THE INTERACTION BETWEEN XANTHATE AND SULPHUR DIOXIDE
IN THE FLOTATION OF NICKEL-COPPER SULPHIDE ORES

by

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We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
July, 1979

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ABSTRACT

Electrochemical methods and small scale flotation tests were used to study the effects of sulphur dioxide and potassium amyl xanthate on the floatabilities of pentlandite, chalcopyrite and nickeliferous pyrrhotite, at pH 5.5.

Mixed potentials of all three mineral systems were positive to the dixanthogen/xanthate redox couple, even in the presence of aqueous SO$_2$. Thus the existence of dixanthogen is thermodynamically favoured in all these systems. The tests also indicated that adsorption of xanthate by:

(i) chalcopyrite is enhanced by SO$_2$;
(ii) pentlandite is impaired by SO$_2$;
(iii) pyrrhotite is unaffected by SO$_2$;

Anodic polarization curves, determined on mineral electrodes, suggested that, in xanthated systems, the collector (probably dixanthogen) forms a film on the electrodes. This film inhibits the continued electron transfer reactions on the surface. The protective character of the film is higher for chalcopyrite (increased by SO$_2$), than for pentlandite (decreased by SO$_2$), than for pyrrhotite (unaffected by SO$_2$).

Cathodic polarization curves indicated that the cathodic process, on pentlandite and pyrrhotite electrodes, is controlled by oxygen reduction. The reduction of oxidized species on the surface is suggested as the controlling mechanism on chalcopyrite electrodes.

Small scale flotation tests showed that the presence of SO$_2$ increases an already very high recovery of chalcopyrite; decreases a high recovery of pentlandite, and decreases further a very low recovery of pyrrhotite.
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This thesis is dedicated to my wife and daughters.
CHAPTER 1

INTRODUCTION

Canada is the world's leading producer of nickel concentrates. The 1977 production of 232,500 t\textsuperscript{(1)} of metal contained represented thirty percent of the world total. Mining activities are presently carried out in Ontario and Manitoba by two companies: INCO Limited and Falconbridge Nickel Limited. Until its closure in 1976, Sherritt Gordon's Lynn Lake mill, in Manitoba, actively contributed to the Canadian production. Purchased concentrates, some of them imported, are now being used to feed their Fort Saskatchewan refinery, in Alberta.

Nickel concentrates produced in Canada come from sulphide ores. Pentlandite (and its alteration products) and nickeliferous pyrrhotite are the nickel bearing minerals. Most nickel sulphide ores contain copper as chalcopyrite. Generally, chalcopyrite and pentlandite are floated in a rougher stage, followed by a scavenger step to recover activated nickeliferous pyrrhotite. Nickel-copper separation is either a mineral processing or a pyrometallurgical operation.

Obtaining a pentlandite-chalcopyrite concentrate, with little pyrrhotite, is possible when the pulp is acidified with SO\textsubscript{2} prior to flotation with alkali metal xanthates. The mechanism of this interaction is presently unclear. Sulphur dioxide is a reducing agent and the current theory states that oxidation of xanthate is often a requirement for flotation.

The present investigation aims to contribute to the understanding of the flotation behaviour of nickel sulphide ores with xanthates, in the presence of sulphur dioxide. This study was deemed worthwhile due to the importance of production of nickel concentrates and the scarcity of information concerning this flotation system.
Starting from the current milling practice of sulphide nickel-copper ores, a natural choice of topics to be reviewed includes utilization of \( \text{SO}_2 \) as a regulating reagent in mineral processing, mechanisms of action of modifying reagents, \( \text{SO}_2 \) water chemistry, nickel-copper ores, principal minerals and their associations, electrophysical properties of these minerals and electrochemical implications related to froth flotation.

The main experimental techniques to be employed in order to achieve the proposed objective are electrochemical methods, such as determination of rest potentials and polarization curves, and small scale flotation experiments.
CHAPTER 2

LITERATURE REVIEW

2.1 Current Milling Practice of Sulphide Nickel-Copper Ores

The conventional milling practice of sulphide nickel-copper ores involves first flotation at a basic pH to produce a bulk concentrate containing most of the pentlandite and chalcopyrite. The tailing at this stage is composed chiefly of the non-sulphide gangue minerals plus most of the pyrrhotite. Magnetic separation can be combined with flotation to produce a pyrrhotite concentrate that is either added to the pentlandite fraction or treated separately in an iron recovery plant. The bulk nickel-copper might follow one of two routes:

(i) be shipped to a smelter, where a pyrometallurgical separation of copper and nickel is performed. The 1966 flowsheet for the Falconbridge mill\(^{(2)}\) (Falconbridge Mines Limited), presented in Figure 1, illustrates this type of operation;

(ii) be separated into nickel and copper concentrates in a selective flotation step in which pentlandite is depressed, at pH 11 or 12, and chalcopyrite is floated. The 1966 flowsheet of the Copper Cliff mill\(^{(2)}\) (INCO Limited), shown in Figure 2, is an example of this procedure.

Some flotation reagents, frequently used in the conventional basic circuit flotation of nickel-copper ores, are listed in Table I.
Figure 1. Flowsheet for Falconbridge Mill, after Boldt (2)
Figure 2. Flowsheet for Copper Cliff Mill, after Boldt (2)
TABLE I

Reagents often used in flotation of nickel-copper sulphide ores
(basic circuit)

<table>
<thead>
<tr>
<th>Function of Reagent</th>
<th>Bulk Rougher</th>
<th>Cu-Ni Separation</th>
<th>Scavenger</th>
</tr>
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<tbody>
<tr>
<td>-gangue-dispersant</td>
<td>Sodium Silicate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-collector</td>
<td>Xanthates</td>
<td>Xanthates</td>
<td>Xanthates</td>
</tr>
<tr>
<td>-frother</td>
<td>various</td>
<td>various</td>
<td>various</td>
</tr>
<tr>
<td>-pH modifier</td>
<td>Lime</td>
<td>Lime</td>
<td>Copper Sulphate</td>
</tr>
<tr>
<td>-activator</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-depressant</td>
<td></td>
<td>Lime*</td>
<td></td>
</tr>
</tbody>
</table>

*Cyanide, dextrin and oxidizing agents are also used.

2.2 Use of Sulphur Dioxide as a Flotation Reagent

Sherritt Gordon's Lynn Lake mill modified the conventional practice. Instead of operating all their flotation cells in the basic range of pH, one acidic step was introduced. The nickel-copper rougher concentrate was reground and conditioned with sulphur dioxide, before being cleaned. The insoluble gangue and probably pyrrhotite, liberated at the finer sizes, were depressed, yielding a cleaner nickel-copper bulk fraction that was next directed to a copper-nickel separation circuit. Figure 3 presents the flowsheet for the Lynn Lake mill\(^2\), as it was operated in 1966.

Another report of a Canadian nickel-copper operation to use SO\(_2\), as an acidifying agent in their flotation circuit, came from INCO's Thompson mill,
Figure 3. Flowsheet for Lynn Lake Mill, after Boldt (2)
in 1974\(^{(3)}\).

The use of sulphur dioxide as a flotation reagent dates back at least to 1913, when tests carried out at Broken Hill, Australia, showed that \(\text{SO}_2\) inhibited the flotation of sphalerite\(^{(4)}\). Since that time depression of sphalerite and marmatite by means of \(\text{SO}_2\) has been reported by several investigators\(^{(5),(6),(7),(8),(9),(10),(11)}\). Different results were obtained by Kosherbaev and Sokolov\(^{(12)}\). In their small-scale laboratory experiments, 1 g samples of sphalerite were tested in a modified Hallimond tube, with 5.00 mg of butyl xanthate as collector and 6.25 mg of pine oil as frother. These authors concluded that the floatability of \(\text{ZnS}\), with any length of treatment between 2 and 20 minutes, increased upon increasing \(\text{SO}_2\) concentration.

The explanation for this apparently opposite action of \(\text{SO}_2\) might be based on a differentiation between depression and deactivation, as defined below\(^{(5)}\):

-"Activation is a process whereby the surface of a mineral particle is modified so as to make it react more readily or more strongly with a collector.

-Deactivation is a process whereby an activating agent is removed from the surface of a mineral, thereby rendering it less able to react readily and strongly with a collector.

-Depression is a process whereby the surface of a particle is modified in such a way as to render it more wettable by water".\(^{(5)}\)

Sulphur dioxide could be a deactivator for copper-activated sphalerite, but would not be a depressant for the unmodified mineral.

A depressing action of \(\text{SO}_2\) on the floatability of galena was reported
by several authors\(^{(10),(12)}\) and\(^{(13)}\). Shimoiizaka et al\(^{(13)}\) stated that either sodium sulphite or sulphur dioxide depress the flotation of galena only when the surface of this mineral is oxidized.

Recent bench and pilot plant scale testwork carried out by Arauco F. et al\(^{(14)}\) indicated that the depressing action of \(\text{SO}_2\) increased over the following sequence of sulphide minerals:

\[\text{chalcopyrite} < \text{copper arseno sulphides} < \text{chalcocite} < \text{covellite} < \text{galena} < \text{pyrite} < \text{marmatite} < \text{sphalerite}.\]

Totally depressed minerals can often be rendered floatable by the addition of more xanthate collector. Each mineral requires a certain level of collector to acquire the necessary floatability.

References to the utilization of \(\text{SO}_2\) as a modifying agent in the flotation of pentlandite and related minerals are scarce and usually brief. Chalcopyrite is claimed to be activated by \(\text{SO}_2\)\(^{(10),(11),(12)}\), while pyrrhotite is depressed\(^{(6)}\). The flotation of several western Australian pentlandite-pyrrhotite ores was studied by Eltham and Tilyard\(^{(15)}\). Better nickel recovery was obtained in basic circuits, than when the pulp was acidified with \(\text{SO}_2\). Claridge and Tenbergen\(^{(16)}\), describing flotation developments for "Pipe ore" in the Thompson mill of INCO Limited, claim that pilot plant work revealed that \(\text{SO}_2\) depressed pentlandite. The detailed conditions of these tests were not specified, however.

A common problem associated with the flotation of nickel sulphide ores is the presence of talc. Talc is a naturally floatable mineral which tends to end up in the flotation concentrates, thereby diluting their grades. The consequent high MgO content also interferes with smelting processes. Preflotation or depression are the two available routes to eliminate this talc dilution. Even in the absence of frother, talc particles can stabilize
a viscous froth. Such a froth tends to entrap both nickel and copper sulphide particles, which often results in unacceptable losses when attempting a talc-preflotation step. Sulphur dioxide combined with dextrin\footnote{17},\footnote{18} or Guartec\footnote{19} has proved to be effective in talc depression during flotation of the copper and nickel sulphides. This is the more normal route to follow in treating talcose nickel ores.

Recent work by Poling\footnote{18} indicated that \( \text{SO}_2 \) can reinforce the action of dextrin as a talc depressant. In addition he found that \( \text{SO}_2 \) could enhance the floatability of pentlandite and chalcopyrite in a particular ore from South Africa.

A review of the literature on utilization of \( \text{SO}_2 \) as a sulphide flotation modifying agent shows that very little has been published about the mechanism of action of this compound. The information concerning its effect on nickel-copper ores is even less. Nickel-copper flotation is a well established plant practice, but little has been published about its fundamentals.

2.3 Level of Hydrophobicity at the Surface of Minerals

The selectivity of froth flotation is based on the principle that, when air is bubbled through a water suspension of mineral particles, some species stay in suspension while others adhere to the air bubbles and are buoyed to the surface. A near-ideal example of selective flotation is a system containing quartz and molybdenite particles. The preferential cleavage of molybdenite along '001 planes generates naturally hydrophobic surfaces on these planes. The \( \text{MoS}_2 \) particles adhere to air bubbles and float. Naturally hydrophilic quartz is wetted by water and is not floated. Very few natural systems are constituted of only two minerals, one hydrophobic, the other hydrophilic. Most minerals are hydrophilic and have to be, at least partially, coated with a collector to acquire the
necessary degree of hydrophobicity required for flotation. In many instances activation of the mineral surface must precede the addition of collector. Deactivation and depression are also very common actions in mineral processing.

The action of modifying agents is one of the fields in which practical achievements are far ahead of theoretical considerations. Among recent work in this area, significant advances have been made by Finkelstein and co-workers\textsuperscript{(20), (21), (22), (23)}. This work deals specifically with the modification of the surfaces of sphalerite and chalcopyrite. Many of their conclusions can be extrapolated to other systems as discussed next.

In systems containing sphalerite and chalcopyrite, depression is due to the presence of insoluble precipitates (mostly Zn(OH)\textsubscript{2} and Zn(CN)\textsubscript{2}). These precipitates are weakly and non-selectively attached to the mineral particles, through physical adsorption. Differences in relative hydrophobicities of the different minerals are responsible for the selectivity of this depression. The concept of a hydrophobicity scale is introduced, including the following contributions:

(i) "the hydrophobicity of the natural mineral surface and the change in this hydrophobicity as a result of activation of the surface;

(ii) further contribution to the overall hydrophobicity by the presence of films of a particular collector reaction product on the surface;

(iii) the hydrophilicity of a depressant film at the surface."\textsuperscript{(20)}

A knowledge of the species present in aqueous solutions of sulphur dioxide might contribute to the understanding of the effect of SO\textsubscript{2} on the "level of hydrophobicity" of sulphide minerals.
2.4 Sulphur Dioxide Water Chemistry

Most of the recent study in the field of sulphur dioxide water chemistry and electrochemistry refers to the corrosion accelerating effect of SO$_2$ on metallic surfaces in humid atmosphere. The objectives of these studies differ from those of the present investigation in two major aspects:

(i) the concentrations of SO$_2$ involved are low compared with those used in flotation;

(ii) the solid surfaces on which SO$_2$ adsorbs are metals and not metallic sulphides.

Sulphur dioxide solubility in water decreases with increasing temperature, as shown in Table II, after Schroeter$^{(24)}$.

**TABLE II**

Sulphur dioxide solubility in water at various temperatures, at 1 atm of total pressure, after Schroeter$^{(24)}$

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>SO$_2$(g/100 g of H$_2$O)</th>
<th>SO$_2$(moles/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>22.8</td>
<td>3.56</td>
</tr>
<tr>
<td>5</td>
<td>19.3</td>
<td>3.01</td>
</tr>
<tr>
<td>10</td>
<td>16.2</td>
<td>2.53</td>
</tr>
<tr>
<td>15</td>
<td>13.5</td>
<td>2.11</td>
</tr>
<tr>
<td>20</td>
<td>11.3</td>
<td>1.76</td>
</tr>
<tr>
<td>25</td>
<td>9.4</td>
<td>1.47</td>
</tr>
<tr>
<td>30</td>
<td>7.8</td>
<td>1.22</td>
</tr>
<tr>
<td>35</td>
<td>6.5</td>
<td>1.01</td>
</tr>
<tr>
<td>40</td>
<td>5.4</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The list of sulphur containing species existing when SO$_2$ is dissolved in water is controversial in the literature. Duncan and Spedding$^{(25)}$ report SO$_2$(aq), H$_2$SO$_3$, HSO$_3^-$, SO$_3^{2-}$, HS$_2$O$_5^-$ and S$_2$O$_5^{2-}$ as the main species present in aqueous solutions of SO$_2$. Lyons and Nickless$^{(26)}$ reported
molecular or solvated $\text{SO}_2$ as the most abundant species, in addition to less abundant $\text{H}_2\text{SO}_3$, $\text{HSO}_3^-$ and $\text{S}_2\text{O}_5^{2-}$. Falk and Guiguere\(^{(27)}\) repeatedly attempted to detect stable $\text{H}_2\text{SO}_3$ in aqueous solutions of $\text{SO}_2$, by infrared spectrometry, with no success. Sulphur dioxide in the molecular state and $\text{HSO}_3^-$ and $\text{HS}_2\text{O}_5^-$ were the only species observed. Early investigation indicated that 50% of the $\text{SO}_2$ present in a 5% solution at 22°C was uncombined\(^{(28)}\). Lynn et al\(^{(29)}\) reported that a saturated solution of $\text{SO}_2$ at normal pressure and temperature is ionized approximately 11%, in close agreement with the 10% ionization suggested by Falk and Guiguere\(^{(27)}\) under the same conditions.

Kosherbaev and Sokolov\(^{(12)}\) studied the effect of pH on the conversion of $\text{SO}_2$ (g) into $\text{H}_2\text{SO}_3$, $\text{HSO}_3^-$ and $\text{S}_2\text{O}_5^{2-}$. Table III, reproduced from their paper, indicates a complete transformation of $\text{SO}_2$ into these species. It could be possible that the distribution presented refers to the fraction of $\text{SO}_2$ which is changed into other species. If this is true, there is no disagreement between these data and those indicating a prevalence of molecular $\text{SO}_2$, reported by other investigators. Table III indicates that $\text{HSO}_3^-$ is the most abundant sulphur containing ionic species of aqueous $\text{SO}_2$ in the pH range of typical acidic flotation circuits (approximately pH 5.5).
**TABLE III**

The effect of pH on the conversion of 1 mg/l of SO₂ gas into H₂SO₃, HSO₃⁻ and SO₃²⁻, after Kosherbaev and Sokolov (12).

<table>
<thead>
<tr>
<th>pH</th>
<th>H₂SO₃ (mg/l)</th>
<th>HSO₃⁻ (mg/l)</th>
<th>SO₃²⁻ (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.06</td>
<td>0.21</td>
<td>1.24 x 10⁻⁷</td>
</tr>
<tr>
<td>2</td>
<td>4.26 x 10⁻¹</td>
<td>0.84</td>
<td>4.96 x 10⁻⁶</td>
</tr>
<tr>
<td>3</td>
<td>6.1 x 10⁻²</td>
<td>1.20</td>
<td>0.71 x 10⁻⁵</td>
</tr>
<tr>
<td>4</td>
<td>6.4 x 10⁻³</td>
<td>1.26</td>
<td>7.48 x 10⁻⁴</td>
</tr>
<tr>
<td>5</td>
<td>6.4 x 10⁻⁴</td>
<td>1.26</td>
<td>7.48 x 10⁻³</td>
</tr>
<tr>
<td>6</td>
<td>6.0 x 10⁻⁵</td>
<td>1.19</td>
<td>7.05 x 10⁻²</td>
</tr>
<tr>
<td>7</td>
<td>4.0 x 10⁻⁶</td>
<td>0.64</td>
<td>4.67 x 10⁻¹</td>
</tr>
<tr>
<td>8</td>
<td>9.1 x 10⁻⁸</td>
<td>0.17</td>
<td>1.06</td>
</tr>
<tr>
<td>9</td>
<td>1.06 x 10⁻⁹</td>
<td>2.1 x 10⁻²</td>
<td>1.25</td>
</tr>
<tr>
<td>10</td>
<td>1.06 x 10⁻¹¹</td>
<td>2.1 x 10⁻³</td>
<td>1.25</td>
</tr>
<tr>
<td>11</td>
<td>1.06 x 10⁻¹³</td>
<td>2.1 x 10⁻⁴</td>
<td>1.25</td>
</tr>
<tr>
<td>12</td>
<td>1.06 x 10⁻¹⁵</td>
<td>2.1 x 10⁻⁵</td>
<td>1.25</td>
</tr>
<tr>
<td>13</td>
<td>1.06 x 10⁻¹⁷</td>
<td>2.1 x 10⁻⁶</td>
<td>1.25</td>
</tr>
<tr>
<td>14</td>
<td>1.06 x 10⁻¹⁹</td>
<td>2.1 x 10⁻⁷</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Infrared spectroscopy has been used for aqueous SO₂ analysis. Experimentally determined absorption frequencies are listed in Table IV.
TABLE IV

Infrared absorption frequencies of aqueous SO₂

<table>
<thead>
<tr>
<th>Freq. (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(27)</td>
</tr>
<tr>
<td>ν₂</td>
<td>527</td>
</tr>
<tr>
<td>ν₁</td>
<td>1152</td>
</tr>
<tr>
<td>ν₃</td>
<td>1334</td>
</tr>
</tbody>
</table>

* pure liquid SO₂.

Quantitative infrared determination of aqueous SO₂ (g) is possible, if the extinction or absorption coefficient is known. Jones and McLaren obtained a figure of approximately $0.8 \times 10^3$ cm²g⁻¹ for the absorption coefficient associated with the peak at 1157 cm⁻¹ (NaCl prism).

The common characteristic of the species present when SO₂ is dissolved in water is that the oxidation state of sulphur is +4 in each case. The ultimate product of disproportionation of the positive oxidation states is +6. The possibility of oxidation to sulphate explains why sulphur dioxide is described in the literature as a reducing agent.

The thermodynamic stability of sulphur species in water can be visualized with the aid of an oxidation state diagram, as shown in Figure 4. On this figure, the oxidation-reduction potential of a couple formed by two species is given by the gradient of the line joining the points representing these species. A large positive gradient characterizes a strongly oxidizing couple and a large negative gradient is associated with a strongly reducing couple.
Figure 4. Oxidation state diagram for sulphur
The diagram also indicates that, if dithionate is an intermediate in
the oxidation of sulphite to sulphate, an excess of free energy is
required.

A first mechanism for oxidation of sulphur +4 to sulphur +6 was
proposed by Hayon et al \((33)\), and involves initiation, propagation and
termination steps:

\[
\text{Initiation} \quad \text{SO}_3^{2-} + \text{hv} \rightarrow \text{SO}_2^{3-} + e_{\text{aq}} \quad (R-1)
\]

\[
\text{SO}_3^{2-} + M^{n+} \rightarrow \text{SO}_3^{-} + M^{(n-1)+} \quad (R-2)
\]

\[
\text{SO}_3^{-} + \text{O}_2 \rightarrow \text{SO}_5^{-} \quad (R-5)
\]

where \( \text{hv} \) represents a photon of ionizing radiation and \( M^{n+} \) represents
a metal cation susceptible to a one electron oxidation.

\[
\text{Propagation} \quad \text{SO}_5^{-} + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{4-} + \text{SO}_4^{2-} \quad (R-4)
\]

\[
\text{SO}_4^{4-} + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_3^{-} \quad (R-5)
\]

plus unknown termination steps for the species \( \text{SO}_3^{-}, \text{SO}_4^{4-} \) and \( \text{SO}_5^{-} \). Reaction
\( R-1 \) describes the so-called photooxidation of sulphite. Reaction \( R-2 \)
refers to thermal autoxidation, when the photochemical initiation is
replaced by a one-electron transfer step involving a metal cation.

Basset and Parker \((34)\) suggested a second mechanism for sulphite
oxidation. In the presence of ferric or cupric ions, sulphite forms a
sulphite complex such as \([\text{Fe(SO}_3^{2-}]\)\(^{-}\). This complex can be oxidized to
either sulphate or dithionate, according to the following reactions:

\[
2[\text{Fe(SO}_3^{2-}] \rightarrow \text{H}_2\text{O} \rightarrow \text{SO}_3^{4-} + 2\text{H}^+ + 2\text{Fe}^{2+} + 3\text{SO}_3^{2-} \quad (R-6)
\]

\[
2[\text{Fe(SO}_3^{2-}] \rightarrow \text{S}_2\text{O}_6^{2-} + 2\text{Fe}^{2+} + 2\text{SO}_3^{2-} \quad (R-7).
\]

Several conclusions can be drawn from the literature review on sulphur
dioxide water chemistry. Approximately 10% of the total dissolved species
is ionized. At pH 5.5 the most abundant ionized species is \( \text{HSO}_3^{-} \). The
non-ionized portion is composed of solvated and molecular \( \text{SO}_2 \).

The concentration of hydrated molecules has been reported to be low, although a quantitative figure is not available. The oxidation state of sulphur is +4 in all the detected species of aqueous \( \text{SO}_2 \), which shows the reducing character of these solutions.

2.5 Geology of Nickel Sulphide Ores

The most important sulphide nickel deposits of the world are located within 25 miles of Sudbury, Ontario. The orebodies are constituted of either sulphides disseminated in a host rock (two thirds of the total) or inclusion-bearing sulphide ores (one third of the total)\(^{(35)}\). The most common host rock is norite, a basic rock (igneous rocks are ranked as acidic, neutral, basic, ultrabasic, and alkaline according to decreasing silica content). Alteration of the mineral assembly of norite to talc \([\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]\) is possible but not very common. Pyrrhotite, chalcopyrite, and pentlandite account for 95 percent of the total sulphides in Sudbury ores.

The Sudbury District provides most of the nickel mined in Canada, but other deposits are economically significant. Kilburn et al\(^{(38)}\) discussed the Canadian nickel sulphide ores related to ultrabasic rocks. The primary sulphide minerals associated with ultrabasic rocks are pyrrhotite, pentlandite, pyrite and chalcopyrite. Most of the ultrabasic rocks are partially or completely altered to serpentine \([\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]\), chlorite \([\text{(Mg,Fe)}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8]\) or talc. Alteration to serpentine is by far the most widespread. Alteration to talc is the most undesirable for either mining or milling operations. The effects of talc on milling were discussed in section 2.2. Its effects on mining are related to the low mechanical strength of the mineral. Planes of weakness in talc can
sometimes cause block failures due to lubricating action.

The association of nickel and iron sulphides, and the presence of copper minerals, is a characteristic of nickel-bearing deposite. A list of more common minerals in the iron-nickel-sulphur system is presented in Table V. Two copper-iron sulphides are also included. Natural specimens usually depart from the ideal stoichiometric formula. Elemental substitution is common. Cobalt is frequently found to replace iron and nickel.

**TABLE V**

Minerals in the iron-nickel-sulphur system

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Crystal System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Awaruite</td>
<td>(Ni,Fe)</td>
<td>Cubic</td>
</tr>
<tr>
<td>Bravoite</td>
<td>(Ni,Fe)S₂</td>
<td>Cubic</td>
</tr>
<tr>
<td>Gersdorffite</td>
<td>(Ni,Fe)₆S₂</td>
<td>Cubic</td>
</tr>
<tr>
<td>Greigite</td>
<td>Fe₃S₄</td>
<td>Cubic</td>
</tr>
<tr>
<td>Heazlewoodite</td>
<td>Ni₃S₂</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Mackinawite</td>
<td>FeS</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Marcassite</td>
<td>FeS₂</td>
<td>Orthogonal</td>
</tr>
<tr>
<td>Millerite</td>
<td>8NiS</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Parkerite</td>
<td>Ni₃S₂</td>
<td>Orthogonal</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>(Ni,Fe)₉S₈</td>
<td>Cubic</td>
</tr>
<tr>
<td>Polydymite</td>
<td>Ni₃S₄</td>
<td>Cubic</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>Cubic</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Fe₇S₈</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Smythite</td>
<td>Fe₅S₄</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Troilite</td>
<td>FeS</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Vaesite</td>
<td>NiS₂</td>
<td>Cubic</td>
</tr>
<tr>
<td>Violarite</td>
<td>(Ni,Fe)₅S₄</td>
<td>Cubic</td>
</tr>
<tr>
<td>Chalcopryrite</td>
<td>CuFeS₂</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Cubanite</td>
<td>CuFe₂S₃</td>
<td>Orthogonal</td>
</tr>
</tbody>
</table>
The composition of the different phases present in the iron-nickel-sulphur system can be better visualized in a ternary phase diagram. The central portion of such a diagram (for the system at room temperature) is shown in Figure 5.

The compositions described in Table V and Figure 5 refer to the bulk mineral. There is indication that the surface stoichiometry may differ from that in the bulk due to unsatisfied bonds and reaction with atmospheric or aqueous environment. The importance of surface stoichiometry towards the flotation behaviour of sulphide minerals is now recognized. Nevertheless, except for investigations on the galena surface\(^{(37)}\), not much has been published on this topic.

Not all the minerals listed in Table V have industrial importance. However, of the secondary minerals which deserve attention, violarite plays an important role. This mineral has been reported as a common alteration product of pentlandite-pyrrhotite associations\(^{(38),(39),(40),(41),(42)}\). Eltham and Tilyard\(^{(15)}\) successfully floated samples of Western Australian violarite using short chain xanthates as collectors, without the need of any activator. A tendency for violarite to slime during grinding was the only flotation problem disclosed. No reference was found in the literature to milling problems, in the Canadian nickel industry, associated with violarite.

A review of Canadian nickel ores indicates that the most important nickel-bearing minerals are pentlandite and the so-called nickeliferous pyrrhotite. Chalcopyrite is usually associated with these minerals. Nickeliferous pyrrhotite is a broad designation which encompasses nickel in solid solution and exsolved pentlandite as fine flames, spindles, blebs, lenses, granular aggregates or veins within pyrrhotite.
Portion represented in the diagram

- troilite (tr), pyrrhotite (po), smythite (smy), millerite (ml)
- coexisting violarite (vl) and pentlandite (pn)
- polydymite (pm)
- violarite (vl) not related to pentlandite (pn)
- pyrite (py) and bravoite (bv)

Figure 5. Central portion of the Fe-Ni-S triangular diagram, after Misra and Fleet (38)
Pyrometallurgical separation of such nickel is usually the only practical recovery procedure.

2.5.1 Identification of Copper and Nickel Sulphide Minerals

Since pentlandite, chalcopyrite and pyrrhotite have been identified as the minerals relevant to the present investigation, it is necessary to be able to identify them.

Optical properties such as colour and anisotropy are useful for microscopic identification of polished sections. Tables presented by Uytenbogaart and Burke\(^{(43)}\) describe the three minerals under oil immersion. Pentlandite is a light creamy or yellowish colour, much lighter than pyrrhotite, and isotropic. Chalcopyrite is yellow, slightly darker than pyrrhotite, and the anisotropy is weak but distinct. Pyrrhotite is cream with a faint pinkish brown tint, and usually very strongly anisotropic. The intensity of anisotropy depends on the crystal system and orientation. The ferromagnetic properties of monoclinic pyrrhotite can be used to distinguish it from the hexagonal type, which is paramagnetic.

An electron microprobe is very effective for identification of minerals. This method can provide qualitative and quantitative information about the minerals present in a sample, their associations and impurities. Minerals present in quantities above a detection limit of usually 5 to 10 percent, can be identified by X-ray diffraction. The X-ray pattern for the mineral is a very precise identification method, particularly useful when other properties are similar.

Last, but not least, the characterization of a mineral specimen requires elemental chemical analysis.

The importance of surface stoichiometry of sulphide minerals was stressed previously. Analytical techniques that deal specifically with surfaces have been known for decades. Recent improvements in the field
include refinement of older methods, development of new techniques and
production of instrumentation that is easier to operate and less
expensive than the equipment that was available ten years ago. Techniques
such as AES (Auger Electron Spectroscopy)\(^{(44)}\), LEED (Low Energy Electron
Diffraction)\(^{(45)}\), ESCA (Electron Spectroscopy for Chemical Analysis)\(^{(46),(47)}\)
and ISS (Ion Scattering Spectrometry)\(^{(47)}\) seem to be helpful in
elucidating the surface stoichiometry of sulphide minerals. These
techniques can also be used to identify surface compounds formed after
reactions with collectors and other reagents. A cautious interpretation
of the results is recommended when the operating conditions (high vacuum
or high temperature, for example) can change the surface of the sample under
analysis.

2.6 **Electrophysical Properties of Sulphide Minerals**

Pentlandite, pyrrhotite and chalcopyrite are all semiconducting
minerals. The mechanism of charge transfer across a semiconductor-solution
interface is affected by the concentration of charge carriers. When this
concentration is high the behaviour of a metal-solution interface is
approached. In the case of lower concentration of carriers, the space
charge region of the solid can influence processes involving charge transfer.

The role of semiconductor properties on the floatability of sulphide
minerals was first discussed by Plaksin and Shafeev\(^{(48),(49)}\). Their
theory is that negatively charged xanthate ions cannot adsorb on n-type
galena. Further, they suggest that oxidizing agents can act as electron
acceptors and convert galena into a p-type semiconductor, creating the
necessary conditions for adsorption. Tolun and Kitchener\(^{(50)}\) showed
that oxygen raises the electrochemical potential of galena, allowing
xanthate to oxidize to dixanthogen. A change from n- to p-type semi-
conductivity was reported, but this fact was not related to the adsorption of xanthate. Springer\textsuperscript{(51)} concluded that the conduction type of pyrite, galena and chalcopyrite does not play a significant role in the anodic oxidation of these minerals.

Zevgolis and Cooke\textsuperscript{(52)} studied the anodic polarization of chalcopyrite (n-type semiconductor). These investigators concluded that there is a limiting anodic current density. The value of this current density is determined by the concentration of holes, which are the minority carriers in chalcopyrite. The theory behind Zevgolis and Cooke's work was introduced by Brattain and Garret\textsuperscript{(53)}, who studied the germanium-electrolyte interface. These investigators found out that anodically biased n-type germanium in an electrolyte solution behaves as a p-n junction. A p-n junction is the interface between a p-region and an n-region within a single crystal of a semiconductor. It was proven that the saturation of the current crossing such an interface is due to the effect of diffusion of the minority carriers as a rate-limiting step.

The work of Zevgolis and Cooke\textsuperscript{(52)} was criticized by Biegler\textsuperscript{(54)}, with respect to the illumination technique and the wide range of anodic potentials used (0-14V). It is questionable whether the criticism is valid in terms of pure electrochemistry of sulphides. As far as electrochemical influence on flotation is concerned, the limiting current density was detected at a potential too high to be considered important (1.45 V anodic). Biegler found no relationship between the n- or p-type character of pyrite and kinetic parameters for cathodic oxygen reduction on pyrite electrodes.

At present there is no indisputable proof of the effect of semi-
conductivity type on the flotation of sulphide minerals with xanthates. There is an indication that the effect is less pronounced in the case of more conductive minerals. Less conductive minerals, such as galena and sphalerite, should have their response to flotation affected in a stronger way by the semiconductivity type.

The electrical conductivity of sulphide minerals is strongly dependent on composition. Values from the literature for different samples of pentlandite, pyrrhotite and chalcopyrite will be presented in section 5.1, together with experimental data for the samples to be used in the present investigation.

2.7 Electrochemistry of Sulphide Minerals

The use of an electrochemical approach to study sulphide minerals dates back to 1931, when Kamienski investigated the effect of pH on the equilibrium potentials of galena. Most of the work on electrochemistry of sulphide minerals has been directed towards the leaching of these minerals as a hydrometallurgical step. The application of electrochemical methods to flotation research was introduced by Salamy and Nixon, who recognized the gap existing between practical flotation developments and its fundamentals. Their pioneering work, presented in 1953, brought forth the suggestion that the reaction between sulphide minerals and xanthates proceeds via an electrochemical mechanism.

Prior to a discussion of this mechanism, it is pertinent to review briefly the need of a collector for flotation of sulphide minerals. Most of these minerals are only weakly hydrophilic due primarily to their inability to form hydrogen bonds. Thus, for example, their natural surfaces are less strongly hydrated than most oxide minerals. The surface
of sulphide mineral particles must be, partially at least, coated with collectors to provide conditions for the attachment of air bubbles. There are exceptions to this situation, some of them related to industrially important minerals. Molybdenite (MoS$_2$) is one of the naturally hydrophobic minerals. Recent investigations have also indicated the possibility of collectorless flotation of copper-activated sphalerite$^{(61)}$ and chalcopyrite$^{(62)}$.

A complete review of the literature on the topic of interaction between xanthates and sulphide minerals is beyond the scope of this work. The present state of knowledge may be summarized based on the information available in recent publications$^{(63),(64),(65),(66),(67),(68),(69),(70),(71),(54)}$.

The common mechanism of interaction between xanthates and sulphide minerals is of an electrochemical nature. Xanthate ions are oxidized to either dixanthogen or metal xanthate, according to the following reactions:

$$2\text{ROCS}^- \rightarrow (\text{ROCS}_2)^2 + 2e$$  \hspace{1cm} (R-8)

$$\text{MeS} + 2\text{ROCS}^- \rightarrow \text{Me} (\text{ROCS}_2)^2 + \text{S} + 2e$$  \hspace{1cm} (R-9)

$$2\text{MeS} + 3\text{H}_2\text{O} + r\text{ROCS}^- \rightarrow 2\text{Me(ROCS}_2)^2 + \text{S}_2\text{O}_3^{2-}$$

$$+ 6\text{H}^+ + 8e$$  \hspace{1cm} (R-10)

Reaction (R-10) may be considered the result of further oxidation of elemental sulphur, produced in reaction (R-9), to thiosulphate.

Geometrical considerations suggest that, at the surface, reaction (R-9) is unrealistic. The xanthate radical is larger than the metal radicals. There is insufficient space for two xanthate radicals adjacent
to one metal cation at the surface. The evidence indicates the formation of a first layer of a mono-coordinated compound MeROCS₂, which can be coated with one or more layers of Me(ROCS₂)₂.

Not all the steps that cause a particle to be hydrophobic in a flotation environment have been completely established. For example, the simple adsorption of xanthate on the surface may or may not be sufficient to give a hydrophobic character to a mineral:

\[
\text{Surface} + \text{ROCS}^- \rightarrow \text{ROCS}_2^- \rightarrow \text{Surface} + e
\]

The role played by elemental sulphur in the flotation of sulphide minerals is not yet clear. Although sulphur is a naturally floatable species, it is still controversial as to whether it is one of the hydrophobic entities that render the particles floatable.

A relationship appears to exist between the product of oxidation of thiol collectors and the rest potential of the system. Table VI, after Allison et al.(72) and Finkelstein and Goold(73), shows that, if the rest potential is more positive than the reversible potential for oxidation of xanthate or dithiocarbonate to dixanthogen or thiouram disulphide, respectively, the latter compounds are formed. Metal thiolates are formed when the rest potential is more negative than the equilibrium redox potential for the thiol couple. Oxidation of xanthate on covellite does not follow this rule. A plausible explanation for the detection of both dixanthogen and cuprous xanthate is that the predicted cupric xanthate is first formed and then reacts producing cuprous xanthate and dixanthogen. Another exception to the "one oxidation product" rule was observed by Allison et al.(72) in the case of molybdenite. A second oxidation product of xanthate, which could not be identified, was detected in addition to dixanthogen.
TABLE VI

Correlation between rest potentials and the products of interaction of sulphide minerals with thiol collectors

(A) Potassium ethyl xanthate ($6.25 \times 10^{-4}$M at pH 7), from Allison et al(72). (Reversible potential for oxidation to dixanthogen is 0.13V versus NHE).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Rest Potential (V versus NHE)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenopyrite</td>
<td>+ 0.22</td>
<td>$X_2$</td>
</tr>
<tr>
<td>Pyrite</td>
<td>+ 0.22</td>
<td>$X_2$</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>+ 0.21</td>
<td>$X_2$</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>+ 0.16</td>
<td>$X_2 + ?$</td>
</tr>
<tr>
<td>Alabandite</td>
<td>+ 0.15</td>
<td>$X_2$</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>+ 0.14</td>
<td>$X_2$</td>
</tr>
<tr>
<td>Covellite</td>
<td>+ 0.05</td>
<td>$X_2 + MX$</td>
</tr>
<tr>
<td>Bornite</td>
<td>+ 0.06</td>
<td>MX</td>
</tr>
<tr>
<td>Galena</td>
<td>+ 0.06</td>
<td>MX</td>
</tr>
</tbody>
</table>

(b) Sodium diethyldithiocarbamate (100 ppm at pH 8), from Finkelstein and Goold(73). (Reversible potential for oxidation to thiouram disulphide is 0.176V versus NHE).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Rest Potential (V versus NHE)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>+ 0.475</td>
<td>(DTC)$_2$</td>
</tr>
<tr>
<td>Covellite</td>
<td>+ 0.115</td>
<td>Cu(DTC)$_2$</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>+ 0.095</td>
<td>Cu(DTC)$_2$</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>+ 0.045</td>
<td>Mo(DTC)$_x$</td>
</tr>
<tr>
<td>Galena</td>
<td>- 0.035</td>
<td>Pb(DTC)$_2$</td>
</tr>
<tr>
<td>Bornite</td>
<td>- 0.045</td>
<td>Cu(DTC)$_2$</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>- 0.115</td>
<td>Cu(DTC)</td>
</tr>
</tbody>
</table>

? refers to unidentified oxidation product of xanthate
Whichever path the oxidation of xanthates on sulphide minerals follows, this anodic process must be balanced by a cathodic reaction. One of the important roles of oxygen in xanthate-sulphide mineral systems is to provide the balancing cathodic reaction. The final product of oxygen reduction in an aqueous environment can be either $\text{H}_2\text{O}$ or $\text{OH}^-$, according to the reactions:

\[
\begin{align*}
\text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O} & (R-12) \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- & (R-13)
\end{align*}
\]

Reaction (R-12) is more appropriate to describe the process in the acidic range of pH (under the catalytic action of a mineral surface). Reaction (R-13) is more realistic in the alkaline range.

The high activation energy (117 kcal/mol) required for the breakage of the strong triple bonds in the oxygen molecule ($\text{O}_3$) suggests that reactions (R-12) and (R-13) represent only initial and final states. The formation of hydrogen peroxide as a soluble intermediate product in oxygen reduction has been experimentally detected on some metallic electrodes, as well as on pyrite. There are also indications that peroxide formation involves two one-electron transfer steps. The overall process can be described by the following reactions:

\[
\begin{align*}
\text{O}_2 + e^- & \rightarrow \text{O}_2^- \\
\text{O}_2^- + 2\text{H}^+ + e^- & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- & \rightarrow 2\text{H}_2\text{O}
\end{align*}
\]

These equations may be applicable in representing the mechanism of oxygen reduction on other sulphide minerals.

At the present time it is clear that an understanding of electrochemical principles is important to the explanation of the complex
mechanism of interaction between sulphide minerals and xanthates.

Thermodynamics can be used as a first approach to study electrode reactions. A simple method of compiling thermodynamic information for aqueous systems was proposed by Pourbaix (74). It is a graphical method in which the electrochemical potential, $E_h$, is plotted against pH. Figures 6 and 7 show $E_h$ - pH diagrams for pentlandite, combined with the sulphur-water diagram. The activity of metallic cations was taken as $10^{-6}$ for both diagrams. The activity of sulphur-containing ionic species was fixed at $10^{-2}$ for the plot shown in Figure 6. Unit activity was assumed unless otherwise specified. The calculations were carried out with thermodynamic data from Pourbaix (74), except for the free energy of formation of pentlandite, where the value presented by Abramov (75) was employed.

The theory of kinetics of electrode reactions was established to explain the corrosion behaviour of metallic systems. Many investigators in the field of froth flotation apply the same concepts. They assume that the surface of a sulphide mineral particle, in a flotation environment, is at a single equilibrium potential, the so-called mixed potential. Although this may be true for certain systems, there is evidence for the existence of both anodic and cathodic sites on the surfaces of some sulphide minerals.

The published information on the electrochemical behaviour of the mineral pentlandite is sparse. Il'in et al (76) reported the rest potential in 1N KCl solution as +0.22V vs. NHE. Oxygen reduction on noble metal and sulphide mineral electrodes was studied by Rand (77). Some of his results, reproduced in Figure 8, show that the activity of pentlandite for oxygen reduction is high and approaches that of noble metals. The high oxygen reduction activity suggests a low requirement for oxygen in flotation.
Figure 6.  Eh – pH diagram for pentlandite and sulphur-water system

\[ a_{\text{Fe}^{2+}} = a_{\text{Ni}^{2+}} = a_{\text{Fe}^{3+}} = 10^{-6} \]

Other activities = 1
Figure 7. $E_h$ - pH diagram for pentlandite and sulphur-water system

$$a_{Fe^{2+}} = a_{Ni^{2+}} = a_{Fe^{3+}} = 10^{-6}$$

$$a_{SO_4^{2-}} = a_{HS^-} = a_{H_2SO_4^-} = 10^{-2}$$

Other activities = 1
Figure 8. Current-potential curves for oxygen reduction on noble metal and sulphide mineral electrodes, at pH 1 and 9.06, after Rand (77.)
CHAPTER 3

OBJECTIVES

The main objective of the present investigation is to study the mechanism of interaction between xanthate collector and the minerals pentlandite, pyrrhotite and chalcopyrite, in the presence of sulphur dioxide as a regulating reagent. The pH of the tests was selected as 5.5 to provide an acidic condition and yet avoid rapid decomposition of the xanthate at lower pH.

Most researchers now agree that the floatability of unoxidized sulphide minerals with xanthates is associated with the oxidation of xanthate ion to dixanthogen or metal xanthate. Sulphur dioxide should have sufficient reducing power to prevent such oxidation of xanthate ion. Nevertheless, successful flotation of pentlandite and chalcopyrite with xanthates has been reported, in the presence of SO$_2$. At present, only guesses can be made as to the hydrophobic entity. It could be elemental sulphur, dixanthogen, metal xanthate or several other hydrophobic surface species. Other aspects still unclear are the effect of SO$_2$ towards oxidized species at the surface of the minerals and the relevance of these species to floatability. An explanation and experimental verification of this interaction would fill a gap in the fundamental understanding of flotation.

During the course of the present work, emphasis will be placed on the mineral pentlandite, since it is the most important nickel-bearing sulphide mineral.
CHAPTER 4

EXPERIMENTAL METHODS AND APPARATUS

Two main lines of experimentation were pursued in order to achieve the proposed objective:

(i) electrochemical experiments;
(ii) microflotation tests.

4.1 Electrochemical Experiments

The electrochemical experiments were set up initially to monitor the behaviour of each individual component of the system under investigation, namely potassium amyl xanthate, sulphur dioxide and the three sulphide minerals (pentlandite, chalcopyrite and pyrrhotite), and subsequently to study their interaction. The tests were divided into two groups:

(i) rest potentials on a platinum electrode;
(ii) tests with mineral electrodes.

4.1.1 Rest Potentials on a Platinum Electrode

This series of tests was carried out in a cylindrical pyrex cell, provided with a lid containing four orifices. Three of the orifices were used for insertion of electrodes: platinum, calomel reference and standard combination. The remaining orifice was employed for feeding reagents and mineral sample to the system. The platinum and calomel reference electrodes were connected to a Fisher Accumet pH-meter, model 210, operated in the +700 mV scale. The combination electrode was connected
to a Beckmann Zeromatic II pH-meter, operated in the pH mode. The calomel reference and standard combination electrodes were from Fisher and the platinum from Corning.

The cell was supported by a plexiglass frame and placed on a magnetic stirrer. A schematic view of the set up is presented in Figure 9.

The working volume of the cell was 750 ml. A 0.1 N KCl solution was used as supporting electrolyte in all tests, to ensure good electrical conductivity. Dilute solutions of NaOH and HCl were employed for pH adjustment. In the preliminary tests without mineral slurries, and those with pentlandite slurries, SO₂ was added as a gas, by means of a gas dispersion tube. It was found that it was easier to control pH if a water solution of SO₂ was added to the system, instead of the gas. This procedure was then adopted in the tests with chalcopyrite and pyrrhotite slurries. Slurries containing 1% (by weight) solids were used in all tests. The tests were carried out at pH 5.5 to avoid rapid decomposition of the xanthate at lower pH. The half-life for decomposition of amyl xanthate decreases from 989 minutes at pH 5.6 to 11.8 minutes at pH 3.4\(^{78}\). All tests were carried out at room temperature.

A justification for the choice of a platinum electrode follows. Irrespective of the particular metal being used as a rest potential indicator electrode, poisoning of the electrode must always be a major concern of the researcher. The use of platinum electrodes for potential measurements has been extensively studied by Natarajan and Iwasaki\(^{97}\), (80),(81),(82),(83). These authors tested different methods for
Figure 9. Schematic view of the apparatus for the measurement of rest potentials with platinum electrode
cleaning poisoned platinum electrodes and concluded that mechanical polishing is the most adequate technique to reactivate an electrode. Although they appreciated the fact that platinum electrodes were not inert in a simulated flotation environment, it was impossible for them to recommend an electrode that could present better performance under these conditions. A discussion of the possible differences between a mineral electrode and a platinum electrode being struck by particles of the same mineral is presented in section 6.2.1. In the present work the platinum electrode was polished on a wet 600 grit paper immediately before each test. The electrode was always stored in a sealed tube containing distilled water.

4.1.2 Tests with Mineral Electrodes

A round glass flask, with multiple orifices, was utilized for these investigations. Orifices were provided for: a working electrode (mineral); an auxiliary or counter electrode (platinum); a Luggin capillary probe; a microprobe combination electrode (pH); a gas inlet and outlet and a thermometer. The counter electrode was inserted into a glass tube with a fritted glass bottom that permitted a physical separation between anode and cathode compartments, to prevent cross contamination. The Luggin capillary was connected to the reference electrode (saturated calomel electrode) via a salt bridge. The electrochemical cell was complete when the electrodes in the glass flask were connected to a Wenking potentiostat, model 68TS10. Preliminary testwork showed that the resistance of the working electrode and the impedance of the semi-conducting connection to the circuit could be neglected. Because of this fact, a four-wire system was not required. The pH electrode was
connected to a Beckmann Zeromatic II pH-meter. The flask was mounted sitting on a magnetic stirrer. The cell is schematically represented in Figure 10.

The working volume of the cell was 1250 ml. All tests were carried out in 0.1 N KCl supporting electrolyte, at room temperature. NaOH and HCl were employed when pH adjustment was necessary. A buffer solution (potassium hydrogen phthalate - sodium hydroxide buffer), pH 5.5, was employed to keep the pH constant during the polarization tests. Sulphur dioxide was added in the form of an aqueous solution.

Potentiostatic polarization curves were determined according to the following procedure. After the system had reached a stable rest potential, a potential 10 to 20 mV anodic or cathodic with respect to the rest potential was applied to the system. A reading of the current between working and counter electrode was taken one minute later. The potential was then immediately shifted by 10 mV, to its next value, the current again being read after a one minute interval. This procedure was repeated until the curve had been determined.

The mineral electrodes were prepared according to the following technique. Pieces of the minerals were mounted in "quick mount" plastic (2.54 cm in diameter and less than 0.5 cm in thickness), ground and polished to a 1μ finish using diamond compound. The mineral particle was exposed at both faces of the sample. One face was selected to be exposed to the electrolyte and the other face was coated with gold in a vacuum bell jar device. A copper wire was connected to the gold coated face by means of silver conducting cement. A glass tube was bent and mounted in "quick mount" as shown in Figure 11(a). The copper wire was inserted into the glass tube and the two plastic pieces were
Figure 10. Schematic view of the apparatus for tests with mineral electrodes
Figure 11. Preparation of Mineral Electrodes
glued together with fast drying epoxy resin. The final arrangement of the electrode is shown in Figure 11(b).

In all tests the mineral electrode was polished on wet 600 grit paper and immediately inserted into the cell. The aim of this procedure was to generate surface conditions similar to those in an actual flotation environment, where a fresh surface is produced by wet grinding.

4.2 Microflotation Tests

Small scale flotation tests were carried out in two types of cell:

(i) modified Hallimond tube;

(ii) modified Smith-Partridge cell.

4.2.1 Modified Hallimond Tube

This cell is a further modification of the version of the Hallimond tube presented by Fuerstenau et al. The tube is illustrated in Figure 12. The important features are a fritted glass disk for air dispersion, a magnetic stirrer, and a ground glass joint that simplifies handling.

The working volume was 125 ml. Air was supplied by the exhaust of a vacuum pump and went through a flow meter that was set to provide a constant flow rate of 50 ml/min.

The pH of the slurry was adjusted with a buffer solution (borax buffer), pH 9.18, prior to any SO\textsubscript{2} addition. Sulphur dioxide was always added as an aqueous solution. Potassium hydrogen phthalate - sodium hydroxide buffer solution was used to keep the pH at a constant value of 5.5 during the flotation tests. After the addition of either SO\textsubscript{2} or potassium amyl xanthate, a conditioning period of 2 minutes was allowed. Slurries containing 1% (by weight) solids were used in all tests.
Figure 12. Modified Hallimond tube
4.2.2 Modified Smith-Partridge Cell

This cell, shown in Figure 13, is a further modification of the original Smith-Partridge cell (85), that had been previously changed by Finkelstein and Stewart (61). The main features are a fritted glass disk for air dispersion and a mechanical stirrer. The advantage of the mechanical impeller over the magnetic stirrer is obvious when a ferromagnetic mineral (like pyrrhotite) is tested. Except for minerals in that class, both stirring mechanisms are adequate. The major advantage in favour of the Hallimond tube is the ease in handling.

The working volume of the cell was 125 ml. The air flow rate employed was 75 ml/min. The impeller speed was 100 rpm. Air supply and test conditions were the same as those described for the Hallimond tube.
Figure 13. Modified Smith-Partridge cell
CHAPTER 5

MATERIALS

The materials used in the present investigation can be divided into two groups:

(i) sulphide mineral samples;
(ii) chemical reagents.

5.1 Sulphide Mineral Samples

A massive matrix of nickeliferous pyrrhotite from Sudbury, Ontario, containing inclusions of pentlandite, was purchased from Ward's Laboratory. INCO supplied a sample of high grade pentlandite concentrate, produced by flotation in their Thompson mill. High grade chalcopyrite and nickel-free pyrrhotite, originating from Shivataki and Kawagama, in Japan, respectively, were obtained.

Thompson pentlandite was employed in tests involving slurries (rest potential on a platinum electrode and flotation). The sample was carefully washed in di-ethyl-ether, to remove collector that could have been left from the previous concentration. The material, as received, was below 65 mesh and was wet screened at 325 mesh. The fines were discarded. Pentlandite electrodes were prepared by cutting, with a mini cut-off saw, visually selected portions from the massive block, precut with a diamond saw.

Chalcopyrite from Shivataki, Japan, was used as electrode and slurry. The sample for slurries was ground to minus 65 mesh with mortar and pestle and the fraction below 325 mesh was discarded.

Portions of the Sudbury sample, visually selected for being low in pentlandite, constituted the source of nickeliferous pyrrhotite. The electrodes were prepared directly from these portions. Material for
slurries was further cleaned from pentlandite by magnetic separation. A hand magnet and a Frantz Isodynamic Separator were used in this operation. From this point on, any nickeliferous pyrrhotite sample will be referred to simply as pyrrhotite, unless otherwise specified.

The nickel-free pyrrhotite sample from Kawagama, Japan, was utilized as an electrode.

The chemical composition of these mineral samples is listed in Table VII.

Before being mounted as electrodes, the samples were submitted to a line scan with the electron microprobe. A summary of the results follows. Although the pentlandite sample was full of cracks, due to the extreme brittleness of this mineral, the analysis of flat surface regions suggested that nickel, iron and sulphur were uniformly distributed along the sample. Scans along the nickeliferous pyrrhotite showed fairly even distribution for iron and sulphur, the nickel content being variable along the sample. This pattern was an indication that most of the nickel was present as very fine grains of pentlandite in the pyrrhotite matrix. The nickel-free pyrrhotite and the chalcopyrite samples were very pure, as shown by uniform distribution of all elements.

The characterization of the samples included the experimental determination of electrophysical properties. For electrical conductivity measurements, both exposed faces of the mounted specimens were immersed in mercury. The applied voltage and resulting current flowing across the sample were measured by means of a digital multimeter.

The results, expressed as resistivity, are presented in Table VIII. Data published by Parasnis\(^{(86)}\), Keller and Frischknecht\(^{(87)}\), Parkhomenko\(^{(88)}\) and Shuey\(^{(89)}\) are also included in the table.
### TABLE VII

Elemental distribution of sulphide mineral samples and corresponding ideal stoichiometric compounds

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Origin</th>
<th>Elemental Distribution</th>
<th>Ni</th>
<th>Fe</th>
<th>Cu</th>
<th>Co</th>
<th>S</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentlandite Con*</td>
<td>Thompson</td>
<td>33.8</td>
<td>31.3</td>
<td>0.03</td>
<td>0.50</td>
<td>32.7</td>
<td>98.33</td>
<td></td>
</tr>
<tr>
<td>Pentlandite</td>
<td>Sudbury</td>
<td>33.6</td>
<td>32.4</td>
<td>0.27</td>
<td>0.76</td>
<td>33.9</td>
<td>100.93</td>
<td></td>
</tr>
<tr>
<td>Stoich. Fe(<em>{4.5})Ni(</em>{4.5})S(_8)</td>
<td>Sudbury</td>
<td>34.22</td>
<td>32.55</td>
<td>-</td>
<td>-</td>
<td>33.23</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Pyrrhotite**</td>
<td>Sudbury</td>
<td>4.35</td>
<td>57.5</td>
<td>0.06</td>
<td>-</td>
<td>38.8</td>
<td>100.71</td>
<td></td>
</tr>
<tr>
<td>Pyrrhotite***</td>
<td>Sudbury</td>
<td>4.45</td>
<td>55.5</td>
<td>0.14</td>
<td>0.09</td>
<td>40.9</td>
<td>101.08</td>
<td></td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Kawagama</td>
<td>-</td>
<td>60.9</td>
<td>0.38</td>
<td>-</td>
<td>35.9</td>
<td>97.18</td>
<td></td>
</tr>
<tr>
<td>Stoich. Fe(_7)S(_8)</td>
<td>-</td>
<td>60.38</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>39.62</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>Shivataki</td>
<td>-</td>
<td>30.9</td>
<td>33.9</td>
<td>-</td>
<td>34.8</td>
<td>99.60</td>
<td></td>
</tr>
<tr>
<td>Stoich. CuFeS(_2)</td>
<td>-</td>
<td>30.43</td>
<td>34.62</td>
<td>-</td>
<td>-</td>
<td>34.95</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

* Analysis provided by Inco, Thompson. The other samples were analysed in the Department of Mineral Engineering, U.B.C., by atomic absorption (sulphur was analysed gravimetrically). Samples were submitted in duplicate and the confidence interval is ± 2%.

** This represents the matrix surrounding pentlandite.

*** Same as above, after magnetic cleaning.
TABLE VIII

Electrical resistivity of sulphide minerals (in Ω x cm)

<table>
<thead>
<tr>
<th>Source</th>
<th>Pentlandite</th>
<th>Chalcopyrite</th>
<th>Pyrrhotite</th>
</tr>
</thead>
<tbody>
<tr>
<td>(86)</td>
<td>-</td>
<td>10^{-2} - 7x10^{-2}</td>
<td>10^{-3} - 5x10^{-3}</td>
</tr>
<tr>
<td>(87)</td>
<td>10^{-4} - 1.1x10^{-3}</td>
<td>1.5x10^{-2} - 9x10^{-1}</td>
<td>2x10^{-4} - 1.6x10^{-2}</td>
</tr>
<tr>
<td>(88)</td>
<td>-</td>
<td>10^{-2} - 7x10^{-2}</td>
<td>6.5x10^{-4} - 4.1x10^{-2}</td>
</tr>
<tr>
<td>(89)</td>
<td>-</td>
<td>10^{-2} - 1*</td>
<td>2x10^{-4} - 1.6x10^{-2}</td>
</tr>
<tr>
<td>This work</td>
<td>8.2x10^{-2}</td>
<td>4.5x10^{-1}</td>
<td>1.2x10^{-1} - 9.9x10^{-1}**</td>
</tr>
</tbody>
</table>

* range of most incidence in a histogram.

** 1.2 x 10^{-1} for nickeliferous pyrrhotite; 9.9 x 10^{-1} for nickel-free pyrrhotite.

The type of semiconductivity of each mineral specimen was qualitatively determined. The technique employed was based on the Seebeck effect, and the experimental set up is illustrated in Figure 14. The following results were obtained:

(i) the chalcopyrite sample is strongly n-type. After 2 minutes immersion in xanthate solution there is a slight decrease in the n-type character;

(ii) the pentlandite sample is weakly n-type, and does not seem to be affected by xanthate;

(iii) both pyrrhotite samples are weakly p-type and are unaffected by xanthate.

5.2 Chemical Reagents

All tests were carried out in single distilled water. The following chemicals (analytical reagent grade) were supplied by Fisher: KCl; NaOH;
Figure 14. Test for semiconductivity type of a mineral.
HC1; buffer salts of pH 4.01 (potassium hydrogen phthalate), pH 7.41 (potassium phosphate monobasic - sodium phosphate dibasic) and pH 9.18 (borax). Buffer solution, pH 5.5, was prepared from potassium hydrogen phthalate and NaOH. Anhydrous SO₂ was utilized.

The buffer solutions employed were tested for their possible effects on the systems under investigation. The rest potentials and polarization curves were the same in buffered systems as in those which pH was controlled by NaOH or HCl only.

Methyl isobutyl carbinol (MIBC) was utilized as a frother in the flotation tests. The dosage employed was 32 mg/l, which corresponds to 6.4 lbs of frother per ton of mineral. This level is unrealistic, as far as plant practice is concerned, but the froth generated was considered adequate for the present purposes.

The xanthate used in all tests was potassium amyl xanthate from Hoechst (92% pure according to UV analysis). From now on, the word xanthate will be used to mean this potassium amyl dithiocarbonate, unless otherwise specified; KAmX and X⁻ will be used as abbreviations for the salt and anion; X₂ will represent the oxidation product, di-amyl dixanthogen.

The concentration of all xanthate solutions was 0.74 x 10⁻⁴ M. The choice was based on the following reasoning. A realistic picture from plant practice of milling nickel ores indicated that, for an ore containing 1% Ni, the xanthate consumption is about 0.1 lbs per ton of ore processed. The sample in this work assayed 30% Ni and 1% wt slurries were used in the tests. This led to 15 mg of xanthate per liter of solution, or 0.74 x 10⁻⁴ M (assuming that both xanthates added in the mill and used in this investigation are 100% pure).

5.3 Adsorption of Xanthate on Sulphide Minerals

The characterization of the materials used in the present work
included an investigation of the adsorption of xanthate on pentlandite and chalcopyrite. Slurries containing 1% (by weight) of these minerals were kept under agitation by means of a magnetic stirrer. Xanthate was added to the system so that the initial concentration was $0.74 \times 10^{-4}$ M. A certain conditioning time was allowed, immediately after which the slurry was filtered. The filtrate was analysed, by UV spectrophotometry, for xanthate ion. The adsorption of UV radiation by the OCSS$^-$ chromophore, at 301 nm, with an extinction coefficient of $17.7 \times 10^{-1}$ l. mol$^{-1}$ cm$^{-1}$ was the property utilized. The percentage of xanthate not adsorbed on the mineral particles is listed in Table IX, for test conditions there specified. In the systems involving $SO_2$, a conditioning time of 2 minutes was allowed prior to xanthate addition.

**TABLE IX**

Adsorption of xanthate on sulphide minerals

<table>
<thead>
<tr>
<th>System</th>
<th>Conditioning time (sec)</th>
<th>% xanthate not adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentlandite</td>
<td>5</td>
<td>55</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>15</td>
<td>21</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>60</td>
<td>19</td>
</tr>
<tr>
<td>Pentlandite-SO$_2$</td>
<td>15</td>
<td>28</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>5</td>
<td>71</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>15</td>
<td>61</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>60</td>
<td>44</td>
</tr>
<tr>
<td>Chalcopyrite-SO$_2$</td>
<td>15</td>
<td>not detected</td>
</tr>
</tbody>
</table>
The results reported in Table IX show that $\text{SO}_2$ enhanced the adsorption of xanthate on chalcopyrite and slightly hindered the adsorption on pentlandite. The actual specific area of the samples was not determined. There was an indication that the pentlandite samples had larger specific areas than those of chalcopyrite. This fact prevented any conclusion being drawn, related to the apparently larger amount of xanthate adsorbed on pentlandite.
CHAPTER 6
RESULTS AND DISCUSSION

6.1 Rest Potentials on Platinum Electrode

All potentials in the present investigation were measured with respect to the calomel reference electrode. The results were then converted to the normal hydrogen electrode scale, assuming that the calomel reference is at 224 mV anodic on the hydrogen scale.

6.1.1 Preliminary Tests

A. 0.1N KCl solution

The first experiments were conducted to investigate the influence of pH on the rest potential of the 0.1N KCl solution, used as supporting electrolyte. The results are shown in Figure 15. A least squares fit* applied to the data gives the following relationship between $E_h$ and pH:

$$E_h = -53.0 \text{ pH} + 872 \quad (E-1)$$
$$r^2 = 0.9993$$

where $E_h$ = potential converted to the normal hydrogen electrode scale, in mV

$$r = \text{coefficient of correlation (see Appendix 1 for confidence intervals of regression lines)}$$

Potentials calculated using equation E-1 were slightly positive compared to the theoretical equilibrium potential of platinum in aqueous solution, given by equations R-17 and E-2 below:

$$\text{Pt(OH)}_2 + 2H^+ + 2e^- = 2H_2O + \text{Pt} \quad (R-17)$$
$$E_h = -59.1 \text{ pH} + 980 \quad (E-2)**$$

(all thermodynamic data are from ref. (74), unless otherwise specified)

* A least squares fit of data was used in obtaining all the linear equations present in this chapter.

** The standard electrode potential relates to the standard free energy of reaction and equilibrium constant as follows:

$$E^\circ_h = -\Delta G^\circ/(nF) = (RT/F)\ln K$$
Figure 15. Rest potential (on platinum electrode) versus pH for 0.1N KCl solution

\[ \text{Eh} = -53.0 \text{ pH} + 872 \]

\[ r^2 = 0.9993 \]
B. KAmX solutions

A next step was the measurement of rest potentials of KAmX solutions. A plot of the variation of potential with xanthate molar concentration is presented in Figure 16. The relationship between the two variables is expressed by:

$$E_h = -59.6 \log [X^-] - 193$$  \hspace{1cm} (E-3)

$$r^2 = 0.9997$$

The linear behaviour and the value of the slope are in agreement with the redox potential associated with the reaction:

$$X_2 + 2e = 2X^-$$ \hspace{1cm} (R-18)

$$E_h = -59.1 \log [X^-] + E^0_h$$ \hspace{1cm} (E-4)

where unit activity of $X_2$ is assumed.

The standard potential for the redox couple $X_2/X^-$ has been determined in this study and by other investigators, as shown in Table X.

<table>
<thead>
<tr>
<th>$E^0_h$(mV)</th>
<th>Author</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>-160</td>
<td>Majima and Takeda(^{(63)})</td>
<td>potentiostatic</td>
</tr>
<tr>
<td>-158</td>
<td>Winter and Woods(^{(90)})</td>
<td>potentiostatic</td>
</tr>
<tr>
<td>-140</td>
<td>DuRietz(^{(91)})</td>
<td>iodine titration</td>
</tr>
<tr>
<td>-193</td>
<td>present work</td>
<td>potentiostatic</td>
</tr>
</tbody>
</table>

The use of commercial xanthate, as opposed to pure synthesized reagents, probably accounts for the discrepancy between the figure obtained in this work and results from other investigators. However, due to
Figure 16. Rest potential (on platinum electrode) versus log[/X^-] for KAmX solutions.
the fact that relative potentials are compared in the present investigation, a constant shift does not interfere with the interpretation of results.

C. SO$_2$ solutions

The pH of solutions containing the supporting electrolyte was initially raised with NaOH to values between 9.0 and 10.5. Gaseous SO$_2$ was then slowly bubbled into the system. The amount of SO$_2$ injected was not quantitatively monitored. A qualitative indication was given by the pH of the solution. Sulphur dioxide addition resulted in a reducing character being imparted to the system, as shown in Figure 17. In the pH range between 5 and 8, a linear relationship between potential and pH is expressed by:

$$Eh = -27.3 \text{ pH} + 569$$

$$r^2 = 0.6747$$  

(E-5)

The poor correlation between the data could be explained by a lack of adequate control of SO$_2$ addition and to the fact that the results refer to several individual tests. The use of a constant amount of a particular buffer solution is a better method of adjusting the initial pH. This procedure was adopted in later tests.

The oxidation state diagram for sulphur, at pH 7, indicates that when SO$_2$ (oxidation state of sulphur = +4) is added to a system, the following equilibrium should occur:

$$S_{2}O_{6}^{2-} + 2H^{+} + 2e = 2HSO_{3}^{-}$$  

(R-19)

$$Eh = -59.1 \text{ pH} + 455 + 29.6 \log \left[ \frac{a_{S_{2}O_{6}^{2-}}}{a_{HSO_{3}^{-}}} \right]$$  

(E-6)

The discrepancy between equations E-5 and E-6 suggests that redox couples other than S$_2$O$_6^{2-}$/HSO$_3^{-}$ play an important role in SO$_2$ water chemistry.
Figure 17. Rest potential (on platinum electrode) versus pH for SO₂ solutions
D. \( \text{SO}_2 - \text{KAmX} \) solutions

Xanthate added to \( \text{SO}_2 \) solutions caused a potential drift in the negative direction, towards the potential for the \( \text{X}_2/\text{X}^- \) couple, as illustrated in Figure 18. Potential is expressed as a function of pH, as follows:

\[
\text{Eh} = -24.3 \text{ pH} + 237 \quad \text{(E-7)}
\]

\[
\hat{r}^2 = 0.8551
\]

The most significant aspect of these results is that the rest potential of the system is still positive with respect to that of the \( \text{X}_2/\text{X}^- \) couple, at concentrations similar to those employed in plant practice. This indicates that the oxidation of xanthate ion to dixanthogen is thermodynamically favoured under all these conditions. Infrared spectroscopy might be used to confirm the presence of dixanthogen adsorbed on the platinum electrode. Attenuated total reflectance is probably an appropriate technique for detection of adsorbed species on a flat platinum surface.

6.1.2 Tests with Pentlandite

A. Pentlandite slurries

Figure 19 shows the variation of potential as a function of pH for a 1\% (by weight) pentlandite slurry. The points on the curve presented in Figure 19 were determined from lower to higher pH values. The curve exhibits two linear regions, one between pH 4.0 and 5.0, and the other between pH 6.1 and 8.7. In the intermediate region there is a distinct minimum. The two linear portions are represented by:

\[
\text{Eh} = -61.2 \text{ pH} + 774 \quad \text{(pH 4.0 - 5.0)} \quad \text{(E-8)}
\]

\[
\hat{r}^2 = 0.9983
\]
Figure 18. Rest potential (on platinum electrode) versus pH for SO$_2$ - KAmX solutions.
Figure 19. Rest potential (on platinum electrode) versus pH for pentlandite slurry
Eh = -49.2 pH + 773 (pH 6.1 - 8.7)  \[ (E-9) \]
\[ r^2 = 0.9984 \]

The slopes of the straight line regions and the general aspect of the curve exhibited good reproducibility. The depth of the minimum seems to be affected by the rate of pH change.

The Eh - pH diagram for the pentlandite and sulphur-water system, Figure 7, predicts that the oxidation of pentlandite should be independent of pH, in the pH range between 4.1 and 5.6, due to formation of elemental sulphur as one of the oxidation products. A correlation between this mechanism and the minimum in the experimental curve is a possibility. The minimum could represent a metastable situation, and as equilibrium is approached it would change into a horizontal line. The linear region at lower pH values suggests that the cathodic reaction, namely oxygen reduction, dictates the slope of the curve.

A discussion of the relevant anodic and cathodic reactions that contribute to the experimentally determined rest potential will be presented in section 6.1.5. At this point it is pertinent to state that, in systems involving sulphide minerals and xanthate, oxygen reduction plays a major role as a cathodic reaction.

B. Pentlandite slurries - SO₂

The effect of addition of SO₂ to pentlandite slurries is illustrated in Figure 20. Prior to SO₂ injection, the pH of the system was adjusted, in all tests, with NaOH, to a value between 9 and 10. The presence of SO₂ proved to have a reducing effect on the mineral, as compared with only a pH change using HCl. The potential versus pH relationship, for the slurry acidified with SO₂ to a pH between 4.3 and 6.8, obeys the
Figure 20. Rest potential (on platinum electrode) versus pH for pentlandite slurry - SO₂
equation:

\[ Eh = -48.8 \text{pH} + 554 \]  
\[ r^2 = 0.8364 \]

The rest potential after \( S_2O_2 \) injection is positive with respect to that of the \( X_2^-/X^- \) couple. These conditions indicate that the oxidation of xanthate ion to dixanthogen is again thermodynamically favoured.

C. Pentlandite slurries - KAmX

The addition of xanthate to a pentlandite slurry caused an initial fast drift of potential in the negative direction. A minimum in the potential versus time curve was reached, and then the potential started moving in the positive direction, tending to restore the potential of the system to its initial value before xanthate addition. Figure 21 illustrates the change of potential with time for one test. The minimum in the curve occurred 30 seconds after xanthate addition. The general shape of the curve and time of the minimum were reproducible, and were not pH dependent.

The minimum in the potential versus time curve can be explained as follows. When xanthate was added to the system the potential drifted towards its equilibrium position, at a more negative value. Before the expected rest potential was reached, the almost complete extraction of xanthate from solution, due to adsorption on the mineral particles, restored the potential of the system to its initial condition (before xanthate addition).

D. Pentlandite slurries - \( S_2O_2 \) - KAmX

A plot of potential versus time for this system, as shown in Figure 22, reveals similar features to those obtained in the absence of \( S_2O_2 \) (Figure 21). The major difference is that the minimum in the curve is
Figure 21. Rest potential (on platinum electrode) versus time for pentlandite slurry - KAmX
Figure 22. Rest potential (on platinum electrode) versus time for pentlandite slurry - SO₂ - KAmX
now displaced to 2.5 minutes. This fact suggests that $SO_2$ slowed down the adsorption of xanthate by the mineral particles. The present results indicate this delay, but do not provide any clue to its interpretation.

6.1.3 Tests with chalcopyrite

The variation of potential as a function of pH, for a chalcopyrite slurry, is presented in Figure 23. The features of the curve are very similar to those for pentlandite. There are two linear regions, separated by a minimum. Between pH 4.2 and 5.6 the curve follows the equation:

$$Eh = -67.7 \, pH + 858$$

$$r^2 = 0.9998$$

(E-11)

In the pH range between 7.1 and 9.5 the results fit the equation:

$$Eh = -54.0 \, pH + 827$$

$$r^2 = 0.9986$$

(E-12)

Figure 23 also shows one point that represents the effect of $SO_2$ added to a chalcopyrite slurry, originally at pH = 9.35. The reducing character of $SO_2$ is evident.

Figure 24 is a plot of the variation of potential with time, for a chalcopyrite slurry treated with xanthate. A minimum can be seen at time = 1.5 minutes. The same type of plot is illustrated in Figure 25, with the difference that the slurry was acidified with $SO_2$, prior to xanthate addition. The minimum still exists, but now it has been shifted to 30 seconds. Assuming that the minimum is associated with xanthate being adsorbed on the mineral, these tests reveal that $SO_2$ speeds up the xanthate adsorption mechanism on chalcopyrite. This effect seems to be due to the reducing action of $SO_2$, towards oxidized species on the surface of chalcopyrite. Thermodynamically the steps in oxidation of chalcopyrite are quite different from those of pentlandite. At pH 5.5 pentlandite oxidizes producing $Fe^{2+}$ and $Ni^{2+}$. The oxidation of chalcopy-
Figure 23. Rest potential (on platinum electrode) versus pH for chalcopyrite slurry
Figure 24. Rest potential (on platinum electrode) versus time for chalcopyrite slurry - KAmX
Figure 25. Rest potential (on platinum electrode) versus time for chalcopryite slurry - SO₂ - KAmX
rite proceeds via covellite, chalcocite, copper and copper oxides and hydroxides.

6.1.4 Tests with pyrrhotite

The potential of a pyrrhotite slurry varies with pH as shown in Figure 26. Again the curve exhibits two straight line portions. In the pH range between 4.25 and 5.45 the equation followed is:

\[
E_h = -60.5 \, \text{pH} + 798 \\
\frac{r^2}{2} = 0.9995
\]  

(E-13)

At higher pH values, between 7.1 and 9.7, the results fit:

\[
E_h = -57.2 \, \text{pH} + 851 \\
\frac{r^2}{2} = 0.9998
\]  

(E-14)

The effect of \( SO_2 \) addition, on a pyrrhotite slurry initially at pH = 9.7, is also featured in Figure 26.

The behaviour of pyrrhotite slurries in the presence of xanthate was investigated next. The results are reported in Figure 27 (xanthate addition only) and Figure 28 (\( SO_2 \) injected prior to xanthate addition). Both plots are very similar, a minimum in the potential versus time curve being found 1 minute after xanthate was introduced.

The results do not indicate any important effect of \( SO_2 \) on the adsorption of xanthate by unactivated pyrrhotite.

Elemental sulphur is supposed to be formed readily on the surface of pyrrhotite, as an oxidation product. The predicted effect of \( SO_2 \) is to contribute to its further oxidation to thiosulphate, rendering the surface less hydrophobic, in the absence of xanthate. The rest potential from the platinum electrode tests neither confirmed nor denied this hypothesis.
Figure 26. Rest potential (on platinum electrode) versus pH for pyrrhotite slurry

\[
\text{Eh} = -60.5 \, \text{pH} + 798
\]

\[
\text{Eh} = -57.2 \, \text{pH} + 851
\]

\[
\text{r}^2 = 0.9995
\]

\[
\text{r}^2 = 0.9998
\]

△ after addition of SO₂
Figure 27. Rest potential (on platinum electrode) versus time for pyrrhotite slurry - KAmX
Figure 28. Rest potential (on platinum electrode) versus time for pyrrhotite slurry - \( \text{SO}_2 \) - KAmX
One aspect that has to be kept in mind, regarding pyrrhotite, is that adhesion of mineral particles to the stirring magnet interfered with the actual slurry density, and could have affected the results.

6.1.5 Correlation between Redox Couples and Experimental Results

This section consists of an attempt to correlate the experimental results, at pH 5.5, with the redox couples that are supposed to be relevant to the system. Tafel behaviour is assumed for all couples, with constant Tafel slope (see Appendix 2 for the Butler-Volmer equation\(^{(93)}\)). The abscissa axis is not to scale. The initial value of the exchange current density for the individual redox couples was arbitrarily fixed. Figure 29 deals with systems not involving mineral slurries. Figure 30 is an attempt to describe the interaction between pentlandite slurries, xanthate and \(\text{SO}_2\).

The model created seems to agree with the rest potentials that were measured. When only one anodic and one cathodic reaction are significant to the system under investigation, the rest potential lies at the intersection of the cathodic curve for the anodic redox couple and the anodic curve for the cathodic redox couple. An example of this situation is the rest potential for \(\text{SO}_2\) solution, presented in Figure 29. The rest potential of 419 mV is determined by the point at which the oxygen reduction curve intercepts the curve for oxidation of hydrogen sulphite to dithionate. When more redox couples are involved in the determination of potential, equilibrium occurs at the intersection of the net anodic curve and the net cathodic curve. The system pentlandite slurry - \(\text{SO}_2\) - KAmX, shown in Figure 30, illustrates this situation. The anodic curve follows the oxidation of pentlandite, from the redox potential for the couple "pentlandite/oxidation products" to the redox potential for the \(X_2/X^-\) couple. At this potential there is a horizontal shift towards larger
Figure 29. Schematic picture of the system $SO_2 - KAmX$ in terms of activation polarization curves.
Figure 30. Schematic picture of the system pentlandite - SO₂-KAmX in terms of activation polarization curves

A. \( 2H_2O = O_2 + 4H^+ + 4e \)
B. \( 2HSO_3^- = S_2O_5^{2-} + 2H^+ + 2e \)
C. \( 2X^- = X_2 + 2e \)
D. \( pn = 5Ni^{2+} + 4Fe^{2+} + 8S^{0} + 18e \)
current densities and, then, the curve follows the oxidation of xanthate ion to dixanthogen. The cathodic curve follows oxygen reduction at more anodic potentials, shifts to larger current densities at the redox potential for $S_2O_6^{2-}/HSO_3^-$ and then follows dithionate reduction. The expected rest potential of 55 mV is at the intersection of the net curves.

A list of the reactions that are likely to determine the experimentally measured rest potentials follows:

A. **0.1N KCl solutions**

Anodic reaction: $R = O^+ + e$  \hspace{1cm} \text{(R-20)}

where $R$ and $O^+$ refer to unknown reduced and oxidized species

Cathodic reaction: \[ \text{Pt(OH)}_2^+ + 2H^+ + 2e^- = \text{Pt} + 2H_2O \] \hspace{1cm} \text{(R-17)}

Er experimental $= \text{Eh}_1 = 581$ mV

B. **KAmX solutions**

Anodic reaction: \[ 2X^- = X_2 + 2e \] \hspace{1cm} \text{(R-18)}

Cathodic reaction: \[ O_2 + 4H^+ + 4e = 2H_2O \] \hspace{1cm} \text{(R-12)}

Er experimental $= \text{Eh}_2 = 53$ mV

C. **SO$_2$ solutions**

Anodic reaction: \[ 2HSO_3^- = S_2O_6^{2-} + 2H^+ + 2e \] \hspace{1cm} \text{(R-19)}

Cathodic reaction: \[ O_2 + 4H^+ + 4e = 2H_2O \] \hspace{1cm} \text{(R-12)}

Er experimental $= \text{Eh}_3 = 419$ mV

D. **SO$_2$ - KAmX solutions**

Anodic reaction: \[ 2X^- = X_2 + 2e \] \hspace{1cm} \text{(R-18)}

Cathodic reactions: \[ O_2 + 4H^+ + 4e = 2H_2O \] \hspace{1cm} \text{(R-12)}

\[ S_2O_6^{2-} + 2H^+ + 2e = 2HSO_3^- \] \hspace{1cm} \text{(R-19)}

Er experimental $= \text{Eh}_4 = 103$ mV
E. Pentlandite slurries

Anodic reaction: \((\text{Fe, Ni})_8S_8 = 5\text{Ni}^{2+} + 4\text{Fe}^{2+} + 8S^0 + 18e\) \(\text{(R-21)}\)

Cathodic reaction: \(O_2 + 4H^+ + 4e = 2H_2O\) \(\text{(R-12)}\)

Er experimental \(= Eh_5 = 460 \text{ mV}\)

F. Pentlandite slurries - SO₂

Anodic reactions: \((\text{Fe, Ni})_8S_8 = 5\text{Ni}^{2+} + 4\text{Fe}^{2+} + 8S^0 + 18e\) \(\text{(R-21)}\)

\(2\text{HSO}_3^- = \text{S}_2\text{O}_6^{2-} + 2H^+ + 2e\) \(\text{(R-19)}\)

Cathodic reaction: \(O_2 + 4H^+ + 4e = 2H_2O\) \(\text{(R-12)}\)

Er experimental \(= Eh_6 = 285 \text{ mV}\)

G. Pentlandite slurries - KAmX

Anodic reactions: \((\text{Fe, Ni})_8S_8 = 5\text{Ni}^{2+} + 4\text{Fe}^{2+} + 8S^0 + 18e\) \(\text{(R-21)}\)

\(2X^- = X_2 + 2e\) \(\text{(R-18)}\)

Cathodic reaction: \(O_2 + 4H^+ + 4e = 2H_2O\) \(\text{(R-12)}\)

Er expected \(= Eh_7 = 40 \text{ mV}\) (expected potential if exhaustion of xanthate, due to adsorption, had not occurred).

Er experimental \(= Eh_8 = 354 \text{ mV}\) (at the minimum in the potential versus time curve).

H. Pentlandite slurries - SO₂ - KAmX

Anodic reactions: \((\text{Fe, Ni})_8S_8 = 5\text{Ni}^{2+} + 4\text{Fe}^{2+} + 8S^0 + 18e\) \(\text{(R-21)}\)

\(2X^- = X_2 + 2e\) \(\text{(R-18)}\)

Cathodic reactions: \(O_2 + 4H^+ + 4e = 2H_2O\) \(\text{(R-12)}\)

\(\text{S}_2\text{O}_6^{2-} + 2H^+ + 2e = 2\text{HSO}_3^-\) \(\text{(R-19)}\)

Er expected \(= Eh_9 = 55 \text{ mV}\)

Er experimental \(= Eh_{10} = 168 \text{ mV}\)

In systems containing pentlandite and SO₂, elemental sulphur will tend to dissolve in SO₂ solutions, according to the reactions:
\[
\begin{align*}
\text{HSO}_3^- + S^0 &= \text{HS}_2\text{O}_3^- \quad (\text{pH} <3) \quad (R-22) \\
\text{HSO}_3^- + S^0 &= S_2\text{O}_3^{2-} + H^+ \quad (3 < \text{pH} <7) \quad (R-23) \\
\text{SO}_3^{2-} + S^0 &= S_2\text{O}_3^{2-} \quad (\text{pH} >7) \quad (R-24)
\end{align*}
\]

This mechanism leads to the possibility of an additional anodic reaction, in cases F and H:

\[
(\text{Fe, Ni})_9\text{S}_8 + 8\text{HSO}_3^- = 5\text{Ni}^{2+} + 4\text{Fe}^+ + 8\text{S}_2\text{O}_3^{2-} + 8\text{H}^+ + 18\text{e} \quad (R-25)
\]

This method of interpretation of results is omitted in the case of the minerals chalcopyrite and pyrrhotite for two reasons. The emphasis of this investigation is on pentlandite, and also, no major change is expected in the above pattern for the chalcopyrite and pyrrhotite systems.

### 6.2 Tests with Mineral Electrodes

#### 6.2.1 Pentlandite Electrode

**A. Rest potentials**

The effect of changes of pH on the rest potential of the pentlandite electrode is shown in Figure 31. For a system consisting of a 0.1N KCl solution the relationship between potential and pH is given by:

\[
\text{Eh} = -37.2 \text{ pH} + 608 \quad (E-15)
\]

\[r^2 = 0.9995\]

The presence of \(\text{SO}_2\) caused a shift of potential in the negative direction. The results fit the equation:

\[
\text{Eh} = -33.4 \text{ pH} + 551 \quad (E-16)
\]

\[r^2 = 0.9488\]

Rest potentials, measured on a platinum electrode, for pentlandite slurry and pentlandite slurry-\(\text{SO}_2\) systems (from Figure 20), were included in Figure 31. One point representing the potential of a pentlandite
Figure 31. Rest potential (on pentlandite electrode) versus pH for 0.1 N KCl and SO₂ solutions
slurry measured with a pentlandite electrode, is also featured. A difference in behaviour between the platinum electrode being struck by mineral particles and the respective mineral electrode is evident.

The fact that minerals from different sources were used as an electrode and in the slurry did not account for the deviation. The differences reported in Figure 31 were also observed in systems containing the minerals chalcopyrite and pyrrhotite, in which case samples from the same source were used in both sets of experiments.

A much larger surface area was one of the characteristics that made the tests with mineral slurries different from those with mineral electrodes. Also, a platinum electrode being struck by particles has been considered as equivalent to a mineral electrode, but this statement requires further confirmation. A simple series of tests was carried out, in which the rest potential of 1% slurries of pentlandite, chalcopyrite and pyrrhotite, in 0.1N KCl electrolyte, was measured with both platinum and the respective mineral electrodes. The potential on a platinum electrode was, in all cases, approximately 120 mV positive with respect to that measured on the mineral electrode. These results indicate either poisoning of one of the electrodes, or a difference in mechanism between the two systems. The magnetic stirrer provided a very gentle agitation, just enough to keep the particles in suspension. In addition, a very low pulp density was used. It is possible that the platinum electrode was not sufficiently bombarded by the particles, and therefore it did not behave as the mineral electrode.

Potential versus time plots for xanthate solutions, in the presence and absence of $S_2O_3^-$, are presented in Figure 32. In both cases there was an initial drop of potential, which, then, stabilized at a constant
Figure 32. Rest potential (on pentlandite electrode) versus time for KAmX and SO₂ - KAmX solutions
value. This potential was much higher than the equilibrium potential for $X_2/X^-$, as measured with a platinum electrode. It is not clear yet if this effect is due to the mineral electrode itself, or to the fact that the electrode is likely coated with a xanthate species (probably dixanthogen).

B. Polarization curves

Anodic and cathodic polarization curves, as measured with a pentlandite working electrode, are presented in the next four figures, for the following systems:

(i) $0.1\text{N KCl}$ solution, in Figure 33,
(ii) $\text{KAmX}$ solution, in Figure 34,
(iii) $\text{SO}_2$ solution, in Figure 35,
(iv) $\text{SO}_2 - \text{KAmX}$ solution, in Figure 36.

In Figures 33 through 44 two symbols were adopted:

(i) $Y = \log [I/A] = \log_{10}$ of the absolute value of the applied current density,

(ii) $K = \text{potential intercept at current density} = 1 \mu\text{A/cm}^2$ (no physical meaning is attributed to $K$).

It is well understood that linear portions shorter than one decade, in applied current density, in the potential versus log current density curve, do not necessarily characterize Tafel behaviour. Nevertheless there is a possibility that these points do represent a region under activation control, and this region does not extend any further due to a change in mechanism. A least square fit was applied to all regions that seemed to be reasonably linear.
Figure 33. Polarization curves of pentlandite electrode in 0.1N KCl solution

\[ Eh = 185 Y + K \]
\[ Eh = 274 Y + K \]
\[ Eh = -168 Y + K \]

\[ Y = \log |I/A| \]
Figure 34. Polarization curves of pentlandite electrode in KAmX solution
Figure 35. Polarization curves of pentlandite electrode in SO₂ solution
Figure 36. Polarization curves of pentlandite electrode in $\text{SO}_2 - \text{KAmX}$ solution
B1. Anodic polarization

All curves present two linear portions. The first region starts at potentials ca. 100 mV above the rest potential. The second linear region starts ca. $Eh = 750$ mV and extends to the highest potential used in the present investigation. Between potentials 650 and 750 mV (lower in Figure 36) there is an inflection that seems to be associated with a change in the oxidation mechanism. Further oxidation of elemental sulphur is one of the reactions that could affect the anodic curve.

The polarization curves do not indicate the oxidation of xanthate ion to dixanthogen as being part of the anodic process. This reaction probably occurred prior to the measurement of the curve. This would confirm the thermodynamic prediction that dixanthogen was the hydrophobic species in this system. It might be possible to identify dixanthogen adsorbed on the surface of sulphide minerals by means of infrared spectroscopy (attenuated total reflectance).

The effect of xanthate seems to have been the formation of a protective or inhibitor-like film of dixanthogen on the electrode surface. This film increased the resistance to anodic dissolution. The anodic mechanism would still have been controlled by the oxidation of the mineral, but its rate was decreased due to the presence of the film. The decrease in dissolution rate was larger in the absence of $SO_2$, than in its presence. This effect could be due to either a change in the extent of surface coverage or a change in the strength of the film-surface bond. Another action of $SO_2$ was to generate a second inflection (not as pronounced, and at a lower potential than the first) on the polarization curve. The mechanism associated with it is unexplained in the light of the present results.
B2. Cathodic Polarization

All four curves exhibit Tafel behaviour for about one decade, followed by a concentration polarization effect.

Biegler et al.\(^\text{(70)}\) concluded that the mechanism of oxygen reduction on a pyrite electrode involves a rate-determining first step:

\[
\text{O}_2 + e^- = \text{O}_2^-
\]  

(R-14)

Assuming a symmetry factor \(\beta\) of 0.5 in the Butler-Volmer equation, this mechanism leads to a Tafel slope of 120 mV/decade. Tafel slopes ranging from 168 to 116 mV/decade were measured in the present work. If these slopes are associated with \(\beta\) values ranging from 0.36 to 0.52, it can be stated that these results are consistent with the above mechanism.

The existence of a limiting current density also favours the hypothesis that the cathodic reaction was oxygen reduction. Fontana and Greene\(^\text{(94)}\) suggested that in air-saturated non-agitated solutions, the limiting diffusion current for oxygen reduction is approximately 100 \(\mu\text{A/cm}^2\). The present results are in good agreement with their finding.

Sulphur dioxide seems to have shifted the limiting current density to a larger value. The effect was not very pronounced. A possible influence of \(\text{SO}_2\) on the cathodic process is by reaction with \(\text{O}_2\), leading to \(\text{S}_2\text{O}_6^{2-}\). Dithionite is electrochemically active and its reduction may be faster than oxygen reduction because of potentially higher concentrations.

6.2.2 Chalcopyrite Electrode

A. Rest Potential

Rest potentials, measured with a chalcopyrite working electrode, immersed in different solutions, at \(\text{pH} = 5.5\), are reported in Table XI.
Rest potentials measured with chalcopyrite electrode

<table>
<thead>
<tr>
<th>Solution</th>
<th>Eh (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1N KCl</td>
<td>398</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>372</td>
</tr>
<tr>
<td>KAmX</td>
<td>169</td>
</tr>
<tr>
<td>( \text{SO}_2 - \text{KAmX} )</td>
<td>134</td>
</tr>
</tbody>
</table>

These results reveal the same trend as those for the pentlandite electrode. The oxidation of xanthate to dixanthogen is thermodynamically favoured. In the presence of \( \text{SO}_2 \) and xanthate, the chalcopyrite electrode seems to be cathodically polarized to a greater extent than the pentlandite electrode.

B. Polarization curves

Anodic and cathodic polarization curves, as measured with a chalcopyrite working electrode, are presented in the next four figures, for the following systems:

(i) 0.1N KCl solution, in Figure 37,
(ii) KAmX solution, in Figure 38,
(iii) \( \text{SO}_2 \) solution, in Figure 39,
(iv) \( \text{SO}_2 - \text{KAmX} \) solution, in Figure 40.

B1. Anodic polarization

All curves show two linear portions, separated by an inflection, that reflects a change in the oxidation mechanism. The very high initial slope of the systems involving xanthate suggests that the electrode was
Figure 37: Polarization curves of chalcopyrite electrode in 0.1N KCl solution
Figure 38. Polarization curves of chalcopyrite electrode in KAmX solution
Figure 39. Polarization curves of chalcopyrite electrode in KAmX solution.
Figure 40. Polarization curves of chalcopyrite electrode in $\text{SO}_2 - \text{KA}_n\text{MX}$ solution

- $\text{Eh} = 105 \text{ Y+K}$
- $\text{Eh} = 2738 \text{ Y+K}$
- $\text{Eh} = -93 \text{ Y+K}$
- $\text{Eh} = -240 \text{ Y+K}$

$|I/A| \ (\mu A/cm^2)$
coated with a film (probably dixanthogen). The protective character of the film was more pronounced in the presence of \( \text{SO}_2^- \). This fact seems to be associated with the reducing action of \( \text{SO}_2^- \) towards oxidized species on the surface of the electrode. The removal of some of these species is likely to facilitate the adsorption of collector.

In the test with \( \text{SO}_2^- \) solution there was a limiting current density at low current that is yet to be explained.

**B2. Cathodic polarization**

All curves presented a limiting current density at very low current (less than 10 \( \mu\text{A/cm}^2 \)), followed by two linear regions. The slopes were, in all but one case, much higher than the expected Tafel slope for oxygen reduction. There was no indication of a limiting current density around 100 \( \mu\text{A/cm}^2 \). These facts suggest that the cathodic mechanism consisted of the reduction of oxidized species on the surface of the electrode, instead of oxygen reduction. This assumption is supported by the facts discussed above, under anodic polarization. On the other hand, the presence of \( \text{SO}_2^- \) does not seem to have interfered with the aspect of the cathodic curves. The indication is that, even under these circumstances, enough oxidized species were left on the electrode surface to prevent the cathodic process from being under oxygen reduction control.

**6.2.3 Pyrrhotite electrode**

**A. Rest potential**

Rest potentials, measured with a nickeliferous pyrrhotite working electrode, immersed in different solutions, at \( \text{pH} = 5.5 \), are reported in Table XII. The rest potential, measured in a 0.1N KCl solution, of a nickel-free pyrrhotite electrode, is included in the table.
TABLE XII

Rest potentials measured with pyrrhotite electrodes

<table>
<thead>
<tr>
<th>Solution</th>
<th>Eh (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1N KCl</td>
<td>376</td>
</tr>
<tr>
<td>SO₂</td>
<td>340</td>
</tr>
<tr>
<td>KAmX</td>
<td>264</td>
</tr>
<tr>
<td>SO₂ - KAmX</td>
<td>267</td>
</tr>
<tr>
<td>NF py* in 0.1 NKCl</td>
<td>344</td>
</tr>
</tbody>
</table>

*NF py = nickel-free pyrrhotite.

These results are similar to those for pentlandite and chalcopyrite electrodes. They reveal that the need of an activator for the flotation of pyrrhotite in industrial practice is not due to the thermodynamic conditions of the system being unfavourable for the presence of dixanthogen. The rest potential in all tests was positive to the equilibrium potential for the X₂/X⁻ redox couple.

Microprobe analysis proved that the nickeliferous pyrrhotite electrode consisted of very finely disseminated pentlandite in a pyrrhotite matrix. The rest potential of this electrode, in 0.1N KCl solution, did not differ drastically from that of a nickel-free pyrrhotite electrode.

B. Polarization curves

Anodic and cathodic polarization curves, as measured with a pyrrhotite working electrode, are presented in the next four figures, for the following systems:
(i) 0.1N KCl solution, in Figure 41,
(ii) KAmX solution, in Figure 42,
(iii) $\text{SO}_2$ solution, in Figure 43,
(iv) $\text{SO}_2$ - KAmX solution, in Figure 44.

B1. **Anodic polarization**

All curves present three linear regions, the slope of each one decreasing with increasing potential. The pyrrhotite systems containing KAmX exhibit smaller slopes than those obtained in the tests with pentlandite and chalcopyrite electrodes. This fact indicates that the xanthate species film was weaker on the pyrrhotite electrodes than it was on the other two. The presence of $\text{SO}_2$ did not seem to interfere with the stability of the film.

B2. **Cathodic polarization**

All curves display a Tafel behaviour region for approximately one decade, followed by a limiting current density. The limiting current density is consistent with that for oxygen reduction. If a symmetry factor $\beta$ as low as 0.27 is acceptable, the experimental Tafel slopes are in agreement with that for oxygen reduction.

6.3 **Microflotation Tests**

6.3.1 **Tests with Pentlandite**

Results of small scale flotation tests, using pentlandite, in a modified Smith-Partridge cell and a modified Hallimond tube, are presented in Table XIII. These tests were carried out at pH 5.5. The concentration of collector was $0.74 \times 10^{-4}$ M.
Figure 41. Polarization curves of pyrrhotite electrode in 0.1N KCl solution
Figure 42. Polarization curves of pyrrhotite electrode in KAmX solution
Figure 43. Polarization curves of pyrrhotite electrode in SO₂ solution
Figure 44. Polarization curves of pyrrhotite electrode in $\text{SO}_2 - \text{KAmX}$ solution
TABLE XIII

Results of small scale flotation tests with pentlandite

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Flotation Time (min)</th>
<th>%F</th>
<th>%NF</th>
<th>SD</th>
<th>No. of tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smith Partridge cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAmX</td>
<td>3</td>
<td>82</td>
<td>18</td>
<td>1.80</td>
<td>4</td>
</tr>
<tr>
<td>S0₂-KAmX</td>
<td>3</td>
<td>70</td>
<td>30</td>
<td>3.91</td>
<td>4</td>
</tr>
<tr>
<td>KAmX</td>
<td>1</td>
<td>69</td>
<td>31</td>
<td>5.07</td>
<td>4</td>
</tr>
<tr>
<td>S0₂-KAmX</td>
<td>1</td>
<td>61</td>
<td>39</td>
<td>5.10</td>
<td>4</td>
</tr>
<tr>
<td>Hallimond tube</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAmX</td>
<td>3</td>
<td>91</td>
<td>9</td>
<td>1.22</td>
<td>4</td>
</tr>
<tr>
<td>S0₂-KAmX</td>
<td>3</td>
<td>85</td>
<td>15</td>
<td>2.17</td>
<td>4</td>
</tr>
<tr>
<td>KAmX</td>
<td>1</td>
<td>74</td>
<td>26</td>
<td>5.92</td>
<td>4</td>
</tr>
<tr>
<td>S0₂-KAmX</td>
<td>1</td>
<td>53</td>
<td>47</td>
<td>5.07</td>
<td>4</td>
</tr>
</tbody>
</table>

*%F = % floated (mean value), %NF = % not floated (mean value), SD = standard deviation.

These results indicate clearly that S0₂ had a deleterious effect on the floatability of pentlandite with KAmX. Thus these data confirmed the predictions from the electrochemical testwork.

Neither of the minerals under investigation showed any sign of natural floatability. This means that, if elemental sulphur were present on the
surface, it did not impart the necessary hydrophobicity required for flotation under the conditions tested.

6.3.2 Tests with chalcopyrite

Tests with the modified Smith-Partridge cell, in the presence or absence of SO₂, revealed that 1 minute flotation time was enough for all the mineral particles to float. A qualitative observation was made that flotation was faster in the presence of SO₂.

One hundred percent flotation was also reported for the 3 minute tests in the modified Hallimond tube. Results for 1 minute tests in this apparatus are presented in Table XIV.

**TABLE XIV**

Results of small scale flotation tests with chalcopyrite

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Flotation Time (min)</th>
<th>%F</th>
<th>%NF</th>
<th>SD</th>
<th>No. of Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hallimond tube</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAmX</td>
<td>1</td>
<td>61</td>
<td>39</td>
<td>1.09</td>
<td>4</td>
</tr>
<tr>
<td>SO₂-KAmX</td>
<td>1</td>
<td>84</td>
<td>16</td>
<td>4.74</td>
<td>4</td>
</tr>
</tbody>
</table>

The above results show that, according to the prediction from the electrochemical experiments, the floatability of chalcopyrite with KAmX was enhanced by previous conditioning of the mineral with SO₂.

6.3.3 Tests with Pyrrhotite

The magnetic stirrer agitation in the modified Hallimond tube was not compatible with the ferromagnetic character of pyrrhotite, thus only the Smith-Partridge cell was used.
Only negligible amounts of the mineral could be floated in 1 minute tests in the modified Smith-Partridge cell. Results for 3 minute tests are presented in Table XV.

**TABLE XV**

Results of small scale flotation tests with pyrrhotite

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Flotation Time (min)</th>
<th>%F</th>
<th>%NF</th>
<th>SD</th>
<th>No. of tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smith-Partridge cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAmX</td>
<td>3</td>
<td>18</td>
<td>82</td>
<td>5.24</td>
<td>4</td>
</tr>
<tr>
<td>SO₂-KAmX</td>
<td>3</td>
<td>11</td>
<td>89</td>
<td>3.64</td>
<td>4</td>
</tr>
</tbody>
</table>

These results indicate that SO₂ acted as a depressant on the flotation of pyrrhotite with KAmX. The amount floated in either case was so small that no major significance could be attributed to the depressing action.

**6.4 Discussion of the Effect of SO₂ on the Hydrophobicity Level**

In the present investigation SO₂ was the only modifying agent employed, and it was always injected before the addition of xanthate.

Results of flotation tests with pentlandite indicate that the presence of SO₂ caused a decrease in the rate of flotation. A possible explanation for this effect could lie in the action of SO₂ towards elemental sulphur at the surface of the particles. In the absence of SO₂ the film of collector (probably dixanthogen) and elemental sulphur contribute to the overall hydrophobicity. In the presence of SO₂, elemental sulphur reacts to thiosulphate; the surface moves to a lower position in the hydrophobicity scale.
The addition of SO\textsubscript{2} enhanced the floatability of chalcopyrite with xanthate. The surface of this mineral is likely to be coated with one or more layers of hydrophilic compounds, such as hydroxides. Sulphur dioxide would reduce these species and decrease the natural level of hydrophilicity at the surface. Another possibility, that requires further confirmation, is that the reaction product between the surface and collector confers a higher level of hydrophobicity if the surface is at a more reduced state.

Results of flotation tests with pyrrhotite reveal that an activator is required in order to achieve high flotation rates. The slight decrease in floatability due to SO\textsubscript{2} could be attributed to the same reasons presented in the discussion for pentlandite.

One aspect, that does not arise from the present set of results, but should be regarded as a feasible mechanism of action of SO\textsubscript{2}, is the physical adsorption of SO\textsubscript{2} molecules to the surface. The review on SO\textsubscript{2} water chemistry showed that approximately 90\% of SO\textsubscript{2} in solution is constituted of molecular or solvated species. Sulphur dioxide, being a polar molecule, should decrease the degree of hydrophobicity of the minerals.
CHAPTER 7

CONCLUSIONS

1. The effect of SO$_2$ on 0.1N KCl solutions and 1% wt slurries of pentlandite, chalcopyrite and pyrrhotite was to shift the rest potential of the systems in the negative direction, i.e. it acted as a reducing agent.

2. For all systems investigated (SO$_2$ solution, KAmX solution, pentlandite, chalcopyrite or pyrrhotite slurries and combinations of these) the measured rest potential was always positive with respect to that for the $X_2^-/X^-$ redox couple. This fact indicates that dixanthogen should be the hydrophobic entity responsible for flotation of these three minerals.

3. The curve for the variation of rest potential on a platinum electrode versus time elapsed after xanthate addition, for slurries of the three minerals, in the presence and absence of SO$_2$, shows a minimum. The effect of SO$_2$ was to shift the minimum towards longer times in systems containing pentlandite, and towards shorter times in systems containing chalcopyrite. The presence of SO$_2$ did not change the position of the minimum in pyrrhotite systems. UV analysis of the filtrate from slurries conditioned with KAmX revealed that the presence of SO$_2$ increased the amount of non-adsorbed xanthate in solution in the pentlandite systems and decreased it in the chalcopyrite systems. It is suggested that the minimum is associated with the adsorption of xanthate on the surface of mineral particles.
4. The anodic polarization curves for pentlandite, chalcopyrite and pyrrhotite electrodes are determined by the oxidation of the mineral. The action of KAmX is towards the formation of an inhibitor-like film on the surface of the electrode. This effect was stronger for chalcopyrite (enhanced by $SO_2^-$) than for pentlandite (weakened by $SO_2^-$) and for pyrrhotite (unaffected by $SO_2^-$).

5. The cathodic polarization curves for the pentlandite and pyrrhotite electrodes show a one-electron transfer Tafel behaviour, followed by a concentration polarization effect starting at current densities just larger than $100 \mu A/cm^2$. It is suggested that the cathodic mechanism on these two electrodes was oxygen reduction. The cathodic polarization curves for the chalcopyrite electrode present two linear regions, that seem to be associated with the reduction of oxidized species on the surface of the electrode.

6. Small scale flotation tests, with KAmX used as a collector, revealed very good floatability of chalcopyrite (enhanced by $SO_2$); good floatability of pentlandite (impaired by $SO_2$); and very poor floatability of pyrrhotite (impaired by $SO_2$).
CHAPTER 8

RECOMMENDATIONS FOR FUTURE WORK

1. A better understanding of SO$_2$ water chemistry and the interaction between SO$_2$ and the mineral particles is desirable.

2. Electrochemical techniques such as rapid galvanostatic and cyclic voltammetry should shed some light on the mechanism of xanthate ion oxidation and adsorption.

3. Analytical techniques that deal specifically with surfaces should provide useful information on the surface compounds in the presence of SO$_2$ and/or xanthate. Specifically, infrared spectroscopy (attenuated total reflectance) might be an adequate technique for identification of dixanthogen or metal xanthate on the surface of either sulphide minerals or platinum.

4. The interaction between SO$_2$, xanthate and activating agents, such as copper sulphate, should be investigated, specially in relation to pyrrhotite. Different sequences of addition of these reagents should contribute to the understanding of their effective action.
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81. NATARAJAN, K.A. and IWASAKI, I., "Significance of mixed potentials in Eh measurements with platinum electrodes", Transactions AIME, 255, 1974, pp.82-86.


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APPENDIX 1

CONFIDENCE INTERVALS OF REGRESSION LINES

\[ Y = a + bx \pm 2 \left( \frac{s}{\sqrt{n}} \right) \]

where \[ 2 \left( \frac{s}{\sqrt{n}} \right) = \text{confidence interval} \]

\[ S = \text{variance of } Y = \sqrt{\frac{\sum e_i^2}{n-2}} \]

\[ n = \text{number of observations} \]

\[ e_i = Y_{\text{measured}} - (a + bx) \]

<table>
<thead>
<tr>
<th>Equation</th>
<th>Confidence interval (±mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-1</td>
<td>2</td>
</tr>
<tr>
<td>E-3</td>
<td>1</td>
</tr>
<tr>
<td>E-5</td>
<td>5</td>
</tr>
<tr>
<td>E-7</td>
<td>5</td>
</tr>
<tr>
<td>E-8</td>
<td>1</td>
</tr>
<tr>
<td>E-9</td>
<td>2</td>
</tr>
<tr>
<td>E-10</td>
<td>10</td>
</tr>
<tr>
<td>E-11</td>
<td>1</td>
</tr>
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<tr>
<td>E-16</td>
<td>4</td>
</tr>
</tbody>
</table>
APPENDIX 2

THE BUTLER-VOLMER EQUATION

Electron transfer reactions at the interface between an electrode and an electrolytic solution obey the basic electroodic equation: the Butler-Volmer equation. When the overpotential is numerically large (>100 mV) the so-called high-field approximation is applicable, and the equation reduces to:

\[ i = i_o e^{(1-\beta)F\eta/RT} \]

where 
\[ i = \text{net current density} \]
\[ i_o = \text{exchange current density} \]
\[ \beta = \text{symmetry factor} \]
\[ F = \text{Faraday constant} \]
\[ \eta = \text{overpotential} \]
\[ R = \text{gas constant} \]
\[ T = \text{absolute temperature} \]

In a logarithm form, the equation can be arranged to:

\[ \eta = \alpha \ln \frac{i}{i_o} \]

where 
\[ \alpha = \frac{RT}{(1-\beta)F} = \text{Tafel slope} \]
LIST OF PUBLICATIONS


* Recipient of the "oxigenio do Brasil" Annual Award for the best paper on applications of nitrogen and argon. (in Brazil).

** Recipient of the "Metal Leve" Annual Award for the best paper on production of non-ferrous metals (in Brazil).