **14**, pp. 777-786.

Torma, A.E., Walden, C.C., Duncan, D.W. and Branion, R.M.R., (1970), 'Microbiological Leaching of a Zinc Sulphide Concentrate', *Biotechnology and Bioengineering,* **12**, pp. 501-517.

Tuovinen, O.H., Niemala, S.I. and Gyllenberg, H.G., (1971), 'Tolerance of *Thiobacillus ferrooxidans* to Some Metals', *Antonie van Leeuwenhoek*, **37**, pp. 489-496.

van Staden, M., (1991), 'Bacterial Leaching of Refractory Gold-Bearing Ore and Sulphide Concentrates', Masters Diploma Thesis, Department of Metallurgy, Technikon Witwatersrand, South Africa.

University of Cape Town

van't Riet, K., (1979), 'Review of Measurement Methods and Results in Nonviscous Gas-Liquid Mass Transfer in Stirred Vessels', *Industrial Engineering Chemistry Process Design and Development*, **18**, (3), pp 357-364.

Vogel, A.I., (1962), *A Textbook of Quantitative Inorganic Analysis*, Longman Group, London, p. 309.

Wen, C.Y. and Yu, Y.H., (1966), 'Mechanics of Fluidisation', *Chemical Engineering Progress Symposium Series*, **62**, (62), pp. 100-111.

Wong, C.W., Scharer, J.M. and Reilly, P.M., (1973), 'A Discrimination among Microbial Iron Oxidation Mechanisms', paper presented at *4th Joint American Institute of Chemical Engineering-Canadian Society of Chemical Engineering Conference*, Vancouver, Canada, September 9 to 12, 1973.

Woodcock, J.T., (1985), 'SME Mineral Processing Handbook', Ed. N.L. Weiss, *Society of Mining Engineering*, New York, **2**, Chapter 13, p. 25.

Yunker, S.B. and Radovich J.M., (1985), 'Enhanced Growth of *Thiobacillus ferrooxidans* in an Electrolytic Bioreactor', *Biotechnology and Bioengineering Symposium Series*, **15**, pp. 307-319.

Zajic, J.E., (1969), 'Review of Microbes used to Leach Copper Ores', *Microbial Biogeochemistry*, Academic Press, New York.

University of Cape Town

APPENDIX ONE

ANALYTICAL TECHNIQUES

A. ACID DIGEST METHOD

Acid digestion enables a mineral sample to be completely dissolved so that the resulting solution can be analysed for the presence of various metals, using atomic absorption (AA) spectrophotometery. The method outlined below has been adapted from the procedure used by Anglo American Research Laboratories (South Africa).

University of Cape Town

Reagents Required

REAGENT	FORMULA	CONCENTRATION
Hydrochloric acid	HCl	30%
Nitric acid	HNO_3	60%
Perchloric acid	$HClO_4$	70%
Hydrofluoric acid	HF	40%

Hydrofluoric is extremely dangerous, causing severe burns if it comes in contact with the skin. Appropriate protective clothing (Face shield, rubber gloves and plastic apron) must be worn when performing digests. The digestion should be performed in a fume cupboard.

METHOD

1. Make up 1 litre of solution by mixing 4 parts HCl to 1 part HF. Store in a plastic container as HF attacks glass.

2. Weigh approximately 0.2g of sample accurately on a 4 decimal place balance. Let this mass be "a". The mass of sample may have to be reduced to 0.1g if the mineral is a high grade material.
3. Put the weighed sample into an Erlenmeyer flask.
4. Pipette (using a plastic pipette) 10ml of the HCl/HF mixture (made in 1.) into the flask and heat until boiling.
5. When boiling, add 10ml HNO_3 and boil till approximately 2ml remains in the flask and the solution has become colourless.
6. Add 5ml $HClO_4$ and boil till the white fumes that form lift to the neck of the flask and 2ml liquid remains.
7. Remove the flask from the hotplate and allow to cool.
8. Using a funnel, pour the contents from the flask into a 250ml volumetric flask. Rinse the flask using distilled water and pour all washings into the volumetric flask.
9. Make up the remaining volume in the volumetric flask to 250ml with distilled water.
10. Shake the volumetric flask to ensure that the solution is well mixed.
11. Filter the solution using Whatman No.1 filter paper and collect the filtrate in 20ml sample bottles. A half-filled sample bottle is generally sufficient for the determination of one element. It is advisable to retain excess solution, however, until the AA analysis has been performed.
12. Determine the concentration, E (ppm) of a particular element (eg. Fe) in the filtered solution using AA analysis.
13. The composition, C (%) of the element in the original sample is determined as follows:

$$E\ (ppm) = E/1000 \quad (g.l^{-1})$$

$$\text{Mass of sample digested per litre} = a * 1000/250 = 4a \quad (g.l^{-1})$$

So,

$$\text{concentration, } C = (E/1000 * 1/(4a)) * 100\% = E/(40a)\ \%$$

University of Cape Town

B. METHOD FOR DETERMINING FERROUS IRON CONCENTRATION IN SOLUTION

This method for ferrous iron measurement, in solution, was obtained from Genmin Process Research (South Africa), and is based on the method outlined by Vogel (1962).

PREPARATION OF REAGENTS REQUIRED

I. Spekker Acid Preparation.

1. Pour 1.4 litres of distilled water into a 5 litre beaker.
2. Add 300ml concentrated H_3PO_4 to the water.
3. Slowly add 300ml of concentrated H_2SO_4.

II. 0.0895 N $K_2Cr_2O_7$ Standard Solution

1. Dry approximately 20g of $K_2Cr_2O_7$ at 150°C for 1 hour in an oven. Cool to room temperature in a desiccator.
2. Weigh 17.560g (exactly) of $K_2Cr_2O_7$.
3. Dissolve the $K_2Cr_2O_7$ in exactly 4 litres of distilled water.

III. Sodium Diphenylamine Sulphonate Indicator

1. Dissolve 5g of barium diphenamine sulphonate in 500ml concentrated sulphuric acid.

TITRATION METHOD

1. Centrifuge mixed liquor sample for 5 minutes at 4000 rpm. Collect supernatant in sample bottle.
2. Pipette 5ml of supernatant into a 150ml Erlenmeyer flask.

University of Cape Town

3. Pipette 10ml Spekker Acid (made in A) into the flask.
4. Add 2 to 3 drops of sodium diphenylamine sulphonate indicator (made in III) to the contents of the flask.
5. Titrate with the Standard $K_2Cr_2O_7$ solution until the solution turns purple permanently. Swirl the flask throughout the titration to ensure good mixing.

1 ml of the Standard $K_2Cr_2O_7$ solution is equivalent to 1g.l^{-1} Fe^{2+} in the supernatant.

C. HCl ACID WASHING METHOD TO DETERMINE TOTAL IRON CONCENTRATION

During bio-oxidation a portion of the iron that builds up in the liquid precipitates as jarosite, an iron sulphate-hydroxide complex. The precipitation is dependent on the solution ORP, pH as well as the iron concentration. If the iron build-up in solution is being used to monitor the bio-oxidation rate, it is necessary to resolubilse the jarosite, so that all of the iron removed from the sulphide material is accounted for. The jarosite is readily soluble on addition of HCl.

METHOD

1. Take a known volume (*ca.* 10ml) of sample from the reactor.
2. Add sufficient concentrated HCl to the sample to give an HCl concentration of approximately 2.5 M in the resulting solution (i.e. 3ml to a 10 ml sample).
3. Seal the container, mix the contents and allow to stand overnight. Re-mix the contents prior to continuing the next day.
4. Weigh a piece of filter paper and a crucible or evaporating basin on a 4 decimal place balance.
5. Filter the solution through the pre-weighed filter paper. Collect the filtrate and reserve. Put the filter paper and solids residue into the crucible.
6. Dry the filter paper and solids residue in an oven at 100°C for approximately 12 hours. Then, remove the crucible and cool to room temperature in a desiccator.

University of Cape Town

7. Weigh the crucible and contents and determine the mass of solids remaining. The solid material can be analysed for residual iron and sulphur still present (now that the jarosite has been removed).
8. The iron concentration of the filtrate is determined using atomic absorption spectrophotometery. It is important to take the amount of HCl that has been added to the sample in (2.) above into account when calculating the actual iron concentration. The addition of HCl will have had a diluting effect.

The difference between the HCl-washed and the total dissolved iron concentration represents the amount of iron that was precipitated as jarosite in the sample.

University of Cape Town

D. METHOD FOR k_La DETERMINATION IN BATCH STIRRED TANK REACTORS

The "dynamic" method of van't Riet (1979) was used for the measurement of the oxygen mass transfer coefficient, k_La in the batch stirred tank reactors. The method outlined below is only applicable when no bacteria are present in the reactor, or the bacterial oxygen consumption is negligibly small. The method is constrained because the reactors used in this experimental work were unsealed, making it difficult to form a layer of pure nitrogen above the liquid surface. This meant that there was always some surface entrainment of oxygen throughout the test, preventing the measurement of a bacterial oxygen utilisation rate (OUR) during the oxygen depletion phase of the test.

The dissolved oxygen concentration was monitored using a YSI dissolved oxygen meter and probe connected to a JJ Lloyd model CR533 chart recorder (Southampton, England). A schematic diagram of the apparatus is shown in Figure A1.

METHOD

1. Fix the dissolved oxygen probe in the reactor and monitor the initial dissolved oxygen level (C^*) on the chart recorder.

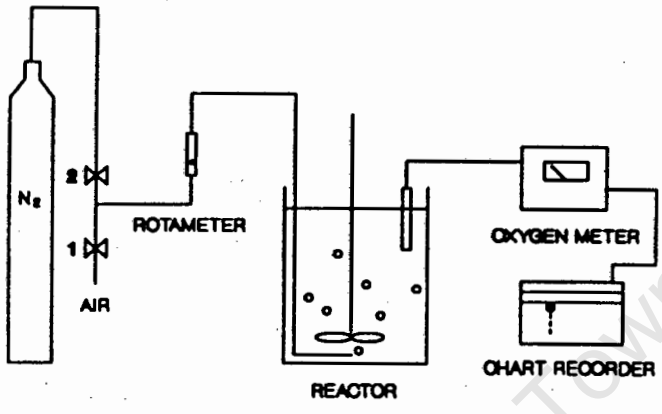


Figure A1: Schematic Diagram of Apparatus used for $k_L a$ Measurement

University of Cape Town

2. To commence oxygen stripping, close valve 1 to switch of the air supply.
3. Open valve 2 to begin sparging with nitrogen. The nitrogen flowrate should be the same as the air flowrate.
4. Continue stripping oxygen until the oxygen level in the reactor has dropped to at least < 1ppm.
5. Close valve 2 and open valve 1 to re-aerate the reactor.
6. Dissolved oxygen concentration data (C) are read off the resulting plot, during the air "on" re-aeration phase of the test, at various times (t). The first data set, read at the commencement of re-aeration, may be taken as time zero.
7. Using Quattro, or similar spreadsheet, calculate $\ln(C^* - C)$ for each of the times, t. In typical tests, a time interval of 4s was allowed between readings.
8. The resulting graph of $\ln(C^* - C)$ versus t should be a straight line. Straight-line regress the data to obtain the slope of the line. Then:

$$k_L a = - (\text{slope})$$

APPENDIX TWO

OXYGEN TRANSFER RATE / OXYGEN TRANSFER POTENTIAL CALCULATIONS

All experimental data quoted in this appendix pertains to data reported by van Staden (1991) in his thesis. The data analysis contained in this appendix is discussed in Chapter Four.

1. CALCULATION OF SPECIFIC OXIDATION RATE

The size analysis of the high sulphide content flotation concentrate is shown in Table A2.1 below, whilst that of the run-of-mine ore is given in Table A2.2.

University of Cape Town

Table A2.1 : Size Analysis of Backfill Pyrite Concentrate

Fraction	% in Range	Average Size
+ 150	0.0	
-150 +106	0.5	128.0
-106 +75	1.3	90.5
-75 +53	6.2	64.0
-53 +38	13.0	45.5
-38	79.0	19.0

Table A2.2 : Size Analysis of Run-of-Mine Ore

Fraction	% in Range	Average Size
+ 150	0.0	
-150 +106	16.4	128.0
-106 +75	14.6	90.5
-75 +53	11.0	64.0
-53 +38	9.1	45.5
-38	48.9	19.0

University of Cape Town

Calculation of Representative Surface Area

A characteristic diameter and a representative surface area can be estimated from the particle size analysis, by using the following calculation scheme:

Assume that the particles are spherical and that the solid density, ρ is constant in all size fractions.

Let:

M_T = total mass of sample
F_i = fraction of sample in size fraction i
D_i = average particle diameter in fraction i
D_c = characteristic particle diameter for sample

Then,

Mass of particles in fraction i = $F_i M_T$
Volume of particles in fraction i = $(F_i M_T)/\rho$
Volume of one particle = $1/6 \times \pi \times D_i^3$

Number particles in fraction i = $\frac{\text{total volume}}{\text{volume of particle}}$

Number particles in fraction i = $6 F_i M_T / (\rho \times \pi \times D_i^2)$

Surface area of particle = $\pi \times D_i^2$

Surface area in fraction i = $6F_i M_T/(\rho \times D_i)$ [A2.1]

Total surface area = $\Sigma\ 6F_i M_T/(\rho \times D_i)$

If the total sample was made up with particles of the characteristic diameter, then

Total surface area = $6 M_T / (\rho \times D_c)$

Equate the two expressions for total surface area :

$$6 M_T / (\rho \times D_c) = \Sigma\ 6F_i M_T/(\rho \times D_i)$$

$$1/D_c = \Sigma\ F_i/D_i \qquad [A2.2]$$

A characteristic diameter, D_c was calculated for both mineral samples using the size analyses. A specific surface area could also be calculated from the information. The results, as well as the density of the two materials, are given in Table A2.3.

Table A2.3 Characteristic Diameter, Density and Specific Surface Area

Sulphide	D_c µm	Density kg.m^{-3}	Specific Surface Area m^2.kg^{-1}
Pyrite Conc.	21.73	3425	79.87
Run-of-Mine ore	31.96	2801	69.19

University of Cape Town

Conversion of Mass Fraction Data to Surface Area Fraction Equivalent

To determine the amount of pyrite surface area available for oxidation, the mass fraction of pyrite, Y_{PY} must be converted to a volume fraction, V_{PY} and then an equivalent surface area fraction, S_{PY}. Assume that the only constituent of the sulphides were pyrite and silica. The silica has a density, ρ_{sil} of 2600 $kg.m^{-3}$. Then:

Pyrite volume	=	Y_{PY}/ρ	
Total volume	=	$Y_{PY}/\rho + (1 - Y_{PY})/\rho_{sil}$	
Volume fraction, V_{PY}	=	Pyrite volume / Total volume	[2.3]
Surface fraction, S_{PY}	=	$V_{PY}^{0.667}$	[2.4]

Table A2.4 summarises the pyrite volume and surface area fractions calculated from the mass fraction data quoted by van Staden, (1991) for the pyrite flotation concentrate and the run-of-mine ore.

University of Cape Town

Table A2.4: Mass, Volume and Surface Area Fractions

Material	Fraction Pyrite		
	Mass Fraction	Volume Fraction	Surface Area Fraction
Pyrite Conc.	0.525	0.364	0.510
Run-of-Mine Ore	0.021	0.011	0.050

Calculate Oxidation Rate Based on Pyrite Surface Area

During oxidation of the pyrite concentrate under steady-state conditions at a solids concentration of 13.6 per cent, van Staden (1991) measured the solids

concentration as 132 kg.m^{-3}. The mineral surface area concentration in the reactor, T_{SA} can be calculated as follows:

$$T_{SA} = 79.87 \times 132 \quad (kg.m^{-3})(m^2.kg^{-1})$$
$$= 10\,543 \ (m^2 \text{ mineral})(m^3 \text{ reactor})^{-1}$$

Measured oxygen consumption rate at 13.6 per cent solids was 26.18 (kg O_2)(m)$^{-3}$(d)$^{-1}$. This rate can be based on the mineral surface concentration in the reactor:

$$\text{Rate} = 26.18 / 10543$$
$$= 2.483 \times 10^{-3} \ (kg\ O_2)(m^2 \text{ mineral})^{-1}(d)^{-1}$$

This rate can be weighted with respect to the surface area of pyrite present in the reactor:

$$R_{PY} = 2.483 \times 10^{-3} / 0.51$$
$$= 4.869 \times 10^{-3} \ (kg\ O_2)(m^2 \text{ pyrite})^{-1}(d)^{-1}$$

2. CALCULATION OF OXYGEN TRANSFER POTENTIAL (OTP)

University of Cape Town

Calculate kLa from Measured OTR

From Equation 4.4

$$OTR = k_L a\ (C^* - C)$$
$$= 26.18 \ (kg\ O_2)(m)^{-3}(d)^{-1}$$

and

$$C^* = 7{,}2 \text{ mg.}l^{-1}$$
$$C = 0.8 \text{ mg.}l^{-1}$$

Rearranging Equation 4.4

$$k_L a = OTR / (C^* - C)$$
$$= 26.18/(7.2 - 0.8)/(1000)$$

$= 4090.6\ d^{-1}$

$= 0.0473\ s^{-1}$

Estimate Slurry Viscosity From Rao (1966) Data

132.1 g solids measured per litre pulp, so:

solids volume $= 0.1321/(\rho)$

$= 0.039\ l$

Specific gravity of pulp $= 0.961(1) + 0.039(3.425)$

$= 1.13$

Corresponds to a relative viscosity of 5.

Express the OTP as a Function of Relative Viscosity

Using OBD correlation [Equation 4.6], lump all unknowns into parameter B, i.e.

$4090.6 = (6.6 \times 10^{-4})(5)^{-0.39}\ (B)$

$B = 1.161 \times 10^{7}$

Then calculate the oxygen transport potential for their system (assuming that the gas sparge rate and power input per unit volume remain constant).

$C^{*} = 7.2\ mg.l^{-1}$

$C = 0.7\ mg.l^{-1}$ (critical value, Liu *et al.* (1988))

$k_L a = 7662.8\ (\mu_{rel})^{-0.39}\ (7.2 - 0.7)$

$OTP = 49.81\ (\mu_{rel})^{-0.39}$

Prediction of Oxygen Demand at a Particular Solids Concentration

$D_C = 21.73\ \mu m$

Particle surface area, A $= 4\ \pi\ (D_C / (2 \times 10^{6}))^2\ m^2$

University of Cape Town

Mass of particle, M_P	=	$1.333 \times \pi \times \rho \, (D_C / (2 \times 10^6))^3$ kg
Mass solids in reactor	=	M $kg.m^{-3}$
Particles per unit volume	=	M/M_P particles
Surface area concentration	=	$M/M_P \times A$ $(m^2)(m^3 \text{ reactor})^{-1}$
Pyrite surface area concentration	=	$M/M_P \times A \times Y_{PY}$ $(m^2 \text{ pyrite})(m^3 \text{ reactor})^{-1}$

Then,

Oxygen Demand	=	$M/M_P \times A \times Y_{PY} \times R_{PY}$ $(kg\ O_2)(m)^{-3}(d)^{-1}$.

Using the calculation schemes outlined above as well as slurry viscosity data of Rao (1966), the oxygen demand and oxygen transfer potential in the van Staden (1991) reactors have been predicted at a range of solids concentrations. The results, for both the sulphide minerals studied, are presented in Tables A2.4 and A2.5, along with experimental bio-oxidation rate data. The rate data were converted so that they could be expressed in the same units as the demand and transfer potential, *viz.* $(kg\ O_2.m^{-3}.d^{-3})$. The data are discussed in Section 3.4.

University of Cape Town

Table A2.5 Oxygen Transfer Potential and Demand Estimates and Rate Data for Backfill Pyrite Concentrate

% Solids	Relative Viscosity	Oxygen Demand $(kg\ O_2)m^{-3}d^{-1}$	OTR $(kg\ O_2)m^{-3}d^{-1}$	Experimental Rate Data $(kg\ O_2)m^{-3}d^{-1}$
5	4.2	10.01	29.26	
10	4.5	20.02	28.48	
13.6	4.7	27.23	28.00	28.43
15	4.8	30.03	27.77	
20	5.04	40.05	27.25	
22	5.12	44.05	27.08	26.71
25	5.31	50.06	26.70	
30	5.61	60.07	26.13	
35	5.94	70.08	25.56	
40	6.26	80.09	25.04	
45	6.67	90.10	24.43	
50	7.18	100.12	23.73	
55	7.68	110.13	23.12	
60	8.20	120.14	22.54	
65	9.6	130.15	21.19	
70	11.5	140.16	19.75	
75	17.28	150.17	16.85	
80	38.4	160.18	12.34	

University of Cape Town

Table A2.6 Oxygen Transfer Potential and Demand Estimates and Rate Data for Run of Mine Ore

% Solids	Relative Viscosity	Oxygen Demand $(kg\ O_2)m^{-3}d^{-1}$	OTR $(kg\ O_2)m^{-3}d^{-1}$	Experimental Rate Data $(kg\ O_2)m^{-3}d^{-1}$
5	4.00	0.84	29.82	
10	4.10	1.68	29.53	
15	4.25	2.53	29.12	
20	4.40	3.37	28.73	
25	4.59	4.21	28.26	
30	4.73	5.05	27.93	
35	4.87	5.90	27.61	
40	5.77	6.74	25.85	
45	7.20	7.58	23.71	
50	9.62	8.42	21.18	
55	15.40	9.26	17.63	8.28
60	25.00	10.11	14.59	

University of Cape Town

APPENDIX THREE

EXPERIMENTAL DATA

The data obtained during the various experiments performed as part of this thesis are presented in this Appendix.

University of Cape Town

A. MALVERN PARTICLE SIZE ANALYSES

A.1 VAAL REEFS PYRITE CONCENTRATE BULK SAMPLE: SIZE ANALYSIS

Size (μm)	% Passing	Size (μm)	% Passing
564	100	59.3	53.5
524	100	55.2	50.5
488	100	51.3	47.7
454	100	47.7	45.2
422	100	44.4	42.9
392	100	41.2	40.8
365	100	38.4	38.7
339	100	35.7	36.6
315	100	33.2	34.5
293	100	30.8	32.5
273	99.9	28.7	30.7
254	99.9	26.7	29.0
236	99.7	24.8	27.6
219	99.4	23.1	26.3
204	98.9	21.4	25.2
190	98.1	19.9	24.2
176	97.1	18.5	23.1
164	95.8	17.2	22.0
153	94.2	16.0	20.8
142	92.2	14.9	19.5
132	89.9	13.9	18.2
123	87.3	12.9	16.9
114	84.4	12.0	15.8
106	81.2	11.2	14.7
98.6	77.9	10.4	13.9
91.7	74.4	9.64	13.2
85.3	70.8	8.97	12.5
79.3	67.2	8.34	11.9
73.8	63.6	7.76	11.2
68.6	60.2	7.21	10.2
63.8	56.8	6.71	9.1
		6.24	7.8
		5.8	6.5

University of Cape Town

A.2 VAAL REEFS PYRITE CONCENTRATE TYPICAL FRACTION PREPARED FOR FLUIDISED BED REACTOR TESTWORK: SIZE ANALYSIS

Size (µm)	% Passing	Size (µm)	% Passing
564	100	59.3	26.7
524	100	55.2	17.9
488	100	51.3	13.0
454	100	47.7	9.8
422	100	44.4	7.4
392	100	41.2	5.6
365	100	38.4	4.3
339	100	35.7	3.5
315	99.9	33.2	3.0
293	99.9	30.8	2.7
273	99.8	28.7	2.3
254	99.7	26.7	1.7
236	99.5	24.8	1.2
219	99.3	23.1	0.7
204	99.1	21.4	0.4
190	98.9	19.9	0.3
176	98.6	18.5	0.2
164	98.3	17.2	0.1
153	97.9	16.0	0.1
142	97.3	14.9	0.1
132	96.3	13.9	0.1
123	94.7	12.9	0.1
114	92.3	12.0	0.1
106	88.9	11.2	0.0
98.6	84.6	10.4	0.0
91.7	80.0	9.64	0.0
85.3	74.8	8.97	0.0
79.3	68.2	8.34	0.0
73.8	58.9	7.76	0.0
68.6	48.2	7.21	0.0
63.8	37.3	6.71	0.0
		6.24	0.0
		5.8	0.0

University of Cape Town

A.3 VAAL REEFS RUN-OF-MINE ORE SAMPLE: SIZE ANALYSIS

Size µm	% Passing
564	100
487	100
420	100
362	100
313	100
270	99.5
233	97.9
201	95.2
173	91.6
150	87.5
129	83.0
111	78.7
96.0	74.5
82.5	70.9
71.5	67.0
61.5	63.0
53.0	59.7
45.8	57.0
39.5	54.4
34.1	51.8
29.5	48.9
25.4	46.0
21.9	43.0
18.9	39.8
16.3	36.3
14.1	33.0
12.1	29.9
10.4	27.1
9.05	24.1
7.80	19.4
6.70	13.9
5.80	0.0

University of Cape Town

A.4 PRIESKA PYRITE CONCENTRATE SAMPLE: ANALYSIS

Size (µm)	% Passing	Size (µm)	% Passing
564	100	59.3	57.1
524	100	55.2	52.7
488	100	51.3	48.4
454	100	47.7	44.5
422	100	44.4	40.9
392	100	41.2	37.7
365	100	38.4	34.7
339	100	35.7	32.0
315	100	33.2	29.4
293	100	30.8	27.0
273	100	28.7	24.6
254	100	26.7	22.4
236	100	24.8	20.4
219	100	23.1	18.6
204	100	21.4	17.1
190	99.9	19.9	15.8
176	99.7	18.5	14.7
164	99.2	17.2	13.6
153	98.3	16.0	12.6
142	97.2	14.9	11.7
132	95.6	13.9	10.9
123	93.7	12.9	10.0
114	91.3	12.0	9.3
106	88.4	11.2	8.6
98.6	85.1	10.4	8.0
91.7	81.5	9.64	7.4
85.3	77.8	8.97	6.9
79.3	73.9	8.34	6.5
73.8	69.9	7.76	6.0
68.6	65.8	7.21	5.4
63.8	61.5	6.71	4.7
		6.24	4.0
		5.8	3.3

University of Cape Town

B. RESULTS OF BATCH BIO-OXIDATION OF VAAL REEFS RUN-OF-MINE PYRITE ORE

B.1 TRIAL ONE AT 20 PER CENT SOLIDS

Material	Vaal Reefs Run-of-mine Ore
Solids Concentration	20 %
Oxidation Rate	0.188 (kg Pyrite)$m^{-3}d^{-1}$
k_La	0.0509 s^{-1}

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} (liquid) $g.l^{-1}$	S (solids) %	ORP mV	pH	Acid ml	pH after	DO_2 $mg.l^{-1}$
0	3.1		0.786	444	1.83	-	-	
1				436				
2				433				
3				432				
4				434				
7				451				
8				470				
9				403				
10	<0.1	2.16	0.285	562	1.75	-	-	7.2
11				597				
12	0.01	1.80	0.222	630	1.78	-	-	7.4
13				623				
14	<0.01	1.67	0.236	631	1.75	-	-	7.6
15				637				
16				651				
17	<0.01	1.74	0.115	656	1.80	-	-	7.5
18				649				
19	<0.01	0.96	0.119	658	1.76	-	-	7.6
20				662				
21	<0.01	1.76	0.094	661	1.72	-	-	7.6
22				668				
23				672				
24	<0.01	1.47	0.061	673	1.68	-	-	7.6
25				674				
26	<0.01	1.63	0.051	674	1.70	-	-	7.6

University of Cape Town

B.2 TRIAL TWO AT 20 PER CENT SOLIDS

Material	Vaal Reefs Run-of-mine Ore
Solids Concentration	20 %
Oxidation Rate	0.239 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.997

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} (liquid) $g.l^{-1}$	S (solids) %	ORP mV	pH	Acid ml	pH after	DO_2 $mg.l^{-1}$
0	3.10		0.628	417	2.06	-	-	
1				414				
2				451				
3	<0.05		0.508	564	1.76	-	-	7.4
4				606				
5	<0.05		0.400	634	1.67	-	-	7.6
7			0.251	655		-	-	7.6
8				664				
9			0.133	675	1.51			7.6
12		1.32	0.116	666	1.59	-	-	7.7
13				650				
14		1.24	0.103	680	1.59	-	-	7.4

University of Cape Town

B.3 TEST AT 40 PER CENT SOLIDS

Material	Vaal Reefs Run-of-mine Ore
Solids Concentration	40 %
Oxidation Rate	0.383 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.980
k_La	0.0543 s^{-1}

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} (liquid) $g.l^{-1}$	S (solids) %	ORP mV	pH	Acid ml	pH after	DO_2 $mg.l^{-1}$
0	3.60		0.774	423	1.8	-	-	
1				405				
2				396				
3				391				
4				385				
7				371				
8				372				
9				372				
10	2.80	2.94		389	2.16	2.5	1.85	6.9
11				419	1.91	0.5	1.85	
12	2.00	2.38	0.663	429	1.91	0.6	1.86	7.3
13				440				
14	1.50	1.87		441	1.87	-	-	7.4
15				455				
16				475				
17	0.30	0.96	0.771	495	1.95	2.5	1.79	7.5
18				520				
19	0.11	0.96	0.719	530	1.81	-	-	7.4
20				538				
21	0.02	0.85	0.593	544	1.82			7.4
22				565				
23				590				
24	0.01	0.89	0.425	611	1.76			7.2
25				624				
26	<0.01	1.63	0.434	646	1.78			5.9
27				664				
28	<0.01		0.207	672	1.93			5.7
31	<0.01		0.124	680	1.60			7.6
33	<0.01		0.093	683				7.6
35	<0.01		0.070	690				7.6

University of Cape Town

B.4 TEST AT 60 PER CENT SOLIDS

Material	Vaal Reefs Run-of-mine Ore
Solids Concentration	60 %
Oxidation Rate	0.591 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.986
k_La	0.0389 s^{-1}

Day	Fe^{2+}	Fe_{total} (liquid)	S (solids)	ORP	pH	Acid	pH after	DO_2
	g.l^{-1}	g.l^{-1}	%	mV		ml		mg.l^{-1}
0	3.30		0.894	398	1.79-	-	-	
1				310				
2				309				
3				316				
4				320				
7				319				
8				333				
9				372				
101.10	1.37	0.848	388	2.62	4.3	1.82	6.8	
11				426	1.96	0.5	1.87	
12	1.20	1.32		430	2.00	1.0	1.84	7.2
13				438				
14	1.00	1.24	0.735	443	1.98	0.8	1.85	7.5
15				458				
16				474				
17	0.20	0.74	0.645	492	2.06	2.0	1.82	7.4
18				512				
19	0.07	0.70	0.632	526	1.87	-	-	7.6
20				552				
21	0.03	0.80	0.513	587	1.82	-	-	4.6
22				613				
23				643				
24	0.01	1.45	0.127	659	1.68	-	-	7.6
25				664				
26	<0.01	1.70	0.178	671	1.78	-	-	7.6
28	<0.01		0.110	684	1.93	-	-	7.5
31	<0.01		0.093	696	1.65	-	-	6.9

University of Cape Town

C. RESULTS OF BATCH BIO-OXIDATION OF PRIESKA PYRITE CONCENTRATE AT 10 PER CENT SOLIDS

C.1 TRIAL ONE

Material	Prieska Pyrite Concentrate
Solids Concentration	10 %
Oxidation Rate	3.60 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.981
k_La	0.0320 s^{-1}

Day	Fe^{2+}	$Fe_{soluble}$	Fe_{total}	ORP	pH	Acid	pH after	DO_2
	$g.l^{-1}$	$g.l^{-1}$	$g.l^{-1}$	mV		ml		$mg.l^{-1}$
0	2.9	9.51	13.10	480				
1				520				
2				600				
3	<0.1	11.73	16.85	625	1.31	-	-	7.6
4				639				7.3
5	<0.1	13.32	16.81	652	1.33	-	-	6.1
6	0.05	15.99	19.58	665	1.32			6.4
7	0.05	17.58	25.51	674	1.34	-	-	6.4
8	0.05	18.81	21.53	678	1.35			6.5
11		24.03	27.42	694				6.5

University of Cape Town

C.2 TRIAL TWO

Material	Prieska Pyrite Concentrate
Solids Concentration	10 %
Oxidation Rate	4.00 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.974
k_La	0.0320 s^{-1}

Day	Fe^{2+}	$Fe_{soluble}$	Fe_{total}	ORP	pH	Base	pH after	DO_2
	$g.l^{-1}$	$g.l^{-1}$	$g.l^{-1}$	mV		ml		$mg.l^{-1}$
0	3.1	13.26	14.66	503				7.2
1				608				
2				612				
3	0.05	17.04	23.62	630	1.16	40	1.32	6.6
4				642				
5	<0.05	19.38	21.09	659	1.44	-	-	6.6
6				678				
7	<0.05	25.17	27.78	690	1.25	40	1.20	4.4
8		31.38	32.64	698				4.5
9	<0.05	31.44	36.93	686	1.26	20	1.30	4.8
10				696				5.1
11	<0.05	32.82	33.38	704				4.6
13				714				4.7
14	<0.05	37.56	34.87	717	1.23	40	1.31	5.3

University of Cape Town

D. RESULTS OF BATCH BIO-OXIDATION OF PRIESKA PYRITE CONCENTRATE-QUARTZ MIXTURES

D.1 BIO-OXIDATION OF 10 PER CENT PYRITE, 10 PER CENT QUARTZ MIXTURE (TOTAL SOLIDS CONCENTRATION = 20 PER CENT)

Material	10% Prieska Conc., 10% Quartz
Solids Concentration	20%
Oxidation Rate	3.52 (kg Pyrite)$m^{-3}d^{-1}$
on pyrite basis	0.0420 (kg Pyrite)(kg pyrite)$^{-1}d^{-1}$
R^2	0.974
k_La	0.0263 s^{-1}

Day	$Fe_{soluble}$ $g.l^{-1}$	Fe_{total} $g.l^{-1}$	ORP mV	pH	Acid ml	pH after	DO_2 $mg.l^{-1}$
0	13.35	14.90	497	1.3			
1			500				
3			501				
6	12.45	15.21	600				7.2
7	14.94	17.63	623				5.5
8			641				4.9
10	18.75	20.98	669				3.8
12	23.64	25.74					

University of Cape Town

D.2 BIO-OXIDATION OF 10 PER CENT PYRITE, 20 PER CENT QUARTZ MIXTURE (TOTAL SOLIDS CONCENTRATION = 30 PER CENT)

Material	10% Prieska Conc., 20% Quartz
Solids Concentration	30 %
Oxidation Rate	3.54 (kg Pyrite)$m^{-3}d^{-1}$
on pyrite basis	0.0420 (kg Pyrite)(kg Pyrite)$^{-1}d^{-1}$
k_La	0.0236 s^{-1}

Day	$Fe_{soluble}$ $g.l^{-1}$	Fe_{total} $g.l^{-1}$	ORP mV	pH	Base ml	pH after	DO_2 $mg.l^{-1}$
0	18.63	20.30	516				6.0
1			536	1.50	-	-	
2			529				
3			524				
4			550				
6	17.34	21.38	570				6.5
10	19.26	22.77	630	1.38	10	1.40	5.2
11	18.99	25.55	632				
12	22.44	25.04	640				

University of Cape Town

E. INITIAL FLUIDISATION INVESTIGATIONS: EXPERIMENTAL AND THEORETICAL BED EXPANSIONS AT DIFFERENT FLUIDISING VELOCITIES

Initial fluidisation studies were conducted using the Vaal Reefs pyrite concentrate in a water-fluidised bed. The flowrate of water was determined by noting the time taken to collect a certain volume of water. The un-expanded bed of solids had a height of 0.024 m. Theoretical bed porosities (e) and theoretical bed expansions (H) were calculated according to the procedures outlined in Coulson and Richardson (1980). A terminal velocity of 26.7 x 10^{-4} $m.s^{-1}$ was used in the estimation.

University of Cape Town

Fluidising Velocity (x 10^4) $m.s^{-1}$	Experimental Bed Height m	Theoretical Bed Porosity	Theoretical Bed Height m
0.0	0.024	0.40	0.024
2.8	0.033	0.59	0.035
5.5	0.042	0.69	0.046
8.7	0.056	0.77	0.062
10.7	0.061	0.80	0.072
11.9	0.072	0.82	0.080
12.4	0.075	0.83	0.085
14.4	0.130	0.86	0.103
15.0		0.87	0.112
16.0		0.89	0.125
17.0		0.90	0.141
18.0		0.91	0.161
19.0		0.92	0.185
20.0		0.93	0.217
21.0		0.94	0.259
21.5		0.95	0.286
21.9	0.360	0.95	0.288
23.3	0.475	0.97	0.480
24.0		0.98	0.574

F. REPRODUCIBILITY TEST

F.1 SIMULTANEOUS REPRODUCIBILITY TEST ONE

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	150 g
Overall solids-to-liquid ratio	3.4 %
Bed solids concentration	20 %
Flowrate	584 $l.d^{-1}$
Bio-oxidation rate	0.439 (g Fe)$l^{-1}d^{-1}$
R^2	0.991
Total system volume	4.47 l

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} $g.l^{-1}$
0	2.2	5.15
1	0.9	5.22
2	0.1	5.17
3	0.1	5.50
4	0.1	6.38
5	0.05	6.54
6	0.03	7.13
7	0.01	7.48
8	0.01	7.99
9	0.01	8.36
10	<0.01	8.80
11	<0.01	9.32
12	<0.01	9.54
13	<0.01	9.33
14	<0.01	9.41
15	<0.01	9.86
16	<0.01	10.16
17	<0.01	10.62
18	<0.01	10.80
19	<0.01	11.12
20	<0.01	11.02

University of Cape Town

F.2 SIMULTANEOUS REPRODUCIBILITY TEST TWO

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	150 g
Overall solids-to-liquid ratio	3.4 %
Bed solids concentration	20 %
Flowrate	584 $l.d^{-1}$
Bio-oxidation rate	0.431 (g Fe)$l^{-1}d^{-1}$
R^2	0.955
Total system volume	4.47 l

Day	Fe^{2+} g.l^{-1}	Fe_{total} g.l^{-1}
0	1.8	5.47
1	0.1	5.50
2	0.01	5.79
3	0.01	6.59
4	<0.01	6.97
5	<0.01	7.49
6	<0.01	7.54
7	<0.01	8.13

University of Cape Town

F.3 CONSECUTIVE REPRODUCIBILITY TEST

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	150 g
Overall solids-to-liquid ratio	3.6 %
Bed solids concentration	20 %
Flowrate	584 $l.d^{-1}$
Bio-oxidation rate	0.442 (g Fe)$l^{-1}d^{-1}$
R^2	0.985
Total system volume	4.15 l

Day	Fe^{2+} g.l^{-1}	Fe_{total} g.l^{-1}
0	2.2	5.31
1	0.9	5.37
2	0.2	5.43
3	0.1	5.6
4	0.1	6.3
5	0.05	6.44
6	0.05	
7	0.01	7.44
8	0.01	7.9
9	0.01	7.94
10	<0.01	8.37
11	<0.01	8.84
12	<0.01	9.03
13	<0.01	9.46
14	<0.01	9.16
15	<0.01	9.66
16	<0.01	9.36
17	<0.01	9.95
18	<0.01	10.88
19	<0.01	11.25
20	<0.01	11.42

University of Cape Town

G. FBR DISSOLVED OXYGEN PROFILE TESTWORK

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	25 %
Bio-oxidation rate	0.0209 (kg Fe)(kg solids)$^{-1}$d^{-1}
R^2	0.990
Total system volume	4.47 l

University of Cape Town

G.1 DISSOLVED OXYGEN CONCENTRATIONS

The table below contains the dissolved oxygen measurements that were made at different levels up the fluidised bed reactor. The segmentation of the reactor is discussed in detail in Chapter Six.

The dissolved oxygen data presented in the table below are quoted in mg.l^{-1}.

DAY		0	1	2	3	4	5
LEVEL							
TOP	1	2.8	1.6	1.6	2.5	2.6	3.7
	2	2.8	1.7	1.7	2.8	3.2	4.0
	3	3.0	2.0	2.3	3.2	4.2	4.8
	4	3.5	2.5	3.2	4.1	4.4	5.2
	5	4.2	3.5	3.8	4.5	5.2	5.8
BOTTOM	6	5.4	5.8	5.7	5.8	6.1	6.2
SURGE TANK	7	5.8	6.3	6.2	6.4	6.6	6.4

G.2 AVERAGE OXYGEN UTILISATION RATES (OUR) FOR THE SEGMENTS

Note that the OUR data in the table below are expressed in units of (kg O_2)d^{-1} x 1000. (i.e. data read off the table should be divided by 1000).

	DAY	0	1	2	3	4	5
LEVEL							
TOP	2 to 1	0	0.095	0.095	0.284	0.568	0.284
	3 to 2	0.189	0.284	0.568	0.378	0.946	0.757
	4 to 3	0.473	0.473	0.851	0.851	0.189	0.378
	5 to 4	0.662	0.946	0.568	0.378	0.757	0.568
	6 to 5	1.135	2.176	1.797	1.230	0.851	0.378
BOTTOM							

University of Cape Town

H. FLUIDISED BED REACTOR TESTWORK AT VARIOUS OVERALL SOLIDS-TO-LIQUID RATIOS, CONSTANT BED SOLIDS CONCENTRATION.

H.1 VAAL REEFS PYRITE CONCENTRATE, SOLIDS LOADING OF 75g

See data table in Section I below.

H.2 VAAL REEFS PYRITE CONCENTRATE, SOLIDS LOADING OF 150g

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	150 g
Overall solids-to-liquid ratio	3.4 %
Bed solids concentration	20 %
Flowrate	554 $l.d^{-1}$
Bio-oxidation rate	5.22 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.985
Total system volume	4.47 l

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} $g.l^{-1}$	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	
0	1.8	5.47			
1	0.1	5.5	6.4	0.5	
2	0.01	5.79	6.3	0.4	
3	<0.01	6.59			
4	<0.01	6.97			
5	<0.01	7.49			
6	<0.01	7.54	6.1	0.4	
7	<0.01	8.13			
8	<0.01		5.8	0.6	
9	<0.01		6.8	0.6	
10	<0.01				

University of Cape Town

H.3 VAAL REEFS PYRITE CONCENTRATE, SOLIDS LOADING OF 200g

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	200 g
Overall solids-to-liquid ratio	4.47 %
Bed solids concentration	20 %
Flowrate	568 $l.d^{-1}$
Bio-oxidation rate	3.34 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.925
Total system volume	4.47 l

Day	Fe_{total} $g.l^{-1}$	ORP mV	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	
0	7.12	503			
1	7.6	510			
2	7.16	582			
3	8.33	620			
4		690			
5	8.49	632	6.8	0.4	
6	9.49	654	6.8	0.6	
7	9.52	643			
8	9.84	651			
9	10.05	674			
10		677			

University of Cape Town

H.4 PRIESKA PYRITE CONCENTRATE, SOLIDS LOADING OF 75g

Material	Prieska Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.68 %
Bed solids concentration	20 %
Flowrate	720 $l.d^{-1}$
Bio-oxidation rate	8.02 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.998
Total system volume	4.47 l

Day	Fe_{total} $g.l^{-1}$	ORP mV	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	
0	3.15	459			
1	3.03	534			
2	3.01	682			
3	3.79	700			
4	4.06	699	7.9	3.1	
5	4.31	695	7.9	2.5	
6	4.56	716	7.8	2.7	
8	5.39	730	7.9	3.4	

University of Cape Town

H.5 PRIESKA PYRITE CONCENTRATE, SOLIDS LOADING OF 200g

Material	Prieska pyrite concentrate
Solids Loading	200 g
Overall solids-to-liquid ratio	4.47 %
Bed solids concentration	20 %
Flowrate	720 $l.d^{-1}$
Bio-oxidation rate	7.16 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.982
Total system volume	4.47 l

Day	Fe_{total} $g.l^{-1}$	ORP mV	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	
0	4.07	442			
1	3.62	618	7.9	3.1	
2	3.62	625	7.0	0.5	
3	4.40	650	6.6	0.2	
5	6.04	722	6.8	0.3	
6	6.68	722	7.2	0.7	
7	7.38	725	7.1	0.6	

University of Cape Town

I. FLUIDISED BED REACTOR TESTWORK AT VARIOUS BED SOLIDS CONCENTRATIONS, CONSTANT OVERALL SOLIDS-TO-LIQUID RATIO

I.1 20 PER CENT BED SOLIDS CONCENTRATION, TRIAL 1

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	20 %
Flowrate	568 $l.d^{-1}$
Bio-oxidation rate	9.38 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.977
Total system volume	4.15 l

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} $g.l^{-1}$	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	
0	1.9				
1	0.1	5.59	6.6	1.4	
2	0.01	5.9	6.5	0.7	
3	<0.01	6.52			
4	<0.01	6.55			
5	<0.01	7.32			
6	<0.01	7.49	6.4	1.1	
7	<0.01	7.97			
8	<0.01	7.67	6.9	1.6	
9	<0.01	8.33	6.8	1.5	

University of Cape Town

I.2 20 PER CENT BED SOLIDS CONCENTRATION, TRIAL 2

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	20 %
Flowrate	771 $l.d^{-1}$
Bio-oxidation rate	9.82 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.988
Total system volume	4.47 l

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} $g.l^{-1}$	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	
0	2.2	6.27			
1	0.05	6.13			
2	<0.01	6.6			
3	<0.01	7.01			
4	<0.01	7.52	6.0	3.1	
5	<0.01	7.74	6.2	3.3	
6	<0.01	8.16	6.4	4.0	

University of Cape Town

I.3 20 PER CENT BED SOLIDS CONCENTRATION, TRIAL 3 (ORE BATCH 2)

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	20 %
Flowrate	864 $l.d^{-1}$
Bio-oxidation rate	8.28 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.984
Total system volume	4.15 l

Day	Fe^{2+}	Fe_{total}	ORP	DO_2 surge	DO_2 top FBR
	$g.l^{-1}$	$g.l^{-1}$	mV	$mg.l^{-1}$	$mg.l^{-1}$
0	2.6	5.9			
1	0.01	6.3			
2	<0.01	6.6	700	6.6	1.5
3	<0.01	7.1			
4	<0.01	7.5			
5	<0.01	7.7	747	6.5	2.1
6	<0.01	8.0			

University of Cape Town

I.4 25 PER CENT BED SOLIDS CONCENTRATION, TRIAL 1

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	25 %
Flowrate	675 $l.d^{-1}$
Bio-oxidation rate	10.23 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.971
Total system volume	4.47 l

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} $g.l^{-1}$
0	2.12	6.45
1	0.02	6.67
2	0.01	7.16
3	<0.01	7.42
4	<0.01	7.60
5	<0.01	8.25
6	<0.01	8.62
7	<0.01	8.98
8	<0.01	9.19
9	<0.01	9.37
10	<0.01	9.53

University of Cape Town

I.5 25 PER CENT BED SOLIDS CONCENTRATION, TRIAL 2

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	25 %
Flowrate	675 $l.d^{-1}$
Bio-oxidation rate	10.45 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.960
Total system volume	4.47 l

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} $g.l^{-1}$
0	2.3	6.69
1	0.1	6.83
2	0.01	7.24
3	<0.01	7.34
4	<0.01	7.68
5	<0.01	7.88
6	<0.01	8.87
7	<0.01	8.65
8	<0.01	9.37
9	<0.01	9.55
10	<0.01	9.45

University of Cape Town

I.6 25 PER CENT BED SOLIDS CONCENTRATION, TRIAL 3 (ORE BATCH 2)

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	25 %
Flowrate	950 $l.d^{-1}$
Bio-oxidation rate	11.20 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.990
Total system volume	4.47 l

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} $g.l^{-1}$	
0		5.81	see Section G for DO_2
1	0.01	6.28	
2	<0.01	6.53	
3	<0.01	6.97	
4	<0.01	7.37	
5	<0.01	7.61	
6	<0.01	7.58	

University of Cape Town

I.7 30 PER CENT BED SOLIDS CONCENTRATION

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	30 %
Flowrate	502 $l.d^{-1}$
Bio-oxidation rate	11.25 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.994
Total system volume	4.15 l

Day	Fe^{2+}	Fe_{total}	DO_2 surge	DO_2 top FBR	
	$g.l^{-1}$	$g.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	
0	2.1	6.34			
1	0.1	6.38			
2	0.01	6.64			
3	<0.01	7.03			
4	<0.01	7.37	6.6	1.9	
5	<0.01	7.63	6.5	1.8	
6	<0.01	7.92	6.1	1.8	

University of Cape Town

I.8 45 PER CENT BED SOLIDS CONCENTRATION, TRIAL 1

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	45 %
Flowrate	514 $l.d^{-1}$
Bio-oxidation rate	18.90 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.952
Total system volume	4.15 l

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} $g.l^{-1}$
0	2.2	7.39
1	0.1	7.08
2	0.01	7.77
3	<0.01	8.1
4	<0.01	8.69
5	<0.01	8.54
6	<0.01	9.59
7	<0.01	9.92
8	<0.01	8.88
9	<0.01	11.35
10	<0.01	9.76

University of Cape Town

I.9 45 PER CENT BED SOLIDS CONCENTRATION, TRIAL 2

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	45 %
Flowrate	514 $l.d^{-1}$
Bio-oxidation rate	19.17 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.982
Total system volume	4.15 l

Day	Fe^{2+} $g.l^{-1}$	Fe_{total} $g.l^{-1}$
0	2.0	6.76
1	0.01	6.78
2	<0.01	7.23
3	<0.01	7.45
4	<0.01	7.60
5	<0.01	7.85
6	<0.01	8.15
7	<0.01	8.57
8	<0.01	9.04
9	<0.01	8.94
10	<0.01	9.21

University of Cape Town

J. RESULTS OF FREE CELL DEPLETION INVESTIGATION

J.1 CONTROL BACTERIAL GROWTH TEST

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.8 %
Bed solids concentration	35 %
Bio-oxidation rate	14.25 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.986
Total system volume	4.15 l

Day	Fe_{total} $g.l^{-1}$	ORP mV	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	Free Cell Conc.x 10^{-7} cells.ml^{-1}
0	6.46	514			
1	6.61	653	6.8	2.9	4.8
2	7.16	691			5.6
3	7.46	710			6.8
4	8.09	710	5.5	1.4	8.0
5		729			12.0
6	8.65	750	6.5	3.0	12.0
7	8.84	755	6.4	4.2	18.0
8	9.15				
9	9.44				

University of Cape Town

J.2 FREE CELL DEPLETION AFTER 4 HOURS OF BATCH OPERATION

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	35 %
Bio-oxidation rate	7.95 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.993
Total system volume	4.47 l

Day	Fe_{total} $g.l^{-1}$	ORP mV	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	Free Cell Conc.x 10^{-7} cells.ml^{-1}
4hours	4.82	508			4.0
1	4.75	600	7.6	5.8	0.1
2	4.87	693			0.4
3	5.14	724			1.6
4	5.30	733	7.0	4.1	2.4
5		735			2.8
6	5.57	742	7.2	4.0	4.0
7	5.89	745	7.2	4.1	5.0
8	6.00				
9	6.13				

University of Cape Town

J.3 FREE CELL DEPLETION AFTER 1 DAY OF BATCH OPERATION

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.7 %
Bed solids concentration	35 %
Bio-oxidation rate	13.73 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.989
Total system volume	4.47 l

Day	Fe_{total} $g.l^{-1}$	ORP mV	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	Free Cell Conc.x 10^{-7} cells.ml^{-1}
0	5.63	475			
1	5.51	640	6.2	3.5	3.2
2	5.76	685	6.2	2.5	0.8
3	5.92	720	6.5	2.7	2.4
4	6.44	704	6.2	1.9	2.4
5	6.68	712	6.1	2.0	4.0
6	7.01	718	6.1	2.0	4.4
7	7.29	722	6.0	2.4	6.8
8		722	6.1	3.3	10.0

University of Cape Town

J.4 FREE CELL DEPLETION AFTER 3 DAYS OF BATCH OPERATION

Material	Vaal Reefs Pyrite Concentrate
Solids Loading	75 g
Overall solids-to-liquid ratio	1.8 %
Bed solids concentration	35 %
Bio-oxidation rate	14.33 (kg Pyrite)$m^{-3}d^{-1}$
R^2	0.988
Total system volume	4.15 l

Day	Fe_{total} $g.l^{-1}$	ORP mV	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	Free Cell Conc.x 10^{-7} cells.ml^{-1}
0	5.66	486			
1	5.62	655	6.4	2.6	2.0
2	6.01	682	6.2	1.4	3.2
3	6.09	712	6.2	1.4	8.8
4	6.28	716	6.7	3.2	0.8
5	6.91	733	6.5	2.9	2.0
6	7.03	743	6.6	2.6	2.8
7	6.97	746	6.6	3.2	4.4
8		747	6.7	3.9	6.8

University of Cape Town

J.5 FREE CELL DEPLETION AFTER 17 DAYS OF BATCH OPERATION

The free cell removal test performed after 17 days of batch operation was a continuation of L.1, the control cell growth tests. Operating details have been given under L.1.

Day	Fe^{2+} $g.l^{-1}$	ORP mV	DO_2 surge $mg.l^{-1}$	DO_2 top FBR $mg.l^{-1}$	Free Cell Conc.x 10^{-7} cells.ml^{-1}
17	4.0	332			<0.05
18	0.1	488			0.4
19		636			0.8

University of Cape Town

K. RESULTS OF STAGED FERROUS SULPHATE ADDITION

The percentages shown in the table below refer to the simulated overall solids-to-liquid ratio. The second row of the table indicates the amount of iron added (as ferrous sulphate) to the reactor on a daily basis.

	1.7%		10%		20%		30%		50%	
	0 g $Fe.l^{-1}.d^{-1}$		2 g $Fe.l^{-1}.d^{-1}$		4 g $Fe.l^{-1}.d^{-1}$		6 g $Fe.l^{-1}.d^{-1}$		10 g $Fe.l^{-1}.d^{-1}$	
DAY	ORP mV	Fe_{tot} $g.l^{-1}$	ORP mV	Fe_{tot} $g.l^{-1}$	ORP mV	Fe_{tot} $g.l^{-1}$	ORP mV	Fe_{tot} $g.l^{-1}$	ORP mV	Fe_{tot} $g.l^{-1}$
0	514	6.46		4.59	457	4.69		4.43	468	4.66
1	653	6.61	522	4.29	664		663	3.52	668	
2	691	7.16	707	5.44	695		744	8.4	682	
3	710	7.46	717		695	9.64	749		695	18.9
4	710	8.09	734		704	13.2	750	22.2	701	25.1
5	729		746	9.17	702	15.1	755	23.7	704	26.9
6	750	8.65	737	9.47	702	18.2	719	25.9	704	37.5
7	755	8.84	734	10.06	703		690	30.6	611	
8			754	10.54	703	28.6	674	28.9	610	
9			754	14.50	710	24.9	650	39.6	562	
10					703	28.31			713	
11					675				546	
12					645	38.58			516	

University of Cape Town