

An Investigation into the Feasibility of Bioleaching Copper Sulphide Ore of Nchanga Mine, Chingola, Zambia

by

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.....

James Manchisi

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Summary

Bioleaching is now well established for extraction of copper from its low-grade, mixed oxide/sulphide ores in bioheap operations (Watling, 2006). It is claimed bioleaching may be a cheaper alternative to other traditional metal extraction techniques such as smelting and therefore more suitable to treat marginal or low-grade ores where high-grade mineral reserves have been depleted. But the degree of microbial oxidation for different copper sulphides varies significantly partly because of different types and level of impurity minerals associated with copper sulphides from different sources. Several authors have reported different mineral leaching kinetics data on account of variability of mineralogical composition and different solution conditions and leaching systems being employed. This has indicated that further work was necessary to determine the kinetics of copper extraction, extent of mineral dissolution and effects of some leaching variables on copper dissolution for an ore from Nchanga mine under various solution conditions.

The preliminary information on the extent of mineral dissolution, microbial activity and leaching kinetics data may be useful for the design, and possible development and operation of tank or heap bioleaching. Therefore, the purpose of this study was to establish the potential of bioleaching a mixed copper oxide/sulphide rougher concentrate of predominantly chalcocite (Cu_2S) from Nchanga mine of the Zambian Copperbelt, using a mixed culture of iron- and sulphur-oxidizing mesophilic bacteria.

Currently, bioleaching is understood to involve both acid (protons) and ferric iron that attack the sulphide mineral to produce metal ions, ferrous iron and reduced sulphur compounds in solution. Ferrous iron is oxidised back to ferric form by iron-oxidising bacteria. The compounds of sulphur are oxidised to sulphate and protons by sulphur oxidising bacteria through either the thiosulphate or polysulphide pathways (Boon, 1996; Sand *et al.*, 1995, 1999; Breed and Hansford, 1999; Schippers and Sand, 1999). The role of microorganisms is to regenerate the ferric iron and acid, maintaining high redox potential and acidity of the bioleaching system hence promoting the dissolution of metal sulphides (Escobar *et al.*, 1993).

A review of literature on copper bioleaching has indicated that secondary sulphide minerals of copper (such as chalcocite, covellite and bornite) have been demonstrated

to show satisfactory bioleach kinetics with mesophilic bacteria (Dew *et al.*, 1999), with several bioheap operations worldwide extracting copper under these conditions (Watling, 2006). However, chalcopyrite has been reported to be very difficult to leach under mesophilic conditions. Attempts to improve chalcopyrite bioleaching now involve the application of controlled solution redox potentials, use of silver as a catalyst and the application of thermophilic bioleaching to quickly and completely leach chalcopyrite (Gericke *et al.*, 2001; Konishi *et al.*, 2001; Mousavi *et al.*, 2005).

Chalcocite is an important secondary sulphide of copper that is reported to leach through a two-stage mechanism. It is rapidly attacked by ferric iron during the first stage to give CuS intermediate product while the second stage proceeds more slowly. About half (50%) of the copper in Cu₂S is leached quickly though a complete dissolution requires much longer times (Dutrillac and MacDonald, 1974; Rossi, 1990; Bolorunduro, 1999). Under mesophilic conditions, high rates of copper extraction from chalcocite have been reported for low pulp densities of typically less than 5% w/v solids, pH 1.3-2.3, temperatures of between 25-40 °C and quite low ferric iron concentration (Rivera-Santillan *et al.*, 1999; Dew *et al.*, 1999; Sakaguchi *et al.*, 1976).

In order to determine the amenability of the ore to microbial leaching it was hypothesised that copper sulphide mineral dissolution is enhanced by the activities of iron- and sulphur-oxidising bacteria and that the extent of mineral dissolution is dependent on solution conditions. To test the hypothesis, batch chemical and bioleaching experiments were conducted under different experimental and solution conditions in laboratory stirred tank bioreactors at 35°C, initial pH 1.50, 5% w/w pulp density and 0k basal salts growth medium, sparged with compressed air. Using Reflected Light Microscopy, the ore was mineralogically characterised to consist mainly of chalcocite, chalcopyrite, pyrite, malachite, cuprite and cupriferous micas, with 15% total copper, 7.01% iron and 9.51% sulphur.

Several studies involving copper sulphides have been conducted in shake flask experiments where cell/microbial growth rates are more often done manually using such techniques as cell counts, protein analysis etc. Due to relatively slow kinetics associated with shake flask experiments, low accuracy and longer time requirements in the more common cell counts technique this study employed stirred tank leaching method using off-gas analysis to enumerate microbial cells following the methods of

Boon (1996) and Breed (2000). Infact reported bioleaching studies involving copper sulphide ores and/or minerals coupled to the off-gas for analysis of microbial growth are rather fewer, therefore it was necessary to conduct this study using the online off-gas technique as a faster and alternative tool to enumerate microbial cells.

Similar solution conditions to those of published studies involving shake flask experiments were therefore applied in this study to investigate the extent of copper extraction in stirred tank bioreactors for Nchanga copper sulphide ore. These include pH of 1.0-2.0, 25-40°C temperature (reported temperature range for mesophilic bacterial growth), low ferric iron concentration of 0.05-0.16 mol/l and a fixed low solids concentration (pulp density) of 5 %w/v. An inoculum of iron- and sulphur-oxidising mesophilic bacteria previously grown on chalcopyrite was obtained from a UCT laboratory stock culture. The progress of bioleaching was then monitored through measurements of $[\text{Fe}^{2+}]$, $[\text{Fe}^{3+}]$, $[\text{Cu}^{2+}]$, pH and solution redox potentials while bacterial activity was monitored online through CO_2 and O_2 utilisation rates.

The extent of copper sulphide oxidation by ferric iron through microbial action depends on the mineral itself, temperatures employed, oxygen availability, pH as well as mass transfer effects. Therefore, it was necessary to investigate the effects of some of these variables on copper dissolution rates in this study. Pyrite and to some extent chalcopyrite have been shown to be a source of soluble iron since the ferric (Fe^{3+}) form is the main oxidant and therefore the driving force in bioleaching systems. The effects of both inherent pyrite in the ore and added ferric iron on copper dissolution were therefore investigated in the present work.

The results and main findings of this investigation are summarised in the following sections. The preliminary experiments were done to determine acid requirement of the ore. The initial rapid consumption of acid was attributed to the reactive alkaline gangue minerals and the chemical (acid) solubilisation of copper oxides/carbonates. Comparatively, bioleaching experiments exhibited highest acid consumption rates and copper extraction than the sterile oxidative acid leaching experiments. The acid demand therefore was 150-300 and 150-240 kg acid/ton ore for bioleaching and sterile oxidative acid leaching experiments respectively.

The results show several differences in copper extraction and leach rates for the abiotic chemical (acid) leaching and bioleaching experiments. The lowest copper extraction (of 20%) was obtained for the non-oxidative acid leaching (without air), followed by a higher copper dissolution (of about 45%) in the oxidative acid leaching experiments (acid + air) in about 50 hours. Finally, nearly 75% copper was solubilised in 50 hours in the bioleaching experiments (acid + air + bacteria), resulting in overall copper extraction of 93% with up to 8.0 g.L^{-1} Cu in solution in 6 days. Thus, the abiotic acid leaching experiments exhibited high leach rates but low copper recovery, corresponding to the dissolution phase of mainly copper oxides/carbonates but not necessarily copper sulphides. It can be concluded that suitable iron-oxidising bacteria oxidised any ferrous iron in solution to ferric iron, which together with acid subsequently oxidised copper sulphides to give high copper recovery and leach rates in the case of bioleaching. These results are consistent with literature data, confirming and recognising the fact that the presence of bacteria increases the rate of leaching.

Bioleaching of a leach residue from non-oxidative acid leach experiment was observed to leach rather slowly relative to the fresh ore, though eventually giving over 90% copper extraction in both cases. It may not be economical to preleach the ore in acid followed by microbial leaching of acid leached residues. Therefore, direct bioleaching of fresh ore may be preferable because of faster oxidation kinetics.

Using off-gas data, the microbial oxygen and carbon dioxide consumption rates were observed to be rapid during the exponential phase where ferrous iron in solution was also high. The growth and activity of bacteria therefore seemed to be dependent on ferrous iron concentration in solution as noted from changes in ferrous iron concentration and microbial off-gas utilisation rates. The result was a high microbial population of up to 10.0 mm C.L^{-1} at the stationary phase. Thus, off-gas analysis is useful for calculating microbial growth rates and other kinetic parameters even in multi-sulphide leaching system as it has been done for single mineral substrates like pyrite and chalcopyrite.

In the final (decay) phase, a gradual decrease in microbial gas uptake was accompanied by low ferrous iron with significantly high ferric iron concentration in solution. Consequently, solution redox potentials increased rapidly before levelling off at about 690 mV (vs. Ag/AgCl). The observed rapid increase in solution redox

potentials was attributed to the fast reduction of ferric iron probably by chalcocite during first stage leaching for which the potential was reflected by changes in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of dissolved iron in the leach slurry. Also, the dissolution of pyrite was only significant at high redox potentials from the observed measurements of total soluble iron. The slurry pH was unstable if uncontrolled but later decreased indicating a microbial sulphur-oxidising capacity after 3 days. It appears therefore that ferrous iron and sulphur compounds (and not chalcocite) are the substrates for bacteria.

The effects of pH, temperature, initial ferric iron concentration and particle sizes on copper leached were then investigated. The results indicated little effect of pH on the amount of copper solubilised in the 0.70-2.00 pH range investigated. An estimated average dissolution of about 90% copper after 6 days was observed in nearly all cases of pH variation. Ferric bioleach experiments showed highest leach rates and amounts of copper leached though jarosite-like precipitates were noticeable on the reactor walls. Copper recovery slightly increased as the initial ferric iron concentration was increased. After just 2 hours 45% copper was leached at $3.0 \text{ g.L}^{-1} \text{ Fe}^{3+}$ iron, increasing to about 58% copper dissolution at $9.0 \text{ g.L}^{-1} \text{ Fe}^{3+}$ iron concentration. The kinetics of microbial ferric leaching were influenced only initially (< 48 hours) though about 94% copper was leached in all cases.

The amount of copper leached did not depend on temperature initially but later increased as temperature was increased from 25 to 40°C . Highest copper recovery of about 95% was obtained after 6 days at 40°C . The highest microbial growth rate was obtained also at this temperature contrary to optimum mesophilic temperatures of around 35°C reported in the literature. The activation energy calculated was 71.4 KJ.mol^{-1} which indicates that the chemical reaction was rate controlling. Furthermore, the smaller the particle sizes the greater the amount of copper solubilised and the higher the leach rates as expected. This means fine grinding gives faster leaching kinetics.

The results of this investigation have established that bioleaching of Nchanga copper sulphide ore requires high solution redox potentials, low solution pH (0.6-2.0) and a certain amount of ferrous iron for high copper extraction and microbial activity. The leaching profile for this ore progressed in a three phase sequence. In phase one, 20% copper was abiotically leached in dilute acid without air (oxygen) corresponding to

the chemical (acid) dissolution of copper oxides/carbonates. The second phase resulted in 58% copper being abiotically and chemically extracted in the presence of air. The last phase involving bioleaching resulted in over 93 % copper recovery.

Finally, this study has established a pH range of 1.00-1.50, temperature of 40 °C and an initial ferric iron concentration of 9.0 g.L⁻¹ as being optimum for bioleaching of Nchanga copper sulphide ore. The best microbial activity and highest copper recovery of up to 94% were obtained under these conditions. Also, the finest particle size range gave the best leach rates and copper recovery. Hence ore grinding to the smallest particle size possible would result in higher copper extraction. The highest leach rate of 0.737 g Cu (g Cu in ore)⁻¹day⁻¹ was obtained in the bioleaching experiment with the largest initial ferric iron concentration (of 9.0 g.L⁻¹) than for any other experimental conditions employed. This leach rate was significantly higher than a rate of 0.548 g Cu (g Cu in ore)⁻¹day⁻¹ for a case of bioleaching without any added ferric iron. The extent of copper dissolution was 94% both for bioleaching experiments involving inherent iron (pyrite) and added ferric iron. This means ferric iron does not increase copper recovery but rather increases the leach rates. Therefore, bioleaching of Nchanga copper sulphide ore by utilising its inherent pyrite as a source of soluble ferric iron may be a better option than the deliberate addition of ferric iron to the leaching system.

On the basis of high copper extraction and leach rates obtained, and satisfactory microbial activity, Nchanga copper sulphide ore has the potential to be bioleached under mesophilic conditions. It is therefore recommended that further investigations involving column trials should be done to ascertain the leachability and scale-up of the present experimental data to a possible heap bioleaching. It is also proposed that a rigorous mathematical treatment of degree of reduction balances must be applied to a multi-substrate system such as this one in order to relate the rate of copper dissolution to microbial oxygen and carbon dioxide consumption rates as it has been done for single substrate (such as ferrous iron and sulphur). One limitation in this study was the inability to determine the qualitative and quantitative mineralogical analysis of the leach residues. This is very important in order to fully interpret the bioleaching data.

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Notation

E°	standard redox potential	mV
E	redox potential	mV
$mV \ RT/nF$	Nernst parameter	mV
AAS	atomic absorption spectroscopy	
SHE	standard hydrogen electrode	mV
XRD	X-ray Diffusion	
XPS	X-ray photoelectron spectroscopy	
G_f°	standard Gibbs free energy	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
C_f°	specific heat capacity	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
H_f°	standard enthalpy of formation	$\text{kJ} \cdot \text{mol}^{-1}$
E_a	activation energy	$\text{kJ} \cdot \text{mol}^{-1}$
$[\text{Fe}^{2+}]$	ferrous iron concentration	$\text{mol} \cdot \text{L}^{-1}$
$[\text{Fe}^{2+}]_{\text{thres}}$	threshold ferrous iron concentration	$\text{mol} \cdot \text{L}^{-1}$
$[\text{Fe}^{3+}]$	ferric iron concentration	$\text{mol} \cdot \text{L}^{-1}$
$[\text{Fe}]^{\text{tot}}$	total iron concentration	$\text{mol} \cdot \text{L}^{-1}$
k, K	rate constants	
K_i	inhibition constant	$\text{mol} \cdot \text{L}^{-1}$
K_s	monod constant	
n	stoichiometric constant	
d	particle diameter	
q_{O_2}	bacterial specific O_2 utilisation rate	$(\text{mol } O_2) \cdot (\text{C} \cdot \text{mol})^{-1} \cdot \text{s}^{-1}$
$q_{O_2}^{\text{max}}$	max bacterial specific O_2 utilisation rate	$(\text{mol } O_2) \cdot (\text{C} \cdot \text{mol})^{-1} \cdot \text{s}^{-1}$
q_s	bacterial specific substrate utilisation rate	$(\text{mol } O_2) \cdot (\text{C} \cdot \text{mol})^{-1} \cdot \text{s}^{-1}$
$r_{Fe^{2+}}$	rate of ferrous iron production	$\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
rpm	revolutions per minute	
R	universal gas constant	$8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
t	time	
T	temperature	
n	number of electrons transferred	

C_x	bacterial concentration	mol C.L^{-1}
F	Faraday constant	
m_o	maintenance coefficient on oxygen	$(\text{mol O}_2).(\text{mol C})^{-1}.\text{h}^{-1}$
m_s	maintenance coefficient on substrate	$(\text{mol O}_2).(\text{mol C})^{-1}.\text{h}^{-1}$
r_{CO_2}	rate of carbon dioxide utilisation	$\text{mol.L}^{-1}.\text{h}^{-1}$
r_{O_2}	rate of oxygen utilisation	$\text{mol.L}^{-1}.\text{h}^{-1}$
r_x	rate of bacterial growth	$\text{mol C.L}^{-1}.\text{h}^{-1}$
μ	specific growth rate of bacteria	h^{-1}
$X_{\text{CO}_2}^{\text{in}}$	mole fraction of carbon dioxide in feed air	mole.mole^{-1}
$X_{\text{CO}_2}^{\text{out}}$	mole fraction of carbon dioxide in off-gas	mole.mole^{-1}
$X_{\text{N}_2}^{\text{in}}$	mole fraction of nitrogen in feed air	mole.mole^{-1}
$X_{\text{N}_2}^{\text{out}}$	mole fraction of nitrogen in off-gas	mole.mole^{-1}
$X_{\text{O}_2}^{\text{in}}$	mole fraction of oxygen in feed air	mole.mole^{-1}
$X_{\text{O}_2}^{\text{out}}$	mole fraction of oxygen in off-gas	mole.mole^{-1}
Y_{ox}	yield of bacteria on oxygen	$(\text{mole C}).(\text{mole O}_2)^{-1}$
Y_{sx}	yield of bacteria on substrate	$(\text{mole C}).(\text{mol substr})^{-1}$
$Y_{\text{ox}}^{\text{max}}$	max. yield of bacteria on oxygen	$(\text{mole C}).(\text{mole O}_2)^{-1}$
$Y_{\text{sx}}^{\text{max}}$	max. yield of bacteria on substrate	$(\text{mole C}).(\text{mole substr})^{-1}$
$\phi_{\text{CO}_2}^{\text{in}}$	flow rate of carbon dioxide in	mole.h^{-1}
$\phi_{\text{CO}_2}^{\text{out}}$	flow rate of carbon dioxide out	mole.h^{-1}
$\phi_{\text{N}_2}^{\text{in}}$	flow rate of nitrogen in	mole.h^{-1}
$\phi_{\text{N}_2}^{\text{out}}$	flow rate of nitrogen out	mole.h^{-1}
$\phi_{\text{O}_2}^{\text{in}}$	flow rate of oxygen in	mole.h^{-1}
$\phi_{\text{O}_2}^{\text{out}}$	flow rate of oxygen out	mole.h^{-1}
ϕ_{in}	flow rate of inlet air	mole.h^{-1}
ϕ_{out}	flow rate of outlet air	mole.h^{-1}
$r_{\text{Fe}^{2+}}$	rate of ferrous iron production	$\text{mol.L}^{-1}.\text{h}^{-1}$

$r_{Fe^{3+}}$	rate of ferric iron production	$\text{mol.L}^{-1}.\text{h}^{-1}$
r_{H^+}	rate of proton production	$\text{mol.L}^{-1}.\text{h}^{-1}$
r_{H_2O}	rate of water production	$\text{mol.L}^{-1}.\text{h}^{-1}$
$r_{NH_4^+}$	rate of ammonium production	$\text{mol.L}^{-1}.\text{h}^{-1}$
r_{FeS_2}	rate of pyrite production	$\text{mol.L}^{-1}.\text{h}^{-1}$
r_s	rate of substrate production	$\text{mol.L}^{-1}.\text{h}^{-1}$
$r_{SO_4^{2-}}$	rate of sulphate production	$\text{mol.L}^{-1}.\text{h}^{-1}$
gpt	grammes per tonne	
gpl	grammes per litre	
Wt %	Weight percent	
TCu	Total Copper	
ASCu	Acid soluble Copper	
AICu	Acid insoluble Copper	

Chapter 1

Introduction

1.1 Background

Bioleaching is fairly well established for the treatment of certain base metal sulphide minerals, where suitable iron and sulphur oxidising bacteria participate in the leaching of usually low-grade ores, and for the pre-treatment of pyritic refractory gold ores and concentrates (Brierley and Brierley, 2001). The microbial leaching of low-grade copper sulphide deposits and other mine wastes to recover copper has been practiced for many years. An early report on copper bioleaching application treated sub-marginal grade, run-of-mine copper bearing rock in dumps at Kennecott Bingham Mine (Murr, 1980).

Though the role of iron-oxidising bacteria was recognised after the discovery of iron and sulphur-oxidising bacterium *Acidithiobacillus ferrooxidans* in acid mine drainage by Colmer and Hinckle (1947) as reported by Murr (1980), not much was made to optimise dump design to allow for maximum solution contact with rock masses and to promote the activity of bacteria (Murr, 1980; Ehrlich, 1999; Brierley and Brierley, 1999; Olson *et al.*, 2003). More recently, bioleaching is carried out in constructed heaps to recover copper from much higher grade ores (Brierley and Brierley, 2001). Thus, bioleaching is now being applied to treat low-grade ores in bioheap operations or high-grade ores and concentrates in stirred tank bioreactors.

At present, the microbial heap leaching of copper from low-grade ores containing secondary sulphide minerals such as chalcocite has been successfully applied at several operations worldwide (Brierley and Brierley, 2001; Watling, 2006). Chalcopyrite is the most abundant primary copper sulphide mineral and thus economically the most important (Dresher, 2004). Although it is refractory to bioleaching with mesophilic bacteria, other secondary copper sulphide minerals such as chalcocite, covellite and bornite are bioleachable (Dew *et al.*, 1999). This thesis reports on feasibility study of

bioleaching of a mixed copper oxide-sulphide rougher concentrate from Nchanga mine of the Zambian Copperbelt with a view to establishing its bioleaching potential.

This chapter describes the project background and the motivation for the research work. It also describes the overall objectives, key questions and hypotheses, and the thesis layout.

1.1.1 Mineralogy of Zambian Copperbelt

An extensive review of the geology and mineralogical distribution of Copperbelt ores can be found in the work done by Tapa (1998). However, only an overview of the characteristic mineralogy of some ores is briefly discussed here.

The Copperbelt ores contain over 30 known minerals of mainly copper and cobalt. Chalcopyrite, bornite and chalcocite are the major copper sulphide minerals with carrollite, linnaeite and cobaltferrous pyrite being some of the cobalt sulphides. Smaller amounts of other base metal sulphides such as galena, sphalerite, molybdenite and uranium minerals have been identified at some mines as cited by Tapa (1998).

Chalcopyrite is the main source of copper in most ore bodies and it occurs mainly as disseminated grains. Following chalcopyrite is bornite occurring as disseminations and more massive aggregates. Chalcocite is dominant in certain ore bodies but the most abundant secondary copper sulphide in Nchanga ores. It is found both as disseminated particles and reaction rims around the copper-rich sulphides. Covellite and digenite have also been identified in Copperbelt ores. Malachite is the major copper carbonate, classified metallurgically as an 'oxide', at Nchanga mine and contributes substantially to copper production. It is found in oxidised zones in some Copperbelt ores. In the Nchanga ore, malachite is found as blebs, disseminations or as vein coatings. For weathered ores, it occurs as replacements of the mineral from which it is derived (Tapa, 1998)

The main source of cobalt is carrollite. It has disseminated grains and often associated with chalcopyrite or bornite with proportions of copper and cobalt in carrollite found to

be close to 20% and 38% stoichiometric ratios respectively. Linnaeite has also been identified as an intergrown phase in carrollite grains in some ore bodies (Tepa, 1998).

A great variety of copper-containing oxides, sulphates, phosphates and silicates exists. Cuprite is a more common copper oxide mineral. It is found to occur as earthy masses intergrown with malachite and iron oxides. Tenorite is another oxide that occurs as fine-grained, earthy material intimately intergrown with cuprite but found less in proportions than cuprite. Chrysocolla is a common copper silicate mineral in Copperbelt ores particularly at Nchanga mine. Other forms of micaceous copper minerals are cupriferrous micas and wad. The hydrated copper phosphates which occur in the weathered zones of Copperbelt ores is mainly Pseudomalachite. A summary of the mineralogy of Copperbelt ores is given in appendix.

Nchanga mine has a predominantly mixed copper oxide-sulphide mineral deposit with substantial amounts of cobalt minerals. The mineralogy of the ore is mainly secondary copper sulphides of chalcocite and covellite with significant quantities of chalcopyrite while malachite/azurite, some cuprite and copper silicates (chrysocolla) are some of the important copper oxide minerals (Tepa, 1998).

1.1.2 Brief Process Description of Nchanga Operations

The Nchanga Concentrator of Konkola Copper Mines (KCM) currently treats open pit and underground copper ores for the recovery of copper sulphide minerals by froth flotation. A bulk sulphide concentrate with targeted final grade of about 44% copper is obtained and taken to Nkana smelters. The underground mine produces approximately 250 000 tonnes of copper ore per month at a grade of about 3% total copper. The output from open pit operations is about 480 000 tonnes of copper ore with varying grades from 1.0 to 2.9% copper. The principal sulphide mineral in the copper feeds is chalcocite, while chalcopyrite and bornite occur to a lesser extent. Malachite, azurite and cuprite are the main oxide minerals. There are small amounts of relatively non-floatable chrysocolla and cupriferrous mica. The tailings (containing mainly oxide copper) from current operations, together with reclaimed tailings from old dams constitute the feed to the

Tailings Leach Plant (TLP) designed for recovery of oxide copper through acid leach-solvent extraction-electrowinning circuit as copper cathodes. The resulting leach residues are neutralised and subsequently pumped to a tailings dam for disposal.

1.1.3 Project Background and Motivation

The future and sustainability of operations at Nchanga Mine are uncertain due to the fact that high-grade mineral reserves are almost depleted. This prompted investigations to look at ways of exploiting large and abundant stockpiles of low-grade mineral resources using alternative and cheaper extraction techniques. Further, the bioleaching response of individual copper sulphide ores and minerals from different localities is remarkably different. Many authors have reported different mineral leaching kinetics data on account of variability of mineralogical composition and different solution conditions and leaching systems being employed. This has indicated that further work was necessary to determine the kinetics of copper extraction and extent of mineral dissolution under various solution conditions. This preliminary leaching kinetics data may be useful for a possible development of tank or heap bioleaching.

The use of conventional technology such as smelting may not be economically feasible because of the need to have sufficiently high metal concentrations in the feed ore. Even the capital costs and energy input for smelting are very high (Dreisinger, 2005). One of the process options is bioleaching as it has been successfully and widely applied to leach oxides and secondary sulphides of copper in heaps (Watling, 2006). Microbial leaching has virtually no lower limit of feed grade in the ore making it more suitable to treat a much lower grade more economically than pressure leaching or smelting (Miller, 1997). Bioleaching is generally cheaper and simple to operate and maintain. It uses non sophisticated equipment and requires less specialist skills (Miller, 1997).

Consequently KCM has embarked on an extensive test work program that is looking at possibilities of heap acid leaching and bacterial leaching. Part of the investigations underway includes testing of foreign copper ore such as those from Western Zambia and neighbouring DR Congo. This particular investigation focused on the feasibility studies

of bacterial leaching and thus forms part of the whole test work program. It is not doubted that the interest in bioleaching at Nchanga mine may lead to bioleaching operations and scale up at some stage for sustainability. In this work the amenability of bacterial leaching to treat copper sulphides from Nchanga Mine was investigated.

The iron and sulphur laboratory of Bioprocess Research Unit in Chemical Engineering at UCT is currently investigating rate processes of bioleaching of sulphide minerals, and the kinetics of microbial ferrous iron and sulphur oxidation. This particular investigation focussed on the kinetic studies of bacterial leaching in stirred tank bioreactors using Nchanga Copper Sulphide Ore as a case study, with a view to obtaining kinetic data that may be useful in developing tank or heap bioleaching. The work further seeks to gain some understanding on the bioleaching profiles of mixed oxide-sulphide feeds. Thus, the purpose of the present work was to explore the potential of bioleaching Nchanga copper ore by determining the kinetics and extent of copper dissolution, and also to give definition of how the rates and recoveries of copper are affected by the operating conditions.

Dew *et al.* (1999) conducted experiments for the continuous bioleaching of a Zambian concentrate from unspecified mine site with mesophilic culture at 40°C. The relative rates of copper sulphide mineral dissolution are shown in Figure 1.1. Their work demonstrated that it is possible to attain complete dissolution of most secondary copper sulphide minerals including chalcocite, covellite, bornite and enargite. However, chalcopyrite bioleaching was not satisfactory probably due to passivation of the mineral during leaching. The overall copper dissolution achieved was 88%. They attributed the residual copper to chalcopyrite. This can be seen from its dissolution which was limited to 43%. Perhaps due to proprietary nature of their work, Dew *et al.* (1999) did not discuss their detailed experimental and solution conditions they employed.

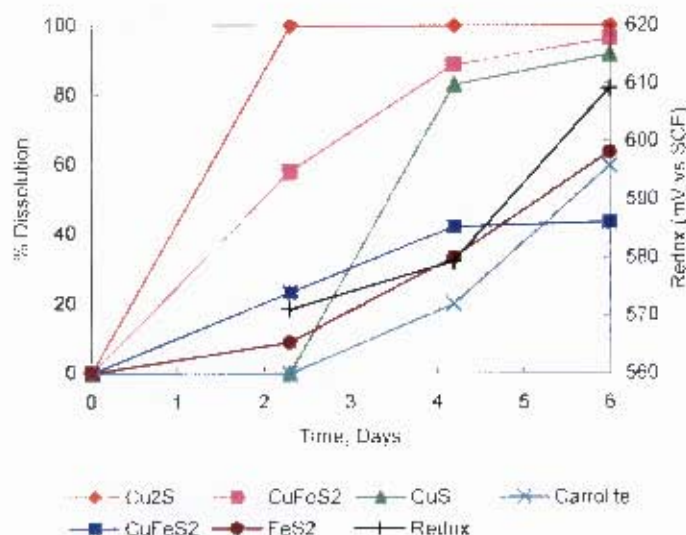


Figure 1.1: Dissolution of copper sulphide minerals plotted against time for a Zambian concentrate in a continuous bioleaching system with mesophilic culture. (Redrawn from Dew *et al.*, 1999)

1.2 Key Questions and Hypotheses

In order to design and operate bioleach heaps for maximum metal extraction, preliminary information on the extent of mineral dissolution, microbial activity and leach kinetics is necessary. Previous work has shown that such information is still lacking. Therefore, in order to determine the amenability of the ore to microbial leaching it is hypothesised that copper sulphide mineral dissolution is enhanced by the activities of iron and sulphur oxidising bacteria and that the extent of mineral dissolution is dependent on solution conditions. Some of the key questions that were addressed to test the hypothesis include:

- [1] Is Nchanga copper sulphide ore amenable to microbial leaching?
- [2] What is the extent of mineral dissolution under various solution conditions?
- [3] Under what solution conditions is the mineral dissolution greatest?

1.3 Research Objectives

The purpose of this study was to establish the potential of bioleaching Nchanga copper sulphide ore using a mixed culture of iron and sulphur oxidizing mesophilic bacteria in batch stirred tank bioreactors. Specifically, the objectives were to;

- [1] Carry out an extensive review of the literature on copper bioleaching for a thorough understanding of the conditions under which the bioleaching window is possible.
- [2] Determine the extent of mineral dissolution and kinetics of copper extraction under laboratory conditions and to compare the experimental data with published literature.
- [3] Determine the microbial growth rates and kinetics under these conditions
- [4] Determine the metal dissolution as a function of pH, redox potential, temperature, particle size and initial ferric ion concentration and
- [5] Determine the acid consumption so as to approximate the acid requirement of the ore and also to infer the extent of acid soluble copper, and other slow leaching oxide/sulphide copper minerals.

1.4 Outline of the Thesis

This thesis is split into 6 chapters:

Chapter 1 is an introduction to this thesis. It gives the background, motivation and research objectives to the project.

Chapter 2 goes into the details of the mechanisms and kinetics of the sub-processes in microbial leaching. It includes the microbial ferrous and sulphur oxidation kinetics, relevant microbial species and the fate of sulphide sulphur (S^{2-}) as occurring through the polysulphide or thiosulphate pathways.

Chapter 3 is a review of the literature on the current understanding of the bioleaching behaviour of copper sulphides. It covers the mineral kinetics of leaching, including influence of leaching parameters, and mass and energy balances in a bioleaching context. A survey of process alternatives and heap bioleaching practice for copper extraction is presented.

Chapter 4 describes the experimental apparatus and techniques employed in this investigation. This includes mineral samples used, bacterial strains and their source, and adaptation as well as the chemical and analytical measurements performed to obtain the experimental data.

Chapter 5 is discussion of the experimental bioleaching results that were obtained. The data is interpreted relative to the published literature. The results are further discussed in terms of their merits in a general bioleaching context and their applicability to Nchanga ores in particular.

Chapter 6 provides a summary of the main findings and conclusions drawn from the research work and gives recommendations for further work.

Chapter 2

General Principles of bioleaching

2.1 Introduction

Bioleaching may be defined as the acid-ferric leaching of metals from their sulphide minerals by the action of microorganisms. The technique has long been applied to extract copper from tailings and dumps of low-grade ores (Murr, 1980). More recently, microbial leaching is carried out in properly designed bioheaps to extract copper from much higher grade ores (Brierley and Brierley, 2001), with a lot of success in copper bioheap leaching operations treating predominantly oxides and secondary copper sulphides using mesophilic bacteria (Watling, 2006).

Bioleaching has also extended into other base metal extraction such as zinc, cobalt, and nickel, and it is now widely accepted as a pre-treatment step for refractory gold ores and concentrates in both heap and tank biooxidation operations (Miller, 1997; Brierley and Brierley, 2001) to liberate and expose gold values for the subsequent cyanide leaching process. Biooxidation is currently being applied to treat arsenic-containing refractory gold ores and concentrates for the dissolution and removal of arsenic (Miller, 1997). These types of minerals cannot be processed pyrometallurgically due to arsenic impurity.

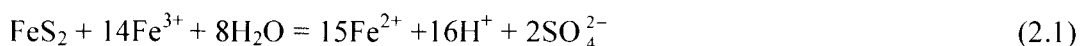
The bacteria that have found commercial application in bioleaching of metal sulphides are mesophiles of the genera *Acidithiobacillus* and *Leptospirillum* (Rossi, 1990; Barrett *et al.*, 1993). Studies on the use of higher temperature (thermophilic) microorganisms in metal sulphide ore solubilisation have given promising results. The most extensively studied mesophilic bacterium is *Acidithiobacillus ferrooxidans*. It has been found to oxidise both ferrous iron and elemental sulphur and other reduced sulphur compounds. However, some organisms are solely ferrous iron oxidisers such as *Leptospirillum ferrooxidans* and *Leptospirillum ferriphillum*. *Acidithiobacillus thiooxidans* on the other hand can only oxidise elemental sulphur and other reduced sulphur compounds (Rossi, 1990). In this investigation a mixed culture of iron and sulphur oxidising mesophilic bacteria were applied in the batch bioleaching experiments using stirred tank bioreactors.

This chapter describes the mechanisms and kinetic aspects of the principal chemical and microbial sub-processes that have been identified in bioleaching systems, with emphasis on microbial ferrous iron and sulphur oxidation. It also describes the microbial species relevant to bioleaching. The bioleaching behaviour of copper sulphide ores and their corresponding pure sulphide minerals is introduced but fully discussed in Chapter 3.

2.2 Fundamental Bioleaching Mechanisms, Kinetics and Rate-limiting Sub-processes

In their study to understand bioleaching mechanisms, Boon (1996) and co-workers considered the bacterial oxidation of sulphide minerals to involve several sub-processes. They then assumed that each sub-process can be identified and studied separately in order to understand the mechanisms and kinetics of the critical or rate determining sub-processes.

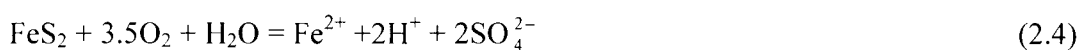
In what was termed as two-step bioleaching sub-processes, Boon *et al.* (1995) ascertained that the sulphide mineral is chemically oxidised by ferric ions to produce the metal cation using pyrite as a case study. If the chemical oxidation reaction is complete, ferrous iron and sulphate ions are produced. The ferric ion is regenerated by the bacterial oxidation of ferrous ions (Boon *et al.*, 1995; Brierley and Brierley, 1986; Schippers and Sand, 1999). However, if the chemical oxidation does not go to completion, elemental sulphur and ferrous iron are produced. In this case, the role of bacteria is to oxidise both elemental sulphur and ferrous iron to sulphate and ferric iron respectively (Rossi, 1990; Boon, 1996). It is assumed here that the bacteria are not associated with the surfaces of the minerals. An illustration of the ferric leaching of pyrite is given below.



The reaction products like ferrous iron and elemental sulphur are oxidised by the relevant bacterial species according to the reactions that follow.



Another possible mechanism of sulphide mineral oxidation is the assumption that the bacteria contact or attach (or adhere) to the mineral surface, oxidising the mineral in a 'direct' manner (Brierley and Brierley, 1986; Konishi *et al.*, 1990; Boon, 1996). This sub-process is now known as the contact leaching sub-process (Tributsch, 1999) and that the role of bacteria is to facilitate the mineral attack through an electrochemical dissolution by ferric iron that is present in the organisms' extracellular polymeric substances (EPS). The sulphur moiety of the mineral is microbially oxidised to sulphate without any intermediate sulphur compounds. For example, it is postulated that pyrite may be oxidised by the microorganisms as follows.



Tributsch (1999) proposed multiple bioleaching mechanisms including contact and cooperative bioleaching where there is a mutual relationship between the bacteria attached to the sulphide mineral surfaces and those that are freely suspended in solution. The attached bacteria through the mechanism of contact bioleaching release suitable substrates into solution that constitute the energy source for the organisms that are free in solution.

Boon (1996) also reviewed other sub-processes that may be significant in overall mechanisms of bioleaching besides the bacterial and chemical oxidation sub-processes. For example, the diffusion of oxygen and carbon dioxide from the gaseous phase to the liquid phase, the formation of jarosite precipitates or other reaction products on the mineral surfaces, and the mass transfer of reactants and products across the reaction interface. Further, acid leaching and the galvanic interactions of different metal sulphides may be important processes in the overall oxidation of metal sulphides (Murr, 1980).

There is a general agreement among authors on the much debated direct and indirect mechanisms that the chemical ferric leaching is the main solubilisation step for the metal sulphides although the attachment of bacteria to the mineral surfaces greatly enhances the process (Rawlings, 2002). The next sections discuss what is currently accepted as a true bioleaching process.

2.2.1 Three Sub-Process Mechanism

The present theory of bioleaching is based on three fundamental sub-process mechanisms of bioleaching of metal sulphides. These sub-processes have been identified as the chemical ferric iron leaching of sulphide minerals involving protons, and the microbial ferrous iron and sulphur oxidation processes (Breed and Hansford, 1999).

It is believed the mechanism of sulphide oxidation involving bacteria is initiated by a chemical acid-ferric attack of the sulphide mineral particle causing it to break down, releasing or solubilising the metal ions and producing ferrous iron and other reduced compounds of sulphur in solution. The iron oxidising bacteria oxidise ferrous iron to the ferric form while the sulphur oxidising bacteria oxidise sulphide-sulphur to sulphate and protons (Schipper and Sand, 1999; Sand *et al.*, 1999). The degree of sulphide oxidation is dependant on the type of the mineral and may follow either of the two sulphur oxidation pathways proposed by Schippers and Sand (1999). The ferrous to ferric iron conversion by bacteria is a cyclic process that continues in the entire bioleaching process and only limited by their relative concentrations in solution.

Thus, the current understanding of bioleaching is that it involves a combination of both acid (protons) and ferric iron to leach the sulphide mineral, solubilising the metal ions and producing ferrous iron and reduced sulphur compounds in solution. Ferrous iron is oxidised back to ferric form by iron oxidising bacteria. The compounds of sulphur are oxidised to sulphate and protons by sulphur oxidising bacteria (Boon, 1996; Sand *et al.*, 1995, 1999; Schippers and Sand, 1999). Therefore, the role of microorganisms is to regenerate the ferric iron and acid. By so doing, a high redox potential and high acidity of the bioleaching system is achieved hence promoting the dissolution of metal sulphides (Escobar *et al.*, 1993). See Figure 2.1 below.

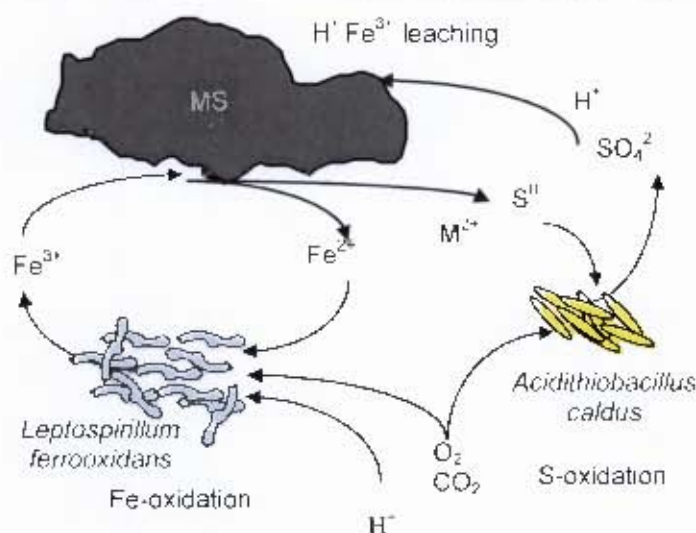


Figure 2.1: Proposed three sub-process mechanisms for bioleaching of sulphide minerals (Breed and Hansford, 1999)

2.2.2 Sulphide Oxidation Pathways

The bacterial oxidation of metal sulphides by ferric ions and /or protons may follow either the thiosulphate or polysulphide pathways as proposed by Schippers and Sand (1999) and Sand *et al.* (1999). The pathway which predominates in the leaching system is dependent on the type of the mineral. Thus, the reaction pathway is firstly determined by both the type of the metal sulphide and reactivity in acid. Since the solubility of the sulphide mineral in acids may be determined by its electronic configuration, those metal sulphides with valence bands that are derived only from orbital of the metal atoms cannot be attacked by protons. These minerals are thus regarded as acid insoluble metal sulphides and their oxidation proceeds through a thiosulphate pathway (for example, pyrite). On the other hand, those metal sulphides with valence bands that are derived from both the metal and sulphide orbitals are soluble in acid. These minerals are termed acid soluble metal sulphides (for example, chalcopyrite and chalcocite) and their oxidation is through the polysulphide pathway (See also the details in the review by Rohwerder *et al.*, 2003).

2.2.2.1 Thiosulphate Pathway

The acid insoluble metal sulphides are solubilised through ferric iron attack, producing thiosulphate as the main intermediate with sulphate and protons being the

final products (Schippers and Sand, 1999; Sand *et al.*, 1999). Sand (1999) and co-workers established that pyrite oxidation by ferric ions goes through mainly thiosulphate and protons, and other minor polythionates by-products. That is, they are oxidised via electron extraction by ferric iron (Tributsch, 1999). Thiosulphate is subsequently oxidised to tetrathionate through disulphane-monosulphonic acid to trithionate (polythionates) and finally to sulphate as shown in Figure 2.2 (Sand *et al.*, 1995, 1999; Schippers and Sand, 1999). Elemental sulphur occurs in minor amounts as a by-product. An example of pyrite oxidation through the thiosulphate pathway is depicted through the overall chemical reactions given below.



As shown in the Figure 2.2 for thiosulphate mechanism, the metal sulphide (MS) is attacked by ferric iron by electron extraction, where the ferric iron is reduced to ferrous iron with the release of the metal cation (M^{2+}) and water soluble intermediary sulphur compounds. The iron-oxidising bacteria such as *Leptospirillum ferriphilum* (*Lf*) and *Acidithiobacillus ferrooxidans* (*Af*) regenerates ferric iron by oxidising ferrous iron (Schippers and Sand, 1999)

2.2.2.2 Polysulphide Pathway

In this pathway, the acid soluble metal sulphides are in general solubilised through a combined attack by ferric iron and protons (acid), giving elemental sulphur as the main product. Sulphur and minor compounds of sulphur produced by side reactions are oxidised by sulphur oxidising bacteria such as *Acidithiobacillus ferrooxidans* (*Af*) and *Acidithiobacillus thiooxidans* (*At*) to sulphate. The polysulphide pathway as proposed by Sand *et al.*, (1995, 1999) starts with the dissolution of mineral sulphides with protons present in the bioleaching medium. The metals are liberated as ions and produces hydrogen sulphide. For all the sulphide minerals that are acid soluble to some extent, the reaction with ferric iron yields elemental sulphur. See the summarised (main) reactions below.





The ferrous iron produced during metal dissolution is re-oxidised by iron oxidising bacteria to ferric iron.

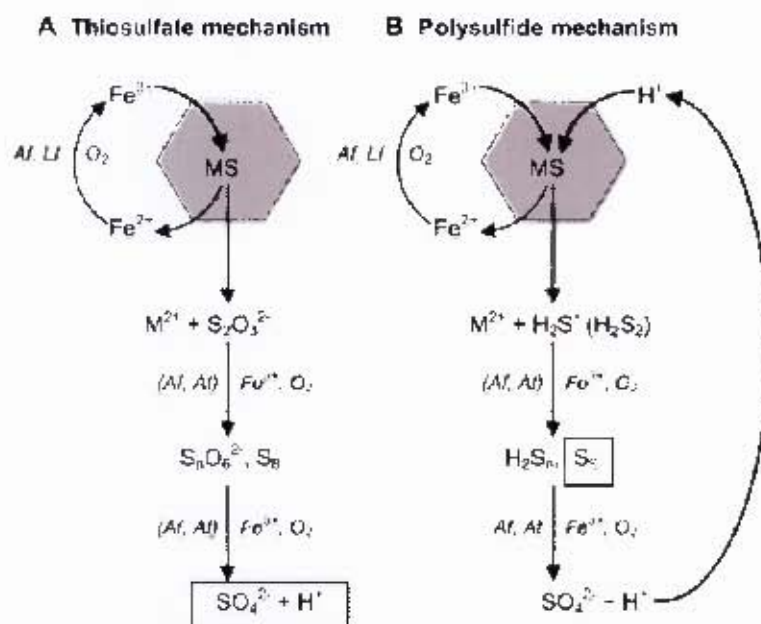


Figure 2.2: The thiosulphate (A) and polysulphide (B) reaction pathways in the bioleaching of metal sulphides (Schipper and Sand, 1999) Adapted from Rohwerder *et al* (2003).

According to Schippers and Sand (1999) the chemical bonds between the metal and sulphur moiety is initially broken down by protons to produce hydrogen sulphide. If ferric iron is present in solution the sulphur moiety is oxidised to $\text{H}_2\text{S}^{\cdot-}$ in one electron step which can react further to form free hydrogen disulphide (H_2S). This is oxidised further to higher polysulphides and elemental sulphur.

During polysulphide oxidation, more than 90 % of the sulphide is oxidised to elemental sulphur if there is no sulphur oxidising bacteria in solution (Schipper and Sand, 1999). Since the chemical bonds between the metal and sulphide are broken by proton attack, the presence of ferric iron in solution may not be an absolute necessity because acid soluble metal sulphides may not be solubilised by the activity of sulphur oxidising bacteria. Therefore, in the absence of ferric iron, hydrogen sulphide that results from proton attack on the metal sulphide is oxidised to elemental sulphur and

finally to sulphuric acid by sulphur oxidising bacteria. This regenerates the protons needed for the metal sulphide dissolution.

Thus, the role of the microorganisms in the metal sulphide solubilisation is to provide sulphuric acid for a proton attack and maintain the iron in the oxidised ferric state for an acid ferric oxidative attack on the mineral (Rawlings *et al.*, 2003).

2.2.3 Electrochemical (Galvanic) Interactions

The metal sulphides are in general semi-conducting solids, and thus set up corrosion (electrical) currents when one particular metal sulphide mineral comes into contact with another, whereby the one with the more positive redox potential becomes an oxidant. This results in the anodic dissolution of the mineral and cathodic reduction of the oxidant (Wadsworth, 1987). In some cases, the effects of galvanic interactions among sulphide minerals may be significant in the overall bioleaching processes. The (galvanic) reactions have been observed during the leaching of low-grade waste among the copper minerals that make intimate contact with one another in the host igneous rock matrix (Murr, 1980). Natarajan (1982) established that galvanic interactions in chalcopyrite concentrate showed preferred oxidation of specific minerals.

According to Natarajan (1982) a mineral assumes a mixed potential value between the anodic and cathodic half cell potentials. If the potential is more positive than the equilibrium potentials the half-cell reaction goes in the anodic direction whereas more negative potential values will drive the reaction in the cathodic reaction. The mixed potential of the system is then established when the anodic and cathodic currents are equal and opposite. Thus, the electrode voltages determined by the mixed potential controls the kinetics of the electrochemical process.

The rate of leaching for pyrite is normally greater than chalcopyrite when these minerals occur as separate inclusions as observed from quantitative measurements of metal solubilisation rate and also from other observed corrosion phenomena. But when chalcopyrite and pyrite make an intimate contact, chalcopyrite leaches faster while pyrite is passivated (Murr, 1980). Natarajan (1992) studied the galvanic dissolution behaviour of pyrite, chalcopyrite and sphalerite in a bioleaching system.

The dissolution of the more active sphalerite to give zinc ions was found to be enhanced due to galvanic effect. Sphalerite dissolution greatly increased when the mineral was coupled to either chalcopyrite or pyrite than in the absence of any galvanic contacts (Natarajan, 1988; 1992)

Further, the dissolution of chalcopyrite increased about three times when it was coupled to pyrite than when it was bioleached alone. However, purely galvanic effects without any bacterial action produced minimal increase in the selective dissolution of zinc and copper. Thus the extent to which the active mineral can be solubilised relative to the noble minerals is dependent on among other things the potential differences in their rest potential values and the magnitude of galvanic currents in the mineral couples (Natarajan, 1988; 1992)

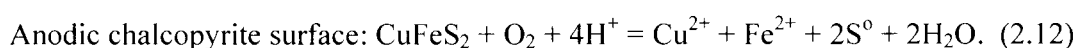
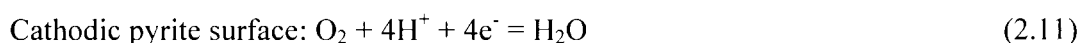
The rest potential series for Cu-Pb-Zn-Fe sulphide mineral system is given in table 2.1 below; taken from Holmes and Crundwell (1995). See also other publications by Natarajan (1990 & 1992).

Table 2.1: Rest potentials of some sulphide minerals according to Mehta and Murr (1983) as cited by Holmes and Crundwell (1995).

Mineral	E vs SHE (V)	
Pyrite (FeS ₂)	0.63	 Noble Active
Chalcopyrite (CuFeS ₂)	0.52	
Chalcocite (Cu ₂ S)	0.44	
Covellite (CuS)	0.42	
Galena (PbS)	0.28	
Sphalerite (ZnS)	-0.24	

Thus, galvanic contacts among various sulphide minerals may lead to selective dissolution of the more active sulphide while the more noble sulphide is passivated. These anodic oxidation processes are enhanced in the presence of bacteria. Pyrite in most sulphide mineral system will normally have the highest rest potential (Murr, 1980; Natarajan, 1988).

An example of the electrochemical reactions between pyrite and chalcopyrite in an acid medium can be described as;



Several factors may influence the rate of galvanic dissolution. For example, the magnitude of rest potential values between the sulphides in contact, anode to cathode area ratio, the nature and duration of contact, presence or absence of bacteria and the properties of the electrolyte e.g. pH, conductivity, availability of oxygen etc.

2.3 Microorganisms Associated with Bioleaching

Several different bacterial species have been identified and characterised from a variety of natural habitats, and applied in bioleaching systems. Only a brief description of these bacterial species associated with bioleaching is presented here. An extensive description and reviews can be found elsewhere (Rossi, 1990; Barrett *et al.*, 1993; Norris, 1997 and Rawlings, 1997; 2002).

The bacteria concerned with oxidation of sulphide minerals have been broadly classified as mesophiles of the genera *Acidithiobacillus* and *Leptospirillum*, moderate thermophiles of the genus *Sulfobacillus*, and extreme thermophiles belonging to the genera *Sulfolobus*, *Acidanus*, *Metallosphaera* and *Sulfurococcus* on the basis of their preferred temperatures for growth. They are often isolated from sites of natural mineral oxidation, and grow in low pH, metal rich inorganic mineral environments (Barrett *et al.*, 1993; Rawlings, 1997).

The bacteria of importance in bioleaching are mainly aerobic chemolithotrophic species. They are able to oxidise ferrous iron, elemental sulphur and reduced sulphur compounds and minerals containing iron (II) and sulphide by consuming oxygen and H^+ (protons) to obtain energy for CO_2 fixation and cell growth (Ingledew, 1981; Barrett *et al.*, 1993). These bacteria fix carbon dioxide via the Calvin cycle and use ammonium ions as their source of nitrogen. The terminal electron acceptor is normally molecular oxygen which penetrates the cell membrane where it is reduced to water (Barrett *et al.*, 1993).

The bacteria that have found industrial application in metal sulphide leaching are acidophilic mesophiles of the genus *Acidithiobacillus spp* (Rossi, 1990). The use of moderate and extreme thermophiles in mineral biooxidation has been demonstrated in both laboratory and pilot plant studies but only one commercial bioreactor process plant is operated with moderate thermophiles at 45-50 °C to extract gold from the

refractory pyrite/arsenopyrite concentrate (Miller, 1997). Among the characteristic requirements for these microorganisms are their ability to oxidise ferrous iron and / or reduced compounds of sulphur, acceptable or faster oxidation kinetics and be able to tolerate low pH, and high metal concentrations and pulp densities for successful industrial applications (Rawlings, 2005).

The bioenergetics of *Acidithiobacillus ferrooxidans* have been widely studied (Ingledew, 1981; Rossi, 1990). The mechanism for energy conservation is shown in Figure 2.3 below for the case of ferrous oxidation, showing the movement of various reaction species.

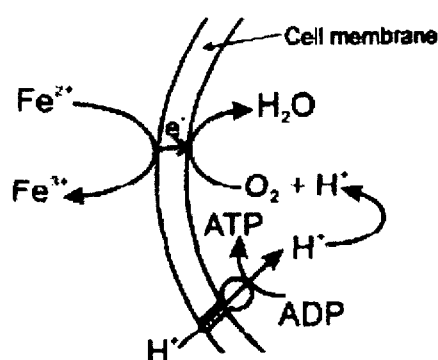


Figure 2.3: Diagrammatic representation of the proton circuit of *Acidithiobacillus ferrooxidans*, showing the movement of the various reaction species. Adapted from Crundwell (1997)

The electrons from Fe^{2+} oxidation on the periplasmic side of the cell membrane are transported through the electron transport chain where O_2 is reduced to water on the cytoplasmic side of the cell membrane. Thus, energy from Fe^{2+} oxidation generates a proton electrochemical gradient across the cell membrane which drives ADP phosphorylation and ATP formation.

This section will briefly review the characteristics and metabolism of some bacterial species associated with bioleaching of metal sulphide minerals.

2.3.1 Acidophilic Mesophile Bacteria

The mesophilic bacteria of importance in bioleaching of metal sulphides belong to the genus *Acidithiobacillus spp* (formally *Thiobacillus*). They are gram-negative and non-spore forming rod-shaped organisms that grow in acidic and inorganic habitats under aerobic conditions. They have optimum temperature and pH of about 25-40 °C and

1.80-2.50 respectively. These microorganisms are normally obligate chemolithoautotrophs that use carbon dioxide from the atmosphere as their source of carbon for synthesis of new cell material. The energy for carbon dioxide fixation is obtained from the oxidation of ferrous iron, reduced sulphur compounds, sulphides, elemental sulphur and thiosulphate. Sulphate is normally the final product (Bosecker, 1997; Rawlings, 1997; 2005). The bacteria are easily destroyed at higher temperature because their proteins are denatured. The use of higher temperature thermophiles is considered as an alternative to mesophiles (Niemela *et al.*, 1994; Torres *et al.*, 1995).

The commonly isolated mesophilic bacteria are *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*. They are all acidophilic and obligately autotrophic, gram-negative bacteria. *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* are both rod-shaped while *Leptospirillum ferrooxidans* has a distinct spiral shape. These organisms are all regarded as the most important in major industrial bioheap leaching operations (Rawlings, 1997). Of these, *Acidithiobacillus ferrooxidans* has been extensively studied and was previously thought to be the only organism of importance in leaching of metal sulphides for many years (Hutchins *et al.*, 1986).

Acidithiobacillus ferrooxidans (formally *Thiobacillus ferrooxidans*) as reviewed by Rawlings (2005) was first isolated in 1947 by Colmer and Hinkle (1947) from the drainage of acid coal mine. The bacterium is a gram-negative, acidophilic, mesophilic chemolithoautotroph with straight rods of approximately 1.0 μm long and 0.5 μm in diameter. It derives the carbon required for cell mass synthesis from carbon dioxide in the air via the Calvin cycle. The energy for carbon dioxide fixation and other metabolic functions is obtained by oxidising ferrous iron and / or reduced sulphur compounds. This unique ability to oxidise both ferrous iron to ferric form, and sulphur and reduced sulphur compounds to sulphuric acid leads to the dissolution of most base metal oxides and sulphides. Consequently, this organism has found commercial application in bioleaching operations (Hutchins *et al.*, 1986; Rawlings, 1997; Devasia and Natarajan, 2004). This organism has been found to adapt to quite high concentrations of most metal ions but arsenic, silver, mercury etc have been found to be toxic even at very low concentrations (Rawlings, 1997).

Leptospirillum ferriphilum is another gram-negative spiral-shaped, acidophilic chemolithoautotrophic mesophile. This organism can only oxidise ferrous iron and not sulphur compounds. It has been established that the organism cannot oxidise sulphide minerals except in the presence of sulphur oxidising bacteria such as *Acidithiobacillus ferrooxidans* or *Acidithiobacillus thiooxidans*. Bioleaching systems with high ferrous iron concentrations or low redox potentials favours the growth of *Acidithiobacillus ferrooxidans* but for solutions with high ferric iron concentrations or high redox potential, *Leptospirillum ferriphilum* may be the predominant iron oxidiser. Other *Leptospirillum*-like bacteria have also been isolated from acidic mine waters (Rawlings *et al.*, 1999; Rawlings, 2005; Hutchins *et al.*, 1986).

Acidithiobacillus thiooxidans is known to oxidise elemental sulphur rapidly but it can even utilise reduced sulphur compounds to produce sulphate and protons (Bosecker, 1997). The acid is responsible for the dissolution of acid soluble metal oxides. However, *Acidithiobacillus thiooxidans* cannot oxidise ferrous iron to give ferric ions, the oxidant required in attacking the metal sulphide minerals. The organism can, however, grow on pyrite in association with either *Leptospirillum ferriphilum* or *Acidithiobacillus ferrooxidans* (Rawlings, 1997; Hutchins *et al.*, 1986). Table 2.2 below gives a summary of the physiological and metabolic characteristics for some mesophilic bacterial species.

Table 2.2: Some physiological and metabolic characteristics for mesophiles (Rossi, 1990).

Strain	Habitat	Oxidisable substrates	pH	Temperature range for growth(°C)
<i>Acidithiobacillus ferrooxidans</i>	Sulphide mine wastes	Fe^{2+} , S^{2-} , S^0 , $\text{S}_2\text{O}_3^{2-}$, Sulphide moiety, reduced sulphur compounds	2.0-3.5	28-35
<i>Leptospirillum ferrooxidans</i>	Sulphide deposits	Fe^{2+}	3.0	30
<i>Acidithiobacillus thiooxidans</i>	Soil	S^{2-} , S^0 , $\text{S}_2\text{O}_3^{2-}$, Sulphide moiety, reduced sulphur compounds	2.0-3.5	10-37

2.3.2 Moderate and Extreme Thermophiles

The moderate thermophiles are generally rod-shaped eubacteria that grow at temperatures of up to 55 °C. Their natural habitats include hot acid soils and acidic thermal springs but are also found in copper leach dumps, metalliferous ore deposits and coal mine wastes. Extreme thermophiles of the *Sulfolobus*-like archaea thrive at temperatures of up to 85 °C. These microorganisms are isolated from sulphurous hot springs, copper mine drainages and the self heating heaps of coal wastes (Brierley, 1978; Brock *et al.*, 1972; Norris, 1997; Brierley and Brierley, 1986).

The higher temperature or extreme thermophilic bacteria are mainly archaeobacteria of the *Sulfolobaceae* family that survive extreme conditions of high temperature and acidity. The other families include Sulfofobaceae of the genus *Sulfolobus*, *Acidianus* and genera *Metallosphaera* and *Sulphurococcus*. These bacteria can be strictly aerobic or facultatively anaerobic. Morphologically, they can be rod-shaped, spherical, spiral, plate shaped or lobed and stain either gram-negative or gram-positive with cell sizes of 0.1-1.5 µm in diameter (Barrett *et al.*, 1993; Rawlings, 2005).

The iron and sulphur oxidising *Sulfolobus* species are spherical, acidophilic thermophiles. They are found in hot springs and coal waste heaps. The *Sulfolobus* strain BC, known as *Sulfolobus Metallicus* has been the widely studied bacteria that grow autotrophically at pH 1-3 and temperatures of 50-90°C. Members of the genus *Sulfolobus* are aerobic, facultatively chemolithoautotrophs that can oxidise sulphur, ferrous iron and metal sulphides for their energy (Hutchins *et al.*, 1986; Bosecker, 1997). These microorganisms have been reported to show faster leaching kinetics when treating refractory sulphides such as chalcopyrite under laboratory scale (Dew *et al.*, 1999; Gericke *et al.*, 2001).

Attempts to apply high temperature bioleaching have been done in both columns and stirred tank bioreactors. At low-solids loading *Sulfolobus*-like organisms have produced fastest rates of sulphide mineral oxidation. The leaching of gold bearing pyrite/arsenopyrite concentrates at 5% w/v solids with mesophiles, moderate thermophiles and *Sulfolobus*-like organisms gave the highest extraction rates with *Sulfolobus*-like organisms that tolerate higher temperature than the others. Many

authors have shown that the use of *Sulfolobus*-like bacteria to leach sulphide mineral concentrates at around 70°C was much faster than mesophiles. Infact, *Sulfolobus Metallicus* was found to dominate at 70°C whereas *Metallosphaera*-like dominating at 80°C (Norris and Bar, 1988; Konishi *et al.*, 1995; Rawlings, 2005).

Acidithiobacillus caldus is a sulphur oxidiser, moderate thermophile that is found in hot springs but it has also been isolated from bioleaching processes that operate at 30-40°C, with an optimum temperature for its growth at 45°C (Rawlings, 1997; Norris, 1997). The work of Rawlings *et al* (1999) identified *Acidithiobacillus caldus* and *Leptospirillum*-like bacteria to be the dominant ones in a continuous biooxidation process plant that was treating several ores at temperature range of 45-50°C. These bacteria can grow in mixed cultures with either mesophiles or extreme thermophiles. At temperatures of 50-55°C, growth of moderate thermophiles is less favourable than *Sulfolobus*-like archaea whose growth progressively increases with temperature, even up to 85 °C with some strains (Norris, 1997).

The iron oxidiser, *Leptospirillum ferrooxidans* has been used together with *Acidithiobacillus caldus* to provide the sulphur oxidising capacity for the dissolution of chalcopyrite concentrates. This demonstrated the use of the thermo-tolerant *Acidithiobacillus caldus* rather than the low-temperature *Acidithiobacillus thiooxidans* to grow is association with *Leptospirillum ferrooxidans*, which is an illustration of the capacity of iron oxidisers to promote the dissolution of sulphide minerals at higher temperatures that do not favour the growth of *Acidithiobacillus ferrooxidans* (Norris, 1997).

Other moderate thermophiles of *Sulfobacillus* spp have been characterised. Two of these strains include *Sulfobacillus thermosulfidooxidans* and *Sulfobacillus acidophilus* which have been differentiated by using both phenotype and 16S rRNA sequence analysis. *Sulfobacillus thermosulfidooxidans* is an acidophilic bacterium that grows on both ferrous iron and mineral sulphides. Their growth on ferrous iron or pyrite is greatly enhanced in the presence of yeast extract though the culture must be supplemented with carbon dioxide (Hutchins *et al.*, 1986; Rawlings, 1997). There are other moderate thermophilic *Acidithiobacillus*-like (called Th bacteria) bacteria that grow on ferrous iron, pyrite and copper sulphides at temperature range of 50°C (Bosecker, 1997).

2.4 Kinetics of Sulphide Mineral Biooxidation

The leaching of sulphide minerals is now believed to consist of principally the chemical ferric leaching of sulphides, microbial ferrous oxidation and microbial sulphur oxidation sub-processes (Breed and Hansford, 1999). The overall rate of bioleaching is then fixed by the kinetics of the critical or rate determining sub-process (Boon, 1996), which may be a function of ferrous and ferric concentration, pH, temperature, biomass concentration and particle diameter.

Apart from the chemical and bacterial oxidation reactions other sub-processes may be rate limiting. For example, oxygen and carbon dioxide mass transfer from the gas phase to liquid phase, formation of precipitate layers such as jarosite on the mineral surfaces, the mass transfer of reactants and products between the bulk liquid and the reaction surface through layers on the surface, attachment of bacteria to the mineral surfaces etc (Boon, 1996).

The rate of sulphide mineral bioleaching may be governed by the kinetics of both ferric leach of the mineral and the microbial ferrous iron oxidation, which show a strong dependence on the redox potential of the bioleach solution (Breed and Hansford, 1999). According to these authors, the chemical ferric leach of pyrite and bacterial ferrous iron oxidation are balanced by the rate of turnover of iron between the bacteria and the sulphide mineral. This defines the rate and redox potential at which the system will operate for a continuous system at steady state. Thus the balance between the two rates will in turn depend on the bacterial species used, the microbial concentration, the residence time employed, the nature of sulphide mineral being leached and its active surface area (Hansford, 2002).

In general, the kinetics are driven by the microbial ferrous iron oxidation provided that the ferric (and proton) leaching of the mineral is not limiting as in the case of chalcopyrite (Munoz *et al.*, 1979; Hackl *et al.*, 1995). Microbial sulphur oxidation is important for the removal of sulphur layers and production of acid (protons) (Schippers and Sand, 1999). This may play an important role in the bioleaching of chalcopyrite in removing a possible passivation sulphur layer if the oxidation is

limited by diffusion. Thus, the bacterial removal of the sulphur layer might improve the overall metal sulphide dissolution rate.

2.4.1 Rate Equation based on the Logistic Equation

According to Hansford (1997), the work of Pinches *et al.* (1996) has shown that the logistic equation could be used to predict and determine the rate of bioleaching, where the kinetic data from both batch and continuous microbial leaching of pyritic minerals have been shown to fit the logistic equation well. For a mineral sulphide, the rate of conversion based on the logistic equation can be written as;

$$\frac{dX}{dt} = K_m X \left(1 - \frac{X}{X_{\max}} \right) \quad (2.13)$$

Where X = conversion (fraction of sulphide mineral leached)

In a batch system, the fraction leached is obtained by integration of the above equation to get;

$$\int \frac{dX}{K_m X \left(1 - \frac{X}{X_{\max}} \right)} = \int dt \quad = \quad X(t) = \frac{X(0)e^{K_m t}}{\left(1 - \frac{X(0)}{X_{\max}} \right) (1 - e^{K_m t})} \quad (2.14)$$

Through simplification the equation above becomes;

$$\ln \left(\frac{X}{X_{\max} - X} \right) = K_m t + \ln \left(\frac{X(0)}{X_{\max} - X(0)} \right) \quad (2.15)$$

2.5 Kinetics and Kinetic Models of Microbial Ferrous iron Oxidation

The oxidation of metal sulphides with ferric ion is accompanied by its reduction to ferrous iron. For the reaction to be sustained ferrous iron thus produced must be reoxidised back to the ferric form by iron oxidising bacteria. The oxidation of ferrous iron is therefore an important sub-process and its kinetics is of considerable importance. The rate of microbial ferrous oxidation has been found to be about 10^6

times faster than the chemical ferrous oxidation rate in the absence of bacteria (Murr, 1980).

A lot of kinetic and physiological data has been published by several researchers. Many kinetic models exist that account for the bioenergetics of cell production, maintenance energy requirements, and inhibition of rates of ferrous oxidation and cell growth by ferric ions (Ojumu *et al.*, 2006). The consequence is that substrate limitation and product inhibition may affect both specific growth rate and cell yield (Rossi, 1990).

Work done on ferrous oxidation with *Acidithiobacillus ferrooxidans* has shown that the kinetic data follows Monod kinetics (Rossi, 1990). The growth of the microorganism using ferrous iron as substrate is inhibited by the ferric ion and in the absence of product inhibition, by ferrous iron as a limiting substrate. As reviewed by Hansford (1997) early work done by Lacey and Lawson (1970) indicated that specific growth rate decreased at increasing iron concentration using the Monod based rate equation:

$$\mu = \frac{r_x}{C_x} = \frac{\mu_{\max} [Fe^{2+}]}{K_s + [Fe^{2+}]} \quad (2.16)$$

The growth yield coefficient was found to be a function of ferric ion concentration. Different authors have reported different values of yield on account of different experimental conditions and different methods of microbial population evaluation. According to Rossi (1990) many authors have reported growth yields as ranging from 0.30 – 0.40 g of dry cell weight per g Fe^{2+} oxidised while the maintenance coefficient, m , varied from 0 – 4.30 depending on experimental conditions. An equation that accounted for ferric inhibition was given as;

$$\mu = \frac{\mu_{\max}}{1 + \frac{K_s}{Fe^{2+}} + \frac{K_i}{K_s} \frac{[Fe^{3+}]}{[Fe^{2+}]}} \quad (2.17)$$

Later investigations by Braddock *et al* (1984) have reported a threshold Fe^{2+} ion concentration to the organism for growth using the equation;

$$\mu = \frac{\mu_{\max}}{1 + \frac{K_s}{[Fe^{2+}] - [Fe^{2+}]_{thres}}} \quad (2.18)$$

More recent studies by Boon (1996) and others used off-gas measurements to determine CO₂ and O₂ uptake to measure the growth, concentration and activity of bacteria. They employed both batch and continuous cultures with pure *Acidithiobacillus ferrooxidans* but used continuous culture only for *Leptospirillum-like* bacteria. They described the kinetics in terms of specific oxygen utilisation rate, q_{O_2} and included both growth and maintenance in terms of the Pirt equation:

$$q_{O_2} = \frac{-r_{O_2}}{C_x} = \frac{\mu}{Y_{ox}^{\max}} + m_o \quad (2.19)$$

An earlier rate equation that was developed and later used by Braddock *et al.* (1984) to incorporate both ferric ion inhibition and threshold value of ferrous iron:

$$q_{O_2} = \frac{-r_{O_2}}{C_x} = \frac{q_{O_2}^{\max}}{1 + \frac{K_s}{[Fe^{2+}] - [Fe^{2+}]_{thres}} + \frac{K_s}{K_i} \frac{[Fe^{3+}]}{[Fe^{2+}] - [Fe^{2+}]_{thres}}} \quad (2.20)$$

The above equation was simplified by ferrous iron term and the threshold ferrous iron concentration or in terms of specific ferrous iron oxidation (Boon *et al.*, 1995) as:

$$q_{O_2} = \frac{q_{O_2}^{\max}}{1 + K \frac{[Fe^{3+}]}{[Fe^{2+}]}}; \quad q_{Fe^{2+}} = \frac{q_{Fe^{2+}}^{\max}}{1 + K \frac{[Fe^{3+}]}{[Fe^{2+}]}} \quad (2.21)$$

Breed *et al.*, (1999) showed that the maximum specific ferrous oxidation rate increased with increasing temperature while pH affects the value of K. The equation above gave a satisfactory fit to kinetic data for ferrous oxidation. The consequence for this rate equation is that the kinetics are assumed to be determined by ferric-ferrous ratio or the redox potential.

The equation for the specific growth rate is given as:

$$q_{O_2} = \frac{-r_{O_2}}{C_x} = \frac{m_{\max} + m_O q_{O_2}^{\max}}{1 + \frac{K_s}{[Fe^{2+}] - [Fe^{2+}]_{thres}} + \frac{K_s}{K_i} \frac{[Fe^{3+}]}{[Fe^{2+}] - [Fe^{2+}]_{thres}}} \quad (2.22)$$

Through measurements of oxygen and carbon dioxide uptake, Boon (1996) determined the kinetics of ferrous iron oxidation using continuous cultures of *Acidithiobacillus ferrooxidans* and *Leptospirillum-like* bacteria at 30 °C and pH 1.60. For growth the bacteria use carbon dioxide and ammonium ions (NH_4^+) as source of carbon and nitrogen respectively. The bacterium is assumed to have the stoichiometric formula of $CH_{1.8}O_{1.5}N_{0.2}$ as given by Roels (1983). Thus the oxidation of ferrous is accompanied by the bacterial growth:



The rate of bacterial growth, r_x is equal to the rate of carbon dioxide utilisation rate i.e. $r_x = -r_{CO_2}$.

Defining yield, Y_{SX} as moles of biomass produced per mole of substrate or in terms of oxygen, Y_{OX} yield is written as;

$$Y_{SX} = \frac{r_x}{-r_{Fe^{2+}}} ; \quad Y_{OX} = \frac{r_x}{-r_{O_2}} \quad (2.25)$$

Often it becomes necessary to define the activity of bacteria in terms of biomass specific ferrous or substrate utilisation rate, $q_{Fe^{2+}}$ and the specific oxygen consumption rate, q_{O_2} i.e.

$$q_{O_2} = \frac{r_{O_2}}{C_x} \quad q_{Fe^{2+}} = \frac{r_{Fe^{2+}}}{C_x} \quad (2.26)$$

So the rate equations using these parameters become:

$$q_{O_2} = \frac{q_{O_2}^{\max}}{1 + K \frac{[Fe^{3+}]}{[Fe^{2+}]}} ; \quad q_{Fe^{2+}} = \frac{q_{Fe^{2+}}^{\max}}{1 + K \frac{[Fe^{3+}]}{[Fe^{2+}]}} \quad (2.27)$$

Chapter 3

Bioleaching of Copper Sulphide Minerals

3.1 Introduction

The major copper sulphide minerals from which copper is extracted include chalcocite (Cu_2S), chalcopyrite (CuFeS_2), covellite (CuS) and bornite (Fe_5FeS_4). Chalcopyrite is the most abundant primary sulphide and economically the most important (Rossi, 1990), followed by chalcocite as being significantly the most common secondary sulphide. The basic carbonates of malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), and several oxides are important sources of copper metal as well (Murr, 1980, Rossi, 1990).

The bioleaching of copper sulphide minerals or low-grade ores and concentrates of mixed oxide-sulphide mineralisation have been extensively studied. This chapter will give a review of some of these studies relevant to the present work and give an up-to-date review of the literature on kinetics of the chemical and bio leaching of copper sulphide minerals. The aim is to have a comprehensive understanding on the solution chemistry and physico-chemical conditions of the minerals under which dissolution is accelerated. It will emphasise on the kinetic behaviour and mechanism of chalcocite bioleaching since this study focussed on the bioleaching of a predominantly chalcocite-bearing ore. It will also include the bioleaching aspects of other copper sulphides such as chalcopyrite, bornite, and covellite as well as pyrite.

Further, this chapter includes a brief survey of process alternatives and heap bioleaching practice for copper extraction. It covers the current understanding of the bioleaching behaviour of copper sulphides with regard to kinetics and effect of leaching variables. The theoretical aspects of mass and energy balances for chalcocite in a bioleaching context are introduced.

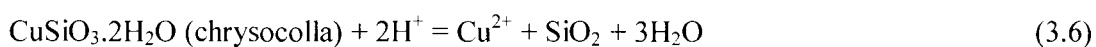
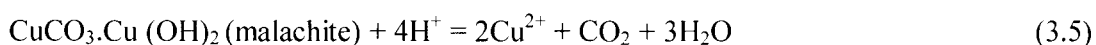
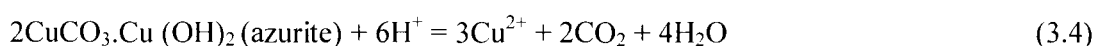
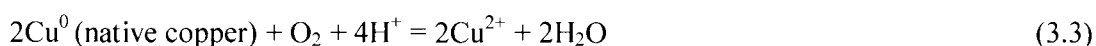
3.2 Review of the chemical and microbial leaching studies of mixed copper oxide/sulphide minerals

3.2.1 General considerations

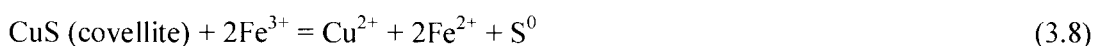
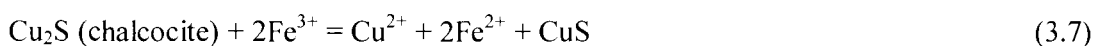
The copper ores of mixed oxide/sulphide mineralisation have been leached for a very long time using solutions of sulphuric acid/ferric sulphate mixtures mainly in ore dumps and heaps (Murr, 1980). Although the oxidised copper minerals are easily leached with sulphuric acid, the sulphide minerals are practically insoluble in acid solutions (Rossi, 1990; Dresher, 2004). An acidic ferric sulphate solution has been found to be a powerful and efficient leachant of sulphides though the actual dissolution rates are low and longer leaching times are required especially in heaps and dumps (Murr, 1980; Hutchins *et al.*, 1986; Rossi, 1990). However, the kinetics of the dissolution process is greatly improved if the iron- and sulphur-oxidising microbial species are introduced to the system (Rossi, 1990; Dresher, 2004). Therefore, one of the main goals of this investigation on the basis of microbial action was to explore the bioleachability of copper sulphide ore from Nchanga mine through chemical (acid) and microbial leaching experiments, under different solution conditions of acid strength, temperature, iron concentration etc.

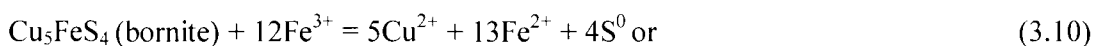
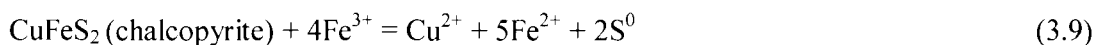
Some leaching reactions of the common oxides and sulphides of copper with dilute solutions of acid and ferric iron solutions are shown below (Murr, 1980; Hutchins *et al.*, 1986; Rossi, 1990);

Copper oxides, carbonates and silicates



Copper sulphides

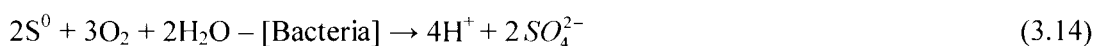
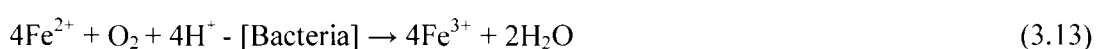
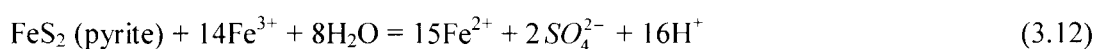




Thus, the dissolution of copper sulphides by ferric iron is highly accelerated in the presence of iron- and sulphur-oxidising bacteria (Rossi, 1990; Drescher, 2004). However, the extent of sulphide oxidation by ferric iron through microbial action depends on the mineral, temperatures employed, oxygen availability, pH as well as mass transfer effects (Murr, 1980). Therefore, it was necessary to investigate the effects of some of these variables on copper dissolution rates in this study.

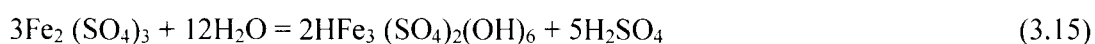
Pyrite (FeS_2) often occurs naturally with copper sulphide minerals (Murr, 1980). Its oxidation is therefore very essential in bioleaching systems since it is considered the driving force in microbial leaching of copper sulphides (Schnell, 1997). Pyrite has been shown to be a source of soluble iron since the ferric (Fe^{3+}) form is the main oxidant in bioleaching systems (Murr, 1980). The effects of both inherent pyrite in the ore and added ferric iron on copper dissolution were therefore investigated in the present work.

Boon (1996) proposed a two-step bioleaching mechanism of pyrite in which it is initially chemically oxidised by ferric iron to produce ferrous iron and acid. Later studies by Schippers and Sand (1999) have elucidated the reaction pathway as occurring through the thiosulphate intermediate where sulphate and protons are the main end products. Refer to Chapter 2 for the details of the bioleaching mechanisms involving iron. Ferrous iron is subsequently oxidised microbially to regenerate ferric iron. Any elemental sulphur produced in the ferric leaching reactions with sulphides is also microbially oxidised to sulphuric acid. These reactions are given as follows;



The above reactions are considered significant in acid-ferric-bacterial leaching systems where ferric iron and sulphuric acid produced are the main leachants required for the

dissolution of sulphide ores (Murr, 1980; Hutchins *et al.*, 1986; Rossi, 1990). The sulphuric acid so produced contributes towards the maintenance of the suitable solution acidity for microbial growth and can also leach several copper oxide minerals as exemplified by the various reactions given at the beginning of this section. A low solution pH (below about 2.0) also helps maintain the iron in the ferric oxidation state, thus preventing it from precipitating as basic ferric sulphate (jarosite) precipitates i.e.



The following sections describe the chemical and bioleaching kinetics of some copper sulphide minerals and/or ores under typical bioleaching conditions.

3.2.2 Bioleaching studies of whole copper ores and concentrates

The secondary copper sulphides such as chalcocite, covellite and bornite have been shown to give satisfactory and nearly complete dissolution under mesophilic bacterial conditions (Dew *et al.*, 1999). For instance, about half (50%) of the copper in chalcocite (Cu_2S) is leached quickly within hours in stirred tank reactors though a complete dissolution requires much longer times (Dutrillac and McDonald, 1974). However, chalcopyrite is very difficult to leach as it shows slow, unsatisfactory leach kinetics with mesophilic bacterial culture, reaching a maximum of about 50 % copper extraction (Murr, 1980; Hackl, 1995; Dew *et al.*, 1999). Copper-bearing waste dumps that were irrigated for 4-6 years only recovered about 15 % copper from chalcopyrite (Schnell, 1997). Presently, there are several bioheap operations extracting copper from secondary copper sulphide ores mixed with oxides in mainly Australia, North America and Chile (Brierley and Brierley, 2001; Watling, 2006).

The use of thermophilic bioleaching has been exploited to overcome the slow bioleaching kinetics of chalcopyrite with mesophiles. Mintek and BHP Billiton conducted studies with thermophilic bacteria to leach copper from chalcopyrite-rich concentrates. The finely ground concentrates were effectively leached with thermophilic bacteria in a pilot plant using stirred tank reactors, giving up to 95 % copper recovery (Miller *et al.*, 1999; Dew *et al.*, 1999).

Several laboratory studies for the bioleaching of chalcocite/covellite ores and/or minerals under specific solution and experimental conditions have been published. These studies provide reagent concentration, temperature, pH limits etc as well as the extent of copper recovery achieved for a particular ore mineralisation and experimental set up used. A few of these investigations are described below.

Earlier work by Sakaguchi *et al.* (1976) investigated the bioleaching of synthetic chalcocite and covellite using *Thiobacillus ferrooxidans* (now *Acidithiobacillus ferrooxidans* (Kelly and Wood, 2000)) in the shake flask experiments. The dissolution of chalcocite at 1.3% w/v solids was 90-100% at pH 1.7-2.3, 35°C temperature and a range of ferric iron concentration of 0.004-0.01 mol.L⁻¹. The observed dissolution for covellite at 5.3% w/v solids was 45-60% at pH 2.3, temperature of 35°C and 0.004-0.02 mol.L⁻¹ ferric iron concentration. At higher than 0.02 mol.L⁻¹ ferric iron, the rate of copper solubilisation decreased with jarosite formation being observed.

The data of Sakaguchi *et al.* (1976) may be difficult to correlate with that of naturally occurring chalcocite and covellite. Infact, Dutrizac and MacDonald (1974) reported that many authors have observed different relations between leaching rate and ferric iron concentration.

Rivera-Santillan *et al.* (1999) conducted experiments in shake flasks to leach copper sulphide concentrate using mixed cultures of mesophilic and thermophilic microorganisms. They observed that the sulphide dissolution occurred sequentially, starting with chalcocite, then digenite followed by chalcopyrite. They achieved a higher copper dissolution of 85% with a moderate thermophilic culture at 45°C than the thermophilic culture at 68°C. This is quite contrary to many publications that have reported much higher dissolution of copper sulphides with thermophilic culture (Norris *et al.*, 1988; Dew *et al.*, 1999; Gericke *et al.*, 2001).

Palencia *et al.* (2002) applied BRISA (which means Fast Indirect Bioleaching with Actions Separated) process to treat chalcocite and covellite bearing ore in shake flasks and stirred tank reactors. The BRISA technique basically employs separate stages for acid-ferric leaching of metal sulphides and the microbial ferrous iron oxidation sub-

processes. It is claimed the BRISA process improves the overall bioleaching kinetics since each sub-process is conducted separately where optimisation is easily done. Briefly, the acid-ferric leaching in the BRISA process is done in a separate stirred tank reactor where copper extraction is enhanced by the possibility of using higher temperatures and pulp densities where bacterial growth may be very limited. The regeneration of ferric iron is done in another flooded packed-bed reactor by oxidation of ferrous iron using bacteria. The bacteria attach to inert particles forming a biofilm. Here bacterial growth conditions are highly and easily optimised.

However, the work of Palencia *et al.* (2002) investigated only the acid-ferric leaching stage in the BRISA process using one concentrate and two ores of predominantly chalcocite and covellite minerals. They studied the effects of temperature, pulp density and particle sizes on copper extraction at fixed values of pH (1.25) and ferric iron concentration of 12 g.L^{-1} for a residence time of 8 hours.

The ferric leaching of the concentrate in stirred tanks at pH 1.25 gave higher copper extraction at 70°C than at 20°C . At both temperatures, copper leached was observed to decrease with increase in pulp densities. Palencia and co-workers attributed the decreased copper extraction at higher pulp densities to the depletion of ferric iron which became rate limiting at pulp densities greater than 2% and 1.5% at 20°C and 70°C respectively. The authors reported an increase in copper extracted from 34-93% as temperature was increased from 20 - 90°C at pH 1.25, 1% w/v solids and ferric iron of 12 g.L^{-1} .

A predominantly chalcocite ore was leached at 25 and 70°C for several size fractions and pulp densities at fixed conditions of pH (1.0) and ferric iron concentration (of 12 g.L^{-1}) for 8 hours. At 25°C , copper extraction did not show any dependence on pulp densities for the range 10-30% w/v solids except at 70°C where the highest solids loading (30%) gave a decrease in copper extraction. The copper extraction increased with decreasing particle sizes and about 54% copper was leached at 25°C regardless of particle size. Copper extraction also increased as temperature was increased from 25 - 70°C .

3.2.3 Chemical and microbial leaching kinetics of copper sulphides

An overview of some published chemical and microbial leaching kinetics data for the common copper sulphide minerals including pyrite are briefly discussed to review the biochemical leaching response of individual minerals.

3.2.3.1 Chalcopyrite (CuFeS_2)

Early studies on the dissolution of chalcopyrite in acidified ferric sulphate solutions have reported different kinetics under different solution conditions. Parabolic kinetics has been reported in some publications (Dutrillac and MacDonald, 1974; Munoz *et al.*, 1979; Dutrillac, 1982) while other investigations have observed linear dissolution rates (Dutrillac, 1978; Dutrillac and MacDonald, 1974). According to Dutrillac and MacDonald (1974) many authors have reported a direct proportionality between the rate and ferric iron at low concentrations but an independent relationship was observed for ferric iron concentrations of greater than 0.01 M. But the rate of chalcopyrite dissolution was found to increase as the grind size became finer and also as temperature was increased. In ferric chloride medium, the rate was observed to be higher than in ferric sulphate medium and that the rate was related to the ferric iron concentration in a direct manner over a wider range of ferric concentration. The reported activation energies in the sulphate and chloride media are 75 kJ/mole and 42 kJ/mole respectively (Dutrillac, 1982). Several authors accept the fact that chalcopyrite has been very difficult to leach.

The bioleaching of chalcopyrite including several other sulphides involves the indirect ferric iron leaching of the sulphide mineral as well. The role of bacteria is to provide an active ferric sulphate lixiviant (See Chapter 2). The leaching of chalcopyrite has been reported to be initially rapid but the dissolution curves level off rapidly at about 50% copper extraction (Pinches *et al.*, 1976). Several investigations on ferric leaching of chalcopyrite have proposed several reasons for the slow, unsatisfactory leach kinetics and its passivation (Hackl *et al.*, 1995; Dutrillac, 1989; Munoz *et al.*, 1979). This has been attributed to the coating of the mineral surface with jarosite precipitates (Pinches *et al.*, 1976), elemental sulphur layer (Munoz *et al.*, 1979; Dutrillac and MacDonald, 1974; Dutrillac, 1978; 1989) or other iron deficient polysulphide layers (Hackl *et al.*, 1995) on the surface of leached chalcopyrite.

Surface analysis techniques such as Scanning Electron Microscopy (SEM), X-Ray Diffraction Analysis etc have often been employed to study the nature of leached chalcopyrite surface. It is believed that a passivating layer coats the surface of the mineral and prevents the ferric iron from contacting the active chalcopyrite surface. This leads to the decreasing rate of leaching with time due to diffusion limitation of ions through the layer (Munoz *et al.*, 1979). Factors such as redox potential, pH and temperature are believed to affect the formation of passivating layer. Hackl *et al.* (1995) observed that this layer breaks down at higher than 200°C temperatures.

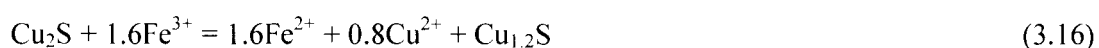
The rate of ferric leaching of chalcopyrite in acidified sulphate medium strongly depends on redox potential, temperature and surface area and to some extent on pH and ferric iron concentration (Munoz *et al.*, 1976; Dutrizac, 1978). An increase in temperature increases the rate of copper extraction (Munoz *et al.*, 1979; Dutrizac, 1978) and a finer grind also increases the rate of chalcopyrite leaching (Munoz *et al.*, 1979). Kametani and Aoki (1985) and Hiroyoshi *et al.* (2000) have established that chalcopyrite leaching occurs at low-redox potentials of 550-700 mV (vs. SHE) and 520-580 mV (vs. SHE) respectively.

Attempts to overcome the passivation effects on chalcopyrite now involve the use of thermophilic bioleaching. Gericke *et al.* (2001) conducted batch experiments at 70°C using extreme thermophiles in which they obtained copper extraction of over 98%. It also was also observed by Konishi *et al.* (2001) that *A. brierleyi* leached chalcopyrite at a faster rate at 65°C than the mesophilic *Acidithiobacillus ferrooxidans* at 30°C. Mousavi *et al.* (2005) obtained highest copper recovery of 85% with thermophilic *Sulfobacillus* and only 70% copper extraction was noted with mesophilic *Acidithiobacillus ferrooxidans* at 10% w/v pulp density after 10 days in batch airlift bioreactors.

3.2.3.2 Chalcocite (Cu₂S) and covellite (CuS)

The behaviour of chalcocite in acidified ferric sulphate solutions in the absence of bacteria has been extensively reviewed by Dutrizac and MacDonald (1974). According to these authors several earlier investigations established that chalcocite leaches by a two-stage mechanism. In the first stage, chalcocite is rapidly attacked by ferric iron to give CuS intermediate product which is different from the natural mineral covellite. About

half (50%) of the copper in Cu_2S is leached quickly though a complete dissolution requires much longer times. In bioleaching systems chalcocite (and covellite) dissolution also involves an oxidative attack by ferric iron derived from the dissolution of either pyrite or chalcopyrite (Schnell, 1997). The first stage produces non-stoichiometric pseudo covellite or blue-remaining covellite (or blaubleibender covellite) which reacts further and rather more slowly to produce elemental sulphur, copper and iron ions in solution. No free sulphur was formed until about 50% had been dissolved (Dutrizac and MacDonald, 1974). The first stage reaction is given as;



The consequence of this rather high initial dissolution phase is that the rate is controlled by the ferric iron diffusion to the mineral surface. This phenomenon was supported by low activation energies (4.2-29.3 kJ/mole) (Bolorunduro, 1999). This initial dissolution rate was found to vary directly (first order) with respect to ferric iron concentration though other studies found different relations. The rate was also observed to be a weak function of pH, temperature and particle size.

The second stage leaching of chalcocite (or pseudo covellite) by ferric iron is given by the following reaction;



The rate of dissolution at the second stage strongly depends on temperature and is thus controlled by a chemical reaction. High activation energies of about 63-105 kJ/mole have been reported in the sulphate system. Kinetically, the second stage dissolution rate is much slower, which increases as temperature is increased. Different authors have reported different relations between rates and ferric iron concentration. Some investigations observed a direct relationship for dilute ferric iron concentration whilst others reported almost an independent relationship between rate and ferric iron for higher concentration. A half order and fractional order dependencies of rate on ferric iron and ferric/ferrous iron ratio respectively have also been reported (Dutrizac and MacDonald, 1974; Bolorunduro, 1999). Current bioleaching studies have established that during bacterial leaching of chalcocite, bacteria oxidise ferrous iron to the ferric state which is

the main oxidant that attacks sulphides such as chalcocite (Schippers and Sand, 1999). Some of the copper dissolution data for first and second stage leaching of chalcocite from Bolorunduro (1999) studies is redrawn in Figure 3.1 below.

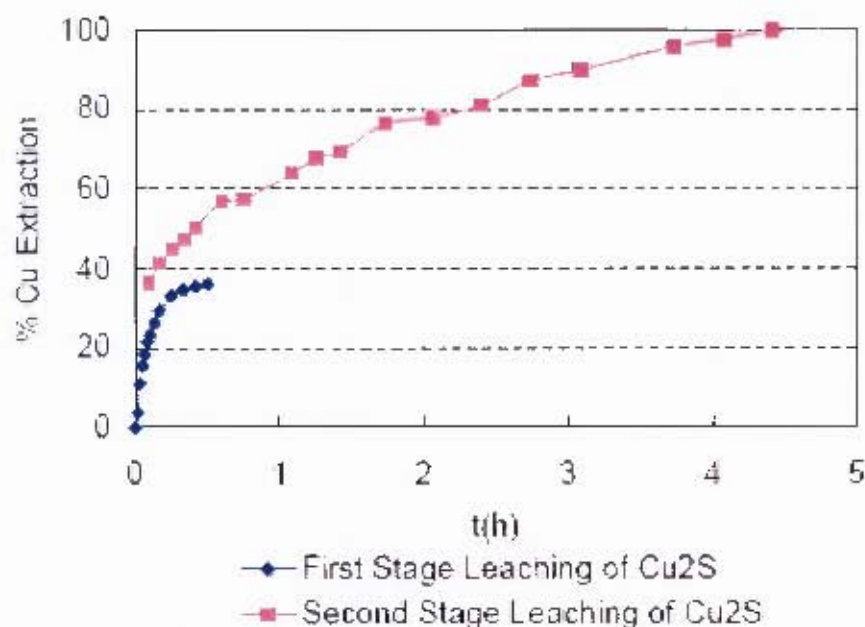


Figure 3.1: Depiction of first and second stage abiotic dissolution data for chalcocite particles (-250 - 212 μm) at 35 $^{\circ}\text{C}$, 0.116 mol/l ferric and 0.0202 mol/l ferrous (Redrawn from Bolorunduro, 1999).

In acidic solutions of ferric sulphate, natural covellite (CuS) leaches according to the reaction below;



There have been different reported dissolution rates for covellite from different sources. This variation was attributed to widely varying amounts of impurities commonly found with natural covellite. Generally, the rate was independent of acid concentration and ferric iron strength of greater than $1\text{g.l}^{-1} \text{Fe}^{3+}$, but the rate increased as temperature was increased. Oxygenated solutions of sulphuric acid at normal atmospheric pressure dissolved copper at about half the rate of acidified ferric sulphate solutions. For studies involving bacterial leaching of covellite, the dissolution was attributed to ferric iron.

which was maintained by iron oxidising bacteria (Dutrizac and MacDonald, 1974). More recent bioleaching studies of covellite in columns (Acar *et al.*, 2005) have established that extraction of copper at 20-23°C by mesophilic bacteria ranged between 12-20% using species of *Acidithiobacillus/Leptospirillum/Sulfobacillus* species. After the temperature was increased to 60-65°C using thermal-tolerant *Acidianus* and *Metallosphaera Archaea*, copper extraction increased to about 62-65% after 346 days.

Published studies on the (bio)chemical leaching of bornite are rather fewer than those of chalcopyrite and chalcocite. However, the ferric leaching of bornite has been reported to show a rapid initial dissolution step followed by a much slower secondary stage. The initial stage has been found to be mass transfer controlled with low activation energy. The initial rate showed a direct proportionality (first order) with ferric iron at low concentrations but was independent at higher ferric strengths. The various intermediate reaction products and other rate-controlling processes in the later stage of dissolution of bornite are not clear (Dutrizac and MacDonald, 1974).

3.2.3.3 Pyrite (FeS₂)

The oxidation of pyrite (and hence ferrous) is very essential in bioleaching systems since it is considered the driving force in bioleaching of copper sulphides (Schnell, 1997). The sub-process reactions involved including sulphur oxidation are given in Equations 3.12-3.14. The overall bioleaching reaction for pyrite is given as;



The ferric leaching of pyrite is slow and limited in the absence of bacteria (Dutrizac and MacDonald, 1974; Schnell, 1997). The slow kinetics was thought to be caused by the formation of a protective layer on the pyrite surface. However, the rate of ferric iron attack is considered to be more rapid than either the direct air oxidation of pyrite or the air oxidation of ferrous iron to ferric form (Dutrizac and MacDonald, 1974).

The rate of pyrite oxidation has been found to be a function of redox potential (May, 1997). Kinetic models presented by Hansford (2002) in a short course indicated that the fraction of the mineral leached or rather mineral conversion is a function of the

ferric/ferrous iron ratio (or redox potential), the residence time, bacterial species and the characteristics of the pyrite itself.

3.2.4 Summary of bioleaching of copper sulphides

The kinetics of copper sulphide mineral dissolution are greatly improved if the iron- and sulphur-oxidising microbial species are introduced to the leaching system. But the degree of microbial oxidation for different copper sulphides varies significantly partly because of different types and level of impurity minerals associated with copper sulphides from different sources. Therefore, one of the main goals of this investigation on the basis of microbial action was to explore the bioleachability of copper sulphide ore from Nchanga mine through chemical (acid) and microbial leaching experiments. Also, the extent of copper sulphide oxidation by ferric iron through microbial action depends on the mineral itself, temperatures employed, oxygen availability, pH as well as mass transfer effects. Therefore, it was necessary to investigate the effects of some of these variables on copper dissolution rates in this study. Furthermore, the different solution conditions and leaching methods employed have an effect on the overall leaching kinetics.

Pyrite has been shown to be a source of soluble iron since the ferric (Fe^{3+}) form is the main oxidant and therefore the driving force in bioleaching systems. The effects of both inherent pyrite in the ore and added ferric iron on copper dissolution were therefore investigated in the present work.

The extent of mineral dissolution for the common secondary copper sulphides (such as chalcocite and covellite) generally varies between 80-100 % under typical bioleaching conditions with mesophiles. For example, about half (50%) of copper in chalcocite may be leached within an hour but a complete dissolution requires much longer times. However, chalcopyrite is very difficult to leach under mesophilic conditions but the kinetics are enhanced in the presence of silver as a catalyst. Several publications have reported high dissolution rates for chalcopyrite using high temperature thermophiles. Conditions under which chalcopyrite is reported to leach include low (controlled) redox potential range of typically 520-580 mV (vs. SHE), high temperatures of 55-80 °C, fine

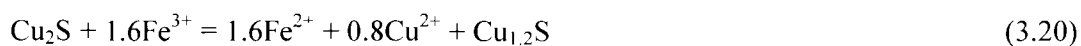
grinding of 6-12 μm particle size range and a low pH values of 1.1-2.0 for satisfactory dissolution rates.

It can be concluded that many of the laboratory bioleaching studies involving copper sulphides have been conducted in shake flask experiments, where cell/microbial growth rates are done manually using such techniques as cell counts, protein analysis etc. Due to relatively slow kinetics associated with shake flask experiments, low accuracy and longer time requirements in the more common cell counts technique this study employed stirred tank leaching method using off-gas analysis to enumerate microbial cells following the methods of Boon(1996) and Breed(2000). The off-gas analysis technique was successful in establishing the microbial oxidation kinetics of pyrite and arsenopyrite by these authors. Infact reported bioleaching studies involving copper sulphide ores and/or minerals coupled to the off-gas for analysis of microbial growth are rather fewer, therefore it was necessary to conduct this study using the online off-gas technique as a faster and alternative tool to enumerate microbial cells.

Similar solution conditions to those of published studies involving shake flask experiments were therefore applied in this study to investigate the extent of copper extraction for copper sulphide ore of predominantly chalcocite from Nchanga Mine. These include pH of 1.0-2.0, 25-40⁰C temperature (reported temperature range for mesophilic bacterial growth), low ferric iron concentration of 0.05-0.16 mol/l and a fixed low solids concentration (pulp density) of 5 %w/v.

3.3 Theoretical mass and energy balances for bioleaching of chalcocite (Cu_2S)

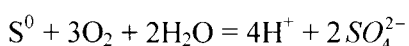
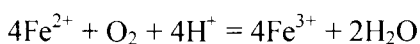
Literature survey (See Section 3.2) has shown that the ferric leaching of chalcocite occurs through a two-stage mechanism. The first stage reaction occurs rapidly according to the following reaction;



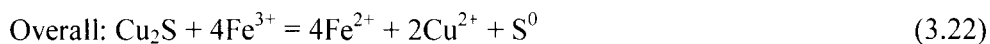
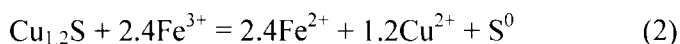
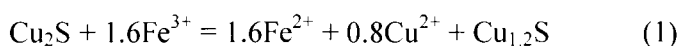
The second-stage ferric leaching of chalcocite is the reaction of $\text{Cu}_{1.2}\text{S}$ (non stoichiometric pseudo covellite) with ferric ions to produce copper, ferrous iron and elemental sulphur in solution.



At the same time ferrous iron and elemental sulphur are microbially oxidised to regenerate ferric ions and produce acid respectively according to the reactions shown earlier (Equations 3.12-3.14) and repeated here i.e.



The overall oxidation of chalcocite is then given by the summation of first and second stage reactions;



Thus, the bioleaching of chalcocite takes place according to the overall stoichiometry shown above. However, it was assumed that only mesophilic iron oxidising bacteria are present such that elemental sulphur remains unoxidised.

As shown previously the off-gas analysis of CO_2 and O_2 has been applied to measure the rates of bacterial growth and substrate (pyrite, ferrous iron) oxidation and conversion through the use of elemental and charge balances and the degree of reduction balances (Boon, 1996). This technique was similarly applied to theoretically determine the bacterial oxidation rate of chalcocite.

The degree of reduction balance was utilised to calculate the substrate (Cu_2S) oxidation rate from the oxygen and carbon dioxide consumption rate. Basically, the degree of reduction balance, γ_i , for any organic/inorganic compound is the number of electrons that are liberated in a redox half-reaction when one (1) C-mole of an organic or one (1) mole

of an inorganic compound is converted into H^+ , CO_2 , H_2O , N-Source, N_2 , SO_4^{2-} or Fe^{3+} . Hence, the degree of reduction is a measure of the electron content of the compound relative to these species chosen as the reference compounds. The consequence of this definition is that values of the degree of reduction balances for H^+ , CO_2 , H_2O , N-Source, N_2 , SO_4^{2-} and Fe^{3+} are taken as zero.

Therefore, the degree of reduction expresses that electrons are conserved

i.e. $\sum r_i \gamma_i = 0$

The degree of reduction of compounds that are involved in the bacterial growth on chalcocite are calculated as follows;

- | | |
|---|---|
| 1. Biomass ($CH_{1.8}O_{0.5}N_{0.2}$);
- $CH_{1.8}O_{0.5}N_{0.2} + CO_2 - 1.5H_2O + 0.2NH_3 + 4.2H^+ + 4.2e^- = 0$, $\gamma_i = +4.2$ | |
| 2. Oxygen (O_2);
- $O_2 + 2H_2O - 4H^+ - 4e^- = 0$
$\gamma_{O_2} = -4.0$ | 3. Ferrous iron (Fe^{2+});
- $Fe^{2+} + Fe^{3+} + e^- = 0$
$\gamma_{Fe^{2+}} = +1.0$ |
| 4. Sulphur (S^0);
- $S^0 + SO_4^{2-} - 4H_2O + 8H^+ + 6e^- = 0$
$\gamma_{S^0} = +6.0$ | 5. Chalcocite (Cu_2S);
- $Cu_2S + 2Cu^{2+} + SO_4^{2-} - 4H_2O + 8H^+ + 10e^- = 0$
$\gamma_{Cu_2S} = +10.0$ |

Thus, $\sum r_i \gamma_i = 0$

$$\therefore 10r_{Cu_2S} + 4.2(r_x) + (-4.0)r_{O_2} = 0$$

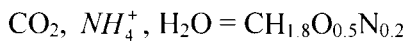
$$-10r_{Cu_2S} = -4.2r_x - 4r_{O_2}$$

where negative rates means that species are consumed and vice versa.

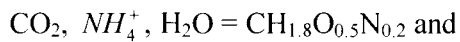
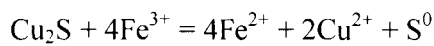
Hence, in cases where chalcocite is the only (single) substrate, knowledge of microbial carbon dioxide and oxygen consumption rates can be used to calculate the rate of microbial chalcocite oxidation directly.

3.3.1 Derivation of stoichiometric equation for chalcocite bioleaching

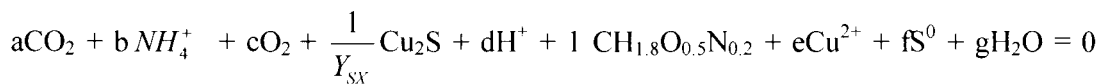
A stoichiometric equation for the bioleaching of chalcocite accompanied by growth of bacteria on ferrous iron is derived from the elemental and charge balances. The term $1/Y_{SX}$ is used and defined as the amount of substrate (Cu_2S) to be oxidised to produce 1 C-mole of biomass. The stoichiometric formula for biomass is taken as $\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.2}$ (Roels, 1983). Other quantities are as previously defined (Section 4.3.2) where r_x is the rate of biomass production determined from the carbon dioxide consumption rate, r_{CO_2} . The bacteria use carbon dioxide and ammonium ions as the only carbon and nitrogen sources respectively for growth.



Therefore, the stoichiometric equation for the bioleaching of chalcocite accompanied by growth of microorganisms is written for;



as;



(3.23)

The coefficients in the stoichiometric equation are then determined from elemental and charge balance calculations;

1. Charge balances

Chemical Species	$\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.2}$	CO_2	NH_4^+	Cu_2S	Cu^{2+}	H^+	O_2	H_2O	S^0
Charge Balances	$1 \times 0 = 0$	$a \times 0 = 0$	$b \times 1 = b$	$1/Y_{SX} \times 0 = 0$	$e \times 2 = 2e$	$d \times 1 = d$	$c \times 0 = 0$	$g \times 0 = 0$	$f \times 0 = 0$

The overall charge balance equation from the above table becomes;

$$\underline{b + 2e + d = 0} \quad (i)$$

2.0 Elemental balances

Element	Balanced equation
C	$a + 1 = 0; a = -1$ (ii)
H	$1.8 + 4b + d + 2g = 0$ (iii)
O	$2a + 2c + 0.5 + g = 0$ (iv)
N	$b + 0.2 = 0; b = -0.2$ (v)
Cu	$2/Y_{SX} + e = 0; e = -2/Y_{SX}$ (vi)
S	$1/Y_{SX} + f = 0; f = -1/Y_{SX}$ (vii)

From equations (i) and (v);

$$d = -b - 2e = -(-0.2) - 2(-2/Y_{SX}) = -0.2 + 4/Y_{SX} \quad (viii)$$

From equation (ii);

$$1.8 + 3b + d + 2g = 0 \Rightarrow 1.8 + 3(-0.2) + 4/Y_{SX} + 2g = 0$$

$$\Rightarrow g = \frac{1}{2} \left(-1.2 - \frac{4}{Y_{SX}} \right) = -0.6 - \frac{2}{Y_{SX}} ; \quad (ix)$$

From equation (iii) and (ix);

$$2a + 2c + 0.5 + g = 0 \Rightarrow 2(-1) + 2c + 0.5 + \left(-0.6 - \frac{2}{Y_{SX}} \right) = 0 \therefore c = \frac{1}{Y_{SX}} + 1.05$$

Hence, substitution of the coefficients in the stoichiometric equation and rearranging gives;

$$\begin{aligned} & CO_2 + 0.2NH_4^+ + \left(\frac{1}{Y_{SX}} - 1.05 \right) O_2 + \frac{1}{Y_{SX}} Cu_2S + \left(\frac{4}{Y_{SX}} - 0.2 \right) H^+ \\ & = \\ & 1CH_{1.8}O_{0.5}N_{0.2} + \frac{2}{Y_{SX}} Cu^{2+} + \frac{1}{Y_{SX}} S^0 + \left(\frac{2}{Y_{SX}} - 0.6 \right) H_2O \end{aligned} \quad (3.24)$$

3.3.2 Estimation of mass and energy requirements for chalcocite (Cu₂S) bioleaching

In this section, an attempt was made to use the established stoichiometric equation above to calculate the theoretical oxygen, carbon dioxide, ammonium, acid/base requirements and heat load for the bioleaching of chalcocite with mesophilic bacteria. The following were the assumptions:

- (1) 1 ton Cu₂S to be treated per day
- (2) Cu₂S concentration of 15% w/w solids in the feed
- (3) pH of 1.50 and temperature of 35⁰C.

The bacterial yield, Y_{sx} on chalcocite is first computed using standard free energy changes.

Calculation of Y_{sx}:

Compound	Biomass	NH ₄ ⁺	O ₂	Cu ₂ S	H ₂ O	Cu ²⁺	H ⁺	S ⁰	CO ₂
ΔG _{f,i} ⁰¹ (kJ.mol ⁻¹)	-67	-79.4	0	-86.21	-237.18	65.3	-39.87	0	-394.36

$$\therefore \sum \alpha_i \Delta G_{f,i}^{01} + \frac{D_S^{01}}{r_x} = 0$$

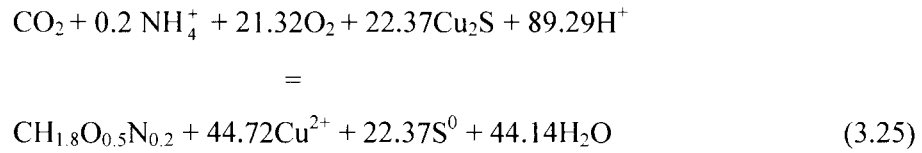
For autotrophic growth the Gibbs energy dissipation term $\left(\frac{D_S^{01}}{r_x} \right) = 3\ 500$ kJ/mole.

The Gibbs energy values are substituted in the stoichiometric equation:

$$\begin{aligned}
 & 1(-394.36) + 0.2(-79.4) + \left(-1.05 + \frac{1}{Y_{sx}} \right) (0) + \frac{1}{Y_{sx}} (-86.21) + \left(-0.2 + \frac{2}{Y_{sx}} \right) (-39.87) \\
 & = \\
 & 1(-67.0) + \frac{2}{Y_{sx}} (65.3) + \frac{1}{Y_{sx}} (0) + \left(-0.6 + \frac{2}{Y_{sx}} \right) (-237.18) + 3500
 \end{aligned}$$

Hence, **Y_{sx} = 0.0447 C-mol.(mol Cu₂S)⁻¹**

Thus, the stoichiometric equation becomes;



Based on the above equation, the masses are calculated as follows;

Basis of Calculation: 1000 Kg Cu₂S

Cu₂S : CO₂

22.37 : 1

$$1000 \text{ Kg} : ? \quad \therefore \frac{1000(1)44}{22.37(159.16)} = 12.36 \text{ kg CO}_2$$

Similar calculations for other terms are done and values are as entered in the table below.

Chemical species	Biomass	NH ₄ ⁺	O ₂	Cu ₂ S	H ⁺
Mass (kg)	6.91	1.01	191.62	1000	25.33

Also at pH 1.50, pH = -log [H⁺], thus [H⁺] = 10^{-1.5} = **0.0316 mol/l H⁺**

But mols of H⁺ produced = 25.33 x 10³/1.01 = 25 kmol/l H⁺.

Hence, to maintain the pH at 1.50, a base is required to neutralise excess protons (acid) as depicted by the above calculations.

Heat Load:

To bioleach chalcocite at 35⁰C, T = 308 K, heat produced by chalcocite oxidation is estimated as follows;

$$C_{p,\text{Cu}_2\text{S}}^O = 81.6 \text{ J/mol.k}; H_{f,\text{Cu}_2\text{S}}^O = -79.6 \text{ kJ/mol}$$

$$\therefore H_{\text{Cu}_2\text{S}} = H_{\text{Cu}_2\text{S}}^O(298) + (T - 298)C_{p,\text{Cu}_2\text{S}}^O(298) = -79.6 \times 10^3 \frac{\text{J}}{\text{mol}} + (308 - 298)k \left(86.6 \frac{\text{J}}{\text{mol.k}} \right)$$

$$= - 78.78 \text{ kJ/mol as heat load}$$

The standard heat of reaction for bioleaching of chalcocite;

Chemical species	Biomass	NH ₄ ⁺	O ₂	Cu ₂ S	H ₂ O	Cu ²⁺	H ⁺	S ⁰	CO ₂
ΔH_f^O (kJ.mol ⁻¹)	-91	-132.6	0	-79.6	-286.1	65.7	0	0	-394.36

The standard heat of reaction, ΔH_R^O is given as;

$$\Delta H_R^O = \sum H_{\text{Products}} - \sum H_{\text{Reactants}}$$

$$\sum H_{\text{Products}} = 1(-91) + 44.72(65.7) + 22.37(0) + 44.14(-286.10) = -9781.35$$

$$\sum H_{\text{Reactants}} = 1(-394) + 0.2(-132.6) + 21.32(0) + 22.37(-79.6) = -2201.17$$

Therefore, $\Delta H_R^O = -338.85$ kJ/mol Cu₂S

The heat load of about 78.78 KJ/mol is less than what the system is producing (-338.85 kJ/mol). The consequence of this is that the system does not infact require any heat input but needs to be provided with cooling mechanism to maintain the temperature at 35°C.

It is often necessary to develop rate expressions from laboratory kinetics data for modelling the performance of stirred tank reactors. However, no such kinetic models have been published in literature for the bioleaching of chalcocite in stirred tank reactors from which estimates of chalcocite conversion could have been calculated. However, Dixon and Petersen (2003) have published models that fit kinetic data from column bioleaching experiments fairly well.

3.4 Heap Bioleaching Practice

There are currently four (4) principal leaching methods that have been utilised for metal extraction from oxide and sulphide ores. These include agitated leaching in vats and tanks, in-situ, dump and heap leaching techniques (Rossi, 1990). Heaps differ from dumps in that it has to be ascertained from the start that heaps would be employed and so deliberate steps are taken to prepare the ore and stockpile. That is, there is a careful selection and placement of ore to be leached. This section describes the basic principles of heap design, construction and operation from the chemical (acid) leaching and bioleaching context. The existing bioleaching operations worldwide are briefly reviewed.

Historically, heap leaching was utilised as means of treating oxide and sulphide ores of mainly copper that were too low in content to be concentrated (by such methods as froth flotation) and smelted economically (Murr, 1980; Rossi, 1990). However, heap (bio)leaching is now evolving as an alternative process to smelting and pressure oxidation as low cost technique that can treat waste dumps/rocks and deposits found in remote sites containing marginal or sub-marginal metal values or low-grade ores (e.g. $< 0.4\%$ Cu) (Murr, 1980; Dixon and Petersen, 2003). There are practically no gaseous emissions from heap operations. However, heap leaching has been observed to take several months or even years to leach about 20-60% of the total copper (Murr, 1980).

There are several types of heap leaching processes. Notable examples as given by Dixon and Petersen (2003) and Rossi (1990) are;

- Gold/silver cyanide leaching
- Acid leaching of copper oxide minerals
- Bioleaching of copper sulphide minerals e.g. dump leaching of chalcopyrite wastes and heap leaching of secondary copper sulphides
- Biooxidation of gold-bearing pyrites
- Leaching from waste dumps and low-grade deposits and
- Leaching of zinc and nickel sulphide deposits

3.4.1 Heap Design, Construction and Operation

Rossi (1990) has discussed the general considerations in assessing the suitability of any ore to heap bioleaching. Special attention should be paid to factors such as mineralogical composition, structural and physical properties of the rock e.g. porosity, clay content as well as particle size distribution. Upon ensuring that the minerals of interest can be bioleached, it must also be certain that there are no toxic or poisonous gangue components of the ore that might hinder the growth of bacteria.

The porosity and particle size distribution of the rock must be such that the leach solutions and dissolved oxygen reach the most inaccessible mineral grains containing the desired metal values. Also, the clay content must be as low as possible otherwise the clays once wetted may increase in volume (by 25-30%) leading to reduced porosity of the

rock. This in turn reduces the flow rate of the leach solution through the rock mass. The laboratory filtration experiments have demonstrated that increases in clay content of 15-60% may reduce filtration rate from 25 to 0.4 cm/day. Consequently, leaching times for heaps 2.5-3.0 m high increases from about 15 to 160 days. Further, copper ions may be lost from the leach solutions to the clay matrix (Rossi, 1990).

Construction of Heaps

Generally, the first step in overall heap design is to clear all vegetation followed by grading the soil surface and subsequent compaction on a suitably chosen site (Rossi, 1990). The ore is then prepared by crushing to a suitable particle size range. The rock pieces normally vary in size from about 250 mm in diameter down to very small particles. The crushed ore is then stacked onto prepared impervious pads to form properly designed piles. The bases of pads are inclined (2-5 degrees) to facilitate the solution to gravitate through and collect into drains and sumps (Barrett *et al.*, 1993). Some design considerations of the pad include the available area, duration of the leaching cycle, maximum practical heap height etc (Rossi, 1990). These pads may be used only once or several times depending on factors such as surface availability, environmental regulations etc. For repeated use pads can be made from compacted clay, asphalt, PVC (Polyvinyl Chloride) sheeting or concrete lined with HDPE (High Density Polyethylene) sheeting. The ground for the base must be geologically sound because fractures, faults or cracks and cleavages may cause an unacceptable solution losses and pollution of aquifers (Rossi, 1990; Barrett *et al.*, 1993).

Sometimes, however, pads for heap bioleaching can only be used once. Rossi (1990) has given several options of pad construction for such usage to ensure that they are impermeable. For example, soil can be cemented and then covered by a layer of diluted tar which effectively cures and seals the pad. Alternatively, a fine sand layer of 20-30 cm thick may be placed on a properly levelled ground. This is followed by 10 mm polyethylene plastic sheeting and finishing with another 30 cm layer of fine sand. Other methods include the placement of approximately 50 cm layer of clay on a properly prepared ground level. Another option is to use an impermeable thin sheet (e.g. 1 mm) of butyl plastic strips (reinforced with fibreglass) which can be joined together on the heap

site. The puncture of the plastic sheet must be avoided by initially putting a protective covering of fine sand.

The crushed ore is placed onto a heap by such methods as movable and tripper distribution conveyors or dumping from haul trucks and positioning the rock pieces into place by bulldozers, front end loaders or drag lines. The movable conveyor system transports the crushed ore from the crushing and screening plant to a tripper distribution conveyor. The distribution conveyor then places the ore on the end of the pad that is furthest away from the ore preparation plant. The conveyor is made shorter and shorter as the pad is filled. This minimises ore segregation. Alternatively, haul tracks may transport the crushed ore from the ore preparation plant to heap pads. Bulldozers or front end loaders finally push the ore into place. Dumpers and bulldozers tend to cause compaction of the ore. Also, the method inevitably produces segregation of the ore, reducing heap porosity (Rossi, 1990; Barrett *et al.*, 1993).

When front end loaders are employed compaction is nearly eliminated but it is difficult to get heaps higher than 3.0 m. Bulldozers can, however, attain heights of 3.5-4.0 m but this technique causes some compaction of the ore. Heap heights of about 4 m have been recommended though optimum values must be obtained from laboratory and pilot plant tests (Rossi, 1990; Barrett *et al.*, 1993). The detailed description of these and other methods of heap construction can be found in Rossi (1990) and Barrett *et al.* (1993). Figure 3.2 below gives a picture of a heap being constructed.



Figure 3.2: The sociedad minera cerro verde s.a.a., Arequipa, Peru; Crushed, agglomerated, ore conveyed to stacker (Hansford, 2005) presented at IBS'05, Cape Town

Operation of Heaps

Once the heap reaches the design height, leach solution is then applied to the heap by pumps that feed a network of pipes that are fitted with a mechanism of distributing the solution to the top of the heap. Solution distribution is mainly by means of small drippers or emitters although wobblers and wigglers are also available. Emitters/drippers discharge the leach solution onto the ore slowly around where they are fitted. These fittings are regularly positioned so that they overlap to wet the ore completely, thus giving a total coverage of the heap surface. During operation drippers may be blocked sometimes by precipitation of dissolved solids once the solution comes into contact with air. Wigglers and wobblers discharge the solution into the air. This aids the dissolution of oxygen and carbon dioxide though a high amount of solution is lost through precipitation. Drippers apply the solution directly onto the heap surface. Therefore, drippers may be more efficient in places where the rate of evaporation is high (Barrett *et al.*, 1993).

3.4.2 Fundamentals of Heap Bioleaching

Heaps are constructed such that the penetration of the leaching solution into the rock mass, mineral dissolution as well as oxygen and carbon dioxide diffusion is optimum. Because heaps are composed of complex mixtures of oxides and sulphides, leaching is achieved through oxidative action by acidified ferric sulphate solution. The leaching process is not a steady-state phenomena since all factors and parameters change with time. For higher leach efficiencies, the leach solution/lixiviant must get inside the particles of the ore and be able to attack the minerals of interest. The minerals must be solubilised by the chemical reaction with the lixiviant. Finally, the leach solution with the dissolved metal in it must diffuse out of rock voids into the main stream (Murr, 1980).

Recent studies by Dixon and Petersen (2003) and many other publications by these authors have given greater understanding of various sub-processes involved in heap bioleaching. Briefly, the overall process starts with oxygen and carbon dioxide uptake from the gas phase into the liquid phase followed by complex interactions of microorganisms with mineral surfaces (See Chapter 2). With suitable concentrations of acid, oxygen and carbon dioxide (for carbon source), bacteria are able to grow and

propagate leading to oxidation of ferrous iron to ferric form (or sulphur to sulphate) and consequent oxidation of minerals by ferric ions. Thus, through intra- and inter-particle diffusion dissolved ions like copper are transported to the bulk solution through cracks and fissures within particles.

Further, many other transport phenomena are at play such as solution, heat and gas flow across heaps. Solution flow is assumed to be uniform but practically follows preferential channels within heaps (Dixon and Petersen, 2003). The Table and Figures below show reaction pathways and sub-processes involved in heap bioleaching.

3.4.3 Biochemical reactions in heaps

The chemical and microbial reactions are similar to those found in stirred tank leaching (See Chapter 2). Some of these reactions such as gas adsorption, ferrous oxidation and the subsequent ferric leaching of the mineral are depicted in Figure above.

The chemical composition of the pregnant solution coming out of the heap is dictated by several factors as discussed by Murr (1980), Rossi (1990), Barrett *et al.* (1993) and Dixon and Petersen (2003). Among the factors is the rate of irrigation since higher rates of (feed) solution application may cause unnecessary dilution of copper values. Furthermore, temperatures within heaps vary considerably and thus the temperature of the leach solution should be controlled where possible since cold or low temperature solutions reduce the reaction rates. Much bigger heaps may heat up excessively giving higher temperatures, thus application of high rates of irrigation lowers the temperatures.

Heap temperatures higher than optimum values reduce the bacterial activity and may affect overall reaction rates. The variation of temperature within heaps is affected by such factors as ambient temperatures, size of the heap, and quantity of sulphide minerals to be leached and the extent of various chemical reactions (Barrett *et al.*, 1993).

Table 3.1: Major Sub-Processes Involved in Heap Bioleaching at various scales (Adapted from Dixon and Petersen, 2003)

Scale	Sub-Processes	Illustration
Mineral Grain	Ferric reduction Mineral oxidation Sulfur oxidation Surface processes	The diagram shows a vertical bar representing a mineral grain. To its left, a cycle shows Fe^{3+} at the top and Fe^{2+} at the bottom, with arrows indicating a downward flow. To the right of the bar, MeS is written at the top and SO_4^{2-} at the bottom. A small arrow points from the bar towards the SO_4^{2-} label.
Ore Particle	Topological effects Intra-particle diffusion Particle size distribution	Three diagrams of ore particles are shown. The first is a solid, irregular shape labeled 'pure mineral particle'. The second is a similar shape with small circles on its surface, labeled 'particle with mineral grains at surface'. The third is a porous, irregular shape with small circles inside, labeled 'porous particle with mineral inclusions'.
Stagnant Cluster	Gas adsorption Inter- and intra-particle diffusion Microbial growth Microbial attachment Microbial oxidation	The diagram shows a cluster of irregular shapes representing particles. Arrows indicate 'D₂, CO₂ adsorption' entering from the top. Arrows between particles indicate 'inter-particle diffusion'. Arrows within particles indicate 'intra-particle diffusion'. Small circles representing 'attached and floating micro-organisms' are shown on and around the particles.
Heap	Unsaturated solution flow Gas advection Water vapour transport Heat balance	The diagram shows a cross-section of a heap. Three vertical arrows point upwards, labeled 'solution flow'. Wavy lines represent 'gas flow'. A shaded area in the center is labeled 'internal heat generation'.

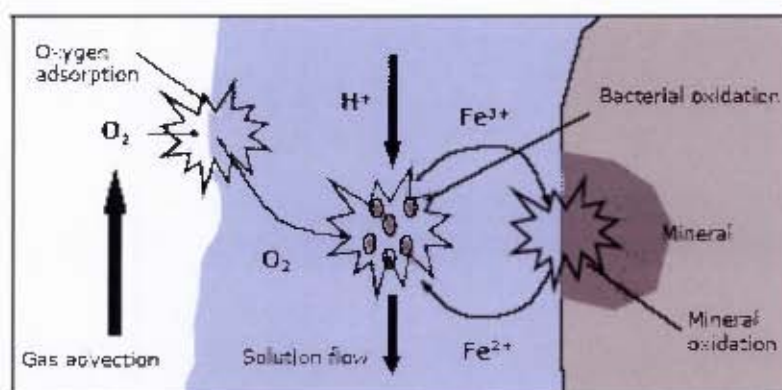


Figure 3.3: Reaction Pathways in heap bioleaching (Adapted from Dixon and Petersen, 2003)

Generally, the mineral oxidation kinetics are specific to a particular ore and may be a function of bacterial action, heat and oxygen balances, air convection along with actual heap dimensions and rates of irrigation. Typically, leach solution composition will have approximately 10^5 cells.cm⁻³, less than 0.40 g.L⁻¹ Fe²⁺ or Fe²⁺/Fe³⁺ ratio of greater than 1.0, while total iron concentration can be as high as 20-40 g.L⁻¹ in the effluent solution or Fe²⁺/Fe³⁺ ratio of less than 1.0 (Murr, 1980).

The control of bacterial oxidation kinetics in heaps is very limited. As acidity is critical for bacterial growth, it can be controlled by adjusting the influent pH of the solution being applied to the heap whereas the uniformity of acidity inside the heap matrix may be ascertained by ensuring uniform nature of leach solution flow through the stacked rock. The optimum bacterial culture growth may be attained by maintaining a constant pH, supply of nutrients and proper gas transfer (oxygen and Carbon dioxide) by convection, diffusion and solution flow (Barrett *et al.*, 1993).

The way heaps are constructed will determine the degree of gas transfer (oxygen and carbon dioxide) from the gas phase to the aqueous phase and sometimes may control the transfer of these gases by the leach solution. Heaps are normally constructed to have sufficient porosity for air to diffuse throughout the heap. The pore spaces further provides the free movement and relatively uniform distribution of the leach solution. If the level of sulphides to be oxidised is very high, positive aeration may be applied whereby pipes are laid underneath the ore and then pumping compressed air into the base of the heap for

increased air transfer. The source of nutrients for bacterial growth in heaps may come from either the ore (rock) or the leach solution itself percolating through the heap. The latter can be achieved by deliberate addition of chemical nutrients to the leach solution being applied to the surface of the heap to make up any deficiency of nutrients coming from the ore (Barrett *et al.*, 1993).

In summary, important considerations in bioheap construction and operation include heap height or volume, irrigation rate and mode, air convection, nature of exothermic reactions and the rock size distribution and consolidation (or heap permeability). Dixon and Petersen (2003) during bioleaching of chalcocite in columns have shown that the oxidation is mainly affected by microbial growth kinetics, influent acid concentration and temperature, gangue acid dissolution, among others. The authors noted that the major challenge facing heap operation include slow rate of metal recoveries, long extraction times, process is inefficient, problems of effluent handling, open circuit water losses, logistical problems for remote mine sites and that heap bioleaching is still undeveloped science. A bioheap modelling tool called HeapSim has been developed (Dixon and Petersen, 2003) for understanding the dynamics of heap mineral kinetics, bacterial growth, particle level effects, oxidation and gas adsorption, pore diffusion etc.

3.4.4 Brief overview of heap bioleaching operations worldwide

Several mineral bioprocessing plants/heaps have been commissioned including aerated stirred tanks, bioheaps, dump bioleaching and in-situ operations (Brierley, 1997). Only an overview of some bioheaps currently in operation is presented here. Basically, bioheaps are reactors in use today to extract copper through bacterial action from both copper oxides and chalcocite ores as well as to pretreat refractory, low-grade sulphidic gold ores. Examples of bioheaps include Cerro Colorado, Quebrada Blanca and Ivan-Zar in Chile.

Quebrada Blanca mine, found in Northern Chile, is an Open Pit operation that produces about 6.3 million mt/yr of high grade, secondary copper sulphide ore. It is located at a high altitude (4 400m above sea level) which means low (oxygen) partial pressures (0.6 atm) and low ambient temperature ranges of -15 to 18°C. The mine produces 75 000 mt/yr of copper cathodes using Thin Layer Bacterial heap leaching of predominantly

secondary sulphides of copper ore (chalcocite and covellite) with copper content of 1.3%, followed by solvent extraction (SX) and electrowinning (EW). The bacterial leaching technique was developed by Sociedad Minera Pudahuel (SMP). Other low-grade sulphides and some oxide resources are yet to be leached (Canello and Schnell, 1995; Report No.2 of E & MJ Magazine, 1995)

The ore is crushed in three stages at 17 300 mt/yr to 80% - 6 mm, agglomerated with 5 Kg/mt sulphuric acid and hot water in drums to form about 6m heap heights. The leach pads (6 degrees slope) are lined with High Density Polyethylene (HDPE). The monitoring wells down stream detect any potential groundwater contamination. The optimum bacterial activity is achieved by aeration using a network of air pipe lines installed at the bottom of heaps using low-pressure fans. It has been established that bacterial activity decreases to half for every 6⁰C temperature drop and completely finishes at the solidification point of the culture. The leach solution is applied by HDPE irrigation pipes fitted with drippers along each pipe that are positioned on the surface of the heap in summer. These pipes are buried beneath heap surface in winter to prevent freezing of leach solution. Copper extraction is 85% in 210 days, to give a pregnant leach solution of 3.5 g.L⁻¹ (Report No.2 of E & MJ Magazine, 1995; Brierley, 1997; Schnell, 1997).

Cerro Colorado, also found in Northern Chile at an altitude of 2600 m above sea level, is an Open Pit Mine that produces about 16 000 mt/day of ore grading 1.4% Cu with an estimated ore reserves of about 193 million tonnes. Ambient temperature range is between 3-30⁰C. The mine produces 60 000 mt/yr of copper cathodes through heap bioleaching by electrowinning via solvent extraction. Leaching process involves the use of Thin Layer Bacterial heap leaching technology that was developed by Sociedad Minera Pudahuel (SMP). The mineralogy of Cerro Colorado ore body is mainly mixed oxides and secondary copper sulphide minerals of chalcocite and covellite (replacement of primary pyrite, chalcopyrite, bornite etc) and oxides of copper such as chrysocolla, atacamite and some malachite, cuprite, bronchantite mineralisation (Porcile *et. al.*, 1996; Brierley, 1997). See also the article by Bernard (1995).

The ore is crushed in three stages at about 22 800 mt/day to give -13mm product size. The crushed product is agglomerated in drums using sulphuric acid and hot water and

then transported by the mobile conveying and stacking system of conveyors to heaps of about 6m on pads that have slopes of 3 degrees. Besides the passive aeration of heaps from air diffusion and convection, active (positive) aeration system is utilised to supply air needed by bacteria. Once heaps reach the required heights (6m), a solution distribution and spray system is then installed. Using drippers, the ore is leached by 10 g. L⁻¹ concentration of sulphuric acid solution (raffinate) with 0.3 g.L⁻¹ Cu at a flow rate of 2500 m³/h for a period of 300 days. The leach solution pH is about 1.2 with bacterial concentration of over 10⁶ cells/ml. In Cerro Colorado bioheaps, the solution nutrient composition for bacterial growth is about 3.5 g.L⁻¹ Fe²⁺, 6.1 g.m⁻³ O₂, 0.32 g.m⁻³ CO₂, 20 ppm NH₄⁺ and 120-230 ppm PO₄³⁻. The overall copper extraction is 80%. The pregnant leach solution from the leach pads contain tenors of 3.2 g.L⁻¹ Cu²⁺ and 3.7 g.L⁻¹ sulphuric acid, which is sent to electrowinning via solvent extraction for production of copper cathodes (Porcile *et. al.*, 1996).

Once leaching is completed, the spent ore is removed using trucks and loaders after which the pad is levelled and prepared again for the next series of heaps to be leached.

As cited by Porcile *et. al.* (1996) column testwork has shown that leaching of sulphide ores with 20% fines gave copper extraction of 46.8% in 50 days while those with 10% fines gave 61.7% copper recovery. This meant that high fines content in the reduces the hydrodynamic properties and oxidation capacity of the bed.

Zaldivar mine, located in Northern Chile at an altitude of 3 300m above sea level, produces copper cathodes at 125 000 mt/yr through heap bioleaching, solvent extraction and electrowinning. The mineralogy of Zaldivar ore body is a mixed oxide/sulphide minerals of bronchantite, chrysocolla and chalcocite. The ore reserves for heap operations contain about 185.7 million tonnes at 1.06% copper, of which 0.32% is acid soluble. The rest of the ore (60.6 million tonnes) with 0.42% copper is processed through dump leaching (Garcia *et. al.*, 1999).

The ore is crushed at 60 000 mt/day to 100% - 100mm and then placed on leaching pads to form heaps. The operation utilises drip emitters to irrigate the heaps, reducing heat loss effects while improving conditions for bacterial activity. A two-stage leaching is utilised

whereby the dilute pregnant leach solution from the first stage is recirculated to fresh ore, giving about 2-4 g.L⁻¹ copper. The pregnant leach solution is collected via pipes and sent to electrowinning via solvent extraction. The solution pH varies in the range 1.6-2.8 while ambient temperature range is -10 to 25°C (Garcia *et al.*, 1999). Several other bioheaps are in operation today. Table 3.2 below gives a summary of some of them.

3.5 Process Alternatives for Copper Extraction

3.5.1 Roasting and Smelting

The conventional extraction of metals from sulphide concentrates is done by roasting, smelting, converting and electro refining process steps (Hayes, 2003). The sulphidic refractory gold ores are firstly concentrated followed by roasting at high temperatures of up to 600-800°C to drive off the sulphides as gases. Roasting is then a pre-treatment step that is aimed at liberating gold from refractory sulphide concentrates by breaking down the sulphide matrix, rendering them more amenable to the subsequent cyanide leaching process (Poulin and Lawrence, 1996). Gold is then recovered from the solid residue that is left behind. Overall gold recovery improves from about 20% without pre-treatment to over 90% after biooxidation (Brierley, 1997). For an ore with arsenopyrite, a two stage roaster is often required, first to remove arsenic as arsenic trioxide and then to oxidise the remaining sulphides. Gas handling devices such as gas scrubbers are necessary to contain sulphur dioxide and arsenic trioxide emissions (Poulin and Lawrence, 1996). The final disposal and containment of arsenic (III) oxide for environmental protection is an expensive remedial step (Barret *et al.*, 1993).

For base metal extraction, both roasting and smelting result in gaseous sulphur dioxide emissions. Thus, the prevention of atmospheric pollution by sulphur dioxide because of its eventual conversion into acid rain is expensive (Barret *et al.*, 1993). The capital costs of smelter and refinery complexes are also very high and these smelters are limited in their ability to treat concentrates that contain high levels of impurities (Dreisinger, 2005).

Table 3.2: Current Copper Heap Bioleaching Operations (Brierley, 1997; 2001; Watling, 2006)

Name of Bioheap, Location & operational Status	Ore type / Mineralogy	Process Conditions	Productivity
Cerro Colorado, Chile, 1993-Present	Chalcoocite, Covellite & Fewer copper oxides	Bioheap with SX/EW & SMP ¹ process	10 000 mt/day ore at 1.4% Cu; 60 000 mt/yr Cu metal
Ivan Zari, Chile 1994-Present	Mixed oxides/sulphides of predominantly chalcoocite	Bioheap with SX/EW & SMP ¹ process	1 500 mt/day ore at 2.5% Cu; 10 000-12 000 mt/yr Cu metal
Quebrada Blanca, Chile 1994-Present	High-grade secondary copper Sulphides of chalcoocite & covellite	Bioheaps/biodumps with SX/EW & SMP ¹ process	17 300 mt/yr ore; heaps at 1.4% Cu; Dumps at 0.6% Cu; 75 000 mt/yr Cu
Punta del Cobre, Chile 1994-Present	Mixed oxides/sulphides	Bioheaps	Ore at 1.7% Cu; 7 000-8 000 mt/yr Cu
Andacollo, Chile 1996-Present	Chalcoocite ore	Bioheaps/Biodumps	15 000 mt/yr ore at 1.0-0.55% Cu; 21 000 mt/yr Cu
Dos Amigos, Chile 1996-Present	Chalcoocite ore	Bioheaps	3 000 mt/yr ore at 2.5% Cu
Zaldívar, Chile 1996-Present	Chalcoocite ore	Bioheaps/Biodumps	20 000 mt/yr ore; heaps at 1.4% Cu; Dumps at 0.4% Cu
Lomas Bayas, Chile 1996-Present	Mixed oxides/sulphides	Bioheaps/Biodumps	38 000 mt/yr ore at 0.4% Cu; 80 000 mt/yr Cu
Cerro Verde, Peru 1996-Present	Mixed oxides/sulphides	Bioheaps	32 000 mt/yr ore at 0.7% Cu; 54 200 mt/yr Cu
Escondida, Chile	Mixed oxides/sulphides	Bioheaps	Ore at 0.3-0.7% Cu; 200 000 mt/yr Cu
Nifty Copper, Australia 1996-Present	Mixed oxides/sulphides	Bioheaps	5 000 mt/yr ore at 1.2% Cu; 16 000 mt/yr Cu
Whim Creek & Mons Cupri, Australia 2006-Present	Mixed oxides/sulphides	Bioheaps	900 000 mt/yr ore at 0.6-1.1% Cu; 17 000 mt/yr Cu
S & K Copper, Monywa, Myanmar, 1999-Present	Chalcoocite ore	Bioheaps	18 000 mt/yr ore at 0.5% Cu; 40 000 mt/yr Cu
Phoenix Deposit, Cyprus 1996-Present	Mixed oxides/sulphides	Bioheaps	Ore at 0.31-0.78% Cu; 9 000 mt/yr Cu
Jinchuan Copper, China 2006-Present	Chalcoocite/Covellite & Enargite	Bioheaps	Ore at 0.63% Cu; 10 000 mt/yr Cu

¹ Thin Layer Bacterial Leaching Technology developed by Sociedad Minera Pudahuel (SMP)

3.5.2 Bioleaching

As discussed in the previous chapters, the principle application of bioleaching is the direct liberation of gold values encapsulated in the pyritic refractory gold ores and the leaching of mainly copper from its sulphides. The effect is to cause the sulphide matrix to break down yielding soluble iron compounds and/or sulphuric acid. Gold is subsequently recovered from the solid residue left behind while copper goes into solution from which it is recovered (Brewis, 1995). Bacterial oxidation then forms a low cost alternative to roasting or smelting for low grade sulphide deposits because, for instance, it does not create gaseous emissions. The only by-product of bioleaching is iron which is easily controlled and disposed off as inert iron arsenate (Poulin and Lawrence, 1996). Several bioprocesses such as BioCOP, BacTech, BIOX etc have been developed and patented. Details of these and many other processes can be found in several publications (Brewis, 1995; Dew *et. al.*, 1997; Miller, 1997; Taylor and Jansen; Dreisinger, 2005). The BioCOP and BIOX processes are briefly described below.

3.5.2.1 BioCOPTM Process

BHP Billiton has done extensive studies on mesophilic and thermophilic bacterial leaching of metal sulphides. Mesophilic bioleaching (42-45⁰C) has been developed for copper extraction from secondary copper sulphides. This technique uses ferric preleach followed by floating the residue to recover chalcopyrite as a concentrate together with any gold/silver present (Taylor and Jansen, 1999). The BioCOPTM process, developed BHP Billiton, uses thermophilic bacteria to oxidise and leach copper sulphide concentrates of predominantly chalcopyrite at 70-80 ⁰C, followed by solvent extraction (SX) and electrowinning (EW). The process has been commercially applied to treat copper concentrates containing arsenic at the Alliance project in Chile. It uses oxygen in stirred tank reactors at controlled pH in which arsenic is removed separately as solid residue for environmentally safe disposal (Dreisinger, 2005).

The BioCOPTM process results in higher copper extractions because of near total oxidation of sulphides to sulphates, hence significant acid is produced. The acid is partially neutralised by limestone addition to the bioleach slurry. Because of higher temperature bioleaching (70-80⁰C) with thermophiles, chalcopyrite is believed to show

higher rates of dissolution. It has been difficult to leach chalcopyrite with mesophilic bacteria due to passivation effect which prevents high recovery of copper (Dreisinger, 2005; Taylor and Jansen, 1999).

3.5.3 High temperature and pressure oxidation

For high grade ores and concentrates, pressure leaching may be used. It uses higher temperature and pressure oxidation conditions in autoclaves to oxidise nearly all sulphide minerals to sulphates and sulphuric acid (Dreisinger, 2005). The process results in good recoveries and faster kinetics. It does not lead to the production of atmospheric pollutants. However, this technique has several drawbacks; for example, the severe conditions of pressure oxidation demand a high standard of plant design and materials (Barrett *et al.*, 1993), and high operating skill and safety requirement. Pressure leaching is capital intensive because of the need for an associated oxygen plant as well as advanced materials of construction for autoclaves (Poulin and Lawrence, 1996; Dreisinger, 2005). Under these conditions, marginal and low-grade ores cannot be processed at a profit.

Due to severe conditions of pressure and temperature in autoclaves as well as excellent recoveries and faster kinetics, the difficult to leach minerals such as chalcopyrite are easily solubilised under these conditions. As a result several higher temperature and pressure oxidation processes have been developed. Examples include MT Gordon, Activox, CESL, Total Pressure Oxidation, Dynatec and Sepon copper processes. See details in reviews by Dreisinger (2005), and Taylor and Jansen (1999). CESL, Total Pressure Oxidation and Activox processes are briefly discussed below.

3.5.3.1 Activox Process

The Activox process was developed by Western Minerals Technology in Perth, Australia. The copper ore is very finely ground to 5-15 μm followed by low-pressure oxidation in autoclaves at about 100°C. Copper is recovered by SX and EW. The technique has been applied to treat copper sulphide minerals of chalcopyrite and chalcocite whereby gold, if present, is recovered by cyanidation process of the residues. It is claimed the copper recoveries are as high as for smelting. The main advantages of the process include

significantly lower capital costs than smelting though operating costs are similar. The process also produces elemental sulphur as a by-product rather than sulphate. This minimises oxygen consumption and also gives acceptable cyanide consumption for gold recovery. It has the ability to operate smaller plants more economically (< 1000 t/yr) (Taylor and Jansen, 1999).

3.5.3.2 Total pressure oxidation process

This process utilises conditions of high temperature ($\sim 200^{\circ}\text{C}$), pressure and oxygen in autoclaves to effect the dissolution of all sulphides to sulphates and/or sulphuric acid. Very high copper extraction of about 99% is achieved within few hours. Copper is subsequently recovered by conventional SX/EW route. Several other metals such as copper, cobalt and nickel can be recovered while iron is precipitated as haematite. Phelps Dodge operates a copper processing Bagdad plant in Arizona that utilises total pressure oxidation to produce about 16 000 t/yr copper. The acid by-product can be used for copper oxide leaching. The advantages are that the feed material does not require fine grinding nor catalysts, and the process does not produce elemental sulphur in the autoclaves (Taylor and Jansen, 1999; Dreisinger, 2005). However, oxygen consumption is high and capital costs of autoclaves for such applications are also high, though lower than those for smelters (Taylor and Jansen, 1999; Dreisinger, 2005).

3.5.3.3 Cominco Engineering Services Limited (CESL) Process.

In the CESL Process, a predominantly chalcopyrite concentrate is lightly reground to about 95% - 45 μm followed by medium pressure oxidation in autoclaves at 150°C , using chloride as a catalyst. An additional second stage atmospheric leach is used to improve copper extraction, with the final copper recovery by SX/EW route. Elemental sulphur is produced as potential by-product followed by gold recovery from the residue by cyanidation. The main advantage is that the use of higher temperatures avoids the necessity for fine grinding while the production of elemental sulphur lowers the oxygen requirement. As before, iron is precipitated as haematite. It is claimed the capital costs in this process are about half of those for smelters and much lower operating costs. Copper recoveries are as good as smelter figures (Taylor and Jansen, 1999).

3.5.4 Relative advantages of bioleaching, pressure leaching and smelting.

The choice of any particular metal extraction technique is influenced by different factors under different applications, with each technique having its own merits and challenges. The potential advantages of bioleaching are briefly discussed in the sections that follow and compared with other processes.

The traditional metal extraction methods involve the use many expensive steps such as roasting and smelting, which require sufficient concentrations of metals in ores. Microbial leaching, however, has virtually no lower limit of feed grade in the ore as it can often treat a much lower grade more economically than pressure leaching or smelting (Miller, 1997). The microbial leaching process also tends to be more environmentally friendly than traditional methods since the necessary limiting of sulphur dioxide emissions during roasting and smelting is expensive (Barrett *et al*, 1993), Bioleaching is generally cheaper and simple to operate and maintain. It uses non sophisticated equipment and requires less specialist skills. Depending on the project, capital and operating costs may be much lower than smelting or pressure leaching. But, the cost of power to provide air for biooxidation and subsequent down stream process steps such as solvent extraction and electrowinning may significantly contribute to the overall costs.

For a complex base metal deposit associated with gold ores, microbial leaching is able to release valuable base metal into solution and also liberate and expose gold values so as to be recovered by cyanidation (Miller, 1997). This means that the technique has a remarkable ability to adapt to treating a variety of sulphide minerals from a single deposit. Any arsenic arising from processing of arsenical refractory gold ores is easily contained through precipitation instead of impure arsenic by-product which may be difficult to dispose of, expensive to purify and usually of no value. The acidic bacterial effluent liquor can be recycled in the heap leaching of low grade sulphide or oxide material. This might offset the cost of neutralising the final liquor which is necessary to produce a disposable ferric precipitate (Miller, 1997).

Pressure leaching is also less favourable compared to bioleaching in case of low-grade ores. The autoclaves are capital and maintenance intensive because of the advanced materials needed for their construction and complexity of operation. The process also demands a high operator skill and safety.

In summary, the selection of bioleaching technique over roasting and smelting may be dictated by several factors, such as the type and size of the deposit and its head grade. Normally, a copper bioheap leaching may be preferred if the size of the deposit for the project is small such that it cannot sustain the construction cost of a smelter (Miller, 1997). Also, the remoteness of the mine site might not allow the production and subsequent shipment of concentrates to an off-site smelter because of high transportation costs. The high smelter charges incurred in treating dirty concentrates can be avoided if bioleaching is applied (Miller, 1997).

As discussed by Miller (1997), the use of stirred tank biooxidation for gold projects over roasting and pressure oxidation is justifiable for high-grade gold ores and concentrates. The capital and operating costs are comparatively lower as well as less environmental requirements. Other advantages include high gold recoveries, simple and robust process. However, if the mineable gold reserves are too low to support the capital costs of a roaster or pressure autoclave then bioheap leaching may be applied. In this case it may be economically more favourable to apply bioheap operation even though the gold recoveries are much lower. Another reason is that the gold grade is too low in some ores to be concentrated to a value high enough to support the capital costs of a roaster, pressure autoclave to even a stirred tank bioreactor. In some applications, mining of higher grade ore entails the removal of over-burden material containing small amounts of gold. This material is considered waste but can be bioheap leached because of the low capital and operating costs of the process.

A major disadvantage of bioleaching is the very low kinetics of metal extraction compared to smelting (Dreisinger, 2005). This means less profit and introduces a significant delay in cash flow for new plants. However, the concentration of gold in its ores and other base metals is generally very low. The cheaper cost of bacterial leaching in this case outweighs the time it takes to extract the metal. Thus, it is desirable to improve

the kinetics of bioleaching which is a major factor that influences the costs of the process. By reducing operating costs, the processing of lower grade ores and the scavenging of residual metal values from mine wastes becomes feasible (Brieley and Brieley, 1986). Despite some of these technological challenges several commercial bioleaching processes have emerged while others are still pilot plants or at the demonstration stage such as BIOX, Mintek and Bactech Processes.

3.6 Summary of Literature Survey

A survey of the literature has shown that the bioleaching of copper sulphide minerals has been extensively studied. Most of the common secondary copper sulphide minerals such as chalcocite and covellite are bioleachable under typical bioleaching conditions with mesophiles. There are several bioheaps worldwide that are treating mixed copper oxides and secondary sulphides of mainly chalcocite. The major difficulty is to leach chalcopyrite relatively fast and completely since it is refractory to bioleaching with mesophilic bacteria.

It is now believed the present theory of bioleaching is based on three fundamental sub-process mechanisms of bioleaching of metal sulphides; the chemical ferric iron leaching of sulphide minerals involving protons, the microbial ferrous iron and sulphur oxidation sub-processes. Thus, the current understanding of bioleaching is that it involves a combination of both acid (protons) and ferric iron to leach the sulphide mineral, solubilising the metal ions and producing ferrous iron and reduced sulphur compounds in solution. Ferrous iron is oxidised back to ferric form by iron oxidising bacteria. The compounds of sulphur are oxidised to sulphate and protons by sulphur oxidising bacteria through either the thiosulphate or polysulphide pathways. Therefore, the role of microorganisms is to regenerate the ferric iron and acid. By so doing, a high redox potential and high acidity of the bioleaching system is achieved hence promoting the dissolution of metal sulphides.

However, the bioleaching response of individual copper sulphide ores and minerals from different localities is remarkably different. Many authors have reported different mineral leaching kinetics data on account of variability of mineralogical composition and

different solution conditions and leaching systems being employed. From an industrial point of view, there is an ever increasing demand to process low-grade ore using alternative and cheaper hydrometallurgical techniques where bioleaching may be attractive. Further, high grade ore reserves are becoming depleted and the environmental pollution policies getting more and more stiff. This has indicated that further work was necessary to determine the kinetics of copper extraction and extent of mineral dissolution under various solution conditions. This preliminary leaching kinetics data may be useful for a possible development of tank or heap bioleaching and therefore it is necessary to investigate ores from Nchanga Mine as representative of the Zambian Copperbelt.

Chapter 4

Materials and Methods

4.1 Introduction

The use of off-gas measurements as an experimental tool in the biooxidation of sulphide minerals has been successfully applied to study the kinetics of microbial leaching of pyrite (Boon, 1996) and arsenopyrite (Breed, 2000). Therefore the experimental approach developed by Boon (1996) was adopted in this work to study the kinetics of a predominantly chalcocite ore by mesophilic bacteria in batch stirred tank bioreactors.

This chapter describes the experimental apparatus and techniques employed in this investigation. It gives the type of the mineral samples used and the bacterial strains, their source and adaptation. It also describes the main experimental framework which is subdivided into sequential shake flask experimentation for bacterial culture adaptation and growth, measurement of oxygen and carbon dioxide uptake using off-gas analyser, and the actual chemical and microbial leaching batch experiments.

4.2 Mineral Sample Collection and Characterisation

The composite mineral samples for this work were copper sulphide rougher concentrates provided by Nchanga mine, Zambia. These samples were characterised in terms of particle size distribution (PSD), chemical and mineralogical composition as well as the distribution and liberation characteristics of the mineral phases. PSD was done by both wet sieve technique and Malvern Mastersizer at University of Cape Town (UCT)'s Chemical Engineering Analytical Laboratory. The mineralogical composition was done at Nchanga mine, Metallurgical Projects by Mineralogy Section using Reflected Light Microscopy. The chemical composition was done at UCT Chemical Engineering Analytical Laboratory using Atomic Absorption

Spectrophotometry (AAS) Technique, though some of the samples were analysed by Nchanga mine Analytical services laboratory.

As shown in Figure 4.1 below, over 70% of the particles were less than 38 μm . The other characteristic particle sizes are shown below.

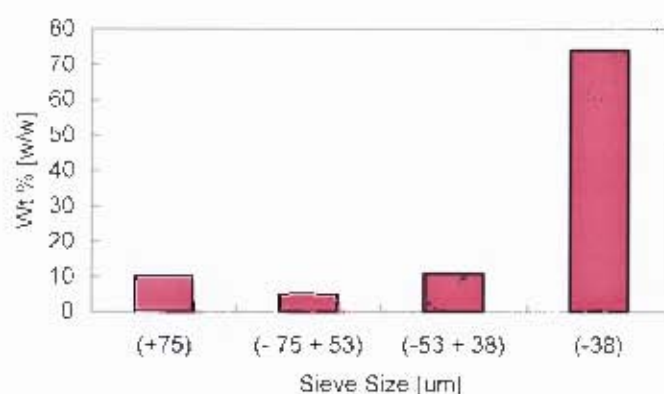


Figure 4.1: Particle size distribution for rougher concentrates

Table 4.1.: Characteristic particle sizes

Specific Surface area [m^2/g]	Density [g/m^3]	d_{50} [μm]	D_{90} [μm]	d_{10} [μm]
3.00	4.5	16	89.91	1.62

4.2.1 Elemental Analysis

A sample was sent to Nchanga analytical services laboratory for elemental analysis. The results provided a guide of the minerals that were present in the sample and the relative abundance of the mineral phases. The average elemental composition is given in Table 4.2 below.

Table 4.2: Chemical Analyses Results

Sample	%TCu	%ASCu	%HFCu	%Fe	%S	%THFCu	%Insols
Rougher Concentrates	15.35	2.21	0.52	7.01	9.51	2.73	49.5

4.2.2 Mineralogical Characterisation

Quantitative mineralogical analysis of the feed samples by Reflected Light Microscopy was carried out to obtain the mineral phase abundance before leaching in combination with elemental analysis. Based on the phases that were identified and from chemical analyses, the phase abundance was determined and summarised below.

Table 4.3: Ore Mineral Data for the Rougher Concentrate

MINERAL	Wt%	Rougher Concentrate			
		%TCu	%ASCu	Free	Locked
Chalcopyrite	1.53	0.528	-	83	17
Bornite	0.267	0.169	0.003	100	0
Chalcocite	15.27	12.185	0.183	92	8
Pyrite	8.755	-	-	97	3
Carrollite	0.022	0.004	-	100	0
Native Copper	-	-	-	-	-
Malachite	1.244	0.717	0.717	90	10
Pseudomalachite	0.278	0.154	0.154	95	5
Chrysocolla	0.141	0.078	0.078	90	10
Azurite	0.093	0.034	0.034	100	0
Cuprite	1.668	1.481	0.921	100	0
Cupriferous Micas	13	0.52	0.13	-	-
Gangue	57.733	-	-	-	-
TOTAL	100	15.87	2.219	-	-
Assays by ASD Nchanga Mine	-	TCu=15.870 HFCu=0.52	2.21	-	-

The concentrate has predominantly a mixed copper oxide-sulphide mineralisation. Chalcocite is the major secondary copper sulphide followed by oxides of malachite, azurite and cupriferous micas. Chalcopyrite also occurs in significant amount. The liberation characteristics are fairly good except chalcopyrite where 17% of it is still locked in the gangue minerals.

4.3 Leaching Apparatus and Procedure

4.3.1 Stirred Tank Reactor (STR)

The experimental setup for both chemical and microbial leaching test work is shown in Figure 4.2. It is essentially a Z61104CT04 Applikon autoclavable stirred tank bioreactor (STR) made of borosilicate glass, which is air tight, double walled and baffled glass reactor with 1 L working volume and H/D ratio of about 1.33. It is fitted with overhead variable speed stirrer with a four pitched (45°C) blade, axial flow turbine impeller fitted at the end of the shaft (about 2 cm from the reactor bottom) to provide proper mixing and ensure effective particle suspension at 400 rpm. The stirrer

assembly was driven by an Applikon P100 motor whose speed was controlled by Applikon 1012 speed controllers.

The air tight stainless steel cover is provided with ports for reflux condenser, stirrer shaft, pH and redox probes, sampling frit and gas sparge line through which compressed air was added. Manual pH control was effected by delivering acid or base as required. The reflux condenser was used to control and reduce evaporative solution losses. Basically, the off-gas from the reactor is passed through a reflux condenser cooled with circulating ethylene/glycol mixture at 6°C from the Grant LTD6G low-temperature bath in order to condense out the water so as to minimise evaporation of water from the bioreactor. The air then passes to the off gas analysers via a cloth filter and a Hartmann & Braun CGEK sample gas conditioner fitted with a CGKA 1 automatic condensate outlet where further drying takes place.

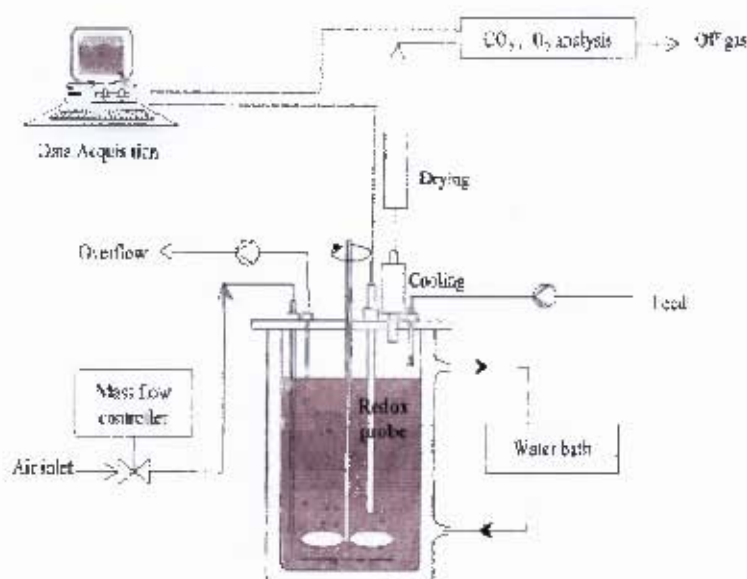


Figure 4.2: Stirred Tank Reactor (STR) with Off Gas Analyser (Breed *et al.* 1998)

The STR was thermostated at 35°C when temperature was not a variable by circulating heated water from an external Grant Y6 constant temperature water bath through the bioreactor jacket. The ingoing gas flow rate was controlled at the required rate by using a Brooks model 5850S mass flow controller and a Brooks model 1054 microprocessor and digital readout/display unit. The carbon dioxide and oxygen concentration in the dried bioreactor off-gas was determined using Hartmann & Braun Uras 4 NDIR (Non-dispersive infrared) industrial photometer and Hartmann & Braun

Magnos 6 G oxygen analyser respectively. The off-gas data was then logged by a computer. The difference between the reference air and off gas concentration was taken as the microbial gas utilisation rate. Therefore, the continuous measurement of oxygen and carbon dioxide consumption rates makes it possible to determine the biomass concentration in terms of moles of organic carbon per litre (C-mole.L⁻¹).

The adopted standard test conditions for all experiments were 35°C, pH 1.50 and 50 g.L⁻¹ solids concentration except where these were variables. Daily slurry samples of about 10 ml were taken from the reactor and suction filtered for analysis of soluble species in solution. The sampling time interval and batch residence time were predetermined and fixed. The residues were thoroughly washed with sufficient distilled water. The essence of this was to wash entrained dissolved copper containing solution out of the filter cake. The final residues (cake) were air dried at ambient conditions to minimise oxidation at high drying temperatures. The residues were then subjected to total acid digestions (see Appendix for the procedure) in order to determine unleached copper and iron.

4.3.2 Chemical Analyses and Copper Extraction Calculations

The progress of bioleaching was monitored through measurements of [Fe²⁺], [Fe³⁺], [Cu²⁺], pH and redox potential while bacterial activity was monitored online by CO₂ and O₂ utilisation rates. The redox potential of the system was monitored online with a gel-filled Metrohm Pt-Ag/AgCl combination redox probe while pH measurements were done by a combination probe using a Model 744 Metrohm pH Meter filled with 3.0 M KCl electrolyte solution. Copper and total iron concentrations were measured by AAS while ferrous iron (Fe²⁺) was determined by both spectrophotometry using 1-10 phenanthroline (C₁₂H₈N₂H₂O) as an indicator and ammonium acetate (NH₄C₂H₃O₂) as a buffer solution, and from values of redox potential and total iron concentration using the Nernst equation. The ferric (Fe³⁺) iron concentration was taken as the difference between total and ferrous iron concentrations.

The calculations of copper extraction were based on both soluble copper in solution and leach residue assays. The percent copper extraction based on copper assays is solution was established by carrying out the mass balances as shown below. The calculated head assay, Cu_{calc}, was defined as;

$$Cu_{calc} = \left\{ \frac{W_{Cu}^{sol} + W_{Cu}^{res}}{W_f} \right\} \times 100\% \quad (4.1)$$

W_{Cu}^{sol} is the mass of copper solubilised, W_{Cu}^{res} is the mass of copper in the leach residue and W_f is the mass of copper in the starting (feed) sample. So % copper extraction was determined as;

$$\therefore \%Cu = \frac{W_{Cu}^{sol}}{\left(\frac{\%Cu_{calc}}{100} \times W_f \right)} \times 100 \quad (4.2)$$

The calculations of percent copper leached based on leached residue assays was done by determining the percentage of copper in the leached residues at any time $t = t$, ($\%Cu_{res}^{t=t}$) and then subtracting from the initial % copper in the starting (feed) sample at time $t = 0$, ($\%Cu_f^{t=0}$) divided by the initial % copper in the feed.

$$\therefore \%Cu = \left(\frac{\%Cu_f^{t=0} - \%Cu_{res}^{t=t}}{\%Cu_f^{t=0}} \right) \times 100 \quad (4.3)$$

Of the two calculation procedures, the one based on the leach residue assays was found to be more consistent and reliable. This procedure was adopted and used in the calculations. Iron dissolution was calculated similarly.

4.3.3 Batch Microbial and Chemical Leaching Experiments

Each experiment was started by first heating the water bath to the desired temperature. In the experiments involving bacteria, a 900 ml modified 9K growth medium was first added to the reactor and brought to be operating temperature in the bath. This was the Silverman and Lundgren basal salts solution without ferrous iron (Equivalent to zero K). Fifty (50) grams of copper sulphide rougher concentrates were then charged into the reactor and pH manually adjusted to the desired value by concentrated (18.4 M) sulphuric acid while redox potential was allowed to evolve freely with time. This constituted a pulp density of about 5% (w/w). After conditioning for about 1 hour the reactor was inoculated with 100 ml (10% v/v) bacterial culture that was obtained from the previous experiment in its late exponential phase. Both microbial and chemical

leaching experiments were conducted in the same reactor type and solution conditions except that for the chemical leaching experiments the bacterial inoculum was replaced with an equivalent volume of sterile growth medium to make up 1 L working volume.

When the pH was higher than the desired value, it was adjusted to this value by acid addition. If pH was lower than desired a free evolution of this valuable was allowed. However, if a constant pH of the solution was needed it was manually controlled by addition of either acid or base.

4.3.3.1 Bacterial Culture, Nutrients and Shake Flask Experiments

A mixed culture of chemolithoautotrophic mesophiles assumed to be predominantly *Acidithiobacillus ferrooxidans*, *Acidithiobacillus caldus*, *Leptospirillum ferriphilum* and *Leptospirillum ferrooxidans* was used in the study. The culture was obtained from a UCT laboratory stock culture previously grown on pyrite/chalcopyrite ore. The bacterial culture was grown in a mineral salt solution of modified 9K growth medium with the composition in the table below. The modified 9K medium was the nutrient solution developed by Silverman and Lundgren (1957) but without ferrous iron (equivalent to zero K). The pH was adjusted to 2.0.

Table 4.4: Modified 9K Growth Medium composition

Basal Salts	Conc., g.L ⁻¹
(NH ₄) ₂ SO ₄	3.00
MgSO ₄ .7H ₂ O	0.50
K ₂ HSO ₄	0.50
KCl	0.10
Ca (NO ₃) ₂ .4H ₂ O	0.013

The Erlenmeyer flasks were used for growth and adaptation of bacteria in rotary shakers using zero K (iron free) medium with the ore as substrate. Both the ore and glassware were sterilised separately by autoclaving at 121°C for 20 minutes. The flasks were then inoculated with the bacterial culture at 10% v/v using aseptic techniques. Substrate (rougher concentrates) dosage was 5% w/w. This was followed by incubating the flasks at 35°C and pH of 1.50 with a shaker speed of 170 rpm. The microbial growth rates were monitored frequently by cell counts. Finally, sequential

sub-culturing of bacteria was done until growth of about 10^9 cells/ml was observed. An inoculum was taken from the flasks for the subsequent batch experiments in stirred tank reactor. For all other experiments that followed, the inoculum was taken from the previous experiment whose microbial growth rates were at the late exponential phase.

4.3.3.2 Oxidative and Non Oxidative (Sterile) Acid Leaching

Following the procedure outlined in Section 4.3.3, the acid consumption and acid leaching tests were conducted to determine acid consumption by oxide copper and gangue minerals. This was approximated by measuring the volume of acid consumed by the ore using a burette, with time. The extent of dissolution of acid soluble copper was assessed through oxidative (with air) and non oxidative (without air) leaching using sulphuric acid. Here, the objective was to determine the role of air (O_2) in the absence of bacteria.

4.3.3.3 Microbial Leaching

The bioleaching experiments were conducted on both fresh rougher concentrate feeds and leach residues from non oxidative acid leach experiments. Details of the procedure are as given in sections above.

Table 4.5: Summary of test work and experimental conditions

Experiment	Experimental solution conditions	Variable
Non Oxidative Acid Leach (Abiotic)	Solids Conc 50 g.L ⁻¹ , Temp 35°C pH 1.50	without bacteria & No air flow
Oxidative Acid Leach (Abiotic)	Solids Conc 50 g.L ⁻¹ , Temp 35°C pH 1.50, air flow @ 400 l.(min) ⁻¹	without bacteria but aerated
Bioleaching Exp ¹ . (Standard conditions)	Solids Conc 50 g.L ⁻¹ , Temp 35°C pH 1.50, air flow @ 400 l.(min) ⁻¹ , 9K growth medium, mesophilic Bacteria	-
Bioleaching Exp. Effect of Leaching parameters:	Solids Conc 50 g.L ⁻¹ , Temp 35°C pH 1.50, air flow @ 400 l/min, 9K growth medium, mesophilic Bacteria	
(a) Ph		pH: 0.70, 1.00 1.50 & 2.00
(b) Temp	"	Temp: 25, 30 35 & 40°C
(c) Particle Size	"	-38 µm, -53 + 38 µm -75 + 53 µm & -106 + 75 µm.
(b) Initial ferric conc.	"	0, 0.0537, 0.1074 & 0.161 moles.L ⁻¹

¹ Mesophilic bacteria were used in all bioleaching experiments.

4.3.3.4 Effect of Leaching Variables

Following the adopted standard test conditions of 35°C, pH 1.50 and 50 g.L⁻¹ solids concentration, the effect of particle size, initial ferric ion concentration, pH and temperature on dissolution kinetics were investigated. The particle size ranges used were -38 µm, -53 + 38 µm, -75 + 53 µm and -106 + 75 µm. The initial ferric (Fe³⁺) ion concentration examined were 0.00 M, 0.0537 M, 0.1074 M and 0.161 M while temperature values were in the range of 26°C, 30°C, 35°C and 40°C. Finally pH values were 0.70, 1.00, 1.50 and 2.00. All the experiments were conducted on fresh rougher concentrate feed without pretreatment.

4.4 Off-Gas Measurements

The online measurement of oxygen and carbon dioxide consumption rates has been shown to be a faster experimental tool to determine bacterial oxidation kinetics (Boon, 1996). This is done by measuring oxygen and carbon dioxide concentration in the off-gas and aeration gas. From carbon dioxide analyses in the off-gas from the reactor and by applying carbon balance, the biomass concentration and growth rate can be determined. The oxygen consumption data are used to determine the specific oxygen consumption rate, which is a measure of bacterial activity.

The biomass concentration is usually determined off-line using cell counts, organic nitrogen, protein analyses or total organic carbon (TOC) (Boon *et al.*, 1998). However, online measurement of oxygen and carbon dioxide consumption rates makes it possible to get more accurate calculations of biomass, substrate and product concentration online from off-gas analyses. The amount of organic carbon is equal to the amount of carbon dioxide consumed from the aeration gas by carrying out carbon balance. Therefore, the amount of bacterial matter is expressed in moles of organic carbon while the concentration of bacteria in C-mole.L⁻¹. Finally, the mineral oxidation rate can be calculated from the oxygen and carbon dioxide consumption rate using the degree of reduction balance.

4.4.1 Determination of Carbon Dioxide and Oxygen Consumption rates

The oxygen and carbon dioxide utilisation rates in the bioreactor were calculated by taking the difference between the inlet and outlet gas concentrations (expressed as mass fractions, x) and flow rates, correcting for the change in the flow rates due to oxygen and carbon dioxide consumption (Boon *et al.*, 1996). A constant inlet air flow rate from the mass flow controller was fed to the reactor. The off-gas or exit air was then passed through the condenser, through to the sampling manifold. The sampling manifold consists of solenoid valves that are controlled by a microcomputer. This allows air from several reactors to be sampled including the inlet air. The off-gas is dried again by a water impermeable membrane before finally going to the off-gas analyser. Oxygen concentration in the gas was measured with a paramagnetic analyser while carbon dioxide with infrared analyser.

For accurate measurements of oxygen and carbon dioxide, oxygen is calibrated to read 19-21% range and carbon dioxide detector is set to measure 0-500 ppm. The measured oxygen and carbon dioxide concentrations in the off-gas and inlet streams are logged and stored in a microcomputer from which rates of consumption are calculated.

Taking ϕ as the total molar flow rate, the total inlet, ϕ_{in} and outlet, ϕ_{out} molar flow rates are defined as the sum total of nitrogen ϕ_{N_2} , oxygen ϕ_{O_2} , and carbon dioxide ϕ_{CO_2} , inlet and outlet flow rates respectively. The mass balances using N_2 as a tie substance are determined as follows (Boon *et al.*, 1996);

$$\phi_{in} = \phi_{N_2}^{in} + \phi_{O_2}^{in} + \phi_{CO_2}^{in} = \left\{ (1 - X_{O_2}^{in} - X_{CO_2}^{in}) + X_{O_2}^{in} + X_{CO_2}^{in} \right\} \phi_{in} \quad (4.4)$$

Molar flow rates of unreacting nitrogen and other species are constants:

$$\phi_{N_2} = \phi_{N_2}^{in} = \phi_{N_2}^{out} \quad (4.5)$$

Thus the total molar flow rate out of the reactor is;

$$\phi_{out} = \phi_{N_2} + \phi_{O_2}^{out} + \phi_{CO_2}^{out} = (1 - X_{O_2}^{in} - X_{CO_2}^{in}) \phi_{in} + X_{O_2}^{out} \phi_{out} + X_{CO_2}^{out} \phi_{out} \quad (4.6)$$

$$\therefore \phi_{out} = \frac{(1 - X_{O_2}^{in} - X_{CO_2}^{in})}{(1 - X_{O_2}^{out} - X_{CO_2}^{out})} \phi_{in} \quad (4.7)$$

Carrying out mole balances on both O₂ and CO₂ give the following rate equations:

$$-r_{O_2} = \frac{\phi_{in}}{V} \left\{ X_{O_2}^{in} - X_{O_2}^{out} \frac{(1 - X_{O_2}^{in} - X_{CO_2}^{in})}{(1 - X_{O_2}^{out} - X_{CO_2}^{out})} \right\} \quad (4.8)$$

$$-r_{CO_2} = \frac{\phi_{in}}{V} \left\{ X_{CO_2}^{in} - X_{CO_2}^{out} \frac{(1 - X_{O_2}^{in} - X_{CO_2}^{in})}{(1 - X_{O_2}^{out} - X_{CO_2}^{out})} \right\} \quad (4.9)$$

4.4.2 Biomass Concentration in Batch Cultures

The measurement of carbon dioxide uptake is a convenient tool to determine the increase in carbon content of cells hence microbial growth rate. The technique was successfully applied to measure bacterial growth rate in pyrite bioleaching and microbial ferrous oxidation in both batch and continuous cultures (Boon, 1996). According to Boon (1996), the biomass concentration calculated from carbon dioxide consumption rates agreed with the measured concentration using total organic carbon (TOC) analysis in a batch microbial leaching of pyrite with mesophiles.

The growth of bacteria, assumed to have a stoichiometric formula CH_{1.8}O_{0.5}N_{0.2} (Roels, 1983), use CO₂ and NH₄⁺ as sole carbon and nitrogen sources respectively.

$$\text{i.e. } CO_2, NH_4^+, H_2O = CH_{1.8}O_{0.5}N_{0.2} \quad (4.10)$$

By carrying out carbon balance, the rate of bacterial growth, r_x , is equal to the rate of carbon dioxide utilisation rate, $r_x = -r_{CO_2}$. Therefore, the biomass concentration in a batch culture at time t can be derived from the integration of the measured carbon dioxide consumption rate (Boon *et al.*, 1994).

$$C_{x,CO_2}(t) = C_x(0) + \int_0^t -r_{CO_2} dt \quad (4.11)$$

$C_x(0)$ has to be known from previous experiments.

The equation above can be rewritten as

$$C_{X,CO_2}(t) = C_X(0) + \sum_{t_i=0}^{t_{i+1}=t} \frac{r_{CO_2}(t_i) + r_{CO_2}(t_{i+1})}{2} * (t_{i+1} - t_i) \quad (4.12)$$

$$\Rightarrow C_{X,CO_2}(t) = C_X(0) + \sum \frac{r_{CO_2} \cdot \Delta t}{2} \quad (4.13)$$

In the equations above, $t_{i+1} - t_i$ is the time interval between two successive CO_2 analyses that gives carbon dioxide consumption rates $r_{CO_2}(t_i)$ and $r_{CO_2}(t_{i+1})$. Therefore biomass concentration is a summation of carbon dioxide absorbed from the air.

4.5 Redox Probe Calibration

The concentrations of ferrous and ferric ions in solution were also determined from values of redox potential and total iron concentration using the Nernst equation:

$$E = E_o + \frac{RT}{nF} \ln \left[\frac{Fe^{3+}}{Fe^{2+}} \right] \quad (4.14)$$

$$\text{Hence } \left[\frac{Fe^{3+}}{Fe^{2+}} \right] = \exp \left(\frac{E - E_o}{\frac{RT}{nF}} \right) \quad (4.15)$$

The ratio of the free ferric to free ferrous iron in iron solutions is related to the measured solution potential through the Nernst equation as shown above. However, the Nernst equation relates the solution potential to the free ferric and ferrous iron activities with ideal values of E_o and RT / nF . Hence, the redox probe must be calibrated for the desired experimental conditions in order to obtain these coefficients, E_o and RT / nF in the Nernst equation.

The solutions of ferric and ferrous sulphate with different concentrations were prepared and initial pH adjusted to 1.50 with sulphuric acid. The different ratios of ferric and ferrous iron ranged from 1 to 1000. Aliquots of ferrous sulphate solution were added to a constant volume of ferric sulphate solution, and the redox potential was then measured at each addition. The potential was finally plotted against $\ln (Fe^{3+}/Fe^{2+})$ which gave a straight line, from which the slope was RT / nF and the

intercept represented the potential of Fe^{3+}/Fe^{2+} couple with reference to the Pt-Ag / AgCl electrode. Calibration curve equation for system at 35°C and pH of 1.50 was

$$E = 26.405 \ln \left[\frac{Fe^{3+}}{Fe^{2+}} \right] + 473.33 \quad (4.16)$$

At each redox potential value and total iron concentration, values of ferrous and ferric ion concentrations were calculated using the equations below;

$$[Fe^{2+}] = \frac{[Fe]^{tot}}{1 + \left[\frac{Fe^{3+}}{Fe^{2+}} \right]} \quad (4.17)$$

$$[Fe^{3+}] = \frac{[Fe]^{tot} \left[\frac{Fe^{3+}}{Fe^{2+}} \right]}{1 + \left[\frac{Fe^{3+}}{Fe^{2+}} \right]} \quad (4.18)$$

Chapter 5

Results and Discussion

5.1 Introduction

This chapter presents a discussion of results for the dissolution of a mixed copper oxide/sulphide rougher concentrate from Nchanga Mine of the Zambian Copperbelt. The bacterial growth kinetics and their effect on the mineral dissolution under different experimental and solution conditions are also discussed. The details of the experimental procedure are given in Chapter 4.

The ore was initially subjected to testing for acid consumption followed by chemical and bio leaching experiments at standardised conditions. The progress of leaching was monitored through measurements of Cu^{2+} , Fe (total), pH, redox potential and the ferrous (Fe^{2+}) and ferric (Fe^{3+}) iron concentrations. The activity of bacteria was monitored by online measurements of carbon dioxide and oxygen consumption rates using the off-gas analyser. From the off-gas data it was possible to determine growth rates and biomass concentration expressed as mmole C.L^{-1} . The specific growth rates and specific oxygen utilisation rates were subsequently computed from values of off-gas consumption rates and biomass concentration which is a measure of bacterial activity. As demonstrated by Boon (1996), these parameters are critical in sulphide mineral oxidation involving bacteria.

The chemical oxidation experiments with dilute sulphuric acid but without bacteria were done in the presence and absence of air (oxygen). The extent of dissolution of acid soluble copper was assessed through oxidation (with air) and non-oxidative (without air) leaching using dilute sulphuric acid. The objective was to establish the effect of aeration and the thermodynamic influence on the dissolution of oxides and sulphides of copper in the absence of bacteria.

The bioleaching experiments followed two routes. The first set of experiments was the direct bioleaching of fresh (without pre-treatment) rougher concentrates. The second set of bioleaching experiments were carried out on the leach residue material that was obtained from the sterile non oxidative (without air) acid leaching experiments. The effects of particle size, initial ferric ion concentration, pH and

temperature on the dissolution kinetics were then investigated by conducting bioleaching experiments on fresh or untreated rougher concentrates. These parameters have been identified as some of the major factors that affect leaching efficiencies and extraction rates.

5.2 Acid Consumption

The acid consumption test was designed to approximate the acid requirement of the ore at the desired pH value and also to infer the extent of acid soluble copper, and slow leaching oxide/sulphide copper minerals. Copper oxides as well as silicates and carbonate gangue minerals consume sulphuric acid during initial reaction with acid. They are broken down to a variety of soluble solution products (Jansen and Taylor, 1998).

The solution/slurry pH was observed to rise upon addition of the ore. The decrease in acidity was due to the chemical solubilisation of mainly copper oxides and the consumption of acid by carbonate gangue minerals as the subsequent sections will show. These minerals if present in any ore are considered as highly acid consuming ones (Murr, 1980). Thus, the acid test is critical to provide quantitative acid requirement of the ore. However, sulphides have very low solubility products in water or acid and are practically insoluble under these conditions (Dresher, 2004; Rossi, 1990).

The variation of cumulative acid consumption rate with time and amount of copper solubilised are given in Figures 5.1(a) and (b) for both abiotic acid leaching and bioleaching experiments at 50 g.L⁻¹ solids concentration, pH of 1.50 and a temperature of 35°C. The cumulative acid consumption was calculated on the basis of volume of sulphuric acid added for pH adjustment.

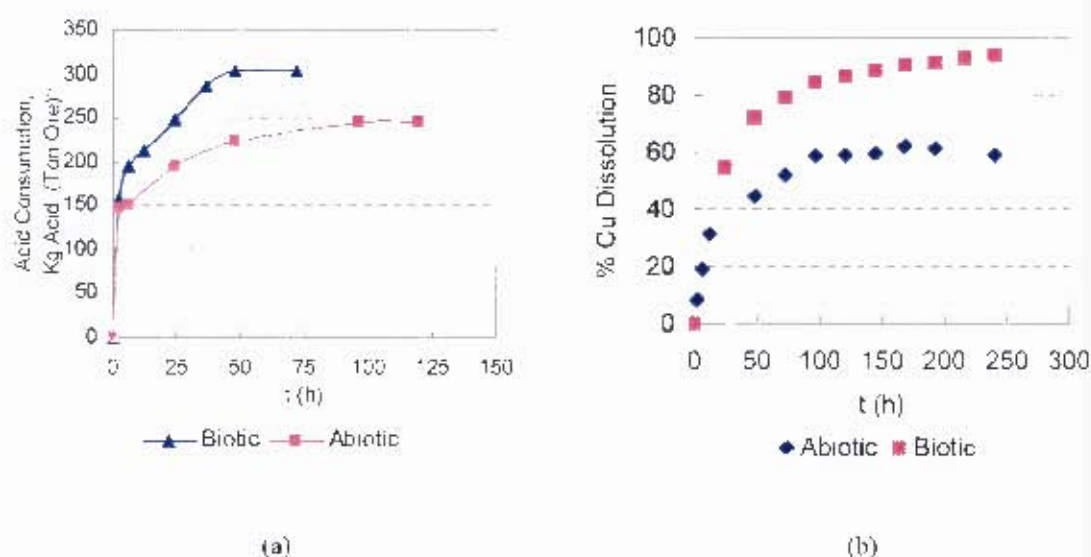
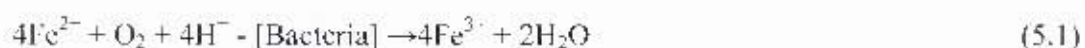


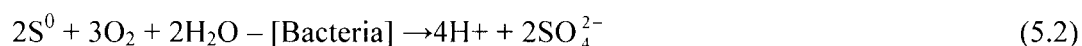
Figure 5.1: (a) Acid consumption rates and (b) copper solubilised plotted with time for both abiotic oxidative acid leaching and bioleaching experiments.

The initial acid consumption rate was rapid at about 150 kg acid per ton of concentrate after about two hours for both oxidative acid leaching and bioleaching experiments. The acid demand therefore was 150-300 and 150-240 kg of sulphuric acid per ton of concentrate for bioleaching and sterile oxidative acid leaching experiments respectively. Similar rates of acid consumption have been reported for predominantly copper oxide leaching (Bustos *et al.*, 2004). Thereafter, the amount of acid consumed increased quite rapidly with time during bio leaching relative to the acid leaching experiment. This trend continued for up to two days during which bacterial activity was highest (Section 5.2). The explanation for this observation might be that during bioleaching, the microbial ferrous iron oxidation sub-process consumes acid in addition to the oxides and carbonates of copper as well as other carbonaceous gangue minerals. The reaction for the microbial oxidation of ferrous iron is shown below.



As bioleaching progressed the system acid demand decreased significantly up until the solution acidity was observed to decrease after about 5 days (Section 5.2). This is due to probably the microbial pyrite or sulphur oxidation sub-processes which supplies acid through oxidation of any elemental sulphur or other reduced sulphur compounds present in the system (Schipper and Sand, 1999). These are products of

metal sulphide oxidation by ferric ions as the next sections will elucidate. The oxidation of sulphur by bacteria is given as follows:



The high acid consumption rates resulted in highest copper solubilised in the bioleaching experiments (Figure 5.1(b)). Over 90% of copper was solubilised during bioleaching compared to 58% copper leached in the oxidative acid leaching experiment. Thus, in the presence of bacteria the rate of sulphide oxidation is enhanced (Rossi, 1990).

It can be concluded that the acid consumption was approximately 150 kg per ton of concentrate at 5% w/w solids. The bioleaching system continued to consume acid at a much slower rate probably due to slow acid consuming silicate minerals (Jansen and Taylor, 1998). Therefore, the solution must be supplemented with additional acid to sustain the solubilisation reactions.

5.3 Abiotic Chemical Oxidation in Sulphuric Acid Medium

5.3.1 Oxidative and Non-Oxidative Acid Leaching

The objective of the oxidative and non-oxidative sterile acid leach tests was to determine the extent to which acid soluble copper can be solubilised in the presence and absence of air (oxygen). The data trends for the amount of copper leached is shown in Figure 5.2. It is expected that copper oxides and carbonates, silicates and other gangue minerals rapidly consume acid during the initial reaction to give different soluble solution products (Jansen and Taylor, 1998). These tests further served as control experiments for the subsequent microbial leaching and were an indication of the slow leaching copper oxide-sulphide minerals.

The dissolution profile of mixed oxide-sulphide copper ore in dilute sulphuric acid medium exhibited in Figure 5.2 above can be explained by considering Pourbaix (Eh-pH) diagram in Figure 5.3.

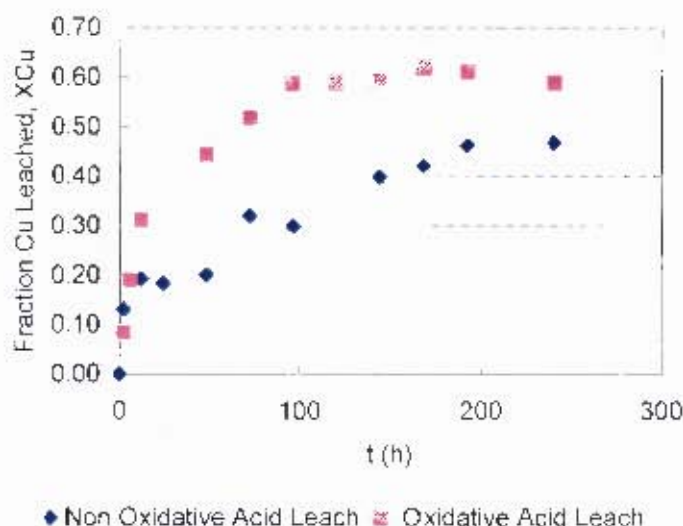
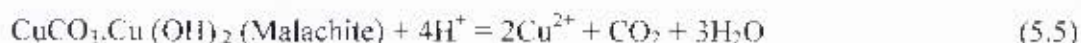
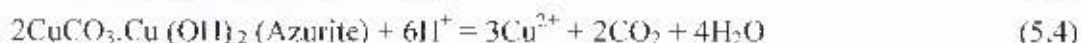
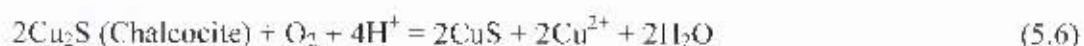


Figure 5.2: Amount of copper leached plotted with time at pH 1.50, temp., 35°C and 50 g.L⁻¹ solids.

The non-oxidative acid leaching solubilised only about 20% copper in the first 50 hours of leaching. This might correspond to complete dissolution of CuO and copper carbonates as these are easily leached in dilute sulphuric acid medium, and about half of Cu₂O (Nyirenda, 2000). These oxides and carbonates of copper minerals in the feed are chemically dissolved in acids by the following reactions;



The introduction of air (O₂) leads to complete dissolution of Cu₂O in addition to CuO. From Figure 5.2 about 45% copper was now solubilised after 50 hours from the oxidative acid leach experiment. In this case chalcocite may also be partially oxidised (Olson *et al.*, 2003) i.e. releasing part of the copper. Most other copper sulphides present are relatively unaffected under these conditions (Drescher, 2004).



CuO (tenorite) is chemically leached by protons without electrons transfer as shown in the Eh-pH diagram. The reaction depends on pH but not necessarily redox potential of the solution. Thus, dissolution of CuO (tenorite) in acids is neither a reduction nor oxidation.

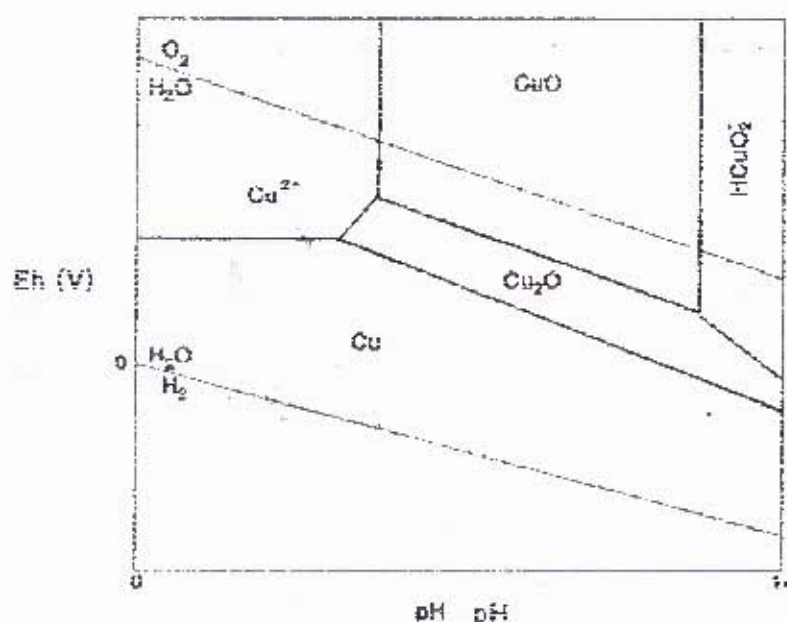
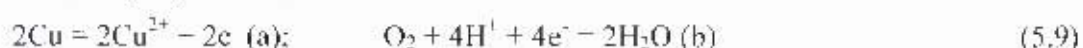


Figure 5.3 Eh-pH Diagram for Cu-H₂O System at 25°C (Nyirenda, 2000)

The complete Cu₂O (cuprite) dissolution to yield Cu²⁺ involves both H⁺ (protons) cations and solution redox potential in a two-stage reaction mechanism. The necessary reactions are:



Reaction (5.8) is a summation of two half cell reactions:



In reaction (5.7) cuprite theoretically solubilises only half of the copper while the other half is converted into metallic copper which subsequently undergoes dissolution in the presence of oxygen as shown in reaction (5.8). This means that in the absence of air (O₂) or any other oxidant native (metallic) copper is unaffected in acids since an electron acceptor or cathodic reaction would not be available to absorb electrons released from any copper dissolution. Thus, without air (O₂) the leachability of copper from cuprite is about half (Nyirenda, 2000).

Thus, the leachability of rougher concentrate under abiotic acid leaching conditions is at best 58% copper dissolution after about 100 hours of leaching. This seemingly high dissolution is mainly drawn from oxides and carbonates of copper. The dissolution of

chalcocite is significant under these conditions, though probably much slower and inefficient.

5.4 Microbial Mineral Oxidation

The kinetics of the oxidation process is vastly improved after the introduction of iron and sulphur oxidising bacteria to the system as shown in Figure 5.4. The initial rate of leaching for the bacterial reaction is very rapid, leaching out over 50% of the initial copper in less than 24 hours. Thus, the overall copper dissolution substantially increased in the presence of bacteria reaching about 90% in 6 days compared to 58% in abiotic chemical oxidation experiments (Figure 5.2). This might be chemical dissolution of copper oxides and probably first stage chalcocite leaching and to a lesser extent other sulphides by ferric ions, resulting in the reduction of iron (III) to iron (II). Since the solution potential of the system is fixed by the ferric/ ferrous concentration ratio the resultant is a low solution potential due to high concentration of ferrous iron in solution.

The results for bioleaching of a pre-treated rougher concentrate through a non-oxidative acid leach are shown in Figure 5.4 (b). Most of the acid soluble oxide and carbonates of copper are assumed to have been removed with the resulting residue assumed to be predominantly chalcocite with minor chalcopyrite and other slow leaching minerals copper oxides. As expected the dissolution rate is much slower when compared to that of untreated ore (Figure 5.4(a)) in the early stages, though eventually giving over 93% in both cases. The consequence for these trends is that bioleaching of untreated ore may be preferable because of the faster kinetics.

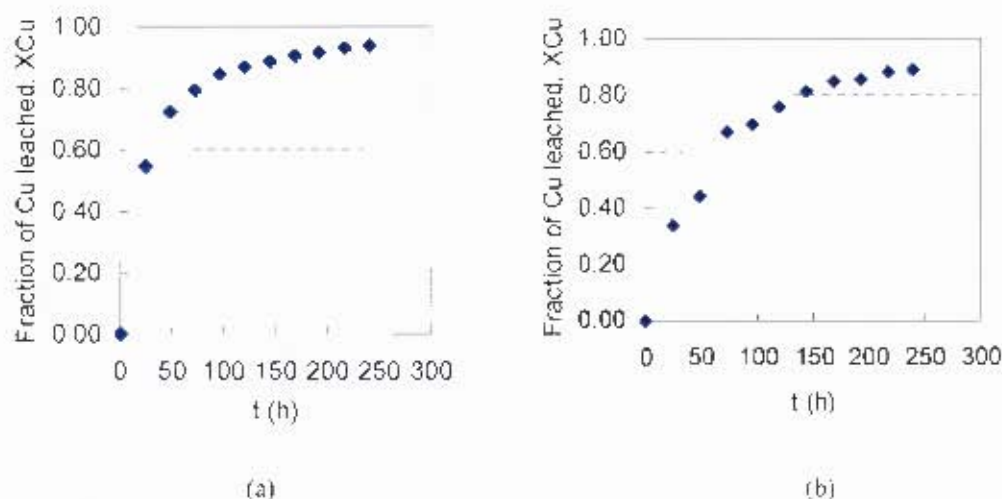
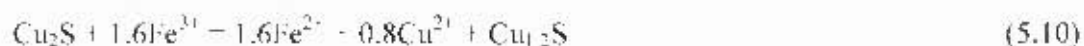


Figure 5.4 Amount of copper solubilised for bioleaching (a) untreated (fresh) rougher concentrate feed and (b) leach residues from non-oxidative acid leach experiment at 35°C, pH 1.50 and 50 g.L⁻¹ solids concentration.

In the first stage leaching of chalcocite the rate of mineral oxidation has been reported to occur much faster than the bacterial ferrous iron oxidation rate (Dutrizac and MacDonald, 1974; Bolorunduro, 1990; Petersen and Dixon, 2003). Work done by Bolorunduro (1990) reported 40% chalcocite dissolution within an hour at the first stage in acid-ferric solutions at a fixed redox potential of 525 mV. However, a slightly lower recovery was obtained for a freely changing redox potential of the solution. The proposed reaction mechanism for first stage leaching of chalcocite occurs through the reactions shown below. According to Bolorunduro (1990), the first stage produces non-stoichiometric pseudo-covellite (or blaubleibender, CuS) which reacts further to produce elemental sulphur, copper and iron ions in solution. At the same time ferrous iron is oxidised to ferric form. Thus, the bacterial ferrous oxidation rate governs or regenerates the concentration of ferric iron in solution:

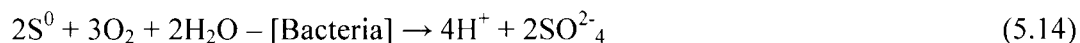
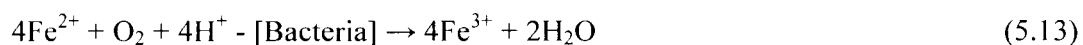
First Stage Oxidation of Chalcocite:



As the first stage leaching proceeds the dissolution rate falls off corresponding to the onset of second stage chalcocite or pseudo-covellite dissolution. At this stage all the copper sulphides present in minor amounts including pyrite are possibly leached to varying degrees. The second stage leaching of chalcocite proceeds much more slowly

relative to the first stage (Dutrizac and MacDonald, 1974; Bolorunduro, 1990; Petersen and Dixon, 2003), in this case producing about 90% copper in 6 days. The reactions involving other copper sulphides are relatively slow as well. The second stage leaching reactions for chalcocite (Petersen and Dixon, 2003) are as follows;

Second Stage Oxidation of Chalcocite:



The bacterial lag phase was taken to happen at the same time with the time of low redox potential. The initial phase of increasing redox potential was probably because of relatively fast reduction of ferric iron by chalcocite during the first stage leaching. This is followed by concurrent oxidation of ferrous iron as reflected in the increase of redox potential. This might be the explanation for rapid increase in solution potential as shown in Figure 5.5(a). However, the rate of mineral ferric consumption at the second stage is now much lower and solution redox potential attains high values (see Figure 5.5(a)). Redox potentials are reflected by changes in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of dissolved iron in the leach slurry, reaching values of > 690 mV (vs. Ag/AgCl) as shown in Figure 5.5(b). The bacterial ferrous oxidation reaction is probably limited by low ferrous iron concentration in solution as depicted in Figure 5.5(a) & (b).

The other copper sulphides are leached according to the reactions shown in Chapter 3. Competition for ferric iron is possible among these minerals. Dew *et al.* (1999) have reported the preferential order of mineral bioleaching with mesophile bacterial culture as;



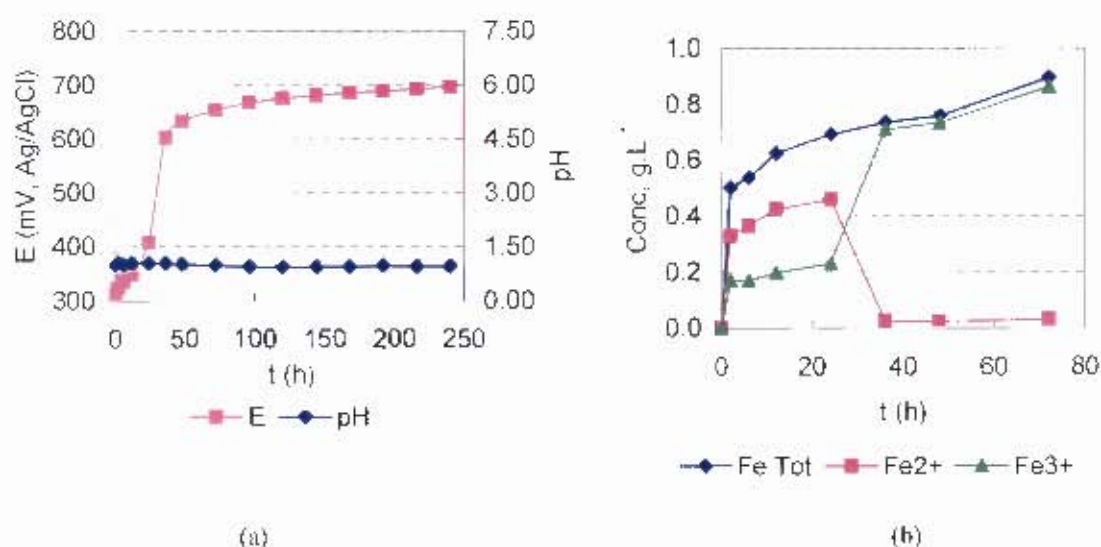


Figure 5.5: (a) Variation of solution redox potential with time and (b) soluble iron speciation during bioleaching at 35°C, pH of 1.50 and 50 g.L⁻¹ solids loading

On the basis of the above preferential order of mineral bioleaching series proposed by Dew *et al.* (1999), the residual copper might be attributed to chalcopyrite due to the refractory nature of the mineral with mesophilic bacterial leaching (Dew *et al.*, 1999). However, pyrite and to some extent chalcopyrite dissolution occurs after considerable dissolution of secondary copper sulphide minerals and at high redox potential (May, 1997) as shown in Figure 5.6 below. It is likely that the dissolution of pyrite starts to occur after about 75 hours when the solution redox potential was above 550 mV (vs. Ag/AgCl) through observed measurements of total soluble iron (Figure 5.6).

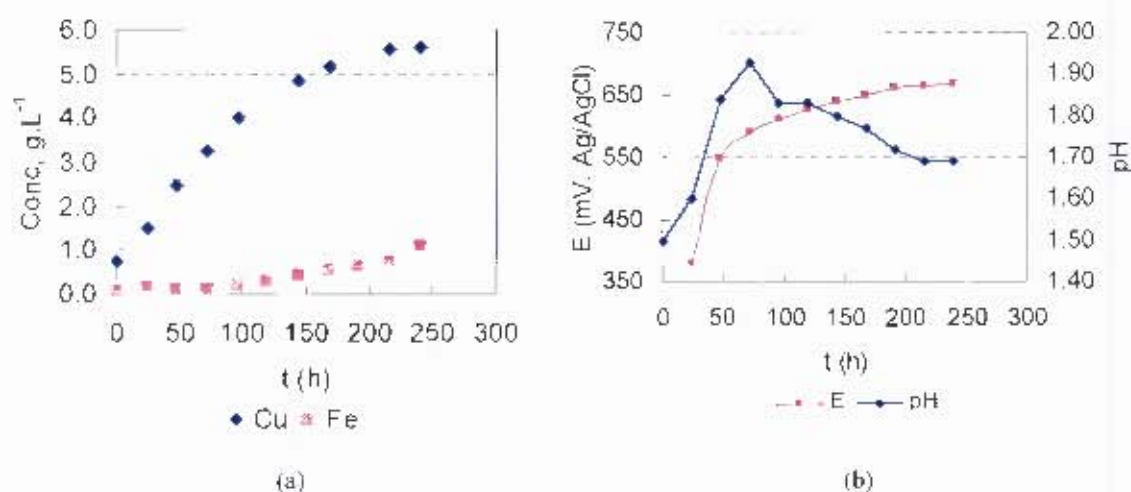
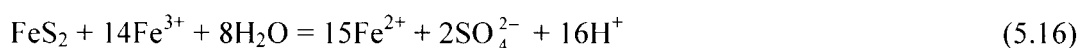


Figure 5.6: Variation of (a) copper and iron concentrations, and (b) pH and redox potential for bioleaching of residue from non-oxidative acid leach experiments.

The mineral and bacterial ferrous oxidation reactions consume acid as observed in the early stages of the experiments where acid was added to the system. However, the bacterial activity was then assessed by determining the acid producing capacity by subjecting the residue from non oxidative acid leach to bioleaching. The pH was initially fixed at 1.50 and then allowed to evolve freely. The evolution of solution pH given in Figure 5.6(b) indicated bacterial activity after 3 days with the generation of protons. This means that sulphur oxidising bacteria were able to oxidise sulphur or any sulphur compound in solution to generate acid, resulting in the lowering of pH. The redox potential evolution was rapid in the first 3 days but later stabilised. The bioleaching system did not initially generate acid because pyrite which can produce acid leaches slowly at such low redox potentials (May, 1997). Also, the first stage leaching of chalcocite does not produce elemental sulphur which when present can be oxidised by sulphur oxidising bacteria to generate acid as shown below.



The experimental data in Figure 5.4(a) was compared to earlier work done by Dutrizac and MacDonald (1974) and Bolorunduro (1990) after normalising the time scales to hours and the percent dissolution to fraction leached. Bolorunduro (1990) leached a narrowly sized chalcocite ore ($-250 + 212 \mu\text{m}$) at 35°C , 0.5% w/w pulp density at an initial ferric iron concentration of $0.0172 \text{ mol.L}^{-1}$ with mesophilic bacteria. The work of Dutrizac and MacDonald (1974) was the ferric leaching of chalcocite ore at 35°C .

The present data compares well with that of Dutrizac and MacDonald (1974) and Bolorunduro (1990) as shown in Figure 5.4. However, the leaching rate for data from Dutrizac and MacDonald (1974) was slightly slower between 50-200 hours though the maximum amount of copper solubilised was nearly the same in all cases. Rivera-Santillan *et al.* (1999) conducted shake flask experiments to leach copper sulphide concentrate of mainly chalcopyrite with secondary copper sulphides with mesophiles. They reported dissolution of 85% copper over an extended period of leaching. (Dew *et al.*, 1999) obtained similar results under continuous bioleaching conditions in stirred tank reactors.

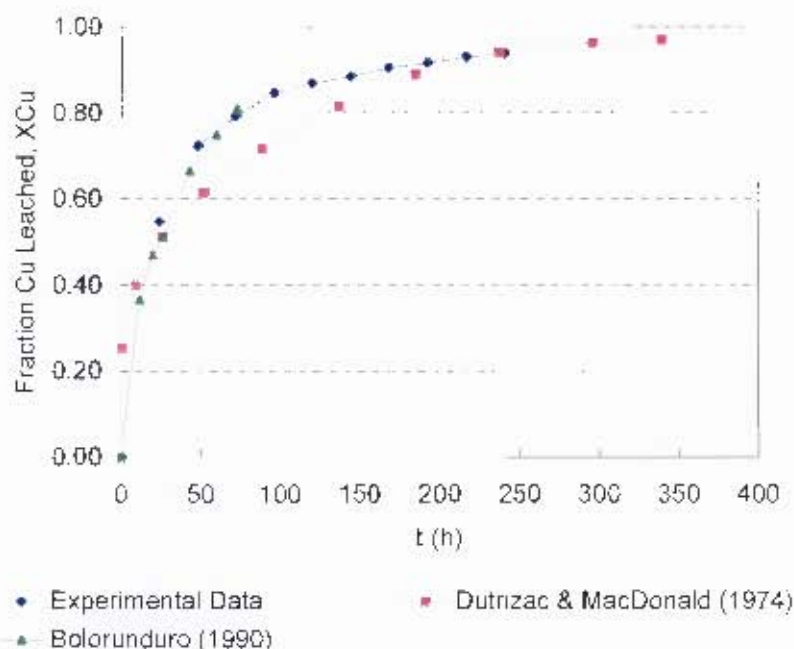


Figure 5.7: Comparison of literature data with experimental values.

5.5 Microbial Growth and Kinetics

The quantitative determination of biomass concentration is usually done by such methods as cell counts, organic nitrogen, protein analyses or total organic carbon (TOC). In this investigation the online measurement of O_2 and CO_2 consumption rates was applied to determine the microbial growth and their kinetics. This method however, has been shown to be a faster experimental tool to determine the bacterial oxidation kinetics (Boon, 1996). The measurement of CO_2 uptake is thus a convenient tool to determine the increase in carbon content of cells from which the microbial growth rate is easily computed. The technique was successfully applied to measure the bacterial growth rates in the bioleaching of pyrite and in the microbial ferrous iron oxidation in both batch and continuous cultures (Boon, 1996).

The growth of chemolithoautotrophic bacteria uses CO_2 from the air and NH_4^+ in solution as the sole carbon and nitrogen sources respectively. The amount of organic carbon is then equal to the amount of CO_2 consumed from the aeration gas by carrying out carbon balance. Therefore, the amount of bacterial matter is expressed in moles of organic carbon while the concentration of bacteria in $mmole\ C.L^{-1}$.

The bacterium cell's stoichiometric formula has been determined as $\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.2}$ (Roels, 1983). The unbalanced equation for bacterial growth using organic carbon and nitrogen is:



The CO_2 consumption rate is then used to determine the biomass concentration and biomass growth rates while data for O_2 consumption are used to calculate the specific oxygen utilisation rate. This gives a measure of bacterial activity. Thus, the rate of bacterial growth, r_x expressed in $\text{C-mole.L}^{-1}.\text{h}^{-1}$ is equal to the rate of carbon dioxide utilisation rate, r_{CO_2} , i.e. $r_x = r_{\text{CO}_2}$. The biomass concentration, C_x expressed in C-mole.L^{-1} for a batch culture at time t was calculated from the integration of the measured carbon dioxide uptake data (Boon, 1996) as follows;

$$C_{x,\text{CO}_2}(t) = C_x(0) + \int_0^t -r_{\text{CO}_2} dt \quad (5.19)$$

$C_x(0)$ has to be known from previous experiments.

The equation above can be rewritten as

$$C_{x,\text{CO}_2}(t) = C_x(0) + \sum_{t_i=0}^{t_{i+1}=t} \frac{r_{\text{CO}_2}(t_i) + r_{\text{CO}_2}(t_{i+1})}{2} * (t_{i+1} - t_i) \quad (5.20)$$

$$\Rightarrow C_{x,\text{CO}_2}(t) = C_x(0) + \sum \frac{r_{\text{CO}_2} \cdot \Delta t}{2} \quad (5.21)$$

In the equations above, $t_{i+1} - t_i$ is the time interval between two successive CO_2 analyses that gives CO_2 consumption rates $r_{\text{CO}_2}(t_i)$ and $r_{\text{CO}_2}(t_{i+1})$. Therefore biomass concentration is a summation of CO_2 absorbed from the air.

5.5.1 Microbial Carbon dioxide and Oxygen Uptake

The measured oxygen and carbon dioxide consumption rates and the biomass concentration as calculated from the off-gas data are plotted against time in Figure 5.8. The plot shows a steep exponential increase of gas consumption rates after about 6 hours (lag phase) before the bacteria could start consuming O_2 and CO_2 which are essential for growth. The lag phase was observed to depend on the growth phase of the inoculum. The maximum consumption rates of oxygen and carbon dioxide reached after 24 hours were about $2.00 \text{ mmol.l}^{-1}.\text{h}^{-1}$ and $0.131 \text{ mmol.l}^{-1}.\text{h}^{-1}$

respectively and then there was a gradual drop in the final phase. The off-gas data in the first 6 hours were ignored since this is the lag phase of the bacteria. The increase in oxygen and carbon dioxide consumption rates is mainly caused by the increase of biomass concentration (Boon *et al.*, 1998). During the final phase of the experiment the decrease in carbon dioxide uptake by bacteria is faster than that of oxygen. Boon *et al.* (1998) observed similar trends for microbial ferrous oxidation in batch experiments and proposed that this effect may be due to the maintenance requirement of bacteria.

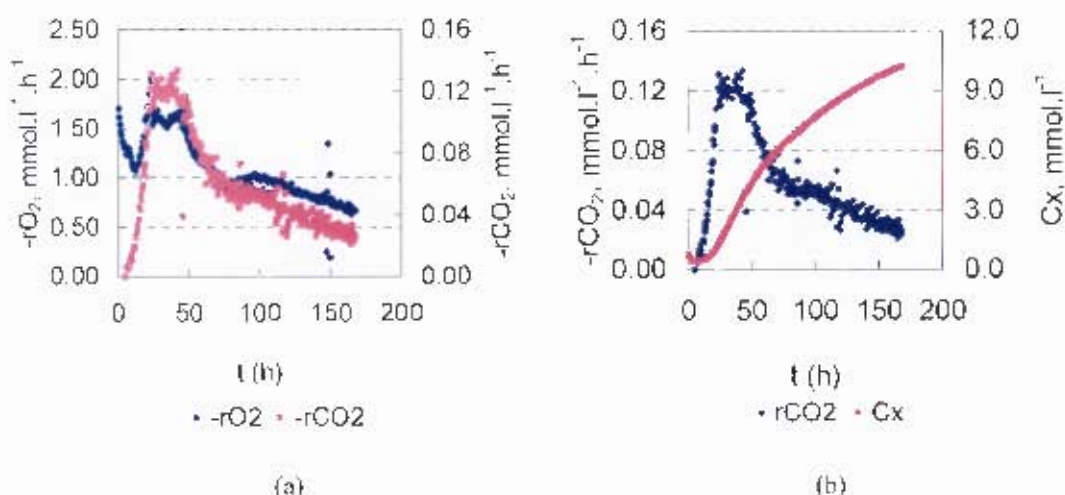


Figure 5.8 Variation of (a) carbon dioxide and oxygen utilisation rates and (b) biomass concentration plotted against time at 35°C, pH 1.50 and 50 g.L⁻¹ solids concentration.

The concentration of biomass as calculated from the carbon dioxide consumption rate is plotted against time in Figure 5.8(b), together with the carbon dioxide utilisation rate data from the off-gas analyser for the entire experiment. In this case, the total amount of carbon dioxide consumed per litre is the total amount of biomass produced which is just the total surface area under the r_{CO_2} graph between time $t = 0$ and time $t = t$. The biomass concentration, Cx is then determined according to the expressions given earlier in this section.

In the exponential growth phase, the increase in biomass concentration was significantly faster during the first 24 hours as shown in Figure 5.8(b). This is expected since the carbon dioxide uptake required for growth was increasingly high in the same period. Finally, the concentration of bacteria was maximum in the last phase at about 10.0 C-mmol.L⁻¹ during which there was negligible rate of growth other

than bacterial maintenance terms. As the concentration of bacteria is high, further growth may be substrate limited and therefore more substrate and oxygen may be required for maintenance of bacteria and indeed less energy is available for growth (Boon *et al.*, 1998)

The consequence for Nchanga copper sulphide ore, on the basis of observed microbial growth and activity is that the material is suitable for microbial oxidation as probably suitable substrates are released into solution leading to the dissolution of the ore. Refer to Section 5.3 of the present chapter for a full discussion of metal and/or copper solubilised.

Figure 5.9 below shows the biomass specific growth rate, $\mu = r_{CO_2}/C_x$ and biomass specific oxygen consumption rate, $q_{O_2} = r_{O_2}/C_x$ both plotted against time, as calculated from the measured oxygen and carbon dioxide off-gas data, $r_{O_2}(t)$ and $r_{CO_2}(t)$ as well as the biomass concentration, $C_x(t)$. It is expected that in the initial phase of the experiment, maximum specific utilisation rates, $q_{O_2}^{\max}$ and $\mu^{\max}$ occur since substrate concentration (mainly ferrous iron) is high while the ferric iron is low. From the Figure 5.9, the specific oxygen consumption rate q_{O_2} was high in the initial phase when ferrous iron (substrate) concentration was also high. During this phase, ferric iron concentration which has been found to inhibit microbial growth was low. The maximum specific oxygen utilisation rate, $q_{O_2}^{\max}$ was about 3.00 (mmole O₂). (C-mmole)⁻¹.h⁻¹ after about 12 hours and then decreased at decreasing ferrous iron and increasing ferric iron concentration (see Section 5.3).

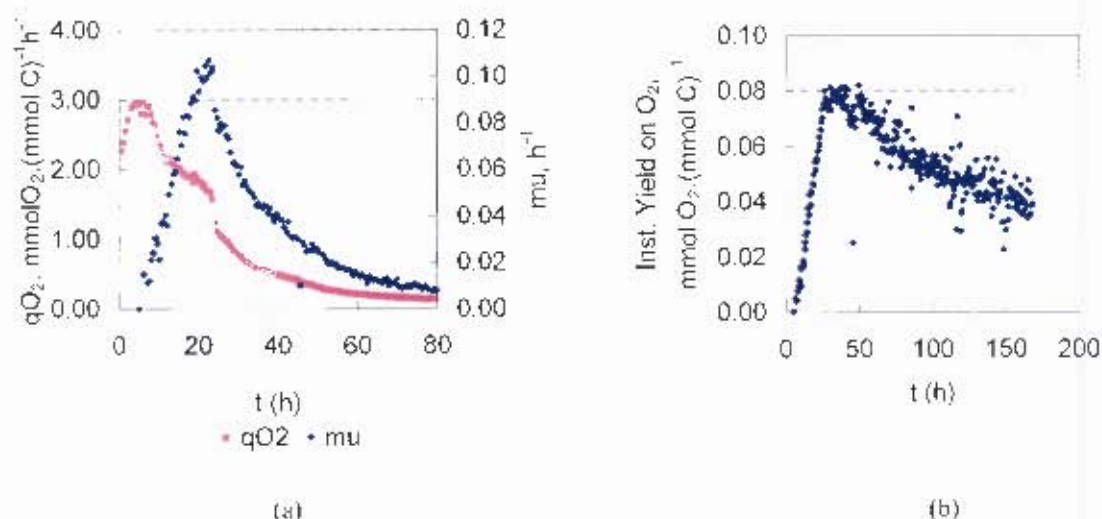


Figure 5.9: (a) Biomass specific growth rate, μ and specific oxygen consumption rate, q_{O_2} plotted against time and (b) biomass yield based on oxygen also plotted with time.

By referring to Figure 5.9(a), the specific growth rate, μ quickly increased in a nearly linear manner to $\mu^{\max}$ of about $0.1 \text{ (mmol CO}_2\text{)} \cdot (\text{C} \cdot \text{mmol})^{-1} \cdot \text{h}^{-1}$ after 24 hours and thereafter decreased towards the end of the experiment.

The calculated biomass yield based on oxygen, Y_{O_2} is plotted against time in Figure 5.9(b). The trend for biomass yield showed an increase with time up to about 24 hours, giving maximum yield of about $0.08 \text{ mmol C} \cdot (\text{mmol O}_2)^{-1}$. This was followed by a gradual decrease in yield probably due to the reduced uptake of carbon dioxide by bacteria as shown in to Figure 5.8(a).

Figure 5.10(a) below shows that an increase in redox potential decreases the rate of oxygen consumption ($q_{O_2} = r_{O_2}/C_c$). This might mean that the rate of substrate oxidation (probably ferrous iron and sulphur and / or reduced sulphur compounds) is reduced as the redox potential increases. Another possible explanation might be that microbial growth is limited by less available substrate in solution. The biomass specific growth rate increased at low redox potentials before becoming constant, and then showed a steep decrease at high redox potential values. Again, this can be attributed to changing concentration of both the substrate and biomass in the entire experiment.

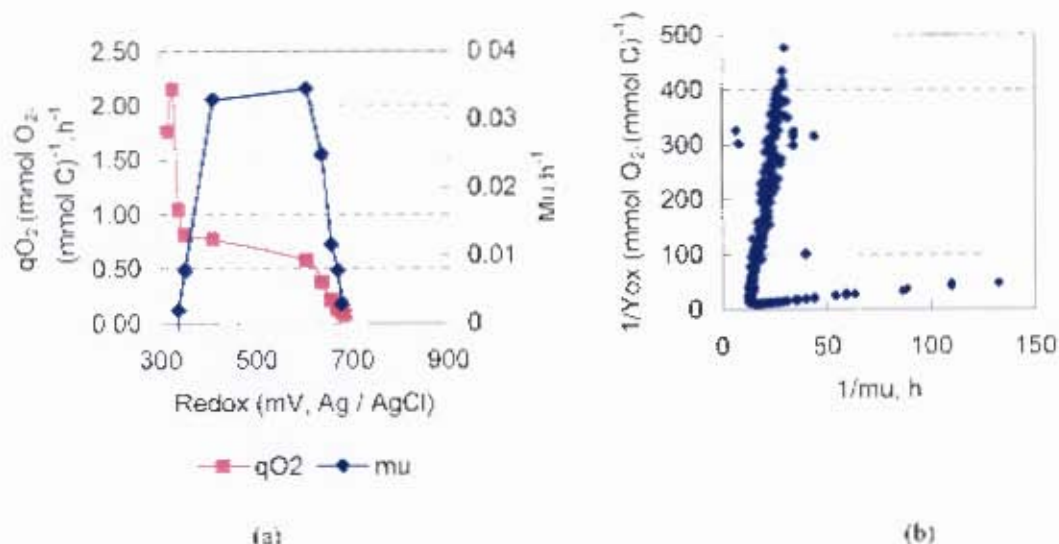


Figure 5.10: Variation of (a) biomass specific oxygen utilisation rate and specific growth rate plotted against redox potential (vs. Ag / AgCl) and (b) inverse biomass yield on oxygen plotted against inverse specific growth rate.

From Figure 5.10(b), the biomass yield on oxygen, Y_{Ox} is quite low early in the experiment since the inverse yield ($1/Y_{Ox}$) is very high. Towards the end of the experiment, however, the actual yield was high as expected since its inverse values are low, as $1/\mu$ increased.

5.6 Effect of Leaching Variables on Mineral Dissolution and Bacterial Activity

The effects of particle size, initial ferric iron concentration, pH and temperature on the dissolution kinetics and bacterial growth were investigated by conducting bioleaching experiments on fresh rougher concentrates. The solids concentration and temperature were kept constant at 50 g.L⁻¹ and 35°C respectively where these were not variables. These parameters have been identified as some of the major factors that affect leaching efficiencies and metal extraction rates.

5.6.1 Effect of pH

The acidity of a bioleaching system must be carefully controlled such that the entire system remains in the Eh-pH region where leaching is possible. The dissolution of copper from oxide and sulphide ores depends to some extent, on the acid concentration and the level of ferric ion concentration present in solution. Acid (protons) participates in the initial attack of sulphide minerals (Schipper and Sand, 1999) though ferric ion is the major oxidant for the dissolution of sulphide ores (Bustos *et al.*, 2004). Any side reactions that either consumes or generates acid will shift the system from the bioleaching window to a different region where leaching may be limited or not possible. Gangue minerals consume acid as well as the microbial oxidation of ferrous to ferric iron though the later is a necessity in order to maintain ferric iron in solution. Thus a low pH prevents iron hydrolysis and subsequent precipitation (Munoz *et al.*, 1979; Dutrizac, 1981; Dutrizac and MacDonald, 1974).

According to Bustos *et al.* (2004) the growth of bacteria also depends on the existence of suitable pH and temperature profiles that promotes the metabolic reactions at the appropriate interphases. This means that solution/slurry pH affects the activity of bacteria. Highly acidic solutions increase the bacterial lag phase to attain exponential growth and also the final bacterial concentration. For solutions with low concentrations of acid, the system may shift from the wanted redox reactions resulting in hydrolytic ferric iron precipitation and subsequent passivation of reaction surfaces by these precipitates and may also slow down the growth of bacteria (Bustos *et al.*, 2004).

Bustos *et al.* (2004) further pointed out that sulphuric acid speciates to free protons (H^+) and bisulphate (HSO_4^-) at pH below about 2. This creates a buffering effect to maintain the pH nearly constant in the range 1.50-1.80. Under these conditions of pH, ferric iron is soluble and thus promotes the dissolution of copper sulphides to give copper ions in solution with ferrous iron going back into solution. As the dissolved sulphate species increase, the bisulphate ions also increases whereby the reaction of acid with gangue minerals reduces, giving a reduction in the overall acid consumption.

The results for the effects of pH on the dissolution of a predominantly chalcocite ore are graphically presented in Figure 5.11 below.

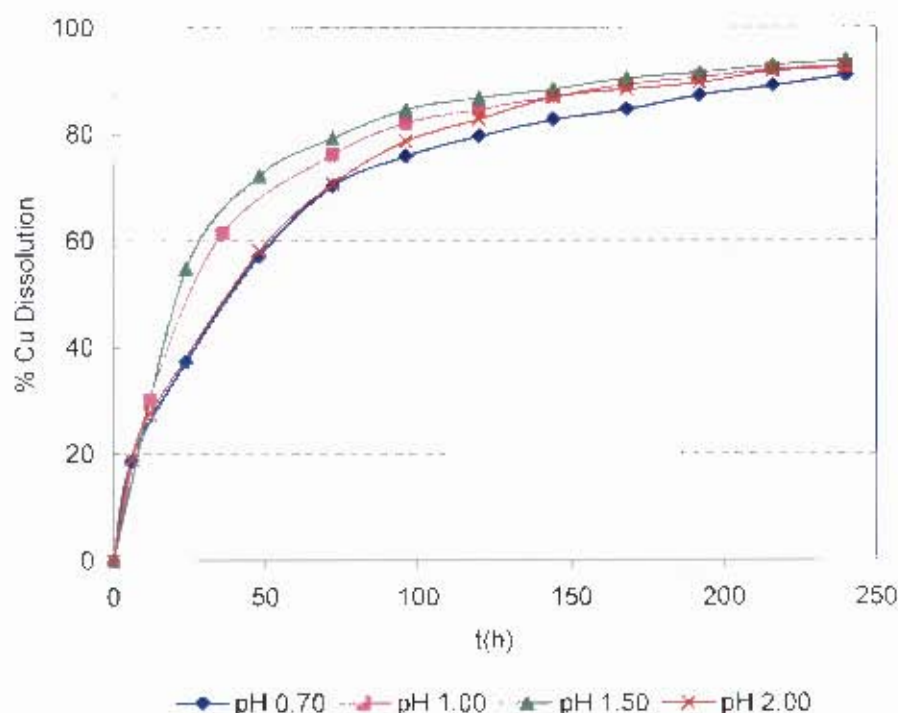


Figure 5.11: Percent (%) copper solubilised plotted against time for different values of pH at $T\ 35^{\circ}C$, and 5% w/w ($50\ g.L^{-1}$) Solids.

The percentage (%) of copper solubilised at various levels of pH is shown in Figure 5.11 above. There was little effect of pH on the amount of copper solubilised in 0.70-2.00 pH range that was investigated. An estimated average copper dissolution of about 90% after 6 days was observed in nearly all cases of pH variation. During the initial phase of the experiments where the bacterial growth was still in the lag phase (~ 8 hours), the percentage of copper extraction were similar regardless of pH value.

The solubilisation mechanism may be attributed to mainly chemical (acid) leaching of copper oxide minerals (see Section 5.3 for the detailed acid leaching reactions).

However, the slight differences in the amount of copper leached for pH range investigated are worth mentioning. In general, the pH values of 1.00 and 1.50 gave highest copper extraction (> 90%) after 6 days and leaching rates (Figure 5.12) compared to the extreme pH values of 0.70 and 2.00 that gave slightly lower copper recovery (~ 85%). The leaching rates shown in Figure 5.12 below were calculated by drawing tangents to the % extraction vs. time graphs (Figure 5.11) between 20-100% copper extraction.

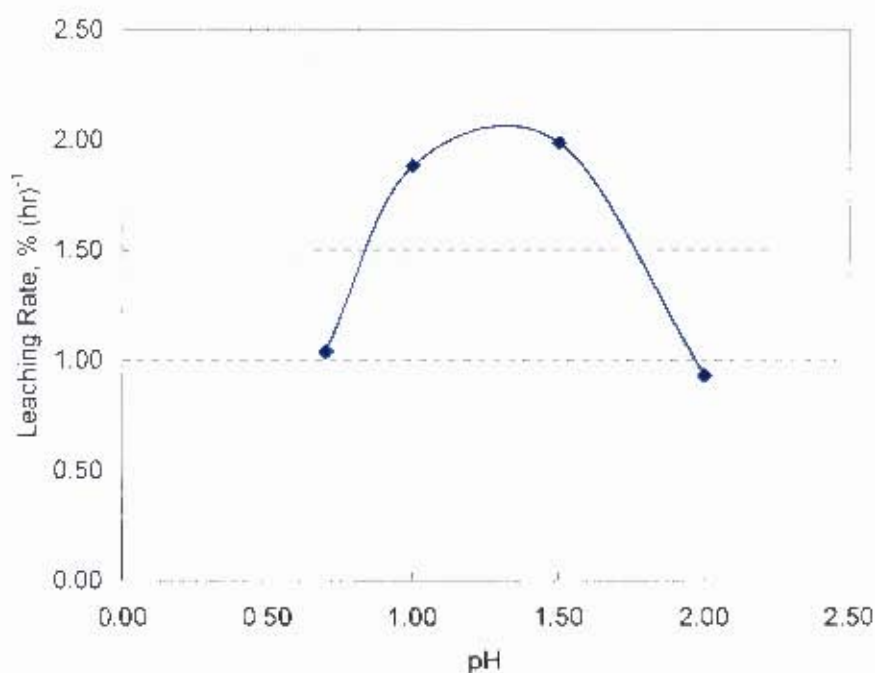


Figure 5.12: Rates of leaching plotted against pH at T 35°C, and 5% w/w (50 g.L⁻¹) Solids

Many researchers have identified suitable pH ranges during which both metal dissolution and bacterial activity is highest. Bioleaching of base metal sulphides such as those of copper is generally conducted in the pH range of 1.50-3.00 where most metal ions remain in solution as soluble species (Bosecker, 1997). The loss of ferric iron through precipitation as jarosite is prevented if the pH of bioleaching solution/slurry is kept below about 1.3 (Rossi, 1990). However, the optimum pH range for the growth of mineral leaching bacteria has been reported as 2.0-2.5 (Bosecker, 1997; Rossi, 1990) although different authors have given slightly different

ranges. According to Rossi (1990) the lower pH limit for optimum growth of *Acidithiobacillus ferrooxidans* is about 1.0 and above 5.5 the bacterial activity is inhibited.

5.6.2 Effect of Initial Ferric Iron Concentration

The extent of copper dissolution from sulphide oxidation by ferric iron at several solution concentrations for a predominantly chalcocite ore is shown in Figure 5.13 below. The figure depicts three different leaching regimes for sterile acid-ferric leaching at 3.0 g.L⁻¹ (0.054 mol.L⁻¹ Fe³⁺), the acid-bacterial leaching without any initial ferric iron addition and also the acid-ferric-bacterial leaching for a range of ferric iron concentration of 3.0-9.0 g.L⁻¹ (0.054-0.161 mol.L⁻¹ Fe³⁺). From the graph, significant differences in the amount of copper solubilised can be observed in the three different categories.

The abiotic acid-ferric leaching at 3.0 g.L⁻¹ Fe³⁺ concentration gave the lowest leaching rates and percentage of copper solubilised compared to the acid-ferric leaching at the same ferric iron concentration (3.0 g.L⁻¹ Fe³⁺) but in the presence of bacteria as shown in Figure 5.14 below. The amount of copper leached after 24 hours was about 51.2% for the abiotic acid-ferric leaching relative to about 66% copper dissolution at the same initial ferric iron concentration but in the presence of bacteria. It appears the role of bacteria is to regenerate the ferric iron (Boon *et al.*, 1995; Brierley and Brierley, 1986; Schippers and Sand, 1999) needed for sulphide attack. In the sterile leaching, it is possible that the ferric iron concentration was continuously being depleted without regeneration. Further, the redox potential values observed in the acid-ferric bioleaching experiment were much higher (715.3 mV vs. Ag/AgCl) than the sterile one (400 mV vs. Ag/AgCl) for the same initial ferric iron concentration. Finally, at the end of the experiments about 92% copper was leached in the bioleaching experiment compared to 79% copper in the sterile one after 150 hours at the same 0.054 mol.L⁻¹ Fe³⁺ initial concentration for both cases.

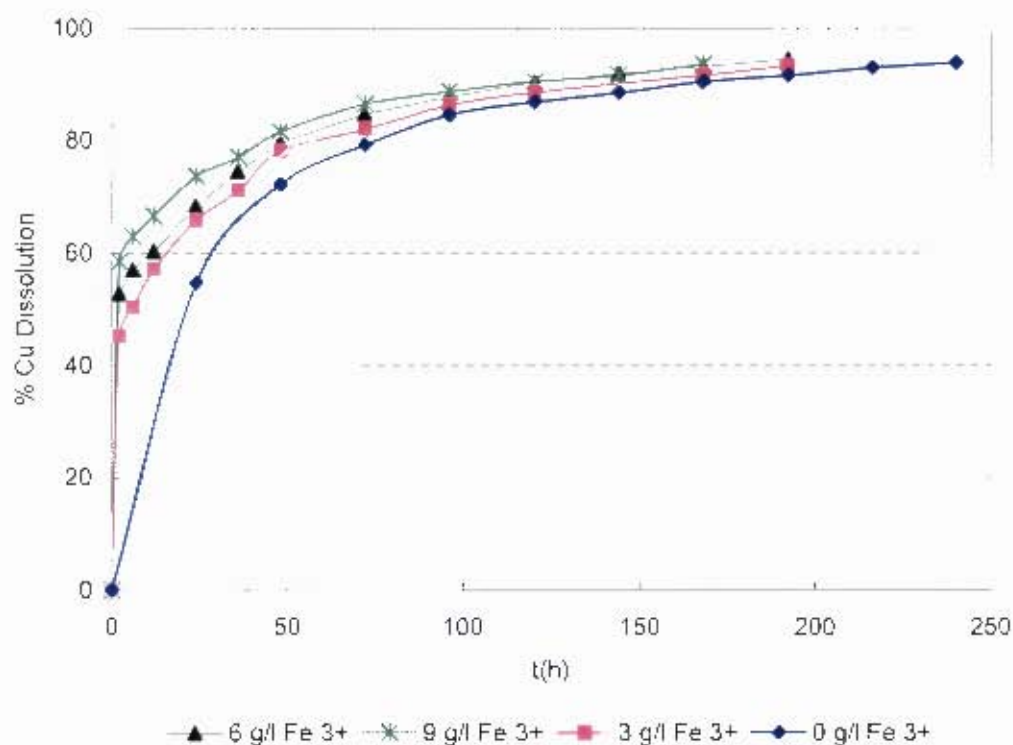


Figure 5.13: Effect of initial ferric ion concentration on the amount of copper solubilised measured against time; pH 1.50, T 35°C, Solids 5% w/w (50 g.L⁻¹).

By referring to Figure 5.13 above, the acid-bacterial leaching experiment without any external ferric iron addition gave higher amounts of copper leached than the abiotic acid-ferric leaching experiment with an initial 3.0 g.L⁻¹ Fe³⁺ iron concentration. However, the copper solubilised for the bioleaching experiment without any external ferric iron addition was much lower than the other bioleaching experiments that had various levels of ferric iron concentration added. After 24 hours of leaching about 54.8% copper was leached for bioleaching at zero initial ferric iron concentration compared to 66-74% copper being solubilised for rest of the bioleaching experiments at various levels of initial ferric iron concentration.

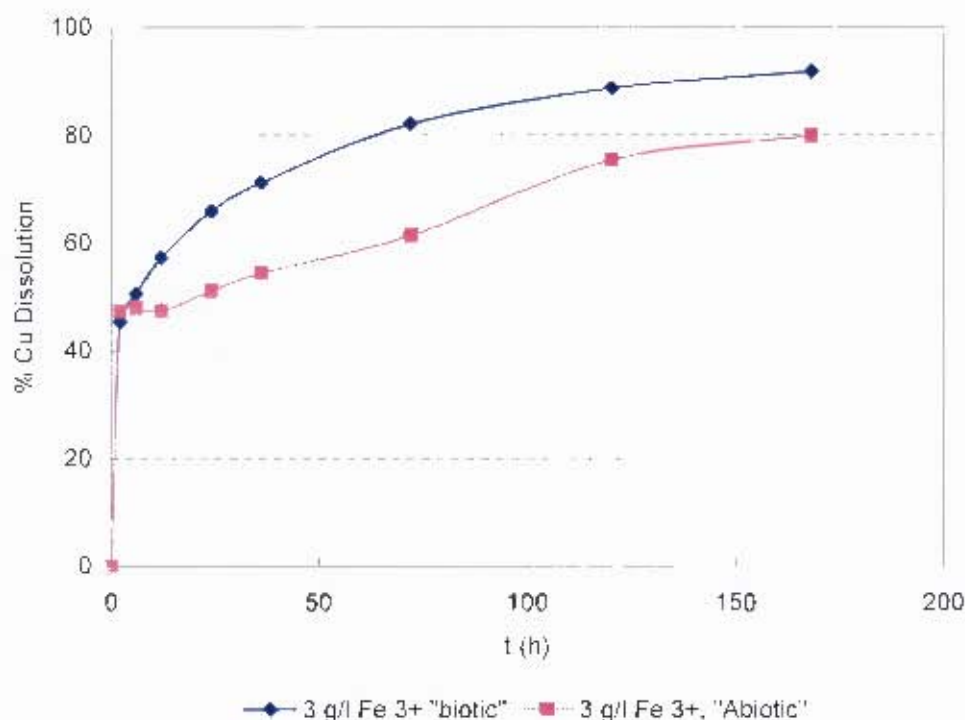


Figure 5.14: Percent (%) copper extraction vs. time at initial $3.0 \text{ g.L}^{-1} \text{ Fe}^{3+}$ iron concentration for abiotic and biotic leaching experiments at pH 1.50, $T 35^{\circ}\text{C}$, Solids 5% w/w (50 g.L^{-1})

After about 100 hours the amounts of copper solubilised were similar for all the bioleaching experiments including the one without any external addition of ferric iron. The explanation for this observation might be that the chalcocite ore used in this study had significant quantities of pyrite that has been reported to leach only at higher redox potentials (May, 2007) and thus provides the ferric/ferrous ions needed for other sulphide oxidation such as chalcocite. This could only happen later in the course of experiments when solution redox potentials attained high values ($> 450 \text{ mV}$ vs. Ag/AgCl). Thus, the kinetics of acid-ferric-bacterial leaching was influenced only initially in the experiments (under 48 hours) where the amounts of copper leached were significantly different but ultimately gave over 90% copper dissolution in all cases. In view of this, the inherent pyrite present in the chalcocite ore may be sufficient to provide the soluble iron species required for leaching though probably longer residence times would be required.

In general, the amount of copper leached was observed to increase with an increase in the initial ferric iron concentration added. After 2 hours of leaching about 45% copper was leached at $3.0 \text{ g.L}^{-1} \text{ Fe}^{3+}$, which increased to about 59% copper being solubilised

at $9.0 \text{ g.L}^{-1} \text{ Fe}^{3+}$. However, a relatively pure chalcocite mineral has been reported to leach at relatively low ferric iron concentrations ($0.004\text{--}0.01 \text{ mol.L}^{-1}$) with *Acidithiobacillus ferrooxidans* (Rossi, 1990). Actually, there seems to be different relationships reported between leaching rates and initial ferric iron concentration in the earlier studies as observed in a review by Dutrizac and MacDonald (1974).

5.6.3 Effect of Temperature

The effect of temperature on copper leached is shown in Figure 5.15 below for a temperature range of $25\text{--}40^\circ\text{C}$ in which optimum mesophilic bacterial growth has been reported (Rossi, 1990).

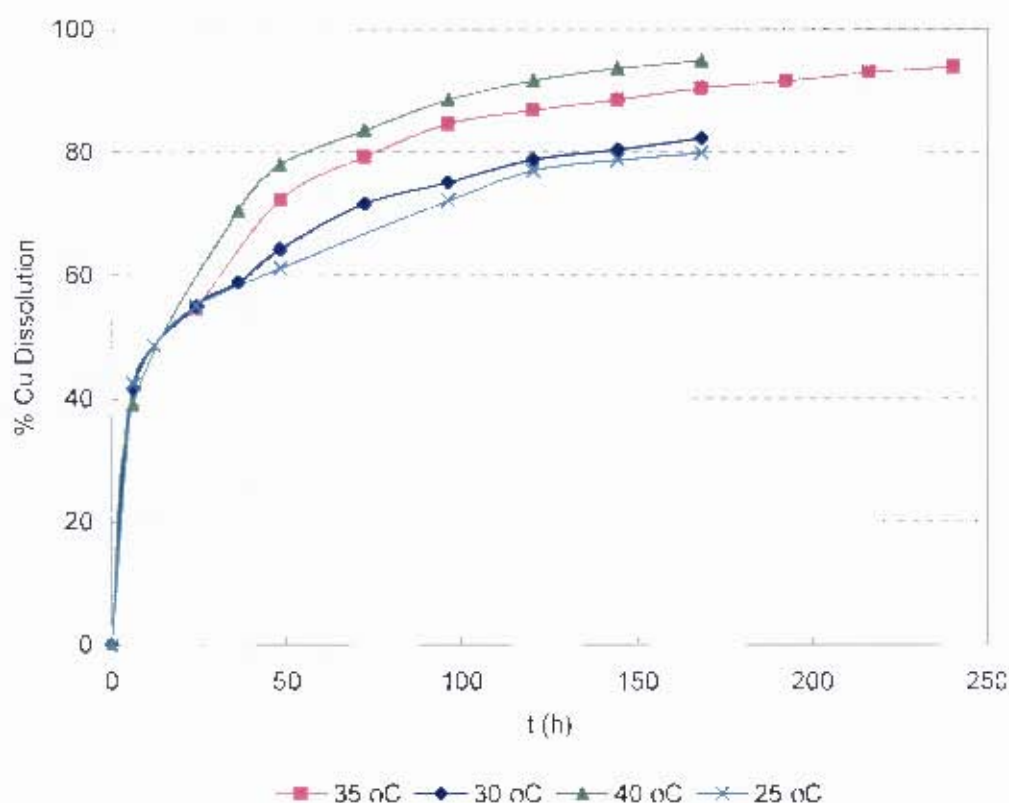


Figure 5.15: Effect of temperature on copper dissolution measured against time at pH 1.50 and 5% w/w (50 g.L^{-1}) solids loading.

From Figure 5.15, the amount of copper solubilised in the first two hours was similar regardless of temperature. This is probably copper oxide mineral dissolution phase and possibly first stage dissolution of chalcocite which has been reported to release about 40% copper within 30 minutes of leaching (Bolorunduro, 1999). After 2 hours,

the percentage of copper solubilised increased with increase in temperature. About 95% copper was leached after 6 days at 40°C. This is the second stage leaching of chalcocite which is much slower and has been found to be temperature dependent. Bolorunduro (1999) reported nearly 99% copper being released from chalcocite after 3 hours of leaching at 75°C in the absence of any bacteria.

An Arrhenius plot for the overall bioleaching experiments is shown in Figure 5.16. Basically, the method of initial rates was applied whereby tangents were drawn to the dissolution-time graphs shown in Figure 5.15. The slopes of the tangents drawn to each curve between 40-100% copper extraction were then taken as the leaching rates in each experiment. The activation energy obtained was 71.4 kJ (mol)⁻¹ which indicates that the chemical reaction was rate controlling.

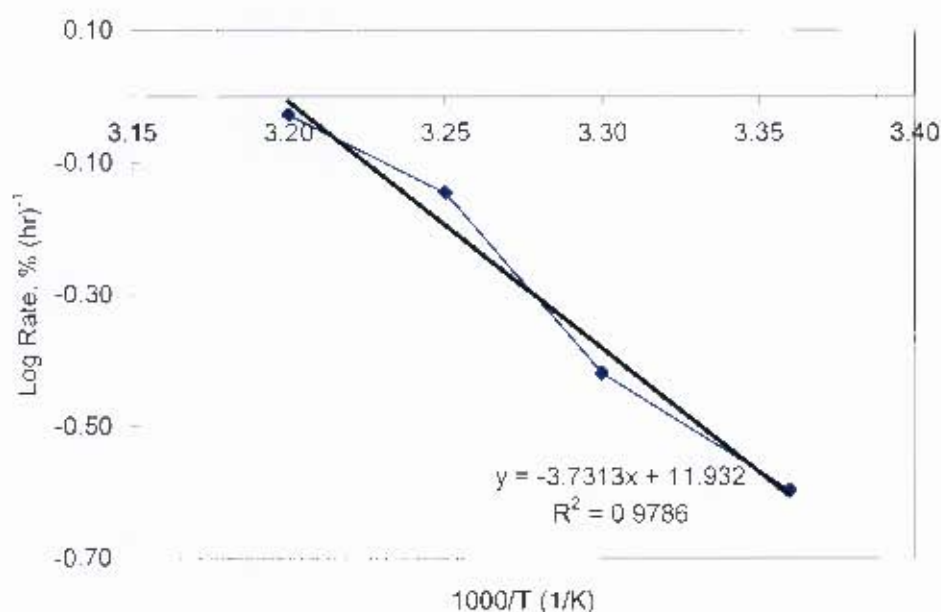


Figure 5.16: Arrhenius plot for overall bioleaching of Chalcocite ore at four different temperatures.

5.6.4 Effect of Particle Size

The distribution of copper in the various size fractions is shown in Figure 5.17. The amount of copper contained in the various particle sizes was observed to increase with increase in particle sizes. This phenomenon might be attributed to the occurrence of mineral values as coarse size grains. The unsatisfactory liberation characteristics, low surface area and possibly intimate locking of mineral grains in the courser size fractions may have resulted in low metal extraction as shown in Figure 5.18 below.

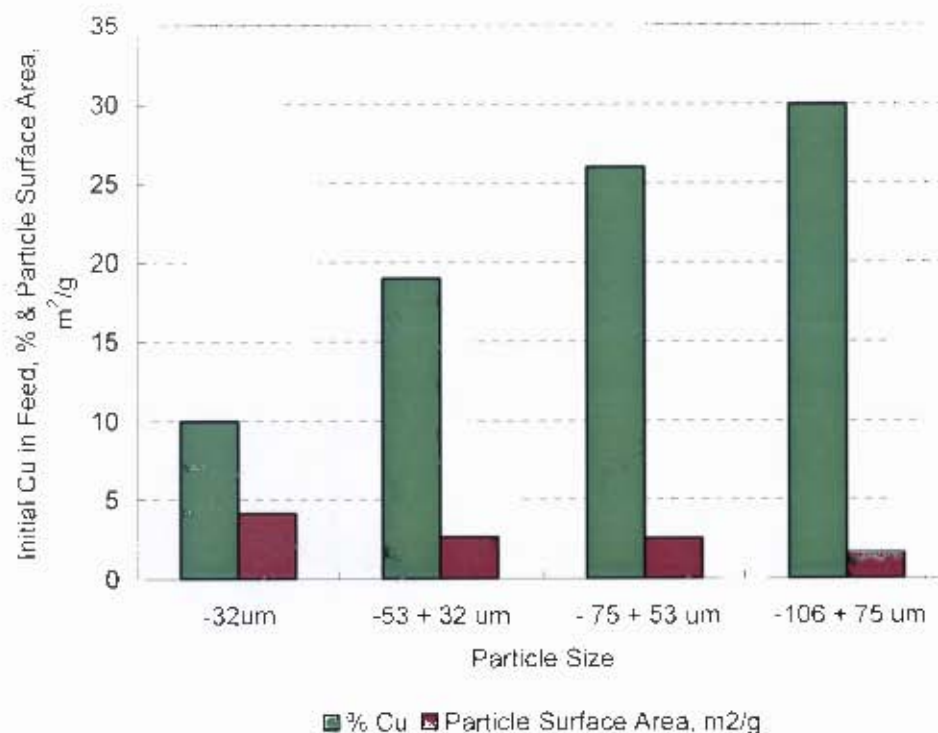


Figure 5.17: Distribution of copper and surface area in different particle sizes.

Figure 5.18 below shows the effect of particle sizes on copper solubilised with time. Unexpectedly, the copper dissolution data for $-75 + 53 \mu\text{m}$ and $-106 + 75 \mu\text{m}$ particle sizes showed much higher dissolution of copper than the smaller particle sizes in the first 2 days of leaching. Consequently, this data was discarded on account of the fact that the smaller particle sizes had higher surface area per unit mass (Figure 5.17), and thus are expected to show highest reaction rates in any heterogeneous system.

Beyond two days of leaching, the smaller the particle sizes the greater the amount of copper solubilised as expected. This means that the finer the grind size the faster the leaching kinetics.

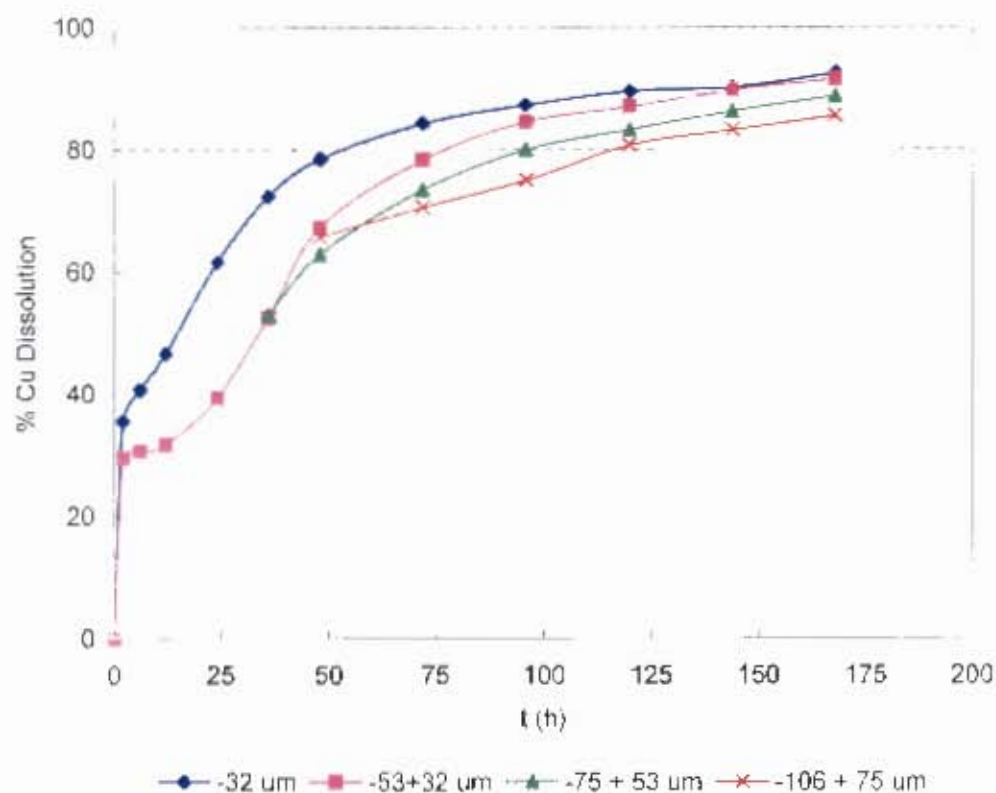


Figure 5.18: Effect of particle size on copper dissolution measured against time at pH 1.50 and 5% w/w (50 g.L^{-1}) solids loading.

A summary of the major findings and conclusions drawn from this investigation is given in the conclusions and recommendations section (Chapter 6).

Chapter 6

Conclusions and Recommendations

In this study, the potential of bioleaching a mixed copper oxide/sulphide rougher concentrate of Nchanga Mine was investigated in batch stirred tank bioreactors, using a mixed culture of iron- and sulphur-oxidising mesophilic bacteria. The main findings and conclusions drawn from this investigation are presented below.

A review of the literature has shown that the chemical and bio leaching of copper sulphides has been extensively studied. However, the bioleachability of different copper sulphide ores and minerals from different sources varies significantly partly because of different types and level of impurity minerals associated with these minerals. Several authors have reported different mineral leaching kinetics data on account of variability of mineralogical composition and different solution conditions and leaching systems being employed. It was therefore necessary to determine the kinetics of copper extraction and extent of mineral dissolution for Nchanga's rougher concentrate under various solution conditions. The preliminary leaching kinetics data may be useful for a possible development of tank or heap bioleaching.

Knowledge of acid consumption of the ore is an important task in industrial tank or heap leaching operations. The preliminary experiments revealed initially rapid acid consumption rates and this was attributed to reactive alkaline gangue minerals and the chemical (acid) solubilisation of copper oxides/carbonates. Comparatively, bioleaching experiments exhibited highest acid consumption rates and copper extraction than abiotic oxidative acid leaching experiments. The acid demand was therefore 150-300 and 150-240 kg acid/ton ore for the bioleaching and abiotic oxidative acid leaching experiments respectively.

The results of this study have established that bioleaching of Nchanga copper sulphide ore requires high solution redox potentials, low solution pH (0.6-2.0) and a certain threshold concentration of ferrous iron for high copper extraction and microbial activity. The leaching profile for this ore progressed in a three phase sequence. In phase one, 20%

copper was abiotically leached in dilute acid without air (oxygen) corresponding to the chemical (acid) dissolution of copper oxides/carbonates. The second phase resulted in 58% copper being abiotically and chemically extracted in the presence of air. The last phase involving bioleaching resulted in over 93 % copper recovery. The abiotic acid leaching experiments exhibited high leach rates but low copper recovery relative to bioleaching experiments where both leach rates and recovery were significantly high. These results are consistent with literature data, confirming and recognising the fact that the presence of bacteria increases the rate of leaching. The role of bacteria therefore is to provide acid and the ferric iron oxidant (through sulphur and ferrous iron oxidation) required for dissolution of copper oxides/carbonates and sulphides as reported in the literature.

The leach rates for bioleaching of a leach residue from non-oxidative acid leach experiments were rather low relative to direct bioleaching of the fresh ore, although eventually giving over 90% copper extraction in both cases. Therefore, it may not be economical to preleach the ore in acid followed by microbial leaching of residues. Therefore, direct bioleaching of fresh ore may be preferable because of faster oxidation kinetics.

Using off-gas data, the microbial oxygen and carbon dioxide consumption rates were rapid in the exponential microbial growth phase where ferrous iron in solution was also high. The result was a high microbial population of up to 10.0 mm C.L^{-1} at the stationary phase. Thus, off-gas analysis is useful for calculating microbial growth rates and other kinetic parameters even in multi-sulphide leaching system as it has been done for single mineral substrates like pyrite and chalcopyrite. In the final (decay) phase, decreased microbial gas uptake was accompanied by low ferrous iron with significantly high ferric iron concentration in solution. Consequently, solution redox potentials increased rapidly before levelling off at about 690 mV (vs. Ag/AgCl). Also, the dissolution of pyrite was only significant at high redox potentials from the observed measurements of total soluble iron. The slurry pH was unstable if uncontrolled but later decreased indicating a microbial sulphur-oxidising capacity after 3 days. It can be concluded therefore that ferrous iron and sulphur compounds (and not chalcocite) are the substrates for bacteria.

The effects of pH, temperature, initial ferric iron concentration and particle sizes on copper leached were then investigated. The results indicated little effect of pH on the amount of copper solubilised in the 0.70-2.00 pH range investigated. An estimated average dissolution of about 90% copper after 6 days was observed in nearly all cases of pH variation. Ferric leach experiments showed highest leach rates and amounts of copper leached though jarosite-like precipitates were noticeable on the reactor walls. Copper recovery slightly increased as the initial ferric iron concentration was increased. After just 2 hours 45% copper was leached at 3.0 g.L⁻¹ Fe³⁺ iron, increasing to about 58% copper dissolution at 9.0 g.L⁻¹ Fe³⁺ iron concentration. The kinetics of acid-ferric-microbial leaching were influenced only initially (< 48 hours) where the leach rates varied for the different initial ferric iron dose rates though about 94% copper was leached in all cases.

The amount of copper leached did not depend on temperature initially but later increased as temperature was increased from 25 to 40 °C. Highest copper recovery of about 95% was obtained after 6 days at 40 °C. The highest microbial growth rate was obtained also at this temperature contrary to optimum mesophilic temperatures of around 35 °C reported in the literature. The activation energy calculated was 71.4 KJ.mol⁻¹ which indicates that the chemical reaction was rate controlling. Furthermore, the smaller the particle sizes the greater the amount of copper solubilised and the higher the leach rates as expected. This means fine grinding gives faster leaching kinetics.

Finally, this investigation has established a pH range of 1.00-1.50, temperature of 40 °C and an initial ferric iron concentration of 9.0 g.L⁻¹ as being optimum for bioleaching of Nchanga copper sulphide ore. The best microbial activity and highest copper recovery of up to 94% were obtained under these conditions. Also, the finest particle size range gave the best leach rates and copper recovery. Hence ore grinding to the smallest particle size possible would result in higher copper extraction. The highest leach rate of 0.737 g Cu (g Cu in ore)⁻¹ day⁻¹ was obtained in the bioleaching experiment with the largest initial ferric iron concentration (of 9.0 g.L⁻¹) than for any other experimental conditions employed. This leach rate was significantly higher than a rate of 0.548 g Cu (g Cu in ore)⁻¹ day⁻¹ for a case of bioleaching without any added ferric iron. The extent of copper dissolution was

94% both for bioleaching experiments involving inherent iron (pyrite) and added ferric iron. This means ferric iron does not increase copper recovery but rather increases the leach rates. Therefore, bioleaching of Nchanga copper sulphide ore by utilising its inherent pyrite as a source of soluble ferric iron may be a better option than the deliberate addition of ferric iron to the leaching system.

On the basis of high copper extraction and leach rates obtained, and satisfactory microbial activity, Nchanga copper sulphide ore has the potential to be bioleached under mesophilic conditions. It is therefore recommended that further investigations involving column trials should be done to ascertain the leachability and scale-up of the present experimental data to a possible heap bioleaching. It is also proposed that a rigorous mathematical treatment of degree of reduction balances must be applied to a multi-substrate system such as this one in order to relate the rate of copper dissolution to bacterial oxygen and carbon dioxide consumption rates as it has been done for single (such as ferrous iron, sulphur) substrate. One limitation in this study was the inability to determine the qualitative and quantitative mineralogical analysis of the leach residues. This is very important in order to fully interpret the bioleaching data.

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Appendices

Appendix 1: Zambian Copperbelt Mineralogical Data Table

Copper Bearing Minerals of the Copperbelt Ore Deposits

Mineral	Formula	Total Copper % Cu	Relative Abundance in Local Ore Bodies	Acid Soluble Copper % ASCu	Metallurgical Classification
Chalcocite	Cu_2S	78.9	Major Mineral	1.5	Sulphide Cu
Bornite	Cu_5FeS_4	63.3	Major Mineral	2.0	Sulphide Cu
Chalcopyrite	CuFeS_2	34.6	Major Mineral	Nil	Sulphide Cu
Digenite	Cu_9S_5	78.8	Present	Not Known	Sulphide Cu
Covellite	CuS	66.5	Present	Not Known	Sulphide Cu
Carrollite	CuCo_2S_4	20.5	Present	Not Known	Sulphide Cu/Co
Native Copper	Cu	100.0	Present, Sometimes abundant	Nil	Native
Malachite	$\text{Cu}_2(\text{OH})_2\text{CO}_3$	57.6	Major Mineral	100.0	Oxide Cu
Azurite	$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	55.3	Present, Sometimes abundant	100.0	Oxide Cu
Chrysocolla	$\text{CuSiO}_3 \cdot n\text{H}_2\text{O}$	36.2	Present, Sometimes abundant	100.0	Oxide Cu
Pseudomalachite	$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$	55.2	Present, Sometimes abundant	100.0	Oxide Cu
Cuprite	Cu_2O	88.8	Present, Sometimes abundant	50-70	Oxide/Sulphide
Cupriferrous Vermiculite	Hydrated Mg, Fe, Al, silicate	0 to 8	Present, major mineral in certain strata	Variable, 18 to 60	Oxide/sulphide
Copper Manganese Wad	Variable Fe, Mn, Cu, Co	0 to 15	Present	100.0	Oxide/sulphide
?	$\text{Cu}_2\text{PO}_4\text{OH}$	53.1	Present to rare	100.0	Oxide Cu
Diopside	$\text{CuSiO}_3 \cdot \text{H}_2\text{O}$	40.3	Rare	61.5	Oxide Cu
?	$\text{Cu}_3\text{PO}_4(\text{OH})_3$	56.3	Rare to present	100.0	Oxide Cu

Appendix 2: Analytical Methods

(a) **Digestion Method (ex Karbochem R & D Lab)**

Principle

The finely milled ore sample is dissolved in aqua regia with the addition of hydrofluoric acid and perchloric acid. The sample is made up to a known volume, filtered and read on the AA spectrophotometer.

Reagents

Hydrofluoric acid	CP	approx. 40%
Nitric acid	CP	approx. 60%
Perchloric acid	CP	concentrated
Hydrochloric acid	CP	approx. 30%

For use: Mix 4 parts HCL to 1 part HF per volume.

Method

1. Sample is weighed out according to the type into a 250 ml wide-mouthed Erlenmeyer flask as follows:

Concentrates	0.1g
Tails and Feed (head)	0.5g

2. Digest:

Add 10 ml of the HCL/HF mixture to sample and heat to boiling.

Add 10 ml HNO₃ to flask and boil until sample volume is approx. 2 ml

Add 5 ml HClO₄ to flask and boil until sample volume is approx. 2 ml

(A white cloud will form which will rise once reaction has taken place)

3. Make up to volume and filter:

Transfer the sample quantitatively to a 100 ml volumetric flask and make up to 100 ml with distilled water. Filter through Whatman No 1 into sample bottle. Filtrate to be read on AA. Store in fridge if delay in reading.

4. Read on AA.

5. Calculation:

$$\text{e.g. \% Cu in sample} = \frac{R \text{ (in ppm)}}{100 \times a \text{ (sample mass)}}$$

(b) Analytical procedure for the determination of soluble iron species in bioleach solution samples:

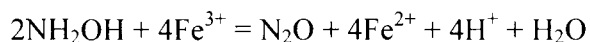
The titrimetric method of determining total iron and ferrous iron in copper-containing samples using a solution of dichromate was tested but not applicable since the concentration of ferrous iron was below the detection limit. However, the method of hydroxylamine to reduce ferric iron to ferrous form was used as described below.

Procedure for determination of soluble iron species in solutions as compiled by Mfandaizda Hove

1. Introduction

The procedure described here is based on two facts:

- The formation of orange red complexes when Fe^{2+} is mixed with 1-10 phenanthroline. Three molecules of 1-10 phenanthroline chelates with one Fe^{2+} ion.
- The reduction of Fe^{3+} by hydroxylamine according to the well known stoichiometry shown below:



By first reducing all the Fe^{3+} present in a sample, total iron can be determined by use of 1-10 phenanthroline complexing agent. The amount of Fe^{3+} is found as the difference between total iron obtained after reduction with hydroxylamine and Fe^{2+} obtained without reduction.

2. Reagents and Procedure

2.1 Standard Fe^{2+} stock solution (100 ppm Fe^{2+})

Slowly add 20 ml of concentrated H_2SO_4 to 50 ml of distilled water and dissolve 497.629 mg of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Dilute to 1000 ml with distilled water and mix thoroughly. Standard solutions of lower concentrations are obtained by dilution as indicated in Table 1.

2.2 1-10 phenanthroline indicator solution

Dissolve 2127.708 mg of 1-10 phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$) in about 100 ml of water. Dilute with more distilled water to 1000 ml mark. This gives a concentration of 1-10 phenanthroline in excess of the stoichiometric requirements.

2.3 Ammonium acetate buffer solution

Dissolve 250 g of ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) in 150 ml of distilled water. Add 700 ml of concentrated glacial acetic acid.

2.4 Calibrating the instrument

Prepare standard samples for the calibration of the spectroquant/spectrophotometer according to Table 1 below. Read off the absorbance at wavelength of 510 nm.

Standard (ppm Fe^{2+})	Vol of stock (ml)	Vol of dist. Water (ml)	Vol of Buffer (ml)	Vol of Indicator(ml)	ABSORB.
1	0.01	0.99	2.00	2.00	
10	0.10	0.90	2.00	2.00	
20	0.20	0.80	2.00	2.00	
30	0.30	0.70	2.00	2.00	
40	0.40	0.60	2.00	2.00	
50	0.50	0.50	2.00	2.00	
60	0.60	0.40	2.00	2.00	
70	0.70	0.30	2.00	2.00	
80	0.80	0.20	2.00	2.00	
90	0.90	0.10	2.00	2.00	
100	1.00	0.00	2.00	2.00	
Blank	0.00	1.00	2.00	2.00	

2.5 Dissolved Fe^{2+}

Premix buffer solution and indicator solution in the prescribed test tubes according to the last two columns of Table 1. Pipette 1.00 ml of sample in the test tube and mix thoroughly. Allow to react for 3 minutes. Read off the concentration from the spectroquant.

2.6 Total Iron

Add buffer and indicator solutions into test tube according to Table 1. Pipette 1.00 ml of sample into the test tube. Add one scoop of hydroxylamine and vortex for 2 minutes. Allow to stand for 5 minutes and then read off the concentration of iron from the spectroquant.

2.7 Dissolved Fe³⁺

Determine the concentration of Fe²⁺ according to 2.5 above. Add one scoop of hydroxylamine to the same test tube. Vortex for 2 minutes and allow to stand for 5 minutes. Read off the total iron concentration. Concentration of Fe³⁺ is the difference between total iron and Fe²⁺ concentration.

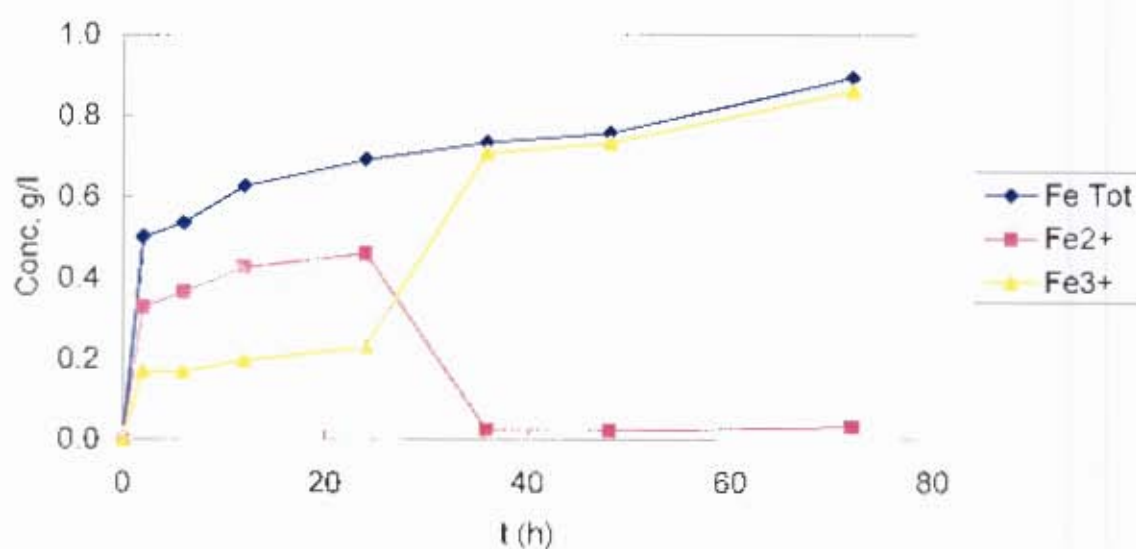
Note: Filter all turbid or coloured samples before analysis.

2.8 Calculation of soluble iron species

$$\text{abs} = 0.0438x + 0.0002 \text{ where } x = \text{conc}$$

$$\text{Conc} = \text{Abs}/0.0438$$

Time (hrs)	E, Mv	Fe (Total)	Abs	Conc (mg/l)	Actual Conc (mg/l)	Conc, g/l	Fe3+
0	313.40	0		0	0	0	0
2	324.45	0.5021	0.290	6.62	331.05	0.3311	0.17105
6	337.23	0.5379	0.322	7.35	367.58	0.3676	0.17032
12	351.08	0.6275	0.375	8.56	428.08	0.4281	0.19942
24	409.12	0.6937	0.405	9.25	462.33	0.4623	0.23137
36	604.55	0.7364	0.023	0.53	26.26	0.0263	0.71014
48	635.43	0.7594	0.021	0.48	23.97	0.0240	0.73543
72	656.20	0.8949	0.029	0.66	33.11	0.0331	0.86179
96	670.04	1.0409	0.028	0.64	31.96	0.0320	1.00894
120	678.03	1.1200	0.030	0.68	34.25	0.0342	1.08575
144	683.89	1.3500	0.033	0.75	37.67	0.0377	1.31233
168	687.65	1.4700	0.034	0.78	38.81	0.0388	1.43119
192	690.81	1.5200	0.036	0.82	41.10	0.0411	1.47890
216	695.07	1.6700	0.039	0.89	44.52	0.0445	1.62548
240	697.73	1.5500	0.038	0.87	43.38	0.0434	1.50662
Inoculum			0.058	1.32	66.21	0.0662	



Concentration of various iron species in solution for run2

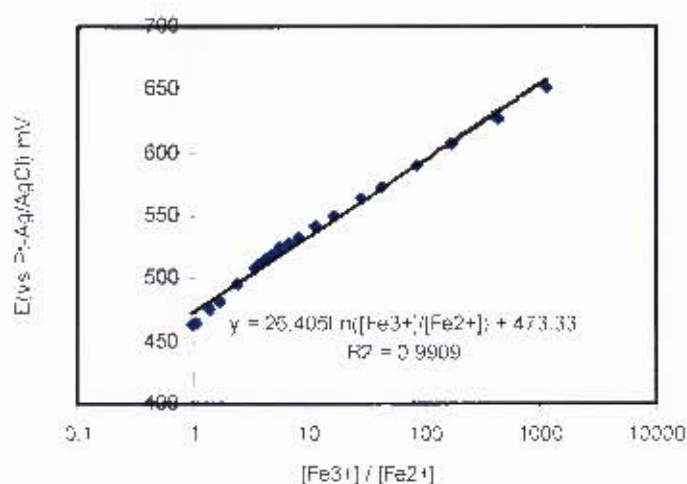
(c) Reactor Redox potential Probe calibration data (See procedure in Chapter 4)

Molar mass of $\text{Fe}_2(\text{SO}_4)_3$	399.6	g/mol	Fe	55.85
Molar mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278.03	g/mol		

$[\text{Fe}^{3+}]_i$	5000	mg/l =	$\text{Fe}_2(\text{SO}_4)_3$	17887.19785	mg/l =	0.044763
$[\text{Fe}^{2+}]_i$	12000	mg/l =	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	59737.86929	mg/l =	0.214861

CALIBRATION CALCULATIONS

$V_{\text{Fe}^{3+}} \text{ (ml)}$	$V_{\text{Fe}^{2+}} \text{ (ml)}$	$V^T \text{ (ml)}$	$[\text{Fe}^{3+}] \text{ (mg/l)}$	$[\text{Fe}^{2+}] \text{ (mg/l)}$	$[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$	E
400	0.15	400.15	4998.125703	4.498313133	1111.111111	652.47
400	0.4	400.4	4995.004995	11.98801199	416.6666667	627.98
400	1	401	4987.531172	29.92518703	166.6666667	606.68
400	2	402	4975.124378	59.70149254	83.33333333	590.17
400	4	404	4950.49505	118.8118812	41.66666667	573.66
400	6	406	4926.108374	177.3399015	27.77777778	563.54
400	10	410	4878.04878	292.6829268	16.66666667	550.23
400	15	415	4819.277108	433.7349398	11.11111111	541.71
400	20	420	4761.904762	571.4285714	8.333333333	533.19
400	25	425	4705.882353	705.8823529	6.666666667	527.87
400	30	430	4651.162791	837.2093023	5.555555556	524.67
400	35	435	4597.701149	965.5172414	4.761904762	519.35
400	40	440	4545.454545	1090.909091	4.166666667	516.15
400	45	445	4494.382022	1213.483146	3.703703704	511.36
400	50	450	4444.444444	1333.333333	3.333333333	508.7
400	70	470	4255.319149	1787.234043	2.380952381	495.38
400	100	500	4000	2400	1.666666667	482.07
400	120	520	3846.153846	2769.230769	1.388888889	475.15
400	160	560	3571.428571	3428.571429	1.041666667	465.56
400	170	570	3508.77193	3578.947368	0.980392157	463.43



Calibration curve for redox probe

Appendix 3: (a) Chemical and bioleaching Data

Acid Consumption Calculation

H₂SO₄ Density 1.83 g/ml

(a) Bioleach run at standard conditions

Time (hrs)	Acid used (ml)	Wt of Ore (g)	Acid Consumption (kg/tonne ore)
0	0	50	0
2	4.3	50	157.38
6	5.3	50	193.98
12	5.8	50	212.28
24	6.8	50	248.88
36	7.8	50	285.48
48	8.3	50	303.78
72	8.3	50	303.78
96	8.3	50	
120	8.3	50	
144	8.3	50	
168	8.3	50	

(b) Abiotic run at standard conditions

Time (hrs)	Acid used (ml)	Wt of Ore (g)	Acid Consumption (kg/tonne ore)
0	0	50	0
2	4.0	50	146.4
6	4.1	50	150.06
12		50	
24	5.3	50	193.98
		50	
48	6.1	50	223.26
		50	
96	6.7	50	245.22
120	6.7	50	245.22
144		50	
168		50	

Run 01

pH 1.5, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Inoculum concentration 10 % v/v, Mixed mesophilic bacterial culture, 0K Basal salts growth medium (without ferrous iron)

					Feed			Filtrate			Residue		Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(Days)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ^I (g/l)	Cu (%)	Fe (%)	Cu	Fe
23.04.06	S0	0	1.50	306.88	50.0	17.23	7.01	0.0088	2.980	0.991	17.23	7.01	0	0
24.04.06	S1	1	1.78	465.03	50.0	17.23	7.01	0.0084	5.200	1.010	7.79	5.33	54.76102	23.95437
25.04.06	S2	2	1.45	638.63	50.0	17.23	7.01	0.0080	5.840	1.060	4.77	5.48	72.29835	21.77795
26.04.06	S3	3	1.43	653.54	50.0	17.23	7.01	0.0080	7.350	1.260	3.57	5.52	79.2704	21.27441
27.04.06	S4	4	1.47	664.72	50.0	17.23	7.01	0.0082	6.570	1.420	2.65	5.22	84.64115	25.55916
28.04.06	S5	5	1.44	673.24	50.0	17.23	7.01	0.0080	8.230	1.640	2.26	4.94	86.88563	29.56909
29.04.06	S6	6	1.49	679.10	50.0	17.23	7.01	0.0080	8.600	1.620	1.98	4.97	88.52653	29.15433
30.04.06	S7	7	1.46	683.89	50.0	17.23	7.01	0.0080	7.480	1.790	1.64	4.95	90.49623	29.34544
01.05.06	S8	8	1.47	688.68	50.0	17.23	7.01	0.0080	8.290	1.880	1.45	4.88	91.60992	30.32037
02.05.06	S9	9	1.42	695.07	50.0	17.23	7.01	0.0078	8.870	1.950	1.21	4.81	92.99634	31.34807
03.05.06	S10	10	1.40	696.67	50.0	17.23	7.01	0.0080	8.900	1.930	1.06	4.53	93.8623	35.42987

Run 02

pH 1.00, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Inoculum concentration 10 % v/v, Mixed mesophilic bacterial culture, 0K Basal salts growth medium (without ferrous iron)

					Feed			Filtrate			Residue			Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ⁺ (g/l)	Cu (%)	Fe (%)	S (%)	Cu	Fe
15.05.06	S0	0	1.00	313.40	50.0	17.23	7.01		0.000	0.000	17.23	7.01		0	0
15.05.06	S1	2	1.07	324.45	50.0	17.23	7.01	0.0080	2.940	0.502	12.61	6.24		26.81882	10.92121
15.05.06	S2	6	1.01	337.23	50.0	17.23	7.01	0.0080	3.440	0.538	13.31	6.22		22.73007	11.29888
15.05.06	S3	12	1.06	351.08	50.0	17.23	7.01	0.0084	4.290	0.628	12.01	6.46		30.30943	7.830312
16.05.06	S4	24	1.05	409.12	50.0	17.23	7.01	0.0076	5.490	0.694	7.19	5.34		58.28706	23.77218
16.05.06	S5	36	1.05	604.55	50.0	17.23	7.01	0.0070	6.540	0.736	6.63	6.53		61.52422	6.900648
17.05.06	S6	48	1.03	635.43	50.0	17.23	7.01	0.0078	6.920	0.759	4.76	5.61		72.38099	20.04196
18.05.06	S7	72	1.00	656.20	50.0	17.23	7.01	0.0084	7.540	0.895	4.10	6.86		76.21859	2.12434
19.05.06	S8	96	0.96	670.04	50.0	17.23	7.01	0.0078	8.100	1.041	3.08	5.98		82.12353	14.6283
20.05.06	S9	120	0.95	678.03	50.0	17.23	7.01	0.0080	8.170	1.120	2.64	6.40		84.68813	8.729826
21.05.06	S10	144	0.95	683.89	50.0	17.23	7.01	0.0072	9.220	1.350	2.21	6.35		87.15592	9.384592
22.05.06	S11	168	0.95	687.65	51.0	17.23	7.01	0.0080	9.380	1.470	1.83	6.07		89.40391	13.43567
23.05.06	S12	192	0.99	690.81	52.0	17.23	7.01	0.0076	9.060	1.520	1.61	6.22		90.65919	11.20214
24.05.06	S13	216	0.97	695.07	53.0	17.23	7.01	0.0078	9.220	1.670	1.34	6.52		92.23336	7.06044
25.05.06	S14	240	0.96	697.73	54.0	17.23	7.01	0.0082	8.970	1.550	1.24	6.69		92.78074	4.599697

Run3

pH 2.0

					Feed			Filtrate			Residue		Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ⁺ (g/l)	Cu (%)	Fe (%)	Cu	Fe
29.05.06	S0	0	1.97	0.00	50.0	17.23	7.01	0.0000	0.000	0.000	17.23	7.01	0	0
29.05.06	S1	2	1.82	231.80	50.0	17.23	7.01	0.0074	2.640	0.333	10.51	5.15	39.0259	26.46691
29.05.06	S2	6	1.94	300.49	50.0	17.23	7.01	0.0078	3.010	0.344	13.96	5.86	19.00333	16.3439
29.05.06	S3	12	2.09	307.94	50.0	17.23	7.01	0.0078	3.430	0.352	12.45	6.23	27.73223	11.06197
30.05.06	S4	24	1.91	323.92	50.0	17.23	7.01	0.0080	4.080	0.353	8.74	5.99	49.27316	14.50551
30.05.06	S5	36	2.29	485.27	50.0	17.23	7.01	0.0078	5.090	0.259	10.84	5.90	37.08738	15.8986
01.06.06	S6	48	1.90	573.13	50.0	17.23	7.01	0.0080	5.830	0.252	7.22	6.25	58.09668	10.79633
02.06.06	S7	72	1.97	599.22	50.0	17.23	7.01	0.0080	6.990	0.335	5.05	7.02	70.71116	-0.10592
03.06.06	S8	96	1.94	620.52	50.0	17.23	7.01	0.0080	8.050	0.423	3.67	6.43	78.69317	8.2589
04.06.06	S9	120	1.95	632.77	50.0	17.23	7.01	0.0076	8.820	0.546	2.96	6.09	82.81953	13.1615
05.06.06	S10	144	1.95	643.95	50.0	17.23	7.01	0.0080	9.180	0.720	2.25	5.07	86.95127	27.67322
06.06.06	S11	168	1.97	648.74	51.0	17.23	7.01	0.0084	9.550	0.791	1.98	5.98	88.52308	14.67346
07.06.06	S12	192	1.92	657.80	52.0	17.23	7.01	0.0086	9.750	0.976	1.78	6.36	89.69764	9.285687
08.06.06	S13	216	1.96	660.99	53.0	17.23	7.01	0.0078	9.870	1.110	1.41	5.58	91.82956	20.34957
09.06.06	S14	240	1.95	666.85	54.0	17.23	7.01	0.0080	9.900	1.200	1.27	5.45	92.64319	22.26507

Run 4

pH 0.70

					Feed			Filtrate			Residue				Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ¹ (g/l)	Wt (g)	Cu (%)	Fe (%)	S (%)	Cu	Fe
09.06.06	S0	0			50.0	17.23	7.01	0.0000	0.000	0.000		17.23	7.01		0.000	0.000
09.06.06	S1	2	0.70	311.00	50.0	17.23	7.01	0.0070	2.140	0.265		10.94	5.27		36.512	24.820
09.06.06	S2	6	0.71	333.50	50.0	17.23	7.01	0.0084	3.590	0.462		14.01	5.88		18.690	16.158
10.06.06	S3	12	0.72	345.75	50.0	17.23	7.01	0.0082	4.270	0.513		11.38	5.93		33.945	15.449
10.06.06	S4	24	0.70	376.64	50.0	17.23	7.01	0.0074	5.390	0.617		10.79	6.12		37.377	12.676
10.06.06	S5															
11.06.06	S6															
12.06.06	S7	48	0.75	583.24	50.0	17.23	7.01	0.0076	6.750	0.721		7.38	5.66		57.193	19.191
13.06.06	S8	72	0.72	623.72	50.0	17.23	7.01	0.0080	7.640	0.795		5.12	5.16		70.302	26.330
14.06.06	S9	96	0.70	637.03	50.0	17.23	7.01	0.0080	8.280	0.921		4.15	5.13		75.928	26.805
15.06.06	S10	120	0.69	646.08	50.0	17.23	7.01	0.0074	8.570	1.043		3.51	5.97		79.611	14.821
16.06.06	S11	144	0.69	652.47	51.0	17.23	7.01	0.0072	8.980	1.230		2.97	5.79		82.748	17.471
17.06.06	S12	168	0.80	657.26	52.0	17.23	7.01	0.0076	8.790	1.230		2.64	6.24		84.684	10.974
18.06.06	S13	192	0.75	660.99	53.0	17.23	7.01	0.0070	9.400	1.400		2.19	6.04		87.318	13.899
19.06.06	S14	216	0.73	664.19	54.0	17.23	7.01	0.0078	9.680	1.480		1.87	5.83		89.147	16.857
	S15	240	0.71	666.85	55.0	17.23	7.01	0.0078	9.370	1.540		1.53	4.99		91.111	28.812

Run 6

pH 1.50, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Initial Ferric (Fe³⁺) iron conc.; 3 g.L⁻¹, Inoculum concentration 10 % v/v, Mixed mesophilic bacterial culture, 0K Basal salts growth medium (without ferrous iron)

					Feed		Filtrate				Residue			Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ⁺ (g/l)	Cu (%)	Fe (%)	S (%)	Cu	Fe
	S0	0			50.0	17.23	7.01	0.0000	0.000	0.000	17.23	7.01		0.000	0.000
26.08.06	S1	2	1.48	383.03	50.0	17.23	7.01	0.0080	5.280	5.240	9.42	6.91		45.304	1.445
26.08.06	S2	6	1.51	389.95	50.0	17.23	7.01	0.0078	5.640	5.320	8.52	6.72		50.538	4.181
26.08.06	S3	12	1.49	399.00	50.0	17.23	7.01	0.0080	6.120	5.500	7.37	5.90		57.230	15.887
27.08.06	S4	24	1.53	419.77	50.0	17.23	7.01	0.0080	6.850	5.480	5.88	6.08		65.893	13.272
27.08.06	S5	36	1.55	483.67	51.0	17.23	7.01	0.0078	7.230	5.260	4.95	6.93		71.257	1.169
28.08.06	S6	48	1.50	660.99	52.0	17.23	7.01	0.0084	7.640	4.470	3.74	6.33		78.290	9.700
29.08.06	S7	72	1.45	683.89	50.0	17.23	7.01	0.0078	8.450	6.010	3.07	6.24		82.165	10.967
30.08.06	S8	96	1.45	698.27	50.0	17.23	7.01	0.0076	8.450	6.080	2.34	5.78		86.443	17.580
31.08.06	S9	120	1.47	703.59	50.0	17.23	7.01	0.0090	8.600	6.280	1.94	5.41		88.743	22.884
01.09.06	S10	144	1.45	709.45	50.0	17.23	7.01	0.0084	8.340	6.050	1.03	5.20		94.004	25.815
02.09.06	S11	168	1.52	712.11	50.0	17.23	7.01	0.0086	8.880	6.420	1.41	5.23		91.807	25.324
03.09.06	S12	192	1.53	715.31	50.0	17.23	7.01	0.0082	9.390	6.970	1.13	4.28		93.425	38.940

Run 7Initial Ferric (Fe^{3+}) iron conc.; 3 g.L⁻¹

					Feed			Filtrate			Residue		Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ^I (g/l)	Cu (%)	Fe (%)	Cu	Fe
	S0	0			50.0	17.23	7.01	0.0000	0.000	0.000	17.23	7.01	0.000	0.000
26.08.06	S1	2	1.51	457.58	50.0	17.23	7.01	0.0076	5.240	0.000	8.12	5.50	52.877	21.541
26.08.06	S2	6	1.47	456.51	50.0	17.23	7.01	0.0078	5.620	0.000	7.40	5.80	57.073	17.283
26.08.06	S3	12	1.48	454.91	50.0	17.23	7.01	0.0080	5.710	0.000	6.83	5.60	60.353	20.136
27.08.06	S4	24	1.53	460.24	50.0	17.23	7.01	0.0072	6.780	0.000	5.46	5.87	68.294	16.299
27.08.06	S5	36	1.55	496.98	51.0	17.23	7.01	0.0074	7.250	0.000	4.39	5.65	74.509	19.359
28.08.06	S6	48	1.48	664.72	52.0	17.23	7.01	0.0080	7.850	0.000	3.51	5.61	79.635	20.027
29.08.06	S7	72	1.45	689.79	50.0	17.23	7.01	0.0074	8.370	0.000	2.63	5.10	84.748	27.294
30.08.06	S8	96	1.42	703.59	50.0	17.23	7.01	0.0074	8.570	0.000	2.10	5.33	87.838	24.002
31.08.06	S9	120	1.48	703.59	50.0	17.23	7.01	0.0076	9.180	0.000	1.65	5.22	90.447	25.468
01.09.06	S10	144	1.45	709.45	50.0	17.23	7.01	0.0084	10.340	0.000	1.38	5.47	91.997	21.945
02.09.06	S11	168	1.47	709.45	50.0	17.23	7.01	0.0084	9.890	0.000	1.17	5.89	93.206	15.970
03.09.06	S12	192	1.45	715.31	50.0	17.23	7.01	0.0080	10.470	0.000	0.95	6.25	94.487	10.793

Run 8

pH 1.50, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Initial Ferric (Fe³⁺) iron conc.; 3 g.L⁻¹, sterile ferric iron leaching

					Feed			Filtrate			Residue			Leach Efficiency (%)	
Sample	Sample	Leach	pH	Redox	Wt	Cu	Fe	Vol.	Cu ²⁺	Fe ^I	Cu	Fe	S	Cu	Fe
Date	Code	Time(hrs)		(mV)	(g)	(%)	(%)	(L)	(g/l)	(g/l)	(%)	(%)	(%)		
	S0	0		411.78	50.0	17.23	7.01	0.0000	0.000	0.000	17.23	7.01		0.000	0.000
11.09.06	S1	2	1.51	375.04	50.0	17.23	7.01	0.0080	4.950	6.170	9.07	6.48		47.366	7.576
11.09.06	S2	6	1.50	377.70	50.0	17.23	7.01	0.0080	4.750	5.770	8.95	6.80		48.044	3.007
11.09.06	S3	12	1.54	380.36	50.0	17.23	7.01	0.0078	5.080	5.850	9.06	6.85		47.441	2.328
12.09.06	S4	24	1.57	383.56	50.0	17.23	7.01	0.0084	5.410	6.240	8.41	6.11		51.191	12.849
12.09.06	S5	36	1.53	388.35	51.0	17.23	7.01	0.0088	0.000	0.000	7.84	6.63		54.492	5.462
13.09.06	S6	48	1.51	388.88	52.0	17.23	7.01	0.0080	6.120	6.320	6.45	5.72		62.589	18.464
14.09.06	S7	72	1.53	393.14	50.0	17.23	7.01	0.0082	6.120	6.170	6.63	6.47		61.497	7.714
15.09.06	S8		0.00	0.00	50.0	17.23	7.01	0.0000	0.000	0.000	0.00	0.00			
16.09.06	S9	120	1.45	403.26	50.0	17.23	7.01	0.0090	7.530	6.450	4.21	5.49		75.557	21.701
17.09.06	S10	144	1.46	408.05	50.0	17.23	7.01	0.0082	7.480	6.170	3.64	5.98		78.880	14.672
18.09.06	S11	168	1.47	413.91	50.0	17.23	7.01	0.0082	7.880	6.500	3.45	6.32		79.960	9.787
19.09.06	S12	192	0.00	0.00	50.0	17.23	7.01	0.0000	0.000	0.000	0.00	0.00		100.000	100.000

Run 9pH 1.50, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Particle size: – 32 µm

					Feed			Filtrate			Residue			Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ⁺ (g/l)	Cu (%)	Fe (%)	S (%)	Cu	Fe
	S0	0			50.0	10.06	4.80348	0.0000	0.000	0.000	10.06	4.80		0.000	0.000
26.09.06	S1	2	1.49	312.74	50.0	10.06	4.80348	0.0084	2.540	0.392	6.48	4.55		35.551	5.317
26.09.06	S2	6	1.52	322.32	50.0	10.06	4.80348	0.0084	2.630	0.384	5.97	4.70		40.671	2.100
26.09.06	S3	12	1.52	343.09	50.0	10.06	4.80348	0.0080	3.050	0.378	5.38	4.30		46.551	10.518
27.09.06	S4	24	1.49	479.41	50.0	10.06	4.80348	0.0080	3.960	0.333	3.86	4.52		61.600	5.996
27.09.06	S5	36	1.55	590.17	51.0	10.06	4.80348	0.0080	4.870	0.429	2.78	4.52		72.322	5.804
28.09.06	S6	48	1.47	620.52	52.0	10.06	4.80348	0.0086	5.140	0.499	2.16	4.47		78.499	6.903
29.09.06	S7	72	1.46	645.45	50.0	10.06	4.80348	0.0080	5.660	0.698	1.58	4.31		84.300	10.341
30.09.06	S8	96	1.45	662.59	50.0	10.06	4.80348	0.0086	5.810	0.813	1.28	4.21		87.300	12.308
01.10.06	S9	120	1.46	671.11	50.0	10.06	4.80348	0.0082	5.740	0.888	1.05	4.01		89.573	16.483
02.09.06	S10	144	1.46	682.29	50.0	10.06	4.80348	0.0084	5.580	0.963	0.98	3.54		90.242	26.286
03.09.06	S11	168	1.46	688.15	50.0	10.06	4.80348	0.0082	6.160	1.113	0.75	3.58		92.542	25.406

Run 10

pH 1.50, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Initial Ferric (Fe³⁺) iron conc.; 9 g.L⁻¹, Inoculum concentration 10 % v/v, Mixed mesophilic bacterial culture, 0K Basal salts growth medium (without ferrous iron).

					Feed			Filtrate			Residue		Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ⁺ (g/l)	Cu (%)	Fe (%)	Cu	Fe
	S0	0			50.0	17.23	7.01	0.0000	0.000	0.000	17.23	7.01	0.000	0.000
26.09.06	S1	2	1.52	474.08	50.0	17.23	7.01	0.0088	4.706	13.880	7.14	5.49	58.569	21.730
26.09.06	S2	6	1.53	471.62	50.0	17.23	7.01	0.0086	5.083	13.130	6.38	5.80	62.991	17.255
26.09.06	S3	12	1.49	466.10	50.0	17.23	7.01	0.0084	5.773	14.740	5.75	5.65	66.611	19.395
27.09.06	S4	24	1.46	463.43	50.0	17.23	7.01	0.0086	6.258	14.190	4.52	5.51	73.742	21.389
27.09.06	S5	36	1.55	473.55	51.0	17.23	7.01	0.0084	6.801	14.090	3.94	5.88	77.123	16.141
28.09.06	S6	48	1.55	545.44	52.0	17.23	7.01	0.0088	7.096	14.510	3.16	6.29	81.672	10.292
29.09.06	S7	72	1.46	690.28	50.0	17.23	7.01	0.0086	7.731	15.230	2.32	6.38	86.560	8.984
30.09.06	S8	96	1.45	709.98	50.0	17.23	7.01	0.0086	8.190	14.710	1.95	6.95	88.702	0.890
01.10.06	S9	120	1.48	713.71	50.0	17.23	7.01	0.0084	8.234	13.990	1.63	7.81	90.561	-11.402
02.09.06	S10	144	1.46	720.63	50.0	17.23	7.01	0.0090	8.027	13.280	1.44	8.02	91.629	-14.385
03.09.06	S11	168	1.46	721.16	50.0	17.23	7.01	0.0084	8.388	13.810	1.10	8.56	93.597	-22.179

Run 11pH 1.50, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Particle size: – 53 + 32 µm

					Feed			Filtrate			Residue			Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ^t (g/l)	Cu (%)	Fe (%)	S (%)	Cu	Fe
	S0	0			50.0	19.55	5.89345	0.0000	0.000	0.000	19.55	5.89		0.000	0.000
07.10.06	S1	2	1.53	313.27	50.0	19.55	5.89345	0.0082	2.210	0.231	13.76	5.52		29.619	6.321
07.10.06	S2	6	1.51	318.06	50.0	19.55	5.89345	0.0080	2.970	0.257	13.53	5.63		30.771	4.424
07.10.06	S3	12	1.56	321.26	50.0	19.55	5.89345	0.0080	3.470	0.276	13.34	5.77		31.767	2.108
08.10.06	S4	24	1.62	337.23	50.0	19.55	5.89345	0.0082	4.370	0.302	11.84	5.73		39.441	2.841
08.10.06	S5	36	1.57	482.07	51.0	19.55	5.89345	0.0080	5.330	0.271	9.27	5.80		52.578	1.589
09.10.06	S6	48	1.47	591.23	52.0	19.55	5.89345	0.0084	6.900	0.331	6.39	6.00		67.318	-1.874
10.10.06	S7	72	1.45	627.44	50.0	19.55	5.89345	0.0080	8.210	0.406	4.22	5.73		78.414	2.736
11.10.06	S8	96	1.48	643.95	50.0	19.55	5.89345	0.0082	8.570	0.532	3.00	6.04		84.655	-2.533
12.10.06	S9	120	1.46	656.20	50.0	19.55	5.89345	0.0080	9.200	0.633	2.52	5.90		87.116	-0.096
13.10.06	S10	144	1.45	666.85	50.0	19.55	5.89345	0.0082	7.660	0.819	1.99	5.66		89.839	3.969
14.10.06	S11	168	1.45	675.37	50.0	19.55	5.89345	0.0088	7.320	0.931	1.64	5.49		91.593	6.907

Run 12pH 1.50, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Particle size: – 75 + 53 µm

					Feed			Filtrate				Residue		Leach Efficiency	
														($\%$)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ⁺ (g/l)	Fe ²⁺ (g/l)	Cu (%)	Fe (%)	Cu	Fe
	S0	0			50.0	26.10	7.38235	0.0000	0.000	0.000		26.10	7.38	0.000	0.000
07.10.06	S1	2	1.53	317.53	50.0	26.10	7.38235	0.0084	2.120	0.219		13.18	5.19	49.486	29.704
07.10.06	S2	6	1.53	321.26	50.0	26.10	7.38235	0.0084	2.470	0.242		12.78	5.71	51.026	22.708
07.10.06	S3	12	1.54	325.52	50.0	26.10	7.38235	0.0086	2.870	0.266		12.72	5.58	51.261	24.395
08.10.06	S4	24	1.62	335.10	50.0	26.10	7.38235	0.0086	3.840	0.313		12.96	5.82	50.360	21.159
08.10.06	S5	36	1.63	400.07	51.0	26.10	7.38235	0.0084	5.530	0.329		12.26	6.22	53.034	15.700
09.10.06	S6	48	1.58	579.52	52.0	26.10	7.38235	0.0086	7.150	0.292		9.69	5.81	62.868	21.233
10.10.06	S7	72	1.53	623.18	50.0	26.10	7.38235	0.0088	9.120	0.413		6.93	5.78	73.458	21.660
11.10.06	S8	96	1.50	644.48	50.0	26.10	7.38235	0.0082	8.660	0.564		5.21	6.15	80.026	16.712
12.10.06	S9	120	1.47	657.80	50.0	26.10	7.38235	0.0082	10.050	0.602		4.37	6.80	83.268	7.941
13.10.06	S10	144	1.45	666.32	50.0	26.10	7.38235	0.0086	11.120	0.713		3.58	6.92	86.283	6.211
14.10.06	S11	168	1.45	673.24	50.0	26.10	7.38235	0.0084	11.450	0.831		2.93	6.45	88.766	12.591

Run 13pH 1.50, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Particle size: – 106 + 75 µm

					Feed			Filtrate			Residue		Leach Efficiency	
													(%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ^t (g/l)	Cu (%)	Fe (%)	Cu	Fe
	S0	0			50.0	30.56	9.94175	0.0000	0.000	0.000	30.56	9.94	0.000	0.000
17.10.06	S1	2	1.48	354.27	50.0	30.56	9.94175	0.0086	2.410	0.240	11.99	5.89	60.764	40.728
17.10.06	S2	6	1.46	367.58	50.0	30.56	9.94175	0.0086	3.090	0.224	11.18	5.89	63.411	40.780
17.10.06	S3	12	1.55	374.51	50.0	30.56	9.94175	0.0088	3.540	0.222	10.87	7.76	64.419	21.941
18.10.06	S4	24	1.55	420.30	50.0	30.56	9.94175	0.0086	5.590	0.249	11.53	7.50	62.260	24.585
18.10.06	S5	36	1.60	577.92	51.0	30.56	9.94175	0.0082	7.400	0.242	11.15	8.28	63.533	16.750
19.10.06	S6	48	1.46	601.35	52.0	30.56	9.94175	0.0082	8.450	0.282	10.44	9.74	65.850	2.064
20.10.06	S7	72	1.53	619.46	50.0	30.56	9.94175	0.0082	9.330	0.309	8.97	11.88	70.666	-19.458
21.10.06	S8	96	1.51	635.96	50.0	30.56	9.94175	0.0080	10.030	0.339	7.60	10.71	75.126	-7.694
22.10.06	S9	120	1.51	645.02	50.0	30.56	9.94175	0.0080	10.280	0.376	5.86	12.49	80.834	-25.610
23.10.06	S10	144	1.47	650.34	50.0	30.56	9.94175	0.0080	11.600	0.286	5.10	13.93	83.305	-40.095
24.10.06	S11	168	1.47	655.67	50.0	30.56	9.94175	0.0082	12.050	0.456	4.39	12.26	85.640	-23.362

Run 14pH 1.50, Temp., 30 °C, Solids concentration 50 g.L⁻¹

					Feed			Filtrate			Residue		Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ^I (g/l)	Cu (%)	Fe (%)	Cu	Fe
	S0	0			50.0	18.40	6.35164	0.0000	0.000	0.000	18.40	6.35	0.000	0.000
17.10.06	S1	2	1.48	321.26	50.0	18.40	6.35164	0.0086	2.080	0.221	10.69	4.45	41.905	29.879
17.10.06	S2	6	1.45	332.44	50.0	18.40	6.35164	0.0084	2.920	0.270	10.76	4.76	41.547	25.109
17.10.06	S3	12	1.55	345.75	50.0	18.40	6.35164	0.0090	3.210	0.253	9.13	4.57	50.389	28.123
18.10.06	S4	24	1.55	392.08	50.0	18.40	6.35164	0.0084	4.180	0.287	8.27	4.18	55.039	34.244
18.10.06	S5	36	1.54	584.31	51.0	18.40	6.35164	0.0084	5.120	0.290	7.56	4.76	58.935	25.035
19.10.06	S6	48	1.45	601.35	52.0	18.40	6.35164	0.0086	6.130	0.352	6.57	4.60	64.280	27.547
20.10.06	S7	72	1.52	624.25	50.0	18.40	6.35164	0.0086	6.860	0.369	5.21	4.39	71.692	30.858
21.10.06	S8	96	1.50	641.82	50.0	18.40	6.35164	0.0084	6.860	0.411	4.58	4.48	75.105	29.536
22.10.06	S9	120	1.48	647.68	50.0	18.40	6.35164	0.0080	7.790	0.511	3.91	4.32	78.757	32.031
23.10.06	S10	144	1.45	658.33	50.0	18.40	6.35164	0.0086	7.980	0.586	3.61	4.23	80.402	33.403
24.10.06	S11	168	1.45	664.72	50.0	18.40	6.35164	0.0086	8.170	0.648	3.27	4.12	82.236	35.207

Run 15pH 1.50, Temp., 40 °C, Solids concentration 50 g.L⁻¹

					Feed			Filtrate			Residue		Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ^I (g/l)	Cu (%)	Fe (%)	Cu	Fe
	S0	0			50.0	17.76	6.46363	0.0000	0.000	0.000	17.76	6.46	0.000	0.000
17.10.06	S1	2	1.53	323.92	50.0	17.76	6.46363	0.0078	3.100	0.228	11.69	5.41	34.192	16.298
17.10.06	S2	6	1.51	331.37	50.0	17.76	6.46363	0.0080	3.380	0.255	10.81	5.30	39.141	18.036
17.10.06	S3	12	1.53	342.56	50.0	17.76	6.46363	0.0082	3.850	0.245	9.53	4.99	46.351	22.765
18.10.06	S4	24	1.53	420.30	50.0	17.76	6.46363	0.0082	5.300	0.531	7.77	5.13	56.252	20.643
18.10.06	S5	36	1.55	584.31	51.0	17.76	6.46363	0.0080	6.740	0.217	5.23	5.11	70.567	21.019
19.10.06	S6	48	1.45	621.05	52.0	17.76	6.46363	0.0080	7.360	0.339	3.91	4.54	78.013	29.713
20.10.06	S7	72	1.45	647.15	50.0	17.76	6.46363	0.0080	8.530	0.474	2.92	5.50	83.569	14.961
21.10.06	S8	96	1.48	660.99	50.0	17.76	6.46363	0.0082	8.960	0.569	2.04	4.89	88.522	24.380
22.10.06	S9	120	1.48	670.58	50.0	17.76	6.46363	0.0076	9.580	0.703	1.48	4.83	91.656	25.270
23.10.06	S10	144	1.45	680.16	50.0	17.76	6.46363	0.0078	9.500	0.811	1.13	4.72	93.621	26.970
24.10.06	S11	168	1.45	686.55	50.0	17.76	6.46363	0.0076	9.610	0.905	0.91	4.75	94.874	26.572

Run 16pH 1.50, Temp., 25 °C, Solids concentration 50 g.L⁻¹

					Feed			Filtrate			Residue		Leach Efficiency	
													($\%$)	
Sample Date	Sample Code	Leach Time(hrs)	pH	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe ³⁺ (g/l)	Cu (%)	Fe (%)	Cu	Fe
	S0	0			50.0	18.72	6.88749	0.0000	0.000	0.000	18.72	6.89	0.000	0.000
17.10.06	S1	2	1.49	315.40	50.0	18.72	6.88749	0.0086	2.390	0.200	11.17	5.34	40.357	22.400
17.10.06	S2	6	1.51	320.19	50.0	18.72	6.88749	0.0084	2.850	0.220	10.78	5.26	42.431	23.599
17.10.06	S3	12	1.53	326.58	50.0	18.72	6.88749	0.0086	3.180	0.283	9.61	5.02	48.655	27.137
18.10.06	S4	24	1.45	334.04	50.0	18.72	6.88749	0.0088	3.780	0.236	8.40	5.15	55.144	25.258
18.10.06	S5	36	1.55	351.08	51.0	18.72	6.88749	0.0084	4.380	0.256	6.18	4.20	67.012	39.028
19.10.06	S6	48	1.55	408.05	52.0	18.72	6.88749	0.0084	5.180	0.387	7.26	5.27	61.214	23.550
20.10.06	S7	72	1.55	585.91	50.0	18.72	6.88749	0.0084	5.970	0.233	6.54	4.75	65.042	31.087
21.10.06	S8	96	1.51	614.13	50.0	18.72	6.88749	0.0086	6.730	0.315	5.21	5.39	72.170	21.780
22.10.06	S9	120	1.53	628.51	50.0	18.72	6.88749	0.0084	7.180	0.347	4.31	4.80	76.983	30.379
23.10.06	S10	144	1.50	638.09	50.0	18.72	6.88749	0.0082	7.340	0.404	3.98	4.72	78.720	31.513
24.10.06	S11	168	1.49	645.02	50.0	18.72	6.88749	0.0076	7.770	0.459	3.77	4.95	79.834	28.123

Run 17

Sterile and non-oxidative acid leach, pH 1.50, Temp., 35 °C, Solids concentration 50 g.L⁻¹

					Feed			Filtrate			Residue		Leach Efficiency (%)	
Sample Date	Sample Code	Leach Time(hrs)	Ph	Redox (mV)	Wt (g)	Cu (%)	Fe (%)	Vol. (L)	Cu ²⁺ (g/l)	Fe' (g/l)	Cu (%)	Fe (%)	Cu	Fe
22.05.06	S0	0	1.45	200.91	50.0	17.23	7.01	0.0000	0.000	0.000	17.23	7.01	0	0
22.05.06	S1	2	1.55	246.71	50.0	17.23	7.01	0.0068	1.390	0.216	14.98	6.36	13.08549	9.235926
22.05.06	S2	6	1.46	265.88	50.0	17.23	7.01	0.0070	1.450	0.248	13.16	5.71	23.64892	18.55637
22.05.06	S3	12	1.52	277.59	50.0	17.23	7.01	0.0072	1.570	0.281	13.93	6.02	19.13635	14.05558
23.05.06	S4	24	1.47	283.45	50.0	17.23	7.01	0.0070	1.840	0.325	14.06	6.15	18.37484	12.23567
23.05.06	S5	36	1.48	289.84	50.0	17.23	7.01	0.0070	2.080	0.347	14.51	6.48	15.80517	7.578839
24.05.06	S6	48	1.52	294.63	50.0	17.23	7.01	0.0070	2.320	0.366	13.80	6.36	19.90827	9.306294
25.05.06	S7	72	1.54	300.49	50.0	17.23	7.01	0.0066	2.770	0.398	11.71	5.66	32.01709	19.28278
26.05.06	S8	96	1.50	306.35	50.0	17.23	7.01	0.0068	3.250	0.422	12.08	6.09	29.90543	13.16752
27.05.06	S9	120	1.53	320.19	50.0	17.23	7.01	0.0068	3.700	0.430	9.77	5.37	43.32197	23.40741
28.05.06	S10	144	1.54	346.82	50.0	17.23	7.01	0.0066	4.020	0.439	10.38	5.94	39.76626	15.23817
29.05.06	S11	168	1.51	362.79	51.0	17.23	7.01	0.0068	4.180	0.441	9.98	5.99	42.07417	14.5324
30.05.06	S12	192	1.46	371.31	52.0	17.23	7.01	0.0068	4.100	0.422	9.27	5.48	46.19189	21.81099
31.05.06	S13	216	1.46	375.04	53.0	17.23	7.01	0.0070	4.340	0.442	0.00	0.00		
01.06.06	S14	240	1.48	376.64	54.0	17.23	7.01	0.0072	4.444	0.454	9.19	5.71	46.66218	18.58658

Truncated table for part of a batch off-gas data for about 24 hours of data logging for Run 1,
pH 1.5, Temp., 35 °C, Solids concentration 50 g.L⁻¹, Inoculum concentration 10 % v/v, Mixed mesophilic bacterial culture, 0K Basal salts
growth medium (without ferrous iron)

hrs	dT(hrs)	δT	rO2	rCO2	dCx=rCO2δT	Cx	Mu	qO2	$dCx = (rCO2(1) + rCO2(2))/2 \cdot \Delta t$	$Cx = \Sigma(rCO2 \cdot \Delta t)$	Yo/x = rx/Ro2	I/Y	I/Mu
13.82	0.00	0.50	1.701592	-0.13486	-0.06743	0.780477	-0.17279		-0.06766	0	-0.07926	-12.6174	-5.78728
14.32	0.50	0.50	1.615977	-0.13579	-0.06789	0.713046	-0.19043	2.2663	-0.06809	-0.06766	-0.08403	-11.9007	-5.25114
14.82	1.00	0.50	1.544611	-0.13659	-0.06829	0.645152	-0.21171	2.394181	-0.05778	-0.13576	-0.08843	-11.3086	-4.72337
15.32	1.50	0.50	1.470154	-0.09454	-0.04727	0.576858	-0.16389	2.548553	-0.03875	-0.19354	-0.06431	-15.5504	-6.10168
15.82	2.00	0.50	1.436334	-0.06045	-0.03023	0.529588	-0.11415	2.712173	-0.02719	-0.23229	-0.04209	-23.7606	-8.76072
16.82	3.00	0.00	1.372254	-0.03323	0	0.475209	-0.06993	2.887686	0	-0.27986	-0.02422	-41.2942	-14.3001
16.82	3.00	0.57	1.372254	-0.03323	-0.01883	0.475209	-0.06993	2.887686	-0.0136	-0.27986	-0.02422	-41.2942	-14.3001
17.38	3.57	0.50	1.348583	-0.01478	-0.00739	0.456378	-0.03239	2.954969	-0.00617	-0.29346	-0.01096	-91.228	-30.8727
17.88	4.07	0.50	1.307125	-0.00991	-0.00496	0.448987	-0.02208	2.911278	-0.00368	-0.29964	-0.00758	-131.847	-45.2884
18.38	4.57	0.50	1.322711	-0.00479	-0.00239	0.44403	-0.01079	2.97888	-0.00118	-0.30331	-0.00362	-276.18	-92.7126
18.88	5.07	0.50	1.295473	8.09E-05	4.04E-05	0.441635	0.000183	2.933358	-0.00031	-0.30449	6.24E-05	16016.16	5460.009
19.38	5.57	0.50	1.238124	-0.0013	-0.00065	0.441675	-0.00295	2.803244	0.001318	-0.3048	-0.00105	-951.701	-339.5
19.88	6.07	0.50	1.311432	0.006575	0.003287	0.441025	0.014908	2.9736	0.001474	-0.30348	0.005013	199.4669	67.07927
20.38	6.57	0.50	1.238286	-0.00068	-0.00034	0.444312	-0.00153	2.786972	0.001071	-0.302	-0.00055	-1824.66	-654.712
20.88	7.07	0.50	1.29671	0.004961	0.002481	0.443973	0.011175	2.920697	0.002593	-0.30093	0.003826	261.3646	89.48706
21.38	7.57	0.50	1.296861	0.005412	0.002706	0.446454	0.012123	2.904805	0.003719	-0.29834	0.004173	239.6109	82.48779
21.88	8.07	0.50	1.255224	0.009465	0.004732	0.44916	0.021072	2.794604	0.005126	-0.29462	0.00754	132.6226	47.45666
22.38	8.57	0.50	1.212911	0.01104	0.00552	0.453892	0.024324	2.672244	0.006261	-0.28949	0.009102	109.8616	41.1121
22.88	9.07	0.50	1.213697	0.014002	0.007001	0.459412	0.030478	2.641846	0.006775	-0.28323	0.011537	86.6792	32.81009
23.38	9.57	0.50	1.156503	0.013097	0.006549	0.466413	0.028081	2.479566	0.005803	-0.27646	0.011325	88.30147	35.61166
23.88	10.07	0.50	1.112991	0.010114	0.005057	0.472962	0.021385	2.353236	0.006924	-0.27066	0.009088	110.0405	46.76136
24.38	10.57	0.50	1.114934	0.017581	0.00879	0.478019	0.036778	2.332403	0.008951	-0.26373	0.015768	63.41859	27.19023
24.88	11.07	0.50	1.086617	0.018225	0.009113	0.486809	0.037438	2.232119	0.009573	-0.25478	0.016773	59.62108	26.71053
25.38	11.57	0.50	1.087082	0.020068	0.010034	0.495922	0.040467	2.192042	0.009558	-0.24521	0.018461	54.16859	24.71147
25.88	12.07	0.50	1.072351	0.018162	0.009081	0.505956	0.035896	2.119454	0.010903	-0.23565	0.016937	59.04347	27.85787

26.38	12.57	0.50	1.116966	0.02545	0.012725	0.515037	0.049414	2.168709	0.013489	-0.22475	0.022785	43.88863	20.23721
26.88	13.07	0.50	1.132011	0.028506	0.014253	0.527762	0.054013	2.144926	0.015007	-0.21126	0.025182	39.71161	18.51421
27.38	13.57	0.50	1.132811	0.031524	0.015762	0.542015	0.05816	2.089998	0.016117	-0.19625	0.027828	35.93526	17.19392
27.88	14.07	0.50	1.147416	0.032942	0.016471	0.557777	0.05906	2.057122	0.017539	-0.18013	0.02871	34.83102	16.93192
28.38	14.57	0.50	1.148512	0.037215	0.018608	0.574248	0.064807	2.000027	0.020601	-0.16259	0.032403	30.86152	15.43055
28.88	15.07	0.50	1.207545	0.045191	0.022595	0.592856	0.076226	2.036827	0.022126	-0.14199	0.037424	26.72106	13.11897
29.38	15.57	0.50	1.235512	0.043315	0.021657	0.615451	0.070379	2.007489	0.023979	-0.11987	0.035058	28.52393	14.20876
29.88	16.07	0.50	1.237911	0.0526	0.0263	0.637109	0.082561	1.943014	0.025684	-0.09589	0.042491	23.53428	12.11226
30.38	16.57	0.50	1.294194	0.050137	0.025069	0.663409	0.075575	1.950824	0.026844	-0.0702	0.03874	25.81312	13.23191
30.88	17.07	0.50	1.310242	0.057239	0.02862	0.688477	0.083139	1.903101	0.02911	-0.04336	0.043686	22.89064	12.02807
31.38	17.57	0.50	1.367691	0.0592	0.0296	0.717097	0.082555	1.90726	0.031343	-0.01425	0.043284	23.10304	12.1132
31.88	18.07	0.50	1.426443	0.066173	0.033086	0.746697	0.08862	1.910338	0.034309	0.017093	0.04639	21.55641	11.28408
32.38	18.57	0.50	1.42764	0.071065	0.035533	0.779783	0.091135	1.830817	0.036058	0.051403	0.049778	20.08914	10.97277
32.88	19.07	0.50	1.584844	0.073168	0.036584	0.815316	0.089742	1.943841	0.040087	0.087461	0.046168	21.66021	11.14299
33.38	19.57	0.50	1.602723	0.087181	0.04359	0.8519	0.102337	1.881351	0.042733	0.127548	0.054395	18.38392	9.771659
33.88	20.07	0.50	1.6303	0.08375	0.041875	0.89549	0.093524	1.820567	0.044274	0.170281	0.051371	19.46626	10.69241
34.38	20.57	0.50	1.718227	0.093348	0.046674	0.937365	0.099585	1.833039	0.047432	0.214556	0.054328	18.40675	10.04166
34.88	21.07	0.50	1.733251	0.096379	0.04819	0.984039	0.097942	1.761363	0.051062	0.261987	0.055606	17.98369	10.21009
35.38	21.57	0.50	1.85438	0.10787	0.053935	1.032229	0.104502	1.796482	0.054078	0.31305	0.058171	17.19082	9.569157
35.88	22.07	0.50	1.85448	0.108443	0.054222	1.086164	0.09984	1.707366	0.057544	0.367128	0.058476	17.10094	10.01598
36.38	22.57	0.50	1.929812	0.121735	0.060867	1.140385	0.106749	1.692245	0.060995	0.424672	0.063081	15.8526	9.367794
36.88	23.07	0.50	2.016277	0.122244	0.061122	1.201253	0.101764	1.678479	0.063369	0.485667	0.060628	16.49391	9.826702
37.38	23.57	0.50	1.989855	0.13123	0.065615	1.262375	0.103955	1.576279	0.061307	0.549036	0.06595	15.16306	9.619531
37.88	24.07	0.50	1.654625	0.113997	0.056998	1.32799	0.085841	1.245962	0.057059	0.610342	0.068896	14.5147	11.64939
38.38	24.57	0.43	1.554027	0.114241	0.049504	1.384988	0.082485	1.122051	0.048635	0.667402	0.073513	13.60308	12.12341
38.82	25.00	0.50	1.567384	0.110226	0.055113	1.434492	0.07684	1.09264	0.057186	0.716036	0.070325	14.21968	13.01406
39.32	25.50	0.50	1.598301	0.118517	0.059258	1.489606	0.079562	1.07297	0.059879	0.773222	0.074152	13.48589	12.56875
39.82	26.00	0.50	1.598969	0.120997	0.060499	1.548864	0.07812	1.032349	0.062042	0.8331	0.075672	13.2149	12.8008
40.32	26.50	0.50	1.586194	0.127172	0.063586	1.609363	0.07902	0.985604	0.063046	0.895143	0.080174	12.47281	12.65499
40.82	27.00	0.50	1.614372	0.125012	0.062506	1.672949	0.074726	0.964986	0.063065	0.958189	0.077437	12.91369	13.38226
41.32	27.50	0.50	1.686879	0.127248	0.063624	1.735455	0.073323	0.972009	0.062145	1.021254	0.075434	13.25657	13.63831

