AN ELECTROCHEMICAL INVESTIGATION INTO THE FLOATABILITY OF PYRRHOTITE

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Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

M. Bartt.

20/02/98

Abstract

Impala's Minerals Processing Plant in the Rustenburg Area, South Africa, uses flotation to beneficiate precious metal bearing ores from the Bushveld Complex. Pyrrhotite is one of the sulphide minerals that is targeted but it is the least amenable to current flotation conditions having the lowest recovery. Electrochemical techniques (mixed potential measurements, cyclic voltammetry and current transient techniques) were used to study the relevant reactions on the surface of pyrrhotite mineral electrodes. Aspects investigated included the oxidation of the mineral in aqueous alkaline solutions, activation by copper sulphate, kinetics of oxygen reduction and the adsorption of isobutyl xanthate. Mixed potential measurements of mineral electrodes were taken in batch flotation test work. In addition a novel qualitative measure of hydrophobicity was investigated. The oxidised surface of pyrrhotite is likely to be covered with iron hydroxides and a sulphur rich sub-lattice. No direct evidence was found for the activation of pyrrhotite by copper sulphate in alkaline solutions. It was shown however that activation could be achieved in mildly acidic media and that the surface remained activated if subsequently exposed to alkaline conditions. When achieved under acidic conditions activation was observed to enhance the degree of interaction between the mineral and the xanthate collector. Also copper sulphate appeared to aid the formation of a more hydrophobic surface (as indicated by the hydrophobicity tests). Copper activation conducted in acidic media did not significantly enhance the kinetics of oxygen reduction, a reaction seen as crucial to the adsorption of xanthate. No evidence was found for the initial chemisorption of xanthate onto the mineral surface. However evidence was found for the oxidation of xanthate to dixanthogen at sufficiently anodic potentials. It was concluded that the relatively poor flotation performance of pyrrhotite could be combated by minimising the extent of the oxidation, adding reagents as soon as possible before the mineral becomes extensively oxidised and by removing surface hydroxides through lowering the pH during conditioning.

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List of Abbreviations

DETA	-	diethylenetriamine
DTP	-	dithiolphosphate
EDTA	-	ethylenediamine tetraacetate
E_h	-	electrochemical potential
FTIR	-	Fourier transform infra-red spectroscopy
IR	-	infra-red
KAX	-	potassium alkyl xanthate
KEX	-	potassium ethyl xanthate
LIMS	-	line of site ion mass spectroscopy
MBT	-	mercapto-benzothiozole
MS	-	metal sulphide
NHE	-	normal hydrogen electrode
PGM	-	precious group metals
QEM*SEM	-	quantitative evaluation of minerals by scanning electron microscopy
UV	-	ultra-violet
SAG	-	semi-autogenous
SEM	-	scanning electron microscope
SHE	-	standard hydrogen electrode
SIBX	-	sodium isobutyl xanthate
TOF-SIMS	-	time-of-flight secondary ion spectrometry
XPS	-	X-ray photoelectric spectroscopy

1. Introduction

Impala's Minerals Processing Plant in the Rustenburg area uses flotation as an initial means of beneficiating run of mine ore and preparing it for subsequent matte smelting. PGM's are found in the ore body as discrete minerals, as metal alloys and in solid solution within other non-precious metal sulphides. The minerals containing PGM's in solid solution that are targeted include chalcopyrite, pyrite, pentlandite and pyrrhotite. The basic flotation process comprises of activation with copper sulphate, followed by collection with SIBX (see Figure 1.1 for schematic of circuit). It is believed that the relatively poor pyrrhotite recovery is responsible for a large portion of unrecovered PGM's, although the exact extent to which pyrrhotite is individually responsible is not known.
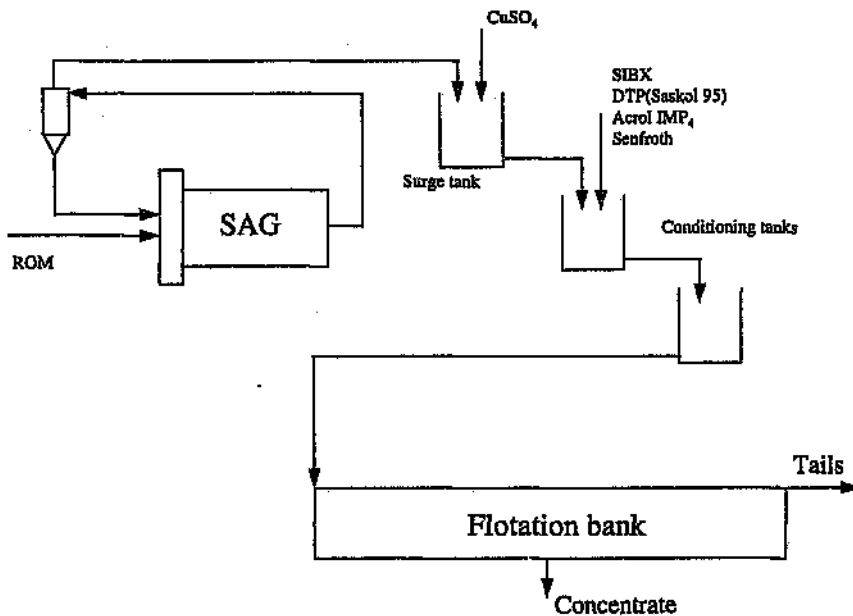
Figure 1.1: **Schematic of milling and flotation circuit at Impala's Minerals Processing Plant**

A detailed QEM*SEM analysis (Latti and Nolle, 1995) revealed a number of interesting points regarding the performance of the sulphide minerals in general, and

specifically in the case of pyrrhotite. The report concluded that pyrrhotite was the least amenable to the current flotation conditions. Although pyrrhotite was identified as a slow floater it was not considered that additional flotation cells would significantly improve the recovery. Pyrrhotite should therefore be targeted either magnetically or chemically. It was from this work that the motivation for the current research evolved.

On a microscopic scale flotation is predominantly dependent on solid/liquid/gas surface interactions. It relies on rendering certain targeted minerals hydrophobic so as to facilitate adhesion to gas bubbles. For minerals that do not show self induced hydrophobicity the technique involves the use of surface active reagents, commonly termed collectors, that attach to the mineral thereby achieving hydrophobicity. Certain minerals however do not collect and it is then necessary to activate the mineral. One of the most important activation techniques is copper activation.

All of these processes involve surface reactions. Thus although bulk composition and liberation characteristics are important aspects, surface composition and topography control the surface reactivity of mineral particles. Consequently these considerations play a key role in determining the flotation behaviour of minerals. Knowledge of surface composition allows for a fundamental understanding of the reaction mechanisms that occur between mineral surfaces and reagents.

Electrochemical techniques have been extremely useful in studying aqueous mineral systems *in situ*. They are especially suited to following electrochemical reactions on the surface of a mineral electrode and can be used diagnostically to study the nature of the reacted mineral surface in terms of surface composition and concentration. This research therefore aims to use electrochemical techniques to develop a fundamental electrochemical understanding of the flotation of pyrrhotite. It is anticipated that once such fundamental knowledge is available it can be translated into practical steps to achieve the necessary recoveries of pyrrhotite, thereby enhancing overall PGM recovery.

2. Literature Review

2.1 Chemistry of pyrrhotite

Pyrrhotite is an iron deficient sulphide mineral, $Fe_{(1-x)}S$, with a range of stoichiometries. A detailed discussion of the structures and properties of pyrrhotites can be found in Power $et\ al.$ (1976). There are two principal crystalline forms: monoclinic and hexagonal, which can be distinguished by X-ray diffraction techniques. The monoclinic form is richer in sulphur and is ferromagnetic, whilst hexagonal form is poorer in sulphur, and is non- or weakly magnetic (Iwasaki, 1988). This varied structure leads to a diverse chemistry which is only partially understood.

The E_h-pH diagrams for the relevant systems are shown in Figure 2.1.
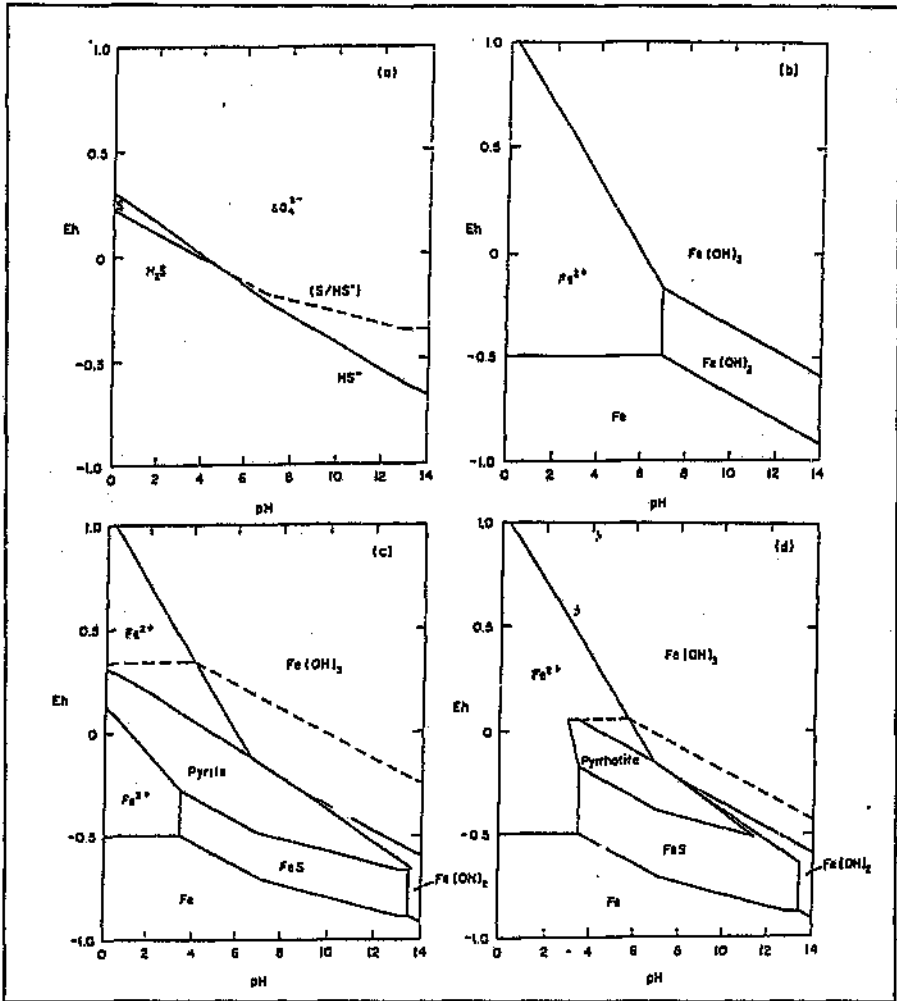
Figure 2.1: E_h-pH diagrams for iron, sulphur, pyrite and pyrrhotite systems (Hamilton and Woods, 1981)

Sulphur is not stable at high pH. Reactions involving sulphate are however irreversible and sulphur can be formed from the oxidation of the sulphide (Hamilton and Woods, 1981). The stable species in the Fe-H_2O system, at alkaline pH's, are insoluble $Fe(OH)_2$ and $Fe(OH)_3$ depending on the E_h. The stability phase diagram for pyrrhotite indicates that, in oxidative alkaline solutions, the products of pyrrhotite oxidation will include ferric hydroxide. At pH 9 pyrrhotite is unstable above $\approx$-0.25 V.

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It is expected that pyrrhotite will be oxidised in conventional alkaline flotation circuits.

Hamilton and Woods (1981) used linear sweep voltammetry to study the oxidation of pyrite and pyrrhotite electrodes in acidic and alkaline conditions. In acidic solutions (pH 4.6), and below 0.400V, they considered the dominant oxidation reactions to be:

$$FeS_{1.13} \rightarrow Fe^{2+} + 1.13S + 2e^- \qquad (1\text{-}1)$$

and

$$FeS_{1.13} + 4.52H_2O \rightarrow Fe^{2+} + 1.13SO_4^{2-} + 9.04H^+ + 8.78e^- \qquad (1\text{-}2)$$

At higher potentials, above 0.400V, they considered that Fe^{2+} was oxidised directly to Fe^{3+}:

$$FeS_{1.13} + 3OH^- \rightarrow Fe(OH)_3 + 1.13S + 3e^- \qquad (1\text{-}3)$$

and

$$FeS_{1.13} + 4.52H_2O \rightarrow Fe(OH)_3 + 1.13SO_4^{2-} + 9.04H^+ + 9.78e^- \qquad (1\text{-}4)$$
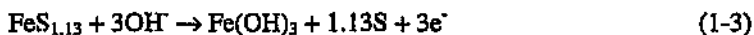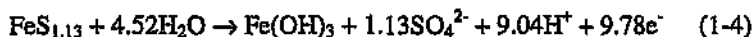
In alkaline solutions (pH 9.2) they considered reactions (1-3) and (1-4) to be the dominant oxidation reactions. The authors conducted a mass and charge balance in order to determine the amounts of pyrrhotite oxidised to either sulphur or sulphate. It was found that, in acidic and alkaline solutions, more pyrrhotite was oxidised to sulphur than to sulphate, although to a lessor extent in alkaline solutions. The amount of sulphate produced increased as the potential increased.

Buckley et al. (1982), in an extension of the above study, used XPS to determine the species formed on sulphide minerals after treatment at different oxidising potentials. Their results for pyrrhotite supported the above electrochemical research with the exception that in alkaline solutions the main oxidation reaction involved the formation of sulphate. The authors resolved this discrepancy by considering the different time scales between the two approaches, that is, a sulphur-rich surface could form initially and then be oxidised to sulphate. The overall conclusion reached was that the oxidation of pyrrhotite proceeds through the progressive removal of iron, leaving a metal-deficient sulphide with the sulphur lattices unaltered.

Hodgson and Agar (1989) studied the effect of Ca^{2+}, $S_2O_3^{2-}$ and SO_4^{2-} on the oxidation of pyrrhotite and pentlandite. They identified two areas of oxidation for pyrrhotite.

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The initial reaction involves the oxidation of $Fe_{0.9}S$ to $Fe(OH)_x(S_2)S$. At higher potentials $(S_2)S$ oxidises to S and SO_4^{2-}. In their analysis of the cathodic waves forms, after anodic treatment, they attributed three cathodic reactions to: the reduction of $Fe(III)$ to $Fe(II)$, $S°$ to S_2^{2-} and reduction of S^{2-} and $Fe(II)$ to reform a metal sulphide. It was observed that the thiosulphate and sulphate ions caused the anodic peaks to move cathodic, but it was considered that these ions would have no adverse affect on flotation response. Ca^{2+} ions were thought to adsorb at surface sulphur sites. The authors also studied the interactions of the mineral with xanthate, but this will be discussed in section 2.2.4.

Sui *et al.* (1995) studied the galvanic interaction between pyrite, pyrrhotite, galena and sphalerite by comparing the metal ion production of minerals by themselves and in pairs. In terms of the theory of sulphide mineral galvanic interactions, minerals with more positive rest potentials should act as cathodes in a galvanic couple, whilst the less noble sulphide minerals act as the anodes (Holmes, 1994). The reaction at the cathode is the reduction of oxygen:

$$^1/_2O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{1-5}$$

The authors used a chelating agent, EDTA, to extract metal ions from the minerals surface. When a mineral was coupled with another mineral with a higher rest potential, in neutral aqueous solutions, the former mineral produced more metal ions than when in solution without other minerals present. Metal ion production was also enhanced on the cathodic mineral. The authors thought that OH^- produced during oxygen reduction may react with the mineral, however no specific reaction mechanism to support this was put forward. It was also found that the amount of metal ion production per unit surface area was independent of particle size, implying that fine particles were not more susceptible to dissolution.

One of the criticisms of galvanic interactions between mineral particles in flotation systems is that it is unlikely that sufficient physical contact occurs between mineral particles in actual flotation pulps, where the sulphide mineral concentration is very low. It is possible that intermediary reactions could still make it possible, for instance a ferrous/ferric couple could act as a charge carrier between minerals that are not in contact, but this has not been investigated.

2.2 Flotation of pyrrhotite

2.2.1 Electrochemical potential and mixed potential

A significant proportion of electrochemical research into sulphide flotation has concentrated on the role of electrochemical potential (E_h) on the recovery and selectivity of flotation processes treating complex sulphide ores (Ralston, 1991, Goktepe and Williams, 1995, Hintikka and Leppinen, 1995). The main drive has been to identify electrochemical potential ranges where the flotation of various specific sulphide minerals becomes favourable over that of other sulphide minerals. Examples include the suppression of arsenopyrite and pyrite from the flotation of gold bearing ores (Hintikka and Leppinen, 1995) and the targeting of chalcopyrite over pyrite in the exploitation of copper bearing ores (Goktepe and Williams, 1995).

Tolley *et al.* (1995) pointed out that there is considerable disagreement over the appropriate method to measure E_h. On the one hand inert precious metal electrodes are advocated, whilst others maintain that the use of electrochemically prepared mineral electrodes is necessary. There are also problems associated with placing too much significance on E_h and its effect on flotation, due to the practicalities of controlling E_h effectively under plant conditions.

Part of this disagreement arises due to the inconsistent use of some of the potential terms mentioned previously. For instance, Ralston (1991) noted that when considering single sulphide minerals in the presence of collectors, the various reactions that occur between the collector and the mineral surface are dependent on the potential across the mineral-solution interface. The most effective measure of this potential is the mixed potential of the mineral itself. Most often however, the flotation of individual minerals is correlated with electrochemical potential, as measured by an inert precious metal electrode, and termed E_h. The effect of the various potential determining ions may not be the same between the two different systems, although there will generally be a correlation between the potential measured by for instance a platinum electrode and a pyrrhotite electrode.

The potential across the mineral-solution interface is only relevant to the flotation response of a mineral, in terms of the extent to which it controls what reactions may occur on the surface of the mineral. It is then these surface products that directly affect the hydrophobicity of the mineral surface and thus the flotation. This point was well illustrated by Allison et al. (1972), who correlated the mixed potential of various sulphide minerals with the surface product from xanthate interaction. This type of fundamental understanding is not possible if only the overall electrochemical potential is considered and this would help explain the apparent frustration at obtaining clear correlation's between pulp potential (E_h) an ftation response (Goktepe and Williams, 1995). Therefore, in terms of developing a fundamental understanding of the flotation of specific sulphide minerals, the mixed potential of the mineral itself is of great importance.

Allison et al. (1972) studied the interaction of xanthate collectors with a number of sulphide minerals including pyrrhotite. They found that all minerals with a rest potential more anodic than the equilibrium potential of the dixanthogen/xanthate couple, of which pyrrhotite was one, formed dixanthogen as a major surface product, and that an electrochemical mechanism was responsible for this formation. For pyrrhotite they reported a rest potential, after 10 minutes, of 0.21 V (vs NHE) in a pH 7, 6.25×10^{-4}M potassium ethyl xanthate solution. The corresponding equilibrium potential for the dixanthogen/xanthate couple was found to be 0.13V. The importance of the sample origin was noted. Different samples of the same mineral may have different rest potentials due the differences in the relative rates of reactions that make up the mixed potential. These differences may arise from slight differences in stoichiometry, and due to the presence of impurities. Obviously it follows that these differences in rest potential could alter the nature of the xanthate product formed on the surface of the mineral.

Goktepe and Williams (1995) studied the flotation of copper ores, of which the principal minerals were sphalerite, chalcopyrite and pyrite. They conducted batch flotation tests investigating the effects of pH, oxygenation and nitrogenation on recovery of copper, iron and zinc. During the flotation tests the mixed potential of

chalcopyrite electrodes was measured, as well as the potential of a platinum electrode. Although the authors did not interpret the mixed potential measurements in terms of the work done by Allison *et al.* (1972), they did attempt to correlate the potential of the chalcopyrite electrode at the point of KAX addition with overall copper recovery (chalcopyrite being the principal copper bearing mineral). The authors noted in their final conclusion that "A general relationship between flotation and pulp potential *(ed. as measured by a chalcopyrite electrode at the point of KAX addition)* could not be found for the complex ore system.". This conclusion, however, cannot be accepted as final. If the oxidation of xanthate to dixanthogen by the reduction of oxygen is controlled by an electrochemical mechanism then the mixed potential after KAX addition would be more relevant to a correlation with flotation recovery.

The above discussion highlights an important point, namely that mixed potential measurements, and more generally E_h measurements, need to first be considered in terms of an understanding of actual surface reactions. Without this the correlation and understanding of potential measurements and flotation recoveries of sulphide minerals will continue to be inconclusive.

2.2.2 Activation by Cu^{2+} ions

Under certain conditions, sulphide minerals do not respond readily to flotation collectors. The problem is often combated by the addition of heavy-metal cations, most commonly lead and copper, to the flotation slurries. For instance, the flotation of sphalerite with xanthate collectors does not occur readily but, after activation with copper ions, the flotation improves substantially (Woollacot and Eric, 1994).

In the simplest sense activation is achieved by altering the chemical composition of the mineral surface to that which is more amenable to collector adsorption. Originally this was thought to occur through simple ion exchange mechanisms. Bushell *et al.* (1961), considered the following reactions for the activation of sphalerite (ZnS) and pyrrhotite (FeS) by copper ions:

$$ZnS + Cu^{2+} \rightarrow CuS + Zn^{2+} \tag{1-6}$$

and

$$FeS + Cu^{2+} \rightarrow CuS + Fe^{2+} \tag{1-7}$$

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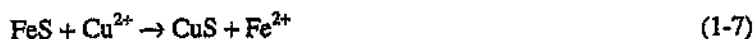
The driving force for these reactions was considered to be the lower solubility of the heavy-metal sulphide, CuS in the above case, as compared to the other metal sulphides, MS (Nicol, 1984). This ion exchange mechanism is however, too simplistic for a general description of activation of sulphide minerals, and, depending on the sulphide, more advanced mechanisms have been proposed.
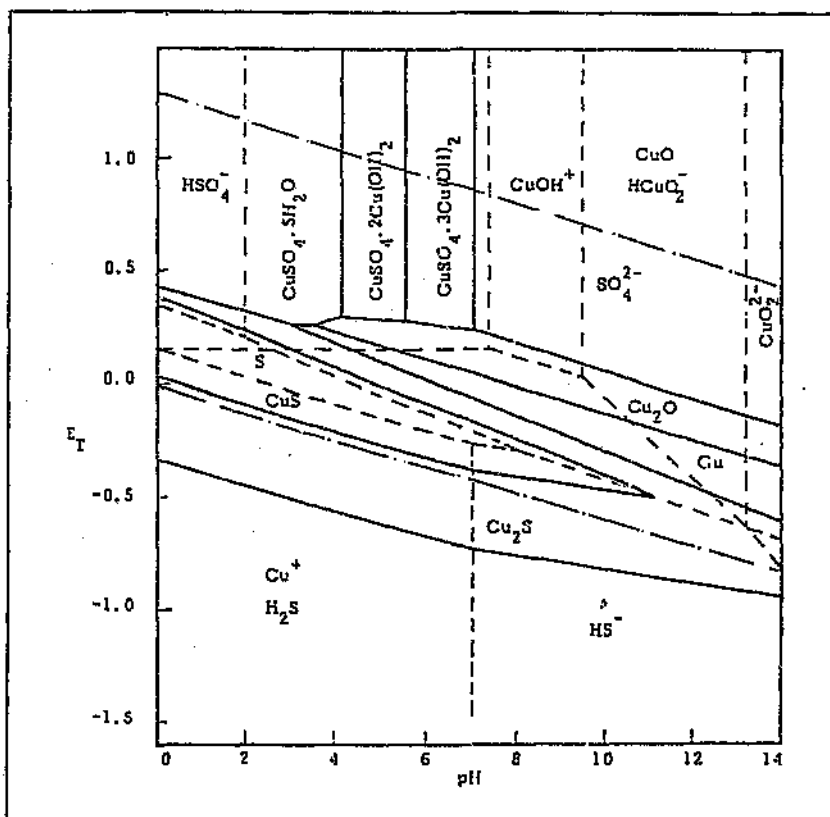
Figure 2.2: E_h-pH diagram at 25°C for the Cu-S-H$_2$O system (Robins, 1987)

Figure 2.2 shows the stability diagram for the aqueous copper-sulphur system. The solubility product, K_s, of $Cu(OH)_2$ is given as 6×10^{-20} (Stranks et al., 1979). At pH 9, this calculates to a maximum Cu^{2+} concentration of $6 \times 10^{-15}M$. Some of the Cu^{2+} will be stabilised through complex formation. The concentration of Cu^{2+} available for activation under alkaline conditions may however be extremely low.

Nicol (1984) used electrochemical techniques to study the reaction of copper ions with the minerals galena, pyrite and pyrrhotite. It was proposed that the activation of galena proceeded via two coupled electrochemical reactions (as opposed to ion exchange):

$$PbS \rightarrow Pb^{2+} + S + 2e^{-} \qquad (1-8)$$

$$PbS + 2Cu^{2+} + 2e^{-} \rightarrow Pb^{2+} + Cu_2S \qquad (1-9)$$

A similar mechanism was proposed for pyrrhotite, the overall reaction being:

$$Fe_9S_{10} + 9Cu^{2+} \rightarrow 9Fe^{2+} + 9CuS + S \qquad (1\text{-}10)$$
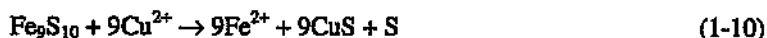
The effect of pH on the activation and floatability of pyrrhotite was investigated by conducting micro-flotation tests. These flotation results are discussed further in section 2.2.5. At pH 5 activation significantly enhanced the flotation response of pyrrhotite. At pH 8 however, activation had no significant effect, even with excessive amounts of collector. Rest potential measurements indicated that the effect of copper ion addition on the electrode mineral potential decreased with increasing pH. At pH 8 the oxidation of xanthate to dixanthogen was negligible compared to the oxidation of the mineral itself, and the rest potential was similar to that in xanthate free solutions.

Iwasaki (1988) notes, in a review of pyrrhotite flotation, that copper activation of pyrrhotite under alkaline conditions has proved virtually ineffective, and that this may, in part, be related to the extent of iron hydroxide coating.

Leppinen (1990) used FTIR and micro-flotation tests to study the effect of copper activation on ethyl xanthate adsorption on the minerals pyrite, pyrrhotite, chalcopyrite and sphalerite. The dominant surface product for pyrite, activated in dilute solutions (10^{-5}M) of copper sulphate, was dixanthogen, and it was suggested that this was an indication of a lack of activation. At higher concentrations (3×10^{-5}M) FTIR spectra indicated copper xanthate became the dominant product, although dixanthogen was still present. At 10^{-4}M only copper xanthate was detected. The same behaviour was reported for the other sulphides, and in the case of pyrrhotite, the copper ion concentration required for only copper xanthate to be detected was 3×10^{-4}M. It is unfortunate that rest potential measurements were not taken in this study, as one would expect, based on the work by Allison et al. (1972), that if metal xanthate is the dominant product on well a..... ed sulphide minerals, then the rest potential of the mineral in xanthate soluti. is should fall below the dixanthogen/xanthate equilibrium potential. Although the flotation results from this study are discussed in section 2.2.5, it is appropriate to point out that the authors did report improvements in recovery due to copper activation up to pH 9.

Stowe et al. (1995) used TOF-SIMS to map the surface distribution of positive cations on sphalerite, pyrrhotite, pyrite and quartz particles. The mineral particles were

separated from a final zinc concentrate produced at Geco Mine, Ontario, Canada. The authors found that the distribution of copper ions on pyrrhotite particles was not uniform. Lead ions were uniformly distributed and were in higher concentration than copper ions. The authors suggested on this basis that pyrrhotite is more effectively activated by lead than by copper. They did not however report what conditions the particle had been subjected to, nor what the concentration of the respective ions was in the flotation solutions.

Yoon *et al.* (1995) found that LIMS analysis indicated the presence of copper and nickel on the surface of pyrrhotite particles which were floated in batch tests using KAX, Dowfroth 1263 and DETA. The amount of ions present was greater on particles from the concentrate than on particles from the tails. This led the authors to believe that pyrrhotite could be activated by heavy metal ions. The authors did not report the pH that the flotation tests where conducted at, although the pH was measured during the flotation. It is likely that the flotation solutions were alkaline, since all the other fundamental work in this study was conducted in pH 9.2, borate solutions. Without knowing the flotation conditions more thoroughly it is difficult to comment on the finding that pyrrhotite was successfully activated.

Recent studies (Leppinen, 1990, Senior *et al.*, 1995 and Kelebek *et al.*, 1996) on pyrrhotite flotation have indicated that activation is possible in alkaline (pH 9) conditions, and that recoveries are significantly improved. The basis for these findings have been batch and micro flotation tests. These findings are discussed in section 2.2.5.

2.2.3 Pyrrhotite as a catalyst for oxygen reduction

It is generally accepted that oxygen reduction plays a crucial role in the adsorption of xanthate onto the mineral surface (Wood, 1984). A mixed potential mechanism exists in which the anodic process is, for example in certain systems, the oxidation of xanthate to dixanthogen, and the cathodic process is the reduction of oxygen:

$$2X^- \rightarrow X_2 + 2e^- \qquad (1-11)$$

$$O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad (1-12)$$

The rates of these reactions are determined by the potential across the mineral surface/solution interface. According to the mixed potential model the interface will assume a potential where the rates of the anodic and the cathodic reactions are equal.

Rand (1977) studied oxygen reduction kinetics on sulphide minerals, including pyrrhotite, in both acidic and alkaline media using cyclic voltammetry. Well defined limiting currents for oxygen reduction where observed for pyrrhotite in acidic solutions at potentials below -0.050V. At more cathodic potentials hysteresis became more significant and the electrode showed enhanced activity on the return anodic sweeps. This was explained in terms of pyrrhotite being reduced to iron, which is a better catalyst for oxygen reduction than the sulphide. In alkaline solutions limiting currents were not observed and the hysteresis was significant over the entire scan. The kinetically controlled region showed a similar dependence of current density on potential in both acidic and alkaline solutions and yielded a Tafel slope of 183mV. He presented a comparison of the requirement for oxygen during flotation with xanthate collectors, described by Plaksin and Bessonov (1957), and the oxygen reduction activity at pH 9.06, as given by the potential of the activation-controlled currents at the foot of oxygen reduction waves (Figure 2.3).

galena

pyrrhotite

arsenopyrite

chalcopyrite

pyrite

Decreasing oxygen reduction activn

Increasing oxygen requirement during flotation
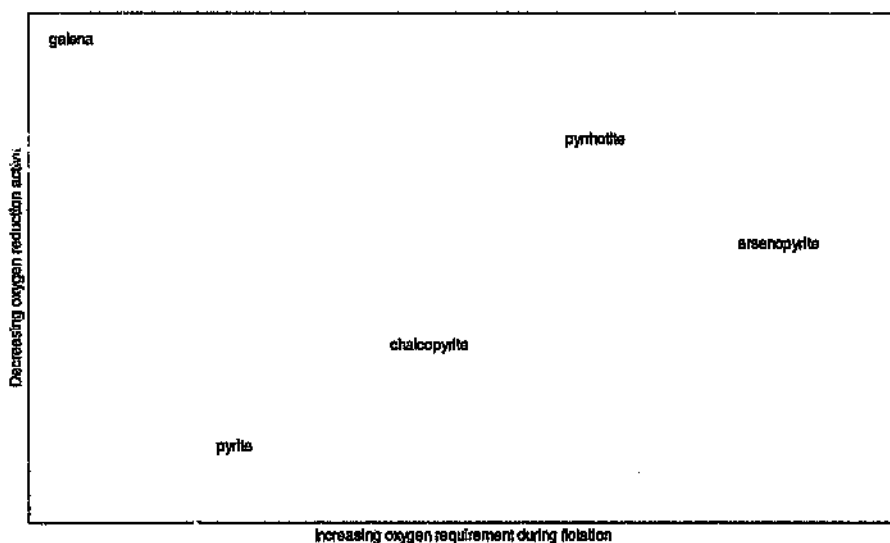
Figure 2... Comparison of O_2 reduction activity and requirement for O_2 (not to scale) (order of minerals taken from Rand (1977), and Plaksin and Bessonov (1957) respectively)

The discrepancy of galena being the poorest catalyst for oxygen reduction yet having the least requirement for oxygen is due to galena forming metal xanthate compounds at potentials where galena floats whilst the other minerals form dixanthogen. There is therefore a general correlation between the requirement for oxygen and oxygen reduction activity. Pyrrhotite is the poorest catalyst for oxygen reduction of the minerals that form dixanthogen. This may in part explain the slow floating characteristics of pyrrhotite.

Attempts to explain the oxygen reduction kinetics on pyrite, and therefore indirectly sulphide minerals, in terms of semiconducting properties have failed. Biegler (1976) found no systematic dependence of kinetic parameters on semiconducting type and in subsequent work (Biegler *et al.*,1977) he considered that the most important factor in activity for oxygen reduction may be the level, and form, of impurities in the mineral.

2.2.4 Adsorption of xanthate

It is well accepted that the interaction of thiol collectors and sulphide minerals follows a mixed potential mechanism. A thorough review of the development of this theory is

given by Woods (1984). Depending on the mineral system there are different classes of mechanism that may be relevant (Yoon and Basilio, 1993). One mechanism involves the chemisorption of the thiol ion onto the mineral surface to form a metal thiol compound. This mechanism appears most relevant to chalcocite and galena. A second mechanism involves the heterogeneous catalytic oxidation of xanthate to dixanthogen coupled to the reduction of oxygen, where the mineral acts as the passage for electron transfer between the two reaction sites. This mechanism is considered to be relevant to, amongst other minerals, pyrite and pyrrhotite. There may be variations in these mechanisms where the mineral participates in the adsorption reactions.

Hodgson and Agar (1989) investigated xanthate interactions on pentlandite and pyrrhotite. On the basis of their cyclic voltammetry results they argued that xanthate interaction was not a direct chemisorption. The reasons for their conclusion were that reduction reactions moved to more anodic potentials in the presence of xanthate. If chemisorption were the mechanism then a cathodic shift in potentials would have been expected. Rather xanthate was considered to adsorb onto the pyrrhotite surface forming an $Fe(OH)_2X$ product. This adsorption occurs through coulombic attraction between cationic $Fe(III)$ sites and xanthate ions, the $Fe(III)$ sites being generated through oxidation of the mineral. No additional peak was detected for the oxidation of xanthate to dixanthogen when the potential was swept anodically in the presence of xanthate. Due to this observation the authors considered that dixanthogen formation occurred adjacent to the oxidised mineral surface and that it is subsequently physisorbed.

A problem with reaching this conclusion is that the magnitude of current associated with xanthate oxidation may be significantly smaller than the background current due to the oxidation of the mineral. This is particularly a problem in the case of pyrrhotite as the mineral oxidises at potentials where the oxidation of xanthate is expected. One therefore requires a very sensitive current scale in order to detect any xanthate oxidation. The classic view of xanthate oxidation is that it is kinetically very slow and that significant oxidation of xanthate to dixanthogen in the bulk solution is unlikely to occur. The formation of dixanthogen only occurs, to significant degrees, on the

sulphide mineral surface, as the mineral acts as a catalyst for the reactions. Therefore it is unlikely that dixanthogen could be formed adjacent to the mineral surface.

Rao and Finch (1991) studied the adsorption of amyl xanthate on pyrrhotite in the presence of nitrogen at pH 6 and 8.4. UV spectrophotometry was used to measure xanthate and dixanthogen in solution, whilst mineral surface products were extracted using hexane followed by UV spectrophotometry tests. When nitrogen was used to condition the slurry the total uptake of xanthate from the solution decreased. No diamyl dixanthogen was formed with nitrogen (neither on the mineral surface nor in solution). Air resulted in dixanthogen both in solution and on the mineral surface, at both acidic and alkaline pH's. Generally the overall uptake of xanthate was significantly enhanced when Cu^{2+} ions were present, although dixanthogen formation on the mineral surface was inhibited. The amount of dixanthogen in solution was however enhanced with Cu^{2+} ions. When nitrogen was used as the conditioning gas, and in the presence of Cu^{2+} ions, dixanthogen was found in the solution, but not on the mineral surface. In micro-flotation tests conducted at pH 6 and 8.4 the use of nitrogen resulted in recovery values for pyrrhotite approximately half of that when air was used. The authors put forward the following interpretation of their results. They concluded that, since xanthate uptake still occurs with nitrogen, at pH 8.4, the adsorption of xanthate onto the mineral surface does not follow a charge transfer mechanism. Rather the negatively charged xanthate ions are electrostatically attracted to $Fe(OH)^+$ sites. These sites are formed through oxidation of the mineral surface. When nitrogen is used these sites are considered to arise through the superficial prior oxidation of pyrrhotite. At pH's above 9 the formation of $Fe(OH)_3$ hinders the uptake of xanthate. The presence of dixanthogen in solution when Cu^{2+} ions are present and nitrogen is used is considered to arise due to the oxidising power of the Cu^{2+} ions, which oxidise the xanthate to dixanthogen. Dixanthogen in solution is however not adsorbed onto the surface of the mineral.

Prestige et al. (1993) studied the competitive adsorption of cyanide and ethyl xanthate on pyrite and pyrrhotite. The study was conducted in pH 9 solutions and the E_h was controlled through gas and reagent addition. They confirmed the formation of dixanthogen at high E_h (>0.250V), and pH 9, using UV-vis and FTIR spectroscopy. At

lower E_h values (<0.250V) the rate and extent of ethyl xanthate adsorption was significantly reduced. It was noted that pyrrhotite appears to adsorb xanthate more strongly than pyrite under low pH conditions. This may be due to the higher susceptibility of pyrrhotite to superficial oxidation and dissolution, which results in increased formation of sites for xanthate adsorption as iron xanthate and iron hydroxy xanthate species. In this study E_h was measured using a platinum electrode and the E_h values were correlated with reactions on both pyrite and pyrrhotite, even though these minerals have different mixed potentials.

Fornasiero *et al.* (1995) used UV and IR spectroscopy to follow the adsorption of ethyl xanthate on pyrrhotite as a function of time, pH and ethyl xanthate concentration. UV spectroscopy was used to monitor the solution species and IR spectroscopy was used to monitor the species on the surface of the mineral. They found that their absorbance spectra could be explained in terms of the spectra for ethyl xanthate in solution, diethyl dixanthogen in solution and pyrrhotite dissolution products. No other xanthate derivatives were observed. In the case of ethyl xanthate its concentration decreased with time as it adsorbed onto the mineral surface. The concentration of diethyl dixanthogen increased with time until it reached its solubility limit. From their IR analysis they concluded that the only surface species on pyrrhotite was dixanthogen. These authors note that the IR spectrum of ferric xanthate and dixanthogen are very similar in the sense that the two main peaks occur at the same positions. The intensity ratio of these peaks is, however, totally different in each spectrum. The confusion regarding the dominant surface species, that is ferric xanthate or dixanthogen, may be partly due to the relatively high mineral contribution in the infrared spectrum which makes interpretation in terms of surface species difficult. The following kinetic model was proposed for the interaction of ethyl xanthate with pyrrhotite:

$$M + EX_f \rightarrow MEX \qquad\qquad (1\text{-}13)$$

$$MEX + EX_f \rightarrow EX_{2a} + M \qquad\qquad (1\text{-}14)$$

$$EX_{2a} \rightarrow EX_{2f} \qquad\qquad (1\text{-}15)$$

where EX_f refers to negatively charged ethyl xanthate ions in solution, MEX refers to ethyl xanthate bound to a pyrrhotite adsorption site, M represents a positively charged ferric or ferrous hydroxide site (e.g. $-Fe(OH)^+$), EX_{2a} refers to adsorbed dixanthogen

and EX_{2f} refers to dixanthogen in solution. An important aspect of this model is the de-sorption of dixanthogen from the mineral surface. Fornasiero et al. (1995) note that in a study conducted by Montalti (1994) it was shown that additions of dixanthogen produced only slight improvements in pyrrhotite recovery. The conclusion reached was that dixanthogen is only weakly adsorbed onto the mineral surface.

Yoon et al. (1995) studied the mechanism of depression of pyrrhotite by DETA at pH 9, using a variety of techniques including batch flotation, LIMS, XPS and FTIR. The flotation tests confirmed that DETA was effective in depressing pyrrhotite flotation as born out by the lower recoveries for this mineral. The FTIR spectra of pyrrhotite samples contacted with 10^{-3}M potassium amyl xanthate in borate solutions at pH 9 under potential control, indicated the presence of both iron xanthate and dixanthogen. The results also appear to indicate that iron xanthate is favoured at the higher potentials (>0.3V). The explanation put forward for this was that at higher potentials the formation of iron hydroxide adsorption sites is favoured due to the more severe oxidation of the mineral surface. Contact angle measurements were conducted on pyrrhotite samples under potential control. These results were correlated with IR intensity values which were also made under potential control. The contact angle and IR intensity signal matched each other. Above 0mV there was a sharp rise in both the contact angle and the xanthate adsorption signal (above $E^o_{xan/dix}$ dixanthogen formation is favourable). In the presence of DETA the contact angles remained zero until the potential reached 0.25mV and small amounts of dixanthogen were only detected above this potential.

2.2.5 Studies of the recovery of pyrrhotite by flotation

The aim of the following section is to try and present an overview of some of the recent pyrrhotite flotation recovery data that has been reported from micro and batch flotation tests. As far as possible the conditions under which the flotation data was generated will be summarised.

Nicol (1984) conducted micro-flotation tests on crushed natural pyrrhotite. KEX was used as the collector and the flotation was conducted at pH 8. The effects of KEX concentration, copper sulphate conditioning, and the pH of the conditioning stage

were investigated. When no copper sulphate was used at pH 8, the recovery of pyrrhotite was approximately 20% regardless of the collector concentration. At pH 8 copper sulphate had no effect on the recovery. When the pH of the activation stage was dropped to 5 there was a significant improvement in recovery with xanthate concentrations of 1mg/l and 5mg/l (recoveries of 32% and 41% respectively). From these results it was concluded that pyrrhotite cannot be expected to float above pH 6 and that copper activation is only effective when carried out below pH 7.

Leppinen (1990) performed micro-flotation tests on non-activated and activated pyrrhotite. The flotation of activated pyrrhotite showed a marked improvement up to pH 9, as compared to unactivated pyrrhotite ($\approx$10% recovery for non-activated and $\approx$60% for activated pyrrhotite at pH 9). The minerals were activated in separate solutions. The pH was controlled to within 0.05 units by additions of sodium hydroxide and hydrochloric acid. It is possible that on addition of copper sulphate the pH may have become mildly acidic initially, even though the pH would have been re-adjusted. If this was the case then the flotation results may be misleading as conditions were not strictly at pH 9. These considerations are however not discussed by the authors.

Heiskanen *et al.* (1991) studied the collectorless flotation of nickel ores containing pentlandite and pyrrhotite as the principal minerals, with chalcopyrite the only other sulphide mineral. When the ore was ground in steel mills pyrrhotite, pentlandite and chalcopyrite all floated readily in acidic conditions (pH 3-5). Pyrrhotite floated especially well at acidic pH's (iron recovery of $\approx$90%), but in alkaline conditions its recovery was so low ($\approx$10%) that the authors attributed it to mechanical entrainment (although this was not substantiated by water balance data). Ceramic grinding improved the flotation compared to steel mills, especially for pentlandite and pyrrhotite (iron recovery at pH 9 $\approx$50%). This affect was not interpreted extensively by the authors, and there are varying ideas on what the role of abraded iron from milling media are. These results support the model of pyrrhotite oxidation, that is a sulphur-rich surface at acidic pH's and a less sulphur-rich, hydroxide surface in alkaline conditions. The results also point to the importance of grinding media.

Senior *et al.* (1995) investigated the selective flotation of pentlandite from a nickel ore containing pentlandite, pyrrhotite and talc as the principal minerals. They used batch flotation tests to investigate the possibility of talc and pyrrhotite rejection by differential flotation. Factors varied included KEX concentration, and the addition of copper sulphate. The tests were conducted at pH 9 and the recoveries reported are for an eight minute float time. The recovery of pyrrhotite from milled ore, with no copper sulphate and 80g/t KEX, was ≈30%. The recovery of pyrrhotite improved to ≈50% when a collectorless talc pre-float was conducted on the ore prior to standard flotation on the tails from this pre-float. Doubling the collector concentration to 160g/t resulted in a ≈70% recovery of pyrrhotite from milled ore. The addition of 200g/t copper sulphate resulted in pyrrhotite recoveries in excess of 90%. Particle size analysis of the tails and concentrates identified that the fine pyrrhotite (sub 20μm) had the lowest recoveries. It was concluded from the results that pyrrhotite rejection can only be achieved effectively, and without excessive pentlandite losses, at low collector concentrations, without copper sulphate and in alkaline conditions. The finding that pyrrhotite was significantly activated by copper sulphate at pH 9 is contrary to the generally accepted result that pyrrhotite cannot be activated by copper sulphate under alkaline conditions.

Kelebek *et al.* (1996) investigated the differential flotation of chalcopyrite, pentlandite and pyrrhotite from Ni-Cu sulphide ores using batch flotation tests. Most of the work was done without a collector, although some tests with SIBX were conducted. Other reagents included the depressants, sulphur dioxide and DETA, and copper sulphate as an activator. The pH was between 9 and 9.5 for all the tests, and all flotation recoveries were quoted for a flotation time of twelve minutes. In the baseline test it was established that the collectorless flotation recovery of pyrrhotite was ≈40%. The use of both sulphur dioxide and DETA effectively depressed pyrrhotite and pentlandite recoveries to below 5%, whilst chalcopyrite was unaffected. The addition of 120g/t (≈40ppm Cu^{2+}) of copper sulphate resulted in an improved recovery of pyrrhotite to ≈80%, even with sulphur dioxide and DETA depressants. After a pre-float to remove chalcopyrite the separation of pentlandite and pyrrhotite was

investigated. It was found that good pentlandite recoveries could be obtained whilst suppressing pyrrhotite recovery to below 20% by using sulphur dioxide and DETA, but with SIBX as a collector.

2.3 Summary

There is good agreement (Hamilton and Woods, 1981 and Hodgson and Agar, 1989) that pyrrhotite oxidation, at the anodic potentials of interest to flotation, occurs through the progressive removal of iron from the sulphide lattice leaving an increasingly sulphur rich surface. The collectorless flotation results for pyrrhotite in acid media support this overall model (Heiskanen *et al.*, 1991).

It is difficult to interpret electrochemical results in terms of whether elemental sulphur exists on the surface of the oxidised mineral. In acidic conditions the formation of sulphate is less favoured than in alkaline conditions, meaning that surfaces are likely to be more sulphur rich in acidic conditions. Hodgson and Agar (1989) attempted to assign a more specific structure to the oxide products but this may be speculative. In alkaline conditions the iron from the sulphide mineral is likely to precipitate onto the mineral surface as ferrous and ferric hydroxide depending on E_h.

Oxygen reduction is critical to sulphide mineral flotation with thiol collectors (Woods, 1984). It has been shown that pyrrhotite is a poor catalyst for oxygen reduction as compared to other sulphide minerals (Rand, 1977). This may, in part, explain pyrrhotite's slow floating characteristics. Attempts to correlate the oxygen reduction kinetics of sulphide minerals on semi-conducting properties have not been successful (Biegler, 1976 and Biegler *et al.*, 1977). It is likely that the stoichiometry and level of impurities within the mineral plays an important role in defining the kinetics of oxygen reduction.

There is growing agreement that the initial adsorption of xanthate onto the mineral surface occurs through physisorption rather than chemisorption (Hodgson and Agar, 1989, Rao and Finch, 1991, Fornasiero *et al.*, 1995). It is proposed that the adsorption occurs through electrostatic attraction between the negatively charged xanthate ions

and positively charged iron hydroxide sites. The iron hydroxide sites are considered to arise through oxidation of the mineral, although there is still controversy regarded the exact nature of the sites. For instance, although a certain degree of oxidation appears necessary for xanthate adsorption, it is clear that heavily oxidised particles are not floated effectively due to the presence of hydrophilic passivating ferric hydroxide layers.

The dominant surface product on pyrrhotite from interaction with xanthate, at pH 9, has been identified as dixanthogen (Allison et al., 1972, Prestige et al., 1993, Fornasiero et al., 1995). There are however reports of metal xanthate being detected in addition to dixanthogen depending on conditions (Rao and Finch, 1991, Yoon et al., 1995). No evidence has been found for the physisorption of dixanthogen onto the mineral surface and it would appear that dixanthogen can only form on the mineral surface through an electrochemical mechanism occurring on the mineral surface.

It is plausible that xanthate physisorbs onto the mineral surface, and that, provided there is a significantly anodic mixed potential, subsequent oxidation of xanthate to dixanthogen occurs. Conventional theory suggests that dixanthogen formation is a prerequisite for hydrophobicity, although its necessity is debatable in terms of a metal xanthate species being effective to achieve hydrophobicity.

There is considerable controversy regarding the role and effectiveness of copper ions for the activation of pyrrhotite under alkaline conditions. Fundamental work appears to indicate that copper activation is not possible at pH 9 (Nicol, 1984). The justification for this is, firstly that copper ions precipitate out of solution at pH 9 and thus may not be available for reaction with the surface of the mineral, and secondly that pyrrhotite particles are likely to be well oxidised and covered with iron hydroxides which inhibit any reaction with the underlying mineral surface.

On the other hand, recent studies by Leppinen (1990), Senior et al. (1995) and Kelebek et al. (1996) have shown that pyrrhotite recoveries are significantly improved when copper ions are present. Copper has been detected on concentrate particles from

actual flotation circuits operating at pH 9 (Stowe *et al.*, 1995, Yoon *et al.*, 1995), thus suggesting that pyrrhotite was effectively activated.

There has been relatively little work on understanding by what me hanism/s copper ions help with rendering the mineral surface hyd hobic. It is thought that activation results in a copper sulphide surface, which is then more beneficial for collector adsorption. In this case the activated mineral is expected to behave similarly to bulk copper sulphide minerals like chalcocite, forming metal xanthate compounds as opposed to dixanthogen in the case of pyrrhotite. The activation reaction may aid the formation of a sulphur rich surface due to a coupled oxidation of the mineral (Nicol, 1984). Another possible mechanism would be to protect the iron sulphide from forming passivating hydroxide layers.

3. Experimental

3.1 Samples

Table 3-1 describes the pyrrhotite mineral samples that were obtained for this study.

Tab. 3-1: Pyrrhotite samples

Code	Description	Origin	Source
A	pentlandite in pyrrhotite (massive)	Sudbury, Canada	Ward's Natural Science
B	nickelferrous pyrrhotite (massive)	Falconbridge, Ontario	Ward's Natural Science
C	pure pyrrhotite (massive)	unknown	Ward's Natural Science
L	pyrrhotite (massive)	unknown	Local mineral dealer

The samples are referred to by their respective codes with a subscript indicated their number (i.e. C_1, C_2 and C_{rot} would all refer to the same pure pyrrhotite sample).

Table 3-2: SEM spot analysis of pyrrhotite samples

Code	Description	Major elements	Trace elements
A	pentlandite in pyrrhotite	Fe, S	Al, Si, P, K, Ca, Ni, Cu, Zn
B	nickelferous pyrrhotite	Fe, S	Al, Si, P, Ni, Cu
C	pure pyrrhotite	Fe, S	Al, Si, P, K, Ni, Cu

SEM spot analysis was conducted on samples A, B and C. This gave a qualitative indication of the elemental composition of each sample which is shown in Table 3-2. Detailed quantitative analysis was not performed.

3.2 Electrode preparation

Small pieces of mineral were cut from the main sample. These pieces were ground to form a cylindrical piece of approximately 5mm diameter. Copper was electrochemically plated onto one end of the cylindrical piece. This allowed for a contact to be soldered onto the mineral end.
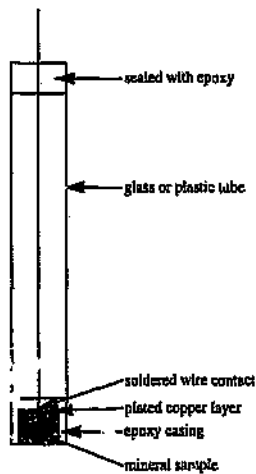
Stationary electrode   Rotating electrode
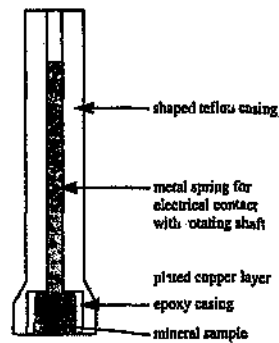
Figure 3.1: Schematic of electrode construction (not to scale)

Figure 3.1 gives a schematic of the electrode construction. For stationary electrodes the mineral sample, with the wire contact, was encased in epoxy resin within a glass or plastic tube. In the case of rotating electrodes Teflon tubes were manufactured.

Table 3-3: Areas of electrodes used in cyclic voltammetry

Code	Description	Area/(cm²)
C_3	stationary, pure pyrr. (Ward's)	0.21
C_4	stationary, pure pyrr. (Ward's)	0.26
C_{rot}	rotating, pure pyrr. (Ward's)	0.28
L_{rot}	rotating, pyrr. (local)	0.71

The areas of the electrode surfaces are given in Table 3-3. In calculating the area for each electrode surface the area of major inclusions (larger than 1mm²) was taken into account and subtracted from the overall area.

3.3 Reagents

Electrolyte solutions were made up from distilled water and AR grade reagents. Anhydrous sodium sulphate and di-sodium tetraborate were supplied by SAARCHEM-HOLPRO ANALYTICAL (Pty) Ltd. Sodium isobutyl xanthate was supplied by SENMIN, a division of SENTRACHEM Ltd, where it was specifically purified by recrystallization. In unbuffered solutions the pH was adjusted by adding small amounts of concentrated sulphuric acid and sodium hydroxide solution which were specifically prepared in distilled water.

Fresh solutions were prepared for each experiment. The solutions were de-oxygenated by sparging with nitrogen gas. Bottled air and oxygen could also be sparged into solutions as necessary.

3.4 Equipment

A potentiostat and sweep generator manufactured by MINTEK were used to measure and control the potential. A rotating disk assembly was obtained with a stepping motor which allowed for rotation speeds of up to 1000RPM. The speed of the controller for the motor was calibrated prior to the rotating disk work. The rotating shaft acted as

the contact to the electrode, with the Teflon casing fitting over the shaft and the spring; within the electrode casing slipping onto the shaft. The spring rested on the copper plated section of the mineral sample (see schematic of rotating disk electrode in Figure 3.1) thus making contact between the shaft and the mineral surface. The current and potential output from the potentiostat was recorded on an HP 7025B X-Y Recorder. A Metrohm 744 pH meter was used to measure the pH of the solutions. All experiements were conducted at 25°C.

3.5 Techniques

The following section describes the experimental techniques used in the various experiments. In some cases more detailed specific explanations are given in the main text.

3.5.1 Potential measurements on the plant

Specially designed electrode probes were assembled. The probes where approximately one meter long and consisted of a hollow PVC tube. Pyrrhotite electrodes were inserted in one end of the tube and the tube sealed so that only the mineral surface was exposed. The electrode was then connected to a contact plug on the other end of the tube via a wire fed through the length of the tube. In addition to three pyrrhotite electrodes, a reference electrode, platinum electrode and pyrite electrode were also assembled in this fashion. By inserting the probes into the various flotation unit operations the mixed potential of the minerals relative to the reference electrode could be measured.

Before each measurement the mineral electrodes were freshly exposed by grinding the surface on 1000 μm emery paper and washing with distilled water. The probes were then inserted directly into the slurry. Measurements were taken at the cyclone overflow surge box, the surge tank, conditioning tank 1, conditioning tank 2 and along the flotation bank stages. These measurements provide a good indication of the electrochemical environment throughout the flotation circuit. It was difficult to measure a steady potential as the potentials tended to fluctuated significantly. This is

probably due to the slurries being vigorously agitated. The measured value is therefore an estimate taking into account the fluctuations.

3.5.2 Potential measurements from batch flotation tests

The details of the batch flotation experiments and results are dealt with elsewhere (Hodgkinson, 1996) and will only be discussed briefly here. Standard flotation tests were conducted in 2 litre batch flotation cells. The concentrations of solids and reagents were the same as those used at the plant. The ore was milled in laboratory mills to 65% -75 microns. The desired pH was maintained throughout the float by small additions of sulphuric acid. Initially a standard float was conducted at the natural pH. The pH was then controlled at 3, 4 and 5.

The tests consisted of a two minute conditioning stage where the required pH was achieved and maintained. Copper sulphate was then added and the pulp was conditioned for 10 minutes. Collectors, depressant and frother were then added and after a further 5 minute conditioning period the flotation was begun. Concentrates were collected at 1, 5, 17 and 33 minutes.

The reagent dosage was similar to that used on a typical local sulphide flotation plant: SIBX, DTP, Acrol IMP₄ and Senfroth. SIBX is not ideally suited to low pH conditions, therefore tests were also conducted using MBT. The addition of SIBX directly into the mill was also investigated.

Allowance was made for electrodes to be immersed directly into the flotation cell during the tests. The mixed potential of the pyrrhotite mineral could thus be measured throughout the various stages of the float. Nickelferrous pyrrhotite (B) and pure pyrrhotite (C) samples were used, each in duplicate. The electrodes were freshly ground at the beginning of each test. Electrodes B_1 and C_1 remained in the slurry throughout the test, whilst electrodes B_2 and C_2 were removed at the end of each stage (conditioning, activating, collecting and floating) and were freshly exposed before being re-immersed in the slurry.

The changes in potential of electrodes B_1 and C_1 and the reactions occurring at the surface of these electrodes are most likely to be the same as those experienced by pyrrhotite mineral particles in the slurry. The measurements taken from B_2 and C_2 give an indication of the potential that the mineral particles would assume were they freshly exposed and non-oxidised.

3.5.3 Potential measurements in the laboratory

Electrodes were freshly exposed by rubbing with 1000 grade emery paper and washing with distilled water. The surface was wiped with tissue paper to remove any residue from the grinding. The electrodes where then immersed in the solution of interest and the potential recorded once it had stabilised. Generally potentials stabilised within 2 to 5 minutes depending in the nature of the solutions. Solutions were prepared as necessary and were de-oxygenated by sparging with nitrogen. All solutions were thermostatted at 25°C.

The electrolyte generally used for experiments was 0.1M Na_2SO_4. In some cases 0.05M di-sodium tetraborate buffer solutions were used. Sodium sulphate was chosen as an electrolyte as plant solutions are known to contain both sodium and sulphate ions. The pH of the solutions was adjusted through small additions of concentrated sulphuric acid and sodium hydroxide.

3.5.4 Cyclic voltammetry

Stationary and rotating electrodes were investigated. 0.1M sodium sulphate and 0.05M di-sodium tetraborate were used as electrolyte solutions. Sodium hydroxide and sulphuric acid were used to adjust the pH of the sodium sulphate solutions to the desired value. All experiments were conducted in a glass titration vessel, with an outer thermostat compartment which was kept at 25°C by circulating water from a water bath. Solutions were de-oxygenated by sparging with nitrogen as necessary. Before each experiment electrodes were freshly ground on 1000 grade emery paper and washed with distilled water. Surfaces were wiped with paper towel to remove residue from the grinding. The electrodes were then immersed directly into the electrolyte solutions. A potentiostat was used to control the potential at the working electrode. The potentiostat was coupled to a potential wave generator which enabled the

potential to be cycled between set limits. Current and potential were recorded directly onto a X-Y recorder (this equipment has been described in Section 3-4).

3.5.5 Hydrophobicity tests

Small bubbles of nitrogen were injected onto the surface of the electrode using a micro-syringe. The volume of the bubble was 6μL which gives a bubble diameter of 2.3mm. Care was taken to inject the bubble onto the surface of the electrode at the same position each time. The electrode was then slowly accelerated until the bubble detached. The set-up is shown in Figure 3.2.
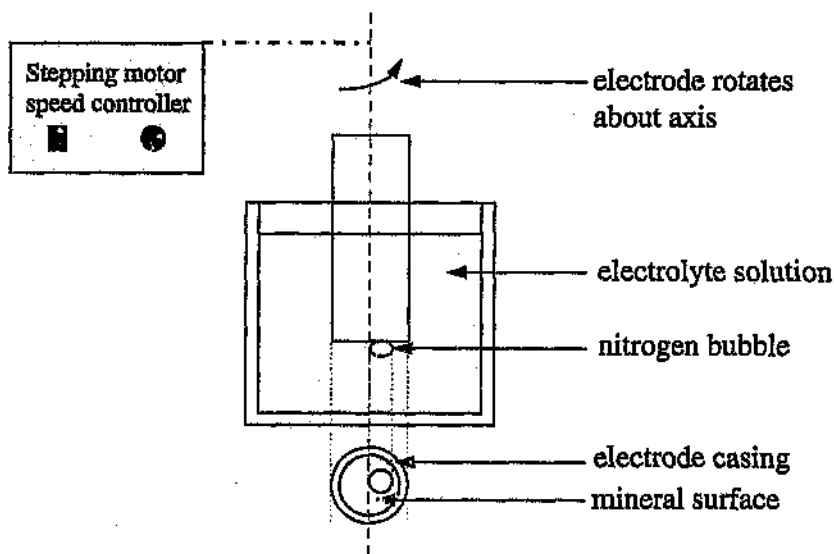
Figure 3.2: Experimental set-up for hydrophobicity tests

The rotation speed of the electrode at the point of detachment was taken as a measure of the strength of attachment of the bubble to the particle surface, and thus by inference a qualitative measure of the hydrophobicity of the surface. The effect of different conditioning treatments could then be qualitatively assessed in terms of strength of bubble attachment. The different types of conditioning employed are described in Table 3-4.

Table 3-4: Description of conditioning stages used for hydrophobicity tests

Treatment no.	Description of conditioning stage
1	0.1M Na_2SO_4 @ pH 9 (no $CuSO_4$)
2	0.1M Na_2SO_4 @ pH 9; 10^{-4} $CuSO_4$
3	0.05M $Na_2B_4O_7$ @ pH 9.3 (no $CuSO_4$)
4	0.05M $Na_2B_4O_7$ @ pH 9.3; 10^{-4} $CuSO_4$
5	0.1M Na_2SO_4 @ pH4 (no $CuSO_4$)
6	0.1M Na_2SO_4 @ pH4; 10^{-4}M $CuSO_4$

The freshly exposed electrode was conditioned for ≈ 2 minutes. In the case of treatments 5 and 6 the pH of the solution when the electrode was first immersed was pH 4. After this the pH was adjusted to ≈ 9. For all other treatments the pH at the start of the test was ≈ 9. SIBX was then added and the electrode conditioned for a further 10 minutes. The concentration of SIBX after addition was 10^{-2}M. All solutions were thermostatted at 25°C with an O_2 sparge. The electrode was rotated at 500 RPM during the conditioning stages. In the case of the acidic conditioning the pH of the solution was increase to ≈ 9.2 before SIBX was added. Following all the conditioning stages the electrode was kept stationary. A 6μL nitrogen bubble was injected onto the inverted surface of the electrode. The electrode was then slowly accelerated until the bubble detached from the surface. The rotation speed at which this occurred was taken as the qualitative measure of the strength of bubble attachment.

4. Results and Discussion

4.1 Mixed potential measurements

The mixed potential of a mineral gives an important indication of the electrochemical state that exists on the surface of the mineral. The mixed potential is defined by competing reactions that occur on the surface. Thus an understanding of what effects the mixed potential leads to an understanding of the reactions that are important to the surface chemistry.

There is an important relationship between thermodynamics and the mixed potential. Thermodynamics gives equilibrium potentials for reacting couples. These equilibrium potentials describe what is possible given sufficiently oxidising or reducing conditions. In the case of mineral-solution systems the oxidising or reducing conditions are defined by the mixed potential that is assumed between the mineral/solution interface.

The mixed potential of pyrrhotite electrodes has been extensively studied in this investigation. Measurements were taken in plant flotation circuits, batch flotation tests and in laboratory experiments.

4.1.1 Equilibrium potential of the dixanthogen/xanthate couple

The equilibrium potential of the xanthate/dixanthogen couple for sodium isobutyl xanthate is not well reported elsewhere. Most research appears to be based on potassium ethyl xanthate. It was thus necessary to measure the potential of this couple.

A 0.1M Na_2SO_4 supporting electrolyte solution was made with the pH adjusted to 9.22. Three different concentrations of xanthate were dissolved into this solution. A platinum electrode was used as a working electrode and the potential was held anodic for several minutes, thereby oxidising xanthate to dixanthogen on the surface of the platinum electrode. The electrode was then open-circuited for ≈ 5 minutes and the resulting rest potential measured.

The following reaction is assumed:

$$X_2 + 2e^- \Leftrightarrow 2X^- \qquad (3\text{-}1)$$
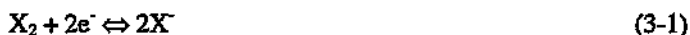
For unit activity X_2, the Nernst equation predicts:

$$E = E° - {}^{RT}/_{2F}.\ln[X^-]^2 \qquad (3\text{-}2)$$

The results are shown in Table 4-1.

Table 4-1: Equilibrium potentials for xanthate/dixanthogen couple (SIBX)

[SIBX]/(M)	E/(V vs. SHE)	E°/(V vs. SHE)
10^{-2}	-0.009	-0.127
10^{-3}	+0.049	-0.128
10^{-4}	+0.108	-0.128

The Nernst equation (equation 3-2) predicts a 59mV increase in equilibrium potential for every order of magnitude decrease in concentration of xanthate. The above results are in accord with this prediction (58 and 59 mV observed change). Using the Nernst equation $E°$ can be calculated and the values are shown for each concentration of SIBX. Winter and Woods (1973) report an $E°$ value of -0.128V for n-butyl xanthate which is in good agreement with the values reported in Table 4-1.

4.1.2 Potential measurements on the plant

The potential which the mineral assumes in the flotation environment is important in understanding how the various flotation reagents will react with the mineral surface, as well as how the mineral will react itself. The mechanism of the oxidation of the mineral, and therefore possibly the products of oxidation, will be dependent on the potential at which the mineral oxidises.

Plant potential measurements were undertaken at the Minerals Processing Plant in Rustenburg. The aim was to gain a better understanding of the potentials to which the pyrrhotite mineral is subjected, and to gauge the change in electrochemical environment down the flotation circuit.

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4.1.2.1 Results and Discussion

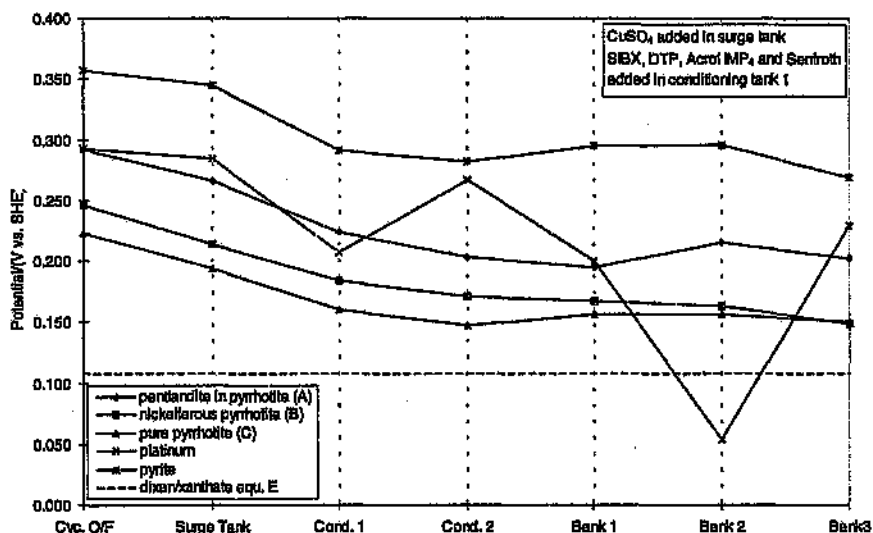The potential measurements taken at the plant down the flotation circuit are shown in Figure 4.1.

Figure 4.1: Plant potential measurements

There is a downward trend in the potential through the circuit. By the end of the second conditioning stage the potential stabilises to some extent. It is expected that the addition of the flotation reagents will lower the mixed potential of the minerals. The erratic readings measured for the platinum electrode are more likely due to experimental error and the poorly poised potential than to any real effect. Pyrite is more noble than the pyrrhotite samples as seen by the more anodic mixed potentials. The pure pyrrhotite sample is the least noble as expected.

The potential range relevant to pyrrhotite flotation is defined on the cathodic side by the equilibrium potential of the xanthate/dixanthogen couple and on the anodic side by the potentials measured by the pyrrhotite electrode prior to xanthate addition. This gives a range from ≈0.100 to 0.250V.

4.1.3 Potential measurements from batch flotation

The slurry at the Minerals Processing Plant tends to be buffered at approximately pH 9. It is thought that und: alkaline conditions the poor flotation response of pyrrhotite is related to the formation of hydroxide layers on the surface of the mineral. These hydrophilic hydroxide layers passivate the surface and inhibit interaction with collectors. It was therefore proposed that the recovery of pyrrhotite could be improved by performing the flotation under acidic conditions thereby minimising the formation of hydroxide layers.

Batch flotation tests were performed on Merensky ore samples at the Gencor Process Research Laboratories in order to test the effectiveness of acid flotation. Mixed potential measurements were taken in order to gain information on the electrochemistry of the flotation.

4.1.3.1 Results and Discussion

Standard flotation with no sulphuric acid addition

The potentials of the electrodes during the test are shown in Figure 4.2. Note that in Figures 4.2, 4.3 and 4.4 the arrows indicate the potential directly after the reagent addition. The abscissa represents stages in the procedure and is not to scale (in time).
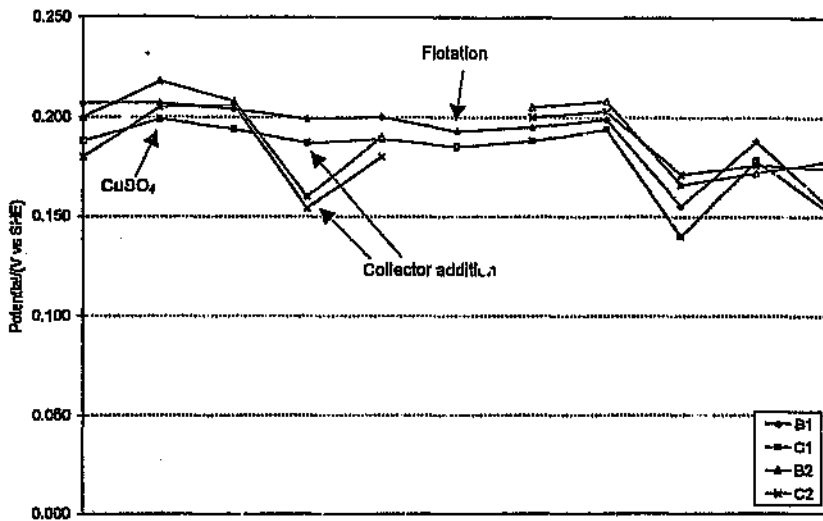
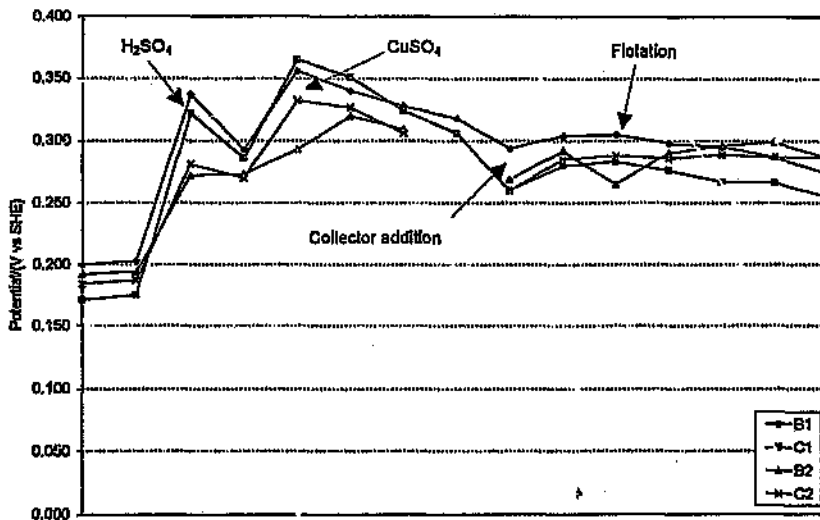**Figure 4.2: Mixed potential measurements - Standard Flotation (pH 9)**

There is very little change in the mixed potential of the B_1 and C_1 electrodes. This would indicate a lack of interaction between the mineral surface and the flotation reagents. The equilibrium potential of the xanthate/dixanthogen couple at plant concentrations ($E=0.108V$) lies more cathodic than the rest potential of the pyrrhotite mineral electrodes. On the addition of xanthate one would expect to see a shift in the mixed potential to more cathodic potentials in line with the predictions of the mixed potential model, and since the rest potential is more anodic than the equilibrium potential for dixanthogen/xanthate couple, the formation of dixanthogen is favoured (Allison *et al.*, 1972).

In the case of electrodes B_2 and C_2 the effect of adding the various reagents is apparent. The mixed potentials of electrodes B_2 and C_2 increases on the addition of $CuSO_4$ and decreases on the addition of SIBX.

The surface of electrodes B_2 and C_2 were freshly exposed at the end of each stage. Electrodes B_1 and C_1 remain in solution throughout the test. It would therefore appear that the lack of interaction between B_1 and C_1, and the flotation reagents is caused by passivation of the surface due to oxidation during the initial conditioning stages.

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Acid Flotation using SIBX

Three different pH's were investigated: pH 3, 4 and 5. The results for pH 4 are shown in Figure 4.3.

Figure 4.3: Mixed potential measurements - pH 4, SIBX

There is a significant increase in the electrode potential when H_2SO_4 is added. The potential decreases slightly by the end of the conditioning stage. On the addition of $CuSO_4$ there is a further increase in electrode potential. The potential decreases again during the conditioning. The addition of SIBX causes a drop in potential. Unlike the standard float conditions (Figure 4.2) the potentials of the electrodes that remain in solution are similar to those of the electrodes that are freshly exposed at the end of each stage. By refreshing the electrode, surface products are removed and the effects of any passivation due to these products are eliminated. Refreshing the electrodes has little effect on the potentials, as compared to those electrodes that are not refreshed. This would indicate that under the acidic conditions investigated the mineral is not being passivated by surface products as is the case under alkaline conditions.
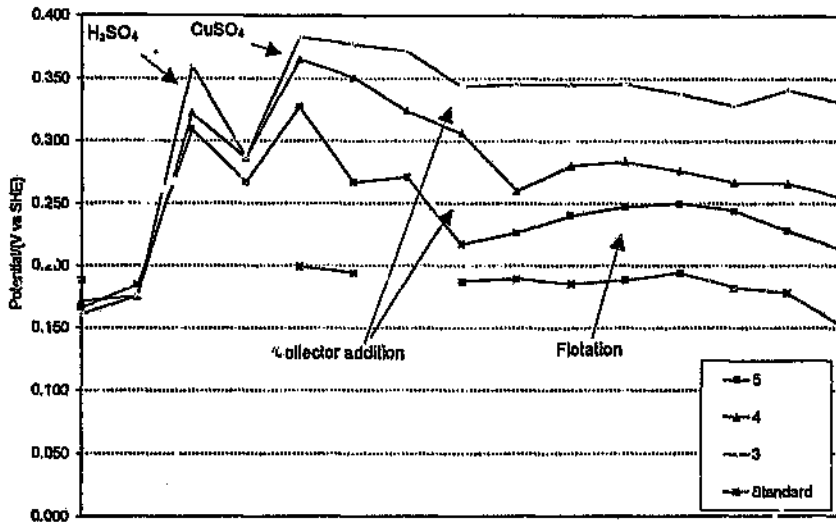
Figure 4.4: Mixed potential measurements - Electrode Cl, SIBX

The potentials of electrode C_1 are shown in Figure 4.4 for the different pH conditions investigated. For standard conditions (pH 9) the potentials are significantly lower than those at more acidic pH's. There is also less change in potential through the various conditioning stages for pH 9.

Acid Flotation using MBT

The use of MBT as the collector should have no significant effect on the initial conditioning stages and the electrochemical results for these stages were found to be similar to those for tests conducted with SIBX. MBT has a similar reducing affect on the mineral as SIBX. The same trends were observed, in that the mineral showed enhanced interaction under acidic conditions.

Mineral Recovery Results

The electrochemical results outlined above suggest that the recovery of pyrrhotite should be enhanced under acidic conditions. In an analysis of the actual recoveries for these experiments, Hodgkinson (1996) found that, for SIBX as the collector, the fraction of slow floating material increased under acidic conditions for all minerals (i.e. flotation kinetics worsened under acidic conditions). It is known that SIBX is not a suitable collector for acidic conditions and, as the pH was maintained at the acidic

levels even during flotation, this could explain the poor flotation. MBT, which is more suitable for acidic conditions, was also tested. This showed an improvement in flotation response. Another draw back of the test is that the effect of the acidic p... on the stability of the froth phase is not known. Thus improved chemical effects achieved by acid conditioning may be masked out by poor physical factors of collector efficiency and froth stability. These problems could be overcome by an alternative experimental procedure whereby the pH is not maintained at acidic levels, but allowed to return to its natural value after the activation stage.

4.1.4 Potential measurements in the laboratory

In order to better understand the potential measurements made under plant conditions and in batch flotation tests it is necessary to have a good understanding of the mixed potential of the mineral under controlled conditions. Under real conditions the mixed potential is likely to comprise of a complex set of competing reactions, due to the large number of potential determining ions in the plant solutions. Under laboratory conditions, however, the mineral can be isolated to some extent. Reagents can then be added to the solution and there respective effects on the mixed potential observed.

4.1.4.1 Results and Discussion

The mixed potential of pyrrhotite electrodes in de-oxygenated sodium sulphate solutions was measured at a number of pH values and the results are shown in Figure 4.5.
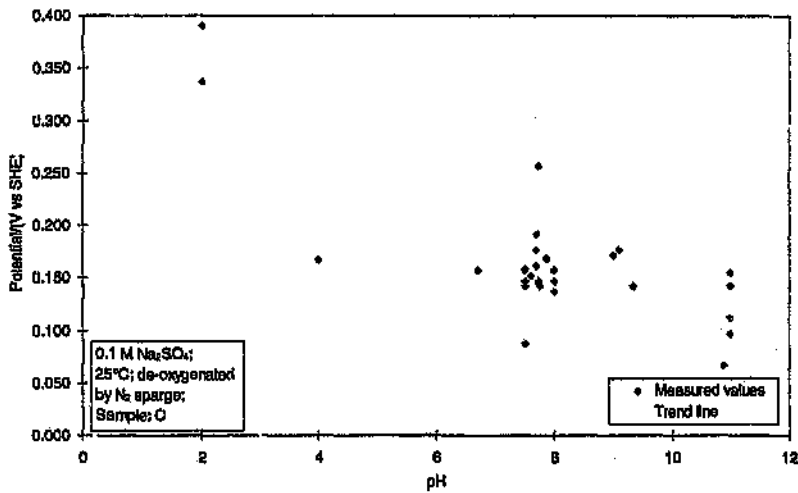
Figure 4.5: Mixed potential of pyrrhotite vs. pH (de-oxygenated)

There is a large amount of scatter in the readings. This indicates that in the absence of any reagents the mixed potential of pyrrhotite is poorly defined making it difficult to obtain reproducible readings.
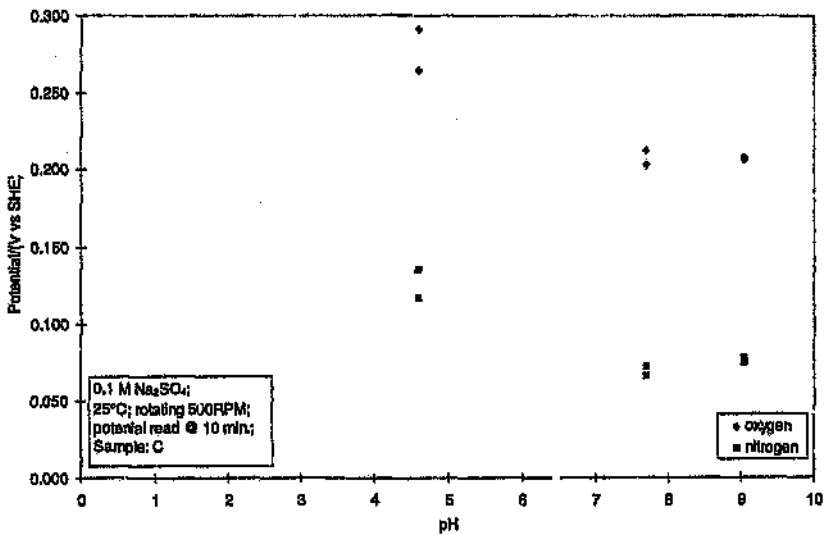
Figure 4.6: Mixed potential of pyrrhotite - effect of oxygen

The effect of oxygen in the solution is evident in Figure 4.6. The potentials are all more anodic in the presence of oxygen by approximately 0.150V.

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The effect of SIBX on the mixed potential of a pyrrhotite electrode is shown in Figure 4.7 and Figure 4.8. Open circuit and anodic pre-conditioning was investigated, and two different xanthate concentrations were considered (10^{-2}M and 10^{-4}M).
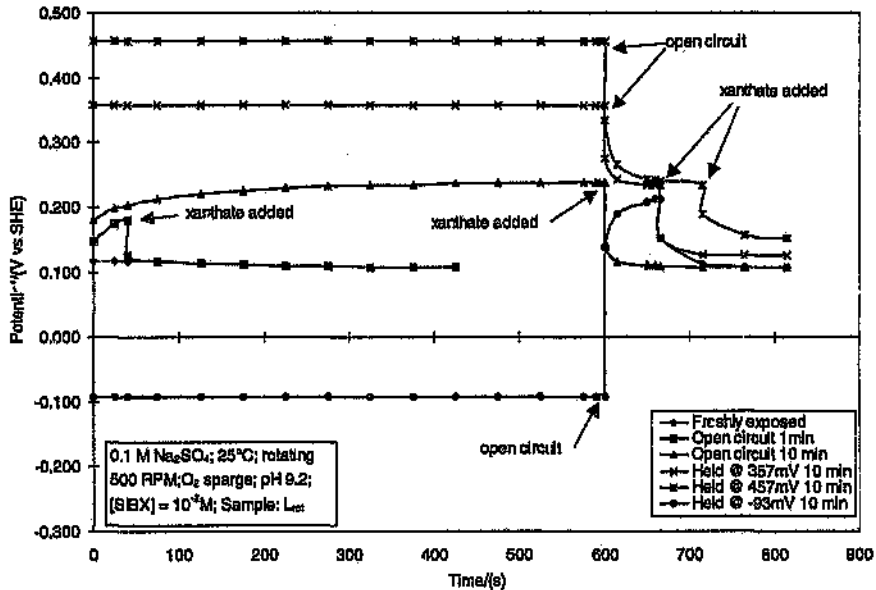
Figure 4.7: Mixed potential of pyrrhotite - effect of xanthate [10^{-2}M]

At a concentration of 10^{-2}M, the dixanthogen/xanthate couple has an equilibrium potential significantly more cathodic than that of pyrrhotite which causes the mixed potential to move cathodic with respect to mixed potentials in xanthate free solutions.

As the concentration of SIBX decreases the xanthate/dixanthogen equilibrium potential moves anodic, and at plant concentrations of 10^{-4}M, lies approximately 100mV cathodic of pyrrhotite's rest potential. Open circuit conditioning of the electrode did not significantly effect the mixed potential as compared to freshly exposed electrodes. Extensive anodic conditioning resulted in the mixed potential, after addition of SIBX, being slightly more anodic than the open circuit condition treatments.
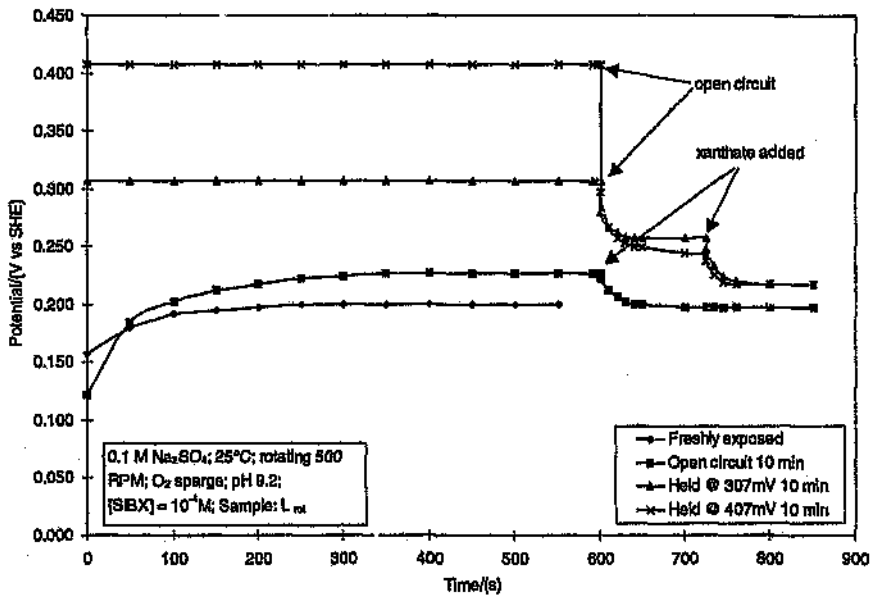
Figure 4.8: Mixed potential of pyrrhotite - effect of xanthate [10⁻⁴M]

Potential measurements in a laboratory simulation were made using a pyrrhotite electrode and solutions of similar composition and concentration to those used under plant flotation conditions (the solution was sparged with air). Figure 4.9 shows the potentials that were measured. The tests were conducted in sodium sulphate and borate buffer solutions. Sodium sulphate is more suitable in terms of corresponding to plant solutions, but it is difficult to control the pH at the desired value (pH 9). For instance on the addition of copper sulphate the pH drops to approximately 6.5 and the pH must be raised by small additions of concentrated NaOH. This then affects the potential that is measured. For this reason a borate solution was also used.
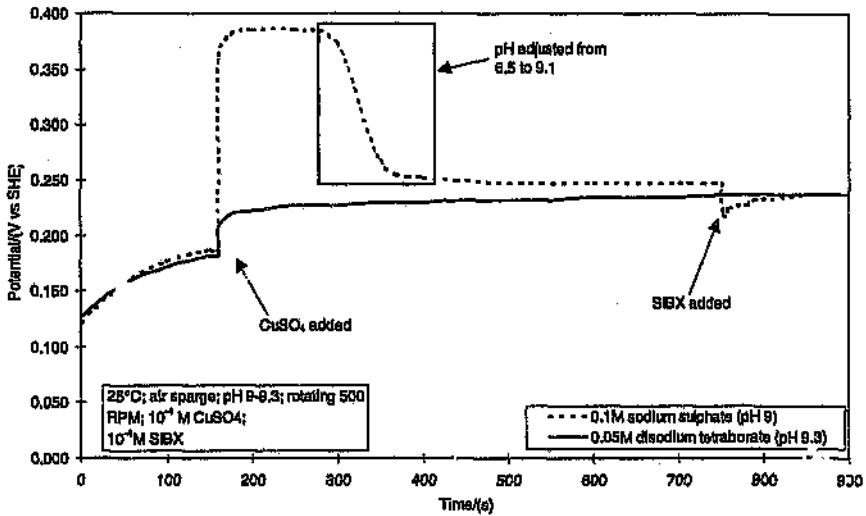
Figure 4.9: Mixed potential of pyrrhotite - laboratory flotation simulation

On addition of copper sulphate the pH of the sulphate solution dropped to
:roximately 6.5. Consequently the measured potential of the pyrrhotite electrode
increased. It is difficult to estimate to what extent the rise in potential is due to the
copper sulphate or the drop in pH. There is a drop in potential on xanthate addition. In
the case of the borate solution there is no significant effect on the measured potential
on the addition of xanthate.

4.1.5 Discussion

Figure 4.10 shows a cor. narison of the various potential measurements, namely: plant, batch flotation test and laboratory potentials.
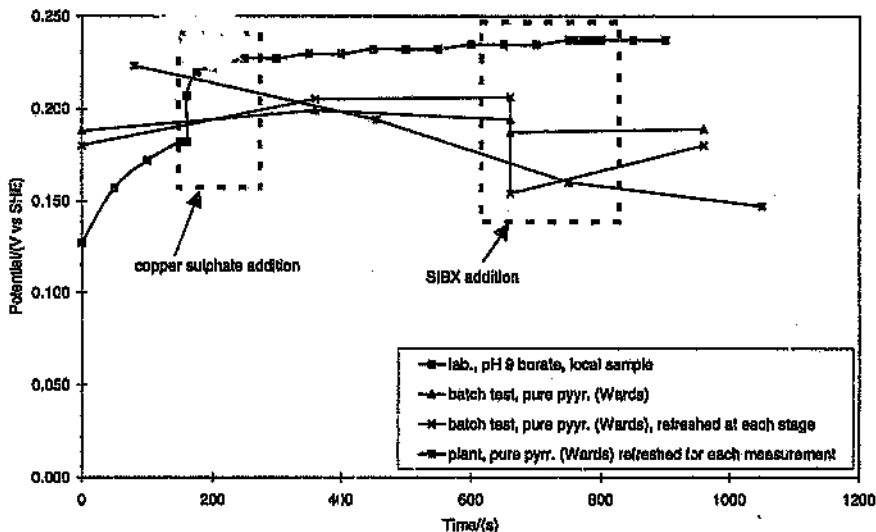
Figure 4.10: **Comparison of plant, batch test and laboratory potential measurements**

All potentials measured are above the equilibrium potential for the xanthate/dixanthogen couple ($E=0.108V$) indicating that dixanthogen is the favoured product from xanthate interaction with pyrrhotite (Allison *et al.*, 1972).

The potential measurements taken from batch flotation tests, under standard conditions, are the most significant (see Figure 4.2). These measurements provide convincing evidence for the passivation of pyrrhotite by surface products. It is not clear what these surface products are, nor how they form, although they are most likely iron oxides/hydroxides formed through oxidative dissolution of the mineral prior to reagent addition.

The role of surface products in passivation could be three fold. Firstly, they may reduce the effective area available for reaction between the xanthate collectors and the mineral surface. Secondly the surface products may be hydrophilic (for example

hydroxides are generally considered hydrophilic). Thirdly, they may have a detrimental effect on the specific collector reactions themselves. These reactions are the anodic adsorption of xanthate coupled to the reduction of oxygen. Interpreting changes in rest potential in terms of the effect on these specific reactions is difficult in the absence of other data.
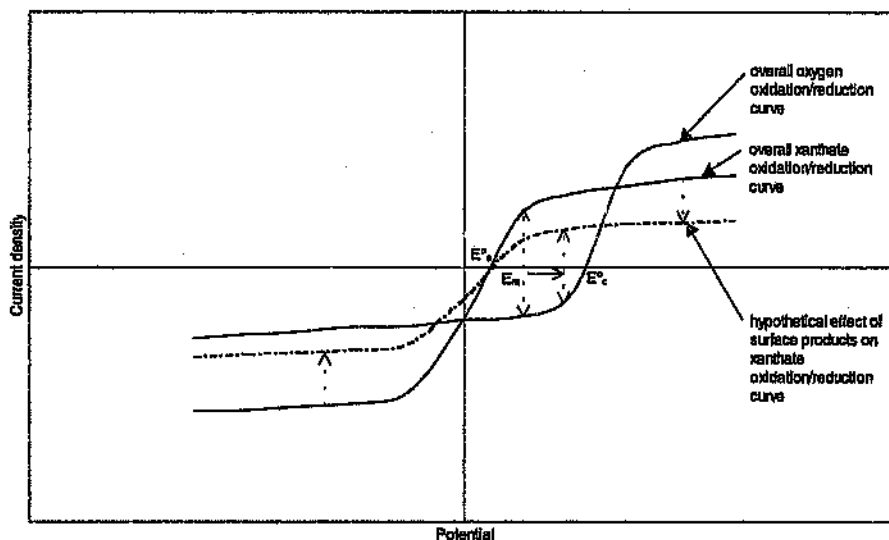
Figure 4.11: Hypothetical schematic of mixed potential model

For instance, as shown in Figure 4.11, the oxygen reduction reaction may be unaffected by surface products yet these products may inhibit xanthate adsorption. In this case an increase in rest potential is expected in accordance with mixed potential theory. It is possible however that an increase in mixed potential could occur through the enhancement of the oxygen reduction reaction only. Equally so there may be effects on both reactions to varying degrees which then yields differences in the mixed potential. Results dealt with later have indicated that the oxygen reduction reaction is not effected by differences in rface composition, at least not to the extent that xanthate adsorption is.

There is a slight disagreement between the batch tests and the laboratory measurements. Laboratory measuremen r showed that open circuit conditioning did not affect the mixed potential of pyrrhotite electrodes in xanthate solutions. It would be expected that, if incipient oxidation leads to passivation, then, after extensive open

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circuit conditioning (10 minutes), potentials should be more anodic in the presence of xanthate as compared to freshly exposed electrodes, where no surface products are expected. Extensive closed circuit conditioning, at potentials of least 100mV more anodic than pyrrhotite open circuit potentials, did give more anodic potentials in the presence of xanthate, as compared to freshly exposed electrodes. This then points to some inhibition of the xanthate oxidation reaction, presuming that the oxygen reduction reaction is unaffected (refer to later sections). Interestingly, in pH 9 borate buffer solutions, the addition of xanthate ha. .o effect on the rest potential of the mineral electrode. This may be due to the buffering action of the solution which minimises local pH effects that may occur in unbuffered sulphate solutions.

Plant potential measurements indicate that the maximum oxidising potential that the mineral experiences is likely to be in the range of 0.2-0.25V. The milling environment is certainly not expected to be more oxidising than this, due to the reducing affect of iron residues. It could be argued, therefore, that these potentials are anodic enough to cause surface oxidation products that inhibit xanthate adsorption.

4.2 Electrochemistry of pyrrhotite in flotation

4.2.1 Electrochemistry of pyrrhotite

The response of pyrrhotite to flotation depends, in a chemical sense, on the effectiveness of the activation and collector adsorption process. These processes occur through reactions on the surface of pyrrhotite mineral particles. The state of the mineral surface, in terms of its composition and concentration of surface products, is likely to play an important role in the effectiveness of subsequent surface reactions. The mineral surface is altered by incipient oxidation during the milling and conditioning stages prior to the addition of flotation reagents. The reactions and subsequent products formed through these reactions will be primarily dependent on the redox potential of the pulp solution and on the pH.

The redox potential (E_h) of the pulp solution gives an indication of the overall oxidising strength of the environment. It is influenced by potential forming ions in solution, oxygen concentration and the various minerals themselves. When considering specific minerals it is better to consider the mixed potential of the mineral itself. This mixed potential will reflect the extent and mechanism of the mineral oxidation. The products formed and the stability of these products will also be dependent on the mixed potential of the mineral. Equally important is the pH of the solutions. This will effect the equilibrium potentials of the reactions as well as the stability of the products.

The oxidation of pyrrhotite has been investigated using cyclic voltammetry. Of particular interest is the extent of oxidation, the products that are formed and the extent of the surface coverage of the products that precipitate on the surface. The knowledge of plant mixed potentials discussed in section 3-1 is important in defining what oxidative potentials are relevant to the ultimate flotation of pyrrhotite. The oxidation of pyrrhotite should be interpreted according to the potential range it can be expected to experience.

4.2.1.1 Results

**Oxidation under highly anodic conditions**

Figure 4.12 shows the voltammogram for a pyrrhotite electrode at pH 9.3 in a borate solution. The sweeps were commenced from the rest potential and the numbers refer to the sweep number.
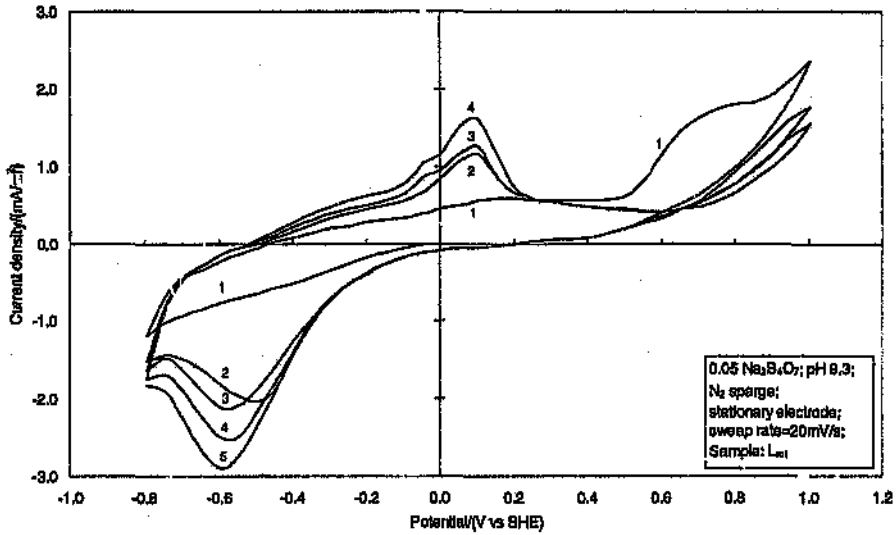
Figure 4.12: Voltammograms of pyrrhotite electrode (L_{rot}) at pH 9.3

Figure 4.13 shows the results of the same experiment but for a different pyrrhotite sample.
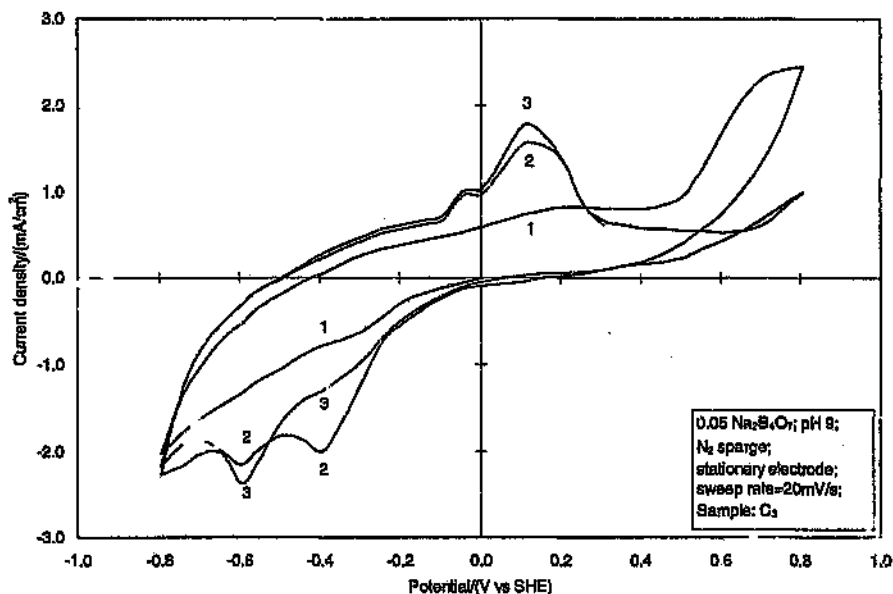
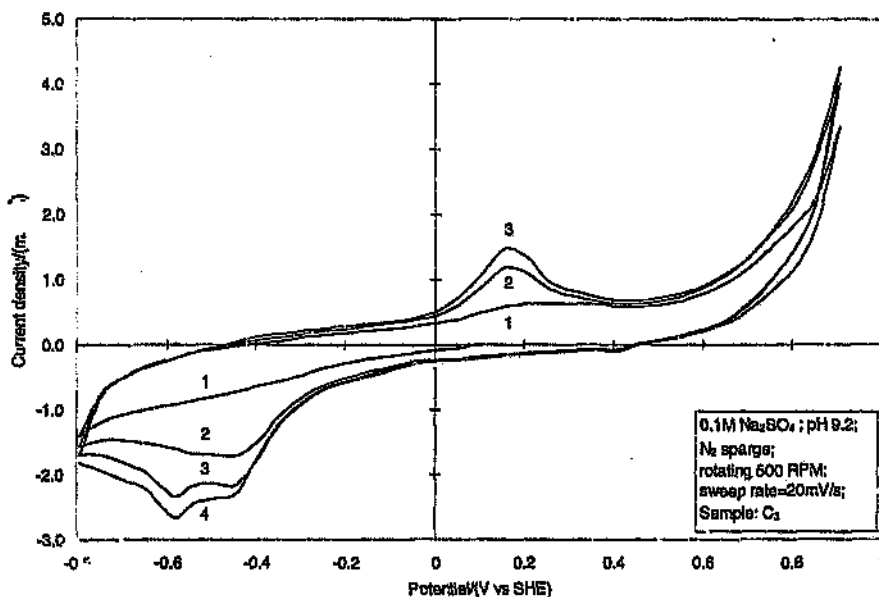**Figure 4.13: Voltammogram for a pyrrhotite electrode (C₃) at pH 9.3**

In both experiments sweeps were initiated from the rest potential in the cathodic direction. The potential was subsequently cycled. On the initial cathodic sweep there is some indication of a reaction occurring at ≈-0.250V. On the first anodic sweep a current plateau is formed at ≈0.200V. At 0.500V the anodic current increases forming a plateau at ≈0.800V. The subsequent increase in anodic current at potentials close to 1V is due to oxidation of H₂O (oxygen evolution was observed at the working electrode).

The second cathodic sweep indicated at least two cathodic reactions. In Figure 4.12 the first cathodic reaction reached its peak current density at ≈-0.500V. For the sample shown in Figure 4.13 this first cathodic peak appears to have occurred at slightly more anodic potentials with a peak current density at -0.400V. For both samples a second cathodic reaction at -0.600V is observed, although in Figure 4.12 this peak is not clearly defined on the second cathodic sweep.

The second anodic sweep indicates at least two anodic reactions at -0.050V and 0.100V. At more an dic potentials the current plateau observed on the first anodic sweep is not present and this would indicate some passivation of the mineral.

On subsequent cycling the first cathodic reaction occurring at ≈-0.500V (Figure 4.12) and -0.400V (Figure 4.13) diminishes. This suggests that the reactants for this reaction are exhausted on the initial cathodic sweep and are not replenished on subsequent anodic sweeps. The second cathodic reaction at -0.600V and the anodic reactions at -0.050V and 0.100V are enhanced on subsequent sweeps.

Experiments were also conducted using rotating electrodes under the same conditions. These voltammograms were similar to the stationary ones indicating that all reactions involved solid reactants and were not controlled by mass transport to or from the electrode.
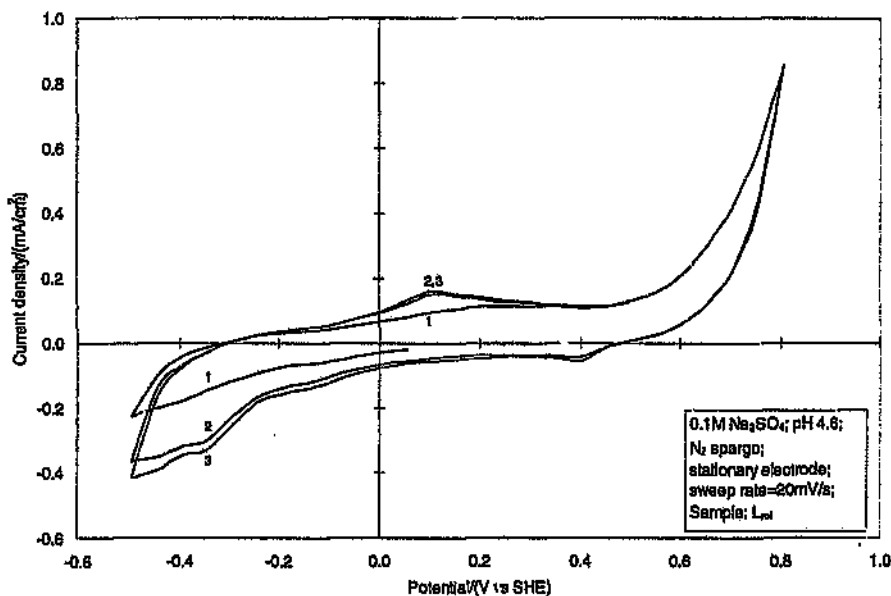

Figure 4.14: Voltammogram of pyrrhotite electrode (C_3) at pH 9.2 (Na_2SO_4)

Figure 4.14 shows the voltammogram for a pH 9.2 Na_2SO_4 solution. There are a number of notable differences as compared to sweeps conducted in borate solutions. The anodic plateau at ≈0.200V on the first anodic sweep is the same as that observed

in borate solutions however there is no evidence of a plateau at higher anodic potentials. There is no clearly distinguishable peak at -0.050V. On the cathodic side there are still at least two main cathodic reactions although the first cathodic reaction at ≈-0.400V does not diminish on subsequent sweeps as was the case with borate solutions, but increases in peak magnitude. The second cathodic peak is again only pronounced on third and subsequent cathodic sweeps. Stationary electrodes gave similar results although the cathodic peaks were more clearly distinguishable when rotating electrodes were used.

Oxidation of pyrrhotite was briefly investigated in acidic conditions in order to aid in the identification and understanding of the alkaline response. Figure 4.15 shows the voltammogram for pH 4.6.

Figure 4.15: Voltammogram of pyrrhotite electrode (L_{rot}) at pH 4.6

At pH 4.6 there was a new cathodic peak at 0.400V. There is an indication of a cathodic reaction at ≈-0.100V. The peaks observed under alkaline conditions at -0.600V and ≈-0.400V appear to have shifted slightly more anodic by ≈0.050V. On the return anodic sweeps there is only one clearly visible anodic peak at 0.100V. Sweeps were also conducted using a rotating electrode. The main difference between rotating

and stationary electrodes was that the cathodic peak at 0.400V disappeared suggesting that this reaction involved soluble reactants.
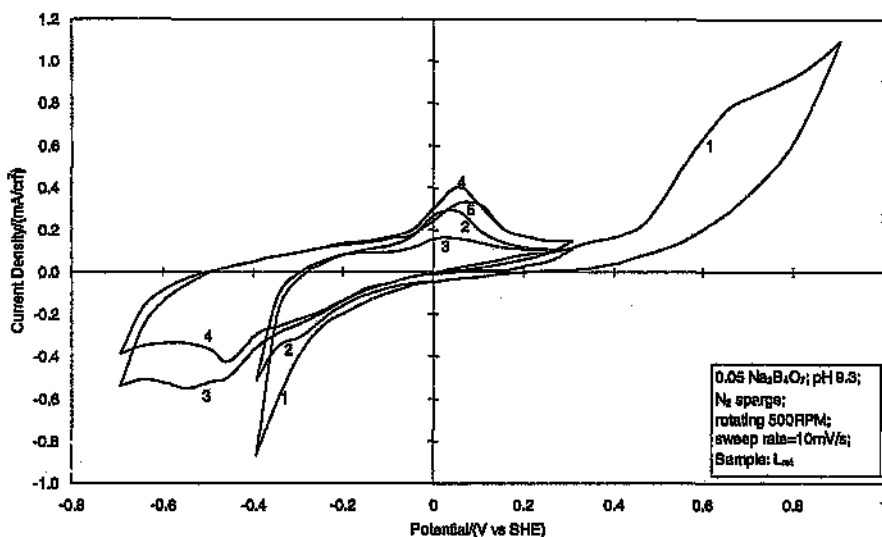
Figure 4.16: **Voltammogram of pyrrhotite electrode (L_{rot}) with varying potential limits**

In Figure 4.16 the potential limits were varied as the sweeps progressed. The initial anodic potential limit was set to 0.800V to allow the mineral to extensively oxidise. On subsequent return anodic sweeps the potential was limited to 0.300V. The cathodic limit was set first to -0.400V and then to -0.700V.

After the first anodic sweep a large cathodic current is observed at -0.400V. The sweep direction was then reversed and a large peak at 0.050V was observed. The potential was then cycled once again between 0.300V and -0.400V. The peak at -0.400V is less pronounced and shifted anodic to ≈-0.300V, although at -0.400V the current increases due to another reaction. On the third anodic sweep the peak is diminished at 0.050V. It would therefore appear that there is a reaction couple occurring at these potentials which involves either a soluble oxidation product or an oxidation product that requires more cathodic potentials to be reduced. This accounts for the peak dying out on subsequent sweeps. The same experiment was conducted using a stationary electrode with the same result. It is therefore more likely that soluble products are not involved but that the oxidation product requires a more

cathodic limit to be reduced. The cathodic limit was then extended to -0.700V (cathodic sweep 3). Two cathodic peaks are visible at -0.450V and -0.500V. On the final cathodic sweep (cathodic sweep 4) only the peak at -0.450V is visible. Corresponding anodic peaks are observed with slightly different peak potentials.

Oxidation under mildly anodic conditions

The oxidation of pyrrhotite appears to occur via two different mechanisms depending on the potential. The one mechanism occurs at potentials of between 0.200V and 0.500V whilst the other mechanism occurs at higher anodic potentials. Mixed potential measurements with pyrrhotite electrodes indicate that the mechanism occurring between 0.200V and 0.500V is more relevant. Pyrrhotite particles are unlikely to experience potentials more anodic than 0.300V in normal alkaline flotation environments. Oxidation of the mineral in this range was therefore investigated more closely.
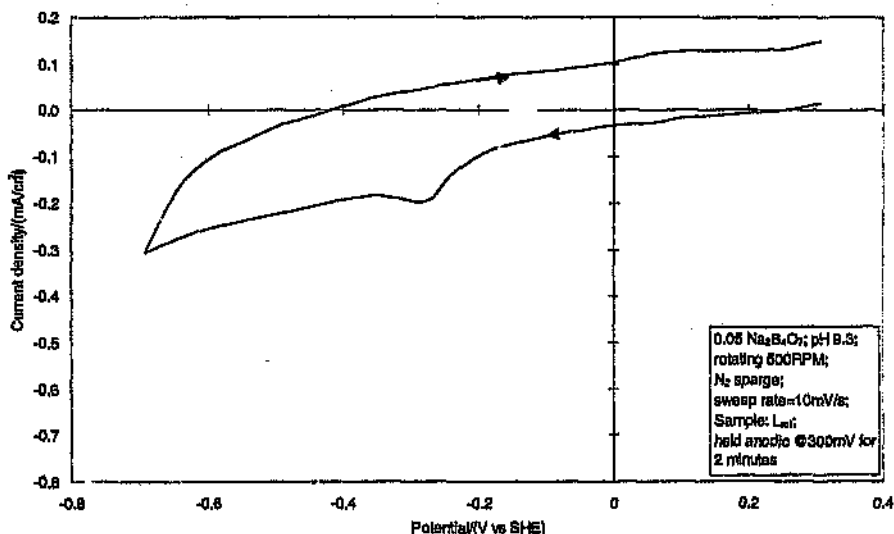
Figure 4.17: Voltammogram of pyrrhotite electrode (L_{rot}) after mild anodic conditioning

In Figure 4.17 the electrode was held at 0.300V for 2 minutes. The potential was then swept in the cathodic direction. There is cathodic peak at ≈-0.250V. No anodic peaks are visible on the anodic scan. The experiment was also performed using a stationary electrode with similar results.
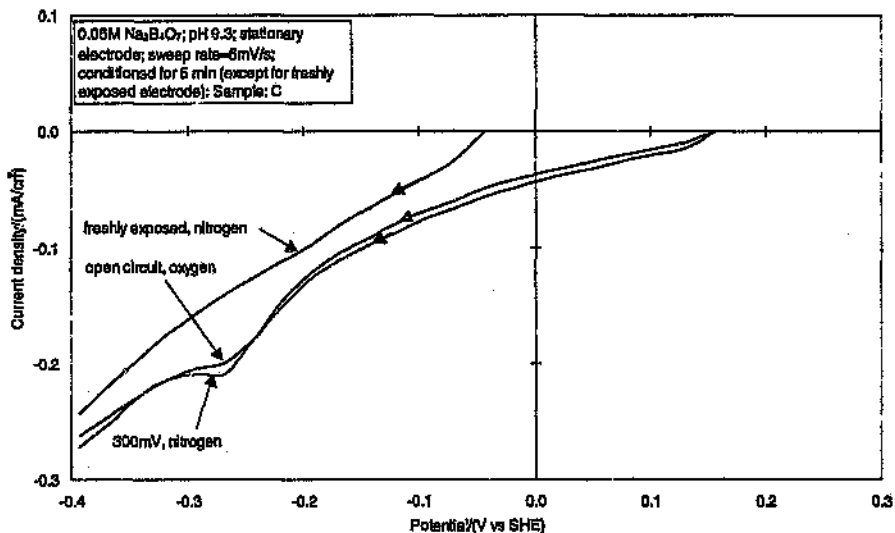
Figure 4.18: Cathodic wave forms for pyrrhotite electrode (C): freshly exposed, mild anodic conditioning and oxygen saturated conditioning

Figure 4.18 shows the results from an experiment conducted on a different pyrrhotite sample. With the exception of the freshly exposed case, the electrode was conditioned for 5 minutes under open circuit, oxygen saturated, pH 9.3 borate solution, and, under closed circuit, 0.300V, pH 9.3 borate solutions.

As already observed the freshly exposed electrode gave no significant cathodic reactions. The conditioning at 0.300V and open circuit yielded similar results with a cathodic reaction occurring at $\approx$-0.250V. After conditioning at open circuit in the oxygenated solutions the rest potential of the electrode was 0.262V. Thus conditioning the electrode at 0.300V is similar to conditioning in open circuit oxygenated solutions were the rest potential approaches 0.300V.
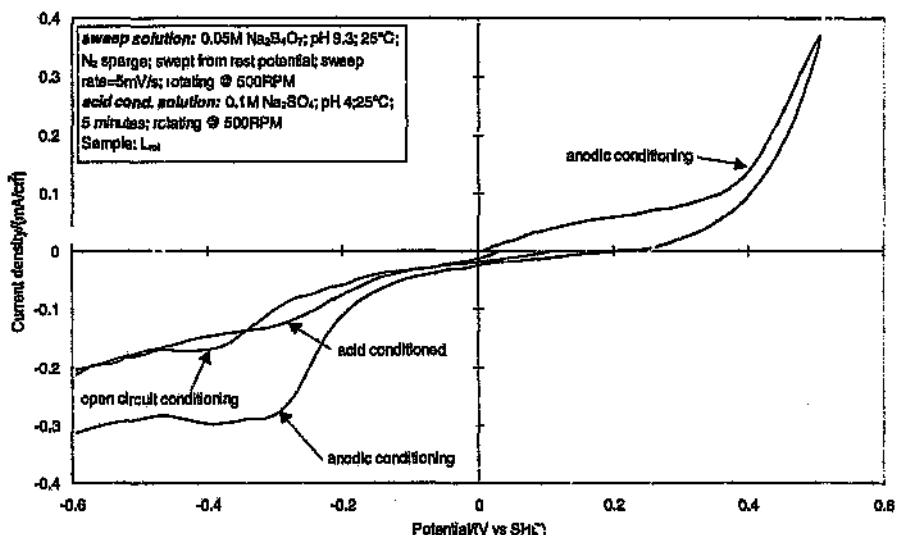
Oxidation under acidic open circuit conditions

There has been considerable interest within industry of acid conditioning sulphide mineral slurries prior to addition of reagents. This interest stems from the generally accepted idea that less noble sulphide minerals, like pyrrhotite, oxidise under alkaline conditions forming oxide/hydroxide surface layers, which then, either inhibit collection directly, or reduce the effective mineral surface area available for collector attachment.

It is anticipated that such an acid conditioning stage would dissolve oxidation products (especially hydroxides) on the surface thus effectively chemically cleaning the minerals and presenting them freshly exposed to the flotation reagents. Practically this would be done by spiking the pH to a low value (pH 4-6) and then allowing the natural buffering capacity of the slurry to bring the pH back up to pH≈9 before the various activators, collectors and frothing agents are added.

There has been no direct experimental evidence to suggest that such a treatment would be effective, and there are a number of issues that remain unresolved. For the specific case of pyrrhotite the mechanism of oxidation in acidic solutions may be different to alkaline solutions resulting in different surface products. The stability of the mineral surface after acidic oxidation is also not known.

The effect of acidic oxidation on the surface was therefore studied. Mineral electrodes were condition in separate pH 4 sodium sulphate solutions. The electrodes were then transferred to a 0.05M sodium tetraborate solution at pH 9.3.

Figure 4.19: Voltammograms showing cathodic wave forms with and without acid conditioning (L_{rot})

Figure 4.19 shows the cathodic wave forms for electrodes after anodic oxidation, open circuit conditioning at pH 9 and acid conditioning at pH4. All solutions were sparged with nitrogen. After the electrode had been swept anodic there are two cathodic peaks on the reverse sweep at 0.300V and 0.400V. When the electrode had been open circuit conditioned only the peak at 0.400V is visible, whilst after acidic conditioning the peak at 0.300V is visible. There are therefore differences in the cathodic behaviour of the mineral between the different treatments.
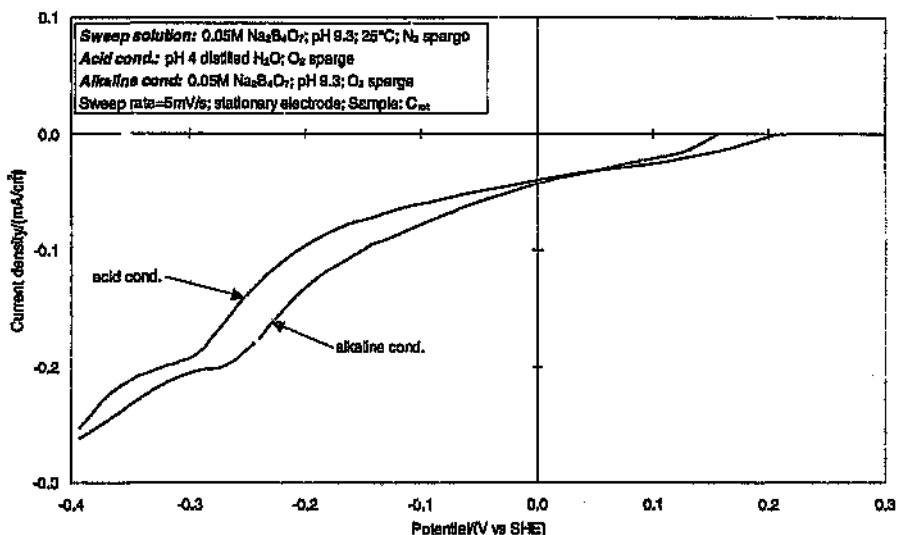
Figure 4.20: Voltammograms showing cathodic wave forms with and without acid conditioning (C_{rot})

In Figure 4.20 a different pyrrhotite sample was investigated. In this case the conditioning solutions were saturated with oxygen, but the sweep solution was de-oxygenated. Unlike the results shown in Figure 4.19 the alkaline conditioned electrode gives a cathodic reaction at slightly more anodic potentials than the acid conditioned electrode.

4.2.1.2 Discussion

The anodic behaviour of the two pyrrhotite samples show very similar oxidation mechanisms and there is good agreement with Hamilton and Woods (1981) and Hodgson and Agar (1989). These researchers have suggested that the initial oxidation occurs through the progressive removal of iron leaving a sulphur rich mineral surface. At higher potentials sulphur is oxidised directly to sulphate (Hodgson and Agar, 1989).

There are differences in the anodic waves between borate and sodium sulphate solutions. Oxidation in borate solutions at higher potentials forms a shoulder before the anodic current increases rapidly due to oxidation of H_2O leading to $O_{2(g)}$ evolution. This shoulder is not visible in sodium sulphate solutions. Related to this is the

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observation that, on second and subsequent sweeps in borate solutions, the oxidation appears to passivate (Figure 4.12 and Figure 4.13). This does not occur in sulphate solutions (Figure 4.14). This could be due to local pH affects at the mineral surface, as the oxidation of pyrrhotite directly to sulphate involves the production of H^+ ions (reaction (1-4)). The use of a buffer solution may counter act this effect.

There is still considerable speculation about the exact nature of the pyrrhotite surface after oxidation. An investigation of the cathodic currents after anodic sweeps reveals at least two, possible three, cathodic reactions that arise through the previous oxidation (these cathodic reactions are not visible when swept cathodically after being freshly exposed). Possible reduction reactions can only include: reduction of sulphur (either elemental or from a sulphur rich lattice), reduction of ferric hydroxide to ferrous hydroxide, further reduction of ferrous to metal, and the re-formation of pyrrhotite or other iron sulphide from oxidation products. The relevant reactions with their equilibrium potentials are given below:

$S_{(s)} + 2e^- + H^+ \Leftrightarrow HS^-$ $\qquad$ $E_{pH\ 9} = -0.328$ V ($E^\circ = -0.062$ V)$\quad$ (4-1)

$Fe(OH)_3 + e^- + H^+ \Leftrightarrow Fe(OH)_2 + H_2O$ $\quad$ $E_{pH\ 9} = -0.250$ V ($E^\cdot = +0.280$ V)$\quad$ (4-2)

$S + Fe(OH)_2 + 2e^- \Leftrightarrow FeS + 2OH^-$ $\qquad$ $E_{pH9} = -0.081$ V ($E^\circ = -0.376$ V)$\quad$ (4-3)

$Fe(OH)_2 + 2e^- \Leftrightarrow Fe(s)\ 2OH^-$ $\qquad$ $E_{pH9} = -0.584$ V ($E^\circ = -0.879$ V)$\quad$ (4-4)
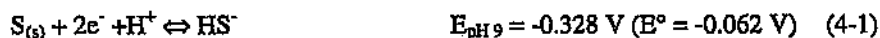
The standard potentials for reactions 4-1 and 4-2 are taken from Hamilton and Woods (1981). The standard potentials for reactions 4-3 and 4-4 where calculated from the bulk thermodynamic properties of the products and reactants involved in the reactions. Thermodynamic data was taken from Perry (1984). Exact identification of cathodic reactions is complicated due to differences in the thermodynamic properties of surface species as compared to bulk thermodynamic properties (Woods, 1984).

The cathodic reactions after anodic sweeps are different for the two samples in that the first cathodic reaction occurs at slightly different potentials depending in the sample.

At slower sweep rates it also appears that the first cathodic peak is in fact two reactions (Figure 4.16 and Figure 4.19). The fact that the potential of the reactions is dependent on sample origin would tend to suggest that the surface species are not elemental, but rather still associated with the mineral lattice.

In terms of the actual flotation characteristics, the surface products after mild oxidation, within the potential range defined by the mixed potential measurements, is of importance. The results show that open-circuit conditioning in oxygen saturated solutions does give rise to a surface product which is reduced on cathodic sweeps (Figure 4.17 and Figure 4.18). There is however no corresponding anodic reaction. This reaction is most likely reduction of $Fe(OH)_3$ and/or S. In the case of sulphur this would explain the absence of any anodic reaction, however stationary electrodes also do not show an anodic reaction. For $Fe(OH)_3$ its reduction may result in the formation of $Fe(OH)_2$ which is considerably more soluble than $Fe(OH)_3$. These factors, combined with the comparatively small amounts of surface product, may explain the lack of any anodic oxidation of reduced surface species resulting from mild oxidation.

Conditioning the mineral in acidic solutions appears to alter the reactivity of the mineral compared to alkaline conditioned cases. It is noted however that the effect is again different for the two samples investigated. Under acidic conditions hydroxides will not precipitate on the mineral surface. Thus oxidation in acidic solutions will leave the mineral surface predominantly sulphur rich. This would then account for the different cathodic behaviours observed. After acidic conditioning the amount of hydroxides available for reduction is very small compared to surfaces conditioned in alkaline solutions.

4.2.2 Interaction with Cu^{2+} ions

Experiments were conducted in two main phases. In the first phase the aim was to identify and characterise an activated pyrrhotite surface. To achieve this acidic pH's and high copper sulphate concentrations were used. In the second phase the effect of oxidation and pH were investigated. The experimental set-up and electrodes used were the same as that used for the previously outlined voltammetry.

4.2.2.1 Results

Characterisation of activated mineral

In Figure 4.21 the pyrrhotite electrode was conditioned in a 5×10^{-3} M $CuSO_4$, sodium sulphate solution at pH 4. An acidic pH was used to counter act any hydroxide layer formation and ensure that the electrode surface was available for activation.

The first anodic sweep in the absence of copper sulphate shows no significant anodic currents. The rest potential of the pyrrhotite is 0.250V more anodic in the presence of copper sulphate. An anodic peak (4) is observed at ≈0.550V. This peak quickly decays. On the reverse cathodic sweep, a cathodic peak (5) is observed at 0.400V. This peak decays into another cathodic reaction which is then followed by a cathodic current plateau. On the second anodic sweep three oxidising reactions are observed at 0.350V, 0.450V and 0.550V.
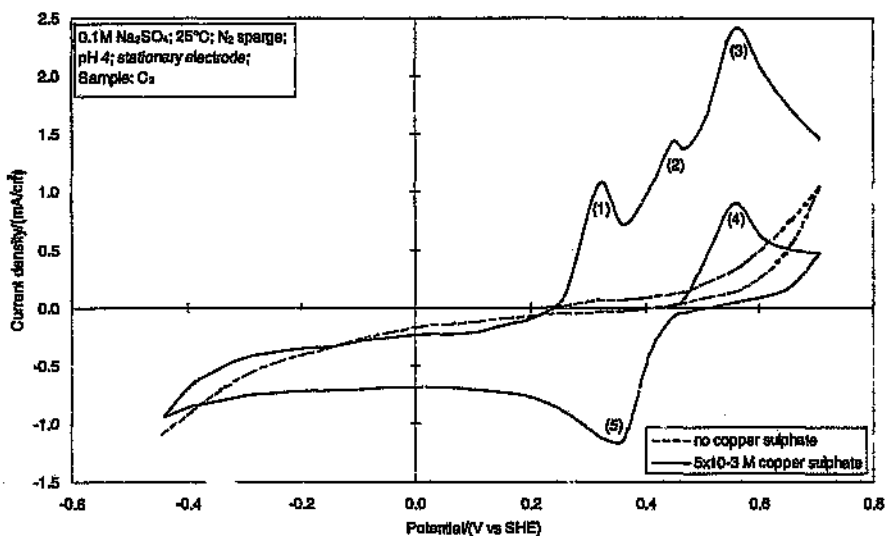
Figure 4.21: Characterisation of activated pyrrhotite surface

There are no anodic peaks in the absence of copper sulphate therefore the anodic peaks observed when copper sulphate is present must be due to the oxidation of copper compounds on the pyrrhotite surface.

The couple

$$Cu^{2+}_{(aq)} + 2e^- \Leftrightarrow Cu_{(s)} \qquad (4\text{-}5)$$

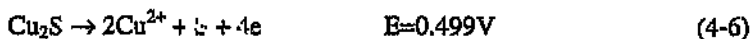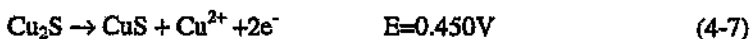has a standard reduction potential of 340mV. Correcting for the concentration of copper ions gives 0.272V. At potentials lower than 0.272V one would expect copper to begin plating out onto the electrode. This would account for the current plateau on the cathodic sweep. The first anodic peak (1) at ≈0.320V after the potential has been swept cathodic is probably therefore the oxidation of a copper layer back to Cu^{2+}.

The second anodic peak (2) may be the oxidation of Cu_2S to either CuS and Cu^{2+}, or Cu^{2+} and S. The reactions with their equilibrium potentials (taking into account Cu^{2+} concentration of $5 \times 10^{-3}M$) are given below (the reactions are written in the direction they occur):

$$Cu_2S \rightarrow 2Cu^{2+} + S + 4e \qquad E=0.499V \qquad (4-6)$$

$$or$$

$$Cu_2S \rightarrow CuS + Cu^{2+} + 2e^- \qquad E=0.450V \qquad (4-7)$$

Thermodynamically the oxidation of Cu_2S to CuS and Cu^{2+} will occur first.

The final anodic peak (3) is probably due to the reaction:

$$CuS \rightarrow Cu^{2+} + S + 2e^- \qquad E=0.548V \qquad (4-8)$$
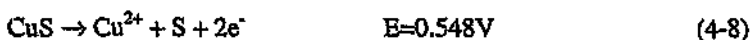
On the first anodic sweep after activation a single anodic peak (4) is observed. This peak occurs at 0.550V, and is likely the same reaction as that occurring on the subsequent anodic sweeps (peak 3).
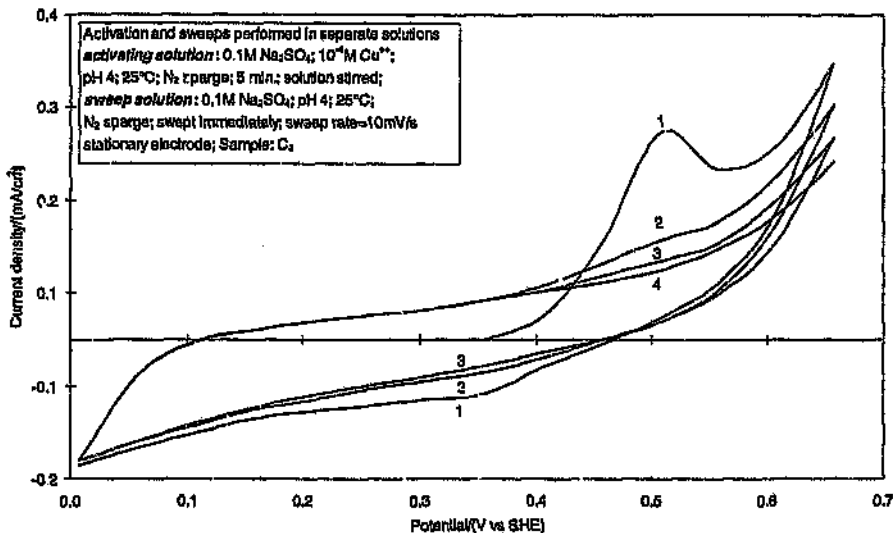
Figure 4.22: **Voltammogram of activated pyrrhotite electrode - swept immediately**

Figure 4.22 shows the voltammogram for a pyrrhotite electrode activated in a stirred pH 4, $10^{-4}M$ copper sulphate solution, before being transferred to a 0.1M Na_2SO_4

solution at pH 4. The sweeps were therefore performed in solutions that did not contain copper sulphate (mineral was activated in a separate solution). The anodic peak at 0.500V is observed indicating an activated surface. The charge density associated with this reaction was calculated from the area of the peak as $910\mu C.cm^{-2}$. There is a cathodic peak at 0.300V. This peak is considerably smaller than the corresponding anodic peak indicating that not all of the oxidised products from the anodic reaction are available for reduction on the cathodic sweep. This indicates that the reaction products of the oxidation are likely to be soluble and thus diffuse away from the mineral surface. On the second anodic sweep there is an anodic reaction of similar magnitude to the preceding cathodic reaction.
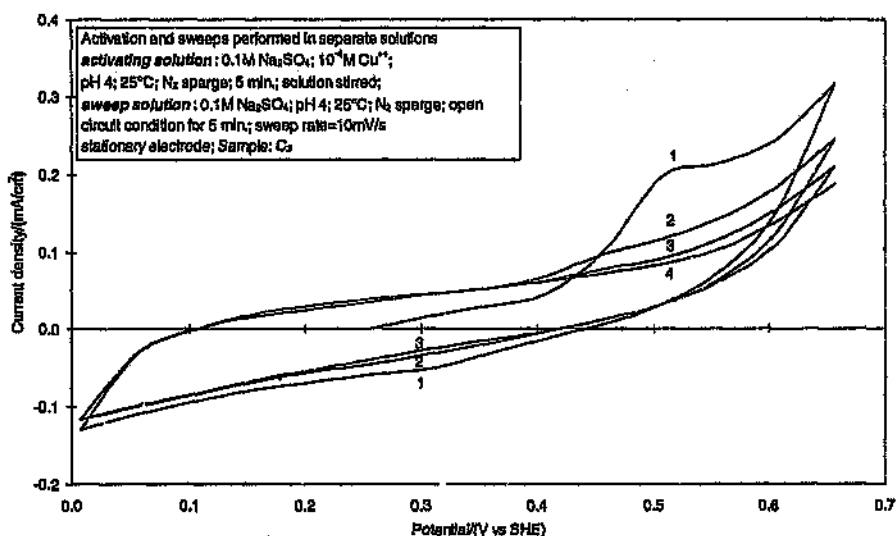
Figure 4.23: **Voltammogram of activated pyrrhotite electrode - conditioned before sweep**

In Figure 4.23 the electrode was conditioned in the copper free solution for 5 minutes under open circuit, after being activated separately. This was done to investigate whether the pyrrhotite surface remained activated even in the absence of copper sulphate. The magnitude of the anodic peak associated with the activated surface is smaller after the electrode has been conditioned compared to Figure 4.22 where the potential was swept immediately (in Figure 4.23 the charge associated with this peak is $\approx 475\mu C.cm^{-2}$). Under open circuit the mixed potential of the activated mineral in copper sulphate free solutions decreases by $\approx 0.100V$ in 5 minutes. The electrodes can

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therefore, within the time scales investigated, be activated in separate solutions, and then transferred to copper sulphate free solutions for further investigation.
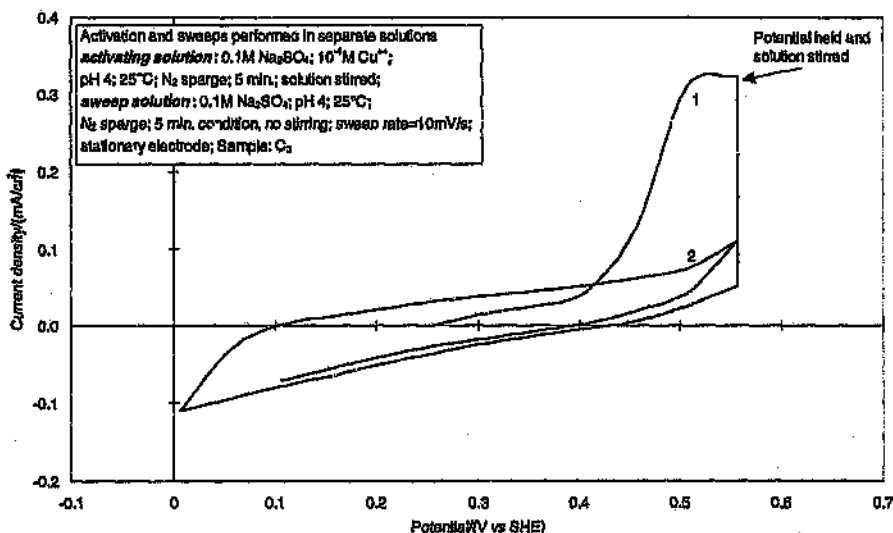
Figure 4.24: Effect of stirring at anodic limit on cathodic wave form

In Figure 4.24 a pre-activated pyrrhotite electrode was swept from its rest potential anodically. At the anodic limit the potential was held whilst the solution was stirred. The stirring action would ensure that any soluble reaction products are removed from the electrode surface. The potential was then swept cathodically. There is no cathodic reaction at 0.300V (as was observed in Figure 4.22 and Figure 4.23). This confirms that the reaction products from the anodic reaction at 0.500V are soluble and are removed from the surface of the mineral.

In Figure 4.22 cycling the potential resulted in a reaction couple at 0.300V and 0.500V which dimished on subsequent sweeps. In Figure 4.21 the following reaction was assigned to the second anodic peak (2):

$$Cu_2S \rightarrow CuS + Cu^{2+} + 2e^-$$ (4-9)
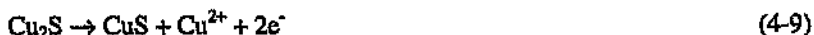
This reaction is absent in Figure 4.22 eventhough the potential has been cycled cathodic. The difference between these to cases is that in Figure 4.22 the Cu^{2+} concentration at the electrode surface is very low and results only from the oxidation of the activated mineral surface via reaction 4-6. In Figure 4.21 copper is plated out onto the electrode surface and it is possible that on oxidation of this copper surface a

Cu_2S species is formed. This species is however not formed when a freshly exposed electrode is immersed in Cu^{2+} solutions.

It is therefore proposed that the surface product of copper activation at pH 4 is CuS. A possible reaction mechanism for the formation of this species was proposed by Nicol (1984):

$$Fe_9S_{10} + 9Cu^{2+} \rightarrow 9Fe^{2+} + 9CuS + S \qquad (4-10)$$
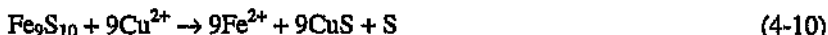
This surface product begins to oxidise off the surface of the mineral at potentials more anodic than $\approx 0.400V$. The oxidation of this surface product can be used to identify an activated pyrrhotite mineral surface. The magnitude of the peak caused through oxidation of this surface activation product is an indication of the degree and extent of the activation.

Factors effecting activation

In the previous section the activation was conducted at pH 4. This is in line with the classic theory of pyrrhotite passivation in alkaline pH's. Activation is often attempted in industrial flotation circuits under alkaline conditions. Alkaline conditions were therefore investigated to check whether activation occurs and to explore ways of enhancing the activation.

Sodium sulphate solutions were prepared at pH's 4, 6.5 and 9. Freshly exposed pyrrhotite minerals were conditioned in the solution for 5 minutes before copper sulphate was added. The concentration of copper sulphate after addition was $10^{-4}M$.

0.1M Na₂SO₄; N₂ sparge; 25°C; pH adjusted to 4, 6.5 and 9; freshly exposed electrode conditioned for 5 min; copper sulphate added; [Cu⁺⁺]=10⁻⁴M; conditioned for further 5 min.;sweep rate 10mV/s;stationary electrode; Sample: C₂
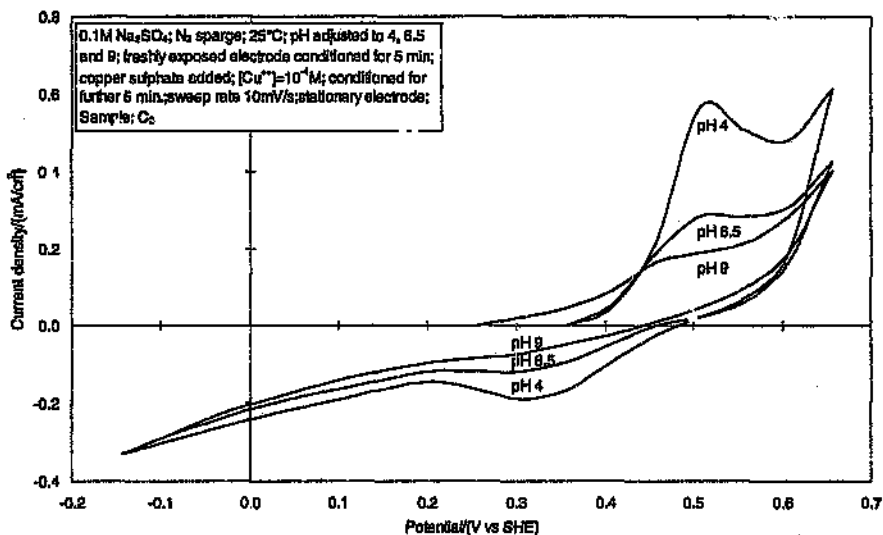
Figure 4.25: Effect of pH on activation of pyrrhotite

After the 5 minute conditioning period the potential was swept anodically from the rest potential. The voltammograms are shown in Figure 4.25. In the case of activation at pH 4 a large anodic peak is visible at 0.500V which is characteristic of an activated pyrrhotite surface. With increasing pH this peak diminishes. In the case of pH 9 the rest potential of the mineral after activation is ≈0.100V more cathodic than in the case of pH 4 and 6.4. As unbuffered solutions were used the pH after copper sulphate addition decreased. This would enhance the activation slightly. The results at pH 9 are therefore not representative of plant solutions where the pH is naturally buffered at pH 9. No evidence was found for activation during experiments conducted in 0.05M borate buffer solutions.

In order to investigate the mechanism of the activation process activation was conducted with the electrode potentiostated at different potentials. If the activation process is coupled with the oxidation of the mineral then it should be possible to inhibit this activation by keeping the potential of the electrode cathodic thus limiting its incipient oxidation. The E_h-pH diagram for the aqueous pyrrhotite system (Figure 1.2) indicates that pyrrhotite is stable between -0.2V and 0V. If the activation process is a coupled process involving oxidation of the mineral, as opposed to a simple ion exchange mechanism, then no activation should be possible when the potential of the

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electrode is held in this region. The situation is complicated however due to the fact that at 10^{-4}M, copper ions are expected to begin plating out onto the electrode at potentials more cathodic than 0.2V. There is therefore no potential region where thermodynamically both pyrrhotite and Cu^{2+} are stable.
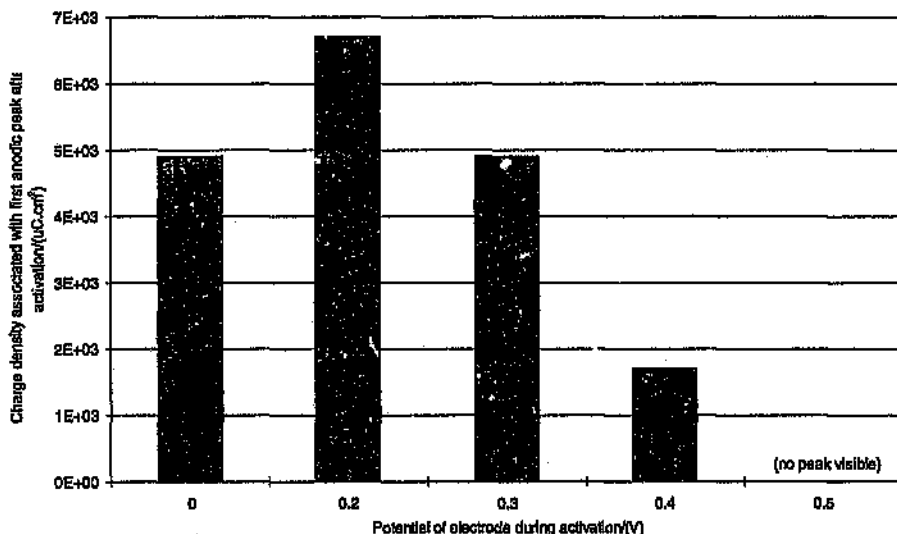
Figure 4.26: Effect of potential during activation on degree of activation

Activation was carried out with the electrode potentiostated at 0, 0.2, 0.3, 0.4 and 0.5V. The activation was done in a stirred, pH 4, 10^{-4}M $CuSO_4$ solution for 5 minutes. The potential was then swept anodically. The charge associated with the characteristic anodic peak at 0.500V was calculated from the voltammograms. These values are shown in Figure 4.26.

As would be expected there is no activation at 0.5V. This is because the product of activation is oxidised at this potential. Similarly the decrease in charge density from 0.2V through to 0.4V may be due to initial oxidation of the product of activation at these potentials, although the cathodic process still dominates. The increase in charge density, and thus the degree of activation from 0V to 0.2V, is consistent with the mechanism of activation whereby it is coupled with the oxidation of the mineral. That is apart from the fact that the activation product becomes unstable at potentials approaching 0.5V, the activation is favoured by more oxidising conditions on the electrode surface.

4.2.2.2 Discussion

The present work indicates that the surface product of activation under acidic conditions is CuS. The activation process is favoured by oxidising conditions, although the activation product is unstable above 0.4V and quickly oxidises to soluble products. The mineral remains activated in alkaline conditions in the absence of copper sulphate within the time-scale investigated, and it is not anticipated that deactivation would be a significant problem in actual flotation conditions.

There is considerable evidence, both from the present investigation, and from previous studies (Bushell *et al.*, 1961, Nicol, 1984 and Iwasaki, 1988) to conclude that activation is ineffective in alkaline, pH 9, solutions. The reason for this may be related to the low solubility of copper hydroxide, as well as to the extent of hydroxide surface coverage on the pyrrhotite mineral itself. There are however reports that indicate that activation can be achieved at pH 9, and that the susequent recovery of pyrrhotite is enhanced (Leppinen, 1990, Senior *et al.*, 1995, Stowe *et al.*, 1995, Yoon *et al.*, 1995 and Kelebek *et al.*, 1996). It is possible that differences arise due to the varying nature of ores that are tested. Different ores have differing pH buffering capacities and the pH may be temporarily affected by copper sulphate addition. From an electrochemical viewpoint there has been no evidence for copper activation at pH 9. This has important implications for alkaline industrial flotation processes where copper sulphate is used as an activator. Activation may have to be performed under acidic to neutral conditions if it is required for effective pyrrhotite flotation.

4.2.3 Oxygen reduction

Xanthate/mineral interaction in most sulphide minerals is thought to occur via a charge transfer mechanism. This mechanism involves oxidation of xanthate to dixanthogen at the mineral surface coupled with the reduction of oxygen. A mixed potential is set up by these reactions.

By using potentiostatic techniques the individual reactions of xanthate oxidation and oxygen reduction have been studied separately. Emphasis has been placed on understanding what effects these reactions and how they may be enhanced. Factors considered includes the effect of oxidation of the pyrrhotite mineral surface and the effect of copper activation.
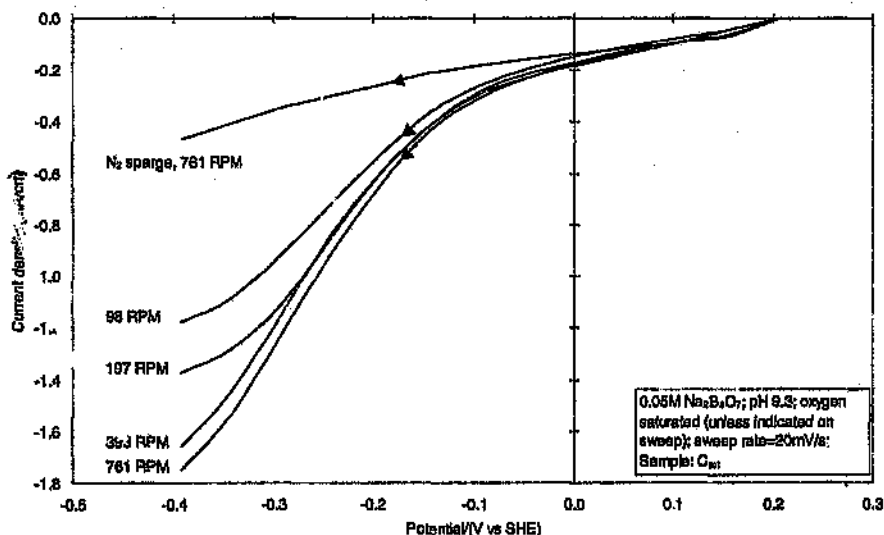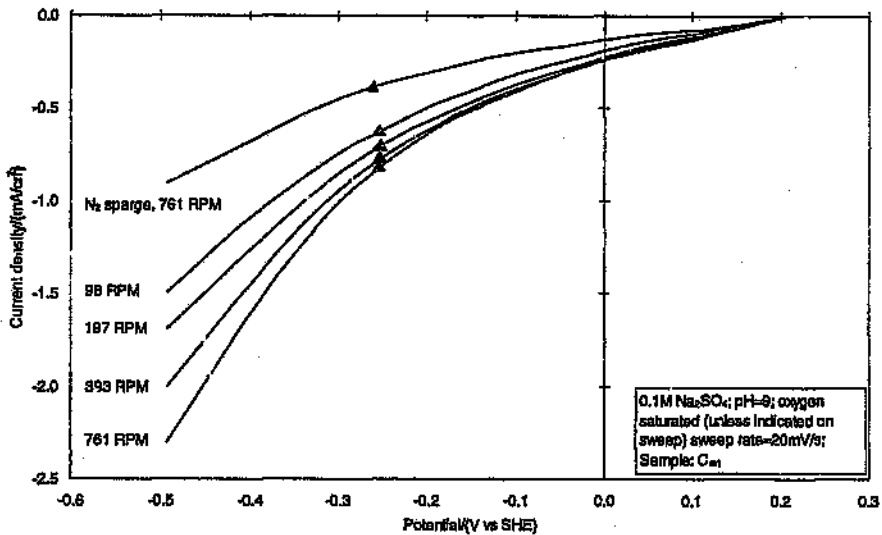
4.2.3.1 Results

Figure 4.27: Oxygen reduction sweeps of pyrrhotite in borate solution

Figure 4.27 shows oxygen reduction sweeps for a freshly exposed pyrrhotite electrode at different electrode rotation speeds. Also shown is the cathodic behaviour in deoxygenated solutions (sparged with N_2).

At potentials more cathodic than ≈-0.300V a limiting current is observed for low rotation speeds.

Figure 4.28: Oxygen reduction sweeps of pyrrhotite in Na₂SO₄ (pH 9) solution

In Figure 4.28 the oxygen reduction sweeps are shown for a freshly exposed pyrrhotite electrode in a pH 9 sodium sulphate solution. Unlike the case for borate solutions no limiting currents are observed even at potentials 0.100V more cathodic, although there is still a dependence of current density on rotation speed. The reduction of oxygen produces H^+ ions and in unbuffered solutions this could result in the pH at the surface of the electrode increasing:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad\quad\quad (4-11)$$

This would account for the more cathodic potentials in Na_2SO_4 solutions.

Pyrrhotite is known to be a poor catalyst for oxygen reduction compared to other sulphide minerals (Rand, 1977). Figure 4.29 shows the oxygen reduction sweeps for freshly exposed pyrite and pyrrhotite in pH 9 sodium sulphate. The current densities are significantly smaller on pyrrhotite as compared to pyrite. Limiting currents are observed on pyrite.
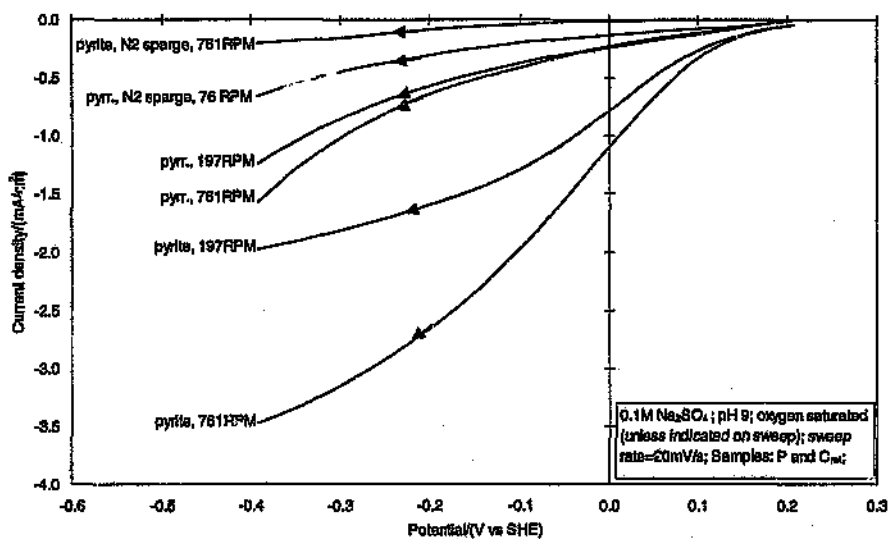
Figure 4.29: Comparison of pyrite and pyrrhotite oxygen reduction curves, pH 9 Na₂SO₄

The effect of oxidation on the kinetics of oxygen reduction was investigated. The electrode was conditioned at different anodic potentials from 0 to 0.600V for ≈5 minutes. The potential was then stepped to a cathodic potential in the region where oxygen reduction occurs. The resulting current transient was then recorded. Cathodic potentials of −0.300V and 0V were investigated. A rotating electrode was used (393RPM). Experiments were performed in 0.05M Na₂B₄O₇ at pH 9.3. Solutions were saturated with oxygen.
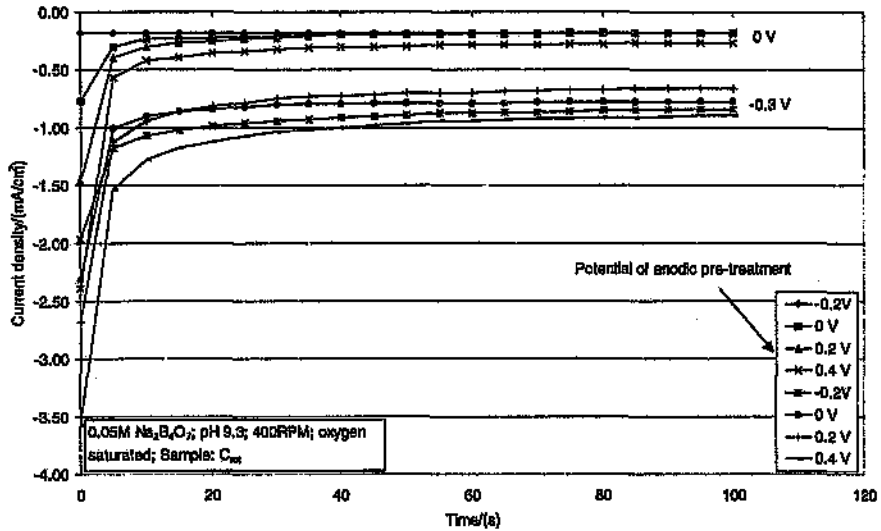
Figure 4.30: Effect of oxidation on kinetics of oxygen reduction

From these experiments (Figure 4.30) it was observed that the magnitude of the current densities at steady state did not exhibit any systematic dependence on the extent of prior oxidation. Initially the current densities were higher for more anodic treatments, but this is likely due to the reduction of oxidation products being enhanced by the more anodic pre-treatment.

If poor oxygen reduction kinetics is an inhibiting factor in pyrrhotite flotation then the effect of copper activation on oxygen reduction is an important consideration. The oxygen reduction sweeps are shown in Figure 4.31 for a pyrrhotite electrode that was activated under favourable acidic conditions prior to being transferred to copper sulphate free solutions. No limiting currents are observed and the dependence of electrode rotation speed does not appear as pronounced as for non-activated electrodes.
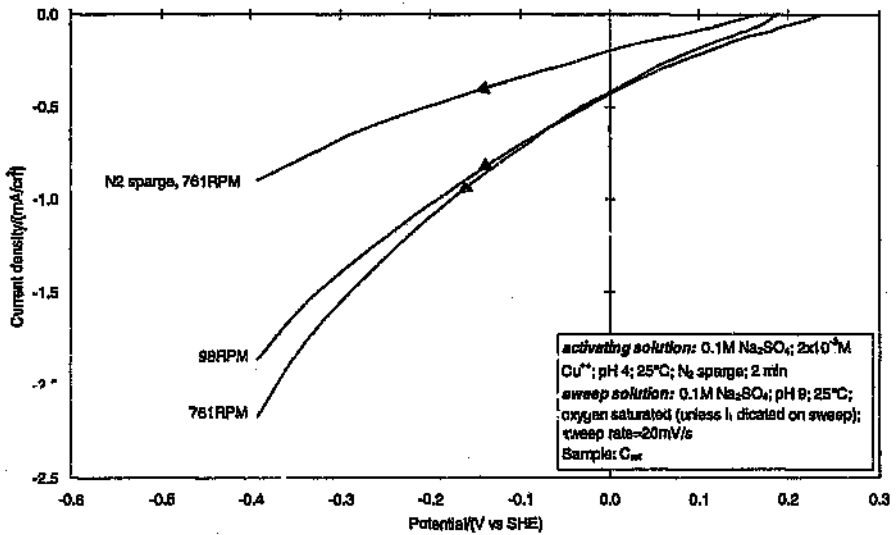
Figure 4.31: Oxygen reduction sweeps for previously activated pyrrhotite electrodes

Figure 4.32 shows a comparison of the oxygen reduction wave between an activated and non-activated pyrrhotite electrode. The current densities for activated electrodes are generally lower than non-activated especially at high cathodic potentials.
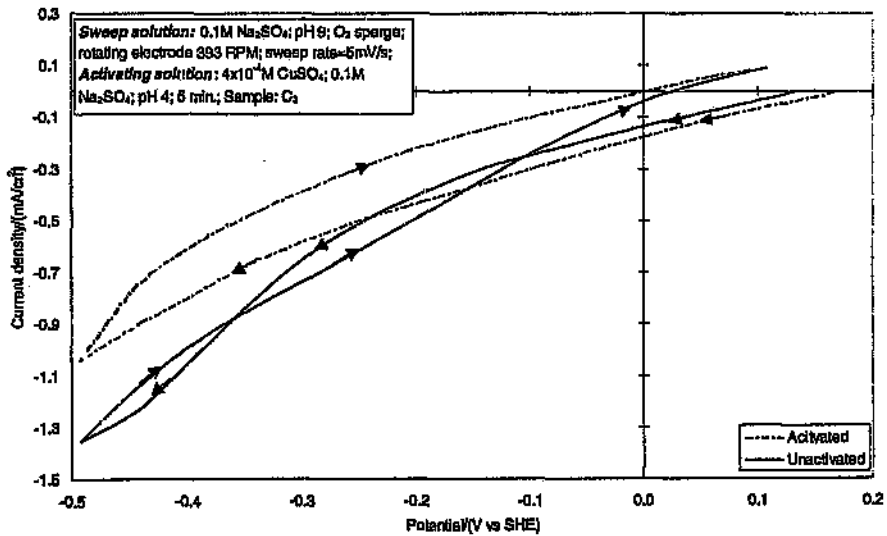
Figure 4.32: Oxygen reduction sweeps for activated and non-activated pyrrhotite electrodes

The kinetics of oxygen reduction in the potential range that the mineral is likely to assume is of particular importance. Such a potential range has been discussed in section 4-1 where a large amount of mixed potential measurements for pyrrhotite electrodes are presented. By considering these potential measurements and the oxygen reduction sweeps presented previously it was decided to study oxygen reduction at 0.107V and 0.157V. The mixed potential of pyrrhotite particles is likely to be slightly more anodic (based on electrode potential measurements) but the current densities at potentials more anodic than 0.157V are very small and difficult to analyse meaningfully.

In order to measure the kinetics of oxygen reduction, current transient techniques were used. A freshly exposed pyrrhotite electrode was conditioned under closed circuit conditions at 0.107V and 0.157V respectively under a nitrogen atmosphere. Once a steady state current had been achieved (typically @ 30s) oxygen was introduced. The steady state current was then measured (@≈2-3 minutes). This was done at both 0.107 and 0.157V. In order to investigate the effect of activation on oxygen reduction, at these potentials, the experiments were repeated, but with electrodes that had been previously activated in $2x10^{-3}M$ CuSO$_4$ (0.1M Na$_2$SO$_4$ base electrolyte) at pH 4 for 2 minutes. Anodic sweeps were performed after the current transients to ensure that the electrode had remained activated throughout the experiment. In all cases the characteristic anodic peak at ≈0.500V confirmed that the mineral surface had remained activated.

Table 4-2: Summary of oxygen reduction current transients

Potential/(V vs SHE)	Non-activated			Activated		
	No. (	Mean current density /(μA/cm^2)	s	No. Obs.	Mean current density /(μA/cm^2)	s
0.107	2	42.7	4.8	4	38.0	5.5
0.157	2	20.3	1.9	4	20.3	1.1
Tafel slope/(-($\delta E/\delta log_{10}i$)/mV)	155			184		

Summary statistics for the current transients are shown in Table 4-2. The reported Tafel slopes were not calculated from a cyclic voltammogram but from the mean current densities at steady-state. Note that when reporting the mean current densities the background current was not subtracted. Thus the current represents O_2 reduction as well as background cathodic currents. It does not appear that the current densities are significantly effected by activation at the potentials investigated. The Tafel slope for the non-activated pyrrhotite was lower than that reported by Rand (1977) who gives 183mV.

4.2.3.2 Discussion
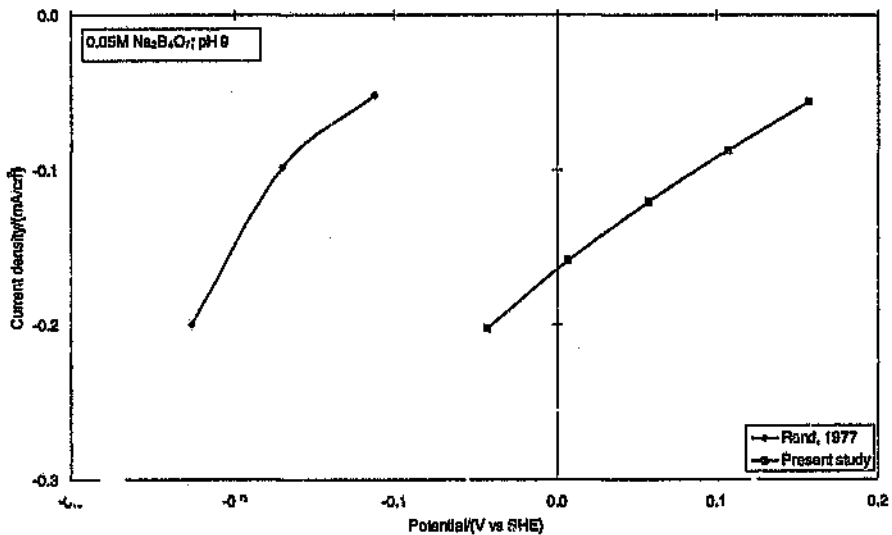
**Figure 4.33: Comparison of activation controlled currents**

Figure 4.33 shows the activation controlled current taken from the foot of the oxygen reduction wave, from the present investigation, and from Rand (1977). There are differences between the two samples. Such differences are not uncommon and Rand (1977) notes that galena samples showed current densities that varied by three times depending on the sample origin.

Evidence suggests that oxygen reduction plays a significant role in the rate of flotation. It is surprising that copper activation does not effect oxygen reduction for pyrrhotite, yet it has been shown that copper activation, carried out at neutral to acidic pH's, does enhance the alkaline floatability of pyrrhotite (Leppinen, 1990). The activation work indicated that the product of copper activation under acidic conditions is CuS. Thus one would expect the oxygen reduction kinetics of well activated pyrrhotite to approach that of covellite. Rand (1977) showed that covellite (CuS) and chalcocite (Cu$_2$S) have better oxygen reduction kinetics than pyrrhotite. The coverage of a copper sulphide species on pyrrhotite may however not be complete and thus the oxygen reduction kinetics may still be dominated by the pyrrhotite surface. The oxygen reduction kinetics of copper activated pyrrhotite at low pH was not investigated and such work may improve the understanding of activation in terms of its affect on oxygen reduction kinetics.

It is significant that galena, which has the poorest kinetics for oxygen reduction, yet has the least requirement for oxygen during flotation (Figure 2.3), forms lead xanthate compounds, and that Leppinen showed that activated pyrrhotite also formed copper xanthate as opposed to dixanthogen. Thus it is possible that in non-activated minerals oxygen reduction is an inhibiting factor in the collection process, but, that upon activation, the mechanism of xanthate adsorption is altered to that forming a copper xanthate product, and thus reducing the need for high oxygen reduction kinetics. The adsorption of xanthate on activated minerals therefore needs more attention.

4.2.4 Xanthate adsorption

4.2.4.1 Results
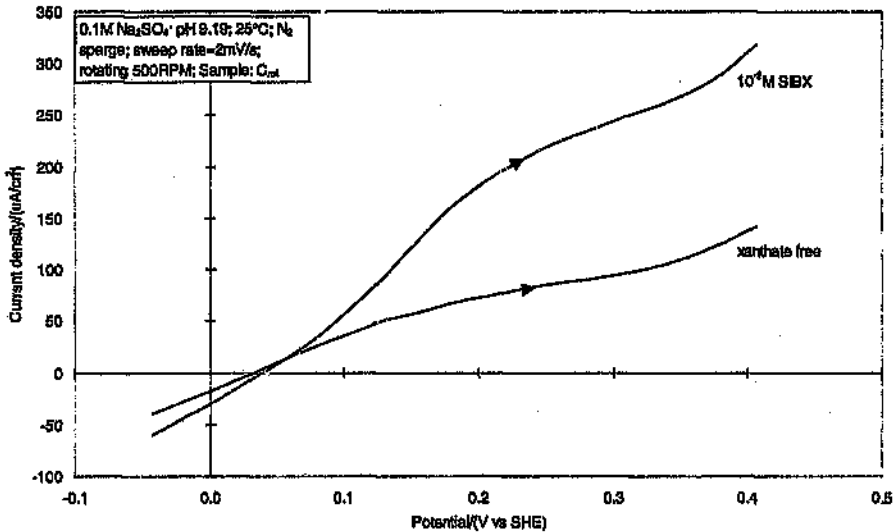
Figure 4.34: Voltammogram in the presence and without SIBX (sodium sulphate solution)

Figure 4.34 shows the anodic behaviour of a pyrrhotite electrode in a pH 9.19, sodium sulphate solution. The electrode surface was freshly exposed and then placed directly into the solution. SIBX was added to the solution before the electrode was immersed. A relatively high $(10^{-2}M)$ concentration of SIBX was used. The anodic currents are larger when SIBX is present than compared to xanthate free solutions. This would indicate either a charge transfer adsorption and/or oxidation of xanthate.
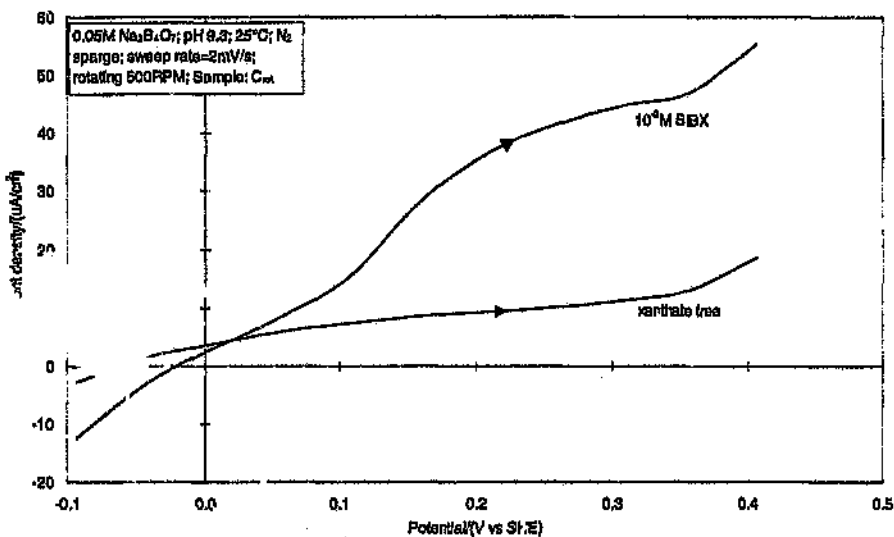
Figure 4.35: **Voltammogram in the presence and without SIBX (borate solution)**

In Figure 4.35 the same experiment was repeated but in a borate electrolyte solution at pH 9.3. Borate solutions in general give lower current densities. As in the case of sodium sulphate solutions enhanced ar odic currents were observed.

The effect of electrode rotation speed on the anodic current in the presence of 10^{-2}M SIBX was investigated. Experiments were conducted in 0.1M Na_2SO_4 at pH 9.2 and the solution was de-oxygenated with nitrogen. A sweep rate of 2mV/s and rotation speeds of 0, 500, 610 and 740 RPM were used. From these experiments no significant dependence of rotation speed on current density was detected.

Attempts to detect reduction reactions associated with the enhanced anodic currents in the presence of xanthate were not successful. If the enhanced anodic currents result in dixanthogen then one would expect to detect the reduction of dixanthogen. This was however not possible. The reasons for this may be related to the sensitivity of the experiments and the magnitude of the background cathodic currents.

At lower SIBX concentrations of 10^{-3}M and 10^{-4}M it was difficult to observe any differences between sweeps conducted with and without xanthate in the solutions, and at 10^{-4}M no differences were observed. This may be caused by the current densities

due to xanthate interaction being to small compared to the actual oxidation of the mineral itself.
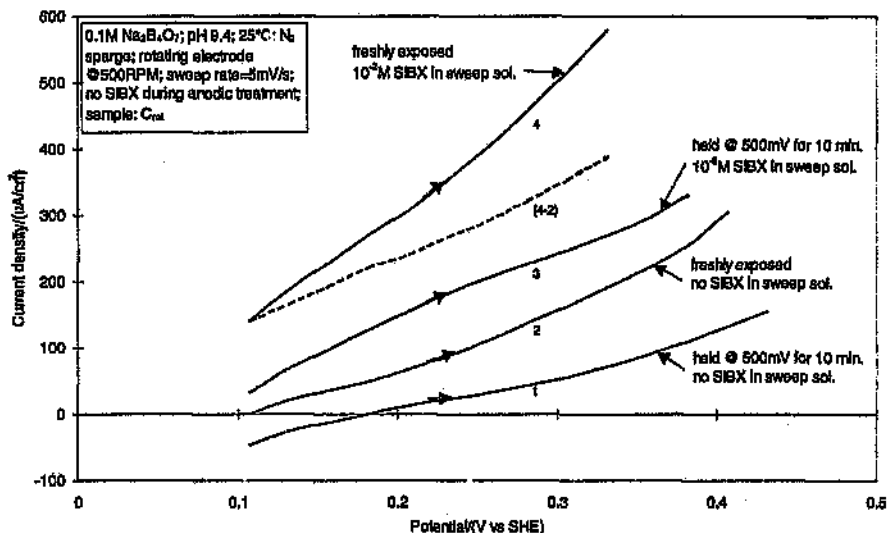

Figure 4.36: Effect of anodic treatment on anodic xanthate interaction

In Figure 4.36 the effect of extensive anodic conditioning on the xanthate interaction wave is shown. The anodic conditioning was achieved by holding the potential of the electrode at 0.500V for 10 minutes. The potential was then set to 0.100V and swept anodically. In solutions without xanthate present the current densities are lower after the anodic treatment. This is expected as after the anodic treatment the mineral is already substantially oxidised. In the presence of 10^{-2}M SIBX there is an enhanced anodic current as compared to the xanthate free sweeps, even after extensive anodic conditioning. There is however a significant increase in the current when the electrode is freshly exposed prior to sweeping in the xanthate solution. Thus the anodic conditioning does inhibit the anodic interaction of xanthate with the mineral but does not completely passivate it.

One of the problems with the above voltammograms is that the mineral is oxidising at the potentials investigated. Thus it is not possible to detect currents that are solely due to xanthate interaction. For this reason current transient techniques were attempted. The mineral was held at a specific potential until the oxidation currents decayed or

stabilised. SIBX was then added to the solutions. The subsequent current transient was recorded.
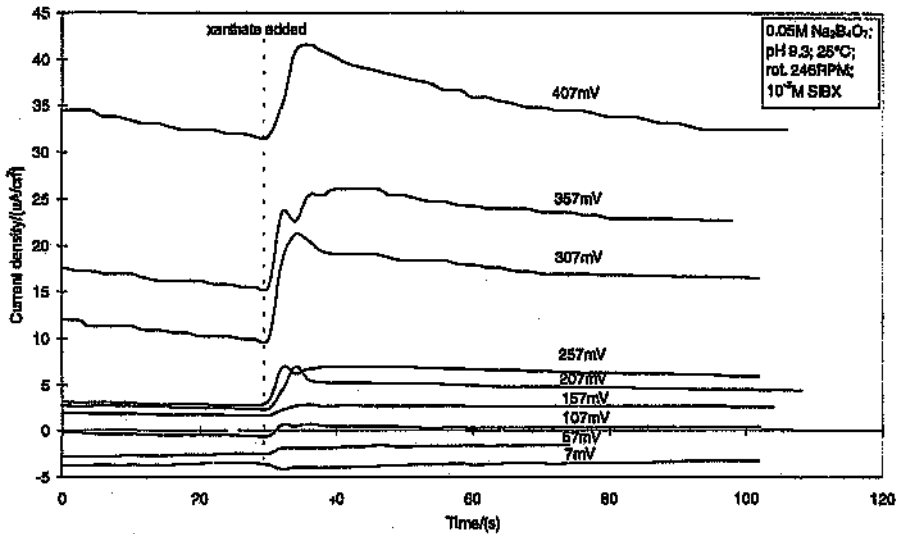
Figure 4.37: Current transients for xanthate addition (250RPM)

Figure 4.37 shows the currents with the electrode rotating at 250RPM. At 0.007V the addition of the xanthate causes a very small cathodic current which diminishes quickly. From 0.057V to 0.257V anodic currents were observed which increased with increasing potential. There is a significant larger increase in current when the potential is above 0.257V. Further increases in potential do not have a significant effect on the magnitude of the current density.
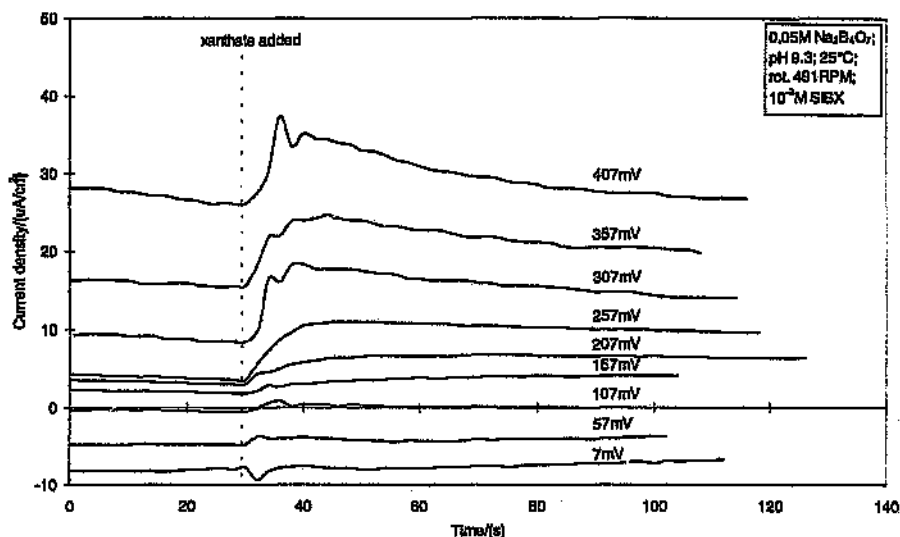
Figure 4.38: Current transients for xanthate addition (500RPM)

In Figure 4.38 the current transients for the addition of SIBX are shown with the electrode rotating at 500RPM. The results are similar to those in Figure 4.37.
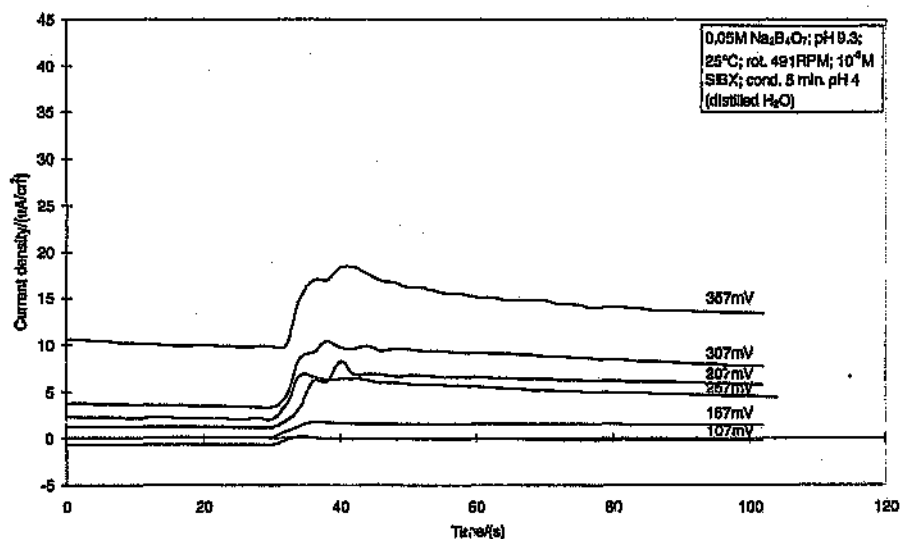
Figure 4.39: Current transients for xanthate addition after acid conditioning

The effect of conditioning the electrode at pH 4 prior to xanthate exposure was investigated. The electrodes were conditioned in separate solutions for 5 minutes and then transferred to a pH 9 borate solution and the potential set. Once the anodic

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current had stabilised SIBX was added as in previous experiments. The resulting current transients are shown in Figure 4.39. Acid conditioning does not appear to have effected the magnitude of the increase in current density on addition of xanthate. The background anodic currents are however smaller after the acidic treatment.
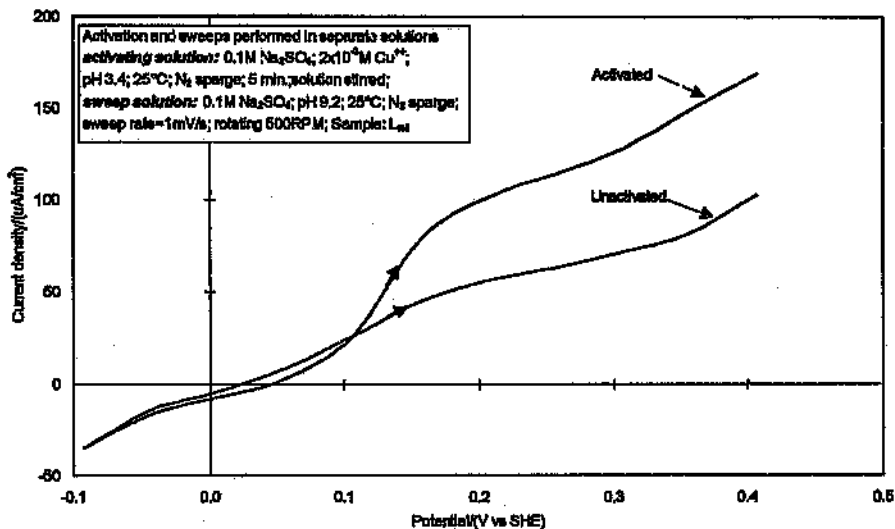
Figure 4.40: Voltammogram for an non-activated and activated pyrrhotite electrode in the presence of SIBX

The effect of activating pyrrhotite on the anodic sweep in the presence of xanthate was investigated. The electrode was activated in a pH 3.4 solution containing 2×10^{-3}M Cu^{2+} ions. The electode was then transfered to a pH 9.2 solution with the potential set to -93mV. The potential was then swept anodically. Figure 4.40 shows the anodic waves from this experiment. The magnitude of the anodic current is larger after activation. This would suggest that the anodic interaction between the mineral and xanthate is enhanced upo . activation.

Figure 4.41 shows the mixed potential of pyrrhotite electrodes after various types of conditioning. The electrode was conditioned for two minutes in solutions with and without copper sulphate being present and at varying pH's. After the conditioning the pH was adjusted to between 9 and 10. SIBX was then added. The potential that the electrode assumed on addition of the SIBX was then recorded.

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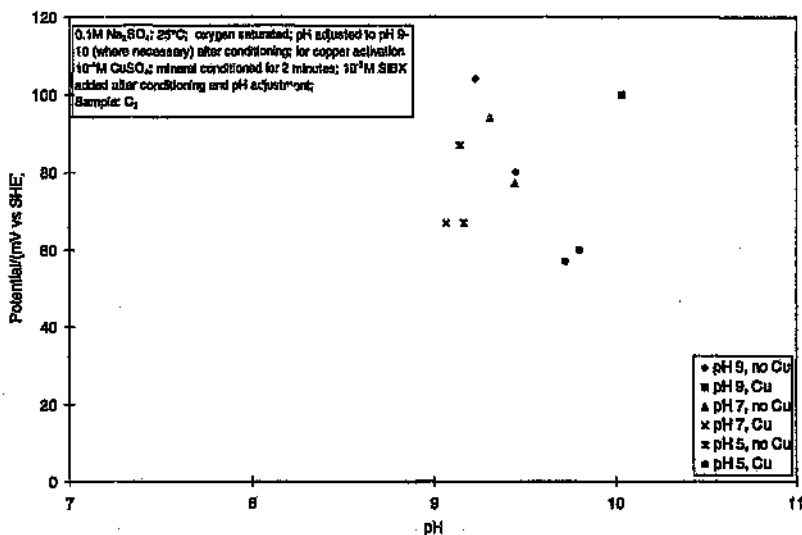
Figure 4.41: Mixed potential of pyrrhotite in the presence of SIBX - effect of activation and pH

There is a general trend for the potential to be lower in the presence of SIBX when the pH of the conditioning stage is acidic. The presence of copper sulphate also appears to result in generally lower potentials. There are insufficient data points to make a statistically significant conclusion, however potential measurements recorded during hydrophobicity tests gave the same general trend (see Figure 4.42).

These lower potentials are expected based on activation enhancing the anodic interaction with xanthate. Due to the enhanced anodic reactions the mixed potential shifts cathodic to balance the nett current.

4.2.4.2 Discussion

Gardner and Woods (1974) studied the interaction between alkylxanthates, and galena and pyrite. In the case of galena the authors were able to detect the chemisorption of ethylxanthate as a distinct anodic peak at ≈0V. The rise in current after the chemisorption peak was due to dixanthogen and lead xanthate formation. On reverse sweeps the reduction of dixanthogen and lead xanthate was also detected. In the case pyrite a distinct chemisorption peak could not be identified although anodic currents were observed above the equilibrium potential for the xanthate/dixanthogen couple.

Cathodic current peaks were observed after anodic treatment in the presence of xanthate.

In this study no anodic peak could be detected for the chemisorp ̧ of xanthate onto the surface of the mineral (as observed by Gardner and Woods (1974) on galena). The voltammograms in Figure 4.34 and Figure 4.35 indicate enhanced anodic reactions above ≈0.050V. The measured equilibrium potential for the xanthate/dixanthogen couple is -0.009V (Table 4-1) at 10^{-2}M SIBX. Current transients confirmed that xanthate interacts anodically with the mineral surface above a certain potential (Figure 4.37 and Figure 4.38).

It is plausible that the anodic currents when xanthate is present are due to the oxidation of xanthate to dixanthogen at the mineral surface. This is supported by dixanthogen being identified as the dominant surface product from a variety of surface analysis techniques (Allison *et al.*, 1972, Prestige *et al.*, 1993, Fornasiero *et al.*, 1995).

Potentials measured in batch tests (Figure 4.2) and plant measurements (Figure 4.1) indicate that the potential of pyrrhotite in the flotation environment is within the potential region where anodic currents related to the oxidation of xanthate are observed. The formation of dixanthogen in flotation pulps at pH 9 is thus thermodynamically possible. In flotation environments there is likely to be significant oxidation of the mineral. Figure 4.36 indicates that oxide layers do inhibit the anodic interaction of pyrrhotite with xanthate but that the interaction is not completely passivated.

Previous researchers have proposed that the mechanism for xanthate adsorption is one of coulombic attraction between positively charged ferrous hydroxide sites, Fe(OH)$^+$, and negatively charged xanthate ions (Rao and Finch, 1991, Hodgson and Agar, 1989). This does not necessarily suggest that the oxidation of pyrrhotite to form ferrous hydroxides sites is a prerequisite for effective xanthate adsorption. Xanthate may chemisorb more effectively on non-oxidised pyrrhotite surfaces. The problem is that non-oxidised pyrrhotite mineral surfaces are unlikely to exist due to the susceptibility

of pyrrhotite to ʿ . . ʾnt oxidation. That is to say that physisorption is not the preferred mecha . . . chemisorption, but that physisorption is the only mechanism available due to the oxidised state of pyrrhotite.

There is probably a delicate balance between favourable ferrous hydroxide adsorption sites and passivating ferric hydroxide. The stability diagram for the Fe-H$_2$O system (Figure 2.1) indicates that ferrous hydroxide becomes more unstable at increasing pH's with ferric hydroxide predominating. Ferrous hydroxide is significantly more soluble than ferric hydroxide. At high pH and under relatively oxidising conditions ferric hydroxide passivation may become an inhibiting factor in the flotation of pyrrhotite. If E$_h$ conditions are such that ferrous hydroxides are favoured then the oxidation of the mineral may not be as inhibiting.

The effect of oxidising the mineral under acidic conditions prior to interaction with xanthate at pH 9 was investigated. Under acidic conditions the formation of a sulphur rich surface without iron hydroxides is favoured. It was anticipated that such a pre-oxidising treatment may favour the interaction of the mineral with xanthate. The current transients in Figure 4.39 did not indicate any signi. ant effect on the interaction. It is possible that the acidic conditioning may merely enhance the extent of hydrophobic species (or minimise hydrophilic species) through the formation of a sulphur rich surface, rather than enhance the collector reactions.

Both the voltammetry results and the mixed potential measurements (Figure 4.39 and Figure 4.41) appear to indicate that the anodic interaction with xanthate is enhanced after effective activation with Cu^{2+}. This is only after the mineral has been activated in acidic conditions. The interaction between xanthate and the mineral at pH 9, with Cu^{2+} ions present, was not directly investigated as previous work indicated that the mineral was not activated under alkaline conditions.

There may be a mechanism for copper interaction with the mineral at pH 9 which is different to acidic conditions and is not electrochemical. For instance copper hydroxide may precipitate on the surface of the mineral, which may or may not enhance xanthate interaction. The justification for this speculation is the indication from flotation tests

by previous researchers that the presence of copper enhances pyrrhotite flotation and that copper ions have been identified on concentrate particles (Leppinen, 1990, Senior *et al.*, 1995, Kelebek *et al.*, 1996, Stowe *et al.*, 1995, Yoon *et al.*, 1995). Additional work will however be required to investigate this.

4.3 Hydrophobicity tests

Flotation is dependent on the attachment of the mineral particles to bubbles. This occurs through rendering the mineral surface hydrophobic, in this study by means of reaction with SIBX, and subsequently contacting the mineral with air bubbles. Generally speaking an increase in the hydrophobic nature of particles results in improved bubble attachment, and correspondingly improved flotation recovery. A thorough review of the meaning of, and relation between, floatability and hydrophobicity is given by Laskowski (1986).

In the present study a qualitative measure of hydrophobicity was developed. A relative measure of the strength of bubble attachment was used to gauge the degree of hydrophobicity. This was correlated with different conditioning treatments. The technique allowed for measurements to be made directly on a rotating disk electrode without removing it from the solution.

4.3.1 Results

Table 4-3 shows the results of the experiments. After each type of conditioning treatment indicated SIBX was added with a concentration after addition of 10^{-2}M. Each type of conditioning treatment was repeated twice, with six separate bubble detachment measurements being made each time. In total twelve measurements were taken for each treatment.

Table 4-3: Hydrophobicity results for different conditioning treatments

Treatment no.	Description of conditioning stage	Average rotation speed at point of detachment/(RPM)	Standard Deviation
1	0.1M Na_2SO_4 @ pH 9 (no copper sulphate)	271	50
2	0.1M Na_2SO_4 @ pH 9; 10^{-4}M $CuSO_4$	410	55
3	0.05M $Na_2B_2O_7$ @ pH 9.3 (no copper sulphate)	no attachment	
4	0.05M $Na_2B_2O_7$ @pH 9.3; 10^{-4}M $CuSO_4$	289	81
5	0.1M Na_2SO_4 @ pH 4 (no copper sulphate)	604	47
6	0.1M Na_2SO_4 @ pH 4; 10^{-4}M $CuSO_4$	648	59

A single factor analysis of variance was conducted on the data sets. This indicated that the treatments gave at least one set of significantly different means. A *Bonferroni Multiple Comparison of Treatment Population Means* (Lapin, 1990) was conducted between different pairs of treatments. To a 95% overall confidence level it was found, in terms of strength of bubble attachment, that:

- with no copper activation the acidic conditioning treatment is significantly better than the alkaline conditioning treatment
- in alkaline sodium sulphate solutions copper activation significantly improves bubble attachment
- in acidic conditioning solutions copper activation does not significantly enhance to bubble attachment

- in buffered borate solutions no bubble attachment is achieved without copper activation

In the case of alkaline sodium sulphate solutions the addition of copper sulphate lowers the pH slightly. The pH then has to be readjusted to 9 before the collector is added. In a follow-up test the copper sulphate was added before the conditioning and the pH adjusted to 9. The electrode was then conditioned as per the previous tests. In this case the average speed for bubble detachment was 260 RPM (±34). This is very similar to the treatment at pH 9 without copper sulphate and would suggest that the enhancement caused by copper sulphate is more related to a slight acidic effect in unbuffered solutions than to activation. It should however be pointed out that in borate buffer solutions copper sulphate was significant in the sense that without it no attachment was achieved. Overall therefore the effect of copper sulphate appears unresolved.

During the conditioning stages the potential of the electrode was recorded. These potential measurements are given Figure 4.42.
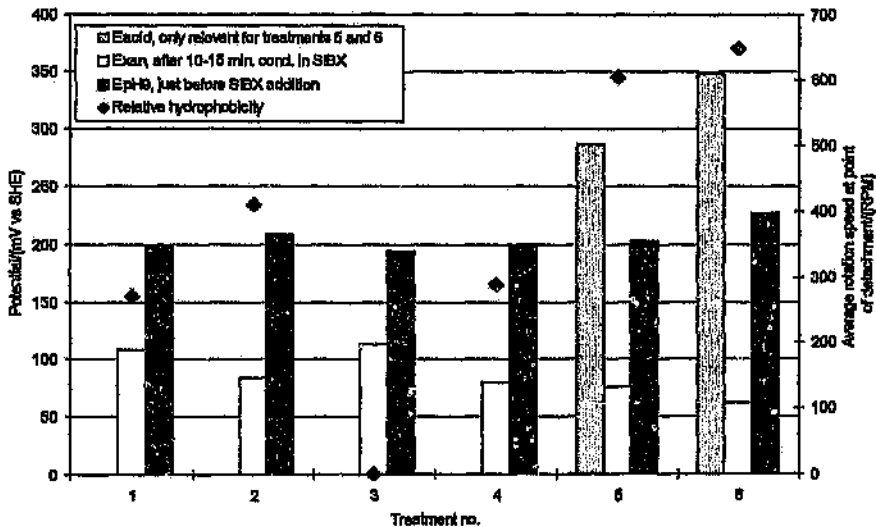

Figure 4.42: Potential measurements of pyrrhotite electrode during conditioning

Consistent trends between relative hydrophobicity and potential are difficult because of the variability of the potential measurements. There does however appear to be a significant inverse relationship between the relative hydrophobicity and the potential after xanthate addition and conditioning. In treatments 5 and 6 the potentials after xanthate addition are the lowest and they correspondingly have significantly stronger bubble attachment. Treatment 3 has the highest potential after xanthate addition and no bubble attachment was achieved.

4.3.2 Discussion

The results give convincing evidence that acidic conditioning significantly enhances the hydrophobicity of the mineral surface even after the pH has been adjusted back to pH 9. There are two possible explanations for this. Firstly the acidic conditioning may leach iron from the mineral lattice leaving a sulphur rich surface. Due to the acidic pH the iron does not precipitate as iron hydroxide. The presence of the sulphur and the lack of hydroxides contribute to the hydrophobicity. Secondly the formation of a sulphur rich surface and the lack of hydroxides may favour the formation of dixanthogen. This is supported by the observation that the mixed potential of the mineral electrode becomes more cathodic after the acidic conditioning than after standard conditioning. Most likely a combination of both of these factors explains the enhanced hydrophobicity.

The results also indicate that copper sulphate does aid the formation of a hydrophobic surface even when added at pH 9. This is contrary to what would be expected from the electrochemical work conducted on copper activation where no evidence for activation of the mineral by copper could be found. A possible explanation is that the activation occurs via a different non-electrochemical mechanism in alkaline environments compared to acidic environments. For instance copper hydroxide may precipitate on the surface rather than form a copper sulphide.

In terms of industrial flotation the results indicate that significant improvements in pyrrhotite recoveries may be possible if the mineral is conditioned in slightly acidic

pH's before reagent addition. It should be noted that it does not appear to be necessary to maintain the acidic pH after initial conditioning.

5. Conclusions and Recommendations

A comparison of the potential measurements made during batch flotation and plant circuit measurements with the stability diagram for pyrrhotite indicates that pyrrhotite is unstable under these potentials. The susceptibility of pyrrhotite for incipient oxidation is well known. The mineral is thus likely to be well oxidised before it comes into contact with flotation reagents. Voltammetric sweeps of pyrrhotite conditioned under mildly anodic conditions (i.e. at potentials that are expected in flotation environments) indicated the formation of surface products. These surface species are likely to include iron hydroxides and a sulphur rich sub-lattice. The potential lies above the equilibrium potential of the xanthate/dixanthogen couple at the concentrations of SIBX used. This would indicate that provided sufficient interaction between the mineral and xanthate occurs, the formation of dixanthogen is thermodynamically favourable.

The potential measurements taken during batch flotation indicated that passivation was occurring and that there was little electrochemical interaction between the oxidised mineral and the flotation reagents. This was gauged by the lack of any effect on the potential of the mineral when the reagents were added to the pulp. Results from this study and the literature favour a physisorption model for the initial adsorption of xanthate onto the surface of the mineral, as opposed to chemisorption.

Tests done in laboratory prepared clear solutions (no mineral particles present) indicated that even after extensive anodic conditioning, at potentials above that likely to occur in flotation environments, there was still an electrochemical interaction between the mineral and xanthate. The interaction was however diminished compared to freshly exposed mineral. Voltammetric and current transient techniques were able to detect anodic interaction between the mineral and xanthate. There may be differences between the extent of oxidation between flotation pulp environments and clear solutions even at similar pH and reagent concentrations. For instance the pulp solutions may contain

significant amounts of dissolved iron which enhance the precipitation of iron hydroxides on the pyrrhotite surface.

There is broad agreement that dixanthogen is the dominant surface product on pyrrhotite as opposed to metal xanthate. It is therefore reasonable to assign the enhanced anodic currents observed when pyrrhotite is swept anodic, in the presence of xanthate, to xanthate oxidation to dixanthogen, however it should be noted that no corresponding cathodic reaction for the reduction of dixanthogen could be detected.

The oxygen reduction kinetics of pyrrhotite are poor compared to other sulphide minerals. In flotation pulps xanthate may be consumed through anodic adsorption with other sulphide minerals which have more favourable oxygen reduction kinetics. This results in pyrrhotite being starved of xanthate interaction. The problem may be aggravated in flotation processes where copper sulphate is added and consumes xanthate by the formation of copper xanthate. This is especially the case when copper sulphate is added in stoichiometric excess to SIBX.

The role of copper ions in activating pyrrhotite remains unresolved. In this study no evidence for activation by an electrochemical interaction could be found at pH 9. In acidic pH's the mineral activated readily with a characteristic surface product that could be oxidised at specific potentials. The surface remained activated even in the absence of copper ions and in pH 9 solutions. The effect of activating the mineral in acidic conditions on oxygen reduction and xanthate interaction were investigated. It was thought that if oxygen reduction could explain pyrrhotites relatively poor flotation kinetics, and that if activation enhanced pyrrhotite flotation, then activation would be expected to effect the oxygen reduction kinetics. It was found however that within the potential range of interest the oxygen reduction kinetics were not significantly effected by prior activation. Activation under acidic conditions did however enhance the anodic xanthate interaction.

Flotation research has indicated that copper ions do appear to activate pyrrhotite under alkaline conditions and that this results in enhanced pyrrhotite recoveries. The hydrophobicity results conducted in this study support the case for some form of activation occurring in alkaline conditions. A possible explanation for this is that copper activation occurs via a different mechanism at pH 9. This may possibly involve the precipitation of copper hydroxides on the surface of pyrrhotite which may then favour xanthate adsorption. This should however be confirmed experimentally by studying the xanthate adsorption wave after interaction with copper ions at pH 9.

There has been considerable interest in conditioning sulphide mineral particles in acidic conditions. The rationale behind this is that during the oxidation hydroxide films form on the mineral particles thus inhibiting interaction with flotation reagents, but that in acidic conditions the hydroxides would be soluble. Thus the particles would be chemical cleaned in acidic conditions prior to reagent addition. Of considerable interest is whether the pulp pH can be allowed to go back to alkaline pH's after the acidic conditioning. This is particularly important for ores that have a natural buffering capacity where keeping the pH acidic would result in significant acid consumption.

Voltammetry results from this study suggest that acidic conditioning does minimise the surface coverage of hydroxides and promote a sulphur rich surface. It appears that these effects remain even after the pH returns to ≈ 9. This is supported by the hydrophobicity results where acidic conditioning significantly enhanced the bubble attachment strength. The mechanism of this enhancement may be two fold: firstly the formation of a sulphur rich surface with minimal hydroxide coverage will naturally contribute to the hydrophobicity of the mineral, and secondly the minimal hydroxide coverage may aid the interaction of xanthate to form dixanthogen at the mineral surface. The first consideration is expected to apply and potential measurements taken during the hydrophobicity tests support the second factor.

The passivation of pyrrhotite appears to be a significant problem in industrial flotation operations. The effects may be enhanced when the dissolved iron content in the pulps is high. This could be combated through more careful selection of milling media to avoid the formation of abraded iron. The problem could be combated by keeping the potential relatively low; firstly to minimise pyrrhotite oxidation, and secondly to favour ferrous hydroxide over ferric hydroxide formation. The pulp potential during the conditioning stage could be controlled by gas composition using nitrogen. Alternatively indications are that a short acidic conditioning stage may significantly enhance the hydrophobicity of the mineral and thus its flotation, particularly if copper sulphate were added during the acidic conditioning stage. The addition of reagents as soon after the milling operation as possible should also combat the problems associated with excessive oxidation of the mineral. The role of copper sulphate needs more attention before a definite conclusion can be reached regarding its use.

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