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PENTLANDITE / PYRRHOTITE INTERACTIONS AND XANTHATE ADSORPTION

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy

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This thesis is dedicated,

To my loving wife, Ebru, for her understanding, support, and encouragement.

To my family, for their emotional support.

At last but certainly not least to my country, The Republic of Turkey.

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ABSTRACT

Xanthate interaction with pentlandite and pyrrhotite has been investigated in the case of single and mixed minerals in the presence of Ni ions and depressants such as meta-bisulfite (MBS), diethylenetriamine (DETA) and MBS plus DETA at two pHs controlled by lime and soda ash. It was found that dixanthogen was the main product and the surface concentration was consistently higher on pentlandite than on pyrrhotite. Ni ions enhanced the dixanthogen adsorption on both minerals in the case of single minerals. Mixed mineral experiments (i.e. pentlandite and pyrrhotite together) showed that dixanthogen formation on penlandite was promoted while on pyrrhotite it was suppressed, interpreted as due to a galvanic interaction between minerals. The ratio of dixanthogen adsorption on pentlandite to pyrrhotite increased to ca 4:1 compared to <2:1 for single minerals and this ratio was maintained in the presence of depressants; overall however, depressants reduced the dixanthogen adsorption on both minerals in the case of single and mixed minerals. For pentlandite in the mixed mineral case, this reduction returned dixanthogen adsorption to values similar to those on the single mineral in the absence of depressants. For pyrrhotite, dixanthogen was reduced below detectable limits. In terms of flotation, the mixture of minerals enhances dixanthogen formation on pentlandite at the expense of pyrrhotite. This is preserved on addition of depressants which serve to reduce the absolute dixanthogen adsorption on pyrrhotite perhaps below a critical level for flotation.

Xanthate adsorption on both minerals is reduced when the pH is adjusted by soda ash instead of lime. The general effects of depressants otherwise were similar regardless of pH modifier.

Open circuit potential measurements showed that pentlandite has a higher rest potential than pyrrhotite. In the presence of xanthate, however, the order was reversed. A mixed potential model was used to explain the effect of mineral interaction on dixanthogen formation. At the potential of the mixed mineral system, the anodic reaction (xanthate oxidation to dixanthogen) occurred preferentially on the pentlandite and the cathodic reaction (reduction of oxygen to hydroxyl ion) occurred on the pyrrhotite.

A new design of spectroelectrochemical external reflectance cell has been developed

for *in situ* analysis under controlled electrochemical conditions. Orientation and stability of xanthate adsorption products on a copper electrode was studied as a model system. Cuprous xanthate was found to be the major product over the potential range -0.5 to -0.1 V (SCE). Further increase in potential to 0.1 V resulted in the formation of dixanthogen in addition to cuprous xanthate. It was also found that the characteristic dixanthogen bands disappeared when the potential was brought back and held at -1.0 V while the cuprous xanthate bands were enhanced. When polarized radiation was used, the appearance of the characteristic peaks of cuprous xanthate changed while that of dixanthogen remained the same, suggesting preferential orientation of the cuprous xanthate molecules but not of the dixanthogen. The probable orientation of cuprous xanthate is given.

In the stability study, the dixanthogen disappeared while the copper xanthate peaks intensified. The rate of dixanthogen disappearance was greater in the case of *ex situ* compared to *in situ* sampling conditions.

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CHAPTER 1

INTRODUCTION

1.1. FLOTATION OF Cu-Ni ORES

In Cu-Ni sulphide ores, the minerals of major economic interest are chalcopyrite $(CuFeS_2)$ and pentlandite ((Ni,Fe)S). These minerals are always associated with pyrrhotite (Fe_7S_8) which is the major gangue sulphide mineral along with minor amounts of other sulphide minerals (e.g. pyrite, marcacite, galena) and precious metal minerals. Rejection of pyrrhotite is essential because it is a significant contributor to SO₂ emissions in the smelting of the concentrates. Pyrrhotite occurs in two different crystallographic forms, monoclinic and hexagonal. Monoclinic pyrrhotite, representing about 70 % of the mineral in the ore, is rejected by magnetic separation and flotation. The hexagonal pyrrhotite is weakly (para-) magnetic and is rejected by flotation.

The two major processors of Cu-Ni ores in Canada are Inco Ltd and Falconbridge Ltd.

In the case of Inco's Sudbury operations, (Figure 1.1), plant feed first goes to rougher magnetic separation. The non magnetic fraction reports to main flotation, concentrates from which go to the bulk concentrate. Tailings from main flotation go either to final tailings or to pyrrhotite rejection. Concentrate from the latter joins the bulk concentrate and tailings report to the pyrrhotite concentrate. The magnetic fraction of rougher magnetic separation is further ground before reporting to primary Cu-Ni flotation. Concentrates from primary Cu-Ni flotation go to another grinding stage and report to secondary Cu-Ni separation. Concentrates from secondary Cu-Ni flotation go to the bulk concentrate and tailings are added to the magnetic fraction of rougher magnetic separation. Tailings from primary Cu-Ni separation report to cleaner magnetic separation. The non-magnetic fraction from here is added to the pyrrhotite rejection flotation feed, while the magnetic fraction reports to the pyrrhotite concentrate.

In the case of Falconbridge (Figure 1.2), after crushing, grinding and classification stages, the ore is subjected to primary and secondary rougher flotation. Primary rougher concentrate goes to Cu-Ni separation which produces a Cu and Cu-Ni concentrate. Primary rougher tailings goes to secondary roughing to produce Cu-Ni concentrate and a tailings



Figure 1.1. INCO Clarabelle Mill flowsheet.

CHAPTER 1. INTRODUCTION

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Figure 1.2. Falconbridge Strathcona Mill nickel ore circuit flowsheet.

which goes to scavenger flotation. Scavenger concentrate goes to a magnetic separation stage and tailings goes to the final tails. The non-magnetic fraction from magnetic separation reports to non-magnetic flotation, while the magnetic fraction is reground and sent to the magnetics flotation circuit. Concentrate from non-magnetic flotation goes to Cu-Ni concentrate and the tailing joins final tails. Concentrate from magnetic flotation goes to the Cu-Ni concentrate and tailings to the pyrrhotite tails.

In both operations, maximum pyrrhotite rejection is an asset. Therefore, both companies have focussed on this area. Approaches have included raising the pH of flotation to partially depress pyrrhotite [1], introducing separate pyrrhotite rejection circuits, which exploit the fact that pyrrhotite floats poorly in alkaline media [2], and using magnetic separation to remove pyrrhotite from feed or concentrate streams [3]. Although these measures have led to significant improvements, for example pyrrhotite rejection at the Thompson concentrator (Inco Ltd.) has increased from 5 to 60 percent [4], none is entirely satisfactory as high levels of pyrrhotite rejection are invariably accompanied by loss of pentlandite.

This problem has prompted research into more efficient ways of separating pentlandite and pyrrhotite. Several procedures have been devised, such as the use of cyanide as depressant [5], nitrogen as flotation gas [6] and pyrrhotite reverse flotation [7, 8]. All the options, however, have deficiencies, either they failed to reduce pentlandite losses sufficiently or were too complex or expensive to implement. Thus, despite some improvements and much attention, the fact remains that a cost effective procedure that gives high pentlandite recoveries and sufficiently selective rejection of pyrrhotite has not yet emerged. Therefore, this remains an ongoing area of research.

Recent studies have indicated the presence of heavy metal ions (Cu, Ni) on pyrrhotite mineral surfaces [9, 10]. These metal ions, resulting from superficial oxidation of sulphide minerals, can cause an unintentional activation. To counter this possibility chelating agents, which readily form complexes with heavy metal ions, have been tested as pyrrhotite depressants. Canada's major Ni producers have concentrated on diethylenetriamine (DETA).

DETA is known to be part of some reagent formulations proposed for pyrrhotite

depression [11, 12]. Recent developments have seen DETA used directly [13, 14], greatly improving pyrrhotite rejection at Inco's (now closed) Copper Cliff Mill [15, 16], while laboratory and pilot scale tests at Falconbridge found that DETA in combination with SO₂ and metabisulphite (MBS) yielded efficient and consistent depression [17, 18].

Flotation at moderate alkalinity is normal practice. The relative merits of lime vs soda ash as pH modifiers are currently of considerable industrial interest. For example at Inco's Thomson Mill, soda ash is used in the primary separation stages because higher flotation rates are obtained compared to using lime [4].

Studies of flotation systems require surface analysis techniques. This has led to the development of spectroelectrochemistry, a technique for obtaining IR spectra under controlled electrochemical potential. With this technique the composition and structure of the topmost adsorbed hydrophobic layers on the mineral surface can be investigated at the molecular level. It is also possible to study the stability of surface products under controlled conditions. One example of this need is the deterioration of performance in a cleaning stage that has been attributed to "disappearance of the collector" [19].

1.2. STATEMENT OF PROBLEM AND OBJECTIVES

From this review of the flotation of Cu-Ni ores, it can be seen that unintentional activation of pyrrhotite by heavy metal ions is a possible cause of loss of selectivity. Therefore, the effect of heavy metal ions needs to be established and possible counter measures investigated. Because these metal ions come from the inevitable contact with other sulphide minerals it is also necessary to conduct experiments on mineral mixtures.

The objectives of this thesis are,

- 1. to determine the effect of mineral contact (mixed minerals) on xanthate adsorption on pentlandite and pyrrhotite.
- 2. to determine effect of Ni ions on xanthate adsorption.
- 3. to determine effect of DETA, MBS and DETA plus MBS on xanthate adsorption.
- 4. to determine effect of soda ash as an alternative to lime for pH adjustment.

5. to establish an *in situ* spectroelectrochemical technique to permit investigation of the adsorption and orientation of collector under controlled potential conditions.

1.3. STRUCTURE OF THE THESIS

The thesis consists of seven chapters.

- Chapter 1. Introduction of the problems associated with the Cu-Ni ore separation and objective and structure of the thesis.
- **Chapter 2.** Discussion on oxidation of sulphide minerals, effect of metal ions on sulphide minerals, galvanic interaction between sulphide minerals and finally xanthate interaction mechanisms with sulphide minerals.
- Chapter 3. Review of surface analysis techniques including: Infrared spectroscopy, electrochemistry and combinations of both as so-called spectroelectrochemistry with application to sulphide mineral flotation.
- Chapter 4. Xanthate adsorption and effect of different reagents on xanthate adsorption in the case of single mineral system is discussed.
- Chapter 5. Xanthate adsorption and effect of different reagents on xanthate adsorption in the case of mixed mineral system is discussed.
- Chapter 6. Xanthate adsorption, orientation and stability on a model copper metal electrode using spectroelectrochemical technique is discussed.
- Chapter 7. Overall conclusions and recommendations for future work.

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CHAPTER 2

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THEORY

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2.1. OXIDATION OF SULPHIDE MINERALS

The flotation of most sulphide minerals varies with oxidation of the surface. In acid solution, the initial oxidation of sulphides corresponds to a reaction of the type [1]

$$M_{\mathcal{S}} - zM^{n^{-}} + S + zne^{-}$$
(2.1)

while in neutral or alkaline solutions it is

$$MS + znH_{2}O = zM(OH)_{n} + S + znH^{-} + zne^{-}$$
(2.2)

Further oxidation may lead to the production of oxy-sulphur species

$$xM_{z}S + (zxn+y)7H_{2}O = zxM(OH)_{n} + S_{x}O_{y}^{2} + (2y+zxn)H^{2} + (2y+zxn-2)e^{-1}$$
 (2.3)

Some form of reaction (2.3) is generally favoured thermodynamically but for some sulphides, it does not proceed rapidly, even in alkaline solution, beyond the production of elemental sulphur (i.e. reaction (2.2)). For other sulphides, the production of thiosulphate or sulphate by reaction (2.3) does proceed at reasonable rates but usually only at overpotentials of varying magnitudes [2].

The type of the oxidation products can determine the subsequent flotation behaviour. If sulphur, or a sulphur-like entity is present (reaction (2.2)), this may lead to floatability in the absence of conventional collectors (self-induced or collectorless floatability). Thiosulphate and sulphate (reaction (2.3)), on the other hand, are hydrophilic species, i.e. they tend to depress flotation. In some cases, however, these species can exchange with collector ions and in that sense can be considered to promote flotation. Reaction (2.2) differs from (2.3) in the consequences for mineral-collector interaction. If the oxidation products remain in the vicinity of the mineral-solution boundary, which is likely the case if they are insoluble, the reaction may reverse under a reducing environment [3, 4]. If the oxidation products are at least partly soluble, as some of the oxy-sulphur species in reaction (2.3), then in the agitated flotation system these will tend to leave the mineral-solution boundary and not be available for reaction if the system is reduced. Any subsequent reduction is then a different reaction, for example

$$M(OH)_{n} + nH^{*} + ne - M^{n^{*}} + nH_{2}O$$
(2.4)

leading to the appearance of free metal on the mineral surface [5] which too modifies any subsequent interaction with collector.

If the metal hydroxide species is formed in situ, it may remain at the boundary as assumed in writing reaction (2.4); if on the other hand, the hydroxide is formed via a soluble intermediate, it would tend to precipitate from solution and may appear on a variety of mineral surfaces as opposed to just the "parent" mineral. The potential significance of metal hydroxide phases in sulphide flotation has made this an on-going area of research.

2.2. THE EFFECT OF METAL IONS

2.2.1. General

Activation and depression effects of metal ions in sulphide mineral flotation have long been suspected. For example, the role of iron oxyhydroxides was discussed by Rose in 1942 [6].

The activation effect of metal ions has been most extensively studied in the case of sphalerite (Sp) because this process is central to Sp flotation with xanthate [7-19]. Sphalerite is activated by copper, lead and iron ions. With Cu ions this is through exchange between $Zn^{2+}_{tantice}$ and Cu^{2+} ions from solution or adsorbed $Cu(OH)_2$; for Pb and Fe, adsorption of hydrolyzed species is suspected. Besides the controlled activation of Sp practiced with Cu ions, unintentional activation of Sp is possible due to both the varying composition of Sp and

the presence of contaminant metal ions [20-24].

Activation of pyrite and pyrrhotite by copper ions is also practised and therefore, has been the subject of investigation [25, 26]. The amount of xanthate adsorbed on activated pyrite was relatively low at pH 4 to 5 but increased steeply up to 8 and then became practically zero at pH 12. In a recent study, lead activation of pyrite has been investigated [27] and it was found that at pH around 10, xanthate uptake by pyrite was promoted in the presence of lead ions at concentrations as low as 1 ppm.

A common non-sulphide gangue (NSG) in sulphide mineral systems is quartz which is not floated by xanthate at any pH. However, in the presence of some metal ions, quartz can be activated and floated with xanthates over a certain pH range [28, 29].

A summary of the principal metal ion/mineral interaction studies is given in Table 1.What follows is a detailed examination of those studies relevant to processing Ni sulphide minerals.

Effect	Mineral	Metal ion/pH	Derived from	Reference
Activation	Sphalerite	Cu(II)/5-10	Solution	[7-14]
Activation	Sphalerite	Pb(II)/5-9	Solution	[12-17]
Activation	Sphalerite	Fe(II)/8-11	Solution	[18, 19]
Activation	Pyrite	Cu(II)/5-8	Solution	[25, 26]
Activation	Pyrite	Pb(II)/9.2/10.5	Solution	[27]
Activation	Quartz	Pb(II)/8-11	Solution	[28, 29]
Activation	Pyrrhotite	Cu(II)/3-9	Solution	[26, 35, 36]
Activation	Pyrrhotite	Ni(II)/3-6	Solution	[36]
Depression	Chalcopyrite	Pb(II)/9	Solution	[38]
Depression	Chalcopyrite	Zn(II)/9	Solution	[38]

 Table 2.1. Summary of metal ions effect

2.2.2. Cu-Ni ore minerals

(i) Pyrrhotite (Po)

Pyrrhotite often occurs as a gangue mineral in base metal ores. In the case of Sudbury area Cu-Ni ores, rejection of Po is the key processing step. Maximum Po rejection is sought to obtain high grade Cu-Ni concentrates to control the subsequent emission of SO_2 from the smelter [30]. Pyrrhotite can be activated by copper ions which was the subject of an early study [25]. The mechanism was considered to be different from that of Sp activation. Rather than replacement of lattice ions it was attributed to adsorption of copper as a hydrolysis product. A later study however, did suggest that activation is via exchange lattice Fe with copper [31]. Thermodynamic considerations indicated that the activation reaction for Po should be analogous to that of Sp [32]:

$$FeS + Cu^{2^{-}} \neq CuS + Fe^{2^{+}}$$
 (2.5)

 $K = [Fe^{2-}]/[Cu^{2-}] = 5x10^{17}$

Comparison of the equilibrium constants for the activation reactions of Sp and Po showed that the thermodynamic driving force for Po activation by copper ions is actually greater than that for Sp. It was also shown that copper abstraction reached no limit on Po in the absence of oxygen. However, in the presence of oxygen in solution, the copper abstraction by Po was negligible due to the formation of a protective ferric hydroxide film on the Po surface. Electrochemical studies on activation of Po with copper ions [33] suggested that activation could be described by the following overall reaction.

$$Fe_9S_{10} + 9Cu^{2*} \neq 9Fe^{2*} + 9CuS + S^0$$
 (2.6)

In another study, the activation effect of copper, lead and zinc on a synthetic iron(II) sulphide and natural Po was investigated [34] and it was shown that Po could adsorb large quantities of these heavy metals. A strongly oxidizing environment, however, not only

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inhibited the adsorption but also led to the release of a large quantity of iron into the aqueous solution. From a subsequent, systematic study [35], the following observations were made: 1. The liberation of iron from a Po surface was reduced significantly in the presence of copper

ions. This was attributed to a coating of copper sulphide.

2. The apparent overall reaction for copper ion activation of Po in an acidic medium is an ionexchange reaction between the lattice iron and copper ions.

3. Solution pH has a crucial effect on the adsorption of copper ions on Po. The adsorption rate of copper ions on Po increased with an increase in solution pH.

4. Oxygen reduced the adsorption of copper ions on Po. In acidic to weakly acidic solutions, prolonged reaction with oxygen lead to the desorption of copper ions from Po. The effect of oxygen on copper ion adsorption decreased with an increase in solution pH.

5. Oxygen combined with a high solution pH retarded but did not prevent the adsorption of copper ions on Po, i.e. a ferric hydroxide oxidation product on Po inhibited to some extent the adsorption of copper.

In the study of Po activation by copper ions by Leppinen [26], it was found that the main product on the Po surface was Cu(I) xanthate. A study of copper and nickel ion activation of Po found that Fe dissolution increased significantly in the presence of both ions. suggesting an exchange of iron from the Po with metal ions in solution [36].

(ii) Pentlandite (Pn)

Pentlandite is not intentionally activated by metal ion additions, but it does react with them. For example, Pn, conditioned with the supernatant from a chalcopyrite suspension, showed significant amounts of copper species present [37].

(iii) Chalcopyrite (Cp)

The depressant effect of metal hydroxides (lead and zinc) on Cp flotation has been studied [38]. It was established that metal hydroxide precipitates on the surface over-rode self-induced floatability and modified collector-induced floatability. That was suggested as the reason Cp does not readily float from complex ores in the absence of collector as predicted from single mineral studies (exceptions to this are known, however [39]).

2.3. GALVANIC INTERACTION

2.3.1. General

Sulphide minerals are semiconductors and assume a particular rest potential in an aqueous medium. The rest potential plays an important role in galvanic interactions. When two sulphide minerals are in contact in an aqueous medium, the mineral with the higher rest potential acts as the cathode, while the mineral with the lower rest potential becomes the anode. At equilibrium the two minerals adopt the same potential called a mixed potential which is a value somewhere between the rest potential of the two minerals. The mixed potential refers to the average steady-state potential measured when two sulphide minerals are short-circuited in an electrolyte. The general electrode reactions, or charge-transfer reactions for this two mineral system [40] are:

Anodic reaction:

$$MS + H_{2}O \neq M(H_{2}O)^{2^{-}} + S^{0} + 2e^{-}$$
(2.7)

Cathodic reaction (reduction of oxygen): at high pH solution:

$$1/2O_2 + H_2O + 2e^- \neq 2OH^-$$
 (2.8)

at low pH solution:

$$1/2O_2 + 2H^+ + 2e^- \neq H_2O$$
 (2.9)

The overall reaction is

$$MS + 1/2O_2 + H_2O = M^{2^-} + 2OH^- + S^0$$
 (2.10)

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For different sulphide minerals the activity for oxygen reduction varies considerably due to their electrocatalytic activity. The order of rest potential of sulphide minerals for oxygen reduction at pH 9.06 was given [41] as,

pyrite > pentlandite > chalcocite > chalcopyrite > covellite >

bornite > arsenopyrite > pyrrhotite > galena > sphalerite > steel grinding media

Of these minerals therefore, pyrite gives the highest rate of oxygen reduction, and sphalerite the lowest. Thus, when pyrite is present with another sulphide, oxygen reduction occurs preferentially on pyrite and the oxidation of the other sulphide is accelerated. That is, pyrite acts as the cathode and the other sulphide becomes the anode (pyrite is also referred to in this context as the more "noble" sulphide). As a result of this enhanced oxidation, more metal ions are released from anodic minerals than would be the case in the absence of galvanic interaction and correspondingly fewer metal ions are released from the cathodic mineral. This is known as *galvanic coupling* or *galvanic interaction*.

An example of galvanic interaction is illustrated in Figure 2.1 for pyrite and sphalerite in water.



Figure 2.1. Mechanism of galvanic interaction between minerals.
The rest potential of pyrite is higher than that of sphalerite, and thus sphalerite is oxidized with Zn^{2-} and S^{0} (in this example) being produced, and oxygen is reduced on pyrite to form OH⁻ ions. The overall electron transfer process is from sphalerite to pyrite, and then to oxygen which is the usual final electron acceptor. If there are no secondary reactions occurring on the pyrite surface, OH⁻ will transfer into solution.

Galvanic interactions have been suspected of playing an important role in sulphide flotation. Several papers on sulphide mineral systems give direct evidence of this [42-51]. One important conclusion is that fundamental studies on single minerals in the sulphide system can be misleading due to the fact that galvanic interactions occur during particle/particle contact in an agitated, mixed mineral system. This may radically alter the flotation response of the minerals.

To illustrate, the flotation behaviour of sphalerite has been investigated in the presence of chalcopyrite, galena and grinding media [42-44]. The order of rest potentials are chalcopyrite > galena > sphalerite > grinding media. The following conclusions were drawn: 1. Galvanic interactions between chalcopyrite and sphalerite significantly reduced the floatability of chalcopyrite, the mineral with the higher rest potential. In contrast the effect on floatability of the sphalerite was not very significant (it was lowered slightly). However after prolonged interaction of sphalerite with chalcopyrite and galena, sphalerite activation by dissolved copper and lead ions occurred.

2. The presence of a steel grinding media (mild steel has a rest potential below even galena) significantly lowered the flotation response of all the minerals.

3. The floatability of a sulphide mineral was found to be most affected after mineral-steel grinding media contact. If, in addition, there was a relatively noble mineral present during the mineral-steel grinding media contact, the effect on floatability was found to be reduced.

2.3.2. Cu-Ni ore minerals

(I) Pyrrhotite (Po)

A number of investigators have studied the flotation behaviour of Po in the presence

of grinding media and other sulphide minerals [45-49].

Po-grinding media; It was reported that contacting Po with mild steel had a detrimental effect on its flotation [45] because of an iron hydroxide (originating from the media) coating, which prevented xanthate from adsorbing on Po.

Po-pyrite (Py); When Po was contacted only with Py. Po floatability was improved, because iron hydroxide formation on Po was retarded due to the shift in the oxygen reduction reaction from Po to Py [46].

Po-Py-grinding media; When Py was introduced to a Po/grinding media combination, the flotation response of Po increased again due to the fact that Py hosted oxygen reduction [47]. *Po-chalcopyrite (Cp)*; When Po was contacted with Cp. Cp acted as the cathode, while Po acted as the anode. The presence of Cp therefore accelerated the oxidation reaction on Po. i.e. the adsorption of collector, and caused increased floatability of Po. On the other hand, a lower floatability of Cp was obtained probably due to the presence of OH⁻ ions on its surface resulting from oxygen reduction. It was confirmed by X-ray photoelectron spectroscopy that the increased floatability of Po was not due to activation by copper ions but instead was due to the absence of hydroxide species [48].

Po-nickel arsenide; The effect of galvanic contact between nickel arsenide and Po on the dissolution of nickel and arsenic has been investigated [49]. Nickel arsenide, having a lower rest potential than Po, behaved as an anode in this system; the concentrations of nickel and arsenic were seen to be higher in the presence of Po than in the absence of Po. The floatability of Po was decreased due to formation of iron hydroxide on its surface.

(ii) Chalcocite (Ch)

Ch-Py: Flotation response of Ch-Py mixtures was studied under controlled electrochemical potential conditions [51]. It was found that the potential-flotation recovery behavior for minerals from mixed-mineral beds was different from that observed for beds of single-minerals. The differences were attributed to galvanic interactions. In this system, Cu(II) ions, produced by anodic dissolution of Ch in the mineral mix, activated the Py, therefore it floated below the reversible xanthate-dixanthogen potential. However, flotation of Ch after contact with Py appeared to be unaffected.

From the examples above, it is evident that galvanic interaction can play an important role in the flotation of sulphide minerals. Galvanic interaction alters the surface properties and reactivity of sulphide minerals and as a result alters the selectivity of flotation.

2.4. XANTHATE ADSORPTION ON SULPHIDE MINERALS

A number of theories have been proposed to describe the xanthate adsorption mechanism on sulphide minerals and include:

The chemical theory The ion exchange theory Neutral molecule adsorption theory Electrochemical theory

2.4.1. The chemical theory

Taggart and co-workers [52] developed this theory which is based on the mineral or the oxidation products of the mineral on the surface being more soluble than the product formed by the interaction between the mineral surface and the collector.

2.4.2. The ion exchange theory

This theory was initially suggested by Wark [53] and discussed by Sutherland and Wark [54]. The basis was the observation that sulphides are generally floated with less than a monolayer coverage of collector, even 1% being sufficient. In contrast to Taggart's theory. Sutherland and Wark stated that there is no need for a direct relationship with the solubility product when the collector is present as a monolayer or less. They believed that the interaction of collector (typically thiols) with sulphides should be considered as adsorption. In support of this, it was demonstrated that competitive adsorption between xanthate and hydroxide ions could explain the Barsky relationship between the upper pH limit of flotation

and collector concentration that had originally been derived empirically. Gaudin [55] agreed with this model.

2.4.3. Neutral molecule adsorption theory

This theory was proposed by Cook and co-workers [56, 57]. They pointed out that adsorption of collector ions would lead to the surface of a mineral being highly charged which is not the expected condition for hydrophobicity. In order to overcome this difficulty, they proposed that the undissociated acid form of the collector is the species adsorbed rather than the ion. The possibility of the acid being the adsorbate was noted earlier by Wark and Cox [58] but it was considered by Sutherland and Wark [54] that co-adsorption of ions of opposite sign better explained the apparent lack of surface charging.

2.4.4. Electrochemical theory

Salamy and Nixon [59] identified another way in which a neutral surface could be generated if the solid phase is an electronic conductor. The electrons, holding the excess negative charge, could be removed by a reaction with oxygen. This concept was supported by investigations that showed the presence of oxygen to be necessary for sulphide minerals to float with xanthate collectors [60-71].

In this model, the collector and oxygen react with the mineral surface by separate electrochemical reactions which proceed simultaneously. An anodic oxidation reaction involving the collector occurs at one site, the electron being returned to the solution phase by the cathodic reduction of oxygen at another site.

$$O_2 + 2H_2O + 4e \neq 4OH^- \tag{2.11}$$

A schematic representation of the electrochemical mechanism is shown in Figure 2.2a.



Figure 2.2. Schematic representation of the mixed potential mechanism for interaction of xanthate with sulphide minerals in which the anodic process is (a) Chemisorption, (b) reaction to form a metal collector compound, (c&d) reaction occurring in two stages: (c) oxidation of the mineral and (d) ion exchange with the collector, (e) formation of dixanthogen [72]. It was recognized that the existing theories of flotation could be reconciled by the electrochemical approach. Thus, Wark's adsorption model would correspond to the anodic process,

$$X^- \neq X_{ads} + e^- \tag{2.12}$$

and Taggart's chemical mechanism would involve an anodic process of the type.

$$MS + 2X^{-} + 4H_{2}O = MX_{2} + SO^{2-} + 8H^{-} + 8e^{-}$$
 (2.13)

This reaction could proceed either in a single stage (Figure 2.2b) or via separate processes occurring at different times (Figures 2.2c-d). For example, oxidation of the sulphide surface to sulphate could occur on exposure of the mineral to air and this species could exchange with a sulphur containing anion when collector is added.

Another anodic process is oxidation of the collector, e.g. xanthate, to dixanthogen,

$$2X^{-} \neq X_{2} + 2e^{-}$$
 (2.14)

The dixanthogen could be produced on an unaltered surface as depicted in Figure 2.2e, or on a surface which has chemisorbed the collector or reacted to form a metal collector compound. Dixanthogen being a neutral species also addresses the concerns of Nixon and co-workers.

Anodic reactions such as reactions (2.12-14) can take place at the surface of an isolated mineral particle if a potential exists at which both this process and the cathodic reduction of oxygen proceed at finite rates. Such a potential is termed a mixed potential. It should be pointed out that the reactions need not be sustained continuously at a finite rate. Transitory currents are expected for adsorption processes which are generally complete at the monolayer level.

The electrochemical model introduced the significance of the electrochemical potential in flotation systems. The potential determines the reactions that take place at the mineral surface and the rates of these reactions. Early investigations to address the importance of the potential across the mineral solution interface, had emphasized its effect on electro-capillarity phenomena associated with the electrical double layer and ion adsorption [73].

Poling [74] pointed out that the xanthate ion appeared to be specifically adsorbed in the double layer at sulphide surfaces since the zeta-potentials of sulphide minerals displayed a negative shift when xanthate ions were present in solution. In the light of this evidence, he questioned the applicability of the electrochemical model which was developed to explain how neutral species were adsorbed. However, xanthate ions can be present in the double layer without contributing to hydrophobicity. This is the situation observed for platinum [75]. The strong attraction for water of charged polar head groups of amphiphilic molecules is known to influence the neighbouring CH₂ groups so that their contribution to the hydrophobic effect is substantially diminished [76]. Thus only when the charge on a short-chain xanthate is removed - by chemisorption, by bonding to a surface metal atom, or by dimerization to dixanthogen - will the hydrophobic character of this hydrocarbon chain dominate. This viewpoint is supported by the fact that alkali xanthates are readily soluble, not an attribute associated with hydrophobicity, while dixanthogen, is only slightly soluble in aqueous systems and behaves as a typical hydrophobic molecule [77].

2.5. PYRRHOTITE DEPRESSION

Pyrrhotite occurs as a gangue mineral in many base metal ore deposits. In the case of Ni-bearing ores, it is usually rejected by a combination of magnetic separation and flotation. Maximum pyrrhotite rejection is sought to obtain high grade Ni concentrates and to minimize subsequent SO₂ emissions from the smelter [30].

Mineral processors have used a number of strategies to reject pyrrhotite. They have raised the pH of flotation to partially depress pyrrhotite [78], introduced separate pyrrhotite rejection circuits, which exploit the fact that pyrrhotite floats poorly in alkaline media [79], or used magnetic separation to remove pyrrhotite from feed or concentrate streams [80]. Although these measures have led to significant improvements, for example pyrrhotite rejection at Thompson concentrator (Inco Ltd.) has increased from 5 to 60 percent [30], none is entirely satisfactory as high levels of pyrrhotite rejection are invariably accompanied by loss of pentlandite.

This problem has promoted a search for more efficient ways of separating pentlandite and pyrrhotite. Several new procedures have been devised, such as the use of cyanide as depressant [81], nitrogen as carrier gas [82] and pyrrhotite reverse flotation [83, 84]. All the options, however, have deficiencies, either they failed to reduce pentlandite losses sufficiently or they were too complex or expensive to implement. Thus despite some improvements and much research, the fact remains that there is no cost effective procedure that gives high pentlandite recoveries and sufficiently selective rejection of pyrrhotite emerged yet. Therefore, this is an ongoing area of research.

The search for selective pyrrhotite depressants has led to the use of chelating agents such as polyamines. The use of polyamines is quite common in hydrometallurgy. Diethylenetriamine (DETA) and other polyamines were highly effective leaching agents for lead sulphate formed in galena acid pressure oxidation [85]. The same type of polyamines were used to extract copper, chromium, cobalt and nickel from their oxide ores [86, 87], and recently it was shown that DETA selectively extracted base metals from waste hydroxide sludges [88]. In flotation research, application of polyamines is illustrated by the use of propylenediamine and ethylenediamine in the study of deactivation of Cu activated sphalerite [89], and the use of ethylenediaminetetraacetate (EDTA) to extract surface metal ions [90-93] and subsequently promote collectorless flotation [94-96] or depression of pyrite in flotation with xanthate [97].

Polyamines, due to their chelating properties, offer a means of controlling contaminant metal ions. However, they have not been used in mineral processing practice till recently, due to a combination of difficulty in controlling selectivity, cost and high consumption. Depression, in principle, could be achieved by adsorbing chelating agents with ligands selective for surface metal sites and hydrocarbon chains sufficiently short so as not to be hydrophobic. Candidate polyamines in this regard are ethylenediamine, dietylenetriamine and triethylenetetramine. Ethylenediamine has been studied along with ethylenediamino tetraacetic

acid and ammonia in an electrochemical study of sphalerite activation and deactivation by copper ions [98]. This study indicated that under certain conditions sphalerite flotation can be suppressed by these reagents.

DETA is known to be part of some reagent formulations proposed for pyrrhotite depression [99, 100]. Recent developments that have taken place in the processing of the Ni-Cu ores involve DETA directly [101, 102]. Using DETA has greatly improved pyrrhotite rejection at Inco's Clarabelle mill (Sudbury) [103, 104]. Also, laboratory and pilot scale tests at Falconbridge with DETA and DETA plus SO₂ found that DETA alone did not ensure depression of pyrrhotite but the combination with SO₂ brought about efficient and consistent depression [105, 106].

The action of DETA was linked to its selective chelation of base metal ions over ferric and alkali metals. Examination of flotation concentrates by Laser Ionization Mass Spectroscopy (LIMS) and X-Ray Photoelectron Spectroscopy (XPS) showed that there was a significant amount of nickel and copper on pyrrhotite upon exposure to plant water [107-109]. The concentration of these base metal ions on pyrrhotite decreased considerably when contacted with DETA [110]. As a result, xanthate adsorption on pyrrhotite was significantly decreased, with a corresponding reduction in floatability [108, 109]. The suspicion that Ni and Cu ions caused accidental activation and that they could be removed by DETA was substantiated by these observations.

Infrared spectra of pyrrhotite treated with DETA solutions showed no trace of this reagent on the surface [108, 109], suggesting the role of DETA was solely as a solubilizing (complexing) or "cleaning" agent. In another study [105], the adsorption of DETA from flotation slurries was monitored during laboratory flotation tests and it was estimated that 75-95% of the DETA, used in the range of 100-600 g/t, disappeared from solution. Interestingly, however, the adsorption of DETA, even at relatively high levels, did not ensure efficient depression of pyrrhotite. There have been questions raised regarding the analytical method used to monitor the DETA concentration in solution. Recently this method has been improved [111].

The use of DETA alone readily depresses pyrrhotite in the collectorless flotation of

Ni-Cu sulphide ores. This aspect of DETA action was the subject of a recent theoretical analysis [112, 113], which focussed on the chelation phenomena taking place in the Ni-Fe-S-DETA, Fe-S-DETA and Cu-Fe-S-DETA systems in an aqueous environment. This work indicated that an important part of DETA action must involve sequestering Ni^{2+} and Cu^{2+} over the wide range of pH and redox potentials encountered in flotation. Also, investigation using time of flight laser ionization mass spectrometry (TOF-LIMS) [107], indicated the presence of a number of metal ions such as copper, nickel, calcium and potassium in the surface layers of nickeliferous sulphides, primarily pyrrhotite. The presence of copper and nickel ions on pyrrhotite surfaces was notable even on ore samples taken directly from the mine. These adsorbed Cu²⁺ and Ni²⁺ ions were assumed to originate from superficial oxidation of chalcopyrite and nickeliferous sulphides, respectively, which naturally come into numerous galvanic contacts after rock fragmentation in humid environments. These ions may affect the flotation characteristics of sulphide minerals by activating gangue minerals such as pyrrhotite. Thus, depression is readily explained by the ability of DETA to chelate Ni²⁻ and Cu²⁻ (and possibly other ions, for example, Fe²⁺) so that these ions are not actively involved in catalysing oxidation reactions promoting the formation of metastable phases (i.e. development of a sulphur-rich hydrophobic surface) on pyrrhotite.

The mechanism for improved depression by the combination of DETA with SO_2 was attributed to complex formation involving SO_2 -derived aqueous products [114]. Whether or not such complexes can form between DETA and sulphoxy species in a flotation environment is not clear. However, exploratory tests carried out in the absence of solids [115, 116] indicated that DETA may extend the stability of sulphides and some other sulphoxy species [102] added or present in flotation pulps. A remarkable stabilization of the ferrous form of iron by DETA has already been demonstrated [106, 113].

These hypotheses regarding the role of SO_2 need to be reconciled with the observation at Inco that improved pyrrhotite rejection occurred only when pyrrhotite was extensively oxidized [108-109]. This was interpreted as follows: The activation products formed on pyrrhotite may be sulphides of Ni, Cu Ag, which are usually insoluble under reducing conditions. When the mineral is oxidized, however, the activation products will be converted to oxides, whose solubility increases in the presence of DETA. Another possibility is that oxidation of pyrrhotite releases sulphoxy species similar to those generated by dissolving SO_2 in water and the reaction products causing depression are essentially the same in both cases.

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CHAPTER 3

SURFACE ANALYSIS

3.1. INTRODUCTION

Surface properties exert a central role in many mineral processing operations such as flotation, flocculation, bioleaching, etc. Flotation is a complex physicochemical process involving many steps that are not yet fully understood. However, it is clear that surface chemistry plays the dominant role, since the reagents (collectors, regulators, etc.) used in flotation all interact in some way with the mineral surface. In an attempt to gain insight into flotation mechanisms, spectroscopic measurements have been and remain very useful in the identification and characterization of the adsorbed species at the mineral-aqueous solution interface.

Most spectroscopic measurements have focussed on mineral-collector interactions. In many instances this is the key reaction. In other instances, reactions with depressants and activators are the key. It is important that all possible adsorption reactions be considered. An important requirement of spectroscopic investigations is the ability to study the adsorbed species on the mineral surface in situ, i.e., at the interface between the mineral and the aqueous solution. However, due to the limited availability of in situ techniques, often it is necessary to use a combination of methods.

One group of methods are electrochemical analysis techniques such as cyclic voltammetry. The electrochemical reactions occurring on electrode surfaces are monitored by changes in current and potential. This technique has provided valuable information on the extent of oxidation as a function of potential for different solution conditions and has allowed surface products to be inferred. Studies have been made on electrodes prepared from mineral specimens, particulate beds, single particles and composites.

The combination of infrared and electrochemical techniques has introduced a new area, spectroelectrochemistry. This technique permits *in situ* surface characterization under electrochemically controlled conditions.

A discussion of the application of infrared, electrochemical, and spectro electrochemical techniques to the study of sulphide mineral flotation follows.

3.2. INFRARED SPECTROSCOPY

3.2.1. Basic theory

Infrared spectroscopy is based on the interaction of infrared light with matter [1-3]. The infrared (IR) region of the electromagnetic spectrum covers radiation with wavenumbers ranging from about 12,800 to 10 cm⁻¹ (Table 3.1). From the application and instrumentation standpoints, the IR spectrum is divided into *near-*, *mid-*, and *far-* regions. However, the majority of applications for identification of organic molecules have been confined to mid-infrared region from 4000 to 400 cm⁻¹.

Quantity	Relationship	Units
wavelength	$\lambda = \frac{1}{v} = \frac{c}{v}$	π, μπ, nm
wavenumber	$\overline{v} = \frac{1}{\lambda} = \frac{v}{c}$	m ⁻¹ , cm ⁻¹
frequency	$v = \frac{c}{\lambda} = c \overline{v}$	s⁻¹ (Hz)
velocity	$c = v \lambda = \frac{v}{\overline{v}}$	m s ⁻¹

Table 3.1. Units of electromagnetic radiation

When IR radiation (i.e. energy) interacts with matter it can be absorbed by a molecule, causing a change in molecular vibration (be excited) from one energy state to another. This transition between two vibrational states of a molecule can be characterized by the frequency of the photons of IR radiation absorbed. The energy difference, ΔE , between the two vibrational states is related to the frequency, v, of this photon by,

$$\Delta E = h v \tag{3.1}$$

where *h* is Plank's constant.

The typical unit used to express the energy of these transitions is the wavenumber $(\bar{\nu})$, and the equation (3.1) can be expressed as follows,

$$\Delta E = h c \overline{v} \tag{3.2}$$

As a result, a vibrational transition can occur when energy interacts with a molecule. In order for this interaction to occur, a molecular vibration must cause a change in the electrical dipole moment of the molecule. When the frequency of the electromagnetic field matches the frequency of the oscillation of the dipole moment, the IR radiation can be absorbed, exciting a vibrational transition.

The vibrational motion of a diatomic molecule can be approximated by the harmonic oscillator model consisting of two masses m_1 and m_2 connected by a spring. If the spring is displaced a distance x from its equilibrium position, the restoring force F is proportional to the displacement (Hooke's law),

$$F = -k x \tag{3.3}$$

where k is the force constant of the spring. The potential energy, V of the system is given by:

$$V = \frac{1}{2} k x^2$$
 (3.4)

These equations of ordinary mechanics do not completely describe the behaviour of particles of atomic dimensions, because they do not take into consideration the quantized nature of molecular vibrational energies. However, by employing the concept one can reach to the following,

$$E = \left(\nu + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$
(3.5)

where v is the vibrational quantum number, which can take only positive integer values (including 0) and $\mu = m_{\Theta} m_{\Theta} / (m_{\Theta} + m_{\Theta})$. The term $(\sqrt{k/\mu} 2 \pi)$ is equal to the vibrational frequency of the mechanical oscillator model, hence by substituting this equation into the previous one gives,

$$E = \left(v + \frac{1}{2}\right) h v \tag{3.6}$$

The harmonic oscillator assumes a simple function for the potential vibrational energy of a diatomic molecule. A more realistic model for the potential energy of such a system is the empirical, Morse function [2]:

$$V = D_{e} \left(1 - e^{-\beta x} \right)^{2}$$
(3.7)

where D_e is the difference between dissociation energy of the diatomic molecule and the bottom of the potential well and β is characteristic of the shape of the curve. This anharmonic function results in a modified equation for the vibrational energy levels of a diatomic molecule. The energy levels are now dependent on the quantum number as well as the displacement of the atoms from their equilibrium positions so that $\Delta E_{01} \neq \Delta E_{12}$. This anharmonic model correctly predicts the appearance of overtones and hot bands.

3.2.2. Instrumentation

There are two type of main spectrometers: dispersive and Fourier transform infrared (FTIR) spectrometers. The dispersive spectrometer uses gratings to disperse the IR radiation into its wavelength components. A spectrum is completed when all wavelengths have been scanned. This type of spectrometer has been superceded by FTIR due to the advent of digital computers that could perform the Fourier transformation rapidly and economically.

Interferometer: This is the device used for modulating optical radiation. The most commonly used interferometer is the Michelson interferometer. The Michelson interferometer splits a beam of radiation into two of nearly equal power and then recombines them in such a way that intensity variations of the combined beam can be measured as a function of differences in the path length of the two. Figure 3.1 shows a schematic of such a device as it is used for optical Fourier transform spectroscopy.

As shown in the Figure, a beam of radiation from a source is collimated and impinges on a beam splitter, which transmits approximately half of the radiation and reflects the other half. The resulting twin beams are then reflected from mirrors, one of which is fixed and the other movable. The beams then meet again at the beam splitter, with half of each beam being directed toward the sample and detector and the other two being directed back to the source. Only the two beams passing through the sample to the detector are employed for analytical purposes.

Horizontal motion of the movable mirror will cause the power of the radiation reaching the detector to fluctuate in a predicable manner. When the two mirrors are equidistant from the splitter, the two parts of the recombined beam will be totally in phase and the power will be a maximum. For a monochromatic source, motion of the movable mirror in either direction by a distance equal to exactly one-quarter wavelength will change the path length of the corresponding reflected beam by one-half wavelength. Under this circumstance, destructive interference will reduce the radiant power of the recombined beams to zero. Further motion to A or D will bring the two halves back in phase so that constructive interference can again occur.



Figure 3.1. Major features of the FTIR spectrometer

The difference in path lengths for the two beams, 2(M-F) in the figure is termed the retardation δ . A plot of the output power from the detector (P(t)) versus δ is called an *interferogram*; for monochromatic radiation, the interferogram takes the form of a cosine curve.

The radiation striking the detector after passing through a Michelson interferometer will generally be much lower in frequency than the source frequency. The relationship between the two frequencies is readily derived by reference to the P(t) versus δ plot. One cycle of the signal occurs when the mirror moves a distance that corresponds to one half a wavelength ($\lambda/2$). If the mirror is moving at a constant velocity of v_M , and we define τ as time required for the mirror to move $\lambda/2$ cm we may write

$$v_{M} \tau = \frac{\lambda}{2}$$
 (3.8)

The frequency f of the signal at the detector is simply the reciprocal of τ , or

$$f = \frac{1}{\tau} = 2 \frac{v_M}{\lambda}$$
(3.9)

and this frequency can be related to the wavenumber $\overline{\upsilon}$ of the radiation.

$$f = 2 v_M \overline{v}$$
(3.10)

The relationship between the optical frequency of radiation and the frequency of the interferogram is readily obtained by substitution of $\lambda = c / v$ into equation. Thus,

$$f = \frac{2 v_M}{c} v \tag{3.11}$$

where v is the frequency of the radiation and c is the velocity of light. When v_{M} , is constant, it is evident that the interferogram frequency f is directly proportional to the optical frequency v. Furthermore, the proportionality constant will generally be a very small number.

The cosine wave of the interferogram shown in Figure 3.1 is described by

$$P(\delta) = \frac{1}{2} P(\bar{\nu}) \cos 2\pi f t$$
 (3.12)

where $P(\bar{v})$ is the radiant power of the beam incident upon the interferometer and $P(\delta)$ is the amplitude or power of the interferogram signal. The parenthetical symbols emphasize that one power $P(\bar{v})$ is in the frequency domain and the other $P(\delta)$ in the time domain. In practise, the foregoing equation is modified to take into account the fact that the interferometer ordinarily will not split the source exactly in half and that the detector response and the amplifier behaviour are frequency dependent. Thus, it is useful to introduce a new variable $B(\bar{v})$, which is the intensity of the spectrum as a function of wavenumber and depends upon $P(\bar{v})$. Equation (3.12) can therefore be re-written as,

$$P(\delta) = \frac{1}{2} B(\bar{\nu}) \cos 2\pi f t$$
 (3.13)

which can be written in terms of wavenumber ($\bar{\nu}$) by substituting frequency (f),

$$P(\delta) = \frac{1}{2} B(\vec{v}) \cos 2\pi \ 2 \ v_M \ \vec{v} \ l$$
 (3.14)

Since mirror velocity can be expressed in terms of retardation $v_M = \frac{\delta}{2t}$; we have

$$P(\delta) = \frac{1}{2} B(\overline{\nu}) \cos 2\pi \ \delta \ \overline{\nu}$$
 (3.15)

For a continuous source, the interferogram can be expressed as a sum of an infinite number of cosine terms. That is,

$$P(\delta) = \int_{-\infty}^{\infty} B(\overline{\nu}) \cos 2\pi \ \overline{\nu} \ \delta \ d\overline{\nu}$$
 (3.16)

The Fourier transform of this integral is,

$$B(\bar{v}) = \int_{\bar{v}}^{\bar{v}} P(\delta) \cos 2\pi \ \bar{v} \ \delta \ d\delta \qquad (3.17)$$

Since the spectrum and the corresponding interferogram are related to each other by the Fourier transformation, this technique of obtaining a spectrum from an interferogram is known as Fourier Transform Infrared Spectroscopy, abbreviated FTIR [4].

The most significant advantage of the FTIR spectrometer over the dispersive spectrometer: is the much higher signal to noise ratio (resulting from the increased throughput), which results in a sensitivity two orders of magnitude higher. Another advantage is greater wavenumber accuracy. There is a high and constant resolution across the scanning range and no steps in the baseline appear in the spectrum. Moreover, its fast scan rate allows kinetic studies to be performed and good quality spectra may be obtained rapidly. The freedom from polarization effects allows study of molecular orientation using polarized radiation [5].

3.2.3. IR spectroscopic techniques and their application

Infrared spectroscopy can be performed in the following modes: transmission, emission, photo acoustic, diffuse reflection, external (specular) reflection and internal reflection (attenuated total reflection, ATR).

3.2.3.A. Transmission

In transmission, the radiation that travels through the sample is detected. i.e., absorption of radiation at the surface and in the bulk is involved. Therefore, to obtain information on the surface, the surface/volume ratio must be high. For this reason, the techniques most commonly adopted, namely KBr pellet and Nujol mull, utilize (dry) fine powdered samples. For flotation studies this represents, therefore, an ex-situ technique (i.e., water has been removed). Many studies on mineral surface/collector interaction have been performed using transmission IR, by comparing treated with untreated minerals [6-10]. From major changes such as band shifts, and appearance and disappearance of peaks in the spectrum, IR transmission spectroscopy provides an indication of chemical bond formation between the mineral and the adsorption entity (e.g. collectors) [11]. In the case of chemisorption phenomena, a drawback is that the surface species may include agglomerates formed in solution and precipitated in bulk form. In order to get around this, a method has been developed which involves double filtering [12].

3.2.3.B. Emission

Emission IR spectroscopy can be used for surface studies because the detected emitting radiation is mainly from the outer surface layers. It is possible, therefore, to obtain information on the surface species even in regions of the spectrum where the bulk absorption bands occur. The characteristic depth of sample emission is two to four monolayers. This technique can be used to advantage when it is necessary to analyse samples at temperatures well above ambient conditions. In such cases it is much simpler to analyse the spontaneouslyemitted radiation because the incident radiation is absorbed in smaller and smaller amounts as the temperature rises [13].

For infrared emission studies, the sample to be investigated is deposited on an inert support. If the latter is highly reflective, it is a poor emitter and does not contribute to the observed emission spectrum. Since best conditions for this technique are at elevated temperatures, it is not generally of interest in the study of mineral/reagent interactions.

3.2.3.C. Photo acoustic (PAS)

A variety of difficulties, such as highly opaque solutions, and optically diffusing samples make observation difficult with the common optical spectroscopy techniques (UV, VIS, IR). This has led to the development of photo-acoustic spectroscopy (PAS), which is based on the transformation of radiant energy into thermal energy.

The sample holder with the test material is placed in a sealed cell, which is filled with inert gas (helium) and fitted with a microphone and a window through which the sample is irradiated. The photo-acoustic signal is generated when the sample absorbs modulated electromagnetic radiation of specific wavelength. The energy thus absorbed by the sample is converted into heat by non-radiative de-excitation processes. Since the incident radiation is modulated, the thermal energy created in the sample will be periodic, at the frequency of the modulation frequency, which creates thermal waves that move towards the boundary of the sample. The periodic variation in the temperature at the surface of the sample generates a pressure (or acousticwave) in the gas surrounding the sample. The acoustic wave propagates through the volume of the cell, and is detected by a highly-sensitive microphone (Figure 3.2).



Figure 3.2. Schematic view of a photoacoustic cell. (Ph) primary photon beam, (W) window, (G) gas, (S) sample, (AT) acoustic transducer

CHAPTER 3. SURFACE ANALYSIS

As the principal effect of the phenomenon is at the solid-gas contact zone where the thermal energy transfer occurs, a particular strength of the technique is that it primarily investigates the surface. Another aspect of the technique is that it offers the possibility of obtaining depth profiles of the solid by varying the modulation frequency of the incident radiation which is related to the depth of penetration of the incident radiation in the sample. By varying the modulation frequency from 100 Hz to 20 Hz, sampling depths in the range of $0.1-100 \mu m$ can be investigated [14].

So far, most of the work reported in PAS studies on solids and related surfaces have used frequencies in the ultraviolet, visible, and near-infrared regions. The IR spectrum of adsorbed species in these wavenumber regions are broad, structureless, and hence not very informative. The IR-PAS technique does not suffer from this problem. The IR-PAS technique has been used to identify surface species on silica [15]. Sharp well defined peaks were observed for certain adsorbates with a surface area of 300 m²/g, while relatively broad peaks were observed for adsorbates with small surface areas of 50 and 80 m^2/g . The IR-PAS studies require an infrared radiation of sufficient intensity over the whole range of infrared frequencies. This restriction has been overcome by use of infrared laser in FTIR-PAS. A variety of solids have been characterized [16-18] and considerable promise for surface studies in flotation has been demonstrated [19]. In a recent investigation, for example PAS was employed to monitor the stability of the electrogenarated dixanthogen molecule on copper and chalcocite electrodes. The products such as COS, CS2 and CO2 were detected in the gas phase and appeared to be the main decomposition products of the xanthate. This phenomenon was also observed for sulphide mineral powders which had been treated with xanthate. For selected minerals CS₂ was also found in the gas phase. The gas-phase concentration of the decomposition products followed the reactivity of the mineral, suggesting that the mineral was intimately involved in the decomposition process [20].

3.2.3.D. Headspace analysis gas-phase infrared spectroscopy (HAGIS)

The observation of the gas-phase decomposition products of xanthate on sulphide minerals [20] using PAS, raised a number of questions regarding the processes involved in their production and what other decomposition products might be present in the gas phase.

To investigate further the gas-phase species produced from collector treated sulphide mineral surfaces, under more controlled conditions, a headspace analysis gas-phase infrared spectroscopy (HAGIS) cell has been designed [21]. The cell permits the detection and identification of gas-phase species produced *in situ* by thermal decomposition of xanthates on sulphide mineral surfaces. The schematic diagram of HAGIS cell is shown in Figure 3.3.



Figure 3.3. Hagis Cell (a) stainles steel sample boat, (b) teflon endcaps with removable KBr windows, (c) digital thermometer, (d) vacuum

The cell is made of glass and has two vacuum stopcocks which allow the cell to be evacuated and permit the introduction of various atmospheres. The total volume of the cell is 50 cm³. The ends of the cell are constructed to allow the KBr windows to be easily demounted, which is necessary for the placement of the sample in the cell. The heating stage consists of a block of stainless steel equipped with a cartridge heater and a thermocouple. The temperature is regulated manually ($\pm 2^{\circ}$ C) using a digital thermometer. The heating block contains and indentation which allows the sample to be placed in direct contact with the heating stage and is constructed in a way that it does not obstruct passage of the IR beam through the sample cell.

The results of these experiments are of use in two ways: i) the detection and identification of the species produced in the decomposition of alkyl xanthates on mineral surfaces is directly relevant to the stability of surface layers on stored mineral concentrates and ii) the identification of the gas-phase species produced may help in proposing decomposition pathways which provide insight into the original chemical form of the collector on the mineral surface.

3.2.3.E. Diffuse reflection infrared Fourier transform spectroscopy (DRIFTS)

Diffuse reflection results from the multiple scattering and partial absorption of the light flux impingent on (ideally) a matte-finish surface [22, 23] (Figure 3.4). For a perfect diffuse reflector, the reflected radiation is unpolarized and its angular distribution is isotropic. In practice, since an ideal diffuse reflector does not exist, the reflected radiation also has a specular component which arises from mirror or regular reflection and is, therefore, polarized.



Figure 3.4. In diffuse reflectance, the incident beam undergoes absorption and scattering by the powdered sample and is then collected and focussed on the detector.
The dependence of diffuse reflection on the optical absorption coefficient and the scattering properties of the sample can be related to the relative reflectance $r_{\alpha} = r_{sam}/r_{ref} = S/R$ by use of the Kubelka-Munk (K-M) equation.

$$K/s = (1 - r_a)^{\theta} / 2r_a$$
 (3.18)

where K is the optical absorption coefficient and s is the scattering coefficient. The K-M theory assumes an infinitely thick sample (a condition that is usually met for scattering powders 1-3 mm thick), diffuse illumination, and the complete absence of specular reflection. The right side of equation (3.18) is commonly referred to as the K-M function. A plot of this function vs concentration is linear with a slope of s⁻¹ for a limited range of concentrations. The K-M function is dominated by the absorption coefficient for strongly absorbing samples and by the scattering coefficient for weakly absorbing materials. The absorption and scattering coefficients also determine the effective depth of penetration and result in a decrease in the fraction of light available for absorption. This causes an increase in the relative reflectance. For strongly absorbing samples, the depth of penetration is small and is relatively unaffected by changes in scattering or absorption. When this is the case, the drift spectrum can be considered to be optically saturated.

The experiment is performed by preparing a small amount of sample (5-15%) which is lightly ground (if necessary) (e.g., with a mortar and pestle) and then gently mixed with 85-95% KBr powder (KBr has no absorption over the mid IR range). The mixture is then poured into the sampling cup, levelled off (e.g., with a spatula) and measured directly. This technique has been used to investigate the adsorption of amylxanthate on galena [24-29] and pyrite [29-31]. Recently interaction between xanthates and sulphide minerals such as chalcopyrite, marcasite, pentlandite, pyrrhotite and troilite has been investigated by this technique [32]. It was found that dixanthogen was the main product on pyrrhotite and pentlandite with no detectable amount of metal xanthate being present.

3.2.3.F. External (specular) reflectance

The basic requirement for external reflection spectroscopy is the reflection of light from a surface and its return to the spectrometer (Figure 3.5).



Metal Substrate

Figure 3.5. In external reflectance, the beam passes through the coating, reflects off the metal substrate, and again passes through the coating.

The light should focus in the same spot and be going the same direction as it would have been if it were not diverted to the sample. It was shown that for a single reflection the optimum angle is 88° (or nearly glancing) [33].

Accessories for external reflection spectroscopy can be designed so that either single or multiple external reflection techniques can be used. For most routine applications involving external reflection measurements, a single reflection will be sufficient. However, when the reflection spectrum of very thin coating on a metal surface, or adsorbed species, the technique just described may not be sufficient. When light is reflected from the surface of a metal, the incident and reflected waves combine, in most cases, to form a standing wave at the surface. This standing wave has a node at the surface and may not show significant interaction with the sample. However, when the radiation is incident at nearly grazing angles and is also polarized with the electric vector parallel to the plane of incidence, the standing wave has a large amplitude at the surface [33] and this leads to maximum interaction between the sample and the radiation, and good-quality spectra can be obtained. The sensitivity can be enhanced by using multiple, polarized (discussed in detail in), external reflections.

The first detailed application of this technique on metal surfaces was by Greenler [33]. Adsorption and orientation of xanthates and other thiol collectors on copper metal and cuprous sulphide (chalcocite) have been investigated in the presence and absence of electrochemical potential control [34-42]. It was found that it was possible to obtain infrared spectra of mono and multilayer adsorbed species and to determine the orientation of the individual molecular groups and the chemical nature of the adsorbed species by recording the reflection spectra of the adsorption layer at different angles of incidence for both p and s polarizations.

3.2.3.G. Internal reflection

Internal reflection spectroscopy (IRS), alternatively referred to as attenuated total reflection (ATR), is the most commonly used spectroscopy technique in flotation chemistry studies, partly because it allows for in-situ measurements in aqueous solutions. Schematic representation of a ray of light undergoing multiple internal reflections in an internal reflection element (IRE) is shown in Figure 3.6a.

Two requirements must be met before total internal reflection can occur. First, the sample must have a lower refractive index than the IRE. Second, the incident angle of the light beam on the IRE must be greater than the critical angle. As the light is internally reflected at the interface, an evanescent wave penetrates into the outer phase, i.e. into the sample, which propagates typically a few μ m (Figure 3.6b). It is the interaction between the sample and this evanescent wave that produces the IR spectrum. The depth of penetration. d_p (not to be confused with the actual measurement depth in IRS) is arbitrarily defined to be the distance from the IRE where the electric field amplitude falls to 1/e of its value at the surface. The value is given by [43];

$$d_p = \frac{\lambda/n_1}{2\Pi[(\sin^2\theta_1 - (n_2/n_1)^2]^{1/2}}$$
(3.19)



Figure 3.6. In ATR, the IR beam travels through a crystal and undergoes multiple reflections at the crystal/sample interface.

Three possibilities exist for studying flotation systems by in-situ internal reflection spectroscopy: 1) direct adsorption of surfactants from solution onto a reactive IRE mineral substrate of interest [44-52]; 2) vacuum deposition of the desired mineral onto an "inert" IRE such as germanium and monitoring surfactant adsorption from solution [53-56]; and, 3) pressing a mineral/surfactant suspension against an "inert" IRE. The latter is the technique most commonly used in sulphide mineral flotation studies [57-69].

In-situ ATR spectra of ethyl xanthate adsorbed on sulphide minerals (chalcocite, chalcopyrite, pyrite and galena) under controlled potential have been generated [70]. On chalcocite, the spectra resembled that of copper xanthate precipitates at all potentials (from -0.25 V to 0.25 V vs SHE). The IR signals of the characteristic xanthate peaks increased with increasing potential, indicating a corresponding increase in adsorption.

ATR spectroscopy investigations on activated and non-activated sulphide minerals have also been performed [71, 72]. On non-activated pyrrhotite in the presence of ethyl xanthate, dixanthogen was found to be the main product regardless of concentration. However, on copper-activated pyrrhotite, the xanthate was in the form of copper (I) xanthate.

3.3. ELECTROCHEMISTRY

3.3.1. Basic theory

3.3.1.A. Electrode reactions and their nature

Electrochemical reactions are heterogenous chemical reactions which occur via the transfer of charge across the interface between an electrode and an electrolyte. An electrochemical reaction involves an anodic process whereby a species is oxidized by releasing electrons to the electrode, e.g.

$$Fe^{2^{-}} \neq Fe^{3^{+}} + e^{-}$$
 (3.20)

and a cathodic process in which a species is reduced by the gain of electrons from the electrode, e.g.

$$O_2 + 2H_2O + 4e^- \neq 4OH^-$$
 (3.21)

Electrochemical reactions can be quite diverse, for instance: the electroactive species may be organic or inorganic, neutral or charged, a species dissolved in solution, a film on the electrode surface or, the electrode material itself. Moreover, the product may be dissolved in solution, a gas, or a new phase on the electrode surface.

In general, electron transfer reactions require the reactant to be located within molecular distances of the electrode surface. Hence the progress of an electrochemical reaction demands adequate rates of reactant supply to the electrode surface and product removal from it, in addition to charge transfer at the electrode/electrolyte interface.

The overall cathodic process in which a species 'O' is reduced by gain of one or more electrons to yield species 'R', i.e.

$$O + ne^{-} \neq R \tag{3.22}$$

occurs in at least three steps (as shown in Figure 3.7):



Figure 3.7. Steps involved in the overall cathodic process, $O + ne^- \neq R$, where O and R are solution phase species.

(i) reactant supply (mass transport to the electrode surface)

$$O_{bulk} \sim O_{electrode}$$
 (3.23)

(ii) electron transfer (charge transport at the electrode surface)

$$O_{electrode} + ne^{-} \rightarrow R_{electrode}$$
 (3.24)

(iii) product removal (mass transport away from the electrode surface)

$$R_{electrode} - R_{bulk} \tag{3.25}$$

The rate of the overall process is determined by the slowest of these steps. Therefore, in order to understand the rates of electrode processes, it is necessary to consider both electron transfer and mass transfer, as well as the interaction of these processes.

In practice, other fundamental steps may also play a key role in an electrode process.

These include:

(1) Phase formation at the electrode surface

The electrode reaction may involve the formation of a new phase on the electrode surface, the removal of one or the transformation of one phase to another. Such reactions show characteristics determined by the need to first nucleate the new phase, then to allow its early growth.

(2) Chemical reactions

Pure chemical reactions (i.e. those not involving electron transfer at the electrode surface) may precede electron transfer, accompany it, or follow it. A simple example is the reduction of acetic acid to hydrogen which proceeds via dissociation prior to electron transfer,

$$CH_{3}COOH \neq CH_{3}OO^{-} + H^{-}$$

$$H^{-} + e^{-} \neq 1/2H_{2}$$
(3.26)

(3) Adsorption on the electrode surface

An adsorbate may change the rate of the electrode reaction, its pathway and/or its products. In electrochemical technology, important examples of this effect include electrocatalysis, corrosion inhibition, control of deposit properties by organic additives in electroplating, and the variation of product selectivity in organic synthesis. The adsorbate may bond via a wide variety of interactions including electrostatic forces, ion-dipole effects, covalent bonding and metallic bonding. The adsorbed species may be a reactant, a product or an intermediate.

An example of adsorption is hydrogen evolution at the surface of a metal where the common mechanism involves M-H bond formation and cleavage

$$H^{-} + e^{-} + M \neq M - H$$
(3.27)

followed by either

$$2M - H \neq 2M + H_2$$

or
$$M - H + H^- + e^- \neq M + H_2$$

(3.28)

In extreme cases, sufficient hydrogen may enter the lattice of certain metals to permit the formation of a metal hydride, as in the case of titanium and palladium.

(4) Multiple electron transfer

In a majority of electrochemical reactions involving the transfer of two or more electrons, simultaneous transfer of all electrons does not occur. Rather, the electron transfer steps occur sequentially and are often separated by chemical reaction steps. The reduction of Cu(II) in acid sulphate solution is known to occur in two single electron transfer process.

$$\begin{array}{l} Cu^{2^{*}} + e^{-} \neq Cu^{-} \\ Cu^{-} + e^{-} \neq Cu \end{array} \tag{3.29}$$

with the first step being rate determining.

3.3.1.B. Electron transfer

The overpotential (η) at an electrode is defined as the difference between the actual potential (E) and the equilibrium potential (E_e),

$$\eta = E - E_e \tag{3.30}$$

Three cases of electron transfer control can be distinguished according to the magnitude and sign of the overpotential at the electrode,

(1) more negative than E_c : η is -ve, net current density, I is -ve, cathodic current flows.

(2) strictly at E_e : η is zero, I is zero, zero net current flows.

(3) more positive than E_{e} : η is +ve, I is +ve, anodic current flows.

The cases of zero, positive and negative values of overpotential can be discussed in terms of the effect on the net current density, I,

$$I = I^{-} + I^{-}$$
(3.31)

The observed current density is the algebraic sum of the partial cathodic and anodic current densities. As electrons flow in opposite directions during reduction and oxidation, 1⁻ and 1⁻ have opposite signs. According to convention the reduction current is taken to be negative, while the oxidation current is positive, i.e., a cathodic reaction involves a negative current and an anodic reaction involves a positive current.

Equilibrium potential (7=0; I=0)

In the absence of any net current, the concentrations of O and R cannot change and the electrode takes up the equilibrium potential for the system. The equilibrium potential, E_e , can be measured directly or calculated from the Nerst equation,

$$E_{e} = E_{e}^{\theta} + \frac{RT}{nF} \ln (a_{i} / a_{R})$$
 (3.32)

where E_c^{o} is the standard potential for the O/R couple and a_0 and a_R are the activities of the species O and R. It is more practical, however, to restate this equation in terms of the concentrations of the species,

$$E_e = E_e^{\circ} + \frac{RT}{nF} \ln (c_0 / c_R)$$
 (3.33)

where E_c is the formal potential for the couple under consideration (i.e. the equilibrium potential when $c_R = c_0$). This equation can be written in terms of decadic logarithms,

$$E_{e} = E_{e}^{*} + S_{N} \log (c_{O} / c_{R})$$
(3.34)

where the Nernstian slope, S_N , is defined as,

$$S_N = 2.3 \frac{R T}{n F}$$
 (3.35)

and has an approximate value of 0.0592/n V at 298 K.

At equilibrium, a dynamic equilibrium exists where the partial cathodic and partial anodic current densities are equal in magnitude but opposite in sign.

$$I = I^{-} + I^{-} = 0 \tag{3.36}$$

This dynamic equilibrium is characterized by the magnitude of the partial current densities at equilibrium which is known as the exchange current density, I_0 , defined as,

$$I_{o} = -I^{-} = I^{-}$$
(3.37)

 I_0 is an important kinetic parameter which measures the degree of electron transfer activity at the equilibrium potential.

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Non-Equilibrium potentials: The general case

The Nernst equation is only strictly true for the special case of equilibrium, i.e. zero cell current which is achieved under reversible open-circuit conditions. It is inherently, a thermodynamic expression and provides no information on the overall reaction rate. In fact, the magnitude of the current flowing at any potential also depends on the rate of electron transfer. At any potential, the measured current density is given by,

$$I = I^{-} + I^{-}$$
(3.38)

where I^- is negative. These partial current densities are each dependent on a rate constant and the concentration of the electroactive species at the site of electron transfer on the electrode surface, i.e.

$$I^{-} = -n F k^{-}c_{0}$$

$$I^{-} = -n F k^{-}c_{R}$$
(3.39)

The rate constants, however, have a particular property: they vary with the applied electrode potential (i.e. the potential difference at the electrode surface during electron transfer), and invariably it is found experimentally that the rate constants vary with potential according to equations of the form,

$$k^{-} = k_{o}^{-} \exp\left(-\frac{\alpha_{c} n F}{R T} E\right)$$

$$k^{-} = k_{o}^{-} \exp\left(-\frac{\alpha_{A} n F}{R T} E\right)$$
(3.40)

where α_A and α_C are constants (between 0 and 1 and generally around 0.5) known as the transfer coefficients for the anodic and cathodic reactions, respectively. For simple electron transfer reaction $\alpha_A + \alpha_C = 1$, so that one transfer coefficient may be eliminated from any equation.

Algebraic manipulation of Equations (3.38-40), recalling the definition of overpotential from Equation (3.30) as the deviation of the actual potential from its equilibrium value for the O/R couple and noting the definition of the exchange current density, $I_0 = -I^- = I^-$ at $\eta=0$, leads to the Butler-Volmer equation,

$$I = I_o \left[\exp\left(\frac{\alpha_A n F}{R T} \eta\right) - \exp\left(-\frac{\alpha_C n F}{R T} \eta\right) \right]$$
(3.41)

This equation, regarded as the fundamental equation of electrode kinetics, shows that current density varies with exchange current density, overpotential, and the transfer coefficients. In the laboratory it is, however, more common to use one of the three limiting forms of this equation. The first two apply at high overpotentials. At high positive overpotentials $|I^-| \gg |I^-|$, and the second term may be ignored; the anodic current density is then given by,

$$\log I = \log I_o + \frac{\alpha_A n F}{R T} \eta$$
 (3.42)

Conversely, at high negative potentials $|I^{-}| \gg |I^{-}|$, the cathodic current density is given by,

$$\log -I = \log I_o - \frac{\alpha_A n F}{R T} \eta$$
 (3.43)

The third limiting form applies at very low values of η where $\eta \ll (RT/\alpha_c nF)$ and $\eta \ll (R T/\alpha_c nF)$. The two exponential terms of equation (3.43) may then be expanded as a series, and, ignoring quadratic and higher order terms, leads to the simple equation.

$$I = I_o \frac{n F}{R T} \eta$$
 (3.44)

This shows a linear relationship between the current density and the overpotential under the small overpotential approximation.

Zones of the current density vs overpotential curve for simple electron transfer controlled reactions can be summarized in Figure 3.8 as:





- (i) The origin where the electrode is at equilibrium and the Nernst equation applies;
- (ii) At high positive potentials (Equation 3.42);
- (iii) At high negative overpotentials (Equation 3.43);
- (iv) At very low overpotentials (Equation 3.44).

3.3.1.C. Mass transport

The supply of reactant(s) to an electrode surface and the subsequent removal of product(s) are essential steps in an electrochemical process. In the general case, this mass transport occurs in three modes. These modes are driven by a gradient near the electrode surface, i.e. a gradual change in a property with distance from the electrode surface, which gives rise to "boundary layers". These layers of electrolyte near the electrode surface have a different concentration and potential than the surface and the bulk electrolyte. For the convenience of discussion, a few terms are defined as follows.

Diffusion, is the movement of a species down a concentration gradient and it occurs whenever a chemical change takes place at the electrode surface, such as the conversion of O to R. The result of this process is a lower concentration of O at the electrode surface (and a higher R level) than in the bulk.

Convection, is the movement of a species down a velocity gradient due to mechanical forces. There are two types of convection. In the case of "natural convection", small differences in solution density (caused by chemical changes at the electrode surface, or by localised temperature fluctuations) are responsible for the velocity gradient. "Forced convection" is often a dominant mode of mass transport and may be induced by electrode or electrolyte movement (as occurs on deliberate agitation or mixing).

Migration, is the movement of a charged species due to a potential gradient and it is responsible for the passage of ionic current through the electrolyte. Migration is driven by electrostatic forces and does not discriminate between chemically different types of ion, but only the size and sign of their charge.

In an unstirred solution and in the presence of a base electrolyte, diffusion is the only form of mass transport for the electroactive species which needs to be considered. The simplest model is that of linear diffusion to a plane electrode. It is assumed in this model that the electrode is perfectly flat and of infinite dimensions, so that concentration variations can only occur perpendicular to the electrode surface. Diffusion may then be characterized by Fick's law in a one dimensional form as in Figure 3.9.



Figure 3.9. Fick's laws for linear diffusion

Fick's first law states that the flux of any species, i, through a plane parallel to the electrode surface is given by,

$$Flux = -D_{i} \frac{dc_{i}}{dx}$$
(3.45)

where D_i is the diffusion coefficient of the species i which has a concentration, c.

Fick's second law considers the change in concentration of i with time due to diffusion.

$$\frac{dc_i}{dt} = D_i \frac{d^2 c_i}{dx^2}$$
(3.46)

Integration of equation (3.46) with initial and boundary conditions appropriate to the particular experiment, is the basis of the theory of instrumental methods such as cyclic voltammetry. This will be discussed in further detail in the method section. The first law, often applied at the electrode surface, x=0, is used to relate the current to the chemical change at the electrode by equating the flux of O or R with the flux of electrons (Figure 3.9) where

$$\frac{I}{nF} = -D_{ij} \left(\frac{dc_{ij}}{dx}\right)_{x=0}$$
or $\frac{I}{nF} = D_R \left(\frac{dc_R}{dx}\right)_{x=0}$
(3.47)

The zone close to the electrode surface where the concentrations of O and R differ from those in the bulk is known as the diffusion layer. In most experiments its thickness increases with time until it reaches a steady state value. approximately 10⁻² cm thick [73], limited by natural convective stirring of the bulk solution. It takes on the order of 10 s for this boundary layer to form. This also means that for the first 10 s of any experiment, the concentration changes close to the electrode are the result of diffusion. Thereafter the effects of natural convection must be taken into account.

In most practical situations, some convection is present. The combination of convection and diffusion can produce complex velocity and concentration profiles near the

electrode surface. However, a simple treatment known as the Nernst diffusion layer model (Figure 3.10) is possible



Figure 3.10. Nernst diffusion layer model.

This model assumes that the electrolyte layer near the surface of the electrode may be divided into two zones as shown in Figure 3.10a. Close to the surface, it is assumed that there is a totally stagnant layer (of thickness, δ_N) such that diffusion is the only mode of mass transport. Outside of this layer, i.e. $x > \delta_N$, strong convection occurs. In reality, there is no

such demarcation between pure diffusion and pure convection at $x = \delta_N$. Rather, a gradual transition occurs as shown in Figure 3.10b. This behavior may be rationalized by considering a pure mass transport controlled reaction and a series of current values from zero (I=0) to one representing the maximum rate of reaction (I-I_L) as shown in Figure 3.4c. At open circuit, the concentration of reactant remains at the bulk electrolyte value c_O , as no net transformation of O to R occurs. If the current is raised to I₁, O is converted to R and the reactant concentration must decrease near the electrode surface. This decrease is pronounced if the current is raised to I₂. Eventually, the current is so large that the surface concentration of reactant falls to the limiting case of zero. The current corresponding to this condition is the limiting current, I_L, which is (ideally) independent of electrode potential and appears as the plateau in Figure 3.10c.

The current density under convective-diffusion conditions can be obtained from equation (3.47) as,

$$I = nFD_O\left(\frac{c_O - (c_O)_{X=0}}{\delta_N}\right)$$
(3.48)

where the concentration gradient is given by,

$$\left(\frac{dc_{O}}{dx}\right)_{x=0} = \frac{c_{O} - (c_{O})_{x=0}}{\delta_{N}}$$
(3.49)

At the limiting current density, $(c_0)_{x=0} = 0$, equation (3.48) becomes,

$$I_L = \frac{n F D_O c_O}{\delta_N}$$
(3.50)

3.3.1.D. The interaction of electron transfer and mass transport

So far, the extreme cases of pure electron transfer control or pure mass transport control of the overall rate of the reaction $O + ne^- \neq R$ has been discussed. In practice, the reaction rate is partly controlled by the electron transfer and mass transport, i.e. reaction conditions are under "mixed control". In certain cases, it is possible to experience three distinct potential regions. This consequence is illustrated in Figure 3.11 by considering a cathodic reduction as the potential is made progressively more negative from its open circuit. equilibrium, value. The I vs E curve can be divided into three zones.



Figure 3.11. The interaction of electron transfer and mass transport.

Immediately below the equilibrium potential, the reaction is electron transfer controlled because the current density is low, the extent of the resulting chemical change at the electrode surface is small, and hence the surface concentrations of O and R are not significantly different from the bulk concentrations. Hence, mass transport conditions have

a negligible effect on the surface concentrations or the current.

As the potential is made more negative, the surface concentration of reactant falls below its bulk value and mass transport of reactant becomes an important process. The current density continues to increase in the cathodic direction as the potential is made more negative. However, the relationship between current density and potential is no longer exponential; a log I vs E plot is non-linear. The region of mixed control commences when I = 0.05 I_L.

As the potential becomes even more negative, the rate of electron transfer becomes fast compare to the rate of reactant supply (mass transport). The surface concentration of reactant then drops to zero when the current density is fully mass transport controlled. Consequently, I is independent of potential in the plateau (I_L) region, but it is strongly dependent upon the mass transport conditions [73, 74].

3.3.2. Instrumentation

3.3.2.A. Device

The Potentiostat is a basic device for studying electrochemical reactions (Figure 3.12).



Figure 3.12. The principle of a potentiostat.

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It controls the potential across the working electrode-counter electrode pair, and adjusts this potential to maintain the potential difference between the working and reference electrode (which it senses through a high-impedance feedback loop) with the computer to drive a function generator [75]. The potentiostat's job, as an active element, is to force through the working electrode whatever current is required to achieve the desired potential at any time.

3.3.2.B. Electrodes

Working Electrode

The working electrode, where the electrochemical process under study occurs. can be either an anode or a cathode [76]. Designs of the working electrode are diverse. Commonly, they are a small sphere, small disc, or short wire, but it could also be metal foil, a single crystal of semiconductor (or metal), or powder as pressed discs or pellets. There are two types of working electrode used in most mineral processing research. One, the packed bed electrode, is prepared by packing mineral particles in a cell with electrical contact being made through a sensing element, usually platinum or gold. The second is the so called massive mineral electrode, prepared by cutting a (pure) crystal of mineral and mounting it in a nonconducting epoxy after making a connection to the mineral surface [77]. An essential point is that the electrode should not react chemically with the solvent or solution components.

The useful working potential range is difficult to define because, first, it may be limited by different processes such as oxide or complex formation, hydrogen and/or oxygen evolution, or solvent decomposition. A second difficulty is to establish a satisfactory electrode pretreatment procedure which ensures a reproducible state of oxidation, surface morphology, and freedom from adsorbed impurities. Electrodes are polished on cloth pads impregnated with diamond particles down to 1 μ m and then with alumina of fixed grain size down to 0.05 μ m. Care should be taken with the diamond abrasives, as they often contain dyes for easy recognition of the grain sizes, and these may be electroactive. Similarly small particles of alumina may affect the kinetics of a reaction under study owing to the adsorption of reactant at the alumina surface. Those particles can be efficiently removed by cleaning the electrode briefly in an ultrasonic bath. The electrode is often held at a reducing potential before running the test to remove any oxidation product that might have been formed during the cleaning stages.

Counter Electrode

The purpose of the counter electrode is to supply the current required by the working electrode without in any way limiting the measured response of the cell. It is essential that the electrode process is decomposition of the electrolyte medium or oxidation/reduction of a component of the electrolyte so that current flows readily without the need for a large overpotential. In some cases, it can be arranged that the counter electrode reaction is gas evolution or reverse of the working electrode reaction so that the composition of the electrolyte is unaltered. This latter arrangement would be ideal for a photovoltaic cell, the study of kinetics, or electrosynthetic processes.

The products of the counter electrode reaction should always be considered and they must not interfere with the reaction being studied [75]. In practice, such interference is minimized by isolating the anolyte and catholyte with a frit or ion exchange membrane. Ionic conduction is maintained, but the mixing of the respective solutions is prevented.

Reference Electrodes

The role of the reference electrode is to provide a fixed potential which does not vary during the experiment (e.g. it should be independent of current density). In most cases, it will be necessary to relate the potential of the reference electrode to other scales, for example to the normal hydrogen electrode, the agreed standard for thermodynamic calculations.

In potentiostatic experiments the potential between the working electrode and reference electrode is controlled by the potentiostat, and as the reference half cell maintains

a fixed potential, any change in applied potential to the cell appears directly across the working electrode-solution interface. The reference electrode has two main purposes: first, it is a thermodynamic reference; second, it isolates the working electrode as the system under study [76].

Reference electrodes can be classified as fixed potential types (e.g. the calomel electrode and silver-silver halide electrode) and indicator types (e.g. metal/metal ion electrodes, ion selective electrodes, and the glass electrode). In practice the main requirement of a reference electrode is that it has a stable potential and is not substantially polarised during the experiment. Some common electrodes for aqueous systems are:

Standard hydrogen electrode (SHE). This is the ideal reference electrode with the reaction.

$$1/2H_{2} = H^{-} + e^{-}$$
 (3.51)

The standard electrode potential of this reaction is taken as 0 V by convention, the measured potential of such a cell directly gives the rest potential of the electrode. However, it is generally not convenient to set up a cell with a standard hydrogen electrode. Instead, a reference electrode of known rest potential is used.

Mercury-mercurous chloride (saturated calomel electrode, SCE). This is the most widely used reference electrode. It is reversible to chloride ion and is usually made up in a saturated potassium chloride aqueous solution. In commercial electrodes, the solution is often retained with a porous plug or ceramic frit; saturated aqueous KCl, being very dense, leaks out easily. A separate compartment therefore is necessary for the reference electrode if chloride ions must be kept out of the working solution. The half cell reaction for this electrode is,

$$2Hg_{1} + 2CI_{ag} = Hg_{2}CI_{2} + 2e^{-1}$$
(3.52)

The half cell potential for this reaction is given by,

$$E = E^{\circ} + \frac{RT}{2F} \ln \frac{[Hg_2Cl_2]}{[Hg]^2 [Cl^-]^2}$$
(3.53)

The activities of Hg_2Cl_2 and Hg are constant and equal to unity (at 1 atmosphere), and since the KCl solution is in equilibrium with solid KCl, the activity of Cl⁻ is also constant. Therefore equation (3.53) becomes,

$$E = E^{\circ} + \frac{R}{2} \frac{T}{F} \ln \frac{1}{[k^2]}$$
(3.54)

At 25 °C, the value of E for the saturated calomel electrode is 0.244 Volt, positive relative to the standard hydrogen electrode. By using SCE, the potential of the cell thus measured is the potential of the working electrode with respect to SCE. In order to obtain the value of E, the E value of the SCE is added to the measured cell potential.

Mercury-mercurous sulphate. This electrode is prepared in the same way as the calomel, but the mercurous sulphate has to be specially prepared. It is a useful electrode for sulphate solutions but becomes unstable if the sulphate concentration falls below 0.1 mol dm⁻³.

Mercury-mercuric oxide. This electrode is easy to prepare and is recommended for use in alkaline solutions.

Silver-silver halide. These electrodes give very stable potentials in halide solutions providing the halide concentration is not too high (<1 mol dm⁻³), when the increasing solubility of the silver salt causes problems. They are available commercially but are also easily prepared.

Common name	Electrode	Potential (V vs SHE)
Calomel	Hg/Hg_2Cl_2 , 1 M KCl	+ 0.280
Mercurous sulphate	Hg/Hg ₂ SO ₄ , sat K ₂ SO ₄ Hg/Hg ₂ SO ₄ , 0.5 M K ₂ SO ₄	+0.640 +0.680
Mercurous oxide	Hg/HgO, 1 M NaOH	+0.098
Silver chloride	Ag/AgCl, sat KCl	+0.197

Table 3.2. Potential of some typical refer	ence electrodes in ad	jueous solutions at 25 °C
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3.3.2.C. Cell design

Cells are usually constructed in glass or occasionally quartz, but for work in corrosive media and molten salt electrolytes there are polymer materials that can be used. The cell should have a frit for entry of an inert gas to deoxygenate the solution and may have separate anolyte and catholyte compartments. The compartments can be isolated by using ceramic materials, ion exchange membranes, or sintered glass. It is advantageous to have working and counter electrodes close together to minimise the cell resistance and to maximize the current which may be driven through the cell by the potentiostat. Furthermore, the working and counter electrodes should be arranged so that the current distribution over the whole of the working electrode is uniform. This can be achieved if all points on the surface of the electrode are equivalent with respect to the counter electrode. Good arrangements are a plane parallel configuration with the back of the working electrode shielded from the solution, or a small bead electrode at the center of the cylindrical counter electrode. The design features are important in high resistance solutions [74].

The reference compartment often contains a solution sealed tap that can be used in the closed position to create a junction between dissimilar solutions. It is recommended that the reference electrode have a Luggin capillary consisting of a tapered glass probe on a movable syringe barrel that enables the potential to be sampled close to the working electrode and the gap between the Luggin tip and the working electrode to be adjusted easily. The cell should be very easy to clean, therefore it should not contain corners or crevices. Glassware can be cleaned by immersion in strong oxidising solutions like aqua regia, permanganic, or chromic acids. Grease should never be used in the cell.

Electrochemical experiments should be carried out at constant temperature by immersing the cell in a thermostat bath. This minimises the density differences which lead to natural convection. Moreover it must not be forgotten that diffusion coefficients increase by 1-2% per degree increase in temperature, while the temperature variation of rate constants may be up to 10% per degree.

3.3.3. Technique: Cyclic voltammetry

In practice the potential of a mineral is not always the equilibrium value because the mineral reacts with the reagent components at different rates. In order to study such a dynamic state it is necessary to follow the changes occurring when the potential of the electrode varies. This is accomplished by imposing a potential on the electrode by an external power source. When this is done electric current flows through the electrode which is no longer in a state of equilibrium (at equilibrium, the net current flow is zero).

Measurement of the current at the working electrode under applied potential from an external source provides information on the electrode reactions. The technique is called cyclic voltammetry. The experimental curve showing the variation of current with applied potential is called a voltammogram. At specific potentials notable current flow occurs and this indicates a charge transfer reaction between the electrode and the solution. This reaction can be either anodic (oxidation) or cathodic (reduction). When it takes place in the anodic region (positive current), the reaction is called an anodic reaction and vice versa [74].

To describe the theory of cyclic voltammetry, consider a simple reversible reaction and assume that only O is initially present in solution.

$$O + ne^- \neq R \tag{3.55}$$

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If a very slow linear potential sweep is applied to such a system the voltammogram recorded will appear like a steady state I vs E curve. However, as the sweep rate increases, a peak of increasing height develops (Figure 3.13). To explain why this happens the shape of the concentration profiles of O vs potential should be considered.





Under steady conditions, it is assumed that concentrations beyond a certain distance from the electrode are maintained by natural convection. On the other hand, in the region next to the electrode, also known as the Nerst diffusion layer, the concentration gradients are essentially linear. The ratio of c_0/c_R in the Nernst equation is for a reversible reaction, and hence as the potential is made more negative the surface concentration of the reactant must decrease gradually. The concentration gradient is therefore increased, and hence the current. Eventually the surface concentration of the reactant approaches zero and the steady state concentration profile can not change further; then the current reaches a plateau value. When the sweep rate is increased, the diffusion layer does not have enough time to relax to its equilibrium condition; it does not extend far into solution, and the concentration profiles are not yet linear, as in Figure 3.14. As soon as a potential for O reduction is reached, the surface concentration of O decreases from its bulk value in order to



Figure 3.14. C vs x profiles at a. 90, b. 50, c. 0, d. -28, e. -128, f. -280 mV.

satisfy the Nernst equation and a concentration gradient is established (Figure 3.14a). As a result a current proportional to the value of this gradient at the electrode surface flows in the external circuit. Once this gradient exists it does not remain constant but starts to relax (decrease) due to diffusion. However at the same time, the electrode potential is still changing, and therefore the surface concentration of O is further decreased (Figures 3.14b-c) until it effectively reaches zero (Figure 3.14d). It can immediately be seen that for any given potential the concentration gradient at the surface is greater than for the steady state case, and therefore the current is larger. Once c_0 reaches zero the concentration gradient starts to decrease, due to the relaxation effect (Figure 3.14e-f) and the current must also decrease. Overall this behaviour gives rise to a peak shaped current-potential response as shown in Figure 3.13. It can also be seen that the concentration gradients at the surface, and hence current, will increase with sweep rate as a result of the shorter timescale of the experiment (less relaxation).

When the potential sweep is reversed, for slow sweeps, the current should directly track the forward one; however this is not true for faster sweeps. In these cases when the sweep is reversed, there is a significant concentration of R present near the electrode and R continues to be formed on the reverse sweep until the potential again approaches equilibrium. However, as the potential approaches equilibrium, the R present near the electrode starts to

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be reoxidised back to O (in order for the surface concentrations to be those required by the Nernst equation) and a reverse current flows. With the changing electrode potential the surface concentration of R eventually reaches zero. Using similar arguments as were used for the forward sweep, it can be deduced that the current on the reverse sweep will also exhibit a peaked response, but of course with opposite sign. A typical cyclic voltammogram is shown in Figure 3.15. It can be appreciated that current associated with an anodic process is lower as compared to that of the forward reduction process because there is a concentration difference driving R away from the electrode through the bulk solution and therefore, not all R cannot be reoxidized on the timescale of a cyclic voltammetric experiment.



Figure 3.15. A typical cyclic voltammogram.

In order to determine the exact form of cyclic voltammogram it is necessary to solve Fick's 2nd Law for O and R, equations (3.56) and (3.57), with the appropriate initial and boundary conditions,

$$\frac{dc_o}{dt} = D_o \frac{d^2 c_o}{dx^2}$$
(3.56)

$$\frac{dc_R}{dt} = D_R \frac{d^2 c_R}{dx^2}$$
(3.57)

With just O initially present in solution and assuming $D_0=D_R=D$ the initial and boundary conditions are,

$$t = 0, x > 0, c_0 = c_0^{\infty} c_R = 0$$
 (3.58)

$$x > 0, \quad x = \infty, \quad c_{ij} = c_{ij}^{2}, \quad C_{R} = 0$$
 (3.59)

$$t > 0, \quad x = 0, \quad D\left(\frac{dc_o}{dx}\right) + D\left(\frac{dc_R}{dx}\right) = 0$$
 (3.60)

and, therefore

$$\left(\frac{c_o}{c_R}\right)_{x=0} = \exp\left[\frac{nF}{RT} \left(E - E_e\right)\right]$$
(3.61)

$$-I = nFD \left(\frac{dc_0}{dx}\right)_{x=0}$$
(3.62)

For a sweep rate of v,

$$0 < t < \lambda \qquad E = E_1 - \nu t$$

$$t > \lambda \qquad E = E_1 - 2\nu\lambda + \nu t \qquad (3.63)$$

where E_1 is the initial potential and λ the time at which the sweep is reversed. An analytical solution is difficult because of the time dependent potential term, but it can be shown for

planar diffusion that

$$I_p = -0.04463 \ nF\left(\frac{nF}{RT}\right)^{1/2} c_0^{\sim} D^{1/2} v^{1/2}$$
(3.64)

This equation is called the Randles-Sevcik equation, where I_p , the peak current density is in A/cm², D is in cm²/s, v is in V/s, and c_0^{-1} is in mol/cm⁻³. The peak current density is proportional to the concentration of electroactive species and to the square root of the sweep rate and diffusion coefficient.

A reversible cyclic voltammogram (Figure 3.16a) can only be observed if both O and



Figure 3.16. Cyclic voltammograms of (a) reversible and (b) irreversible systems.

R are stable and the kinetics of the electron transfer process are fast, so that at all potentials and potential scan rates the electron transfer process on the surface is in equilibrium, and surface concentration follows the Nernst equation.

In the case of an irreversible system (Figure 3.16b), the rate of mass transport increases and becomes comparable to the rate of electron transfer, hence the mass transport can supply reducible material to the surface faster than the electrons can be made available to react with the reducible material. As a result, the shape of the curve modifies with increasing peak separation and reduced peak height from that of a reversible process.

As the peak for an irreversible process is more drawn out, the surface concentration of O changes more slowly with potential, and at the instant when the surface concentration effectively reaches zero, the concentration profile for O is less steep and flux to the surface lower. The most marked feature of a cyclic voltammogram of a totally irreversible system is the complete absence of a reverse peak. However, such a feature on its own does not necessarily imply an irreversible electron transfer process, but could be due to a fast subsequent chemical reaction. For the reversible case, the peak potential is independent of the sweep rate, while for the irreversible case, the peak potential varies with the sweep rate.

3.3.4. Review of electrochemical studies of pentlandite/pyrrhotite system

Oxidation of pyrrhotite has been investigated [78-83] using cyclic voltammetry at acidic (pH 4.6) and alkaline (pH 9.2) pHs. At pH 4.6, anodic peaks below 0.2 V(SHE) were assumed to arise from pyrrhotite oxidation to Fe(II), elemental sulphur, and sulphate,

$$Fe_{1.13}S \neq Fe^{2^{-}} + 1.13S + 2e^{-}$$
 (3.65)

$$Fe_{1,13}S + 4.52H_2O \neq Fe^{2^-} + 1.13SO_4^{2^-} + 9.04H^+ + 8.78e^-$$
 (3.66)

while above this potential, to Fe(III), elemental sulphur, and sulphate.

$$Fe_{1.13}S + 3H_2O \neq Fe(OH)_3 + 1.13S + 3H^2 + 3e^2$$
 (3.67)

$$Fe_{1.13}S + 7.52H_2O \Rightarrow Fe(OH)_3 + 1.13SO_4^2 + 12.04H^2 + 9.78e^2$$
 (3.68)

Cathodic peaks at 0.2 and -0.3 were attributed to reduction of $Fe(OH)_3$ to Fe(II) and S to H_2S , respectively.

$$Fe(OH)_3 + 3H^2 + e^2 = Fe^{2^2} + 3H_2O$$
(3.69)

$$S + 2H^2 + 2e^2 \neq H_2 S \tag{3.70}$$

At pH 9.2, an anodic peak at 0.5 was attributed to the oxidation of pyrrhotite to $Fe(OH)_3$ and sulphate. A single cathodic peak at -0.4 V was assigned to the reduction of $Fe(OH)_3$ to $Fe(OH)_3$.

Detailed electrochemical studies have been performed on the pyrrhotite and pentlandite system at pH 9 [78, 79]. Two anodic and three cathodic peaks were found on pyrrhotite.

Peaks	Reactions	
A_1	initial oxidation of FeS to Fe(OH) _x (S ₂)S	
A	oxidation of $(S_2)S$ to S and SO_4^{2-}	
C ₁	reduction of Fe(III) to Fe(II)	
C ₂	reduction of S^0 to S_2^{2-}	
C ₃	reduction of S_2^{2-} to $S^{2-}/Fe(II)$ reduction	

Table 3.3. Assignment of reactions associated with pyrrhotite

In the case of pentlandite, three anodic and four cathodic peaks were found,

Peaks	Reactions	
A	FeNiS to (FeS)(NiS); pH independent	
A,	metal site hydroxylation, formation of $Me(OH)_x(S_2)$	
<u>A</u> 3	oxidation of sulphur species, hydroxylation of residual Me(OH),	
C,	Ni(OH), reduction	
С,	Fe(III)(OH) _x reduction	
C,	S^0 reduction to $S_2^{2^-}$	
C₊	S_2^{2-} reduction to $S^{2-}/Fe(II)$ reduction	

Table 3.4. Assignment of reactions associated with pentlandite

In the presence of xanthate [78, 79], it was found that xanthate interaction with pentlandite is a two step process: first xanthate ion adsorbs, probably at nickel sites (a process known as "chemisorption" (reaction 3.71) and subsequently, dixanthogen forms from the chemisorbed xanthate (reaction 3.72).

$$Pn\| + X^{-} = Pn\|X + e^{-1}$$
(3.71)

$$Pn\|X + X^{*} \neq Pn\|X_{1} + e^{-1}$$

$$(3.72)$$

In the case of pyrrhotite however, chemisorption of xanthate was not detected. Instead the following sequence of reactions was postulated to account for the observed hydrophobicity of pyrrhotite:

$$Po_{\parallel} + H_2O \neq Po_{\parallel}(OH)[S]^* + H^* + e^*$$
 (3.73)

$$Po[(OH)[S]^{-} + X^{-} \neq Po[(OH)[S][X]$$

$$(3.74)$$

with xanthate then oxidizing on the surface to dixanthogen,

$$Po\|(OH)[S][X] + X^{-} \neq Po\|(OH)[S][X_{2}] + e^{-1}$$
(3.75)

In all the above oxidation (or anodic) reactions, the common cathodic reaction is reaction 4.57.

$$O_{2} + 2H_{2}O + 4e^{-} \neq 4OH^{-}$$
 (3.76)

i.e. oxygen acts as the final electron acceptor.

3.4. SPECTROELECTROCHEMISTRY

The structure of the electrode/electrolyte interface plays an important role in electrochemistry. On one hand, the distribution of charged particles and dipolar molecules in the electrode/electrolyte interface under the combined influence of diffusion and potential gradients determine the potential barrier, which strongly influences the rate of electrochemical reactions, i.e., reactions involving charge transfer through the interface. On the other hand, many electrode reactions proceed through adsorbed intermediates, which are produced during chemisorption of the reacting molecules on the electrode surface. The mechanisms of these reactions greatly depend on the nature of the electrode material, which determines the structure of the adsorbed intermediates.

Most of the *in situ* investigations concerning the structure of the electrode/electrolyte interface or the nature of the adsorbed intermediates were performed using electrochemical

measurements. However, the accuracy of such determinations is rather poor. Therefore, it is extremely difficult, if not impossible, to determine the reaction mechanism only by electrochemical measurements on a macroscopic scale.

The need for experimental methods allowing investigations of the electrode/electrolyte interface at the molecular level has become acute. More precisely, it has become apparent that physicochemical methods have to be used in conjunction with an electrochemical control of the electrode surface by applying a suitable potential. As one of the common physicochemical methods, infrared spectroscopy is an excellent method of probing a surface because it minimizes the amount of destruction of the surface layer as compared to other surface analysis methods and it can be conducted in the presence of (some) solution (i.e. *in situ*), which makes the information obtained more relevant to practice. Therefore, infrared spectroscopy in conjunction with electrochemistry has led to the development of "spectroelectrochemistry", especially following the introduction of the Fourier transform modification.

Spectroelectrochemistry has been applied in mineral processing research for investigating the interaction mechanisms between collector and sulphide mineral surfaces, due to the ability to investigate under *in situ* conditions.

An internal reflectance technique, *in situ* attenuated total reflection (ATR) spectroscopy, has been used to study the reaction products on sulphide mineral powders [70]. There are two electrochemical problems associated with this type of study. First, the electrode (powder) is often oxidized to some degree during sample preparation. This can result in adsorption of xanthate by simple ion exchange between the surface oxidation products and xanthate ions in solution. The second problem arises from the close proximity of the electrode is polarized to a negative potential in order to reduce the electrode surface, the counter electrode potential increases to a positive value. Hence, during a reduction cycle, common at the beginning of electrochemical studies, the xanthate ion may oxidise to dixanthogen at the counter electrode. If dixanthogen is produced, it can react rapidly with the sulphide mineral in a non-potential controlled reaction, which complicates interpretation of the results. The use of powder type electrodes also suffers from the inability to perform
structural and quantitative evaluation of the reaction products [42].

The other commonly used infrared technique is external reflectance spectroscopy. This technique can be applied both *ex situ* and *in situ* as shown in Figure 3.17.



Figure 3.17. Schematic diagram of (a) ex situ (b) in situ external reflection

Most characterization to date with this technique has been conducted *ex situ*. The examples include both characterization of the orientation of xanthate on a surface and investigation of xanthate adsorption under electrochemical control using metal and sulphide mineral electrodes [34-42].

In the present work, a new *in situ* external reflection spectroelectrochemical cell has been designed. This cell consists of two Teflon cell bodies, top and bottom (Figure 3.18). The top piece holds the working electrode which can be positioned vertically by means of a Teflon screw. The bottom piece contains two ports, able to accommodate the counter electrode and the reference electrode. A CaF_2 window is mounted under the cell. The advantages of this cell can be summarized as: uniform applied potential on the working electrode, high throughput, and the ability to determine molecular orientations of the adsorbed species.



Figure 3.18. Spectroelectrochemical cell.

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CHAPTER 3. SURFACE ANALYSIS

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CHAPTER 4

XANTHATE ADSORPTION ON PENTLANDITE/PYRRHOTITE SYSTEM: SINGLE MINERALS

4.1. EXPERIMENTAL

4.1.1. Electrode preparation

Hand picked specimens of minerals were obtained from Ward's Natural Science Establishment, New York. Carefully selected specimens were cut and ground to circular shape of 5 mm diameter using 1200 grid polishing paper. After connecting a copper wire to the mineral with graphite paste (DOTITE Electroconductives), the electrodes were prepared by mounting these mineral specimens with a nonconducting epoxy in a glass tube with an outside diameter of 11 mm. The electrode was polished on a LeclothTM lapping cloth using 0.3 μ m alumina powder as finishing medium. The polished electrode was washed with distilled water followed by ultrasonication in ethanol for 2 mins. After blow-drying with dry nitrogen, the electrode was transferred immediately to the electrochemical cell where a reducing potential was applied for 2 minutes to remove possible oxidation products formed during the sample preparation. With this procedure, reproducible electrochemical response was obtained.

4.1.2. Mineral particles and reagents

Pyrrhotite and pentlandite samples were obtained from the Strathcora Mill, Falconbridge Ltd and Ward's Natural Science Establishment, New York, respectively. The samples were crushed and screened to various size fractions, and then cleaned with a hand magnet. The processed samples were sealed in a plastic container and stored in a freezer at -4 °C.

Sodium iso-butyl xanthate, NaIX, (American Cyanamid) was purified by repetitively dissolving in acetone and recrystallizing from petroleum ether. The purified xanthate was stored in petroleum ether. The NaIX concentrations were fixed at $2x10^{-3}$ and $5x10^{-5}$ M for cyclic voltammetry and spectroscopic measurements (including UV & FTIR/ATR), respectively.

CHAPTER 4. XANTHATE ADSORPTION ON PENTLANDITE/PYRRHOTITE SYSTEM: SINGLE MINERALS

The pH of the solutions was adjusted to 9.2 using lime for all experiments unless otherwise stated. In the case of cyclic voltammetry measurements, experiments were conducted in 0.01 M KCl electrolyte (to increase solution conductivity).

Nickel sulphate was used to prepare Ni solutions at 10 and 2 ppm concentrations for cyclic voltammetry and spectroscopic measurements, respectively. For cyclic voltammetry, the electrode was treated with 10 ppm Ni solution in a beaker for 10 minutes, washed and then transferred to the electrochemical cell to which xanthate was added. For ATR measurements, the mineral powder was treated with 2 ppm Ni solution in a beaker for 20 minutes, washed and then xanthate solution was introduced to the beaker.

Diethylenetriamine (DETA, 100%) from Aldrich Chemical Co. was reagent grade. The concentrations were 40 and 10 ppm for cyclic voltammetry and spectroscopic measurements, respectively.

Sodium meta-bisulfite Na₂S₂O₅ from Fisher Scientific was reagent grade. The concentration was 10 ppm.

4.1.3. Cyclic voltammetry

All cyclic voltammetry measurements were performed using an EG & G Princeton Applied Research Potentiostat/Galvanostat Model 273 with the Head-Start software. A standard three electrode electrochemical cell (Figure 3.12) was used, with Saturated Calomel Electrode (SCE) being the reference electrode, the mineral the working electrode and the platinum wire (2mm in diameter) the counter electrode. Potentials quoted are on the SCE scale.

The experiments were conducted with pentlandite and pyrrhotite electrodes in the presence and absence of $2x10^{-3}$ M NaIX. The solution was not nitrogenated because in practice, it is open to the environment.

4.1.4. External reflectance FTIR (Fourier Transform Infrared Spectroscopy)

A Bruker IFS66 spectrometer equipped with a liquid nitrogen cooled MCT detector was employed to record *in situ* infrared spectra using an external reflectance attachment (Spectratech Baseline with a fixed incident angle of 45°) with the *in situ* spectroelectrochemical cell (Figure 3.18). The spectra were taken at a wavenumber resolution of 4 cm⁻¹ by co-adding 250 scans in the 4000 - 500 cm⁻¹ region. The IR unit used is defined as log (R/R₀), where R₀ is the reflectivity of freshly polished clean mineral electrode not subjected to an applied potential.

For IR analysis, the electrode was polarized cathodically at -1.0 V for a period of 15 minutes to remove any oxidation products formed during sample preparation. The electrode was brought down against the cell window after it was held at a given polarization potential for a period of 10 minutes. Spectra were taken at a given potential which was stepped anodically.

4.1.5. Attenuated total reflectance (ATR) FTIR

For the powder samples, ATR spectra were obtained using a baseline horizontal ATR sampling unit (Spectra Tech) with the Bruker IFS66 spectrometer. The spectra were taken at a wavenumber resolution of 4 cm⁻¹ by co-adding 250 scans. The clean ATR crystal was used as background. The ATR unit used is defined as ATR (*Init* = $A(v) \times v/100$, where A(v) is the absorbance at wavelength v.

For IR analysis, a 0.5 gram sample of mineral (-200 +400 mesh fraction) was placed in a 100 mL beaker. Fifty-five mL of NaIX solution ($5x10^{-5}$ M) was introduced into the beaker and the slurry stirred gently with a glass bar for 1 min. The beaker was then shaken on a shaker (New Brunswick Scientific) at 250 rpm for 20 minutes. Then a high solid aliquot was taken using a pipette and placed on a strip of filter paper which absorbed some supernatant, but left a thin layer of liquid on the mineral surface. After being uniformly

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covered by particles, the filter paper was placed immediately on a ZnSe ATR crystal with the mineral particles against the crystal and spectra were collected. The technique was considered as pseudo in situ because the mineral samples remained in contact with supernatant during the spectral acquisition. There was no attempt to control the potential with this technique.

4.1.6. UV spectroscopic measurements

A Milton Roy Spectronic 1201 UV spectrophotometer with the SpecScan software was used to monitor the absorbance of xanthate from solution. A narrow scan was conducted from 190-400 nm and the absorbance at wavelength of 300.1 nm was recorded.

For UV analysis, a 0.5 gram mineral sample (-200 +400 mesh fraction) was placed in a 100 mL beaker. Fifty-five mL NaIX solution (5x10⁻⁵ M) was introduced into the beaker and the slurry stirred gently with a glass bar for 1 min. The beaker was then shaken on a shaker (New Brunswick Scientific) at 250 rpm for 20 minutes. Solution was filtered with fast speed qualitative (No:4) filter paper. The filtered solution was transferred to a quartz crystal cell and replaced in the UV spectrometer sample compartment. The spectrum was acquired immediately.

4.2. RESULTS

4.2.1. Effect of xanthate

4.2.1.A. Cyclic Voltammetry

Cyclic voltammograms of pentlandite and pyrrhotite in the presence and absence of NaIX are shown in Figures 4.1 and 4.2, respectively.

For pentlandite, two small anodic peaks (A_1, A_2) and two small cathodic peaks (C_1, A_2) C_{2}) were found in the absence of xanthate. These peaks were attributed to the processes [1] listed in Table 4.1.

One anodic peak (A_{1x}) was observed in the presence of xanthate. Electrochemical

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Figure 4.1. Cyclic voltammograms of pentlandite.



Figure 4.2. Cyclic voltammograms of pyrrhotite.

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investigations [1] have suggested that xanthate interaction with pentlandite is a two step process: first xanthate ion adsorbs, probably at nickel sites (a process known as "chemisorption", reaction (3.71)) and subsequently, dixanthogen forms from the chemisorbed xanthate (reaction (3.72)).

Peaks	Reactions
A	Metal site hydroxylation; formation of Me(OH) _x (S ₂)
A ₂	Oxidation of sulphur species and hydroxylation of residual Me(OH) _x
C ₁	Fe(III)(OH) _x reduction
С,	S^0 reduction to $S_2^{2^-}$

Table 4.1. Attributed reactions for pentlandite

For pyrrhotite, two small anodic peaks (A_1, A_2) and three small cathodic peaks (C_1, A_2) C_2, C_3) were found in the absence of xanthate. These peaks were attributed to the processes [1-6] listed in Table 4.2.

Table 4.2. Attributed reactions for pyrrhotite

Peaks	Reactions
A ₁	Initial oxidation of FeS to $Fe(OH)_X(S_2)S$
A ₂	Oxidation of $(S_2)S$ to S and SO_4^{2-}
C ₁	Reduction of Fe(III) to Fe(II)
C ₂	S^{0} reduction to S_{2}^{2}
C ₃	reduction of $S_2^{2^{-}}$ to $S^{2^{-}}/Fe(\Pi)$ reduction

In the case of pyrrhotite, chemisorption of xanthate was not detected. Instead the sequence of reactions (3.73-75) was postulated to account for the observed anodic peak $(A_{1X}).$

4.2.1.B. External reflectance FTIR (Fourier Transform Infrared Spectroscopy)

In situ external reflection spectra of pentlandite and pyrrhotite at given applied potentials are shown in Figures 4.3 and 4.4, respectively. No xanthate adsorption was detected at low potentials. The spectrum showed xanthate adsorption on both minerals starting at ca 0 V. Xanthate adsorption took place in the form of dixanthogen with characteristic peaks at 1240 (C-O-C), 1260 (S-C-S) and 1019 (S-C-S) cm⁻¹ [7-9].

4.2.1.C. Attenuated total reflectance (ATR) FTIR

ATR spectra of xanthate adsorption on pentlandite and pyrrhotite are shown in Figure 4.5. As can be seen, adsorbed xanthate is in the form dixanthogen with the characteristic S-C-S stretching vibration peaks at 1263, 1048 and 1027 cm⁻¹ [7-10]. From the peak height, xanthate adsorption on pentlandite appears to be higher than on pyrrhotite.

4.2.1.D. UV spectroscopic measurements

Figure 4.6 shows residual xanthate in solution after contact with pentlandite and pyrrhotite. As shown, the amount was lower in the presence of pentlandite compared to pyrrhotite, suggesting that xanthate adsorption on pentlandite was higher than on pyrrhotite. This confirms the observation in Figure 4.5.

4.2.2. Effect of Ni ions

4.2.2.A. Cyclic voltammetry

Cyclic voltammograms of pentlandite and pyrrhotite in the absence of NaIX are shown in Figures 4.7 and 4.8, respectively; the voltammograms for Ni treated minerals were similar to those without Ni treatment. This finding suggests that the Ni ions are not involved in any

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Figure 4.3. ER reflectance spectra of pentlandite.



Figure 4.4. ER reflectance spectra of pyrrhotite.

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Figure 4.5. ATR spectra of pentlandite and pyrrhotite.



Figure 4.6. The amount of residual xanthate in solution: Initial concentration 50x10⁻⁶ М.

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Figure 4.7. Cyclic voltammograms of pentlandite in the absence of NaIX.



Figure 4.8. Cyclic voltammograms of pyrrhotite in the absence of NaIX.

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significant electron transfer processes over this potential range.

In the presence of NaIX, voltammograms for pentlandite and pyrrhotite are shown in Figures 4.9 and 4.10, respectively. The voltammogram for Ni treated pyrrhotite in particular was different from the untreated case. The dixanthogen anodic peak (A_{1X}) at around 0.1 V was enhanced in the presence of Ni suggesting the possible activation of minerals or a catalytic effect of Ni ions in promoting dixanthogen formation [11].

4.2.2.B. Attenuated total reflectance (ATR) FTIR

The ATR spectra of pentlandite and pyrrhotite are shown in Figures 4.11 and 4.12. respectively. Xanthate adsorption on nickel treated minerals was higher than in the absence of treatment. This again suggests that minerals are activated by Ni ions.

4.2.2.C. UV spectroscopic measurements

Residual xanthate concentration in the supernatant of pentlandite and pyrrhotite suspension is shown in Figure 4.13. The amount was lower in the presence of Ni ions for pentlandite and pyrrhotite as compared to that in the absence of Ni ions. This also supports the possible Ni activation of both minerals. Xanthate adsorption on pentlandite remained higher than on pyrrhotite even with Ni treatment.

4.2.3. Effect of diethylenetriamine (DETA)

4.2.3.A. Cyclic voltammetry

Cyclic voltammetry measurements were performed using a platinum electrode as a baseline to establish the electrochemical behaviour of DETA in the presence and absence of xanthate. The voltammograms in the absence of xanthate are shown in Figure 4.14. There is no indication of any characteristic electrochemical reactions, as expected because amines only



Figure 4.9. Cyclic voltammograms of pentlandite in the presence of NaIX.



Figure 4.10. Cyclic voltammograms of pyrrhotite in the presence of NaIX.

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Figure 4.11. ATR spectra of pentlandite.



Figure 4.12. ATR spectra of pyrrhotite.



Figure 4.13. The amount of residual xanthate in solution.



Figure 4.14. Cyclic voltammograms of platinum in the absence of NaIX.

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tend to oxidize in the potential range of 1.0 - 1.5 V (SCE) [12] which is above the range of potential applied here. Therefore, the anodic current starting around 0 V with DETA can not be accounted for by oxidation of DETA itself. However, it might be due to the surface modification of platinum by DETA molecules, or a "cleaning" effect.

The voltammogram in the presence of xanthate is shown in Figure 4.15. There is an anodic peak (A_{LX}) beginning around 0 V, attributed to xanthate oxidation to dixanthogen [13, 14]. This peak is reduced and shifted to a higher potential in the presence of DETA. This may be due to possible complex formation between DETA and xanthate [15].



Figure 4.15. Cyclic voltammograms of platinum in the presence of NaIX.

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Voltammograms of pentlandite and pyrrhotite in the absence of xanthate are shown in Figures 4.16 and 4.17. There was a general small increase in anodic currents as seen on the platinum electrode with DETA. This again could be due to the cleaning effect of DETA on minerals which enhanced their oxidation.

Voltammograms of pentlandite and pyrrhotite in the presence of xanthate are shown in Figures 4.18 and 4.19, respectively. The anodic peak (A_{1X}) for pentlandite disappeared in the presence of DETA suggesting possible interaction between DETA and xanthate or perhaps a blocking effect of DETA covering Ni sites which otherwise act to promote xanthate adsorption. However, the disappearance of the anodic peak on pyrrhotite was not as significant as on pentlandite probably due to the scarcity of Ni sites on pyrrhotite. The same effect was observed on Ni treated pentlandite (Figures 4.20). However, the disappearance of the anodic peak on pyrrhotite was more significant after Ni treatment (Figure 4.21), perhaps because of the establishment of Ni sites on the pyrrhotite.

4.2.3.B. Attenuated total reflectance (ATR) FTIR

The ATR spectra of pentlandite and pyrrhotite are shown in Figures 4.22 and 4.23, respectively. Xanthate adsorption on minerals decreased with DETA but more significantly with pentlandite. The same trend was observed in the case of Ni treated pentlandite and pyrrhotite (Figures 4.24-25), but the disappearance of xanthate with Ni treated pyrrhotite was more significant compared to untreated pyrrhotite. These findings agree with those by cyclic voltammetry.

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Figure 4.16. Cyclic voltammograms of pentlandite in the absence of NaIX.



Figure 4.17. Cyclic voltammograms of pyrrhotite in the absence of NaIX.

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Figure 4.18. Cyclic voltammograms of pentlandite in the presence of NaIX.



Figure 4.19. Cyclic voltammograms of pyrrhotite in the presence of NaIX.

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Figure 4.20. Cyclic voltammograms of Ni treated pentlandite in the presence of NaIX.



Figure 4.21. Cyclic voltammograms of Ni treated pyrrhotite in the presence of NaIX.

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Figure 4.22. ATR spectra of pentlandite.



Figure 4.23. ATR spectra of pyrrhotite.

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Figure 4.24. ATR spectra of Ni treated pentlandite.



Figure 4.25. ATR spectra of Ni treated pyrrhotite.

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4.2.3.C. UV spectroscopic measurements

Residual xanthate in the presence of pentlandite and pyrrhotite is shown in Figure 4.26. The amount was higher with DETA for both minerals with and without Ni treatment. The UV results were therefore in agreement with the ATR spectroscopic and cyclic voltammetry measurements



Figure 4.26. The amount of residual xanthate in solution.

4.2.4. Effect of meta-bisulfite (S₂O₅²⁻) (MBS) and DETA 4.2.4.A. Attenuated total reflectance (ATR) FTIR

ATR spectra of pentlandite and pyrrhotite are shown in Figures 4.27 and 4.28, respectively. Xanthate adsorption was decreased slightly in the presence of MBS. A further decrease was observed upon addition of DETA, but remained more compared to DETA alone. Notably, the decrease on pentlandite was more than on pyrrhotite as observed with DETA alone (Section 4.2.3.B.).

ATR spectra of Ni treated pentlandite and pyrrhotite are shown in Figures 4.29 and 4.30, respectively. The effect of reagents on xanthate adsorption was similar to that without Ni treatment

4.2.4.B UV spectroscopic measurements

Residual xanthate concentrations are shown in Figure 4.31. The amount was higher in the presence MBS and further increased when DETA was also present. The same trend was found for Ni treated minerals. The effect was again more significant on pentlandite.

4.2.5. Effect of substituting soda ash for lime 4.2.5.A. Attenuated total reflectance (ATR) FTIR

The effect of pH being adjusted by lime and soda ash is compared in Figure 4.32 for pentlandite and pyrrhotite. Xanthate adsorption on both minerals was decreased when pH was adjusted by soda ash. A similar effect was observed in the case of Ni treated minerals, shown in Figure 4.33.

The effect of DETA, MBS and DETA+MBS is shown in Figures 4.34 and 4.35. The effect was similar to that observed when pH was adjusted by lime.

The effect of DETA, MBS and DETA+MBS on Ni treated pentlandite and pyrrhotite is shown in Figures 4.36 and 4.37. Their effect is similar to that for pH adjusted by lime.

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Figure 4.27. ATR spectra of pentlandite.



Figure 4.28. ATR spectra of pyrrhotite.

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Figure 4.29. ATR spectra of Ni treated pentlandite.



Figure 4.30. ATR spectra of Ni treated pyrrhotite.



Figure 4.31. The amount of residual xanthate in solution.
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Figure 4.32. ATR spectra of pentlandite and pyrrhotite.



Figure 4.33. ATR spectra of Ni treated pentlandite and pyrrhotite.

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Figure 4.34. ATR spectra of pentlandite with soda ash adjusted pH.



Figure 4.35. ATR spectra of pyrrhotite with soda ash adjusted pH.

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Figure 4.36. ATR spectra of Ni treated pentlandite with soda ash adjusted pH.



Figure 4.37. ATR spectra of Ni treated pyrrhotite with soda ash adjusted pH.

4.3. DISCUSSION

4.3.1. Xanthate adsorption

Experimental evidence suggests that xanthate adsorption on pentlandite and pyrrhotite is in the form dixanthogen and the adsorption on pentlandite is higher than on pyrrhotite. confirming the results of others [2, 10].

It is also apparent that Ni treatment causes increased dixanthogen adsorption on both minerals. This can be attributed to an "activation effect", the adsorbed Ni acting as sites for xanthate adsorption and oxidation to dixanthogen. The active species could be the ion. various hydroxy species or nickel sulphide. Heavy metal sulfides (in this case Ni) are more stable (or less soluble) than pyrrhotite. It has been shown that in the presence of Ni ions pyrrhotite surface is converted to millerite (NiS) [16]. This was also evident from solution analysis giving rise to more Fe in solution [17].

An effect of DETA on xanthate uptake is evident as dixanthogen adsorption on pentlandite, in particular, was significantly reduced. This might be due to complex formation between DETA and xanthate, a complexation effect of DETA with Ni sites which otherwise act to promote xanthate adsorption, or a cleaning effect with DETA removing activating surface species [18-24]. In the case of pyrrhotite interestingly, dixanthogen adsorption did not reduce significantly in the presence of DETA possibly due to the lack of Ni sites. After Ni treatment, the same general observations were apparent for pentlandite, but for pyrrhotite, the effect of DETA was more evident possibly due to the initial presence of Ni on the surface which is removed.

The effect of MBS on dixanthogen adsorption was not as significant as DETA alone. The partial disappearance of dixanthogen with MBS can also be attributed to solubilization of Ni from the surface. The effect of MBS was less significant for pyrrhotite possibly because MBS does not solubilize Fe as well as Ni [22]. However, in the case of Ni treated minerals, the effect of MBS was enhanced due to the presence of Ni ions on the surface. The combination of DETA and MBS reduced the dixanthogen further compared to MBS and DETA alone. This might be because MBS facilitates the solubilization of Ni ions causing more effective action of DETA or simply reflects the sum of the independent effects of these reagents.

The effect of substituting soda ash for lime resulted in reduced adsorption of dixanthogen on the minerals. This suggests a type of "competition" between xanthate and carbonate ions. For example, carbonate complexes may form at the same Ni "activation" sites which promote xanthate adsorption, or the "complexes" may be as precipitates which disperse, effectively removing the activation sites [25]. It has also been suggested that activation by Ca ions on sulphide minerals occurs which might also favour xanthate adsorption when pH is adjusted by lime [26]. The general effects of DETA, MBS and DETA+MBS were similar whether pH was adjusted by either soda ash or lime for minerals both with and without Ni treatment.

4.3.2. Significance to flotation

Overall, these findings suggest that in the case of single minerals xanthate adsorption readily occurs on both minerals. Although xanthate adsorbs on pyrrhotite without metal ion activation, the concentration of xanthate required for significant adsorption is higher than that required for pentlandite. Also, the potential at which xanthate adsorption occurs is higher. Both these observations suggest a basis for separation by flotation. When pyrrhotite is contaminated by Ni ions, however, xanthate adsorbs at low concentration and low potentials, making separation more difficult.

It is interesting to note that the effect of depressing agents (DETA, MBS or DETA+MBS) on reducing xanthate adsorption was more significant on pentlandite than on pyrrhotite. This raises a question regarding the selectivity of these depressants. An important point pursued in this thesis is the effect the minerals have on each other when mixed. This is a closer approximation to the real flotation environment. The mixed pentlandite and pyrrhotite experiments are discussed in the next chapter.

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4.4. CONCLUSIONS

- 1. Xanthate adsorption on both minerals is in the form of dixanthogen.
- 2. Xanthate adsorption on pentlandite is higher than on pyrrhotite.
- 3. Ni treatment enhances xanthate adsorption on both minerals.
- 4. DETA reduces the dixanthogen adsorption on pentlandite significantly, but less significantly on pyrrhotite; Ni treatment enhances the effect of DETA on pyrrhotite.
- 5. The effect of MBS on dixanthogen adsorption on both minerals is not as significant as DETA alone.
- 6. The combination of DETA and MBS resulted in more reduction in dixanthogen adsorption than either alone.
- 7. Xanthate adsorption on both minerals is reduced when the pH is adjusted by soda ash instead of lime.
- 8. The general effects of DETA, MBS and DETA+MBS were similar whether pH was adjusted by either soda ash or lime.

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CHAPTER 5

XANTHATE ADSORPTION ON PENTLANDITE/PYRRHOTITE SYSTEM: MIXED MINERALS

5.1. EXPERIMENTAL

5.1.1. Attenuated total reflectance (ATR) FTIR

For IR analysis, a 0.5 gram sample of each mineral (-200 +400 mesh fraction) was placed in a 100 mL beaker. Fifty-five mL of 5×10^{-5} M NaIX solution was introduced into the beaker and the contents stirred gently with a glass bar for 1 min. The beaker was then agitated on a shaker (New Brunswick Scientific) at 250 rpm for 20 minutes. A high solid aliquot of both minerals was taken using a pipet and placed on a glass dish and pyrrhotite was separated from pentlandite using an automagnet separator (Gilson). The separated minerals were then mounted on the ZnSe crystal as described for the case of single minerals

5.1.2. Open circuit (rest) potential measurements

All open circuit potential measurements were performed using the Potentiostat described before. Solution pH was adjusted to pH 9.2 using lime unless otherwise stated. Open circuit potentials of pentlandite and pyrrhotite electrodes were measured in the presence and absence of 2×10^{-3} M NaIX. To simulate the mixed mineral system, open circuit potentials were measured in the presence of powder of the second mineral and in some cases by maintaining physical contact with the powder. As a check, potentials were also recorded for the mineral in contact with its own powder. Potentials quoted are on the SCE scale.

5.2. RESULTS

5.2.1. Effect of xanthate

5.2.1.A. Attenuated total reflectance (ATR) FTIR

The ATR spectra, along with that for single minerals, are shown in Figures 5.1 and 5.2 for pentlandite and pyrrhotite, respectively. Comparing the mixed to single mineral cases,

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Figure 5.1. ATR spectra of pentlandite.



Figure 5.2. ATR spectra of pyrrhotite.

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the amount of dixanthogen on pentlandite increased while that on pyrrhotite decreased. These results indicate that mineral contact enhances the difference in dixanthogen formation between the two minerals in favour of pentlandite.

5.2.1.B. Open circuit (rest) potential measurements

Figure 5.3 shows the results of open circuit potential measurements. In all cases, the potential changed with time, reaching a constant (equilibrium) value after about 10 mins.



Figure 5.3. Open circuit potentials of pentlandite and pyrrhotite. Note, Po/Pn+X refers to Po in contact with Pn in presence of xanthate, similarly Pn/Po+X.

The equilibrium open circuit potential for pentlandite was found to be ca. 100 mV (SCE) compared to ca. 60 mV for pyrrhotite, which corresponds to the reported order [22]. In the presence of 2×10^{-3} M xanthate, the equilibrium potentials are lowered for both minerals as expected since xanthate acts as a reducing agent in these systems [22]. However, now the

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value for pyrrhotite (40 mV) is higher than that for pentlandite (-55 mV), in reverse order to the situation in the absence of xanthate. These potentials are in the range for xanthate oxidation to dixanthogen and oxygen reduction to hydroxide on various sulphide mineral surfaces [22, 23]. Although xanthate adsorbs on both minerals, the greater reduction in the open circuit potential for pentlandite than for pyrrhotite indicates that xanthate uptake is preferential on pentlandite, as confirmed by the spectroscopic studies.

Figure 5.3 also shows that the open circuit potential of pyrrhotite reduced further to ca. 0 mV when in contact with pentlandite particles (Po/Pn+X), while that for pentlandite increased from -55 to -30 mV when in contact with pyrrhotite particles (Pn/Po+X).

5.2.2. Effect of Ni ions

5.2.2.A. Attenuated total reflectance (ATR) FTIR

The spectra for pentlandite and pyrrhotite are given in Figures 5.4 and 5.5. respectively. After Ni treatment, the same effect of mixed minerals described above is found except that xanthate adsorption on pyrrhotite appears to increase slightly.

5.2.3. Effect of DETA

5.2.3.A. Attenuated total reflectance (ATR) FTIR

The ATR spectra of pentlandite and pyrrhotite are given in Figures 5.6. and 5.7, respectively. Xanthate adsorption on pentlandite decreased in the presence of DETA but this was less significant compared to the case with the single mineral. In the case of pyrrhotite, the decrease in xanthate adsorption was more significant in the mixed mineral case compared to that of pyrrhotite on its own.

ATR spectra of Ni treated pentlandite and pyrrhotite are shown in Figures 5.8 and 5.9, respectively. The effect of DETA is similar to that without Ni treatment.

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Figure 5.4. ATR spectra of pentlandite.



Figure 5.5. ATR spectra of pyrrhotite.

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Figure 5.6. ATR spectra of pentlandite.



Figure 5.7. ATR spectra of pyrrhotite.

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Figure 5.8. ATR spectra of Ni treated pentlandite.



Figure 5.9. ATR spectra of Ni treated pyrrhotite.

5.2.4. Effect of MBS and DETA

5.2.4.A. Attenuated total reflectance (ATR) FTIR

The ATR spectra of pentlandite and pyrrhotite are shown in Figures 5.10 and 5.11, respectively. Xanthate adsorption on both minerals did not change in the presence of MBS and decreased with the addition of DETA.

The spectra of Ni treated pentlandite and pyrrhotite are shown in Figures 5.12 and 5.13, respectively. Similar effects were observed as in the case without Ni treatment.

5.2.5. Effect of substituting soda ash for lime

5.2.5.A. Attenuated total reflectance (ATR) FTIR

The spectra of pentlandite and pyrrhotite are shown in Figures 5.14 and 5.15, respectively. Comparing lime with soda ash, the effects of DETA, MBS and DETA+MBS on xanthate adsorption on pentlandite were similar. In the case of pyrrhotite, however, when soda ash replaced lime, xanthate adsorption was below the detection limit in the presence of MBS+DETA,

The spectra of Ni treated pentlandite and pyrrhotite (Figures 5.16 and 5.17, respectively) show that the effect was similar to that without Ni ion treatment. Again, xanthate adsorption was below the detection limit in the presence of MBS+DETA when soda ash was used.

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Figure 5.10. ATR spectra of pentlandite.



Figure 5.11. ATR spectra of pyrrhotite.

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Figure 5.12. ATR spectra of Ni treated pentlandite.



Figure 5.13. ATR spectra of Ni treated pyrrhotite.

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Figure 5.14. ATR spectra of pentlandite with soda ash adjusted pH.



Figure 5.15. ATR spectra of pyrrhotite with soda ash adjusted pH.

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Figure 5.16. ATR spectra of Ni treated pentlandite with soda ash adjusted pH.



Figure 5.17. ATR spectra of Ni treated pyrrhotite with soda ash adjusted pH.

5.3. DISCUSSION

5.3.1. Xanthate adsorption

The present results clearly show that mineral interactions play a significant role in xanthate uptake in the pentlandite/pyrrhotite system. A mixed potential model can be used to help interpret the observations.

The open circuit potentials in the presence of xanthate showed the order to be $E_{Po\cdot X}$ > $E_{Pn X}$. Assuming the anodic reaction is the oxidation of xanthate to dixanthogen (the IR results show only X₂) and the cathodic reaction is reduction of oxygen, then a schematic Current-Potential diagram can be constructed (Figure 5.18).



Figure 5.18. Schematically constructed Current (I) vs Potential (V) diagram using open circuit potentials.

This represents the current vs potential for the anodic and cathodic reaction couples associated with the minerals. The open circuit potential represents the equivalence of the anodic and cathodic currents (the dotted vertical lines). When together, the system exhibits

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a mixed potential E_m somewhere between the two individual potentials. The E_m again represents an equivalence of anodic and cathodic currents but now the anodic reaction is $2X^2 - X_2$ on Pn and the cathodic reaction is oxygen reduction on Po. A physical interpretation for the case of direct physical contact is sketched in Figure 5.19: the xanthate to dixanthogen oxidation reaction takes place on pentlandite, the released electron is transferred to pyrrhotite and is accepted by the oxygen which reduces to OH².



Figure 5.19. Schematic representation of galvanic interaction between pentlandite and pyrrhotite in the presence of xanthate.

There are at least two aspects of the explanation that merit attention: it appears to apply even if the minerals are not in direct contact; and, the relative open circuit potentials that support the explanation are those in the presence of xanthate.

When the two sulphide minerals are together in the same solution they contribute to the system (or pulp) potential which then falls somewhere between the reversible potentials of the two couples. Thus the system will be oxidizing to one couple, in this case the $Pn(X/X_2/O_2/OH^2)$ couple on pentlandite, and reducing to the other, i.e. the $Po(X/X_2/O_2/OH^2)$ couple on pentlandite, on this basis, is not a requirement but it will add a galvanic interaction (Figure 5.19) to significantly enhance the effect (as observed).

In the absence of xanthate, the relative rest potentials suggest pyrrhotite should be oxidized when in contact with pentlandite. However, the relevant oxidation reaction is not of the mineral but of adsorbed xanthate going to dixanthogen. Hence the rest potentials in the presence of xanthate are the relevant ones. The reason the order of rest potentials changes

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upon addition of xanthate indicates the pentlandite is more reactive to xanthate. This could reflect the different electrochemical reaction pathways (reactions (3.71) and (3.72) for Pn vs (3.73), (3.74) and (3.75) for Po) with Ni in the Pn initiating and promoting the reaction with xanthate; or, that some xanthate adsorbs initially through non electrochemical routes, e.g. ion exchange with surface species, and this is more favourable on pentlandite. Whatever the initiating mechanism, pentlandite adsorbs more X⁻ than pyrrhotite, causing the order of the open circuit potentials to reverse which then sustains the preferential oxidation of X⁻ to X₂ on pentlandite.

As with the single minerals, the depressing agents DETA, MBS and DETA+MBS also decreased dixanthogen adsorption in the mixed mineral case (Figure 5.20). However, compared to single minerals, the ratio of adsorption on pentlandite to pyrrhotite increased substantially (from < 2:1 to > 4:1) (Figure 5.20).



Figure 5.20. ATR spectra peak heights at 1027 cm⁻¹ for pentlandite and pyrrhotite in the case of single and mixed minerals when pH is adjusted by lime.

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The mixed mineral D+M case and the single mineral X case provide an instructive comparison. The level of dixanthogen adsorption on pentlandite is similar but that on pyrrhotite has been significantly reduced. This suggests the importance of studying minerals in physical contact, a condition which is a closer approximation to real flotation. Single minerals doped with Ni ions, as one of the products of interaction, clearly does not substitute for contact itself.

The same pattern was seen when pH was adjusted with soda ash (Figure 5.21). In the presence of DETA+MBS the difference between the minerals was very significant with dixanthogen on pyrrhotite being virtually below the detection limit.



Figure 5.21. ATR spectra peak heights at 1027 cm⁻¹ for pentlandite and pyrrhotite in the case of single and mixed minerals when pH is adjusted by soda ash.

5.3.2. Significance to flotation

The addition of depressants reduced dixanthogen adsorption almost equally on both minerals. This means that the high relative adsorption in favour of the pentlandite, induced by the mineral mix, remained. Flotation selectivity, while requiring preferential collector adsorption on one mineral would also benefit if adsorption on the second was below some threshold to prevent its flotation. The results give a suggestion that this is the mechanism at play here. Consider the D+M case: the relative pentlandite:pyrrhotite adsorption is ca 4:1 while the adsorption on pyrrhotite is now less than half what it was in the single mineral case (and that on pentlandite is virtually the same as it was). The ratio with soda ash is even higher with the apparent additional advantage that dixanthogen adsorption on pyrrhotite is lower (still considering the D+M case); however now, while the two criteria have been met (preferential adsorption on pentlandite and below threshold adsorption on pyrrhotite), the penalty is reduced dixanthogen on pentlandite and therefore, perhaps slower flotation. As always in flotation we seek a compromise.

This interpretation would not have emerged based on the single mineral results. Indeed, these are quite confusing suggesting that depressants had more impact on the pentlandite. If we did not know the process that result may seem reasonable since more xanthate was adsorbed on pentlandite in the first place, i.e., it had greater potential to be affected. But, an additional factor is at play - the interaction between the two minerals that we seek to separate - and this alters the situation sufficiently for the depressants to work as observed in plant practice.

5.4. CONCLUSIONS

- 1. Xanthate adsorption on both minerals remains in the form of dixanthogen.
- 2. Dixanthogen formation on pentlandite was promoted while the opposite occurred for pyrrhotite; the presence of Ni ions moderated this effect.

- 3. A mixed potential model helped to explain the results in 2, provided the open circuit potentials for the minerals in the presence of xanthate were considered.
- 4. Depressants DETA, MBS and DETA+MBS reduced the dixanthogen adsorption on both minerals.
- 5. For pentlandite this reduction returned dixanthogen adsorption to values similar to those of single mineral in the absence of depressants.
- The ratio of dixanthogen adsorption on pentlandite to pyrrhotite increased to ca 4:1 compared to < 2:1 for single minerals and this ratio was maintained in the presence of depressants.
- 7. In terms of flotation, the mixture of minerals enhances dixanthogen formation on pentlandite at the expense of pyrrhotite. This is preserved on addition of depressants which serve to reduce the absolute dixanthogen adsorption on pyrrhotite perhaps below a critical level for flotation.
- 8. The mechanism in 7. only becomes evident on performing a mixed mineral study; indeed the single mineral results were confusing suggesting only small preferential adsorption for pentlandite and a greater effect of depressants on pentlandite, in contrast to plant experience.

CHAPTER 6

ORIENTATION AND STABILITY OF XANTHATE ON COPPER AS A MODEL SUBSTRATE

6.1. INTRODUCTION

Understanding the interaction between reagents and mineral surfaces is the key to understanding flotation mechanisms and essential if there are to be any fundamentally driven improvements in flotation practice. To control selective separation it may be necessary that the composition, structure and orientation of the topmost layers of the mineral be controlled at the molecular level. Xanthates are the most common collectors used in the separation of sulphide minerals. In spite of their extensive application, important details of the composition of the surface layers (xanthate vs dixanthogen for example) remain uncertain, and knowledge of the structure of this layer is still in its infancy. After the characterization of composition and orientation of surface products, it is also important to recognize that the stability of these products is important, an aspect that has received scant attention. There are reasons to question the stability. Many collectors are added at the head of the roughers and are presumed to form products which remain stable throughout the flotation circuit. These circuits can be quite large and involve substantial circulation of material meaning that some surface products are exposed to a changing environment for periods approaching an hour or more. In at least one example, viz., chalcocite flotation with amyl xanthate, a deterioration of performance in the cleaning stage has been attributed to "disappearance of the collector" [1].

Infrared spectroscopy has found its way into these important practical considerations. External reflectance spectroscopy has been employed *ex situ*. The examples include both characterization of the orientation of xanthate on a surface [2-9] and investigation of xanthate adsorption under electrochemical control using metal and sulphide mineral electrodes [10-13]. The use of this technique for orientation studies is relevant to the work here. For ethyl xanthate on copper in the case of p-polarization, the intensities of the three dominant bands, at 1197, 1127, and 1050 cm⁻¹, increased with time [4-7]. These three bands were assigned to a v_a (COC) stretching mode, indicating a close to perpendicular orientation of this molecular group on the copper surface. The absence of bands at 1034 and 1010 cm⁻¹, assigned to the v_a (SCS) stretching mode, indicated that this molecular group is oriented parallel to the

surface. The molecular arrangement of xanthate in the adsorption layer was therefore resolved. However, it is interesting to note that the conclusion regarding orientation was drawn without the use of s- polarization, which gives selective information on molecular groups oriented parallel to the surface.

An *in situ* external reflectance technique has recently been used for orientation studies [2] but no details on the cell were given. In that study on copper sulphide the orientation of the xanthate molecule was found to be random when adsorbed under applied potential whereas it was well oriented in the open circuit case.

In this chapter, the *in situ* external reflection spectroelectrochemical cell has been employed to characterize xanthate adsorption, orientation and stability on copper which was used as a model substrate. The orientation of the adsorbed xanthate was investigated as a function of electrochemical potential.

6.1.1. Theory of molecular orientation study

Consider a beam of light that is incident onto a mirrored surface such as a polished mineral surface (i, in the diagram Figure 6.1a and the reflected beam is r). The plane of incidence is defined as the plane formed by i and r. The angle θ is known as the angle of incidence. If the polarised light is oriented with the electric field vectors in the plane of incidence (i.e. are perpendicular to the surface), this radiation is known as *p* polarised (Figure 6.1b). This contrasts with the case when the electric field vectors are oriented perpendicular to the plane of incidence (i.e. are parallel to the surface), in which case the IR radiation is known as *s* polarized (Figure 6.1c). The behaviour of light varies with these two different orientations of reflection at a mirrored surface. The *s* polarised radiation undergoes a phase change of close to 180° for all angles of incidence whereas *p* polarised light shows a strong dependence on the angle of incidence (Figure 6.1d). The use of this information in determining molecular orientation may be understood by the bottom trace. In this trace the intensity of reflected and incident light for different polarisations is plotted against the angle

of incidence. The *p* polarised light has a greater intensity than the *s* polarised for all angles of incidence (Figure 6.1e).



Figure 6.1. External reflectance.

This difference is maximised at an angle of incidence of about 88°, which is close to being a grazing angle to the surface. The intensity of p polarised radiation is greater than s only very close to the surface. This means that the method is surface sensitive (1-2 μ m). For IR

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radiation to be absorbed by a vibrating molecule, it must have a changing dipole moment. The presence of a strong electric field or strong IR intensity parallel to the plane of incidence means that only vibrational dipoles also oriented in this direction will be observable (i.e., vibrational dipoles oriented parallel to the plane of incidence are enhanced and this enhancement is evident only close to the surface).

This method can be applied to characterize the orientation of surfactant on surfaces by acquiring the spectra under p and s polarization. For s polarization, only those molecular groups that have transition moment components parallel to the surface interact with the incident radiation and result in observable absorption bands in the recorded spectrum. For ppolarization only those molecular groups that have transition moment components perpendicular to the surface can be observed in the recorded spectrum.

6.2. EXPERIMENTAL

6.2.1. Materials

A circular disc of copper (99.999%) was obtained from Aldrich Chemical Company, Inc., and an electrode was fabricated by mounting a 5-mm diameter piece in a glass tube (100mm in diameter, 200-mm in length) with nonconducting epoxy after connecting a copper wire with graphite paste (DOTITE Electroconductives). Potassium ethyl xanthate (KEX) from Cyanamid was purified twice by dissolving in acetone and reprecipitated by petroleum ether following an established technique [14]. A buffer solution (0.05 M sodium tetra borate) was used as supporting electrolyte to provide a solution pH of 9.2.

6.2.2. Spectroelectrochemical measurements

The standard three-electrode spectroelectrochemical cell [15], which is described in Chapter 3 in detail, was used for potential control. The working electrode was held at a constant potential using an EG&G Princeton Applied Research Potentiostat / Galvanostat (Model 273). Prior to adding xanthate, the electrode was polarized cathodically at -1.0 V (SCE) for a period of 10 mins to remove any oxidation products formed during sample preparation. The electrode was brought down against the cell window after the polarization period. Spectra were taken at a given potential which was stepped anodically. In the case of stability studies, a potential of 0.1 V was applied for 20 min. after which the electrode become sufficiently covered to observe the disappearance of collector. The stability experiments were performed *ex situ* and *in situ*. For *ex situ* experiments, the electrode was removed from the cell, quickly rinsed with distilled water and mounted into the specular reflectance accessory in the spectrometer. In the case of *in situ* measurements, the whole cell with the electrode was mounted in the spectrometer. In both *ex situ* and *in situ* conditions, spectra were acquired over time.

Spectra were recorded using a Bruker Model IFS-66 FT-IR spectrometer, equipped with an MCT (mercury cadmium telluride) detector and a specular reflectance attachment (Spectratech Baseline) with a fixed incident angle of 45°. Also, a wire grid polarizer (Harrick Scientific) was used to produce the polarized radiation. Typically, 500 scans at a nominal resolution of 4 cm⁻¹ were co-added. The spectra were ratioed against that of a clean, untreated electrode in the buffer solution, and presented as reflectance data.

6.3. RESULTS AND DISCUSSION

6.3.1. Xanthate adsorption

The electrochemistry of the copper/xanthate system has been investigated extensively [16-19] using cyclic voltammetry. Characteristically three oxidation peaks are found at potentials -0.6 (A_1), -0.5 (A_2) and 0 V (A_3). A_1 is identified with chemisorption of xanthate [16, 19], A_2 is attributed to formation of either bulk copper xanthate [17, 19] or cupric xanthate [18], and A_3 is regarded as either the reaction associated with oxidation of cuprous to cupric or with cuprous xanthate formation alone or in combination with formation of

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dixanthogen, depending on solution concentration [18, 19].

Cyclic voltammograms of the copper electrode in the presence of $2x10^{-3}$ and $2x10^{-4}$ M xanthate are shown in Figure 6.2: The three peaks (A₁, A₂ and A₃) are observed. The peak positions are similar to the literature values and corresponding assignments are given. Chemisorption peak A₁ is concentration independent over this concentration range, while the A₂ and A₃ peaks are concentration dependent as expected [13, 16-19]. The disappearance of the A₃ peak and appearance of A₁ and A₂ peaks upon adding xanthate suggests the adsorption of xanthate through an oxidation step competes with oxidation of cuprous to cupric. These peak potentials were taken into account in the choice of potential values for acquiring spectra.



Figure 6.2. Cyclic voltammograms of copper metal.

The *in situ* infrared reflection spectra of the copper electrode contacted with $2x10^{-3}$ M xanthate solution as a function of potential are shown in Figure 6.3. Xanthate adsorption increased with potential. At -0.5 V (Figure 6.3b) cuprous xanthate was the main product with characteristic bands at 1198 ($v_a(COC)$), 1127 ($v_a(COC)$), 1050 ($v_a(COC)$), 1035 ($v_a(SCS)$)

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and 1010 ($v_a(SCS)$) cm⁻¹ [2-7]. Stepping the potential to 0.1 V (Figure 6.3e) created three additional bands, 1240, 1260 and 1020 cm⁻¹, which are characteristic of dixanthogen [20, 21]. These dixanthogen bands disappeared at a reducing potential of -1.0 V, while the cuprous xanthate bands were intensified, suggesting the conversion (reduction) of dixanthogen to cuprous xanthate (Figure 6.3F).



Figure 6.3. In situ FTIR reflection spectra of 2x10⁻³ M xanthate on copper metal.

The principal spectral difference for the electrode in $2x10^{-4}$ M xanthate solution (Figure 6.4) is the absence of dixanthogen bands. This means that oxidation of adsorbed xanthate to dixanthogen depends on initial bulk xanthate concentration. This may be relevant when comparing laboratory data, often produced with relatively high collector concentrations, with plant data. A common feature observed at both concentrations is the presence of some xanthate at potentials lower than -0.6 V, which is below the calculated potential for chemisorption [19].


Figure 6.4. In situ FTIR reflection spectra of 2x10⁻⁴ M xanthate on copper metal.

6.3.2. Molecular orientation

Xanthate orientation was investigated at $2x10^4$ M. The spectra, shown in Figures 6.5 and 6.6, are for s and p polarizations, respectively.

For s-polarization, three absorption bands, at 1197, 1122, and 1035 cm⁻¹, were observed at and above 0.15 V. These bands are assigned to the v_a (SCS) stretching mode [2-7]. Only these bands and no C-O-C stretching vibration bands (1198, 1127, and 1050 cm⁻¹) were observed with s-polarization. At 0.35 V, a weak band at 1010 cm⁻¹ appeared, which is also associated with S-C-S anti-symmetric stretching. The absence of the bands due to C-O-C vibrational modes and the presence of the bands due to S-C-S molecular groups that have transition moment components perpendicular to the surface suggests a xanthate configuration as shown in Figure 6.7.



Figure 6.5. In situ FTIR reflection spectra of $2x10^{-4}$ M xanthate on copper metal: S polarization.



Figure 6.6. In situ FTIR reflection spectra of 2x10⁻⁴ M xanthate on copper metal: *P* polarization.

In the case of p-polarization five distinct bands were observed (Figure 6.6). Three bands, at 1198, 1127 and 1050 cm⁻¹, are assigned to the $v_a(COC)$ stretching mode while the remaining two, at 1035 and 1010 cm⁻¹, are assigned to $v_a(SCS)$ as in the case of s-polarization. Bands at 1197 and 1122 cm⁻¹, also due to $v_a(SCS)$, are not observed in the p-polarized spectra as expected for a molecule oriented perpendicular to the substrate (as suggested in Figure 6.7).



Figure 6.7. Xanthate orientation on copper surface suggested from polarization study.

It has been suggested [4-6] that the presence of the bands at 1035 and 1010 cm⁻¹ in the ppolarized IR spectrum indicate multiple monolayer adsorption and random orientation. However, it is clear from the remaining s- and p-polarized spectra that the xanthate molecule is not oriented randomly in this case. The results demonstrate that *in situ* orientation of xanthate can be distinguished even under applied potential conditions, in contrast to the previous study [2].

The state of dixanthogen on the surface can also be judged by the use of polarized IR. In the present case, dixanthogen was only observed at higher $(2x10^{-3} \text{ M})$ concentration. As shown (Figure 6.8), the dixanthogen bands, at 1240, 1260 and 1020 cm⁻¹, do not change with the direction of polarization. This suggests that dixanthogen is oriented randomly.



Figure 6.8. In situ FTIR reflection spectra of 2x10⁻³ M xanthate on copper metal: Study of orientation of xanthate.

6.3.3. Stability

The evolution of *ex situ* and *in situ* spectra over time is shown in Figures 6.9 and 6.10, respectively. At the beginning of the experiment (0 min), there is evidence of both copper xanthate [1035 and 1049 cm⁻¹, v (SCS); 1123 cm⁻¹, v (COC); 1190 and 1197 cm⁻¹, v_a (COC) and v_a (SCS)] and dixanthogen [1020 cm⁻¹, v (SCS); 1240 and 1260 cm⁻¹, v_a (COC) and v_a (SCS)] [20, 21]. Over time, the bands at 1020, 1240 and 1260 cm⁻¹, associated with dixanthogen, reduce in intensity. At the same time, a new peak appears at 1009 cm⁻¹ [v (SCS) of copper xanthate] and the intensity of the copper xanthate peaks at 1035, 1049, 1123, 1190 and 1197 cm⁻¹ increases.



Figure 6.9. *Ex situ* FT-IR spectra showing disappearance of dixanthogen on copper metal over time.



Figure 6.10. In situ FT-IR spectra showing disappearance of dixanthogen on copper metal over time.

Figure 6.11 and 6.12 show the intensity changes for the copper xanthate peak at 1197 cm⁻¹ and dixanthogen peak at 1240 cm⁻¹ for *ex situ* and *in situ* conditions. A similar trend is observed for both cases, but the intensity reduces more rapidly for the *ex situ* (where the peaks associated with dixanthogen are no longer discernible after 60 min compared to 200 min for the *in situ* case).



Figure 6.11. Dixanthogen disappearance vs copper xanthate appearance in case of *ex* situ condition.

The instability of dixanthogen on surfaces exposed to air (i.e., *ex situ*), due to its volatility and chemical reactivity, is well known (although the resulting products have only recently been the subject of study [22]). The work here has shown that dixanthogen is also unstable under *in situ* conditions, albeit over a longer time frame. The disappearance of dixanthogen, even if a metal xanthate remains on the surface, as in this case, probably will result in reduced hydrophobicity [23]. This may contribute to reduced floatability in cleaning stages (i.e. after a period of exposure) as reported in that one instance [1].



Figure 6.12. Dixanthogen disapperance vs copper xanthate appearance in case of *in* situ condition.

The spectra in both the *ex situ* and *in situ* situations show not only the disappearance of dixanthogen but also the intensification of the copper xanthate peaks. This can be interpreted in two ways: the dixanthogen is present as an over-layer and its disappearance allows stronger interaction of IR radiation with the underlying metal xanthate; or, the dixanthogen is reduced to copper xanthate. The latter is more probable due to the experimental evidence discussed in Section 6.3.1., Figure 6.3F.

The time frame for disappearance in the *in situ* case, which is the more interesting from a flotation point of view, is of the order of 3 h. This seems long for conditions encountered in flotation, but may be relevant to minerals "caught" in a circulating load. Also, the time may be significantly different in practice due to the presence of other species in the processing stream (e.g., metal ions and sulphoxy species, etc.).

6.4. CONCLUSIONS

- 1. A new cell for *in situ* external IR reflection analysis is described which permits determination of adsorption products on electrodes under applied potentials.
- 2. For the copper/xanthate system, by using s- and p- polarized IR under applied potential, cuprous xanthate was determined to be preferentially oriented perpendicular to the electrode surface while dixanthogen was randomly oriented.
- 3. Dixanthogen, was reduced apparently to cuprous xanthate, by applying a reducing potential.
- 4. Dixanthogen disappeared over time under both ex situ and in situ conditions, but was faster in the ex situ case
- 5. The disappearance of dixanthogen peaks was accompanied by intensification of the copper xanthate peaks.

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CHAPTER 7

CONCLUSIONS AND CONTRIBUTIONS TO KNOWLEDGE AND SUGGESTIONS

7.1. CONCLUSIONS

7.1.1. Pentlandite / Pyrrhotite: Single Minerals

- 1. Xanthate adsorption on both minerals is in the form of dixanthogen.
- 2. Xanthate adsorption on pentlandite is higher than on pyrrhotite.
- 3. Ni treatment enhances xanthate adsorption on both minerals.
- 4. DETA reduces the dixanthogen adsorption on pentlandite significantly, but less significantly on pyrrhotite; Ni treatment enhances the effect of DETA on pyrrhotite.
- 5. The effect of MBS on dixanthogen adsorption on both minerals is not as significant as DETA alone.
- 6. The combination of DETA and MBS resulted in more reduction in dixanthogen adsorption than either alone.
- 7. Xanthate adsorption on both minerals is reduced when the pH is adjusted by soda ash instead of lime.
- 8. The general effects of DETA, MBS and DETA+MBS were similar whether pH was adjusted by either soda ash or lime.

7.1.2. Pentlandite / Pyrrhotite: Mixed Minerals

- 1. Xanthate adsorption on both minerals remains in the form of dixanthogen.
- Dixanthogen formation on pentlandite was promoted while the opposite occurred for pyrrhotite; the presence of Ni ions moderated this effect.
- 3. A mixed potential model helped to explain the results in 2, provided the open circuit potentials for the minerals in the presence of xanthate were considered.
- 4. Depressants DETA, MBS and DETA+MBS reduced the dixanthogen adsorption on both minerals.
- 5. For pentlandite this reduction returned dixanthogen adsorption to values similar to those of

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single mineral in the absence of depressants.

- 6. The ratio of dixanthogen adsorption on pentlandite to pyrrhotite increased to ca 4:1 compared to < 2:1 for single minerals and this ratio was maintained in the presence of depressants.
- 7. In terms of flotation, the mixture of minerals enhances dixanthogen formation on pentlandite at the expense of pyrrhotite. This is preserved on addition of depressants which serve to reduce the absolute dixanthogen adsorption on pyrrhotite perhaps below a critical level for flotation.
- 8. The mechanism in 7. only becomes evident on performing a mixed mineral study; indeed the single mineral results were confusing suggesting only small preferential adsorption for pentlandite and a greater effect of depressants on pentlandite, in contrast to plant experience.

7.1.3. Orientation and Stability of Xanthate on Copper as a Model Substrate

- 1. A new cell for *in situ* external IR reflection analysis is described which permits determination of adsorption products on electrodes under applied potentials.
- 2. For the copper/xanthate system, by using s- and p- polarized IR under applied potential, cuprous xanthate was determined to be preferentially oriented perpendicular to the electrode surface while dixanthogen was randomly oriented.
- 3. Dixanthogen, was reduced apparently to cuprous xanthate, by applying a reducing potential.
- 4. Dixanthogen disappeared over time under both *ex situ* and *in situ* conditions, but was faster in the *ex situ* case.
- 5. The disappearance of dixanthogen peaks was accompanied by intensification of the copper xanthate peaks.

7.2. CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

1. The effect of a mixture of pentlandite and pyrrhotite on xanthate adsorption was specifically determined and an explanation based on a galvanic interaction proposed.

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- 2. The effect of DETA, MBS, and DETA+MBS on xanthate adsorption and flotation was reinterpreted based on the influence of mineral interactions.
- 3. A new cell for *in situ* external IR reflection analysis technique was developed which permits determination of adsorption products on an electrode under applied electrochemical potentials.

7.3. SUGGESTIONS FOR FUTURE WORK

- 1. Study of mixed minerals with different ratios to simulate various locations in a flotation circuit.
- 2. Perform a microflotation tests under various conditions such as single vs mixed minerals, in the presence DETA, MBS, DETA+MBS and metal ions (Ni and Cu).
- 3. Resolve the issue of the use of DETA with,
 - a) oxidizing conditions (Inco),
 - b) sulphur dioxide (Falconbridge)
 - The following approach is suggested,
 - determine effect of mineral oxidation on DETA / metal ion / mineral interaction.
 - determine type of sulphoxy species released by mineral & ore oxidation and generated by adding SO_2 to water.
 - study interaction products between metal ions / DETA / sulphoxy species to see if some products form in common to both the "Inco" and "Falconbridge" processes
- 4. Repeat the study on various types of pyrrhotite.
- 5. Try to devise a way to categorize pyrrhotite in order to be able to compare data from different sources. Some suggestions are using x-ray diffraction and x-ray photoelectron spectroscopy to characterize crystal structure and metal / sulphur ratios.
- 6. Using *in situ* spectroelectrochemical cell, study the decomposition of dixanthogen on minerals under different controlled conditions such as in the presence of N₂, O₂, metal ions, pH modifiers etc.