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Ad Majorem Dei Gloriam

**A Preliminary Investigation of the Ferric Leaching of a Mixed Sulphide
Copper Concentrate at Controlled Redox Potentials.**

by

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Samantha (smile) Govender, Amanda Furamera, Bryne Rwodzi, Njodzi Zizhou, Mukayi Mutsago, Munya and Ku, this one is for you too

Dedication

To my parents who have shown me the power of love and the value of perseverance.

Especially to the memory of my dad Gordian who passed away on 10th September 1999.

To my mom Lucy for all you have and continue to be.

"Zvinhukwazvo nenyasha zvichanditevera mazuva ose oupenyu wangu."

"Ndichagara mumba maJehova nemisi isingaperi." {Mapisarema 23:6}

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Summary

Current work in the Department of Chemical Engineering at the University of Cape Town is looking at understanding the sub-processes of the bioleaching of chalcopyrite rich concentrates. This thesis is part of the greater study and looks into understanding the ferric leaching sub-process by establishing an effective way of measuring the rate of the chemical leach process.

In relation to that of other sulphides, the leaching of chalcopyrite is slow and incomplete and there is agreement that this is a result of a passivating product film (Dutrillac, 1969; Munoz *et al.*, 1979; Ammou-Chokrum *et al.*, 1979). Therefore the emphasis of recent research has been focussed on overcoming the effect of passivation

A review of the literature was undertaken to evaluate the current understanding of the chemical ferric sulphate leaching of chalcopyrite. To date, a significant portion of previous work has been performed under batch conditions in which conditions of pH and redox potential varied during the experiment. There has been little consideration of the potential differences between suspended particles and the solution. However it is possible to overcome this by conducting experiments under constant potential. A reliable method that used potassium permanganate to maintain the solution potential first presented by Kametani and Aoki (1985) was used. The potassium permanganate allowed for the regeneration of the ferric ions by re-oxidising the ferrous ions produced from oxidation of the sulphides, and this allowed the maintenance of a constant redox potential.

This work was aimed at establishing the method developed by Kametani and Aoki (1985) for use in the research group and then applying it at conditions of relevance to bioleaching: temperatures 35 °C and 70 °C, pH = 1.5 and total iron concentration of 10 g.l⁻¹ as reported for the BIOX[®] process by Dew *et al.* (1997). Holmes *et al.* (1999) also reported conditions for bioleaching of pyrite of 9 g.l⁻¹ of total iron, redox potential of 650 mV (SCE), pH of 1.6 and temperature of 35 °C.

Kametani and Aoki (1985) however did not conclusively prove their method *viz.* critical aspects such as showing that potassium permanganate reacted stoichiometrically and rapidly

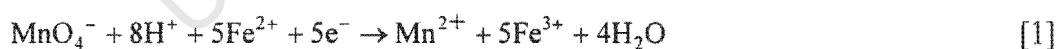
with ferrous ion and it did not react with the concentrate. This report set out to conclusively test these aspects.

This study was conducted using a mixed sulphide copper flotation concentrate which analysed 80.8 % chalcopyrite, 13.1 % pyrite and 1.3 % sphalerite. A particle size fraction of +75 μm - 106 μm was used in all experiments. The locking characteristics of the concentrate showed that 51 % of the grains were composed solely of chalcopyrite, with 20 % being composed of a mixture of the three minerals previously mentioned.

The redox potential was controlled by addition of potassium permanganate using an automatic titration unit. Samples were withdrawn at intervals for copper analysis using atomic adsorption spectroscopy (AAS).

Preliminary results showed a very high rate of copper extraction in the initial period of the leaching. This behaviour was attributed to attached fines material. The concentrate was pre-treated using an ultrasonic bath and subsequently showed leaching more representative of the size fraction of interest.

An important aspect of this work was to validate the use of potassium permanganate for maintenance of a constant redox potential. Experimental determination proved that the stoichiometry of the ferrous ion oxidation by potassium permanganate is correctly represented as:



This stoichiometry was shown to be unaffected by changes in temperature (35 °C and 70 °C) and pH (1.0 – 2.0). The reaction was observed to occur very rapidly as the potassium permanganate decolourised immediately upon addition to the leach medium. The purple permanganate ion (MnO_4^-) was reduced to the pink (colourless in dilute solutions) manganese (II) ion (Mn^{2+}). The potassium permanganate was also shown to not directly oxidise the mineral.

Having established the viability of the use of potassium permanganate, preliminary experiments at different redox potentials was undertaken to determine the rate of chemical leaching. There was observed a strong dependence of the rate on redox potential. Figure 1

shows a comparison of the ferrous ion generation rate at 35 °C and 70 °C. The rate of ferrous ion generation was calculated from the amount of potassium permanganate added to re-oxidise it back to ferric ions. This was on the premise that leaching involved the ferric attack of the mineral and that the ferric ions were reduced to ferrous ions. The iron content of the mineral would also have been released as ferrous ion but was not significant enough to alter the total iron concentration of the leach medium. There appears to be regions of enhanced ferrous ion generation, namely 430 mV – 480 mV and between 560 mV and 600 mV.

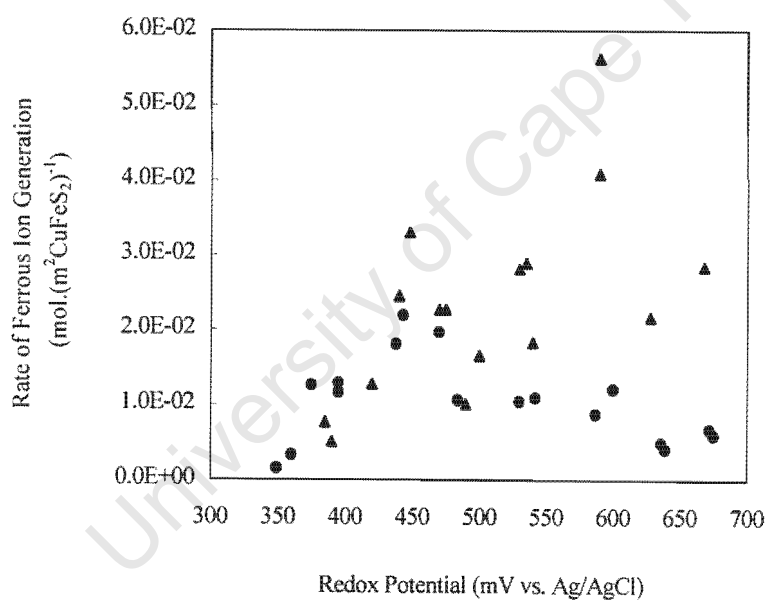


Figure 1 Comparison of Ferrous Ion Generation at 35 °C and 70 °C
 [▲] 70 °C, [●] 35 °C, Total iron = 10 g.t⁻¹, pH = 1.5

The amount of copper extracted was also monitored throughout the duration of the experiments and Figure 2 shows a comparison of the copper extraction rates at 35 °C and 70 °C. The higher temperature was observed to enhance copper extraction. Above 600 mV, the rate of copper extraction decreased, however the rate of ferrous ion generation shown in

Figure 1, increased. This was an indication that the leaching of chalcopyrite alone was not the source of the ferrous ion but one of the other mineral aggregates of the concentrate was undergoing leaching.

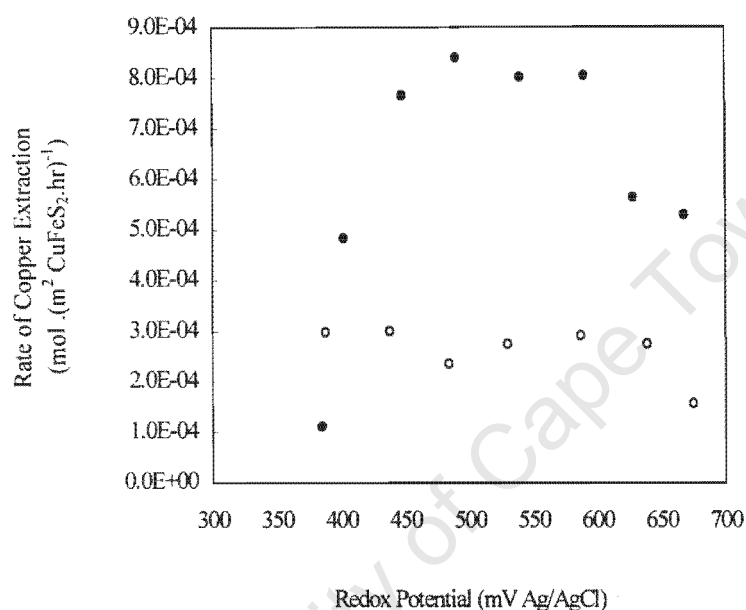


Figure 2 Comparison of the Rate of Copper Extraction at 35 °C and 70 °C
[o] 35 °C, [•] 70 °C, Fe total = 10 g.t⁻¹, pH = 1.5.

A comparison of the work performed in this report and related published work was undertaken. The data presented by Kametani and Aoki (1985) was re-worked. In this procedure, the rates were normalised to rates per unit area of mineral and the differences in temperature were accounted for by using the Arrhenius equation. Figure 3 shows that the data points lie in the same order of magnitude. There is agreement in that the rate of ferrous ion generation increases with redox potential in the range 450 mV to 600 mV.

Kametani and Aoki (1985) observed that at a redox potential of approximately 400 mV, the maximum rate of ferrous ion generation occurred. This report however showed a maximum

rate of ferrous ion generation to occur closer to 450 mV. The difference in observed rates was explained in terms of differences in the mineral compositions of the concentrates used. The interaction of the mineral composites has been shown to affect the rates of leaching (Natarajan, 1992).

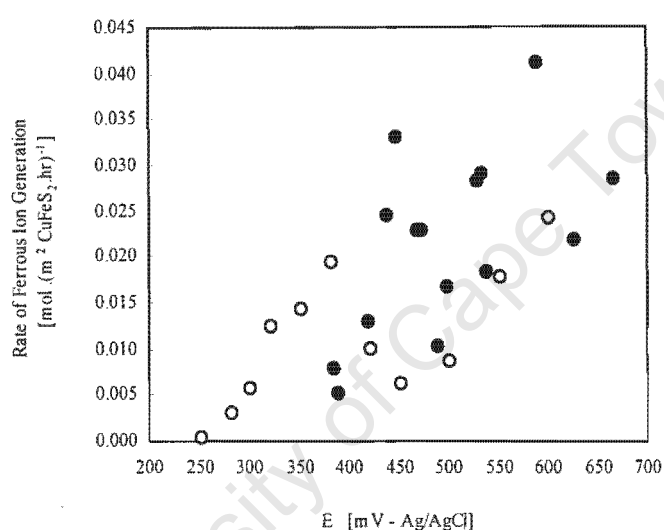


Figure 3 Comparison of Experimental Rate of Ferrous Ion Generation With Kametani and Aoki (1985), [○] Kametani and Aoki (1985), [●] Experimental Results, Fe total = 10 g.l⁻¹, pH = 1.5.

Hiroiyoshi *et al.* (2000) also performed experiments under constant redox potentials. Their data was re-worked and normalised for rate of copper extraction per unit area. From Figure 4 it is observed that maximum mineral oxidation occurs at potential of about 390 mV. This report showed a high rate of copper extraction between 390 and 450 mV. The findings of Hiroiyoshi *et al.* (2000) agreed with Kametani and Aoki (1985) who observed a maximum in the amount of ferrous ion generated at the same redox potential.

The project managed to establish in the research group a reliable method of measuring the ferric leaching of a copper concentrate under constant redox potentials. Preliminary results have shown that the rate of oxidation of the concentrate is dependent on the redox potential and temperature. It appears that leaching of chalcopyrite in the concentrate is favoured at lower redox potentials in the range 390 to 450 mV vs Ag/AgCl. Higher potentials (above 590 mV) show a lower rate of leaching of the chalcopyrite. There is evidence of leaching of the sphalerite in the concentrate in the higher redox potential range.

The results obtained are consistent with previously published work of Kametani and Aoki (1985) and more recently Hiroyoshi *et al.* (2000); who observed high copper extraction and ferrous ion generation at high ferrous ion concentrations and therefore low redox potentials. This phenomenon of enhanced copper extraction at low redox potential for chalcopyrite has formed the basis of a commercial pilot plant (Mintek/Bactech Bioleach Process) for the treatment of chalcopyrite concentrates (van Standen, 1998).

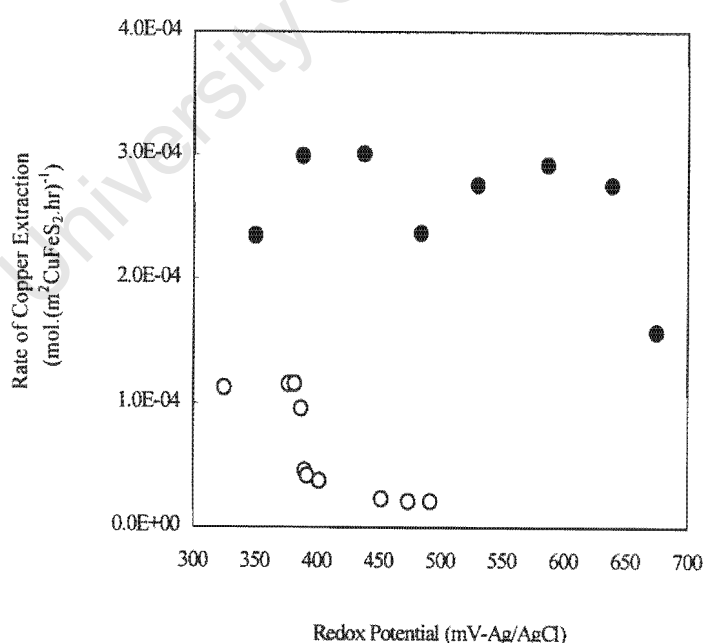


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Nomenclature

		UNITS
α	Transfer Coefficient	m^2
α	Fraction of Copper Extracted	
E^0	Standard Redox Potential	mV
E	Redox Potential	mV
G_f^0	Standard Gibbs Free Energy	$kJ.mol^{-1}$
C_p^0	Specific Heat Capacity	$J.mol^{-1}K^{-1}$
H_f^0	Standard Enthalpy of Formation	$kJ.mol^{-1}$
RT/zF	Nernst Parameter	mV

1. INTRODUCTION

Bioleaching is now a recognised commercial method for the pre-treatment of refractory gold ores and concentrates and for leaching of copper from sulphide ores (Haines and van Aswegan, 1990). On the basis of the current understanding that bioleaching proceeds via a multiple sub-process mechanism under which the ferric and proton attack of the mineral is an important sub-process (Boon *et al*, 1995); this thesis reports on a study of this sub-process, as part of a greater study of the bioleaching of chalcopyrite rich mixed sulphide concentrates.

The oxidation of sulphide minerals is important both economically and environmentally. Sulphide minerals are still the major source of metals and must be oxidised to release the metal value (Torma, 1993). The natural oxidation of sulphide minerals especially in mine dumps leads to acid mine drainage, which has major environmental consequences. These considerations give impetus to the need of understanding sulphide mineral oxidation.

Chalcopyrite is the most abundant of the naturally occurring copper bearing minerals and is a major commercial source of copper. Conventionally copper is obtained from the smelting followed by acid leaching and refining of oxides and secondary sulphides. With ever increasing environmental awareness, smelters are either voluntarily or by legislation reducing levels of sulphur dioxide gas emissions. Importantly sulphides usually contain trace amounts of mercury, tellurium, selenium and arsenic, these impurities are traditionally emitted to atmosphere or entered into the process to make sulphuric acid (Williams and Hunter, 1999).

Economic considerations also make smelting inappropriate for treating metal sulphides. Such cases include small scale operations where the project is not large enough to sustain the cost of running a smelter, operations located close to populated areas and mines producing dirty concentrates containing arsenic, mercury and lead for which high penalty charges imposed by toll smelters (Williams and Hunter, 1999).

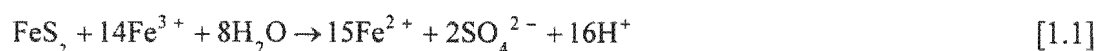
As a consequence, hydrometallurgical processes are considered suitable alternatives to established pyrometallurgical processes. These operations involve exposing the mineral of interest to oxygen, in an acid medium. Pressure leaching is the most efficient of these processes and versions of pressure leaching include the CESL and Activox pressure oxidation processes. The CESL process is a relatively low pressure, low temperature leach developed

for copper concentrates especially chalcopyrite. The Activox process relies on ultrafine grinding of the concentrate. However the application of elevated temperature, pressure and ultrafine grinding results in high operational costs (Williams and Hunter, 1999).

The leaching of chalcopyrite is slow and incomplete in relation to that of other sulphides and there is agreement that this is a result of a passivating product film (Dutrizac, 1969, Munoz *et al.*, 1979). Therefore the emphasis of recent research has been focussed on overcoming the effect of passivation. Biohydrometallurgy has been proposed as a method of achieving this, as certain organisms are associated with sulphide mineral oxidation (Brierley, 1997).

Following the discovery of the iron-oxidizing bacterium *Acidithiobacillus ferrooxidans*¹ in acid mine drainage by Colmer and Hinkle (1947) as cited by Murr (1980), they were soon to be associated with leaching of sulphide minerals along with sulphur oxidising bacterium, *Acidithiobacillus thiooxidans*. Bioleaching is fast becoming the norm in commercial bio-oxidation of refractory gold ores. The BIOX[®] process pioneered by Gencor SA Limited is commercially applied at Ashanti Obuasi in Ghana and treats 960 tonnes per day of concentrate (Dew *et al.*, 1997). Major advantages of bioleaching are the absence of toxic gases, simpler plant maintenance, fewer safety considerations and the tolerance of a wide range and low-grade sulphide minerals, which is unsuitable for processing by conventional smelting. (Haines and van Aswegen, 1990).

As stated earlier, sulphide mineral bioleaching proceeds via a multiple sub-process mechanism. Boon *et al.* (1995) noted that in the case of pyrite, the mineral is firstly chemically oxidised by the ferric ions present in the bioleaching medium.



The ferrous ion is subsequently oxidised to the ferric form by the action of bacteria as shown below.



¹ The genus *Thiobacillus* has been reclassified. *Thiobacillus ferrooxidans* is now *Acidithiobacillus ferrooxidans* and *Thiobacillus thiooxidans* is now *Acidithiobacillus thiooxidans* (Kelly and Wood, 2000).

Subsequently, there has been a concerted effort to elucidate the intermediate sulphur compounds occurring during the bioleaching process. It has been reported that the bioleaching of sulphide minerals proceeds via two pathways namely, the Thiosulphate and The Polysulphide pathway (Schipper and Sand, 1999).

The Thiosulphate mechanism describes the degradation of the disulphides: pyrite, molybdenite and tungstenite. Ferric ions are exclusively the oxidising agents for the dissolution. The thiosulphate intermediate is subsequently biologically degraded to sulphate with elemental sulphur being a side product. The Polysulphide mechanism describes the degradation of the metal sulphides: galena, sphalerite, chalcopyrite, heuretite, orpiment and realgar. This mechanism assumes an initial ferric ion and proton attack of the mineral. The dissolution proceeds via a hydrogen sulphide radical and polysulphides and finally to elemental sulphur (Schipper and Sand, 1999).

The existence of a multiple sub-process mechanism for bioleaching implies that the overall process can be reduced to a number of independent sequential and/or parallel sub-processes. The kinetics of the respective sub-processes may be studied independently and the results used to predict the performance of bioleach reactors for a variety of operating conditions. The ferric ion attack of the mineral is accepted as an important sub-process of the bioleaching mechanism (Boon *et al.*, 1995; Schipper and Sand, 1999).

Current work in the Department of Chemical Engineering at the University of Cape Town is looking at understanding the sub-processes of the bioleaching of chalcopyrite. This thesis is part of the greater study and looks into understanding the ferric leaching sub-process by establishing the most effective way of measuring the rate of the chemical leaching process.

A significant part of previous work to study the ferric leach sub-process was performed under batch conditions under which pH and redox potential varied during the experiment. There has also been little consideration of the potential differences occurring between suspended particles and the solution. A reliable method that used potassium permanganate to maintain solution potential first presented by Kametani and Aoki (1985) was used. The potassium permanganate allows for the regeneration of the ferric ions by re-oxidising with ferrous ions, and this allows the maintenance of a constant redox potential.

This work is preliminary and aims to establish in the research group the method developed by Kametani and Aoki (1985). However, they did not provide conclusive evidence to prove their method regarding critical aspects such as showing that the potassium permanganate used reacted stoichiometrically and instantaneously with ferrous ions and that it did not directly oxidise the concentrate. The effect of temperature and pH on the stoichiometry of ferrous ion oxidation by potassium permanganate was also not reported on.

If the method of Kametani and Aoki (1985) is proved to be viable, preliminary work will be undertaken to observe the dependence of the rate of leaching of the concentrate on the redox potential. Comparison of the experimental results with published literature would be undertaken and this will be valuable in understanding the usefulness of the method.

The organisation of the thesis is as follows: An Introduction and a Review of the literature relevant to the study at hand. Materials and Methods presents chemical and physical analysis of the concentrate used in the experiments. Exact experimental procedures undertaken are also described together with the details of the experimental apparatus used. The Results and Discussion describes all results obtained and evaluates their significance. The Conclusions section outlines the extent to which the objectives of this investigation were met and the direction which future work could follow.

A list of all the references used is provided together with Appendices, which includes some of the analytical and technical aspects of the work.

2. LITERATURE REVIEW

Based on current understanding, bioleaching proceeds via a multiple sub-process mechanism. This implies that the mechanism can be reduced to its component sub-processes and each one can be studied independently. The ferric and proton attack of the mineral is an important sub-process. The literature review begins by outlining the electrochemical nature of the leaching of sulphide minerals. It will then assess the different methods that have been applied to measure the rate of leaching of chalcopyrite.

The review will then outline some of the characteristics of the leaching stoichiometry and kinetics and how the various parameters, for example temperature, affect the observed kinetics. It is the aim of this review to establish the state of the art in chemical leaching of chalcopyrite and outline the contribution of this work to the greater study of bioleaching underway in the research group.

2.1 BACKGROUND OF SULPHIDE MINERAL DECOMPOSITION

It has been proposed that the leaching of sulphide minerals can be classified into the molecular oxygen and sulphur transfer mechanism or an electrochemical mechanism (Peters and Doyle, 1989). The respective mechanisms will be discussed in greater detail.

2.1.1 Molecular Oxygen and Sulphur Transfer Mechanism

The molecular oxygen and sulphur transfer mechanisms can be either inorganic or biologically classified. The mineral can be leached by oxidising sulphur to sulphate and thereby releasing the metal ion into solution. Oxygen is available to achieve this only under conditions of elevated pressure and temperature as found in pressure leaching; under milder conditions other chemical species that exhibit a higher oxidation potential are needed for example chlorine and ferric ions. Ferric ion being a potent oxidant, with an oxidation potential of the order + 700 millivolts is ideal. Ferric ion has the advantage of being generated in the process as most sulphides contain some iron mineral that dissolves during leaching (Hearne *et al.* 1998), (Wadsworth, 1987). Typically the oxidation of the mineral is as shown in Equation 2.1. If ferric ion regeneration occurs, the process is sustainable.



2.1.2 Electrochemical Mechanism

Electrochemical mechanisms are promoted by high over-voltages supplied by high redox potentials, or accelerated by high temperature. If the mineral undergoing the oxidation is a good electrical conductor, as most sulphides are, then the leaching processes may be electrochemical in nature. Electrochemical processes are unique in that the solid assumes a uniform potential provided the ohmic resistance is negligible. The potential may directly affect the kinetics of the reaction and may also serve to stabilise the intermediate solid phase. The dissolution of minerals in which there is no net charge transfer is termed a non-oxidative leach process. The non-oxidative leaching of sulphide minerals is generally not favoured thermodynamically as back reaction with hydrogen sulphide limits the extent of the reaction (Wadsworth, 1987).

It has been proposed that concepts developed in corrosion theory can be extended directly to electron conducting solids in hydrometallurgical systems (Wadsworth, 1987). In this case, there are two regimes operating: the corrosion and the galvanic couples. The corrosion type involves a single phase having both anodic and cathodic reactions on a single mineral surface. A galvanic couple is operative where two or more solid phases are in contact. Each solid assumes either anodic or cathodic behaviour and has its own surface area for reaction. Wardworth (1987) and also Natarajan (1992) studied the galvanic interaction of mixed sulphide chalcopyrite concentrates and reported preferential oxidation of the respective minerals in contact relative to their electrochemical activity.

When a mineral sulphide is in contact with a solution containing an oxidant (e.g. Fe^{3+}) having a more positive equilibrium potential, a corrosion cell will result in anodic oxidation of the metal sulphide, MS, and the cathodic reduction of the oxidant. The half-cell reactions are:



The mineral is essentially a short-circuited electrochemical cell. This assumes a mixed potential between the two reactions above. Potentials more positive than the equilibrium potential drive the half-cell reaction in the net anodic direction and potentials more negative than the equilibrium potential drive the reactions in the net cathodic direction (Wadsworth, 1987).

The net current density for a system is the sum of the anodic and cathodic reactions. The mixed potential, E , occurs where the net current density is zero, i.e. when the anodic and cathodic currents are equal and opposite. Therefore the kinetics of electrochemical processes involve the anodic and cathodic reactions influenced by voltage biases controlled by the mixed potential generated during leaching (Wadsworth, 1987).

2.1.3 Redox Potential Measurement

As a consequence of these mechanisms outlined for sulphide mineral decomposition, monitoring and control of the redox potential is important. The redox potential is measured by simply placing an inert metal electrode e.g. a platinum electrode in solution and comparing its potential with that of a reference electrode. The reference electrode attains a stable potential which is unaffected by the solution potential. The metal electrode acquires the potential of the solution by a process of electron interchange, which can be expressed as the Nernst equation:

$$E = E^0 + \frac{RT}{zF} \ln \frac{[a_{\text{ox}}]}{[a_{\text{red}}]} \quad [2.4]$$

Where a is the activity coefficient, which cannot be determined experimentally for ions, but can be evaluated theoretically. However due to complexity of the ferric leach solution the coefficients can be assumed to be equal to one and we can substitute the ionic concentrations and Equation 2.4 simplifies to:

$$E = E^0 + \frac{RT}{zF} \ln \frac{[M^{\text{ox}}]}{[M^{\text{red}}]} \quad [2.5]$$

Where M is the oxidised or reduced ionic species. The standard potential, E^0 , is related to the ease of removal of electrons from the oxidised species. Thus each system would have a characteristic value. Usual practice is to refer to the Standard Hydrogen Electrode (SHE)

assumed to have zero potential at all temperatures. The standard hydrogen electrode is however not suitable for practical use and other electrodes are more convenient. Table 2.1 lists the different relationships between the different redox electrodes.

Table 2.1 Relationships between various electrode potentials referred to the SHE at 25 °C for common reference electrodes – European convention
(Data obtained from Record, 1965)

<i>Reference Electrode</i>	<i>mV</i>
Saturated Calomel Electrode, SCE	+244
3 <u>M</u> KCl, Calomel Electrode	+250
1.0 <u>M</u> KCl, Calomel Electrode	+285
Saturated Silver, Silver Chloride Electrode	+198
Saturated Mercury, Mercurous Sulphate Electrode	+658

The redox potential of a solution possesses an important property analogous to buffer capacity of a pH solution, namely a resistance to any attempt to alter it by addition of a reducing or oxidising agent. A well poised system is well buffered and is maximum when E_h equals E° of system used. The extent to which the redox of a solution is poised determines the current used in measuring the system. In a poorly poised system the electrode may become polarised and an incorrect potential recorded. In a ferric/ferrous iron system the ferric ions accumulate at the anode, and the ferrous ions at the cathode. A potential difference results across the electrodes because the ferric/ferrous-ratio is not the same at both electrodes. Polarisation can however be minimised by vigorous agitation. Poising is also minimised by using dilute solutions (Record, 1965).

2.2 METHODS OF MEASURING RATE OF FERRIC LEACHING

Several methods have been applied to measure the rate of leaching of sulphide minerals. These vary from simple measurement of the amount of the desired species (e.g. copper in the case of chalcopyrite) that goes into solution through to constant potential methods in which the rate of leaching is determined via the amount of an oxidising agent added. Details of available methods will be discussed in this section. The evaluation of methods is restricted to study of methods using pulverised mineral concentrates.

Crude methods have been applied which involved batch operations with monitoring the amount of ions extracted. These methods however did not take into account the electrochemical nature of leaching of sulphide minerals. There is a firm understanding of the electrochemical nature of sulphide mineral leaching and the most effective methods of applied have taken this into account.

2.2.1 Dynamic Redox Potential Method

May *et al.* (1997) used the dynamic redox method to determine the rate of leaching of pyrite. May carried out experiments in a 0.10 litre jacketed glass vessel. 0.05 litres of ferric sulphate solution were added and a redox probe inserted. The temperature was controlled at 25 °C using an external water bath. The solution was agitated using a glass impeller. Approximately 0.4 g of pyrite was added to the system and the redox potential monitored for the 30 minutes duration of the reaction.

The redox potential behaviour was then related to a rate of leaching for the mineral using the Nernst equation, which was differentiated to give Expression 2.6.

$$r_{\text{FeS}_2} (\text{mol.l}^{-1}.\text{s}^{-1}) = \frac{\frac{zF}{RT} \cdot \frac{dE}{dt}}{\frac{(3n+2)}{[\text{Fe}^{3+}]} + \frac{(3n+3)}{[\text{Fe}^{2+}]}} \quad [2.6]$$

where n is the stoichiometric coefficient of reaction i.e. when $n = 0$ there is elemental sulphur formation and a value of $n = 4$ indicates formation of sulphate.

From Equation 2.6 it can be seen that the change in redox potential was seen as the major variable in the rate expression. There are no reports of this method being applied on copper bearing mixed sulphides.

Oxidation in suspension differs in some respects from an electrode reaction. Firstly it is not possible to measure directly the potential difference occurring between the suspended particles and the solution. This makes it difficult to compare leaching reactions and electrode processes directly. Secondly, semi-conducting properties of pulverised minerals vary during oxidation (Kametani, 1982) as cited by Kametani and Aoki (1985). These problems can be overcome by conducting experiments at constant redox potential.

2.2.2 Constant Redox Potential Methods

The maintenance of a constant redox potential has been achieved in a number of ways predominantly by the use of an externally applied current (Crundwell and Harvey, 1997) or the use of an oxidising agent (Kametani and Aoki, 1985). Crundwell and Harvey (1997) used an electrolysis cell divided into two sections by an ion exchange membrane. The contents of the working compartment were stirred and the compartment sparged with air. The electrodes for measuring the redox potential were suspended in the solution of the working compartment. Redox potential measurements were made using a platinum electrode with an Ag/AgCl reference electrode, using a high impedance differential amplifier and analogue digital control card. A computer program determined the values of the output signals from the card to a relay switch, which varied the direction and magnitude of the current. The current was measured by the potential difference across a precision resistor.

The redox potential was controlled to within 1.0 mV of the set point. This method offered very elaborate control over the applied potential. There are however no reports of this method being applied to leaching of copper bearing mixed sulphides. The method has also only been applied at solids concentration of about 20 g.l⁻¹.

Kametani and Aoki (1985) however reported a method, for studying the leaching of a copper concentrate and at solids concentrations of 40 g.l⁻¹. They conducted experiments in a one-litre jacketed glass vessel reaction vessel. The suspension potential was measured using a rotating platinum electrode with a reference electrode. A controller regulated the addition of potassium

permanganate solution, which allowed the maintenance of the desired redox potential by re-oxidising ferrous ions to ferric ions. They however did not conclusively establish some aspects of this method chiefly, the possible direct oxidation of the mineral with potassium permanganate or conclusively establish the reaction stoichiometry between ferrous ion and potassium permanganate and how temperature and pH affected the stoichiometry.

2.3 STOICHIOMETRY OF FERRIC LEACH OF CHALCOPYRITE

2.3.1 Physical Properties of Chalcopyrite

The chalcopyrite crystal structure is derived from the zinc blende structure ZnS ; the unit cell structure consists of two metal atoms, copper and iron, surrounded by sulphur in a tetrahedral arrangement as shown in Figure 2.1. The bonding scheme is covalent in nature with each atom being bonded to its neighbours by sp^3 hybrid orbitals. Table 2.2 lists some of the physical and electrical properties of chalcopyrite.

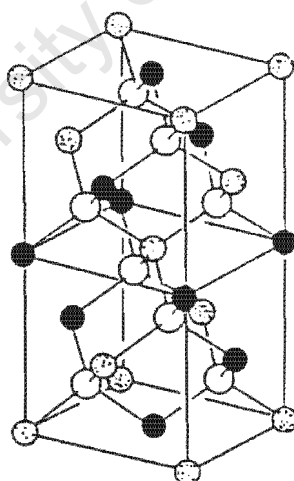


Figure 2.1 The Unit Cell Structure of Chalcopyrite
[○] = copper, [●] = Iron, [⊗] = Sulphur

Table 2.2 Table Illustrating Properties of Chalcopyrite

Data obtained from Hiskey (1993)

<i>Property</i>	<i>Units</i>	<i>Value</i>
Density	(g.cm ⁻³)	4.0878
Hardness	(Moh)	3.5 – 4
Cp ⁰	(J.mol ⁻¹ K ⁻¹) (298 – 830 K)	$88.71 + 5.19e^{-2T} + 7.45 e^{-5T-2}$
ΔG_f^0	(kJ. mol ⁻¹)	- 184.72
ΔH_f^0	(kJ. Mol ⁻¹)	- 183.68
Crystallography		tetragonal
Molar mass	(g.mol ⁻¹)	184
Resistivity	(Ω m)	$2 \times 10^{-4} - 3 \times 10^{-1}$

2.3.2 Stoichiometry Of Ferric Leaching Of Chalcopyrite

It has been reported and agreed that the leaching of chalcopyrite follows two distinct kinetic regions as represented in Figure 2.2 (Dutrizac, 1969; Munoz *et al.*, 1979; Ammou-Chokrum *et al.*, 1979). The region O to A shown in Figure 2.2 is characterised by a high dissolution rate and has been attributed to chemical reaction control of the reaction. The later regime has been attributed to diffusional control of reaction through a growing passivating layer. It has been reported that the first phase is several hundred times faster than the latter stage (Ammou-Chokrum *et al.*, 1979).

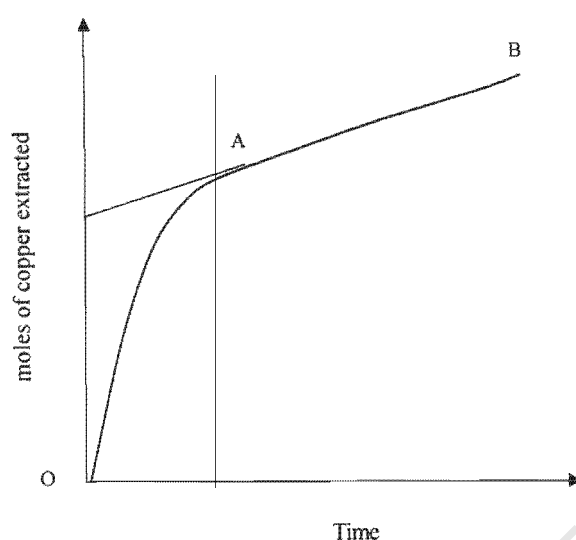
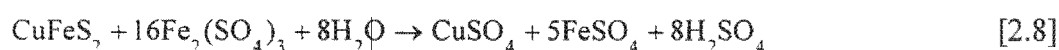
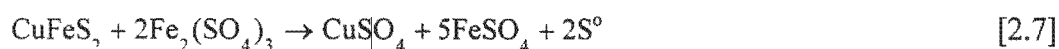


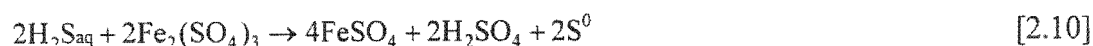
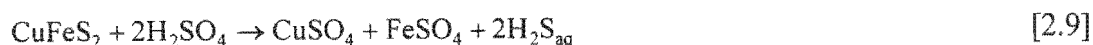
Figure 2.2 A Schematic of Copper Dissolution during Leaching of Chalcopyrite
(Ammou-Chokroum *et al.*, 1979).

Dutrizac (1989) used finely ground (10 - 14 μ m) and polished massive (1 cm²) Transvaal chalcopyrite and monitored Cu²⁺/S⁰ and Fe²⁺/S⁰ molar ratios during the reaction. The finely ground ore gave ratios of 0.56 and 2.9 respectively indicating 94% sulphur generation and 6% SO₄ generation under the stoichiometrys represented in Equations 2.7 and 2.8. The finely ground particles were observed to be extensively coated with sulphur after three hours of attack.



In contrast, examination of the sulphur morphology on the massive particles showed that most of the surface was free of sulphur. The sulphur located at discrete sites on the surface and with sulphur particle size of approximately 20 μ m although on some, particles of size greater than 20 μ m were observed. The surfaces appeared roughened on a micro-scale. The existence of

the larger sulphur particles was explained by deposition of sulphur from the solution onto pre-existing granules. Dutrizac (1989) proposed that the leaching mechanism in this case might involve a direct acid attack of sulphide mineral as follows:



The hydrogen sulphide is rapidly used up and thus not detected above the solution. This finding draws interesting parallels with the findings of Schippers and Sand (1999), who although working with a bioleach system described the leaching of chalcopyrite to proceed via a polysulphide mechanism which involves formation of an intermediate hydrogen sulphide radical. The findings of Dutrizac (1989) point to the possible difference in stoichiometry that occurs with differing experimental condition and also highlights the possibility of the reaction proceeding via the formation of intermediates. However, it would appear that the net overall stoichiometry can be represented by Equations 2.7 and 2.8 as there is agreement that complete oxidation results in formation of cupric ions and elemental sulphur.

2.4 FACTORS AFFECTING FERRIC LEACHING OF CHALCOPYRITE

2.4.1 Galvanic Interactions of Sulphide Minerals

In leaching systems containing more than one mineral, galvanic interactions come into play and make prediction of leach behaviour difficult. When two sulphide minerals establish contact in a leaching medium, a galvanic cell is formed, the more active mineral undergoes corrosion whilst the other is cathodically protected. The galvanic series of some sulphide minerals are listed in Table 2.3.

Table 2.3 Galvanic Series of Sulphide Minerals.

Data obtained from Crundwell (1988)

<i>Mineral</i>	<i>Formula</i>	<i>Rest Potential (mV)</i>	
Pyrite	FeS ₂	630	Noble
Chalcopyrite	CuFeS ₂	530	
Chalcocite	Cu ₂ S	440	
Covellite	CuS	420	
Galena	PbS	280	
Sphalerite	ZnS	-240	
			Active

Natarajan (1992) recorded the interaction of chalcopyrite, sphalerite and chalcocite in a bioleaching system. The measured rest potentials in a bioleach medium at pH of 2.3 for pyrite, chalcopyrite and sphalerite are 700mV, 560mV and 240mV respectively. These indicate that sphalerite is the most electrochemically active mineral, while pyrite and chalcopyrite are more noble. Thus in galvanic combinations involving these minerals, sphalerite will undergo selective anodic dissolution as follows.



On the other hand, while chalcopyrite behaves anodically with respect to pyrite, it remains cathodic to active sphalerite. Thus, depending on the type of mineral with which it is in contact, either anodic dissolution of chalcopyrite occurs as:



or cathodic reduction of oxygen will be promoted on its surface as:



Only Equation 2.14 can be expected on pyrite surfaces in any combinations involving the above three sulphides. Preferential oxidation of chalcopyrite will be enhanced when contacted to pyrite (Natarajan, 1992).

2.4.2 Effect of Temperature on Leaching

It has been reported that an increase in temperature causes an increase in the rate of copper extraction (Dutrizac (1978), Dutrizac (1982), Munoz *et al.* (1979)). Using 12 μm particles, Munoz *et al.* (1979) observed an increase in the fraction of copper extracted with increasing temperature as illustrated in Figure 2.3. It appears that the higher temperatures limit the extent of passivation as a higher copper extraction is obtained.

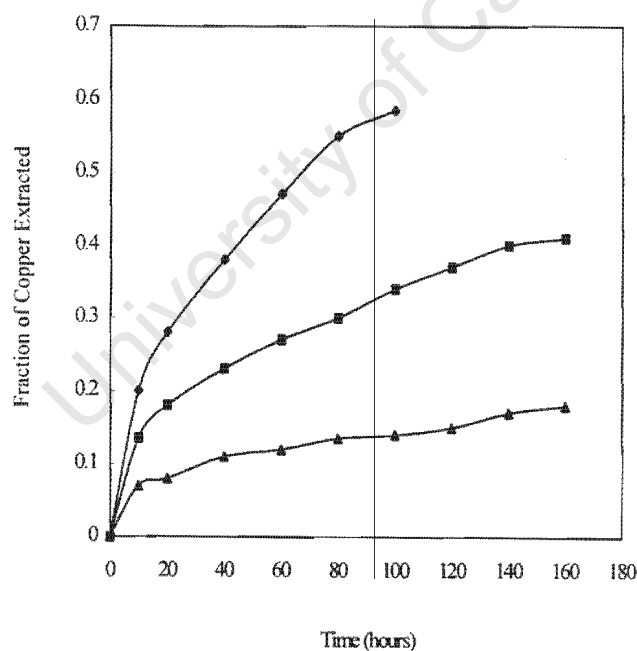


Figure 2.3 A Plot of Copper Extraction from 12 μm Monosize Chalcopyrite
[♦] 90° C, [■] 75° C, [▲] 60° C. 1 M H_2SO_4 , 0.25M $\text{Fe}_2(\text{SO}_4)_3$,
0.5 % solids and 1200 rpm. (Munoz *et al.*, 1979).

2.4.3 Effect of Particle Size on Leaching

As a result of the refractory nature of chalcopyrite, commercial leaching processes need to be carried out using finely ground concentrates (Dutrizac, 1989). Munoz *et al.* (1979) observed an increasing rate of copper extraction with decreasing particle size as illustrated in Figure 2.4. This is expected as the smaller particles offer a greater surface area per gram than the larger particles.

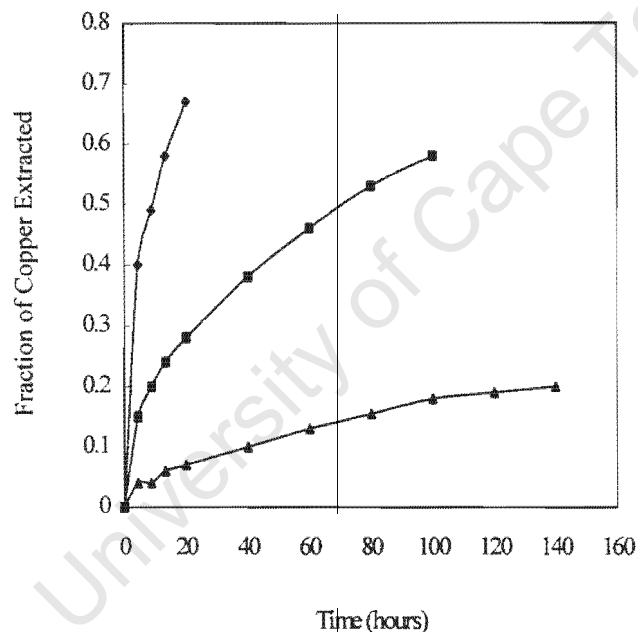


Figure 2.4 Plot of Copper Extraction from mono-size Chalcopyrite Particles
 1 M H_2SO_4 , 0.25M $\text{Fe}_2(\text{SO}_4)_3$, 0.5 % solids and 1200 rpm.
 [♦] 4μm, [■] 12μm, [▲] 47μm. (Munoz *et al.*, 1979)

However, the results of Munoz *et al.* (1979) can be re-interpreted. It is possible to show that the copper extraction per unit area of mineral is the same for all size fractions. In their work they used the same mass for each different size fraction. This meant that the smaller size fractions had a greater available surface area. If we however assume that the particles are

spherical and with similar physical properties, a normalised extraction of copper per unit area can be calculated. Figure 2.5 shows the results of this normalisation procedure on extraction illustrated in Figure 2.4. The normalisation is relative to the extraction pattern of the 12 μm particles.

Munoz *et al.* (1979) did not present any BET surface analysis; which would in all respects not necessarily follow the assumptions above. The similarity in fraction extracted per unit area allows flexibility in the choice of size fraction used for leach studies. The normalisation of the rate also allows for easier comparison with other published work.

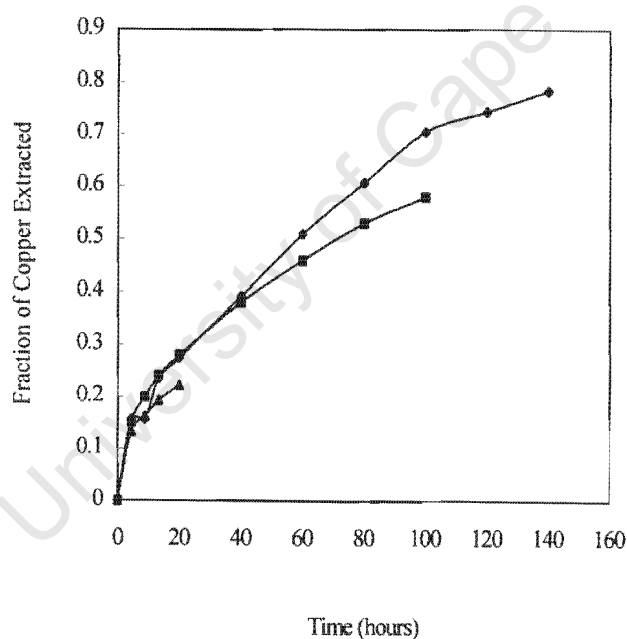


Figure 2.5 Plot of Normalised Copper Extraction for Mono-size Chalcopyrite
1 M H_2SO_4 , 0.25M $\text{Fe}_2(\text{SO}_4)_3$, 0.5 % solids and 1200 rpm.
[♦] 4 μm , [■] 12 μm , [▲] 47 μm . (Munoz *et al.*, 1979)

2.4.4 Effect of Ferric Ion Concentration on Leaching

There have been varied findings on the effect of ferric ion concentration on the rate of leaching of chalcopyrite. Munoz *et al.* (1979) reported a half order dependency on the ferric iron concentration.

Dutrizac *et al.* (1982) reported a decrease in rate constant with addition of ferrous ion up to a ferric/ferrous iron ratio of 0.25. Havlik *et al.* (1995) established two regions of dependency on ferric iron; up to 0.5 M the rate was dependent on the ferric ion and above it was independent. It would appear that concentrations below about 0.5 M provided insufficient ferric ion for the leach reaction. It is possible that workers who have observed a dependence on ferric ion may have provided insufficient ions to complete the oxidation reaction.

However, the ferric ion concentration depends on the total iron concentration and redox potential. Therefore when conducting experiments at constant redox potential it is not possible to measure the effect of ferric ion concentration directly unless the redox potential or total iron concentration are changed. The constant potential methods have been established as being most suitable for determining ferric leaching of chalcopyrite and will be applied in the work of this report.

2.4.5 Effect of Acid on Leaching Kinetics

It has been reported that acid may play a part in the initial attack of the mineral in the leaching process (Dutrizac, 1989). Hearne *et al.* (1999) reported that a low pH prevents iron hydrolysis. In a bioleaching system the optimal pH for operation is between 1.2 and 2.0 for the BIOX[®] process for pre-treatment of refractory gold concentrates and ores (Dew *et al.* 1997). Sand and Schippers (1999) proposed the polysulphide leaching mechanism which chalcopyrite undergoes, involves an initial acid and ferric attack of the mineral.

There is however a need to establish the exact role of acid in the chemical leaching process and quantify it in relation to the ferric leaching.

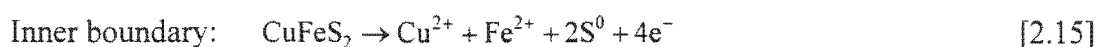
2.4.6 Effect of Mass Transfer Limitations on Leaching

May (1997) found that the agitation speed has no effect on the rate of oxidation of pyrite; experiments were performed using agitation speeds between 300 – 2000 rpm with a solids concentration of 8 g.l⁻¹. This was in agreement with the findings of Sexana and Mandre (1992) working at a solids concentration of 40 g.l⁻¹ found that agitation speeds above 100 rpm had little effect on the leaching of chalcopyrite using a ferric chloride medium. These findings indicate that agitation is only important to keep the solids suspended, and that this is not a mass transfer limitation.

2.5 FORMATION OF SURFACE FILMS ON CHALCOPYRITE

Certain aspects of this have been discussed earlier. There is agreement that ferric leaching of chalcopyrite is slow and incomplete and this has been attributed to passivation (Dutrizac and M^c Donald (1974); Munoz *et al.*, (1979)). However there is disagreement as to the nature of passivation. Some authors have attributed passivation to a film of elemental sulphur as previously discussed (Dutrizac, 1989) or a copper rich polysulphide (Warren *et al.*, 1982); whilst other workers have described formation of a jarosite passivating layer (Braithwaite, 1976).

Dutrizac (1978, 1989) studied elemental sulphur formation during acid ferric sulphate leaching of chalcopyrite. Operating at 95 °C, there was a reported 94% elemental sulphur formation and 6% sulphate formation. Supporting evidence for the formation of elemental sulphur was given by Munoz *et al.* (1979) who cited an activation energy of 83.7 kJ/mol which was approximately the same as transport through elemental sulphur, 96 kJ/mol. Munoz *et al.* (1979) argued using Wagner's theory of oxidation, that the rate limiting process was transport of electrons through elemental sulphur formed on the ore surface. The Wagner theory proposes that the ferric sulphate leaching may be viewed as two half-cell reactions, which occur on both side of the sulphur layer as follows:



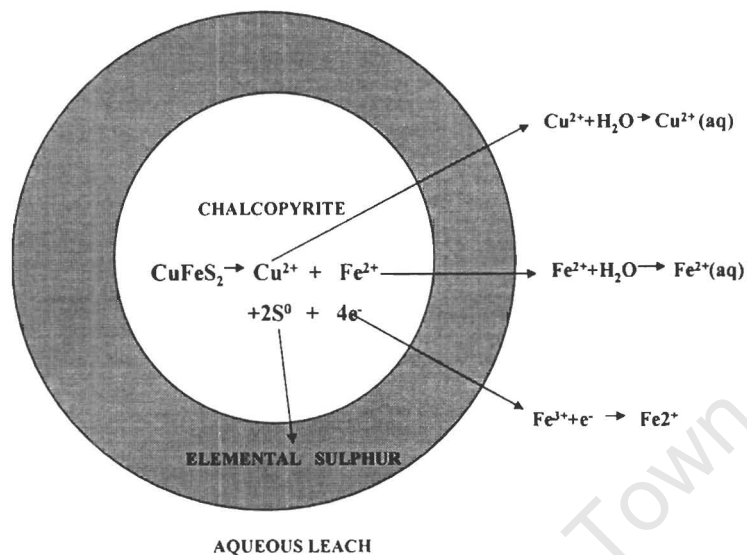


Figure 2.6 Schematic Representation of Wagner's Theory of Oxidation
(Munoz *et al.*, 1979)

Evidence of an intermediary polysulphide passivating layer is dispelling the long held understanding that passivation was due to a sulphur layer. Linge (1976) found that pore diffusion did not limit the rate of oxidation, therefore the sulphur layer was not responsible for the observed parabolic kinetics. The conclusion was that the diffusion layer was composed of a bimetallic sulphide exhibiting chemical and structural differences from the chalcopryrite where it originated.

Subsequent work has shown agreement with the formation of an intermediary polysulphide. Warren *et al.* (1982) using cyclic voltametry found that at low potential (600 mV – 800 mV vs. SHE), chalcopryrite initially formed bornite and at higher potentials (1000-1200 mV) formed covellite. However these findings were based on the use of chalcopryrite electrodes and over a short duration. Kametani and Aoki (1985) using x-ray diffraction analysis of the leach residue found presence of covellite at potentials in the range 0.3 mV to 0.33mV (SCE). They noted that at this redox potential the oxidation of the initial chalcopryrite was

incomplete. However, complete oxidation of the chalcopyrite to elemental sulphur was observed at higher redox potentials up to 650 mV (SCE).

Hiro Yoshi *et al.* (2000) used free energy calculations to support the formation of chalcocite as an intermediate product. They proposed that the chalcopyrite was initially reduced by ferrous ions and the intermediate formed is reduced by oxygen to copper II ions. However no analytical techniques were performed to confirm the presence of the intermediate.

Braithwaite *et al.* (1976) suggested iron precipitates hematite or jarosite were the composition of the passivating layer but provided no substantiation of this assertion.

This conflict over the identity of the passivating layer presents the possibility that the passivating layer formation may be a function of the mineral composition of the concentrate and the particular conditions of the study for example redox potential. Table 2.4 shows some of the proposals for the identity of the passivating layer in addition to those previously discussed.

Table 2.4 Proposed Identity of Passivating Compounds Formed During Chalcopyrite Leaching

<i>Author</i>	<i>Nature of pasivating layer</i>
Jones and Peters	(1976) Porous sulphur
Mc Millan <i>et al.</i>	(1982) Solid electrolyte interphase of polysulphides
Tiwari <i>et al.</i>	(1980) Semi conducting iron deficient polysulphide
Ammou Chokroum <i>et al.</i>	(1979) CuS, Cu ₂ S, Cu ₅ FeS ₄
Parker <i>et al.</i>	(1981) CuS, Cu ₂ S,
Warren <i>et al</i>	(1982) CuS, Cu ₂ S

2.6 MODELLING FERRIC LEACHING OF CHALCOPYRITE

By tracing the rate of copper extracted, chalcopryrite shows two regions of leaching that have been linked to initial chemical control and then to diffusional control of the rate. Because such modelling of the kinetics had been focussed on applying the shrinking particle model for fluid particle reactions. Munoz *et al.* (1979) reported that the oxidation of chalcopryrite was controlled by transport through a reaction product layer and applied the Equation 2.17 for a diffusion limited reaction. The relationship between the fraction reacted (α) and the time was used.

$$F(\alpha) = 1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = k_p t \quad [2.17]$$

Kamatani and Aoki (1985), however found chalcopryrite oxidation rate to be under reaction control and could be represented by:

$$1 - (1 - \alpha)^{1/3} = k_r t \quad [2.18]$$

They further argued that the power term in Equation 2.18 could be eliminated for an ore sample with a logarithmic size distribution.

$$-\log(1 - \alpha) = k_f t \quad [2.19]$$

There are shortcomings in the sole use of fluid particle shrinking core models. These models do not account for the electrochemical nature of the leaching of sulphide minerals, particularly that oxidation can only proceed once the potential at the particle surface exceeds the mineral rest potential. There is mounting evidence of the dependence of leaching on the redox potential (Warren *et al.*, 1982; Verbaan and Huberts, 1988 and Kamatani and Aoki, 1985). There is increasing use of electrochemical theories in modelling sulphide mineral ferric leach kinetics.

The simplest electrochemical model assumes a linear relationship between solution redox potential and mineral rest potential (Nagpal *et al.* 1994). Boon (1996) suggested a Monod type

model, which adopted an inverse relation for the bacterial ferrous ion oxidation of pyrite as shown in Equation 2.20

$$v_{\text{Fe}^{2+}} = \frac{v_{\text{Fe}^{2+}}^{\max}}{1 + B \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}} \quad [2.20]$$

Inspection shows that Equation 2.20 predicts an increase in the leaching rate with an increase in the redox potential; and that the rate tends to zero as potential tends to zero. However leaching can only occur once the potential at the particle surface exceeds the mineral rest potential.

More comprehensive models are based on the Butler–Volmer equation for corrosion reactions, limited by charge transfer at the interphase.

$$i = i_o \left(\exp \left(\frac{(1-\alpha)F\eta}{RT} \right) - \exp \left(\frac{-\alpha F\eta}{RT} \right) \right) \quad [2.21]$$

The values of α and η in the above equation determine the interrelationship between the rate of the charge transfer reaction and the potential difference across the interface. η is the overpotential, which is the difference between the equilibrium potential and the applied potential. α is the transfer coefficient (or in the case for single step reactions, the symmetry factor) and is an intrinsic characteristic of the charge transfer reaction and determines what fraction of the electrical energy, resulting from the displacement of the potential from equilibrium affects the rate of electrochemical transformation i.e. not all of the potential difference across a double layer actually causes reaction. The symmetry factor for the reduction of ferric iron to ferrous iron at a platinum electrode has been shown to be 0.58 (Bockris and Reddy, 1970).

The Butler-Volmer equation does take the rest potential of the mineral into account. Although at extremely high redox potentials a Butler-Volmer type model is inadequate. Dry (1984) and Verbaan and Huberts (1986) reported that the leaching kinetics of triolite and sphalerite respectively was dependent on the electrochemical potential at the mineral surface, which can be approximated to solution redox potential. Using the key assumption that the anodic

dissolution reaction at the surface of the particle is described by the anodic term of the Butler-Volmer equation, they derived the following equation.

$$\frac{dm}{dt} = -k_1 \exp(k_2 E) m^{2/3} \quad [2.22]$$

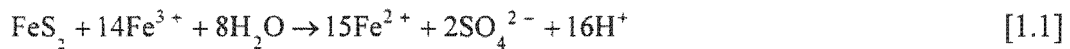
where m is the amount of unleached mineral remaining, E is the electrochemical potential at the mineral surface (or redox of the solution), k_1 and k_2 are constants for the mineral at a given temperature. Mathematical integration was used to determine the values of the constants k_1 and k_2 . Equation 2.22 also assumed the surface reaction could be described by the anodic dissolution reaction at the surface of the particle; that the exchange current density for ferrous/ferric couple is much larger than that of the dissolution of the mineral.

May *et al.* (1997) reported a version of the Butler-Volmer equation that could be used to determine rate directly:

$$r = r_0 \left(\exp \left(\alpha \beta \left(E - E' \right) \right) - \exp \left((1 - \alpha) \beta \left(E - E' \right) \right) \right) \quad [2.23]$$

2.7 BIOLEACHING MECHANISM OF SULPHIDE MINERALS

Boon *et al.* (1995) reported that for pyrite, bioleaching proceeds via a multiple sub-process mechanism and noted that the mineral is firstly chemically oxidised by the ferric iron present in the bioleaching medium as follows:



The ferrous ions generated are subsequently oxidised to the ferric form by the action of bacteria as shown in Equation 1.2; resulting in the maintenance of a constant redox potential.

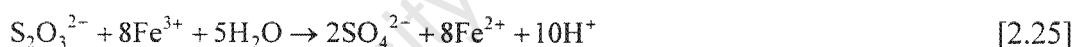
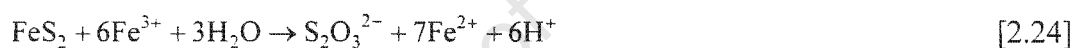


Combined new evidence has resulted in the new integrated model for bioleaching. A characteristic hypothesis of the model is that ferric ions and/or protons are the only (chemical)

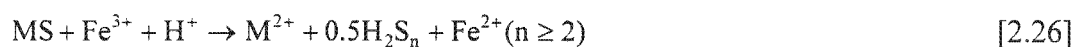
agents directly dissolving a metal sulphide. The bacteria have a sole function of regenerating ferric ion and/or protons and to concentrate them at the mineral/water and mineral/bacterial interface. It is further proposed that a tiny exopolymer layer with nanometer dimensions is the location of the chemical processes causing metal dissolution. (Schippers and Sand, 1999). Due to the concentration of these compounds at the interface, the accelerated dissolution observed in presence of bacterial than in a sterile chemical system can be explained.

Based on the intermediate sulphur compounds formed during bioleaching under the integrated model presented, two mechanisms are observed, the Thiosulphate and Polysulphide mechanism, which will be briefly discussed.

The Thiosulphate mechanism of bioleaching assumes the oxidative attack of ferric ions on the acid insoluble sulphides: pyrite, molybdenite and tungstenite. The intermediate sulphur compound is thiosulphate as illustrated below, which is rapidly oxidised by ferric ion to sulphate.



The Polysulphide mechanism assumes the ferric ion and/or proton attack of mineral. In this case the main sulphur intermediate is a polysulphide. The sulphides: chalcopyrite, sphalerite, galena, huerite, orpiment and realgar are degraded according to this pathway as illustrated by Equations 2.26 to 2.28.



The bioleaching mechanisms discussed highlight the importance of the ferric ions and/or proton attack of the mineral.

Acidophilic bacteria capable of attacking metal sulphides are classified according to their preferred temperatures for growth into three groups: mesophiles, moderate thermophiles and extreme thermophiles. The mesophile bacteria operate optimally at temperatures between 25 °C and 40 °C and are incapable of growth above 45 °C. Most commonly isolated types are *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans* and *Acidithiobacillus thiooxidans*. (Rawlings, 1997).

Moderate thermophiles such as *Acidithiobacillus caldus* species, which operate optimally between 45 °C and 55 °C are applied commercially for extraction of gold from a pyrite/arsenopyrite concentrate (Millar, 1997). The growth of the *Acidithiobacillus*- bacterium becomes restricted at the upper extreme of this temperature range. However the *Sulfolobus*-archaea activity increases with some active up to 85 °C. These strains are associated with sulphurous hot springs with temperatures higher than 60 °C and where pH is as low as one (Brock, 1978).

Bioleaching of chalcopyrite is not successful at low temperatures without uneconomical process manipulation such as regrinding ore (Torma, 1976), or addition of silver ions to leach medium (Brierley, 1999). Enhanced leaching is however possible using thermophile bacteria which operate at temperatures which would damage mesophilic bacteria (Brierley, 1999). Consequently the most notable potential of thermophiles is in overcoming the difficulties experienced at low temperature bioleaching of chalcopyrite.

2.8 STATE OF THE ART IN CHALCOPYRITE LEACHING

When a sulphide mineral comes into contact with a solution containing an oxidant such as ferric ion having a more positive equilibrium potential, a corrosion cell results in an anodic oxidation of the mineral sulphide and cathodic reduction of the oxidant. The mineral is essentially a short-circuited electrochemical cell and the kinetics are influenced by voltage biases controlled by the mixed potential generated during leaching.

In evaluating the methods available to perform ferric leach studies careful note of the electrochemical nature of the reaction is required. Oxidation in suspension differs in some respects from an electrode reaction. Firstly it is not possible to measure directly the potential difference between the suspended particles and the solution. This makes it difficult to

compare directly leaching reactions and electrode processes. Secondly semi-conducting properties of pulverised minerals vary during oxidation (Kametani (1982) as cited by Kametani (1985)). The latter problems of difference in suspension potential can be overcome by conducting experiments at constant redox potential.

A reliable method that used potassium permanganate to maintain solution potential first presented by Kametani and Aoki (1985) was used. The potassium permanganate regenerates the ferric ions by oxidation of ferrous ions, thus maintaining a constant potential. The method is applicable to a wide variation in experimental conditions especially solids concentration and temperatures.

However Kametani and Aoki (1985) did not conclusively show the behaviour of potassium permanganate particularly the stoichiometry and rate of its reaction with ferrous ion and whether chalcopyrite directly oxidised the mineral in question. These factors need to be conclusively proved and theoretical conclusions alone would be inadequate.

There is agreement about some form of surface film inhibiting the rate of leaching. However it is difficult to precisely define the stoichiometry of these compounds and their stability. It appears that the passivating substance formed varies with operating conditions applied. The identification of the exact nature falls beyond the scope of this work. However the dependence on redox potential of the rate of leaching of chalcopyrite will be used to examine the extent of limitation in the reaction.

Table 2.5 below outlines the literature reviewed. It summarises the experimental conditions applied and the observed kinetics of leaching of chalcopyrite.

Table 2.5 Summary of Published Literature Findings on Leaching Characteristics

Reference	Study/lixiviant Conditions Temp, pH, potential	Ore Source/ Size fraction	Kinetics/ nature of passivating layer / Proposed stoichiometry
Beckstead <i>et al.</i> , 1976	Fe ₂ SO ₄ / H ₂ SO ₄ T = 50 - 90 °C pH = 2.5	Pima 53 & 106µm size 10 g.t ⁻¹ slurry conc.	Parabolic, rate limited by diffusion through diffusion layer $\text{CuFeS}_2 + 4 \text{Fe}^{3+} = \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0$
Braithworth <i>et al.</i> , 1976	In situ ferric sulphate leach pass O ₂ at 40 - 1620 psia. SEM,EDAX surface analysis T = 90 °C pH = 1.88 - 2	Bingham +65 - 100µm +200 - 270µm	Parabolic, rate limited by O ₂ diffusion through diffusion layer
Jones and Peters, 1976	1 M Ferric sulphate leach T = 90 °C pH = 0.4	Craigmont	Mixed, linear then parabolic kinetics $\text{CuFeS}_2 + 4 \text{Fe}^{3+} = \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0$ Passivation by S ⁰
	1 M Ferric chloride leach T = 90 °C pH = 0.7	Craigmont	Linear kinetics, rate = 5 times faster than ferric sulphate leach $\text{CuFeS}_2 + 16 \text{Fe}^{3+} + 8\text{H}_2\text{O} = \text{Cu}^{2+} + 17\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 6\text{H}^+$
Dutrizac, 1978	0.1 M Fe ₂ (SO ₄) ₃ leach pH = 0.22 T = 30 - 95 °C	Temagami Lake 150 - 200µm Slurry concentrate = 0.5 - 3 g.t ⁻¹	Parabolic $\text{CuFeS}_2 + 4 \text{Fe}^{3+} = \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0$ Passivation by S ⁰
	Ferric chloride leach T = 50 - 90 °C pH = 0.52	Synthetic	Linear $\text{CuFeS}_2 + 4 \text{Fe}^{3+} = \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0$ No passivation

Munoz <i>et al.</i> , 1979	0.25 M Ferric sulphate leach pH = 0.3 T = 60 – 90 °C	Pima 4, 12, 47 µm slurry concentration = 0.3 - 0.5%	Parabolic kinetics, reaction control followed by diffusion control through S ⁰ product layer. $\text{CuFeS}_2 + 4 \text{Fe}^{3+} = \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0$
Tiwari <i>et al.</i> , 1980	In situ ferric sulphate Leach T = 93 °C XRD surface analysis		$\text{CuFeS}_2 + 2.16\text{Fe}_2(\text{SO}_4)_3 + 0.21\text{H}_2 = \text{Cu}^{2+} + 5.3\text{FeSO}_4 + 1.95\text{S}^0 + 0.21\text{H}_2\text{SO}_4$ $\text{Fe}^{2+} + 4 \text{H}^+ + \text{O}_2 = \text{Fe}^{3+} + 2\text{H}_2\text{O}$ Cu ptn: $\text{Cu}^{2+} + \text{S}^0 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{CuS} + \text{SO}_4^{2-} + 4\text{H}^+$
Parker <i>et al.</i> , 1981	Electrochemical oxidation in ferric sulphate Electrochemical oxidation in ferric chloride Potentiostatic oxidation in chloride and sulphate media Potentiodynamic oxidation in chloride and sulphate media	Messina, Baxter, Springs, Craigmont Used massive ore to make electrodes	Parabolic kinetics, rate limited by slow transport through semi-conducting metal deficient polysulphide layer. Spl is more thermally stable in sulphate lixiviant as compared to chloride.
Warren <i>et al.</i> , 1982	Anodic dissolution of CuFeS_2 in 1 M H_2SO_4 500-1100mV (SHE) Temp= 298 K Potentiodynamic oxidation in acidic sulphate medium Potentiostatic oxidation in acidic sulphate medium	New Mexico, Ontario, Craigmont, Mt Lyle, Mt. Isa, Transvaal	Parabolic kinetics 500 - 700mV (SHE) $\text{CuFeS}_2 = \text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z} + x\text{Cu}^{2+} + \text{Cu}^{2+} + y\text{Fe}^{2+} + z\text{S}^0 + 2(x+y)\text{e}^-$ For $y > x$ For 700 – 750 mV (SHE) $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z} = (2-z)\text{CuS}_{(n-s)} + (1-y)\text{Cu}^{2+} + (1-y)\text{Fe}^{2+} + 2(1-y)\text{e}^-$ At lower potentials less than 700mV(SHE): $\text{CuS}_{(n-s)} = \text{Cu}^{2+} + \text{S}^0 + 2\text{e}^-$ At higher than 700mV: $\text{CuS}_{(n-s)} = \text{Cu}^{2+} + 0.25\text{SO}_4^{2-} + 0.75\text{S}^0 + 2\text{e}^-$

Dutrizac, 1982	0.1 M Ferric sulphate leach $T = 50 - 95\text{ }^{\circ}\text{C}$ $\text{pH} = 0.22$ Ferric chloride leach $T = 50-95\text{ }^{\circ}\text{C}$ $\text{pH} = 0.52$	Transvaal, Arizona, Quebec, Craigmont, Montana, Ontario, Manitoba, Mattagami, Kiddcreek 20 - 29μm, Slurry conc. = 1 g.ℓ^{-1}	Parabolic kinetics in sulphate medium $\text{CuFeS}_2 + 8\text{H}_2\text{O} + 16\text{Fe}^{3+} = \text{Cu}^{2+} + 17\text{Fe}^{2+} + 16\text{H}^+ + 2\text{SO}_4^{2-}$ Paralinear in chloride $\text{CuFeS}_2 + 4\text{Fe}^{3+} = \text{Cu}^{2+} + 5\text{Fe}^{2+} + 2\text{S}^0$ No specification of passivating layer
McMillan <i>et. al</i> , 1982	$T = 22\text{ }^{\circ}\text{C}$ Air oxidation, Ammonia oxidation 0.2 M acetic acid.	Kidd Creek, Messina 20 - 29μm	Solid electrolyte Interphase made up of iron deficient copper sulphide, which is electrochemically insulating but allows transfer of ionic species.
Buckley and Woods, 1984	Anodic dissolution in acidic media 1 M HCl, 1 M HClO₄, 1 M HNO₃ and 1 M H₂SO₄ 200 - 700 mV (SCE) $T = 25\text{ }^{\circ}\text{C}$	Mt Lyle	Iron hydroxyl oxide and CuS₂ species from exposure to air. Metal deficient copper disulphide Cu_{1-x}FeS_{2.8} from acetic acid exposure
Beigler and Horne , 1985	0.01 – 1 mol.ℓ^{-1} Ferric chloride leach $\text{pH} = 0.7$ $T = 70\text{ }^{\circ}\text{C}$	Mt. Lyle	Passivating layer of the form: $2\text{CuFeS}_2 = \text{Cu}_{0.75}\text{S}$ or $\text{CuS} = \text{Cu}_2\text{S}$
Hirato <i>et al.</i> , 1986	0.2 M ferric chloride leach $T = 30 - 90\text{ }^{\circ}\text{C}$	Shakanai mine	Linear kinetics with a half order dependence on ferric chloride Porous S⁰ on fringes of surface causes some passivation

Table 2.5 Summary of Published Literature Findings on Leaching Characteristics

Sexana and Mandre, 1992	Dichromate leach $T = 90\text{ }^{\circ}\text{C}$	Hindustan Cu. Limited 74-104 μm Slurry conc. = 20 g. ℓ^{-1}	Mixed model for sphalerite leaching used.
Murr and Hiskey, 1993	Ferric sulphate leach pH = 0.22 $T = 95\text{ }^{\circ}\text{C}$	Transvaal 48-65, 100-150, 200-270 μm Slurry conc. 1 g. ℓ^{-1}	X-ray spectrum showed presence of sulphur
Dutrizac, 1989	Ferric chloride leaching $T = 30 - 90\text{ }^{\circ}\text{C}$ 0.2 <u>M</u> ferric chloride	Messina 10-14, 20-29, 29-37 μm	Diffusion model applied with limitation of transport through S^0 layer. Ferric sulphate leach accompanied by direct acid attack and H_2S oxidation to S^0 . Following proposed reactions. $\text{CuFeS}_2 + 2\text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 5\text{FeSO}_4 + 2\text{S}^0$ $\text{CuFeS}_2 + 8\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} = \text{CuSO}_4 + 17\text{FeSO}_4 + 8\text{H}_2\text{SO}_4$ $\text{CuFeS}_2 + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + 5\text{FeSO}_4 + 2\text{H}_2\text{S}(\text{aq})$ $2\text{H}_2\text{S}(\text{aq}) + 2\text{Fe}_2(\text{SO}_4)_3 = \text{H}_2\text{SO}_4 + 4\text{FeSO}_4 + 2\text{S}^0$
Sexana and Mandre, 1992	Potentiodynamic oxidation Cyclic voltametry $T = 25 - 68\text{ }^{\circ}\text{C}$ pH = 0-2	Hindustan Cu. Ltd, Rakha Slurry 40 g. ℓ^{-1}	Used mixed reaction control proposed by Bobeck and Su
Hackl, 1995		Messina, Gibraltar 14 μm	At 110 $^{\circ}\text{C}$ passivating layer is iron deficient copper disulphide indicated: $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_2$ where $y \gg x$ At 200 $^{\circ}\text{C}$ no passivation is observed

Gomez <i>et. al.</i> , 1996		Transvaal	Cu rich, Fe poor polysulphide differing structure at 25 – 68 °C
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University of Cape Town

3. MATERIALS AND METHODS

This project aimed to use the method developed by Kametani and Aoki (1985) to generate chemical ferric leach data. The ferric ion and proton attack of the mineral has been established to be an important sub-process in bioleaching of sulphide minerals. However there was seen a need to establish conclusively the validity of the method viz. key factors about the use of potassium permanganate for regeneration of ferric ion. It is necessary to establish experimentally the stoichiometry of the ferrous ion oxidation by potassium permanganate and the effect of temperature and pH on it. There were also doubts about the possibility of the potassium permanganate directly oxidising the mineral.

The mixed sulphide copper concentrate used in the experiments was analysed to obtain its physical and chemical characteristics which are presented. A clear description of the experimental apparatus and the experimental procedures are also presented.

3.1 MINERAL ANALYSIS

A copper bearing mixed sulphide concentrate from Otjihasë mine in Namibia was used. The chemical composition of the concentrate was determined by QuemSEM analysis, and the results are presented in Table 3.1. The mineral phases were determined using x-ray diffraction (XRD) analysis and the results are presented in Table 3.2. Ore in the size range +75-106 μm was used for the experiments and a Malvern Laser Master Sizer was used to determine the size analysis of the ore sample and the results are presented in Table 3.3. The Brunauer Emmett Teller (BET) method for surface area analysis showed an available surface area of $1.9270 \text{ m}^2.\text{g}^{-1}$.

Table 3.1 Quem SEM Analysis of the Concentrate

<i>Element</i>	<i>QuemSEM Assay (%)</i>	<i>Estimated Chemical Assay (%)</i>
Copper	27.99	32.8
Iron	31.55	34.0
Sulphur	35.69	
Zinc	0.85	

Table 3.2 The Mineral Composition of the Concentrate

<i>Mineral</i>	<i>Weight Percent (%)</i>
Chalcopyrite	80.77
Pyrite	13.11
Sphalerite	1.26
Cub/Idiate	0.09
Bornite	0.01
Other Sulphides	0.13
Quartz	1.62
Feldspar	0.05
Other Silicates	1.73
Fe-oxides	1.06
Other	0.16

Table 3.3 Malvern Laser Master Size Analysis of the Concentrate

<i>Size Fraction</i>	<i>Mass Percent (%)</i>
+150	9.81
+106 –150	25.68
-106 + 75	36.21
-75 + 53	22.27
-53 + 38	3.24
-38	2.80

Table 3.4 shows the locking characteristics of the mineral. In the table, “monominerallic” relates to the concentrate grains which consists entirely of chalcopyrite. “Binary” relates the grains that consist of chalcopyrite + 1 other mineral and “composite” are grains that consist of chalcopyrite + 2 or more other minerals.

Table 3.5 shows the degree of liberation of the mineral. The degree of liberation is the grains that consist of 10 volume %, 20 volume % etc. of chalcopyrite. The volume liberated is the total volume % of chalcopyrite that occurs in grains that are 10 volume %, 20 volume % etc.

Table 3.4 Locking Characteristics of the Concentrate

<i>Association category</i>	<i>Volume percent (%)</i>
Monominerallic	51.4
Binary with:	
Pyrite	1.9
Sphalerite	1.9
Other Sulphides	5.5
Silicates	0.9
Other	18.9
Composite	19.5

Table 3.5 Degree of liberation of concentrate

<i>Degree of Liberation</i>	<i>Cumulative volume %</i>
0.	100.0
10	99.8
20	99.5
30	99.2
40	98.6
50	97.7
60	97.2
70	96.3
80	94.4
90	91.8
100	51.4

3.2 STOICHIOMETRY OF FERROUS ION OXIDATION BY POTASSIUM PERMANGANATE

The method developed by Kametani and Aoki (1985) required validation with respect to some aspects listed below. The aim of this particular experiment was to establish the stoichiometry of ferrous ion oxidation by potassium permanganate. 10 g.l⁻¹ total iron in the form of ferrous sulphate was added to a 1 litre working volume stirred reactor. The redox potential was noted and once stabilised a 0.01 litre aliquot of 2.0 g.l⁻¹ potassium permanganate was added; the potential was again allowed to stabilise before a further aliquot of potassium permanganate was added.

After the addition of each aliquot of potassium permanganate, a sample was withdrawn from the vessel for titrimetric determination of the iron concentration (total and ferrous). The ferric ion concentration was determined as the difference of the two amounts. It was also felt important to determine the variation if any of the stoichiometry with temperature and pH. Thus experiments were performed at 35 °C, 50 °C and 70 °C and at pH 1.05, 1.5 and 2.0. These determinations were performed in the absence of mineral.

3.3 RATE OF FERROUS ION OXIDATION BY POTASSIUM PERMANGANATE

These experiments were undertaken to establish the rate at which potassium permanganate oxidised the ferrous ion. Visual observations were undertaken to see if decolourisation of the potassium permanganate occurred when it was added to a ferric/ferrous ion solution. The behaviour of the redox potential value with each addition of potassium permanganate was also observed.

3.4 DETERMINING IF POTASSIUM PERMANGANATE DIRECTLY OXIDISED THE CONCENTRATE

This experiment was done in order to investigate if any direct oxidation of the concentrate by the potassium permanganate occurred. A one-litre working volume jacketed vessel used in the other determinations was used to perform the experiments. In preliminary constant potential experiments performed in this project, the maximum amount of potassium permanganate added in any one experiment was 0.16 mol. l⁻¹. In the interest of completeness, double this amount (0.32 mol. l⁻¹) of potassium permanganate was then added to the reaction vessel and

15 ± 0.686 g of concentrate was then added and the mixture was stirred. Samples were taken at the end of the experiment to determine the change of total iron and copper concentration.

A control experiment was performed in which 15 ± 0.686 g of concentrate was added to 1 litre of deionised water. The amount of copper extracted and change in total iron concentration was determined by atomic adsorption spectrophotometry.

3.5 EXPERIMENTAL EQUIPMENT

Experiments were performed in a 2 litre Applikon™ jacketed vessel in which a 1 litre working volume was used. The temperature was set at the required value using a Grant Y6 constant water bath. Agitation was achieved by using a 6-pitched blade impeller driven by a variable speed overhead electric motor. The redox potential was measured using a platinum wire Ag/AgCl combination Metrohm™ redox probe with a 3 M lithium chloride solution. The pH of the solution was measured with a Metrohm™ glass electrode filled with 3 M potassium chloride solution.

The solution potential was controlled by addition of potassium permanganate, using an automatic titration unit, Metrohm 718 Stat Titrino™, which had an extensive remote control facility that allowed full control of the unit via a desktop computer. Figure 3.1 shows a representation of the experimental apparatus.

3.6 EXPERIMENTAL PROCEDURE

On completion of the validation of the experimental method, the results of which are presented later, the method was then applied to obtain chemical leach data at different redox potentials. The experimental protocols are described in greater detail below.

3.6.1 Ore Pre-treatment

Preliminary findings showed a very high copper extraction in the initial phase of leaching. This behaviour was attributed to attached mineral fines, which were also detected by Scan Electron Microscopy (SEM). Pre-treatment was seen to alleviate the uncharacteristic leaching behaviour. The pre-treatment procedure was performed on all concentrate samples before leaching. 0.10 litres of deionised water was added to 15 ± 0.686 g of concentrate in a 0.25 litre

flask which was then immersed into an ultrasonic bath. The concentrate was exposed to one minute in the ultrasonic bath, then the particles were allowed to settle before the cloudy supernatant was decanted. The procedure was repeated using a fresh amount of deionised water

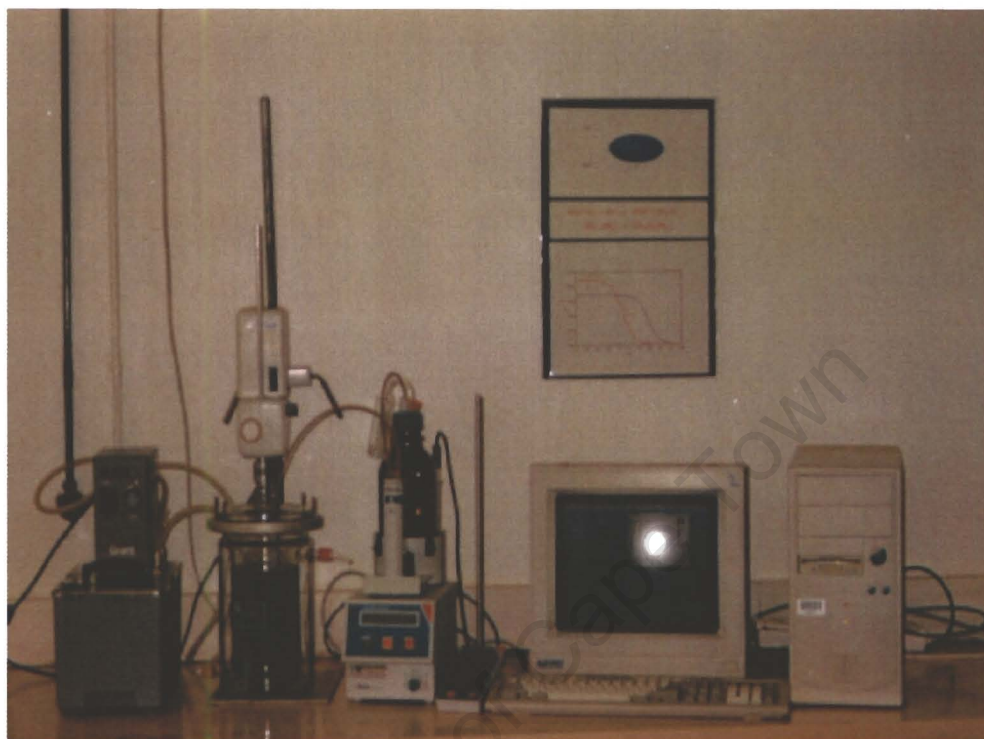
3.6.2 Probe Calibration

The redox probe was calibrated to determine the Nernstian parameters E^0 and RT/zF for the experimental conditions used. Theoretical values for these constants are not applicable as they are based on different experimental conditions notably temperature and total iron concentration.

3.6.3 Constant Potential Experiments Procedure

Using sulphuric acid, one litre of deionised water in the reaction vessel was made up to a pH of 1.5. A total iron concentration of 10 ± 0.36 g was added in the form of ferrous sulphate. The potential was set at the desired value by addition of potassium permanganate; which was also used to maintain the potential upon addition of the concentrate. 15 ± 0.686 g of concentrate was added for each experimental run. The temperature was maintained at the required value using a water bath.

The pH of the solution was maintained using 5 M sodium hydroxide solution and 98% sulphuric acid solution. Analytical grade chemicals and deionised water were used in all the determinations. Mineral oxidation was followed by monitoring the potassium permanganate additions whilst solution samples were also taken at regular intervals to determine the concentrations of dissolved copper and total iron using atomic adsorption spectrophotometry.

**Figure 3.1**

Representation of Experimental Apparatus.

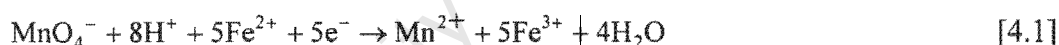
4. RESULTS AND DISCUSSION

In order to test the applicability of the use of potassium permanganate to maintain redox potential, it was necessary to conclusively determine the stoichiometry of the reaction of potassium permanganate and ferrous ion and how it was affected by changes in temperature and pH. There was also a need to verify whether or not potassium permanganate directly oxidised the concentrate.

4.1 STOICHIOMETRY OF FERROUS ION OXIDATION BY POTASSIUM PERMANGANATE.

The method used to determine this has been described in the Materials and Methods. Titration results for ferrous ion and total iron concentration were used to evaluate the amount of ferric ion generated for each aliquot of potassium permanganate added.

Published literature has presented the stoichiometry for the ferrous ion oxidation by potassium permanganate to be represented by Equation 4.1 (Ebbing, 1996).



By applying Equation 4.1, a value for the theoretical amount of ferric ion generated for each aliquot of potassium permanganate added can be evaluated.

In presenting the results, a comparison of the amounts of ferric ion generated calculated from titration results and that calculated using Equation 4.1 was performed. A ratio of 0.994 was obtained indicating that Equation 4.1 accurately describes the stoichiometry of the ferrous ion oxidation by potassium permanganate. Changes in temperature and pH were observed not to affect the stoichiometry as this is represented in Figures 4.1 and 4.2.

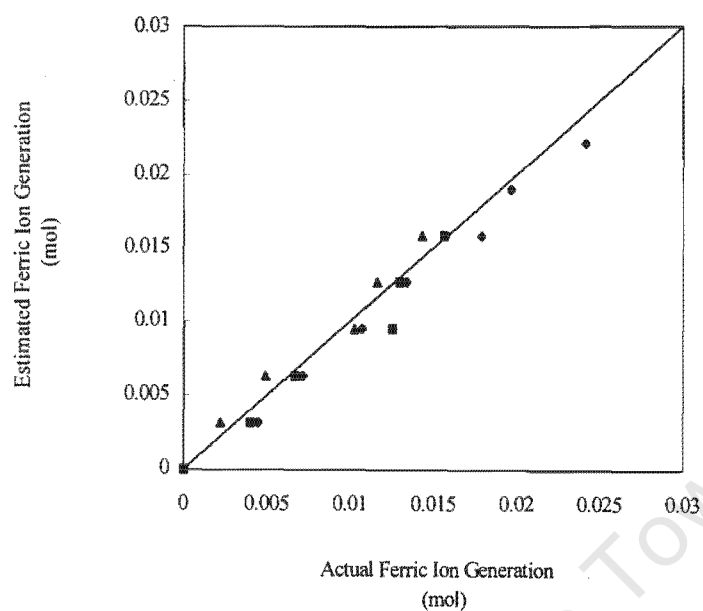


Figure 4.1 Effect of Temperature on Ferrous Ion Oxidation by Potassium Permanganate

[♦] = 35 °C, [▲] = 50 °C, [■] = 70 °C, pH = 1.5, $10 \text{ g} \cdot \ell^{-1} \text{ Fe}^{\text{total}}$.

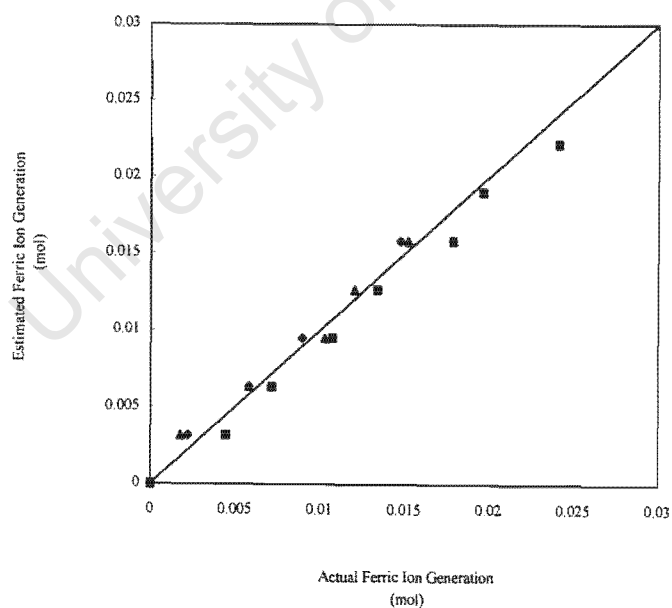


Figure 4.2 Effect of pH on Ferrous Ion Oxidation by Potassium Permanganate

[♦] pH = 1.05, [▲] pH = 1.50, [■] pH = 2.0, 35 °C, $10 \text{ g} \cdot \ell^{-1} \text{ Fe}^{\text{Total}}$.

4.2 RATE OF FERROUS ION OXIDATION BY POTASSIUM PERMANGANATE

In all experiments performed, the potassium permanganate was seen to decolourise immediately upon addition to the ferric/ferrous sulphate indicating a very rapid reaction. The permanganate ion (MnO_4^-) is purple in solution and is reduced to the manganese II ion (Mn^{2+}), which is pale pink or colourless in dilute solutions (Ebbing, 1996). There was also an immediate increase in the redox potential on addition of the permanganate, indicating an increase in the ferric to ferrous ratio of the Nernst equation (previously described).

4.3 DETERMINATION OF EFFECT OF POTASSIUM PERMANGANATE ON CONCENTRATE

Kametani and Aoki (1985) had only presented a theoretical argument of how potassium permanganate only reacted with ferrous ion. They argued that the redox potential during titration corresponds to the redox potential ($[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$) during reaction and it rises rapidly at the endpoint, because the potential for $\text{MnO}_4^-/\text{Mn}^{2+}$ is very high and given by:

$$E_{\text{SCE}}(298\text{K}) = 1.263 - 0.095\text{pH} + 0.012\log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \quad [4.2]$$

Using Equation 4.2, at $\text{pH} = 0$ and $E = 650 \text{ mV (SCE)}$ yields $\log ([\text{MnO}_4^-]/[\text{Mn}^{2+}]) = -51$. The low value is indicative of the absence of free MnO_4^- .

Table 4.1 however shows the results of the analysis for copper and total iron determined experimentally. The results indicate that potassium permanganate does not directly oxidise the concentrate and no enhanced copper or iron release is observed.

Table 4.1 Determination of Effect of Potassium Permanganate on Concentrate

<i>Sample No</i>	<i>With Potassium Permanganate</i>	<i>Sample No.</i>	<i>Control Experiment</i>
Copper Extracted (mg.l^{-1})			
K3	0.370	3	1.635
K4	0.384	4	1.739
Change in Total Iron (mg.l^{-1})			
K3	0.717	3	1.310
K4	0.336	4	1.319

4.4 FERRIC LEACH STUDIES USING CONSTANT POTENTIAL

The results obtained support the use of potassium permanganate as a method for maintaining constant redox potential; in terms of it not reacting directly with the concentrate and its rapid reaction with only ferrous ion. The stoichiometry of the ferrous ion oxidation by potassium permanganate has also been established to be unaffected by changes in temperature and pH.

4.4.1 Ore Pretreatment

Preliminary findings showed an unusually high copper extraction in the initial period of leaching. It was thought that this might have been the effect of fines associated with the mineral particles. It is evident from Figure 2.1 that the untreated concentrate gave uneven extraction of copper, the washed ore showed a smoother extraction pattern.

As expected with the ultrasonic pre-treatment procedure, there is a loss of mass with the decanting of the fines. However, experimental determination showed that the loss of mass (concentrate) was not significant and a loss of $4 \pm 0.7 \%$ resulted. Consistency was maintained in regarding the amount of deionised water added and the volume decanted.

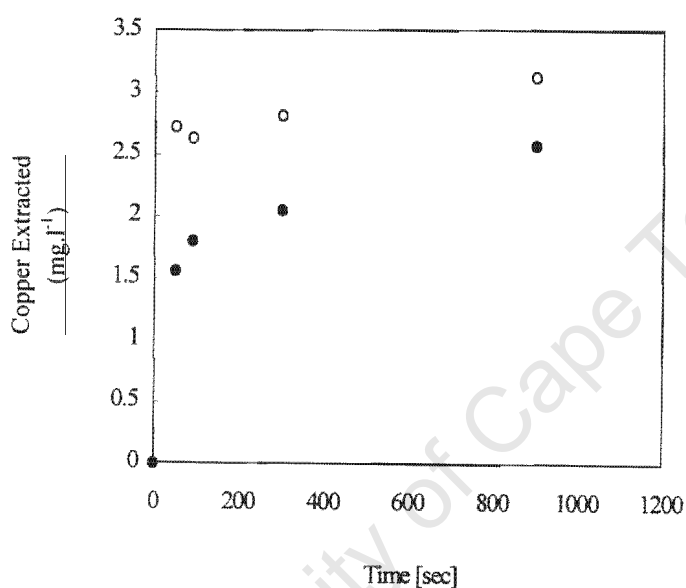


Figure 4.3 | A Comparison of Copper Extracted from Untreated and Pre-treated Concentrate

[●] Pre-treated, [○] Untreated, 35 °C, $E = 450 \text{ mV(Ag/AgCl)}$,

$10 \text{ g. l}^{-1} \text{ Fe}^{\text{Total}}$, pH = 1.5

4.4.2 Probe Calibration

The Nernst parameters E^0 and RT/zF were obtained for the conditions applied in these experiments and the values are given in Table 4.2.

Table 4.2 **Determined Nernst Parameters**

<i>Total Iron Concentration g.ℓ⁻¹</i>	<i>Temperature</i>	<i>RT/zF</i>	<i>E⁰</i>	<i>Correlation Coefficient R²</i>
10	35 °C	24.36	472.35	0.9915
10	70 °C	29.34	539.27	0.9983
Standard Value	25 °C	25.70	573.00	

4.5 CALCULATION OF RATE OF LEACHING OF CONCENTRATE

The stoichiometry of the ferrous ion oxidation by potassium permanganate has been confirmed (Equation 4.1). It follows that the rate of the individual species can be represented as follows:

$$-5r_{\text{KMnO}_4} = -r_{\text{Fe}^{2+}} = r_{\text{Fe}^{3+}} \quad [4.3]$$

Thus the rate of ferrous ion generated from oxidation of mineral can be calculated from the amount of potassium permanganate added to re-oxidise the ferrous ion to ferric ion. Subsequently the rate of addition can be calculated according to the performance equation for a constant volume batch reactor.

$$-r_A = -\frac{dC_A}{dt} \quad [4.4]$$

The assumption of constant volume is valid since for each experimental run performed, it was ensured that the overall volume of sample withdrawn matched the volume of potassium permanganate added. The difference between the two volumes did not exceed 0.02 litres for any given experimental run. This amount would represent a volume change of 2.0 %, which was sufficiently small to ignore the effect of volume change in evaluating the rate.

4.5.1 The Rate of Ferrous Ion Generation

The leaching process involves ferric ion attack of the mineral and the ferric ion is reduced to the ferrous form. The iron content of the mineral is also released as ferrous ions. Through addition of potassium permanganate, the ferrous ion is re-oxidised to ferric ion. It is therefore possible to calculate the rate of mineral oxidation through the amount of potassium permanganate added and relating it to the amount of ferrous ion generated.

Figure 4.4 shows the ferrous ion generation at 35 °C. It can be seen that there is an increase in the rate of ferrous ion generation in the redox potential range from 350 mV to 450 mV. In the range 480 mV to 600 mV, the rate of ferrous ion generation is constant before a slight peak at 600 mV.

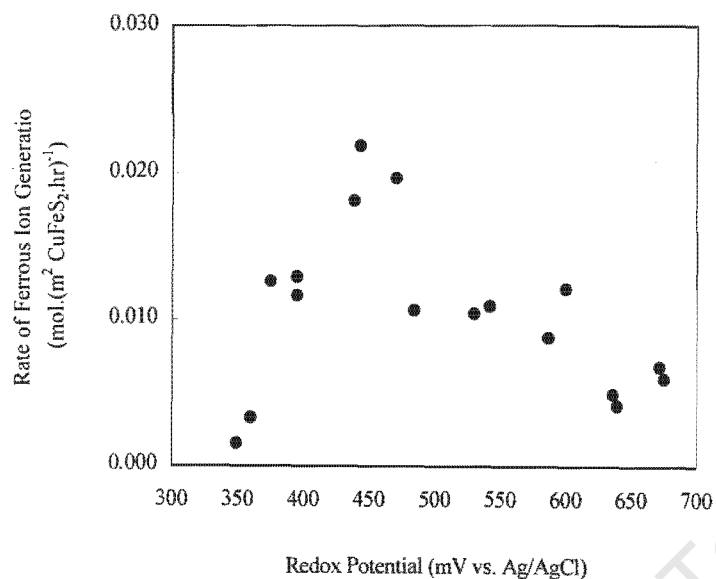


Figure 4.4 The Rate of Ferrous Ion Generation with Redox Potential
 $T=35\text{ }^{\circ}\text{C}$, $\text{Fe total} = 10\text{ g} \cdot \ell^{-1}$, $\text{pH} = 1.5$.

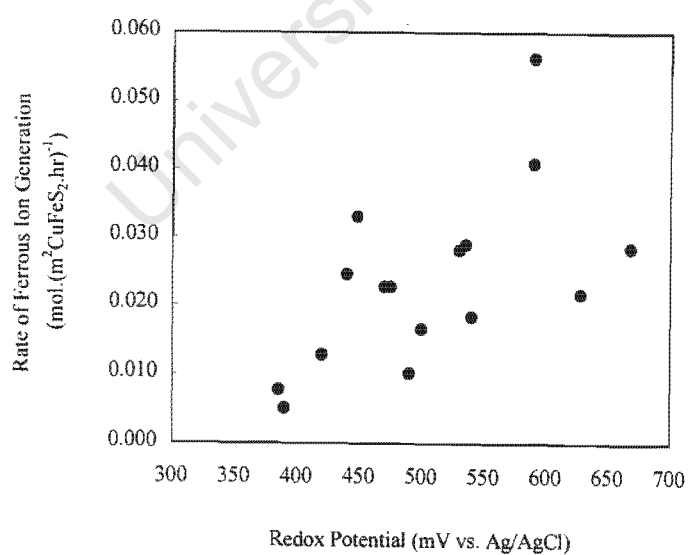


Figure 4.5 The Rate of Ferrous Ion Generation with Redox Potential
 $T=70\text{ }^{\circ}\text{C}$, $\text{Fe total} = 10\text{ g} \cdot \ell^{-1}$, $\text{pH} = 1.5$.

Figure 4.5 shows the rate of ferrous ion generation at 70 °C. There is a similarity with the 35 °C experiment in that the ferrous ion generation rate increases with redox potential till a peak at 450 mV. From 450 mV till 500 mV there is a decrease in the rate with increasing potential. From this value, the rate increases with an increasing potential till 590 mV before decreasing till 650 mV.

Figure 4.6 shows the relative rates at the two temperatures. In contrasting the rates observed at 35 °C and 70 °C, it was observed that the higher temperature results in higher rates of ferrous ion generation. However between 350mV and 400 mV, repetitive experiments showed that the temperature seems to have little effect on the rate of ferrous ion oxidation.

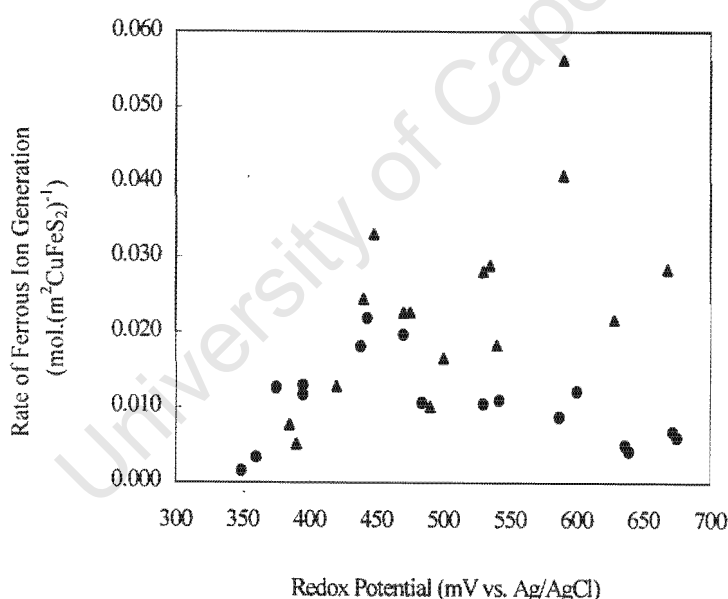


Figure 4.6 Comparison of ferrous Ion Generation at 35 °C and 70 °C

[▲] 70 °C, [●] 35 °C, Total iron = 10 g.l⁻¹, pH = 1.5

4.5.2 Rate of Copper Extraction

The concentrate used in the experiments was predominantly copper and the amount of copper extracted was determined by atomic adsorption spectrophotometry. The rate of copper extraction at different redox potentials is illustrated in Figure 4.7. An increase in temperature gives a rise in observed rates of copper extraction. At 70 °C, the rate of copper extraction increases with an increase in redox potential in the range 380 mV till 460 mV. From this value the extraction rates then stay constant till 600 mV. This constant region could be viewed as the potential window for leaching of the concentrate.

The copper extraction rate at 35 °C, is relatively constant in the range 380 mV to 480 mV, though with a slightly increased rate observed at about 440 mV – 460 mV. From 480 mV, there is observed an increase in the rate with increasing potential till about 600 mV before the rate decrease with increasing potential.

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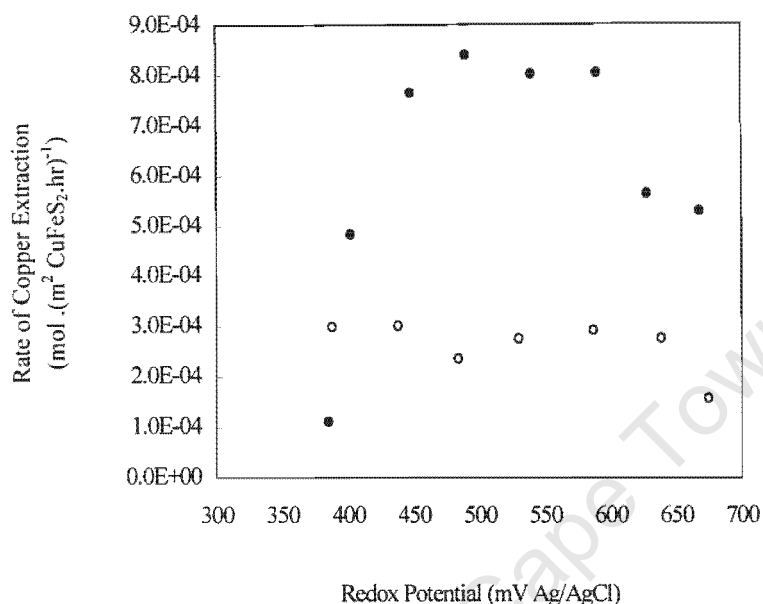


Figure 4.7 Comparison of the Rate of Copper Extraction at 35 °C and 70 °C

[o] 35 °C, [•] 70 °C, Fe total = 10 g.l⁻¹, pH = 1.5.

In comparing the trends observed in rate of ferrous ion generation and rate of copper extraction, some valuable information can be obtained. There appears to be agreement in an increased rate of ferrous ion generation and copper extracted at about 450 mV. The rate of ferrous ion generation also shows a peak at 600 mV.

There is evidence of the possibility of galvanic effects. It can be noted that in the potential range 600 mV till 670 mV, the rate of copper extraction decreases whilst that of ferrous ion generated increases. This can be linked to the possible leaching of another sulphide mineral in the concentrate, as the chalcopyrite in the concentrate cannot account for the ferrous ion generated.

4.5.3 Relationship between Ferrous Ion Generated and Copper Extracted

The observed behaviour above 600 mV was further investigated in order to establish the role of galvanic interactions. In a separate determination at 600 mV, the amount of copper extracted was compared to the amount of potassium permanganate added.

Chalcopyrite oxidation was represented in Equation 2.7 and that of ferrous ion re-oxidation by potassium permanganate is represented by Equation 4.1.

The molar ratio of copper to potassium permanganate observed was 3.7. This value indicated that not all the potassium permanganate was used for re-oxidation of ferrous ion emanating from chalcopyrite leaching. This could be because the stoichiometry presented was incorrect or there was another source of ferrous ion possibly the sphalerite or pyrite.

Subsequently, the amount of zinc extracted was measured. The sphalerite undergoes oxidation as (Crundwell, 1988).



The amount of zinc extracted was used to calculate a theoretical amount of ferrous ion generated and subsequently the theoretical amount of potassium permanganate needing to be added to re-oxidise it to ferric ion. Figure 4.5 shows that there is a significant level of zinc extraction *viz.* Amount initially present. The fraction of zinc extracted in the experiment was 21% in comparison to a copper extraction of 0.6%.

A comparison of the actual amount of potassium permanganate added and that which would be require theoretically (via amount of copper and zinc extracted) gave a value of 1.1. This finding is important as it has shown that at a redox potentials of 600 mV, there was leaching of sphalerite as well as the chalcopyrite.

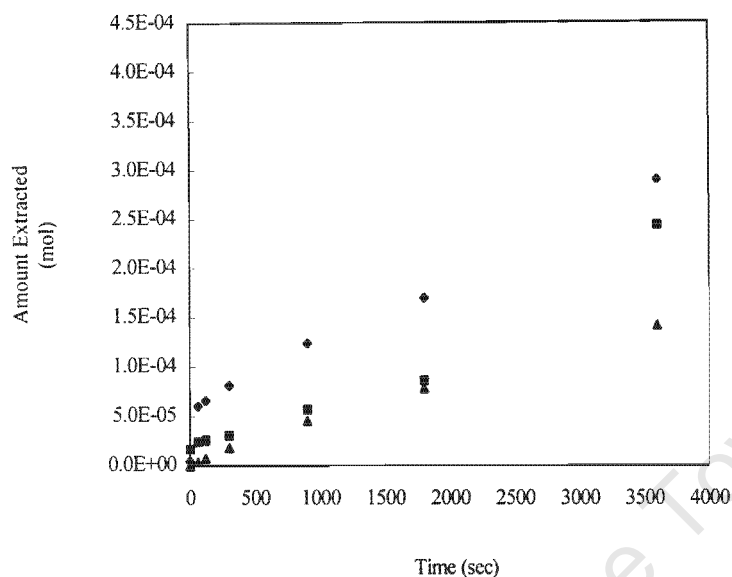


Figure 4.8 Amount of Copper and Zinc Extracted and Potassium Permanganate Added
 [♦] Copper, [■] Zinc, [▲] Potassium Permanganate Added
 70 °C, pH of 1.5 and 15g.l⁻¹ solids concentration

4.6 ROLE OF ACID DURING LEACHING OF THE CONCENTRATE

The role of acid in the leaching of chalcopyrite has been described by some authors as being involved in an initial attack of the mineral with ferric ion (Dutrillac, 1989, Schippers and Sand, 1999). However, some have suggested that acid was more important for preventing iron hydrolysis (Hearne *et al.*, 1998).

Figure 4.9 shows the amount of copper extraction using an iron free acid solution compared with that extracted from a combination ferric/ferrous ion and acid solution. The findings show that acid is not the chief oxidant in the leaching of the concentrate.

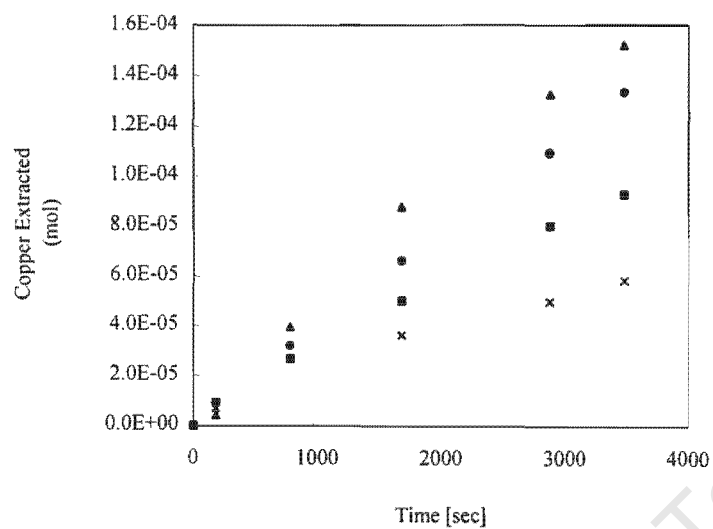


Figure 4.9 The Role of Acid in Leaching Of Concentrate

[▲] 490 mV, [●] 590 mV, [■] 628 mV, [x] H⁺

5. EVALUATION OF RESULTS WITH THE LITERATURE

The raw data presented by Kametani and Aoki (1985) and Hiroyoshi *et al.* (2000) was re-worked in order to determine the rate of leaching as a function of redox potential. It was preferred to use the raw data because of different assumptions made by the different researchers and in this case different experimental conditions. The calculated rates were normalised to rates per unit area. The differences in temperature were also taken into account and the Arrhenius equation was used.

Kametani and Aoki (1985) conducted their studies on chalcopyrite ore comprising 75% chalcopyrite 17% pyrite and 3 % sphalerite. Potassium permanganate was added to maintain the potential by re-oxidising the ferrous ions generated from the mineral oxidation back to ferric ions. Consequently, the rate of oxidation was followed by recording the amount of Potassium permanganate added.

The results they obtained were presented in the form of amount potassium permanganate used vs. log time at the different potential studied. The data was first converted to a normal time scale as in Figure 5.1, which shows an initial fast rate followed by a slower rate. The fast rate has been linked to chemical control of the reaction (Munoz *et al.* 1979, Dutrizac, 1982). The rate of ferrous ion production can be calculated as previously explained and assuming that the work of Kametani and Aoki (1985) was performed under constant volume.

The role of the bacteria in bioleaching is to re-oxidise ferrous ion back into ferric ions; thus maintaining a constant redox potential. As such, determining the rate of ferrous ion generation at constant redox potential is valuable. Figure 6.2 shows the rates calculated at the different potentials. The rate of ferrous iron generated increases with potential up to a critical potential of 440mV(SCE). The rate then drops till about 530mV(SCE). Before increasing with increasing potential (530mV – 650mV)(SCE)

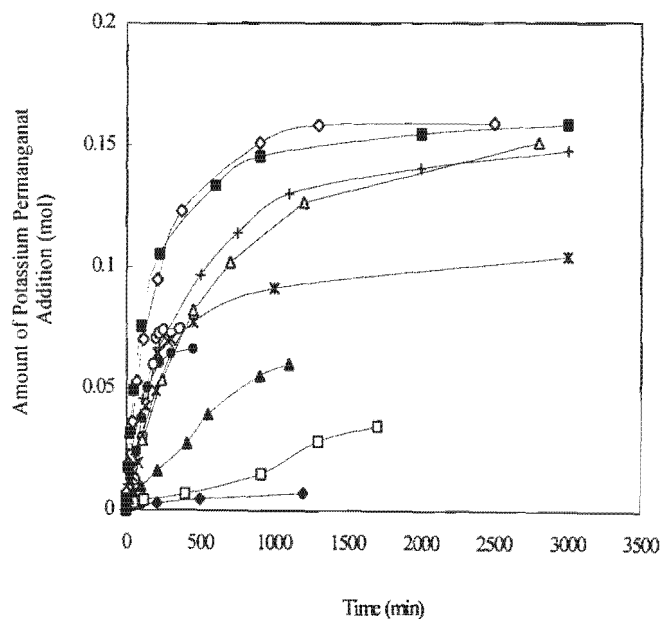


Figure 5.1 Amount of Potassium Permanganate Added (Kametani & Aoki, 1985)

[◆] 300 mV, [□] 330 mV, [▲] 350 mV, [†] 370 mV, [●] 400 mV,
 [○] 430 mV, [*] 470 mV, [Δ] 500 mV, [+] 550 mV, [◇] 600 mV.

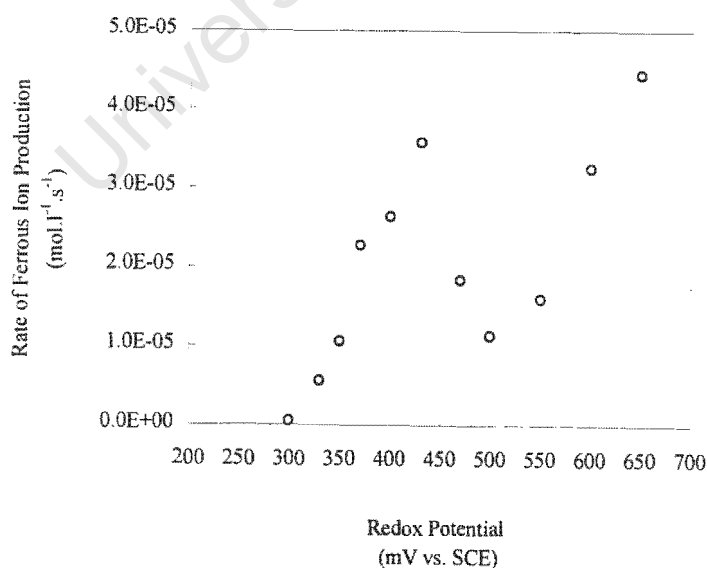


Figure 5.2 Rate of Ferrous Ion Generation vs. Redox Potential (Kametani and Aoki, 1985)

90 °C, 1M H₂SO₄, Redox Potential vs. SCE.

The amount of copper and iron extracted were seen to be equal up to 440mV(SCE). Beyond this redox potential value the amount of iron dissolved increases until a maximum at 500mV(SCE). Kametani and Aoki (1985) initially attributed the rise in iron extracted to oxidation of pyrite in the ore. The fact that there was no accompanying increase in sulphur formed above 500mV(SCE) was used as further evidence to support the oxidation of pyrite. However on verification of this finding using a 96% chalcopyrite ore, the authors found similar behaviour. This finding meant that it was not in fact pyrite leaching but maybe the result of the chalcopyrite changing its nature at potentials above the critical potential.

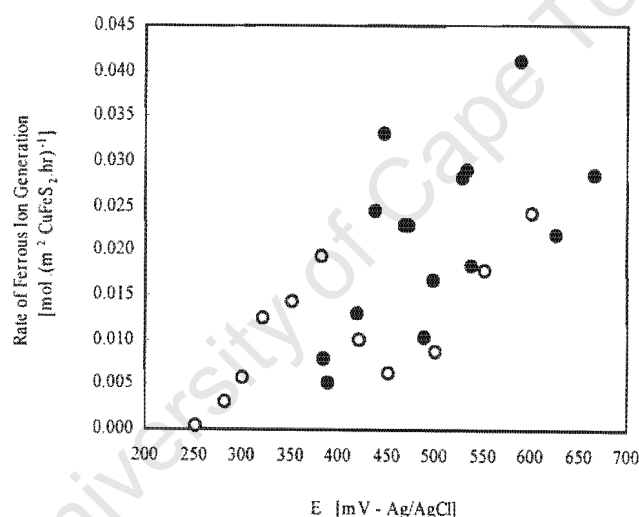


Figure 5.3 Comparison of Rate of Ferrous Ion Generation
 [•] Experimental Result, [o] Kametani and Aoki (1985)
 (all data corrected to 90 °C)

Figure 5.3 shows that the data of Kametani and Aoki (1985) and this report lie in the same order of magnitude once expressed as a normalised rate per unit of available mineral surface area. Both data series have a strong relationship in potential range 490 mV to 600 mV where

there is an increase in rate of ferrous ion generation with increasing potential. This is complemented by a similar trend in the rate of copper extraction with increasing potential observed in Figure 5.4 below.

Hiro Yoshi *et al.* (2000) proposed a model of ferrous ion promoted chalcopyrite oxidation. The ferrous ions are released from chalcopyrite together with cupric ions. The proposed model is as follows:



The first step is achieved by reduction of the chalcopyrite with ferrous ions and the second step by oxidising Cu_2S with oxygen. A thermodynamic argument was used to prove the steps of this reaction. The authors used the Gibbs Free Energy of formation of various possible products. However XRD analysis was not performed to confirm the prediction.

They used a chalcopyrite ore containing 33 % copper, 29 % iron and 0.3 % lead. 0.01 litres of ferrous sulphate and a sulphuric acid concentration of 0.1 M together with 0.1 g of chalcopyrite concentrate was used. The initial amounts and amounts after 24 hours of copper and iron were measured.

They also showed that for the solution redox potential remained constant throughout the leach period. However this was only possible by use of a small amount of concentrate (0.1 g) which would not have contained sufficient iron to change the ferrous ion or total iron content.

They described the amount of copper extracted at the start and after 24 hours of reaction. They did not describe the pattern of extraction during this period. It is therefore plausible that more copper was extracted in the initial hour of leaching. This lack of disclosure about the copper extraction with smaller time increments means that an assumption had to be made that there was an even extraction of copper throughout the entire 24 hours.

Figure 5.4 shows a comparison between the results of this report and those of Hiro Yoshi *et al.* (2000). There is some agreement about the redox potential region for maximum copper extraction. It appears to be between 380 mV and 450 mV. However Hiro Yoshi *et al.* (2000) did not conduct any experiments above 500 mV so the behaviour of a second region of high copper extraction at 35 °C could not be verified.

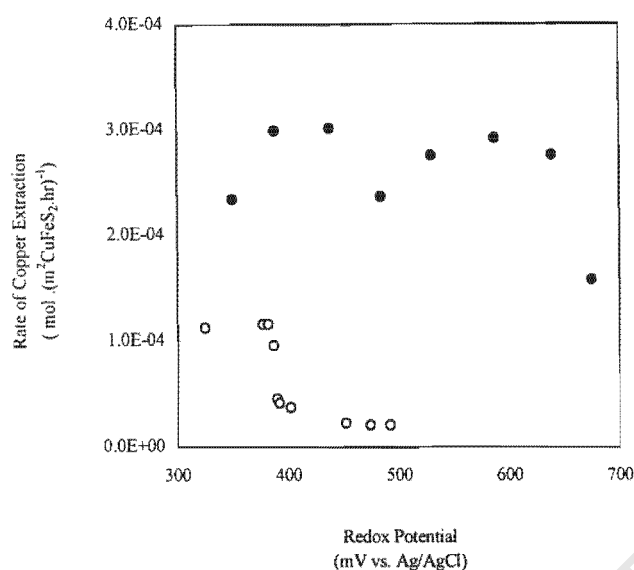


Figure 5.4 A Comparison of Copper Extraction Rate with Hiroyoshi *et al.* (2000)

[•] Experimental results, [o] Hiroyoshi *et al.* (2000), T = 35 °C

Kametani and Aoki (1985) and Hiroyoshi *et al.* (2000) show agreement that at a potential of about 390 mV, maximum leaching of chalcopyrite occurs. This is supported by a coinciding of the rates of ferrous ion generation and copper extracted respectively shown in Figures 5.3 and 5.4. The results from this report show significant oxidation at this potential however with maximum oxidation at a higher redox potential (448 mV).

There is agreement between this report and Kametani and Aoki (1985) on the rate of ferrous ion generation between 490 mV and 600 mV, where there is an increase in rate of with increasing in potential; to reach a maximum value at 590 mV.

6. CONCLUSIONS

This work has established the validity of the method developed by Kametani and Aoki (1985) for studying the chemical leaching of a copper concentrate at constant redox potentials, using potassium permanganate.

Preliminary results have shown that the rate of oxidation of the concentrate is dependent on the redox potential. It appears that leaching of chalcopyrite in the concentrate is favoured at lower redox potentials in the range 390 to 450 mV vs Ag/AgCl. Higher potentials (above 590 mV) show a lower rate of leaching of the chalcopyrite. There is evidence of leaching of the sphalerite in the concentrate in the higher redox potential range.

An increase in temperature from 35 °C to 70 °C shows a higher rate copper extraction and ferrous ion generation.

Pre-treatment of the concentrate was shown to be effective in removing attached fine material. The role of acid during the leaching of the concentrate was shown to be more important for preventing iron hydrolysis.

The results obtained are consistent with previously published work of Kametani and Aoki (1985) and more recently Hiroyoshi *et al.* (2000); who observed high copper extraction at high ferrous ion concentrations and therefore low redox potentials. This phenomenon of enhanced copper extraction at low redox potential for chalcopyrite has formed the basis of a commercial pilot plant (Mintek/Bactech Bioleach Process) for the treatment of chalcopyrite concentrates (van Standen, 1998).

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APPENDIX I

ANALYTICAL METHODS

STANDARDISATION OF A SOLUTION OF POTASSIUM PERMANGANATE

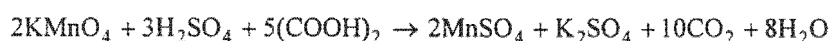
Listed below is the procedure used to calculate the concentration of the potassium permanganate used in the experimental determinations.

Method

The burette was washed with water and allowed to drain. The burette was rinsed four times with about 10ml of potassium permanganate solution and allowed to drain each time. Finally the burette was filled with potassium permanganate solution. The pipette was washed with water and rinsed three times with small amounts of the oxalic acid solution. Exactly 20 ml of oxalic acid solution (0.05 M) was pipetted into a clean flask. Approximately 20 ml of 3M sulphuric acid was added and the solution was heated to about 60 °C (a thermometer was not used to prevent loss of the solution). The hot solution was slowly titrated with the potassium permanganate to the first permanent pink tinge. If a brown suspension or precipitate had occurred, then insufficient sulphuric acid would have been added or the titration could have been carried out too quickly.

The procedure was repeated until three titres within 0.1 ml of each other were obtained.

The equation for the reactions which occurred is:



Calculations

The permanganate ion (MnO_4^-) was converted to the manganese (II) ion (Mn^{2+}) while carbon dioxide was liberated. The reaction involved the hydrogen ion (H^+), thus the addition of sulphuric acid to the oxalic acid solution before titration.

Using the equation above, the following relationship was used to calculate the concentration of the potassium permanganate.

$$\frac{C_{\text{oxalic acid}} \times V_{\text{oxalic acid}}}{5} = \frac{C_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{2}$$

TITRATIONS FOR DETERMINATION OF FERROUS AND TOTAL IRON CONCENTRATIONS

Determination of Ferrous Ion Concentration

The required aliquot (5 ml) was pipetted into a conical flask. 10 ml of spekker was added, followed by 3 – 4 drops of barium diphenyl sulfonate indicator. The sample was titrated with potassium dichromate until the first permanent colour change from orange to purple.

$$[\text{Fe(II)}](\text{mol.l}^{-1}) = \frac{[\text{K}_2\text{Cr}_2\text{O}_7] \times V_{\text{titre}} \times 55.85 \times 6}{V_{\text{titre}}}$$

Determination of Total Iron Concentration

The required aliquot (5 ml) of sample was pipetted into a conical flask. 30 ml ferric acid was added and the solution was heated to boiling point. Stannous chloride was added drop-wise until the yellow colour of the solution disappeared. One extra drop was added and the total amount of stannous chloride added was recorded. The solution was cooled to room temperature and 10 ml mercuric chloride solution was added forming a silky white precipitate. If no precipitate formed, too little stannous chloride would have been added, and if the precipitate was heavy and grey, too much stannous chloride would have been added. In either case the experiment had to be aborted. 4-8 drops of barium sulfonate indicator were added and the sample titrated with potassium dichromate until the first permanent colour change from yellow/green to purple.

$$[\text{Fe(total)}](\text{mol.l}^{-1}) = \frac{[\text{K}_2\text{Cr}_2\text{O}_7] \times V_{\text{titre}} \times 55.85 \times 6}{V_{\text{titre}}}$$

Preparation of Reagents

The chemical reagents used in the procedures mentioned above were prepared as described below.

Potassium Dichromate Solution

About 10 g of potassium dichromate was dried in an oven at about 105 °C for 1-2 hours. About 8.8 g of the dried potassium dichromate was dissolved in 2 litres of distilled water, to form a standard solution of concentration about 0.015 M.

Spekker Acid

450 ml concentrated (98 %) sulphuric acid and 450 ml concentrated (32 %) hydrochloric acid were slowly added to 1200 ml distilled water with stirring. The solution was allowed to cool before transferring to a storage bottle.

Ferric acid solution

300 ml of spekker acid solution and 600 ml concentrated (32 %) hydrochloric acid were slowly added to 1200 ml distilled water with stirring. The solution was allowed to cool before being transferred to a storage bottle.

Stannous chloride solution

50 g stannous chloride (SnCl_2) was weighed out into a 100 ml beaker. 50 ml of concentrated (32 %) hydrochloric acid was added and the solution was heated to about 50 °C and agitated until all the salt had dissolved. After cooling, the solution was diluted to 1 litre with distilled water and stored in a glass container with a few granules of tin metal.

Mercuric chloride solution (saturated)

One litre of distilled water was added to 50 g mercuric chloride (HgCl_2) and agitated for 2 hours. If all the mercuric chloride had dissolved, a further amount was added and the solution agitated for a further 2 hours.

Barium Diphenylamine Sulfonate Indicator

1 g barium diphenyl sulfonate ($C_{24}H_{20}BaN_2O_6S_2$) was weighed out in a 250 ml beaker. 100 ml of concentrated (98 %) sulphuric acid was added and the solution was agitated until the salt had completely dissolved.

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APPENDIX II

CALCULATION OF RATE PER UNIT AREA OF CHALCOPYRITE

$$(\text{m}^2\text{CuFeS}_2)\text{mol}^{-1} = [(\text{m}^2\text{CuFeS}_2).\text{kg}^{-1}][(\text{0.183kgCuFeS}_2)\text{mol}^{-1}]$$

$$= \frac{\pi d^2}{4\pi \frac{d^3}{6}} \cdot [(\text{0.183kgCuFeS}_2)\text{mol}^{-1}]$$

$$= \frac{6}{\pi d} [(\text{0.183kgCuFeS}_2)\text{mol}^{-1}]$$

$$= \frac{6}{4087d} [(\text{0.183kgCuFeS}_2)\text{mol}^{-1}]$$

Assumptions: Molar mass of chalcopryrite = 183 g. mol^{-1}

Density of Chalcopryrite = 4087 kg.m^{-3}