THE ROLE OF DISSOLVED METAL IONIC SPECIES IN THE
PHOSPHONIC ACID FLOTATION OF CASSITERITE

by

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ABSTRACT

The techniques of X-ray photoelectron spectroscopy (XPS), secondary ionization mass spectroscopy, chemical abstraction analysis and microelectrophoresis were used to confirm the existence of iron films on cassiterite grains recovered from the tin concentrator of Renison Limited (Australia). All analyses indicated the level of surface iron contamination to be far in excess of that characteristic of the bulk mineral lattice. No evidence was found in XPS analyses to support the contention that this iron represented lattice iron that had accumulated on the surface due to migration through the lattice, as has been suggested to be the case for certain sulphide minerals. Instead, all of the experimental data supported the hypothesis that the surface film was the result of previous adsorption of hydrous ferric oxide sols onto the cassiterite surface in the plant environment but which had undergone fundamental structural changes when the sample was dried. Specifically, the presence of the iron film did not change significantly the electrokinetic properties of cassiterite, as is known to be the case for other insoluble oxide minerals in the presence of freshly precipitated hydrolyzed metal ionic species. To reconcile these observations, it was shown independently that drying, both thermally and under vacuum, caused the charge reversal phenomena related to hydrolyzed metal ion adsorption either to diminish or disappear.
In the presence of styryl phosphonic acid, the iron contaminated cassiterite exhibited a microflotation response that corresponded remarkably with the actual flotation observed in the plant from which it was taken. A critical examination of the literature revealed that this behaviour was indicative of that reported for other cassiterites in both batch and plant flotation of ores. Most notably the mineral floated strongly between pH 4.0 and 7.5. However, after acid leaching, the pH of maximum recovery moved to more acidic values around pH 2.0 and the mineral floated much less strongly in the slightly acidic to alkaline range. This latter behaviour correlated with a large body of published data for which it was known that the cassiterite used was either a high purity sample, not exposed to solutions containing dissolved metal ionic species, or had been acid cleaned prior to test work. Conversely, results from fundamental studies, where this was known not to be the case, exhibited remarkable consistency with the data obtained for the untreated cassiterite sample.

The principal influence of the iron species adsorbed onto the surface of cassiterite was shown to be flotation activation in the pH range where the adsorbed species were not extensively solubilized. In the acidic range below pH 4.0, solubilization of the surface iron entities occurred which caused a severe flotation depressant effect. This solubilization was promoted in the presence of sodium fluoride, a known complexing agent for iron in acidic solutions, and the phosphonic acid. In the latter case, evidence was found for the formation of a soluble iron phosphonate complex. Independent confirmation was also sought and obtained from light scattering photometry to verify the strong affinity of phosphonic acids for hydrous ferric oxide species. Other ionic entities, such as those of magnesium and calcium were
found to interact far less strongly.

On the basis of this research, it has proven possible to provide a rational interpretation of all previously existing data pertaining to cassiterite flotation with phosphonic acids, for which reasonable sample description and preparation information exist. Such a reconciliation has not previously been provided, either through studies on the effects of cassiterite mineral lattice impurities or other work with dissolved metal ionic species. Furthermore, a significant link has been established between the results of fundamental analyses and industrial related observations. In particular, commercially successful practices, such as fluoride pretreatment of ore slurries prior to cassiterite flotation, now can be interpreted successfully in terms of fundamental ion solution chemistry. The evidence is that such processes involve the solubilization under acidic conditions of adsorbed iron hydroxy sols from the surface of minerals prior to cassiterite flotation. A bulk rejection of the complexed metal ionic species is then made in the water split of the desliming circuit that precedes flotation. The solution chemical evidence obtained supporting such a mechanism is considerable and no finding, in this work or elsewhere, refutes it.
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The pH Dependence of 1 x 10^{-4} M AlCl_3.6(H_2O) Solution Turbidities in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid.

The pH Dependence of the Turbidities of Solutions Containing both 1 x 10^{-4} M AlCl_3.6(H_2O) and 6 x 10^{-4} M NaF in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid.

Turbidities of Ferric Chloride Solutions as a Function of Concentration at pH 5.0 in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid.

The pH Dependence of 1 x 10^{-4} M FeCl_3 Solution Turbidities in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid. Data are given for solution initial pH values of (a) pH_4 = 1.0 and (b) pH_4 = 3.8.

Turbidities of Ferrous Chloride Solutions as a Function of Concentration at pH 1.5 in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid.

The pH Dependence of the Turbidities of Solutions Containing 1 x 10^{-4} M FeCl_3 and/or 6 x 10^{-4} M NaF in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid (SPA). Data are given for the solutions (a) 1 x 10^{-4} M SPA + 6 x 10^{-4} M NaF, (b) 1 x 10^{-4} M FeCl_3 + 6 x 10^{-4} M NaF (pH_4 = 3.7), (c) 1 x 10^{-4} M FeCl_3 + 6 x 10^{-4} M NaF + 1 x 10^{-4} M SPA (pH_4 = 3.7), and (d) 1 x 10^{-4} M SPA + 1 x 10^{-4} M FeCl_3 (pH_4 = 3.8).

Turbidities of Magnesium Chloride Solutions as a Function of Concentration at pH 5.0 in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid.

Turbidities of Calcium Chloride Solutions as a Function of Concentration at pH 5.0 in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid.

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<th>Title</th>
<th>Section</th>
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<td>401</td>
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CHAPTER 1

INTRODUCTION

Cassiterite is the only economically exploitable source of the metal tin. Historically, concentration of the mineral has been by gravity techniques which are well suited to the recovery of coarser cassiterite grains. However, cassiterite in many lode deposits is characteristically of a very fine grain size and not readily amenable to gravity concentration alone. During the past 25 years, flotation has become well established as a complementary recovery technique for the treatment of gravity circuit fines.

Numerous surfactants have been proposed as collectors for cassiterite. However, the selectivity required in industrial flotation can be achieved by few reagents. Phosphonic acid collectors, which first became commercially available in the early 1970's, have been remarkably successful for a number of ore types. At many major tin mines treating complex lode tin ores, phosphonic acids are currently the preferred flotation collectors. This is despite their significant cost disadvantage with respect to all other collector reagents.

The phosphonic acid flotation of cassiterite has been the subject of major research efforts at both the plant and the fundamental surface chemistry levels. However, virtually from its inception, significant discrepancies have been reported between different fundamental studies related to flotation and between laboratory and plant analyses. Invariably, these differences have been ascribed to mineral lattice impurities and to the presence of dissolved metal ionic species in flotation pulps.

The objective of this research was to provide a rational interpretation of the role of dissolved metal ionic species in the phosphonic acid flotation
of cassiterite. The experimental approach was fundamental in nature and involved only studies with the mineral cassiterite. Resolution of the role of interactions between cassiterite and phosphonic acid and ionic species present in solution and adsorbed on the mineral surface was the principal objective. The importance of mineral lattice impurities was examined only in so far as the impurities were a source of dissolved metal ions. While such a single mineral study does represent an ideal flotation system, the influence of dissolved metal ionic species can account for many of the otherwise difficult to explain observations that exist in fundamental studies. It can further provide a plausible reason why single mineral flotation and adsorption study results, in distilled water systems, are seldom consistent with the flotation behaviour of cassiterite in ores.

The need for such research can be justified at both the scientific and technological levels. Resolution of the apparent anomalies that exist in fundamental studies is a necessary prerequisite if further progress is to be made in establishing the controlling mechanisms of cassiterite flotation. Greater understanding of the deleterious effects of dissolved metal ionic species in cassiterite flotation also offers significant opportunity for improving the economics of the flotation process. High phosphonic acid reagent consumptions, together with low selectivity with respect to certain gangue species, are the two major problems encountered in industrial flotation. Considerable evidence has been obtained that these problems are, to an appreciable degree, intimately related to the presence of metal ionic species in industrial flotation pulps.
CHAPTER 2

LITERATURE REVIEW

2.1 Cassiterite Mineralogy and Solution Chemistry

2.1.1 Crystal Structure

Cassiterite (SnO\(_2\)) possesses a tetragonal crystal structure. The tin atoms form a body-centered tetragonal unit cell with basal dimension 4.73 Å and axial dimension 3.18 Å (Figure 1). The distance between the cell corner and centre is 3.70 Å. The oxygen atoms can be considered to be in O\(_2\) groups on a body-centered lattice displaced from the first by 1.59 Å along the tetragonal axis. Shuey (1975) has listed the following crystallographic data for cassiterite:

<table>
<thead>
<tr>
<th>System</th>
<th>Tetragonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO(_2) per cc</td>
<td>2.79 x 10(^{22})</td>
</tr>
<tr>
<td>Sn-O</td>
<td>2.05 Å</td>
</tr>
<tr>
<td>O-O</td>
<td>2.58 Å, 2.89 Å</td>
</tr>
<tr>
<td>Sn-Sn</td>
<td>3.18 Å, 3.70 Å</td>
</tr>
</tbody>
</table>

According to the unit cell structure, each Sn atom has two Sn neighbours at 3.18 Å, eight at 3.70 Å, four at 4.73 Å, etc. Each O atom has three Sn neighbours forming an isosceles triangle in a (110) or (1\overline{1}0) plane. Conversely, each Sn has six O neighbours. There is evidence for electron sharing between the Sn and O atoms as their bond length of 2.05 Å is less than the sum of their ionic radii of 2.11 Å (Shuey, 1975). The O atoms are joined in pairs 2.58 Å apart which is significantly less than the O\(^{2-}\) diameter of 2.8 Å. According to Shuey (1975), it is, therefore, more accurate to consider O\(^{2-}\) molecules. These O\(^{2-}\) molecule-ions are apparently not in contact with each other because their internuclear distance of 2.89 Å is greater than the diameter of 2.80 Å.
2.1.2 Crystal Impurities, Nonstoichiometry and Semiconductor Properties

Natural cassiterite crystals characteristically exhibit a variety of colours (Fander, 1985). Individual grains are most commonly brown to black in colour but can vary from white to yellow (wax-tin) or red (ruby-tin) and often show colour zoning (Uytenbogaardt and Burke, 1971; Patterson, Ohmoto and Solomon, 1981). Colour variations are believed to be the result of impurities, particularly iron, substituting for tin (Baker, 1962).

Iron, tungsten, tantalum, manganese, niobium and titanium are the most frequently reported impurities in the cassiterite lattice (Deer, Howie and Zussman, 1962; Pol'kin et al., 1973; Houchin and Warren, 1986). These impurities can substitute for tin atoms in the crystal structure of cassiterite. The presence of impurity elements has been shown to alter certain physical properties of cassiterite crystals such as their electrical conductivity and thermal emf coefficient (Pol'kin et al., 1973; Balachandran, 1982).
Pure polycrystalline stannic dioxide is an insulator. However, the presence of impurity elements and deviations from stoichiometry can render the material into a broad band n-type semiconductor (Laitinen, Vincent and Bednarski, 1968; Solymosi, Bozso and Hesz, 1976; Balachandran, 1982). Due to crystal defects and impurities, all natural cassiterites are semiconductors. The mineral typically has a band gap of 3.6 eV. The conduction band is derived from the Sn 5s level, while the valence band is derived from the oxygen 2p level (Shuey, 1975). Only n-type cassiterite is known, the apparent cause being that nonstoichiometry is only in the direction of oxygen deficiency (Hoberg, 1969; Shuey, 1975; Balachandran, 1982). Substitutional Fe would be an acceptor, but no natural p-type cassiterite has ever been found. Impurities such as Ta and Nb are donors.

The semiconductive nature of cassiterite led Arbiter (1977) to suggest that reduction of SnO_2 to metallic tin might occur on cassiterite surfaces under flotation conditions. Such reduction was thought possible in an acidic environment due to electrochemical contact with iron or with semiconductive minerals containing ions that could form a suitable galvanic couple with cassiterite. However, in linear potential sweep voltammetric studies on tin oxide conducting electrodes, Laitinen, Vincent and Bednarski (1968) found that the cathodic decomposition of SnO_2 to metallic tin occurred at -0.55 V (SHE) in 0.1 M HCl solution. The potential of this cathodic decomposition, being outside the region of stability of water, was associated with the reduction of hydrogen ions. At higher pH, the required potential became more negative. It is consequently extremely unlikely that any reduction of the surface of cassiterite to metallic tin would occur in aqueous pulps.
2.1.3 X-Ray Diffraction and Infrared Spectra

The structures of natural and synthetic cassiterite crystals have been well characterized by X-ray diffraction. Powder diffraction patterns of cassiterite are referenced in numerous standard handbooks on mineral diffraction. Data from Berry (1974) listing the interplanar spacings, relative intensities and Miller indices of the diffraction pattern of a pure cassiterite crystal are reproduced in Table I.

Infrared spectroscopy has proved to be a particularly useful complementary technique to X-ray diffraction for mineral characterization. In the case of cassiterite, the infrared spectrum is also well understood in principle. This is illustrated by infrared vibrational calculations which achieve favourable agreement with experimental data.

Table II lists the infrared and Raman vibrations of cassiterite. The unit cell of cassiterite belongs to the point group $D_{4h}$ with two formula units per unit cell. Thus, there are 15 lattice vibration modes, the symmetry species of which, obtained by standard group theoretical methods (Wilson, Decius and Cross, 1955) are:

$$\Gamma = A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{2g} + E_g + 2B_{1u} + 3E_u.$$  

The character table for the point group $D_{4h}$ shows that the translation operations are of symmetry species $A_{2u}$ and $E_{2u}$; consequently the four modes belonging to these symmetry species are infrared active. Similarly, the symmetry species of the polarizability tensor are $A_{1g}$, $B_{1g}$, $B_{2g}$ and $E_g$; hence the four modes of these symmetry species are Raman active. The three remaining modes ($A_{2g}$ and $B_{1u}$) do not interact directly with electromagnetic radiation (Summitt, 1968).
### TABLE I

CASSITERITE X-RAY DIFFRACTION DATA (from Berry, 1974)

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>( \frac{I}{I_0} )</th>
<th>h k l</th>
<th>d (Å)</th>
<th>( \frac{I}{I_0} )</th>
<th>h k l</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.35</td>
<td>100</td>
<td>110</td>
<td>1.092</td>
<td>8</td>
<td>312</td>
</tr>
<tr>
<td>2.644</td>
<td>80</td>
<td>101</td>
<td>1.081</td>
<td>8</td>
<td>411</td>
</tr>
<tr>
<td>2.369</td>
<td>25</td>
<td>200</td>
<td>1.059</td>
<td>4</td>
<td>420</td>
</tr>
<tr>
<td>2.309</td>
<td>6</td>
<td>111</td>
<td>1.036</td>
<td>4</td>
<td>103</td>
</tr>
<tr>
<td>2.120</td>
<td>2</td>
<td>210</td>
<td>0.9505</td>
<td>8</td>
<td>402</td>
</tr>
<tr>
<td>1.765</td>
<td>65</td>
<td>211</td>
<td>0.9291</td>
<td>4</td>
<td>510</td>
</tr>
<tr>
<td>1.675</td>
<td>18</td>
<td>220</td>
<td>0.9143</td>
<td>4</td>
<td>332</td>
</tr>
<tr>
<td>1.593</td>
<td>8</td>
<td>002</td>
<td>0.9081</td>
<td>8</td>
<td>501</td>
</tr>
<tr>
<td>1.498</td>
<td>14</td>
<td>310</td>
<td>0.8819</td>
<td>8</td>
<td>422</td>
</tr>
<tr>
<td>1.439</td>
<td>18</td>
<td>112</td>
<td>0.8814</td>
<td>6</td>
<td>303</td>
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<tr>
<td>1.415</td>
<td>16</td>
<td>301</td>
<td>0.8480</td>
<td>6</td>
<td>521</td>
</tr>
<tr>
<td>1.322</td>
<td>8</td>
<td>202</td>
<td>0.8375</td>
<td>2</td>
<td>440</td>
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<tr>
<td>1.215</td>
<td>12</td>
<td>321</td>
<td>0.8261</td>
<td>4</td>
<td>323</td>
</tr>
<tr>
<td>1.184</td>
<td>4</td>
<td>400</td>
<td>0.8125</td>
<td>2</td>
<td>530</td>
</tr>
<tr>
<td>1.155</td>
<td>8</td>
<td>222</td>
<td>0.8026</td>
<td>6</td>
<td>512</td>
</tr>
</tbody>
</table>

Rad. CuKα₁

On the basis of the symmetry and structure of cassiterite, the single vibration of species A₂u₁ corresponds to a displacement of Sn⁴⁺ relative to the O²⁻ ions along the crystal axis while the three E_u species give dipole oscillations perpendicular to this axis. In the latter species, infrared bands at 244–276 cm⁻¹ correspond to Sn⁴⁺ vibrations involving Sn–O stretching. The in-plane and out-of-plane vibrations of O²⁻ give infrared bands at 618–770 cm⁻¹ and 293–366 cm⁻¹, respectively (Farmer, 1974).

#### 2.1.4 Solubility

Pure cassiterite is chemically inert and highly insoluble. For natural cassiterites, the concentration of tin species dissolved into aqueous solution at room temperature is below the 0.5 µg/ml detection level for soluble tin.
TABLE II
INFRARED AND RAMAN VIBRATIONS OF CASSITERITE
(from Katiyar et al, 1971)

<table>
<thead>
<tr>
<th>Species and Activity</th>
<th>Displacements</th>
<th>Sn (D'&quot;2h)</th>
<th>O (C'&quot;2f)</th>
<th>SnO₂ Frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁₆ (R)</td>
<td>0</td>
<td>1a</td>
<td></td>
<td>638</td>
</tr>
<tr>
<td>A₂₆</td>
<td>0</td>
<td>1d'</td>
<td></td>
<td>398</td>
</tr>
<tr>
<td>B₁₆ (R)</td>
<td>0</td>
<td>1d'</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>B₂₆ (R)</td>
<td>0</td>
<td>1a</td>
<td></td>
<td>782</td>
</tr>
<tr>
<td>E₅ (R)</td>
<td>0</td>
<td>1z</td>
<td></td>
<td>441</td>
</tr>
<tr>
<td>A₂u (IR)</td>
<td>1z</td>
<td>1z</td>
<td></td>
<td>477 (TO); 705 (LO) + acoustic</td>
</tr>
<tr>
<td>B₁u</td>
<td>1z</td>
<td>1z</td>
<td></td>
<td>505</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>140</td>
</tr>
<tr>
<td>E¹_u</td>
<td></td>
<td></td>
<td></td>
<td>244 (TO); 276 (LO)</td>
</tr>
<tr>
<td>E²_u (IR)</td>
<td>2p</td>
<td>2h</td>
<td></td>
<td>293 (TO); 366 (LO)</td>
</tr>
<tr>
<td>E³_u</td>
<td></td>
<td></td>
<td></td>
<td>618 (TO); 770 (LO) + acoustic</td>
</tr>
</tbody>
</table>

Directions of the displacements: a = along C₂" axis; z = parallel to c axis; h = perpendicular to c-axis; d' = perpendicular to diagonal axis.

species (Barsukov and Klintsova, 1970). Estimates made with stannic dioxide powder indicate an equilibrium solubility with respect to hydrous stannic oxide of 4 x 10⁻⁷ moles/litre. In the pH range 2.0 - 11.4, this solubility is independent of pH (Barsukov and Klintsova, 1970). Under flotation conditions, equilibrium with respect to solubility would not be expected as the kinetics of dissolution are extremely slow (Gruner and Lin, 1926). The concentration of stannic ion species in flotation pulps is, therefore, negligible in the pH range of interest in tin flotation.

The tin ion in aqueous solution can exist in either the stannic (Sn(IV)) or stannous (Sn(II)) oxidation states. Under the oxidation-reduction potential (Eh) conditions existing in flotation pulps, only stannic ion
species are stable (Pourbaix, 1966). Thermodynamic analyses of the Sn–H₂O system (Appendices A and B) indicate that dissolution of cassiterite in the pH range 0.5 to 11.4 gives rise to the neutral hydrous stannic oxide species Sn(OH)₄ (Figure 2):

$$\text{SnO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Sn(OH)}_4^-$$

These species are metastable with respect to stannic dioxide (Klintsova et al., 1975) and would be expected largely to readsoorb on the cassiterite surface (James and Parks, 1982). The low stability and the readsoorption of the hydrous oxides results in low concentrations of stannic ion species in bulk solution.

Above pH 11.4, cassiterite dissolves to give Sn(OH)₅⁻:

$$\text{SnO}_2 + 2\text{H}_2\text{O} + \text{OH}^- \rightleftharpoons \text{Sn(OH)}_5^-$$

This species has little tendency to readsoorb onto the cassiterite surface and the solubility of cassiterite increases significantly above pH 11.4 (Barsukov and Klintsova, 1970).

No cassiterite solubility analyses have been performed at pH values below 2.0. However, the thermodynamic data of Figure 2 suggest strongly that the solubility of cassiterite will increase appreciably below pH 2.0 commensurate with the greater stability of the lower order stannic hydroxy species and the stannic ion. The strongly hydrated nature of these ions and their positive charge will promote their diffusion away from the cassiterite surface and into the bulk solution.

2.1.5 Cassiterite/Aqueous Solution Interface

In aqueous solution the cassiterite surface becomes strongly hydrated. Hydroxylation of the surface occurs by dissociative adsorption of H₂O, converting surface O²⁻ ions to OH and completing the coordination of exposed
Figure 2 - Distribution Diagram of Individual Sn(IV) Species at a Total Sn(IV) Concentration of $4 \times 10^{-7}$ M (plotted from the data of Appendices A and B).
stannic ions (James and Parks, 1982). A considerably smaller amount of molecular water is attached to oxide anions through hydrogen bonding (Yamazoe et al., 1979; Morishige, Kittawa and Morimoto, 1980; Morimoto, Yokota and Kittaka, 1978; Kittaka, Kanemoto and Morimoto, 1978; Egashira et al., 1981).

Figure 3 shows the stoichiometric (110) cleavage plane of cassiterite. The plane contains equal numbers of surface cations that are four and five-fold coordinate to lattice oxygens whose coordination number is three. The former cation carries two surface oxygens each coordinated to two surface cations whereas the sixth octahedral position of the latter is left vacant by the stoichiometry of the cleavage. Upon exposure to water, this vacant position acts as a coordination site for the oxygen atom of the water molecule. The adsorbed molecule is then transformed into two hydroxyls by proton transfer to an adjacent oxygen ion (Boehm, 1971) producing the hydroxylated state shown in Figure 3a. The same argument holds in the case of the (100) cleavage plane, except that every cation is equivalent. After hydroxylation, the cation carries three hydroxyls with the remaining octahedral positions occupied by lattice oxygens, as shown in Figure 3b.

In Figure 3, both planes contain two types of hydroxyls; those bound to one Sn⁴⁺ site and those bound to two Sn⁴⁺ sites. Furthermore, the hydroxyls are linked with each other or with uppermost lattice oxygen by hydrogen bonding. The mode of this hydrogen bonding is different on different crystal planes (Egashira et al., 1981). These differences are reflected in the different chemical behaviour of hydroxyls bonded to different crystal planes in cassiterite (Morishige, Kittawa and Morimoto, 1980). That there are surface sites of differing acidity on cassiterite also has been suggested by infrared (IR) studies (Thorton and Harrison, 1975).
There appears little doubt that there are a variety of OH sites on hydroxylated cassiterite surfaces that are capable of functioning as proton donors and acceptors. The total surface densities of these ionizable protons (sites nm\(^{-2}\)) have been calculated by a variety of techniques including chemical titration, IR, tritium exchange and crystal structure determination (Boehm, 1971; Morishige, Kittawa and Morimoto, 1980; Egashira et al., 1981; Houchin and Warren, 1984). Values reported range from 0.75 OH groups per nm\(^{-2}\) to 17.8 OH's nm\(^{-2}\).
2.1.6 Electrokinetic Properties

As for other essentially insoluble oxide minerals, the potential determining ions of cassiterite are \( \text{H}^+ \) and \( \text{OH}^- \). The surface charge of the mineral is generally considered to be due to the adsorption-dissociation of \( \text{H}^+ \) from the surface hydroxyls (Jaycock, Ottewill and Tar, 1964):

\[
\begin{align*}
\text{Sn} & \quad \text{OH}^+ \\
\text{Sn} & \quad \text{OH} \\
\text{Sn} & \quad \text{O}^-
\end{align*}
\]

However, Edwards and Ewers (1951) and Wottgen (1969) considered that on the acid side, the hydroxyl ions dissociated to give the structures corresponding to:

\[
\begin{align*}
\text{Sn} & \quad + \\
\text{Sn} & \quad + \\
\end{align*}
\]

The ionization of the cassiterite surface in the form suggested by Edwards and Ewers and Wottgen appears unlikely due to the chemical instability of the four or five coordinated tin(IV) atom (Ball, Cox and Yap, 1978). In aqueous solution, six coordinated tin(IV) is the favoured state and tin(IV) exists as such species as \( \text{SnCl}_6^{2-} \) and \( \text{Sn(OH)}_6^{2-} \) (Masterton and Slowinski, 1978).
Determinations of the isoelectric point (iep) and the point of zero charge (pzc)\(^1\) of cassiterite and stannic oxide have been made by numerous researchers. However, as shown in Table III, the published values often show little agreement. The wide variations of results have been attributed to impurities, sample pretreatment and lattice substitution in natural cassiterite (Blazy, Degoul and Houot, 1969; Edwards and Ewers, 1951).

A number of studies of the effects of lattice substitution on the electrokinetic properties of cassiterite have been made. In early research, the presence of iron in the cassiterite lattice was reported to shift the point of zero charge to higher pH values (O'Connor and Buchanan, 1953) with the magnitude of the shift depending on the iron content (Cibulka and Dobias, 1963). More recent analyses with natural cassiterites (Houchin and Warren, 1986), suggest that the level of substitutional species required to produce observable shifts in the pzc or iep are well in excess of 1000 µg/g. Cassiterites exhibiting a wide range of trace element concentrations were found by these researchers not to have appreciably different points of zero charge or isoelectric points. After due care was taken to remove contaminants prior to size reduction, all measured iep and pzc values occurred in the range 4.1 to 4.7 (Tables IV and V).

\(^1\) The point of zero charge (pzc) denotes the condition under which a direct measurement of the surface charge density gives a zero net charge. The term isoelectric point (iep) denotes the negative logarithm (base 10) of the concentration of potential determining ions at which the electrokinetic potential becomes zero.
<table>
<thead>
<tr>
<th>Source of SnO₂</th>
<th>iep or pzc</th>
<th>Measurement Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stannic Oxide:</td>
<td>iep 4.5</td>
<td>Electrophoresis</td>
<td>Houchin &amp; Warren (1984)</td>
</tr>
<tr>
<td>Aldrich 99.999%</td>
<td>pzc 4.3</td>
<td>Potentiometric Titration</td>
<td></td>
</tr>
<tr>
<td>Stannic Oxide:</td>
<td>iep 4.5,5.4</td>
<td>Electrophoresis</td>
<td>Johansen &amp; Buchanan (1957)</td>
</tr>
<tr>
<td>Sn + HNO₃</td>
<td>iep 5.6,6.5</td>
<td>Electrophoresis</td>
<td></td>
</tr>
<tr>
<td>Above, ignited</td>
<td>pzc 5.5</td>
<td></td>
<td>Huang (1971)</td>
</tr>
<tr>
<td>Stannic Oxide:</td>
<td>pzc 5.5</td>
<td></td>
<td>Kokarev et al (1982)</td>
</tr>
<tr>
<td>Cassiterite:</td>
<td>iep 7.3,7.7</td>
<td>Electrophoresis</td>
<td>Johansen &amp; Buchanan (1957)</td>
</tr>
<tr>
<td>Australia</td>
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<tr>
<td>Cassiterite:</td>
<td>iep 3.4</td>
<td>Streaming Potential</td>
<td>Blazy, Degoul &amp; Houot (1969)</td>
</tr>
<tr>
<td>Rhodesia</td>
<td>iep 3.9</td>
<td>Streaming Potential</td>
<td></td>
</tr>
<tr>
<td>Congo, D.R.</td>
<td>iep 4.5</td>
<td>Streaming Potential</td>
<td></td>
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<td>France</td>
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<td></td>
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<td>Cassiterite:</td>
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<td></td>
<td>Wottgen (1969)</td>
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<td></td>
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<tr>
<td>Cassiterite:</td>
<td>pzc 4.0</td>
<td>Potentiometric Titration</td>
<td>Gutierrez &amp; Pomier (1969)</td>
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<tr>
<td>Potasi (Bolivia)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Catair (Bolivia)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cassiterite:</td>
<td>pzc 5.4,5.5</td>
<td>Potentiometric Titration</td>
<td>Ahmed &amp; Maksimov (1969)</td>
</tr>
<tr>
<td>B.C. (Canada)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cassiterite:</td>
<td>pzc 4.0</td>
<td>Potentiometric Titration</td>
<td>Bellot (1970)</td>
</tr>
<tr>
<td>Potasi (Bolivia)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cassiterite:</td>
<td>iep 3.0</td>
<td>Electrophoresis</td>
<td>de Cuyper &amp; Salas (1977)</td>
</tr>
<tr>
<td>Altenberg (DDR)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cassiterite:</td>
<td>iep 5.5</td>
<td>Electrophoresis</td>
<td>Ball, Cox and Yap (1978)</td>
</tr>
<tr>
<td>Bolivia</td>
<td>iep 4.5</td>
<td>Streaming Potential</td>
<td>Doren, van Lierde &amp; de Cuyper (1979)</td>
</tr>
<tr>
<td></td>
<td>iep 3.9</td>
<td>Electrophoresis</td>
<td>Petruk (1984)</td>
</tr>
<tr>
<td>Cassiterite</td>
<td>iep 4.2</td>
<td>Electrophoresis</td>
<td>Gochin &amp; Solari (1983)</td>
</tr>
</tbody>
</table>
Table IV
TRACE ELEMENT ANALYSIS OF CASSITERITES
(from Houchin and Warren, 1986)

<table>
<thead>
<tr>
<th>Element</th>
<th>South Palmer River</th>
<th>Elsmore</th>
<th>Taronga</th>
<th>Rossarden</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2500</td>
<td>800</td>
<td>1000</td>
<td>300</td>
</tr>
<tr>
<td>Nb</td>
<td>1500</td>
<td>700</td>
<td>&lt;30</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Ti</td>
<td>600</td>
<td>2500</td>
<td>1000</td>
<td>2500</td>
</tr>
<tr>
<td>W</td>
<td>1000</td>
<td>800</td>
<td>600</td>
<td>200</td>
</tr>
<tr>
<td>Si</td>
<td>150</td>
<td>150</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Ta</td>
<td>80</td>
<td>&lt;60</td>
<td>&lt;60</td>
<td>&lt;60</td>
</tr>
<tr>
<td>V</td>
<td>15</td>
<td>15</td>
<td>250</td>
<td>20</td>
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<tr>
<td>Zr</td>
<td>&lt;100</td>
<td>150</td>
<td>&lt;100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table V
COMPARISON OF VARIOUS CASSITERITES IN TERMS OF THEIR POINTS OF ZERO CHARGE (PZC) AND Isoelectric Points (IEP)
(from Houchin and Warren, 1986)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potentiometric Titration</th>
<th>Mular and Roberts Method*</th>
<th>Combined Method</th>
<th>iep Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Palmer River</td>
<td>5.2*</td>
<td>4.6</td>
<td>4.3</td>
<td>4.2</td>
</tr>
<tr>
<td>Elsmore</td>
<td>4.6</td>
<td>4.4</td>
<td>4.3</td>
<td>4.4</td>
</tr>
<tr>
<td>Taronga</td>
<td>4.7</td>
<td>4.5</td>
<td>4.4</td>
<td>4.5</td>
</tr>
<tr>
<td>Rossarden</td>
<td>4.1</td>
<td>4.2</td>
<td>4.1</td>
<td>4.1</td>
</tr>
</tbody>
</table>

δ subject to higher error due to low sample surface area

* Mular and Roberts (1966)
Studies of a more fundamental nature pertaining to the relationship between cassiterite electrokinetic properties and lattice substitution also have been performed. Balachandran (1982), working with stannic dioxide, attempted to correlate shifts in the iep with the temperature of formation and levels of dopant in the dioxide lattice. Increased sintering temperatures were found to shift the iep to more basic pH values (Figure 4). This finding is consistent with the results of Johansen and Buchanan (1957) who established that, while the iep of precipitated hydrous SnO₂ occurred at pH 4.5, ignition of the precipitate at 850°C for two hours increased the isoelectric point to 5.5. Both Parks (1965) and Balachandran (1982) have proposed that heat treatment might result in increased oxygen vacancies in the oxide lattice; the resulting n-type semiconductivity then shifting the iep to more basic pH values.

Figure 4 - Electrokinetic Behaviour of Undoped Synthetic Cassiterite as a Function of Sintering Temperature (from Balachandran, 1982).
Several studies have been performed with doped stannic dioxide crystals. Gruner (1971) measured the electrophoretic mobilities of a series of such samples using streaming potential techniques. The presence of dopants did not change significantly the iep from that of the undoped sample (iep 4.0) except in the case of titanium doped dioxide for which no iep was found in the range pH 3.0 - 9.0. However, measurable differences in zeta potentials of all doped stannic dioxides did occur at pH values above the iep (Figure 5). In similar research, Balachandran found that both antimony (donor impurity) and iron (acceptor impurity) shifted the iep of synthetic cassiterite to more basic pH values (Figure 6). The absence of any correlation between iep and semiconducting properties, in this latter case, was interpreted as indicating that the isoelectric point of the synthetic oxide was controlled by both electronic and atomic defects in the lattice. The precise nature of this effect was, however, not specified.

Comparison of the Gruner and Balachandran data indicates a number of disparities. Immediately evident is that the iep values reported by the researches, for both undoped and doped stannic dioxide crystals, differ by approximately two pH units. Furthermore, the effect of iron doping, for which a direct comparison is possible, shows opposing trends; the Gruner data indicating that iron doping moves the iep to more acidic pH values while the Balachandran data indicating an higher iep value with iron doping. The isoelectric points determined by Balachandran (1982) for pure, antimony doped and iron doped stannic dioxide (6.1, 6.8 and 6.9, respectively) are also much higher than the values generally reported for natural cassiterites. In the latter case, the iep values are typically between 4.0 and 5.5 (Tables III and V).
Figure 6 - Electrokinetic Behaviour of Doped and Undoped Cassiterite Sintered at 1400 °C. (from Balachandran, 1982).
Disparities in electrokinetic properties between different synthetic stannic dioxides and between synthetic and natural crystals presumably reflects variations in the conditions of formation of the crystals. Significant differences in temperature, pressure and oxygen-potential of formation almost certainly exist between geological environments and laboratory conditions of synthesis. For example, Patterson, Ohmoto and Solomon (1981) have established that formation of cassiterite in the Renison Bell deposit (Australia) took place at about 350°C at low \( f_2 \) (about \( 10^{-31.5} \) atm) and low pH (3.9 - 5.4). These conditions are far removed from the conditions of synthesis used by Gruner (1971) (growth of crystals from stannic dioxide powder vaporized at 1300°C and allowed to condense) and Balachandran (firing of pressed stannic dioxide pellets at 1400°C in air for 4 hours).
2.2 Phosphonic Acids

2.2.1 Chemical Structure and Synthesis

Phosphonic acids are compounds of the general form \( \text{RP(O)(OH)}_2 \) where \( R \) can be either an aryl or an alkyl hydrocarbon radical. Various methods for synthesis of the phosphonic acids have been published (Freedman and Doak, 1957). The generally preferred method for aryl phosphonic acids is the Friedel-Crafts reaction between phosphorus trichloride and aromatic hydrocarbons as proposed by Kosolapoff and Huber (1946, 1947). A disadvantage of this method is, however, that mixtures of aryl phosphonic acids are usually obtained. For example, Kosolapoff (1952) showed that the tolyl and ethylphenylene phosphonic acids produced by the Friedel-Crafts reaction, while containing predominantly the para isomer, also contained significant proportions of meta and ortho isomers.

Styryl phosphonic acid was first synthesized according to the Friedel-Crafts reaction by Kosolapoff and Huber in 1946. The phosphonic acid was reported to be quite stable with a melting point of 140 - 144°C. In 1970, an East German patent was granted for a method of commercial production of styryl phosphonic acid for use in cassiterite flotation (Roeder et al., 1970). Reference to the patent indicates that the method of reagent synthesis is identical to that of Kosolapoff and Huber except that the solvent for the initial hydrocarbon reactant is carbon tetrachloride rather than benzene.

A number of major inconsistencies exist in the nomenclature used to describe phosphonic acid flotation reagents.\(^2\) In many cases, this has led to

\(^2\) Much of the phosphonic acid nomenclature used in the flotation literature does not conform to IUPAC convention. Thus styrene rather than the correct term styryl is most commonly used for the radical \( \text{C}_6\text{H}_5-\text{CH=CH-} \) (IUPAC Rule A 13.2 ). Similarly, the correct nomenclature for the radical \( \text{CH}_3-\text{CH}_2-\text{C}_6\text{H}_4- \) is p-ethylphenylene not "ethyl phenyl".
confusion regarding the chemical structures of phosphonic acid collectors. The use of trademark flotation reagents, without disclosure of the nature of the compounds, has further contributed to the problem.

At present, four major tin flotation operations are believed to be using phosphonic acid collectors. Both Altenberg (G.D.R.) and Renison Limited (Aust.) are using styryl phosphonic acid. Renison's styryl phosphonic acid is supplied by Plaistere and Hanger International Limited (U.K.) under the trade name PH-PEP. Phosphonic acid collector is also used at Rooiberg and Union Tin in South Africa. According to both Moncrieff and Lewis (1977) and Bulled (1982), this reagent is "ethyl phenyl" phosphonic acid. However, uncertainty exists as to the actual composition of the collector used at these two mines as Bulled states that "ethyl phenyl" phosphonic acid is otherwise known as "styrene" (styryl) phosphonic acid. This is incorrect and the two compounds have distinctly different structures:

Styryl Phosphonic Acid:

\[
\text{PhCH=CH-P(O)(OH)₂}
\]

p-ethylphenylene Phosphonic Acid:

\[
\text{CH₃-CH₂-Ph-P(O)(OH)₂}
\]

2.2.2 Ultraviolet and Infrared Spectra

The ultraviolet spectra of a considerable number of aryl phosphonic acids have been published (Jaffé and Freedman, 1952; Polestak and Zimmerman, 1956). In general, the phosphonic acid \((\text{P(O)(OH)₂})\) group causes no profound change in
the characteristics of the spectrum of the parent hydrocarbon compound. The absorption maxima of most aryl phosphonic acids show bathochromic shifts of about 10 nm, and the intensity of absorption is increased by a factor between 1.5 and 5. Any fine structure found in the spectrum of the parent compound is usually unaltered by the presence of the P(O)(OH)₂ group. The slight bathochromic shift and the moderate hyperchromic effect have been ascribed to a weak resonance interaction between the P(O)(OH)₂ group and the phenyl ring (Freedman and Doak, 1957; Hudson, 1965). The effects of the P(O)(OH)O⁻ and P(O)(O⁻)₂ groups in aqueous solution are generally less than that of the P(O)(OH)₂ group (Jaffé and Freedman, 1952; Polestak and Zimmerman, 1956; Banks and Davis, 1955) reflecting the increasing ionizing influence which the water solvent exercises on the acid.

A number of studies of the infrared spectra of phosphonic acids have been made. The key phosphorus group vibration frequencies for a range of aryl and alkyl phosphonic acids have been reported by Wottgen and Dietze (1969). Full spectra of phenyl and butyl phosphonic acids also have been published (Daasch and Smith, 1951; Ferraro, Peppard and Mason, 1965). Studies of other related organo-phosphorus compounds have further indicated characteristic frequency ranges for a number of fundamental phosphonic acid vibrations. These are reviewed and summarized in standard references on infrared spectroscopy, such as those of Bellamy (1962), Thomas (1974) and Socrates (1980).

2.2.3 Solution Chemistry

The phosphonic acids are weak dibasic acids. Chavane (1949) gives the first and second ionization constants of styryl phosphonic acid as pK₁ = 2.00 and pK₂ = 7.10. In the pH range of cassiterite flotation, the partially dissociated species is, therefore, the predominant styryl phosphonic acid.
species in solution.

A number of systematic measurements of the effects of hydrocarbon radicals on the pK's of phosphonic acids have been made (Ashby and Kosolapoff, 1953; Crofts and Kosolapoff, 1953). The dissociation constants for aromatic phosphonic acids (Jaffé, Freedman and Doak, 1953; Banks and Davis, 1955) correlate closely with the Hammett substituent parameter (Hammett, 1940) giving a value of $\rho = 0.75$ (Figure 7). This low value of the Hammett reaction constant has been attributed to the low polarizability of the phosphorus ion. Evidence that the dissociation of aryl phosphonic acids is affected by $\pi$-bonding of the aryl ring with the phosphorus atom also has been found in the close correlation between the acid pKₐ values and $\sigma$.

Martin and Griffen (1964) have shown that the pKₐ's of phenyl phosphonic and styryl phosphonic acid are predicted accurately by the Taft $\sigma^*$ inductive parameters (Taft, 1956). The Taft $\sigma^*$ constants also correlate with the pKₐ values of alkyl phosphonic acids (Martin and Griffin, 1964). The pKₐ's of a wide range of alkyl phosphonic acids are given by the equations:

$$\log K_1 = -2.47 + 1.121 \sigma^*$$
$$\log K_2 = -7.77 + 1.177 \sigma^*$$

As in the case of the aryl acids, the reaction parameters for the first and second ionizations (1.121 and 1.177) are relatively low, indicating that electronic effects are not transmitted readily through the phosphorus atom (Hudson, 1965).

In the solid state and in certain non-polar solvents, the phosphonic acids associate in long chains through molecular hydrogen bonding. The existence of these bonds has been demonstrated clearly by molecular weight studies, infrared spectroscopy and X-ray diffraction (Kosolapoff and Powell, 1950;
Freedman, Doak and Ezzell, 1971). In aqueous solution, the phosphonic acids can display striking variations in solubility depending on the nature of the hydrocarbon radical (Ashby and Kosolapoff, 1953). The commercially important styryl phosphonic acid is only sparingly soluble in water and is prepared industrially for flotation circuits as the sodium salt. Kosolapoff (1952) has proposed that, at low pH, hydrogen bonding might persist in aqueous solution for certain phosphonic acids. Thus, the much lower solubility of p-tolyl phosphonic acid compared to the other two tolyl isomers was considered to reflect the greater tendency for polymeric hydrogen bonding of the para isomer (Ashby and Kosolapoff, 1953). On the other hand, Freedman and Doak (1956) have argued that the weak energy of the hydrogen bond would result in rapid dissolution of such associations in a polar solvent such as water. Molecular weight determinations of phosphonic acids in glacial acetic acid (Freedman and
Doak, 1956) and ethanol (Freedman, Doak and Ezzell, 1971) have supported this latter view. At present, there appears to be insufficient evidence for assigning a polymeric structure to phosphonic acids in aqueous solution.

Surface tension measurements of phosphonic acids in aqueous solution have not been published. However, given the poor solubility of the acids in acidic solution, surface tension lowering effects might be expected at low pH.

2.2.4 Ion Interactions

The presence of cations in flotation pulps is well known to affect the flotation of cassiterite with phosphonic acids. High ferric ion levels, in particular, are believed to have a strong depressant effect on flotation (Collins and Jackson, 1967; Iriarte, 1985). Calcium ions also have been reported as interacting but much less strongly than ferric ions (Collins, 1967; Wottgen and Topfer, 1976; Iriarte, 1985).

Despite the widely accepted importance of dissolved metal ionic species in phosphonic acid flotation, few fundamental studies of cation-phosphonic acid interactions have been made. Wottgen and Dietze (1969) prepared the ferric ion precipitates of a number of phosphonic acids and noted some of the key infrared absorption bands. Freedman and Doak (1955) found that magnesium salts of aryl phosphonic acids did not form in cold solution when the acids were treated with magnesia. No other direct studies of the interactions of phosphonic acids with cations of interest in flotation have been reported. Stability diagrams for aqueous phosphonic acid salts have not been defined nor has the interaction of phosphonic acids with cationic hydroxy or hydrous oxide sols been examined experimentally.
2.3 Ions Present in Cassiterite Flotation Pulps

It is well recognised that cassiterite flotation pulps contain appreciable levels of metal cations. Aluminum, iron, magnesium and calcium cations are the most frequently reported such aqueous species (Collins, Hollick and Joy, 1969; Pol'kin et al., 1973; Arbiter, 1977; Bulled, 1982).

The levels of metal ion aqueous species in flotation plant process waters can vary significantly both within an individual circuit and from plant to plant. Factors influencing the concentrations of metal ion species in solution include:

(i) the dissolved ion levels in plant water supplies
(ii) type, solubility and reactivity of associated gangue species
(iii) the flotation plant operating pH and pulp potential
(iv) the extent of ion adsorption on mineral surfaces

Recent analyses (Winby, 1985) of cassiterite flotation pulps in the tin concentrator of Renison Limited (Aust.) are summarized in Table VI. While somewhat variable, the concentrations of aluminum (0.1-4.8 ppm) and iron (0.1-62.0 ppm) in the flotation pulps are appreciable. The level of copper ions is more consistent throughout the circuit but is not considered significant at below 0.05 ppm. The levels of both calcium and magnesium ions (160-520 ppm and 300-600 ppm, respectively) are very high indicating the "hardness" of Renison process water.

The sources of high levels of dissolved metal ions in flotation circuits are of considerable importance in understanding the effects of ions on cassiterite flotation. In the Renison circuit, pyrrhotite, pyrite and siderite are major gangue species (Patterson, Ohmoto and Solomon, 1981). Oxidation of sulphide minerals such as pyrrhotite and pyrite releases iron
### TABLE VI

**SUMMARY OF RENISON CASSITERITE FLOTATION PULP WATER ANALYSES**
(data from Winby, 1985)

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Pulp pH</th>
<th>Pulp Eh (mV)</th>
<th>Ion Concentrations</th>
<th>Total Alkalinity (ppm CaCO₃)</th>
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</thead>
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<tr>
<td></td>
<td>Fe</td>
<td>Al</td>
<td>Cu</td>
<td>Mg</td>
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<tr>
<td>1</td>
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<td>2</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>62.0</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>61.0</td>
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</tr>
<tr>
<td>5</td>
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</tr>
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<td>6</td>
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<td>7</td>
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<td>8</td>
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</tr>
<tr>
<td>9</td>
<td>7.31</td>
<td>-13</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>10</td>
<td>7.30</td>
<td>-10</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>11</td>
<td>7.31</td>
<td>-7</td>
<td>0.3</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>12</td>
<td>5.21</td>
<td>44</td>
<td>17.0</td>
<td>4.8</td>
</tr>
<tr>
<td>13</td>
<td>5.24</td>
<td>39</td>
<td>17.3</td>
<td>4.2</td>
</tr>
<tr>
<td>14</td>
<td>5.21</td>
<td>41</td>
<td>18.2</td>
<td>3.8</td>
</tr>
</tbody>
</table>

into solution. The pyrite in the Renison ore, in particular, is believed to be highly reactive (Trahar, 1985). Dissolution of siderite at low pH (pH < 4.0) can also release iron into solution. However, the kinetics of such dissolution in a flotation environment have not been established. Significant levels of iron in solution undoubtedly also result from the abrasion of grinding media in the Renison comminution circuits. The sources of the aluminum ions are somewhat less certain but might include the dissolution of alumino-silicate minerals such as tourmaline which are present in the Renison ore. Dissolution of tourmaline below pH 4.0 has been demonstrated by both Ticona (1985) and Houchin (1986). The high levels of calcium and magnesium in the flotation circuit are indicative of the high concentrations of these cations in the plant water supplies.
2.3.1 Aluminum Solution Chemistry

2.3.1.1 Hydrolysis of Aluminum Ions

The free aluminum ion exists in aqueous solution as the hexaquo ion i.e. the ion is hydrated by six water molecules. Each hydrated water molecule is in turn hydrogen bonded to other water molecules. When base is added to the solution, hydronium ions are removed and it becomes energetically favourable for the hydrogen atoms on the hydrate water molecules to release electrons to the aluminum ion and transfer through the hydrogen bond to a neighbouring $\text{H}_2\text{O}$ (or $\text{OH}^-$) to form either $\text{H}_3\text{O}^+$ to be neutralized or $\text{H}_2\text{O}$ directly (Figure 8). The hydrated aluminum ion thus acts as a weak Bronsted acid being neutralized. According to this scheme, the aluminum ion can participate in a series of consecutive proton transfers:

$$
\text{Al(H}_2\text{O)}_6^{3+} \rightarrow \text{Al(H}_2\text{O)}_5(\text{OH})^{2+} + \text{H}^+ \rightarrow \text{Al(H}_2\text{O)}_4(\text{OH})^{2-} + 2\text{H}^+ \\
\rightarrow \text{Al(H}_2\text{O)}_3(\text{OH})_3 + 3\text{H}^- \rightarrow \text{Al(H}_2\text{O)}_2(\text{OH})_4^- + 4\text{H}^-
$$

Although the above hydrolysis products of Al(III) are all known and identified, small polymeric ions and nonstoichiometric hydrous oxides also result during aluminum hydrolysis. In the polymeric ions, directional bonding characteristically produces rings or clusters (Stol, van Helden, and de Bruyn, 1976). In the hydrous oxide, hydroxide and oxide ions are coordinated to the aluminum ion, together with a variable amount of water hydrogen bonded into the structure as well as coordinated to the cation (Figure 9).

Several polymeric aluminum ions have been reported in the literature. The simplest polymerized species is the dimer $\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$ which has the structure:
Figure 8 - Schematic Illustration of the Hydroxylation of Aluminum Ions in Aqueous Solution (from Porterfield, 1984).

Figure 9 - Schematic Illustration of the Hydrogen Bonding in Hydrous Aluminum Oxide Sols (from Porterfield, 1984).
Further polymerization of the dimer produces larger polymeric ions such as $\text{Al}_6(\text{OH})_{16}^{3+}$ (Brosset, Biedermann and Sillén, 1954), $\text{Al}_8(\text{OH})_{20}^{4+}$ (Matijevic et al., 1961), $\text{Al}_7(\text{OH})_{17}^{4+}$ and $\text{Al}_{13}(\text{OH})_{34}^{5+}$ (Stumm, 1965), $\text{Al}_4(\text{OH})_8^{4+}$, $\text{Al}_7(\text{OH})_{16}^{5+}$, $\text{Al}_{10}(\text{OH})_{24}^{6+}$, and $\text{Al}_{13}(\text{OH})_{32}^{7+}$ (van Cauwelaert and Bosmans, 1969) and ultimately colloidal dispersions (sols) of aluminum-hydroxy polycations and hydrous aluminum oxides.

Bonding in the low molecular weight polymeric ions is through OH bridges (the formation of which is referred to as olation). Such bonding is possible due to the ability of the OH$^-$ ion to serve as a Lewis base two or three times in bridging metal ions, since it has three pairs of non-bonding electrons. In large polymers, bonding through oxygen bridges (oxolation) can also occur. Due to their reduced charge, species formed in the oxolation process undergo rapid coagulation giving rise to hydrous aluminum oxide sols.

Formation of hydrous oxide precipitates or colloidal dispersions can also occur via condensation of neutral monomeric $\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3$ species (Porterfield, 1984). The absence of monopole electrostatic repulsion allows the $\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3$ molecules to aggregate through olation and hydrogen bonding which can include intermediate water molecules as shown in Figure 9. These hydrous oxide sols are extremely soft and ill defined due to their lack of crystalline symmetry and the weak nature of the hydrogen bond.

In solutions where polymeric aluminum species are formed, the kinetics of formation of these polymers is rapid whereas their breakdown is very slow (Stol, van Helden and de Bruyn, 1976). Kinetic studies have further indicated that the dissolution process is not simply the reverse of the formation process. The degradation of polymers is believed to occur in two stages (Figure 10). The first step in the reaction is the loosening of Al-OH-Al
olation bonds. This step proceeds slowly and is rate determining. It is followed by a fast elementary step in which severance of the bond and the uptake of a water molecule as a ligand occurs.

\[
\begin{align*}
\text{Al}^{n+} \text{OH} & \xrightleftharpoons{\text{slow}} \text{fast} \text{H}^+ \rightarrow \text{Al}^{n+1} \text{OH}_2 \xrightarrow{\text{H}_2\text{O}} \text{Al}^{n+1} \text{OH}_2
\end{align*}
\]

Figure 10 - Proposed Mechanism for the Dissolution of Hydrous Aluminum Oxide Sols. The six coordination of aluminum is indicated schematically with one bridging OH shown (from Stol, van Helden and de Bruyn, 1976).

2.3.1.2 Hydrous Oxide Precipitation

Aging of hydrous oxide sols ultimately results in the formation of precipitates. The chemical and structural composition, particle size and morphology of these precipitates can vary considerably depending on the concentration of aluminum ions, pH, temperature, aging time and the nature of any anions present. The type of anion present, in particular, can affect markedly the course of precipitation. Precipitation is greatly accelerated in sulphate solutions. It has been proposed (de Hek, Stol and de Bruyn, 1978) that the divalent sulphate ion can screen the positive charge of the polynuclear aluminum complexes and thereby assist in the linking together of the complexes that ultimately form the solid precipitate lattice.

Despite innumerable studies of precipitation in hydrolyzed aluminum solutions, the relationships between hydrolysis products in solution and the mechanisms by which a precipitate and ultimately a solid phase is produced are
not completely understood. Precipitation does exhibit aspects of crystal growth phenomena such as nucleation and initial growth phases (de Hek, Stol and de Bruyn, 1978) but crystal growth mechanisms do not apply directly since the process does not involve only the deposition of ionic units upon a growing crystal nucleus. The initial stage in precipitation is probably the linking together by hydrogen bonding and van der Waals interactions of polymeric species in solution to form three dimensional structures. The formation of a solid phase must then necessarily involve the elimination of coordinated water from these structures together with continued oxolation reactions.

2.3.1.3 Electrokinetic Properties of Hydrous Oxides

Numerous determinations of the iep of a variety of hydrous aluminum oxides have indicated values ranging from pH 2.0 to 10.0 with some concentration of values between pH 7.0 and 9.0 (Parks, 1965). These wide variations in iep undoubtedly mirror changes in hydrous oxide chemical and structural composition, particle size and morphology. These characteristics are influenced strongly by the conditions of precipitation.

When first formed, hydrous aluminum oxides are amorphous. With aging, distinct phases such as γ-A1OOH and α-A1OOH are formed. Associated with such aging processes are changes in the degree of hydration and the extent of olation and oxolation bonding in the hydrous oxides. Analyses by Parks (1965) and Robinson, Pask and Fuerstenau (1965) suggest that the iep of hydrous oxides decreases with diminishing degrees of hydration and increased structural perfection accompanying continued oxolation reactions. In the latter case, a decrease in the iep is to be expected as increased oxolation at the expense of olation reduces the number of coordinated hydroxyl ions in the polymer and therefore its basic character.
The purity of hydrous aluminum oxide sols can also affect the iep. Brace and Matijevic (1973) have shown that hydrous aluminum oxide sols containing sulphate ions have a lower iep than those that are sulphate free.

2.3.1.4 Thermodynamic Analyses

A wide variety of experimental techniques has been used in solution preparation and analysis for determination of aluminum ion stability constants. Consequently, it is difficult to assess the degree to which results might have been affected by polymerization reactions and the absence of true equilibria. The polymerization reactions themselves are also extremely difficult to investigate quantitatively because of their complexity and the absence of equilibrium conditions. The instability of aluminum ion solutions therefore adds to the many other sources of error attending equilibrium studies in general.

Following the work of Baes and Mesmer (1976), reliable thermodynamic data are believed available for the four mononuclear species Al(OH)$_2^{2+}$, Al(OH)$_2^+$, Al(OH)$_3^{aq}$, and Al(OH)$_4^-$ and the polynuclear species Al$_2$(OH)$_2^{4+}$, Al$_3$(OH)$_4^{5+}$ and Al$_{13}$O$_4$(OH)$_2^{7+}$. From the Gibbs free energy data of these hydrolysis species, it is possible to calculate the distributions of the various aluminum species present in aqueous solution as a function of pH. These data can be presented graphically in a number of ways. Figure 11 shows the log concentrations of aluminum species in aqueous solution plotted with respect to pH assuming thermodynamic equilibria. An alternative method of presenting the data is to plot the mole fraction of each hydrolysis species as a function of pH. Figure 12 shows the distribution of individual Al(III) species at total aluminum ion concentrations of $5 \times 10^{-6}$ M and $2 \times 10^{-4}$ M. These concentrations represent the limits of the range of aluminum ion levels found
in Renison water analyses (Table VI). Details of all thermodynamic calculations are given in Appendices A and B.

Figure 11 - Equilibrium Diagram for Monomeric and Polymeric Aluminum Species in Contact with Freshly Precipitated Hydrous Aluminum Oxide.
Figure 12 - Distribution Diagrams of Individual Al(III) Species at Total Aluminum Ion Concentrations believed Typical of Industrial Plant Waters. In the shaded areas the solution becomes oversaturated with respect to the hydrous oxide. Additional polynuclear hydrolysis species occur as kinetic intermediates in this pH range.
Reference to Figures 11 and 12 indicates that aluminum ion solutions become saturated with respect to hydrous aluminum oxide precipitates at pH values above 5.0 and 4.25 for Al(III) concentrations of $5 \times 10^{-6}$ M (0.1 ppm) and $2 \times 10^{-6}$ M (5.4 ppm), respectively. Consequently, in the pH range typical of cassiterite flotation circuits (pH 5.0 - 7.5) aluminum exists predominantly in the form of hydrous aluminum oxide species. These hydrous oxides are kinetic intermediates in the usually slow transition to the precipitated solid phase and, while stable almost indefinitely, are in fact metastable with respect to the precipitate.

2.3.2 Iron Solution Chemistry

Iron exists in aqueous solution in one of two possible oxidation states, ferrous (+2) and ferric (+3). In well aerated solutions, ferrous ions can be oxidized to ferric ions or ferric ion hydrolysis species depending upon pH.

2.3.2.1 Ferric Ion Hydrolysis

The hydrolysis of the ferric ion proceeds in a similar manner to that of the aluminum ion, the two ions having identical charge and similar size. The mononuclear species $\text{Fe(H}_2\text{O)}_5\text{(OH)}^2^+$, $\text{Fe(H}_2\text{O)}_4\text{(OH)}_2^+$, $\text{Fe(H}_2\text{O)}_3\text{(OH)}_3$ and $\text{Fe(H}_2\text{O)}_2\text{(OH)}_4^-$ have all been identified together with polymeric ions and hydrous ferric oxide species.

Detailed analyses of ferric ion hydrolysis have been performed by numerous researchers. Evidence for the existence of the dimer was first provided by Hedstrom (1953) and subsequently confirmed by Mulay and Selwood (1954). Simultaneous pH and optical measurements (Dousma and de Bruyn, 1976; Dousma and de Bruyn, 1978) have shown that the dimer can continue to polymerize by abstraction of OH$^-$ from solution to produce small polymers:
Further polymerization leads to larger polymers of general formula:

\[
\left[ \begin{array}{c}
\text{Fe} \\
\text{H} \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{Fe} \\
\text{O} \\
\text{Fe} \\
\text{Fe} \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{Fe} \\
\end{array} \right] \] ^{n+} \left[ \begin{array}{c}
\text{Fe} \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{Fe} \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{Fe} \\
\text{Fe} \\
\text{O} \\
\text{Fe} \\
\end{array} \right] ^{n/2}
\]

According to Dousma and de Bruyn, oxolation of these large polymers produces:

\[
\left[ \begin{array}{c}
\text{Fe} \\
\text{O} \\
\text{H} \\
\text{O} \\
\text{Fe} \\
\text{O} \\
\text{Fe} \\
\end{array} \right] ^{n/2}
\]

which constitutes the hydrous ferric oxide precipitates.

Ultraviolet (Segal, 1984a) and Mossbauer (Music et al., 1982) spectroscopic studies of the hydrolysis of ferric ion solutions have supported the reaction scheme whereby monomers and dimers of ferric ion form initially, followed by the formation of larger ferric-hydroxy polycations and ultimately hydrous ferric oxide.

2.3.2.2 Hydrous Ferric Oxides

The initial phase precipitated from ferric ion solutions is an amorphous hydrous oxide. Analyses of the polymeric species comprising such amorphous sols have shown that they are generally of uniform size with a clearly discernable maximum size (Spiro, Bates and Saltman, 1967; Murphy, Posner and Quirk, 1976-1976c; van der Woude and de Bruyn, 1983). It is generally accepted that the maximum size is approximately 5 nm corresponding to a
molecular weight of the order of $10^5$ (van der Woude and de Bruyn, 1983). It further has been established that the formation of these polymers is independent of total iron (III) concentration, ionic strength and pH.

Recent relaxation experiments (van der Woude and de Bruyn, 1983) have shown that the formation of hydrous ferric oxide sols involves clearly defined nucleation and growth stages. In the nucleation stage, a critical nucleus containing a maximum of 16 to 32 iron atoms is formed. This amorphous precursor phase then grows to an eventual maximum average size of about 5 nm. The rates of nucleation and growth of the amorphous phase are largely dependent on the concentration of polynuclear iron(III) hydroxo-complexes in solution.

Hydrous oxide sols, when allowed to age for extended time periods, transform slowly into crystalline solids. These solid phases can vary markedly in composition, morphology and particle size. In general, three crystalline structures: goethite, lepidocrocite and $\beta$-FeOOH, are formed from ferric solutions. Goethite ($\alpha$-FeOOH) most commonly forms at room temperature.

2.3.2.3 Hydrolysis Kinetics

The kinetics of ferric ion hydrolysis and precipitation are of fundamental importance in flotation environments. The formation of ferric-hydroxy polycations has been shown by many researchers to be rapid while depolymerization and dissociation, even in the presence of excess acid, are very slow (Lamb and Jacques, 1938; Segal, 1984a). In terms of flotation kinetics, colloidal dispersions of polycations and hydrous ferric oxides are stable almost indefinitely. Precipitation from saturated sol solutions generally commences the order of days after initiation of polymerization (Spiro et al, 1966; Segal, 1984a).
2.3.2.4 Electrokinetic Properties of Hydrous Ferric Oxides

The reported iep values of hydrous ferric oxides show little consistency ranging from pH 1.9 to 9.0 (Parks, 1965). As for the hydrous aluminum oxides, these variations are presumably due to the chemical and structural composition, particle size and morphology of the studied hydrous oxides.

The products of ferric ion hydrolysis can vary substantially depending upon the conditions of precipitation and aging time. Initial hydrous oxide products are generally amorphous in character. With reference to the iep compilations of Parks (1965), the reported iep values of such amorphous phases, while showing appreciable variability, do exhibit some clustering of values around pH 8.5. Lepidocrocite ($\gamma$-FeOOH) and goethite ($\alpha$-FeOOH) phases show slightly lower iep values with frequently occurring values around pH 7.4. Clustering of reported iep values of hematite ($\alpha$-Fe$_2$O$_3$) formed by hydrolysis occurs around pH 8.6.

2.3.2.5 Effects of Complexing Reagents

Unlike counterions, such as the chloride and nitrate ions, the presence of chelating agents in ferric ion solutions can affect significantly the polymerization processes of ferric hydrolysis (Gustafson and Martell, 1963; Aasa et al., 1964; Spiro, Bates and Saltman, 1967; Schugar et al., 1967). Chelating agents which form strongly bonded complexes and occupy many of the coordination sites of the ferric ion can restrict the extent of polymerization such that lower molecular weight polycations predominate in solution.

The effects of complexing agents on ferric polycation and hydrous oxide formation have been studied extensively. However, the interaction of hydrous ferric oxides with complexing agents subsequently added to solution has received little attention. In a cassiterite flotation environment, this
latter case would be expected to prevail. Hydrolysis of ferric species would be well advanced prior to complexing agent addition.

Studies by Rubio and Matijevic (1979) have shown that when EDTA is added to a solution containing $\beta$-FeOOH sols, the interactions are complex. Depending upon the pH, the EDTA either adsorbs on the surface of the hydrous oxide or promotes the dissolution of the sol (Figures 13 and 14). Maximum adsorption of the EDTA occurs at low pH. Associated with this adsorption are significant changes in the electrokinetic properties of the sol. In acidic media, the chelating agent causes charge reversal with the iep of the sol decreasing appreciably from an initial value of 6.4 (Figure 15). No effect on the iep is observed at pH above 8.0, the point at which increased dissolution occurs. The anionic complexing agent, therefore, strongly adsorbs in the pH range where the hydrous oxide is positively (and hence oppositely) charged causing the electrophoretic mobility to reverse in sign. Changes in pH during solution equilibration, suggest an exchange of EDTA anions for OH$^-$ of the $\beta$-FeOOH to be taking place in this pH range. In the pH range where the hydrous oxide is negatively (and hence similarly) charged, the EDTA remains in solution and promotes the dissolution of the sol up to pH values of 12.0. This dissolution is, however, kinetically very slow.

2.3.2.6 Ferrous Ion Hydrolysis and Oxidation

In a similar manner to that of the free ferric ion, the free ferrous ion in low pH aqueous solutions is coordinated by six water molecules. Hydrolysis of the ferrous ion in the absence of oxygen gives rise to the hydroxo complex Fe(OH)$^+$ and the hydroxide Fe(OH)$_2$$. In oxygenated aqueous solutions, the ferrous ion hydrolysis and oxidation chemistry is complex. Both the kinetics and the thermodynamics of reaction
Figure 13 - Adsorption Isotherms at 22°C for EDTA on $\beta$-FeOOH at Various pH Values of the Media. Dashed lines at pH 8.5 and 10 represent the expected trend if a Langmuir-type isotherm was obeyed under these conditions (from Rubio and Matijevic, 1979).

Figure 14 - Solubility of $\beta$-FeOOH (expressed as released iron) in the Absence and in the Presence of EDTA in Different Concentrations as a Function of pH at 22°C (from Rubio and Matijevic, 1979).

Figure 15 - Electrophoretic Mobilities of $\beta$-FeOOH in the Absence and Presence of EDTA as a Function of pH at 22°C (from Rubio and Matijevic, 1979).
are strongly dependent on the pH, Eh and ferrous ion concentration in solution. Under highly acidic conditions, kinetically slow oxidation of the ferrous ion to the aquo ferric ion occurs. According to Tamura, Goto and Nagayama (1976), this transition proceeds through reaction of the hydrated oxygen species $O_2OH$ with the ferrous hydroxo complex $Fe(OH)^+$ according to the sequence:

$$Fe(OH)^+ + O_2OH^- \rightarrow Fe(III) + O_2^-$$
$$O_2^- + H^+ \leftrightarrow HO_2$$
$$Fe^{2+} + HO_2 \rightarrow Fe(III) + HO_2^-$$
$$HO_2^- + H^+ \leftrightarrow H_2O_2$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe(III) + OH^- + OH$$
$$Fe^{2+} + OH \rightarrow Fe(III) + OH^-$$

The first stage $Fe(OH)^+$ and $O_2OH^-$ reaction is believed rate determining with the resultant oxygen radical, $O_2^-$, being rapidly consumed by oxidizing three additional $Fe^{2+}$ ions in successive reactions. The kinetics of the hydroxyl radical oxidation are known to be fast; the oxidation of the ferrous ion by $OH$ occurring through simple electron transfer (Jayson and Parsons, 1972).

In slightly acidic solutions with pH below 5.0, oxidation of ferrous ion becomes more rapid. In neutral solutions with pH 6.0 - 8.0, the rate is much faster and increases dramatically with higher pH (Tamura, Goto and Nagayama, 1976). The thermodynamically stable species resulting from oxidation also change significantly with increasing pH. At higher pH, the complex polycations and hydrous oxide of the ferric ion are the thermodynamically stable species. However, the transition of the ferrous ion to these polymeric entities can be very complex proceeding through the formation of polymeric ferrous-ferric species (Misawa et al., 1973).
2.3.2.7 Thermodynamic Analyses

The construction of thermodynamic diagrams for the Fe(II)-Fe(III)-H₂O system is subject to a number of uncertainties. In particular, stability constants for highly polymerized species are generally not known. Reliable thermodynamic data are available only for the free ions Fe(II) and Fe(III), the mononuclear species Fe(OH)₂⁺, Fe(OH)₃⁺, Fe(OH)₆⁻, Fe(OH)⁺ and the polynuclear species Fe₂(OH)₆²⁺ and Fe₃(OH)₆⁵⁺ (Baes and Mesmer, 1976). Gibbs free energy data also exist for the ferrous and ferric hydrous oxide phases (Weast and Astle, 1983).

Figure 16 and 17 show the equilibrium and distribution diagrams for the ferric ion system. The Pourbaix (Eh-pH) diagram for the Fe(II)-Fe(III)-H₂O system at 25°C and 1 atmosphere total pressure is given in Figure 18. Boundaries in the Pourbaix and distribution diagrams are calculated for total activities of dissolved iron species of between 10⁻⁶ and 10⁻³. This represents the range of aqueous iron levels found in the Renison flotation circuit survey.

In the absence of minerals, an iron bearing solution can be interpreted quantitatively with respect to solution composition on the basis of known Nernst potentials, if equilibrium conditions can be assumed to prevail. However, in the presence of conducting minerals, such as certain sulphides and cassiterite, a measuring electrode can adopt a potential that represents both the ion solution chemistry and the potential of the conducting solid components in the pulp (Heyes and Trahar, 1977). In the Pourbaix diagram of Figure 18, pulp potentials and pH values measured in the Renison circuit are shown. A shaded area, representing the range of Eh and pH values generally believed typical of tin flotation pulps, is also included in the figure.
Figure 16 – Equilibrium Diagram for Monomeric and Polymeric Ferric Species in Contact with Freshly Precipitated Hydrous Ferric Oxide.
Figure 17 - Distribution Diagrams of Individual Fe(III) Species at Total Ferric Ion Concentrations Believed Typical of Industrial Plant Waters. In the shaded areas, the solution becomes saturated with respect to the hydrous oxide. Additional polynuclear hydrolysis species occur as kinetic intermediates in this pH range.
Figure 18 - Pourbaix Diagram for the Fe - H₂O System at 25 °C, 1 Atmosphere Total Pressure and Total Iron Species Activities of 10⁻³ and 10⁻⁶. The shaded area represents the range of Eh and pH values believed typical of actual tin flotation pulps.
Unfortunately, fundamental interpretation of such Eh and pH data, in relation to iron solution chemistry, is virtually impossible, since the flotation pulps represent multi-mineral, multi-ion component systems. However, such potentials might be interpreted reasonably as indicating whether conditions are oxidizing (positive potentials) or reducing (negative potentials). On such a basis, it can be concluded that conditions in the cassiterite flotation pulps are neither strongly reducing nor strongly oxidizing. As such, the predominant ferrous species existing at the circuit pH values is most probably the free ion. The predominant ferric species are, presumably, the hydroxy polycations and hydrous ferric oxides which are metastable intermediates in the slow transition to precipitate formation. It is further conceivable that Fe(II)-Fe(III) polycations might exist under the pH and Eh conditions in the flotation pulp, although the lack of thermodynamic data on these species makes their presence difficult to confirm. Conditions seem neither sufficiently oxidizing for the existence of the free ferric ion or lower order ferric hydroxy species nor sufficiently reducing for the existence of significant concentrations of ferrous hydroxide.

2.3.3 Magnesium and Calcium Solution Chemistry

The solution chemistry of magnesium and calcium is considerably less complicated than that of aluminum and iron. In aqueous solution, magnesium and calcium ions have only one oxidation state and undergo olation and oxolation reactions only in concentrated solutions and at high pH. The inability of these metal ions to form polycations and hydrous oxides in all but highly basic solutions is due to their size and charge. The divalent nature of the ions reduces their ability to withdraw electrons from their hydrated water molecules.
At low pH, magnesium exists as the aquomagnesium(II) ion, \( \text{Mg(H}_2\text{O)}_6^{2-} \). At higher pH, magnesium is hydrolyzed to form the polynuclear complexes \( \text{Mg}_2(\text{OH})_2^{2-} \) and \( \text{Mg}_3(\text{OH})_4^{2-} \) (Einaga, 1977; Einaga, 1981). Formation and precipitation of a neutral hydrolyzed \( \text{Mg(OH)}_2 \) species is possible via at least three mechanisms:

\[
\begin{align*}
\text{Mg}^{2+} & \rightleftharpoons \text{Mg}_2(\text{OH})_2^{2+} & \rightleftharpoons \text{Mg}_3(\text{OH})_4^{2+} \\
\text{Mg(OH)}_2(\text{sat.)} & \rightleftharpoons \text{Mg(OH)}_2(\text{sat.}) & \rightleftharpoons \text{Mg(OH)}_2(\text{sat.}) \\
\text{Mg(OH)}_2(\text{ppt.)} & \rightleftharpoons \text{Mg(OH)}_2(\text{ppt.}) & \rightleftharpoons \text{Mg(OH)}_2(\text{ppt.)}
\end{align*}
\]

Thermodynamic analyses suggest that formation of \( \text{Mg(OH)}_2(\text{ppt.)} \) via larger polycationic species is much more favourable than from small polycations or \( \text{Mg(II)} \) ions although accurate kinetic data are lacking.

Figures 19 and 20 show the equilibrium and distribution diagrams for magnesium species in aqueous solution. Polymerization and precipitation of the aquomagnesium ion occurs only at high pH (pH > 9.5) even in concentrated \( (2 \times 10^{-3} \text{ M}) \) solutions. Under the pH conditions of cassiterite flotation, the free magnesium ion is the predominant magnesium hydrolysis species in solution.

The calcium ion similarly exists as the free aqueous species over the pH range of interest in cassiterite flotation. The hydroxo complex \( \text{Ca(OH)}^- \) and hydroxide generally only form above pH 10.0 (Figure 21). No polynuclear complexes are reported in the literature pertaining to calcium ion hydrolysis, although as yet undetected species might exist.
Figure 19 - Equilibrium Diagram for Magnesium Species.
Figure 20 - Distribution Diagrams for Individual Mg(II) Species at Total Magnesium Ion Concentrations Believed Typical of Actual Tin Flotation Pulps.
2.3.4 Carbonato Complexes

Cassiterite flotation pulps characteristically contain detectable levels of carbonate species. These species can be present in mine water supplies or can be derived from dissolution of carbonaceous mineral species in the flotation pulp.

A number of species comprise the aqueous carbonate system — dissolved CO₂, carbonic acid H₂CO₃, and bicarbonate HCO₃⁻ and carbonate CO₃²⁻ ions (Snoeyink and Jenkins, 1980). Figure 22 shows the distribution of carbonate species as a function of pH assuming a closed system i.e. only solution equilibria. Carbonic acid and bicarbonate species predominate in the pH region of cassiterite flotation.
Figure 22 - Distribution of Carbonate Species in Aqueous Solution as a Function of pH Assuming a Closed System.
Carbonato species readily act as ligands for many dissolved metal ions in aqueous solution. Carbonate and bicarbonate complexes have been reported for ferrous, magnesium and calcium ions.

The ferrous ion forms only one rather unstable bicarbonate complex, $\text{Fe(HCO}_3\text{)}^+$ (Stumm, 1965). However, the carbonate ion $\text{CO}_3^{2-}$ can successfully compete with the hydroxyl ion for coordinative positions around ferrous ions. In carbonate bearing water systems, FeCO$_3$ rather than the hydroxide Fe(OH)$_2$ is the predominant ferrous solid (Figure 23).

In the Mg(II)-CO$_2$-H$_2$O system, the complexes $\text{Mg(HCO}_3\text{)}^+$, $\text{Mg(HCO}_3\text{)}_2(\text{aq})$ and $\text{MgCO}_3(\text{aq})$ have been identified (Riesen, Gamsjager and Schindler, 1977). Only two carbonato complexes, $\text{Ca(HCO}_3\text{)}^+$ and $\text{CaCO}_3(\text{aq})$, have been reported for calcium (Stumm, 1965). Thermodynamic data (Appendix A) indicate that for both magnesium and calcium ions the carbonato complexes are relatively unstable. The abundance of magnesium and calcium carbonato complexes in aqueous solution exceeds that of the corresponding free ions only at high pH values (pH > 10.0) and hence in a pH region outside that of interest in cassiterite flotation (Figures 24 and 25).

2.3.5 Fluoro Complexes

Fluoride, added in its various forms (HF, Na$_2$SiF$_6$ and NaF), is used extensively as a modifying agent in cassiterite flotation. In the absence of complexing cations, fluoride ions in aqueous solution can exist in the form of HF, HF$^-$ and in very concentrated solutions, as the dimers (HF)$_2$ (Warren, 1971). At the concentration levels typically present in flotation circuits, the concentration of (HF)$_2$ is infinitesimal while that of HF$^-$ is lower than that of HF by a factor of at least 10$^3$ (Read and Manser, 1975). For $[\text{F}^-] < 1 \times 10^{-3}$ M, it is only below pH 3.0 that significant amounts of HF$^-$ are present.
Figure 23 - Pourbaix Diagram for the Fe - CO$_3$ - H$_2$O System at 25 °C, 1 Atmosphere Total Pressure, Total Iron Species Activities of 10$^{-3}$ and 10$^{-6}$ and a Total Carbonate Species Activity of 5 x 10$^{-4}$. The shaded area represents the range of Eh and pH values believed typical of actual tin flotation pulps.
Figure 24 - Equilibrium Diagram for Magnesium Hydroxy and Carbonato Species Assuming a Closed System.

Figure 25 - Equilibrium Diagram for Calcium Hydroxy and Carbonato Species Assuming a Closed System.
(Warren and Kitchener, 1972). The predominant fluoride species in a cassiterite flotation circuit, in the absence of complexing cations, are therefore HF and F\(^-\). The concentrations of these two species are equal at pH 2.94 (Weast and Astle, 1983).

The fluoride ion is well known to form stable fluoro-complexes with free Al(III) and Fe(III) at low pH values. The aluminum complexes are particularly stable with all the species in the series AlF\(^2+\) to AlF\(_6\)^{3-} having been identified. A very weak complex (FeF\(^+\)) is formed between fluoride and the ferrous ion (Dodgen and Rollefson, 1949) and a weak calcium complex (CaF\(^+\)) also exists (Shergold, 1972). Read and Manser (1975) consider it likely that the fluoride ion would similarly form weak complexes with the magnesium ion although thermodynamic data on such species are generally lacking.

The stability of Al(III) fluoro complexes is critically dependent on ion concentrations and pH. The Pourbaix diagrams for the Al-H\(_2\)O and Al-F-H\(_2\)O systems (Figures 26 and 27) indicate that the fluoro complexes predominate in solution under acidic conditions. In weakly acidic or neutral conditions, the hydroxy species and hydrous oxides of aluminum are present in significantly higher concentrations.

At low pH, the fluoro complexes of aluminum are strongly solvated. They show little or no tendency to polymerize in the manner of the hydroxy species of aluminum essentially because fluorine has such a high electronegativity that it is reluctant to increase its coordination number by donating electrons (Porterfield, 1984).

Fundamental studies of the onset of aluminum ion hydrolysis in fluoride solutions have not been performed. However, based on the effects of chelating agents in iron hydrolysis, it would be expected that the fluoride ion would
Figure 26 - Pourbaix Diagram for the Al - H₂O System at 25 °C, 1 Atmosphere Total Pressure and a Total Aluminum Species Activity of 10⁻⁶.

Figure 27 - Pourbaix Diagram for the Al - F - H₂O System at 25 °C, 1 Atmosphere Total Pressure and Total Aluminum and Fluoride Species Activities of 10⁻⁶ and 10⁻³, respectively.
occupy many of the coordination sites of the aluminum ion and thereby restrict the extent of polymerization.

In a cassiterite flotation system, aluminum ion oxolation and olation reactions would be expected to be considerably advanced prior to fluoride reagent addition. The effects of adding fluoride ion to such a system are, at present, largely a matter of speculation. The strong nature of the Al-F bond, however, might allow the fluoride ion to displace coordinated water and hydroxyl groups in aluminum polycations (and hydrous oxides). This would alter the electrokinetic properties of the sols and possibly promote their solubilization. Solubilization would be expected to be more pronounced at low pH where the fluoro complexes are thermodynamically more stable (Figure 27). At present, the kinetics of such reactions are unknown.

The fluoride ion forms stable complexes with the ferric ion under oxidizing (high Eh) and low pH conditions. However, the stability of ferric fluoro complexes is greatly diminished under low Eh conditions where ferrous ions and polymeric ferric (-ferrous) polycations and hydrous oxides predominate in solution (Figure 28).

In the absence of fluoride reagents, the potentials of cassiterite flotation pulps can be below 100 mV SHE (Table VI). Thermodynamically, fluoro complexes of ferric ion would not be expected to form preferentially under acidic conditions at such low Eh values. However, the Eh and pH values of mineral pulps are well recognised as not being independently variable (Heyes and Trahar, 1977). The simultaneous addition of a fluoride reagent and acidification of the pulp, therefore, might alter significantly the pulp potential such that fluoro iron species were the most thermodynamically stable entities. On the basis of the results of Rubio and Matijevic (1979) for the
Figure 28 - Pourbaix Diagram for the Fe – F – CO₃ – H₂O System at 25 °C, 1 Atmosphere Total Pressure, Total Iron and Fluoride Species Activities of $10^{-3}$ and a Total Carbonate Species Activity of $5 \times 10^{-4}$. The shaded area represents the range of Eh and pH values believed typical of actual tin flotation pulps.

The β-FeOOH/EDTA system, this would presumably promote the dissolution of the hydrous ferric oxide sols. Furthermore, it must be emphasized that equilibrium conditions are frequently not achieved in the time frames characteristic of flotation. Specifically, the reductive dissolution of hydrous ferric oxide sols is kinetically slow. Consequently, once formed, such sols are well known to remain in solution under Eh and pH conditions where the ferrous ion is more stable thermodynamically. Given the strong affinity of fluoride for ferric iron under acidic conditions and its ability to form soluble complexes with the cation (as evidenced by the greater stability of ferric-fluoro complexes over ferric hydroxy complexes at high Eh and low pH), the net effect of fluoride addition to acidic cassiterite
flotation pulps might be enhanced dissolution of ferric (-ferrous) polycations and hydrous oxides irrespective of the Eh.

In the case of calcium ion solution chemistry, the effects of fluoride ion addition would be negligible. Thermodynamic data reported by Shergold (1972) indicate that the concentration of CaF\(^+\) in cassiterite flotation pulps is many orders of magnitude less than that of the free calcium ion (Figure 29).

![Equilibrium Diagram for Calcium Hydroxy and Fluoro Species.](image)

**Figure 29** - Equilibrium Diagram for Calcium Hydroxy and Fluoro Species.
2.3.6 Conclusions

1. Cassiterite flotation pulps contain appreciable levels of metal cations. Aluminum, iron, magnesium and calcium are generally present in the highest concentrations.

2. In the pH range typical of cassiterite flotation, aluminum exists predominantly in the form of complex polycations and hydrous aluminum oxide species. The kinetics of both acid dissolution and aging of these sols to form solid precipitates are very slow.

3. Under the pH and Eh conditions of tin flotation, the predominant ferric iron species are most likely the hydroxy polycations and hydrous ferric oxides which are metastable intermediates in the slow transition to solid precipitate formation. Dissolution of these species in an acidic environment is kinetically very slow.

4. Appreciable levels of free ferrous ions might occur in flotation pulps possibly in conjunction with complex Fe(II)-Fe(III) polycations.

5. The concentrations of the free aquomagnesium(II) and aquocalcium(II) ions in tin flotation solutions are many orders of magnitude greater than those of the possible hydroxy, carbonato and fluoride complexes of these cations.

6. Detailed studies of the effects of fluoride ion additions to solutions containing aluminum polycations and hydrous oxides have not been published. However, it is known that aluminum fluoro species are strongly solvated in acidic solutions. Furthermore, related studies and thermodynamic analyses suggest that the fluoride ion will displace coordinated water and hydroxyl groups in polymeric aluminum sols at low pH. This might promote the dissolution of such sols. At present, the
kinetics of such dissolution is largely a matter of speculation.

7. Thermodynamically, the fluoride ion forms very stable ferric ion complexes under high Eh and low pH conditions. These species are strongly solvated in aqueous solution. Weaker ferrous fluoro complexes are known to exist, but only at concentrations significantly below those of other iron species.

8. As for the aluminum ion case, the effects of fluoride ion additions to flotation pulps containing hydrous ferric oxide sols are largely unknown. If the pulp potential increases sufficiently upon lowering of the pH and addition of the fluoride, ferric fluoro complexes might become thermodynamically stable. Some resolubilization of hydrous ferric oxide sols would then be expected. In the absence of a significant increase in the Eh, the ferric fluoro complexes would be thermodynamically less stable than the free aqueous ferrous ion. However, given the kinetically slow nature of the reductive dissolution of hydrous ferric oxide sols through simple pH decrease, the effects of fluoride ion addition still might be to promote dissolution of such sols. In either case, the kinetics of such dissolution is, at present, not known.
2.4 Phosphonic Acid Flotation of Cassiterite

The phosphonic acids are one of the technologically most important families of reagents in cassiterite flotation. Initially evaluated as collectors during the early sixties, they are currently the preferred flotation surfactants at many major tin mines treating lode ores (Moncrieff et al., 1973; Gerstenberger and Greulich, 1977; Moncrieff and Lewis, 1977; Bilsing et al., 1978; Bulled, 1982; Mosch and Becker, 1985).

The pioneering studies on phosphonic acid flotation of cassiterite were performed at the Freiberg Research Institute in the German Democratic Republic. In early publications on the subject (Wottgen and Lippmann, 1963; Wottgen, 1965; Kirchberg and Wottgen, 1965; Kirchberg and Wottgen, 1967; Wottgen and Luft, 1970), the synthesis and evaluation of a range of phosphonic acids in batch flotation testing of ores from Altenberg and Ehrenfriedersdorf were reported. Alkyl, p-alkylphenylene and various branch chain and substituted phosphonic acids were studied. The alkyl phosphonic acids, except for their shorter chain members such as butyl (C₄) phosphonic acid, were not selective and their evaluation was discontinued in favour of the aryl phosphonic acids. In terms of overall flotation selectivity and recovery, the p-tolyl and p-ethylphenylene phosphonic acids were subsequently concluded by the researchers to have optimal hydrocarbon radical chain lengths (Kirchberg and Wottgen, 1965; Kirchberg, 1969).

In independent research that largely paralleled the Freiberg studies, Collins and coworkers extensively investigated C₆-C₉ alkyl phosphonic acids as cassiterite flotation collectors (Collins, 1967; Collins et al., 1968; Collins, Hollick and Joy, 1969). The primary objective of this work was to prove the technical and economic viability of tin flotation at a number of
Cornish tin mines. While acknowledged as less selective than the aryl phosphonic acids, the alkyl acids were thought to be less expensive to produce in commercial quantities.

The first industrial application of a phosphonic acid collector was at Altenberg (G.D.R.) in the early 1970's. The collector used was styryl phosphonic acid (Wottgen, Luft and Neuber, 1971). This reagent was subsequently introduced at Renison Limited (Aust.) during 1977/78. While having no pronounced metallurgical advantages over other aryl phosphonic acids, such as p-tolyl or benzyl phosphonic acid, styryl phosphonic acid is believed to be the least expensive to produce in commercial quantities. This is a consequence of the use of styrene, rather than other more expensive hydrocarbons, in the reagents synthesis. An aryl phosphonic acid also has been the preferred collector at both Rooiberg and Union Tin in South Africa since the mid 1970's (Moncrieff and Lewis, 1977; Bulled, 1982). The exact structure of the hydrocarbon radical of this surfactant is, however, uncertain. The alkyl phosphonic acids have not found commercial application in cassiterite flotation.

2.4.1 Microflotation Response

The microflotation response of cassiterite with phosphonic acids has been investigated extensively by a number of researchers (Wottgen and Luft, 1971; Raatz and Schubert, 1971). Optimal flotation response in these single mineral studies has been established to exist in the acidic pH range. A recovery maximum at pH 2.0 was found by Wottgen and Luft (1971) in microflotation studies with small additions of n-heptyl phosphonic acid (Figure 30). With increased collector concentrations, the flotation region broadened to higher pH values. A concentration of $1 \times 10^{-3}$ M n-heptyl phosphonic acid produced a
maximum recovery plateau between pH 2.0 and pH 8.0. Measurements of the concentration dependence of cassiterite microflotation recovery with n-heptyl phosphonic acid at fixed pH values (Figure 31) confirmed that the flotation response was strongest at pH 2.0 and decreased at higher pH values.

Data from microflotation studies performed by Raatz and Schubert (1971) indicate a cassiterite flotation response with n-heptyl phosphonic acid (Figure 32) similar to that reported by Wottgen and Luft (1971). The region of maximum recovery at low surfactant concentrations was found to occur in acidic solutions and broadened to higher pH values with increased collector additions. The pH of maximum recovery, however, existed closer to pH 3.0 than the pH 2.0 value reported by Wottgen and Luft (1971). Increased temperatures were found to enhance the flotation response leading to higher recoveries in
Figure 31 - The Concentration Dependence of Cassiterite Microflotation Recovery with n-heptyl Phosphonic Acid at Different pH Values (from Wottgen and Luft, 1971).

Figure 32 - The pH Dependence of Cassiterite Microflotation Recovery with n-heptyl Phosphonic Acid as a Function of Concentration and Temperature (from Raatz and Schubert, 1971).
the more neutral pH range. Flotation at 75°C also significantly lowered the n-heptyl phosphonic acid concentration necessary for the onset of flotation at both pH 3.0 and pH 5.0 (Figure 33).

The microflotation response of various doped and undoped synthetic cassiterite samples have been determined by Balachandran (1982). Figure 34 shows the recovery dependence of undoped, iron-doped and antimony-doped stannic dioxide with styryl phosphonic acid at pH 3.5. Significantly, all three of the stannic dioxides floated strongly with the styryl phosphonic acid. In the case of the undoped sample, this is a most important result in that it confirms that the phosphonic acid genuinely floats the synthetic cassiterite. Flotation cannot be attributed to impurities. The presence of impurity dopants in the mineral lattice might, however, alter the flotation response.

In the Balachandran studies, iron-doped stannic dioxide exhibited a stronger flotation response than undoped stannic dioxide while the effect of antimony dopant was to diminish the flotation response. These results were interpreted as indicating the dopants to affect flotation response through changes either in the semiconductor properties of the synthetic cassiterites (degree of hydration, electron transfer with surfactants) or their chemical properties (stannic or dopant atom solubilities, etc). However, in the absence of further data, it could equally well be argued that differing responses were due to crystal morphology or surface area effects. While Balachandran (1982) used the same size fractions of dioxides in all microflotation tests (-295 + 208 µm), surface area measurements were not conducted. It is conceivable that the synthetic samples containing different dopants varied significantly in their specific surface areas from the undoped
Figure 33 - The Concentration Dependence of Cassiterite Microflotation Recovery with n-heptyl Phosphonic Acid as a Function of pH and Temperature (from Raatz and Schubert, 1971).

Figure 34 - The Concentration Dependence of the Microflotation Response of Different Synthetic Cassiterites with Styryl Phosphonic Acid at pH 3.5 (from Balachandran, 1982).
sample. Solymosi, Bozso and Hesz (1976), working with chromium doped stannic dioxide prepared in a similar manner to that of the Balachandran samples, have reported appreciable variations in surface area between doped and undoped samples. Any significant changes in surface area would influence the concentration of phosphonic acid required for flotation of a fixed weight of stannic dioxide. Evidence that the Balachandran samples were of considerable surface area can be found in the high concentrations of phosphonic acid that were required to achieve flotation.

In test work at pH 6.0, Balachandran found that none of the synthetic cassiterites floated in 5 \times 10^{-4} \text{ M styryl phosphonic acid}. This result is consistent with both the Wottgen and Luft (1971) and Raatz and Schubert (1971) data indicating reduced flotation recoveries at higher pH values where the available surface area to surfactant concentration ratio is large.

2.4.2 Vacuum Flotation Response

In early test work, Collins and coworkers (Collins, 1967; Collins and Jackson, 1967; Collins, Hollick and Joy, 1969) performed a series of vacuum flotation studies to characterize the flotation response of cassiterite with phosphonic acids. Tests were conducted with cassiterites from various origins and with both n-heptyl and isoheptyl phosphonic acids (Figure 35). The straight chain alkyl phosphonic acid was found to produce remarkably similar flotation response for two different cassiterites. Flotation of a third cassiterite with isoheptyl phosphonic acid occurred at significantly lower surfactant concentrations but over essentially the same pH range. In striking contrast to the microflotation results of Wottgen and Luft (1971) and Raatz and Schubert (1971), the optimum flotation response in all tests occurred between pH 5.0 and 6.0. Appreciably greater concentrations of phosphonic acid
were required to achieve vacuum flotation at both more acidic and basic pH values.

At present, no reconciling mechanism exists to explain the different pH ranges of optimal flotation response reported between vacuum and microflotation studies of different cassiterites with n-heptyl phosphonic acid. Presumably the experimental techniques could not themselves so profoundly influence the results. The implication, although currently lacking experimental support, is therefore that the cassiterites varied significantly in their surface properties. It is consequently of relevance to note that Raatz and Schubert extensively acid treated their cassiterite prior to flotation test work. In contrast, no such surface pretreatment is referenced in the publications of Collins and coworkers.
2.4.3 Batch Flotation Response

In investigating the surface properties of undoped and doped synthetic cassiterites, Gruner (1971) performed a series of batch flotation tests on mixtures of the synthetic mineral and pure quartz. The studies confirmed the floatability of undoped synthetic cassiterite in the presence of n-heptyl phosphonic acid over the range of pH 5.0 - 7.0 (Figure 36). Iron-doped stannic dioxide exhibited a similar recovery-pH dependence although Gruner concluded that the effect of all dopants was to reduce floatability. Evidence for such a depressant effect was cited in the batch flotation results for low n-heptyl phosphonic acid concentrations at pH 6.0 (Figure 37). However, flotation results with p-ethylphenylene phosphonic acid, at the same pH, fail to support such a general conclusion.

No batch flotation data were reported by Gruner for tests conducted outside the pH range 5.0 - 7.0. It is consequently not possible to conclude how well Gruner's batch flotation data for synthetic cassiterite correlate with reported microflotation and vacuum flotation analyses with natural cassiterites.

2.4.4 Adsorption Isotherms

The adsorption of phosphonic acids on natural and synthetic cassiterites has been studied extensively by Wottgen (1969) and Gruner (1971). Using P32 marked surfactant, measurements were made of both residual surfactant in solution and that adsorbed at the solid-liquid interface. Figure 38 shows the published data for the adsorption density of three different phosphonic acids on a natural cassiterite with an iep of 5.6. The adsorption density of n-heptyl phosphonic acid on an undoped synthetic cassiterite with iep 4.0 is shown in Figure 39. In all isotherms, adsorption increases with decreasing pH.
Figure 36 - The pH Dependence of Undoped and Fe-Doped Stannic Dioxide Recovery with n-heptyl Phosphonic Acid in Batch Flotation Tests on Stannic Dioxide/Quartz Mixtures (from Gruner, 1971).

Figure 37 - The Concentration Dependence of Undoped and Fe-Doped Stannic Dioxide Recovery at pH 6.0 with n-heptyl and p-ethylphenylene Phosphonic Acids in Batch Flotation Tests on Stannic Dioxide/Quartz Mixtures (from Gruner, 1971).
Figure 38 - The pH Dependence of Phosphonic Acid Adsorption on a Cassiterite with iep of 5.6 (Wottgen, 1969).

Figure 39 - The pH Dependence of n-Heptyl Phosphonic Acid Adsorption on Undoped Stannic Dioxide (from Gruner, 1971).
reaching a maximum at pH 2.0 for the natural cassiterite and pH 3.0 for the synthetic cassiterite. With n-heptyl and p-ethylphenylene phosphonic acids, a sharp decrease in the amount adsorbed occurs at lower pH. Isotherms of similar form were reported by Gruner (1971) for n-heptyl phosphonic acid adsorption on both iron and manganese doped cassiterite (Figure 40). Maximum adsorption for both doped samples occurred at pH 3.0. However, the isotherm for manganese-doped cassiterite was slightly broader than for undoped synthetic cassiterite while iron doping increased both the pH range and the extent of the adsorption maximum.

The Wottgen isotherm data for n-heptyl phosphonic acid (Figure 38) indicate that an excellent correlation exists between the adsorption results and the floatability of the same cassiterite with the surfactant (Figure 30). In the microflotation studies, maximum recovery occurred at pH 2.0 which corresponds to the pH of maximum adsorption. Calculation of the critical surfactant surface coverage necessary for maximum recovery is, however, not possible due to the different size fractions of cassiterite used for the adsorption and microflotation studies and the absence of surface area data for the microflotation samples.

The adsorption study results of Wottgen (1969) and Gruner (1971) were interpreted by both researchers as indicating that phosphonic acid adsorption was both chemical and electrostatic in nature. Chemisorption, it was argued, was evident from adsorption above the iep of cassiterite. The significant increase in adsorption below the iep was thought due to increased electrostatic attraction between (anionic) dissociated surfactant and the cassiterite surface. This increase occurred despite the reduced concentration of dissociated phosphonic acid in solution at acidic pH values. According to
Figure 40 - The pH Dependence of n-heptyl Phosphonic Acid Adsorption on Undoped, Iron-doped and Manganese-doped Stannic Dioxide (from Gruner, 1971).

Wottgen, the decrease in adsorption observed in his data below pH 2.0 was due to a decrease in ionization of the phosphonic acids and an increase in the solubility of the Sn(IV) phosphonic acid species formed at the surface. It was confirmed independently by Wottgen that Sn(IV) phosphonates were readily dissociated in very acidic solutions.

An alternative interpretation of Wottgen's results has been proposed by Fuerstenau and Healy (1972). These authors considered the maximum adsorption at pH 2.0 to be due to neutral molecule-ion coadsorption; the maximum adsorption density occurring at the pK$_i$ of the acid where neutral molecules most effectively neutralized any adsorbed anion-anion repulsion at the positive cassiterite surface. Neutral molecule coadsorption at low pH would
appear highly probable where the hydrocarbon radical is sufficiently long to impart a high degree of hydrophobicity to the neutral phosphonic acid species.

The pH dependence of phosphonic acid adsorption on cassiterite reported by Wottgen (1969) and Gruner (1971) also has been shown to exist for other phosphonic acids. Figure 41 shows the adsorption isotherm for the commercially important styryl phosphonic acid (Wottgen, Luft and Neuber, 1971). The adsorption density of p-tolyl phosphonic acid on a cassiterite with an iep of 5.5 is shown in Figure 42 (Yap, 1975). The isotherms have adsorption maxima at pH 2.0 and pH 2.2, respectively. For both acids, the extent of adsorption decreases significantly at pH values above and below the maximum. The adsorption-concentration isotherm for p-tolyl phosphonic acid at pH 3.0 was also determined by Yap (1975) and is shown in Figure 43. Adsorption was found to increase rapidly at solution concentrations above $1 \times 10^{-5}$ M, reaching a plateau at concentrations in excess of $3 \times 10^{-5}$ M. Monolayer surface coverages were not achieved over the range of concentrations tested. Similar data were obtained by Wottgen for adsorption of n-heptyl phosphonic acid at pH 4.0 and 6.4. However, strikingly different adsorption behaviour occurred at pH 2.0 and 1.0 (Figure 44). At these pH values, adsorption increased many times over that at higher pH.

While not commented on by Wottgen, the data of Figure 44 would suggest that a fundamentally different phosphonic acid adsorption mechanism exists in the pH 1.0 - 2.0 region. Assuming the extreme case of uniform surfactant adsorption and only 25 Å² as the area occupied by an heptyl phosphonic acid molecule on the cassiterite surface (which is conservatively small), monolayer adsorption is exceeded at pH 2.0 and very closely approached at pH 1.0. The existence of an excess of adsorbed phosphonic acid over that necessary for
Figure 41 - The pH Dependence of Styryl Phosphonic Acid Adsorption on Cassiterite (from Wottgen, Luft and Neuber, 1971).

Figure 42 - The pH Dependence of p-tolyl Phosphonic Acid Adsorption on Cassiterite (data from Yap, 1975).
Figure 43 - Adsorption Density of p-tolyl Phosphonic Acid on Cassiterite as a Function of Equilibrium Concentration (from Yap, 1975).

Figure 44 - Adsorption - Concentration Isotherms for Heptyl Phosphonic Acid Adsorption on Cassiterite (from Wottgen, 1969).
monolayer adsorption clearly indicates that coadsorption of phosphonic acid species must be occurring at low pH values. Any chemical adsorption character obviously cannot be maintained for more than one layer of adsorbate on one layer of underlying adsorbent. The data of Wottgen, therefore, strongly support the contention that coadsorption of neutral species is associated with phosphonic acid adsorption in very acidic solutions. Such coadsorption might reflect the incipient precipitation or deposition of hydrophobic neutral phosphonic acid molecules at low pH.

2.4.5 Electrokinetic Studies

The specific adsorption of phosphonic acids on the surface of cassiterite has been confirmed in studies of the electrokinetic properties of the mineral (Yap, 1975). In the presence of p-tolyl phosphonic acid, the positive zeta potential of the mineral was found to be reduced at low surfactant concentrations and to reverse in sign at high concentrations (Figure 45). Some evidence was also found for a chemical adsorption component in that high surfactant concentrations increased the magnitude of the negative zeta potential above the iep of the mineral. Adsorption of the anionic surfactant consequently occurred when the mineral surface charge was negative.

To further understand the mechanism of phosphonic acid adsorption on cassiterite, Yap attempted to correlate the results of the electrokinetic studies with those from similar studies with sodium dihydrogen phosphate. Figure 46 shows the results of these measurements together with the appropriate proportions of the phosphonate species present in solution. The results clearly show that phosphonate ion species such as:

\[
\text{HO} \quad \text{P} \quad \text{OH}
\]

\[
\text{O} \quad \text{O}^{-}
\]
Figure 45 - Electrophoretic Mobility of Cassiterite in the Presence and Absence of p-tolyl Phosphonic Acid (from Yap, 1975).

Adsorb specifically onto the surface of cassiterite. However, for similar cassiterite test suspensions and identical solution concentrations, the sodium dihydrogen phosphate produced greater charge reversal effects than the p-tolyl phosphonic acid. This presumably reflects a fundamental difference in the adsorption mechanism of the inorganic ion and the surfactant, despite the structural similarity of the ion to the polar group of the surfactant.

Assertions of direct chemical and surface activity correspondence between inorganic ions and structurally similar surfactants appear rather tenuous. The presence of an hydrocarbon radical, for example, changes such fundamental properties as the ionization constants of the acid. The hydrocarbon radical might further alter the chemical character of the polar group through radical-polar group interactions. The presence of an hydrocarbon radical also would
Figure 46 - Electrophoretic Mobility of Cassiterite in the Presence and Absence of Increasing Concentrations of Sodium Dihydrogen Phosphate. Also shown are the distributions of the phosphonate species in an aqueous solution as a function of pH (from Yap, 1975).
be expected to introduce steric effects into the adsorption process. In the inorganic ion, the additional hydroxyl group which replaces the radical might itself play an active role in the adsorption process and fundamentally alter the adsorption mechanism.

A number of researchers have successfully correlated the changes in the electrophoretic mobility of a mineral in the presence of a long chain surfactant with the adsorption isotherms of the surfactant on the mineral (Wakamatsu and Fuerstenau, 1968; Shergold and Mellgren, 1969). Yap attempted a similar analysis for the cassiterite/p-tolyl phosphonic acid system but found a number of major inconsistencies. No reconciling explanations were proposed. The difficulties in the data interpretation were attributed to the "unreliable nature of electrophoresis measurements of minerals in the presence of surfactants".

In comparing adsorption and electrokinetic data, due consideration must be given to the relative mineral surface areas in the tests. The small particle size and dilute nature of suspensions used in electrokinetic measurements generally means that the mineral surface area available for adsorption is considerably less than that in adsorption studies. As a consequence, low surfactant concentrations can produce large zeta potential changes that are seemingly inconsistent with adsorption isotherms for the same concentration. Furthermore, in electrokinetic studies, monolayer surface coverage can be achieved at surfactant concentration levels well below those necessary in adsorption studies. Taking due regard of the above, the data of Yap can be reinterpreted.

Figure 45 indicates that a p-tolyl phosphonic acid concentration of $4 \times 10^{-5}$ M produces measurable changes in the electrophoretic mobility of
cassiterite particles. No evidence for adsorption saturation at this concentration exists, as shown by the electrophoretic mobility curve at the higher concentration of $1 \times 10^{-4}$ M. Figure 47 compares the change in the electrophoretic mobility of cassiterite in the presence of $4 \times 10^{-5}$ M p-tolyl phosphonic acid with the adsorption isotherm at the same concentration. In the pH 4.0 - 6.0 range, the adsorption density increase observed in the isotherm is paralleled by an increasing change (decrease) in the zeta potential. These data are consistent and indicate that species with a negative charge character are adsorbed inside the inner Helmholtz plane of the cassiterite electrical double layer. In the pH range 2.5 to 4.0, the change in the electrophoretic mobility is essentially constant while an almost three-fold increase occurs in the adsorption density. Given the apparent absence of any adsorption saturation effects in the electrokinetic data, adsorption presumably does increase between pH 2.5 and 4.0, but the adsorbed species produce no measurable change in the electrophoretic mobility. The additional adsorption in this pH range is consequently of species that are fundamentally different, or have a different adsorption mechanism, to those that produce charge reversal at higher pH.

Figure 48 shows the distribution of p-tolyl phosphonic acid species in solution as a function of pH. The distribution diagram is plotted from the data of Ashby and Kosolapoff (1953). The absence of discernable changes in the electrophoretic mobility of cassiterite with continued adsorption between pH 4.0 and 2.5, and the correlation of this adsorption with the onset of formation of neutral species in solution, provides strong support for the contention that neutral phosphonic acid species coadsorb on the cassiterite surface at pH values lower than 4.0.
Figure 47 - Comparison of the Change in Zeta Potential of Cassiterite in the Presence of $4 \times 10^{-5}$ M p-tolyl Phosphonic Acid with the Adsorption Isotherm at the Same Concentration (replotted from the data of Yap, 1975).

Figure 48 - Distribution of p-tolyl Phosphonic Acid Species in Solution as a Function of pH (from the data of Ashby and Kosolapoff, 1953).
Below pH 2.5, the magnitude of the change in the electrophoretic mobility of cassiterite in the presence of p-tolyl phosphonic acid decreases. This correlates broadly with the decrease in adsorption observed in the adsorption isotherms at low pH. A small pH displacement between the points of decrease is discernable. However, this might reflect small errors in pH measurement and control associated with the adsorption and electrokinetic studies.

2.4.6 Spectroscopic Studies

Wottgen and Dietze have extensively investigated the infrared spectra of both phosphonic acid treated cassiterite and the precipitates formed by reacting stannic ions with phosphonic acids (Wottgen, 1969; Wottgen and Dietze, 1969). Analyses were performed for a range of phosphonic acids including those with heptyl, styryl, and p-ethylphenylene radicals. Formation of the Sn(IV) phosphonates was found possible only under highly acidic conditions near pH 0 and hence where only undissociated phosphonic acid existed in solution. At this pH, the excessive precipitation of hydrous stannic oxide was avoided. Adsorption of phosphonic acids onto the cassiterite surface was conducted at various pH values in the range pH 2.0-6.0.

Figures 49 and 50 show the infrared spectra of the stannic ion phosphonates of heptyl and p-ethylphenylene phosphonic acid. On forming stannic compounds, the infrared spectra of both phosphonic acids undergo significant changes, particularly in the 1000-1200 cm\(^{-1}\) range. In the heptyl phosphonic acid spectrum, Wottgen (1969) assigned bands at 960 cm\(^{-1}\) and 1280 cm\(^{-1}\) to (P)OH deformation vibrations. Bands at 1070 cm\(^{-1}\) and 1170 cm\(^{-1}\) were considered to be PO valence vibrations. In the stannic phosphonate spectrum, the (P)OH deformation vibrations were absent and a very broad band centered at
Figure 49 - Infrared Spectra of (1) Heptyl Phosphonic Acid, (2) Sn(IV)-Heptyl Phosphonate, (3) Cassiterite-Heptyl Phosphonic Acid Adsorbate (from Wottgen and Dietze, 1969).

Figure 50 - Infrared Spectra of (1) p-ethylphenylene Phosphonic Acid, (2) Sn(IV) - p-ethylphenylene Phosphonate, (3) Cassiterite - p-ethylphenylene Phosphonic Acid Adsorbate (from Wottgen and Dietze, 1969).
1080 cm\(^{-1}\) was formed. Similar spectral changes occurred for the p-ethylphenylene phosphonate.

On the basis of the disappearance of the (P)OH deformation vibrations, Wottgen and Dietze proposed that the stannic phosphonates were of the general structure:

\[
\begin{array}{c}
\text{R} - \text{P} - \text{O} \\
\text{Sn} - \text{O} \\
\text{P} - \text{R}
\end{array}
\]

Elemental analyses confirmed the dibasic nature of the phosphonates but indicated that coordinated water was present in many of the precipitates. This water could not be removed even during prolonged drying as shown by the presence of strong water bands in the phosphonate spectra. The coordination of water molecules into the structure of the phosphonate precipitates suggests that they might be polymeric in nature. Sandhu, Manhas and Kohli (1976), in investigating the metal ion precipitates of the chemically similar arsonic acids, concluded that the metal arsonates were polymeric.

Stannic dioxide and cassiterite particles treated with phosphonic acids at pH 2.0 - 3.0 were found by Wottgen and Dietze to display clear evidence of spectral changes. The absence of (P)OH bands and the similarity of the spectra to those of the corresponding stannic phosphonates led to the conclusion that stannic phosphonates were formed on the tin oxide surfaces and that the divalent surfactant anion was the chemisorbed species.

Figures 49 and 50 show the published spectra of Wottgen and Dietze for cassiterite treated with heptyl and p-ethylphenylene phosphonic acids, respectively. Both spectra show the presence of adsorbed phosphonate species.
similar to the corresponding stannic phosphonates. However, the lack of spectral detail associated with the poor signal to noise ratio of the KBr infrared analyses does not allow definitive confirmation of the nature of the adsorbed species.

Evidence for chemisorption was also cited by Wottgen (1969) in the inability of acetone washing to remove the characteristic peaks of the phosphonate adsorbates from the cassiterite spectra (Figure 51). Phosphonic acids are completely soluble in acetone and phosphonate bands would not be expected in the infrared spectra if only physical adsorption of phosphonic acids was occurring.

Figure 51 - Infrared Spectra of (a) Cassiterite (b) Cassiterite-Heptyl Phosphonic Acid Adsorbate and (c) Cassiterite-Heptyl Phosphonic Acid Adsorbate After Treatment With Acetone (Wottgen, 1969).
The lack of resolution of peaks in the infrared spectra of phosphonic acid treated cassiterite has resulted in many questions of fundamental importance in phosphonic acid flotation remaining unanswered. In particular, it has not proven possible to ascertain the nature of molecular interactions between adsorbed phosphonic acid species. Such interactions would be of key importance in an understanding of the marked increase in phosphonic acid adsorption on cassiterite at pH values below 4.0.

The role of cassiterite lattice impurities in surfactant adsorption is similarly one of conjecture. Wottgen and Dietze (1969) found that the infrared spectrum of a natural cassiterite treated with phosphonic acid at pH 6.0 was not distinguishably different from that for cassiterite treated at pH 2.0. This result was thought to be inconsistent with adsorption isotherm measurements (Figure 38) which had been interpreted as indicating little surfactant adsorption above pH 5.0 (in fact, the surface coverage with heptyl phosphonic acid at pH 6.0 is at least 7.5 percent; assuming 25 Å² per molecule). It was subsequently proposed that iron in the lattice of natural cassiterite might be responsible, at least partially, for the adsorption at pH 6.0. However, corroborative evidence for this hypothesis, sought in the infrared studies, proved inconclusive due to the difficulty of distinguishing individual iron and stannic phosphonate bands in the spectrum of phosphonic acid treated cassiterite.

Mossbauer isomer shifts have been reported for a range of stannic ion phosphonates including styryl phosphonate (Pietzsch, Fritzsch and Braun 1981). These analyses have proven conclusively the existence of the Sn–O–P bond in the phosphonates. Furthermore, the effective charge at the tin ion and the ionicity of the Sn–O–P bond have indicated strong ionic bonding.
The Mossbauer results indicating a predominance of ionic bonding in the tin(IV) phosphonates are not entirely incompatible with the Wottgen and Dietze conclusion from infrared spectral analyses of covalent bonding character. Bonding is presumably both partially ionic and partially covalent. Support for a partial ionic-covalent bond is also evident in the Mossbauer isomer shifts themselves which, while indicating the high ionicities of the tin(IV) phosphonates, typically give values around 90.0%.

2.4.7 Adsorption Mechanisms

Considerable evidence exists supporting the contention of a significant chemical component in phosphonic acid adsorption on cassiterite. Support for such a conclusion comes from flotation, adsorption and electrokinetic studies all of which indicate appreciable surfactant adsorption above the isoelectric point of cassiterite. Enhanced microflotation response with increasing temperature (Figure 32) also suggests adsorption to be largely chemical in nature. Chemisorption generally requires an appreciable energy of activation and tends to be favoured at higher temperatures (Leja, 1982). Systems in which collectors exhibit only physisorption behaviour are characterized by an exothermic heat and, as a consequence, adsorption decreases with increase in temperature (Fuerstenau and Raghavan, 1976).

The infrared studies of Wottgen and Dietze (Wottgen, 1969; Wottgen and Dietze, 1969) have provided important information as to the nature of the chemisorbed phosphonic acid species. By analogy with the bonding in stannic ion salts, Wottgen proposed that the adsorption involves the displacement of coordinated hydroxyls from the cassiterite surface with subsequent formation of stannic phosphonate species. The infrared spectral changes observed on treating cassiterite with phosphonic acid were interpreted as indicating the
bonding between the phosphorus species and the stannic ions of the cassiterite lattice to be covalent in character (Wottgen and Dietze, 1969). The Mossbauer analyses performed by Pietzsch, Fritzsch and Braun (1981) on stannic phosphonate salts would, however, suggest the bonding is predominantly ionic.

As has been recognized by both Balachandran (1982) and Somasundaran and Nagaraj (1984), the mechanism proposed by Wottgen is a chelating mechanism in which the phosphonic acid acts as a bidentate 1:1 chelating molecule:

\[
\begin{align*}
\text{O} & \quad \text{Sn} \quad \text{O} \\
\text{OH} & \quad \text{Sn} \quad \text{OH} \\
\text{O} & \quad \text{Sn} \quad \text{O} \\
\end{align*}
\]

A chelating mechanism is consistent with the Sn–O–P bond being highly ionic in character as shown by the Mossbauer spectroscopy. Presumably, the specific nature of the chelation bond is fundamentally responsible for the high degree of selectivity that can be achieved with phosphonic acids in cassiterite flotation.

Ball, Cox and Yap (1978), in discussing the adsorption of inorganic phosphonate ions on cassiterite, have been critical of a simple ligand
exchange mechanism due to:

(a) the formation of unstable intermediate tin sites which lack complete coordination and,

(b) the breaking of Sn–O bonds which have a dissociation energy of 132 kcal per mole.

A considerably more complex mechanism has been proposed by these researchers. According to this mechanism, the surface hydroxyls first become deprotonated. The phosphorus atom of the phosphonate ion then undergoes a nucleophilic attack on the surface oxygens resulting in the breaking of the original P–O bonds. As proposed by Ball, Cox and Yap, this process involved attachment only at one surface hydroxyl site. However, given the consistent spectroscopic results indicating bidentate adsorbed species, the mechanism can be modified for phosphonic acid surfactants and represented as follows:
A number of criticisms of the Ball, Cox and Yap nucleophilic attack mechanism are immediately apparent. In particular, the breaking of P–O bonds in the phosphonic acid polar group with the formation of phosphonate radicals appears less energetically favourable than simple ligand exchange. Furthermore, the ligand exchange reaction does not involve the breaking of Sn–O bonds with high dissociation energy as claimed by Ball, Cox and Yap. Exchange of only coordinated hydroxyl groups is involved and these are well known to have much lower dissociation energy than that of a Sn–O bond in a solid lattice structure (the dissociation energy quoted by Ball, Cox and Yap is for a diatomic molecule and more closely approximates the latter case). The thermal desorption of hydroxyl groups from the surface of cassiterite at temperatures well below that necessary for the decomposition of the oxide (Morishige, Kittawa and Morimoto, 1980) clearly illustrates this fact.

Irrespective of the underlying reaction mechanism, the formation of bidentate phosphonate chelate species on the cassiterite surface would appear to be a key component of phosphonic acid adsorption over the entire pH range of interaction. However, as shown in adsorption studies, additional adsorption occurs at pH values below 4.0. The mechanism of this coadsorption is at present a matter of conjecture. There is evidence that the coadsorbing entity is an hydrophobic neutral phosphonic acid species although unequivocal confirmation of this is lacking. The electrokinetic studies of Yap (1975) further suggest that the mechanism of coadsorption is such that no measurable change in the electrophoretic mobility of the mineral occurs. The coadsorption is, therefore, fundamentally different to the chelation type reaction which produces a significantly more negatively charged cassiterite surface.
It is well established in other cassiterite flotation systems that surfactant adsorption occurs over specific areas or several scattered areas on the mineral surface (Kitchener, 1965; Pol'kin et al., 1973). These sites can be considered as high energy sites and probably represent areas on the mineral surface where chemical and steric compatibility of surface and surfactant exists (Scamehorn, Schechter and Wade, 1982). In the case of the phosphonic acids, this might correspond to cleavage planes where exposed stannic ions have two vacant sites which can act as coordination sites for the oxygen atoms of a phosphonic acid molecule.

At any one high energy site, significant numbers of phosphonic acid molecules would be expected to be coordinated to available stannic ions in the cassiterite lattice. These molecules might further interact through polar group and hydrocarbon radical interactions to form a close packed surfactant layer on the surface site. Cooperative bonding effects between hydrocarbon radicals, in particular, are well recognised as being important in immobilizing surfactant at an adsorption site. Such immobilization is necessary to prevent the shearing of surfactant from a surface in the turbulent environment of a flotation cell (Leja, 1982).

Phosphonic acid chelation at high energy sites on the cassiterite surface presumably takes place over the entire pH range of surfactant/mineral interaction. The phosphonic acid coadsorption that occurs in acidic pH solution most probably then complements this adsorption. However, since no further change in the electrophoretic mobility of the cassiterite occurs, the coadsorption must involve species that lack polar character or are orientated in such a way inside the inner Helmholtz plane as not to alter measurably the mineral charge character. Such might be the case for neutral phosphonic acid
species adsorbing through π-bonding interactions whereby they lie flat on the mineral surface. Any change in the electrophoretic mobility would then be due only to water dipole reorientation resulting from displacement of water molecules. Conway and coworkers (Conway, 1976) proposed that the small surface potential changes of the mercury electrode in the presence of low concentrations of pyrazine were due to such an interaction.

Another possibility (Fuerstenau and Healy, 1972) is that neutral phosphonic acid molecules coordinate in a parallel adsorption mode between chelated phosphonic acid molecules. Neutral molecules coadsorbed in this manner inside the inner Helmholtz plane might not alter measurably the electrokinetic properties of cassiterite particles on which chelate type adsorption already exists. Such a coadsorption mechanism would be consistent with the enhanced floatability that accompanies increased adsorption in the acidic pH range. Inverted mode coadsorption (i.e. polar groups of the neutral phosphonic acid molecules orientated toward the aqueous phase) would be expected to reduce the hydrophobicity and conversely is inconsistent with reported flotation results. Similarly, the formation of multilayer surfactant films appears unlikely since inverted mode coadsorption would again presumably be favoured by van de Waal's attraction forces between the hydrocarbon chains of the chelated and coadsorbed species.

The analyses of the adsorption study and electrokinetic measurements of Wottgen (1969) and Yap (1975), presented earlier in this chapter, clearly indicate that adsorption of neutral phosphonic acid species according to a chelating type mechanism is unlikely. Intuitively, such a result is not unexpected. For a 1:1 bidentate stannic ion chelate to form, two hydroxyls must be displaced from their coordination sites around a stannic ion.
Simultaneously, deprotonation of the chelating phosphonic acid molecule must occur. For a singly charged molecule only one hydroxyl must undergo deprotonation while two protons must be removed from the neutral species. Neutral phosphonic acid species only exist at low pH and hence in solutions where the proton concentration is in excess. Deprotonation under strongly acidic conditions is obviously inherently unfavourable.

2.4.8 Conclusions

1. Phosphonic acids are one of the most technologically successful families of collectors for cassiterite flotation. They are currently the preferred flotation surfactants at many major tin mines treating lode ores.

2. Flotation studies performed with undoped synthetic cassiterites indicate that phosphonic acids genuinely float cassiterites through interaction with surface stannic ions. Phosphonic acid flotation cannot be attributed solely to mineral lattice impurities.

3. There is no evidence available, at present, to indicate that cassiterite lattice impurities profoundly influence the flotation of cassiterite in the pH range of interest in industrial flotation (pH 4.5 - 7.0). Batch flotation data for doped synthetic cassiterite/quartz mixtures demonstrate that lattice impurities have only a small influence on the cassiterite floatability in this pH range.

4. Single mineral microflotation tests have consistently shown that maximum recovery of cassiterite with phosphonic acid occurs in acidic solution between pH 2.0 and 3.0. At high surfactant concentrations, the range of optimum flotation broadens towards more neutral pH values. In contrast, vacuum flotation studies performed on cassiterites from various origins have indicated optimum flotation between pH 5.0 and 6.0. No
experimentally verified mechanism for these differing flotation behaviours has been advanced.

5. Published adsorption isotherms for different phosphonic acids and various synthetic and natural cassiterites all indicate an adsorption maximum in acidic solution between pH 2.0 and 3.0. Excellent correlation exists between adsorption study and microflotation data for tests performed on the same mineral samples with identical solutions of n-heptyl phosphonic acid. Maximum flotation recovery occurred at the pH of maximum adsorption.

6. Strong experimental evidence exists that a significant chemical component is involved in phosphonic acid adsorption on cassiterite over the entire pH range of surfactant/mineral interaction. Flotation, adsorption, and electrokinetic studies all indicate appreciable surfactant adsorption above the iep of cassiterite.

7. Infrared spectra of phosphonic acid adsorbates on cassiterite are consistent with the formation of stannic phosphonates on the mineral surface. Mossbauer, infrared and chemical analyses have confirmed that stannic phosphonates are dibasic. Bonding in these phosphonates, while exhibiting some covalent character, is predominantly ionic.

8. A chelation mechanism involving the displacement of coordinated hydroxyls from the cassiterite surface with subsequent formation of bidentate 1:1 stannic phosphonate chelate species correlates with all current data pertaining to the chemisorption of phosphonic acids on cassiterite. A more complex mechanism has been proposed but appears considerably less plausible. The specific nature of the stannic phosphonate chelation bond would appear fundamentally responsible for the high degree of selectivity
that can be achieved with phosphonic acids in cassiterite flotation.

9. In acidic solution below pH 4.0, there is considerable evidence that the chemical component of phosphonic acid adsorption is complemented by coadsorption of undissociated phosphonic acid molecules. Strong support for this conclusion comes from reinterpretation of adsorption study data and correlation of adsorption isotherms with changes in the electrokinetic properties of cassiterite in phosphonic acid solutions. Independent confirmation of the latter data would provide irrefutable evidence for such coadsorption.

10. The coadsorption mechanism is at present a matter of conjecture. Increased floatability in the acidic pH region is, however, consistent with a proposed parallel mode coadsorption mechanism in which neutral phosphonic acid molecules are coordinated between chelated phosphonate species with their polar heads orientated towards the mineral surface.
2.5 Ion Interactions in Oxide Mineral Systems

2.5.1 Cation Adsorption

2.5.1.1 Electrokinetic Effects

Oxide minerals in the presence of hydrolyzable metal cations characteristically exhibit a series of charge reversals. In the general case, three charge reversals occur: a positive to negative charge reversal at low pH, followed by a negative to positive reversal and finally, at high pH, a positive to negative charge reversal. James and Healy (1972a) have denoted these charge reversals as CR.1, CR.2 and CR.3, respectively, in order of increasing pH. A schematic illustration of the general electrophoretic mobility behaviour of colloidal systems in the presence and absence of hydrolyzable metal ions is shown in Figure 52.

The general form of electrophoretic mobility curves for oxide minerals in the presence of hydrolyzable cations has been confirmed in many systems. However, in some systems, significant differences exist. For minerals with high iep values, CR.1 and CR.2 can both be absent (Figure 53). Charge reversal CR.1 has been interpreted as corresponding to the iep of the mineral and, consequently, where the iep is high, onset of specific adsorption can occur prior to the surface obtaining a net negative charge. The concentration of metal ionic species in solution and the surface area of the mineral available for adsorption are both also critical factors in determining the form of electrophoretic mobility curves. For large surface areas or for low concentrations of cations in solution, the magnitude of the charge reversal effects are generally diminished. The specifically adsorbing species cover a smaller percentage surface area and the mineral charge character therefore corresponds more closely to that of the original mineral surface. These
Figure 52 - Schematic Illustration of the General Electrophoretic Mobility Behaviour of Colloid Systems in the Presence and Absence of Hydrolyzable Metal Ions (from James and Healy, 1972a).

Figure 53 - The Variation of the Zeta Potential of TiO₂ Colloid (0.05 g liter⁻¹; iep 5.8) in 10⁻⁴ M KNO₃ with pH at 25°C, in the Presence and Absence of 5.2 x 10⁻⁶ M Al(NO₃)₃ (from Weise and Healy, 1975).
effects are clearly shown in Figure 54. As the mineral concentration and hence the available surface increases at a fixed cation concentration, the magnitude of the charge reversal is reduced, CR.2 increases while CR.3 decreases, and ultimately the mineral fails to exhibit a charge reversal effect.

A diversity of experimental procedures has been used in preparing suspensions for electrokinetic measurements. In ideal systems obtaining rapid thermodynamic equilibrium, variations in solution preparation procedure would not affect the nature of adsorption on minerals. However, metal cation systems are far from ideal. As discussed in detail previously, the kinetics of cation hydrolysis are very rapid up to the point of polycation and hydrous oxide formation. These polymeric species, while in fact metastable with respect to the formation of a final crystalline phase, are for most practical purposes, stable almost indefinitely. Of even greater importance, however, is that the kinetics of depolymerization and transformation from the hydrolyzed to the free aquated ion state are very slow. Consequently, a mineral suspension initially at a high cation concentration and pH between CR.2 and CR.3 will, when acidified to a pH below CR.2, give an electrophoretic mobility different from a similar suspension of identical cation concentration and final pH but initially at a pH below CR.1. In the former case, the reaction kinetics are very slow and equilibrium is not normally attained in the time frame of electrokinetic studies while, in the latter case, the reaction kinetics are rapid.

The importance of the method of mineral-cation suspension preparation and its influence on electrokinetic data have been overlooked frequently. Some inconsistencies in data interpretation have resulted. Iwasaki and coworkers
(Heerema and Iwasaki, 1980; Krishnan and Iwasaki, 1983) have recently recognized the importance of test procedure in electrokinetic studies involving quartz suspensions and magnesium and calcium ions. These researchers identified two fundamentally different types of tests which they denoted as surface precipitation and heterocoagulation, respectively.

In surface precipitation tests, cation salts were added to a mineral suspension at the natural pH of the suspension. In the case of magnesium and calcium, this pH was well below that required for charge reversal. The pH was then adjusted, using an acid or base, to the test pH. In the high pH studies, the effects of adsorption of hydroxylated species on the electrokinetic properties of the mineral were measured. In contrast, heterocoagulation tests involved preparing the mineral suspension and the cation solutions separately,
but both at the desired test pH. These were then mixed and the electrokinetic measurements made. Under high pH conditions, hydroxylation of the cations occurred in solution prior to contacting with the mineral. The tendency of the mineral particles and the cationic hydroxylated species to heterocoagulate was therefore measured. The electrokinetic data obtained according to the two procedures was found to be distinctly different. In general, surface precipitation tests produced more positive electrophoretic mobilities at high pH than those obtained in heterocoagulation tests.

A comprehensive examination of the literature relevant to the effects of cations on the electrokinetic properties of minerals reveals that a number of other experimental procedures, in addition to those recognised by Iwasaki and coworkers, exist. This is particularly the case for ferric and aluminum cations which undergo hydroxylation readily at low pH values. Four fundamentally different procedures can be identified. Figure 55 presents schematic illustrations of each of these four procedures which are denoted as surface nucleation, surface condensation (types I and II) and heterocoagulation, respectively.

In surface nucleation tests, a cation salt is added to a mineral suspension initially at a pH well below that necessary for specific adsorption and charge reversal. The pH is then raised to the test pH. At some critical pH, specific adsorption occurs. Tests at higher pH values then reflect the effects of increasing hydroxyl ion concentrations on this initial adsorption. As has been shown in studies on hydrolyzable metal cations in the absence of mineral substrates, the hydroxyl ion concentration and, in particular, the cation/hydroxyl ratio, can influence profoundly the nature of the polymerization reactions of polycationic and hydrous oxide species.
Figure 55 - Schematic Illustrations of Surface Nucleation, Surface Condensation (Types I and II) and Heterocoagulation Test Procedures.
An experimental disadvantage of the surface nucleation procedure is that for cations such as ferric and aluminum, the initial pH must be very low (pH < 2.0) to avoid the formation of hydrolysis species. Consequently, large additions of base are necessary for high pH electrophoresis measurements which, in turn, can increase significantly the suspension ionic strength.

In surface condensation tests, addition of the metal cation is to a mineral suspension at a pH value where bulk solution hydrolysis can occur. In type I tests, this pH is the test pH and no base is added other than that necessary to maintain a constant pH. The tendency for specific adsorption under the test conditions is then indicated by the electrophoresis measurements. In type II tests, there is an adjustment to the test pH. Interpretation of the electrophoresis results is consequently in terms of the effects of added acid or base on the initial adsorption. For cations forming polymeric or hydrous oxide species under the initial conditions, subsequent acidification might be expected to produce results significantly different to those obtained under surface nucleation conditions even at identical final pH values. Such variations would reflect differences in the forward and reverse kinetics of cation hydroxylation.

The fourth and final classification is that of Iwasaki's heterocoagulation tests. This procedure is fundamentally different to both surface nucleation and surface condensation in that specifically adsorbing species are allowed to form in solution prior to contacting with the mineral suspension. Under conditions of sol formation, adsorption would be expected to depend not only on the solution chemistry but also on factors such as the frequency of collision of the sol and mineral particles.
In studies relating flotation response in the presence of metal ions to electrokinetic measurements, the choice of procedure to obtain the most appropriate electrophoretic data is generally given little consideration. Cassiterite flotation pulps are characteristically naturally buffered around pH 4.5 - 7.5. Calcium and magnesium ions entering a circuit, whether through mineral dissolution or from plant water supplies, are therefore predominantly present as the free aquo ions. Electrokinetic effects, as measured in surface nucleation tests, consequently correspond most closely to the cassiterite flotation environment.

The situation for the ferric, ferrous and aluminum ions is considerably more complex. As discussed in detail in Section 2.3, pH conditions are generally not low enough for the free aquo ferric or aluminum ions to exist in solution. Therefore, for ferric and aluminum ions entering a flotation circuit from an external water supply, the prevailing conditions correspond closely to those in heterocoagulation tests. However, for such ions generated by mineral dissolution, surface condensation tests bear a closer correspondence to the flotation environment. The situation is more complicated in the case of ferric hydroxy species in that the source of such species can be ferrous ions entering solution under the reducing conditions of grinding and subsequently oxidizing to ferric hydroxy species. Surface nucleation tests involving ferrous ions would most closely parallel this latter case.

A number of analyses of the effects of metal cations on the electrokinetic properties of cassiterite have been published. However, much of the work is incomplete and in many respects difficult to interpret due to poorly specified sample preparation techniques. Nevertheless, sufficient data do exist to
indicate that certain dissolved metal ionic species can have profound effects on the electrokinetic properties of cassiterite.

In early work, Gaudin and Sun (1946) established that an initially negatively charged cassiterite surface became highly positively charged in the presence of 125 mg/l \( \text{FeCl}_3.6\text{(H}_2\text{O)} \) at pH 5.0 (Figure 56). A similar charge reversal effect occurred at pH 6.0 in the presence of 60 mg/l \( \text{AlCl}_3 \). No charge reversal effects were found when 100 mg/l \( \text{CaCl}_2 \) was added. Gutierrez and Pommier (1969) and Bellot (1970), using potentiometric titration techniques, also established that changes in the charge sign of cassiterite occurred in the presence of certain ions. Bellot (1970) found that the pzc of cassiterite was moved to higher pH in the presence of ferrous and ferric ions but not in the presence of calcium ions. A concentration of \( 5.7 \times 10^{-6} \text{ M} \)

![Figure 56 - Zeta Potential of Cassiterite in the Presence and Absence of (a) 125 mg/l \( \text{FeCl}_3.6\text{(H}_2\text{O)} \) (b) 60 mg/l \( \text{AlCl}_3 \) (c) 100 mg/l \( \text{CaCl}_2 \) (plotted from the data of Gaudin and Sun, 1946).]
ferric chloride was reported to move the cassiterite pzc from 4.0 to 6.0. The same concentration of ferrous chloride gave a pzc of 5.0. Data published by Gutierrez and Pommier (1969) indicate similar findings. It should be noted, however, that no Eh values were measured in any of the ferrous ion studies. It is, consequently, impossible to ascertain whether the reported electrokinetic effects were due to the free ferrous ion or to the products of its oxidation and hydroxylation in solution at higher pH values.

Undoubtedly, the most definitive studies of the effects of cations on the electrokinetic properties of cassiterite have been performed by Schubert and coworkers (Schubert, Baldauf and Raatz, 1969; Raatz and Schubert, 1971a). Results of these studies with calcium, magnesium and ferric chloride salts are shown in Figures 57 and 58. In all tests, the pH of the ion solutions was initially maintained below pH 2.0 to avoid formation of hydroxy species. The test procedure, therefore, was that of surface nucleation. In agreement with the results of other workers, the calcium and magnesium ions were found not to produce charge reversal in the pH range of interest in cassiterite flotation (Figure 57). Above the mineral iep and below pH 8.0, only reduction in the magnitude of the zeta potential occurred; presumably due to compression of the electrical double-layer. In contrast, ferric chloride additions were found to cause charge reversal in the manner characteristic of the James and Healy model. Charge reversal CR.3 occurred at pH 5.7 and pH 6.8 for 1.8 x 10^{-5} M and 1.8 x 10^{-4} M FeCl₃, respectively (Figure 58). Charge reversal points CR.1 and CR.2 were absent due to specific adsorption of ferric species below the cassiterite isoelectric point (iep 3.0). These data provide clear evidence for adsorption of a positively charged ferric species onto the surface of cassiterite at pH values above 2.0.
Figure 57 – Zeta Potential of Cassiterite in the Presence and Absence of Calcium and Magnesium Ions (from Raatz and Schubert, 1971a).

Figure 58 – Zeta Potential of Cassiterite in the Presence and Absence of Ferric Chloride (from Schubert, Baldauf and Raatz, 1969).
2.5.1.2 Adsorption Isotherms

A variety of experimental techniques has been used in determining the adsorption of cationic metal species on oxide mineral surfaces. In general, all the test procedures can be classified according to the scheme shown in Figure 55 and denoted as either surface nucleation, surface condensation (types I and II) or heterocoagulation tests, respectively. Reference to published data suggests that observable differences in adsorption measurements can result depending upon the test procedure adopted (Figure 59). Interpretation of results, consequently, must be made with appropriate regard to test procedure.

Figure 59 - The Abstraction of Magnesium Species by Quartz in the Presence of $10^{-6}$ M, $10^{-3}$ M and $10^{-2}$ M Magnesium Chloride as a Function of pH (from Krishnan and Iwasaki, 1983).
Irrespective of the method of contacting ion solutions with minerals, it is well recognised that considerable difficulty exists in measuring adsorption isotherms at pH values where significant cation hydroxylation occurs and where hydrous oxide species form in bulk solution (Weise and Healy, 1975; Letterman and Iyer, 1983). A significant fraction of unadsorbed sols tends to be removed from suspension during either centrifugation or membrane filtration, thereby complicating such adsorption measurements. The problem appears particularly acute in the aluminum and ferric ion systems where extensive polymerization can occur.

A number of experimental procedures have been adopted to overcome the problems of sol abstraction in adsorption measurements. The most widely used is the determination of residual ion concentrations in solutions prepared in the presence and absence of the test mineral. Differences in the residual ion levels are then considered as estimates of adsorption at the solid/liquid interface. However, implicitly assumed in such a procedure is that precipitation in bulk solution is the same irrespective of the presence of the mineral. Given that bulk solution precipitation might be diminished in the presence of a preferential adsorption site, such as a mineral surface, the residual concentration difference can underestimate the true mineral adsorption density. An alternative procedure is to attempt a direct measurement of cationic species adsorption. This involves recovering the mineral after contacting with the cation solution (usually by decantation), washing to remove loosely adhering precipitates and then acid leaching to resolubilize the adsorbed cationic species. Solution analyses are then performed as in the case of indirect adsorption measurements. The procedure suffers from the principal disadvantage that the mineral must be such that
dissolution does not interfere with the determination of the cations of interest in the leach liquor.

The only published data for cationic species adsorption on cassiterite are the ferric and calcium ion adsorption isotherms of Raatz and Schubert (1971a). In these studies, contacting of the ion solutions and the mineral was according to a surface nucleation procedure. A direct measurement of adsorption was used and the cassiterite test mineral was extensively acid leached prior to the adsorption measurements to avoid interference effects. Results from the studies are shown in Figure 60. Adsorption of calcium species occurred only in strongly alkaline solution above pH 8.0. In contrast, ferric ion species adsorbed strongly between pH 2.0 and pH 5.0.

Figure 60 - Adsorption of Ferric and Calcium Ion Species on Cassiterite as a Function of pH (from Raatz and Schubert, 1971a).
The pH values reported by Raatz and Schubert (1971a) for the onset of ferric and calcium species adsorption onto the cassiterite surface are consistent with the data obtained for other mineral substrates (Figures 61 and 62). Furthermore, the data are consistent with the corresponding electrokinetic measurements performed by Schubert and coworkers (Figures 57 and 58). In particular, maximum adsorption of ferric ion species in the range pH 3.0 - 4.0 corresponds to the pH of maximum charge reversal (Figure 58).

No isotherms for the adsorption of aluminum or magnesium species onto the surface of cassiterite have been published. However, data for the adsorption of aluminum species on rutile and quartz, which might reasonably be expected to correlate with the cassiterite system, do exist.

In Figure 63 the adsorption data of Weise and Healy (1975) for aluminum in the presence and absence of a rutile suspension are reproduced. The data confirm the tendency for depletion of aluminum ion levels in solutions containing no mineral to occur over the pH range 4.0 - 8.0. However, from the difference curve, an estimate of the adsorption of aluminum species on the rutile surface can be obtained. These data indicate that adsorption does not vary significantly between pH 5.0 and 9.0 but is significantly lower outside this range. The data of Araujo and Coelho (Figure 64) for the quartz-aluminum system are similar, although adsorption passes through a more distinct maximum in the region of pH 7.5 - 8.0.
Figure 61 - Adsorption Isotherms at 25°C for $1.2 \times 10^{-4}$ M Fe(III) and $1.4 \times 10^{-4}$ M Ca(II) on SiO$_2$ as a Function of pH (from James and Healy, 1972a).

Figure 62 - Adsorption Isotherms for Ca(II) Contacted with Quartz According to a Surface Condensation (Type II) Procedure (from Clarke and Cooke, 1968).
Figure 63 - The Residual Concentration of Al(III) as a Function of pH at 25°C in Solutions of $1.2 \times 10^{-5} \text{ M Al(NO}_3\text{)}_3$ in the Presence and Absence of 0.05 g litre$^{-1}$ TiO$_2$. In the absence of TiO$_2$, solutions analyzed without prior centrifugation are shown by full circles (from Weise and Healy, 1975).

Figure 64 - Abstraction of Aluminum onto Quartz as a Function of pH Expressed as a Percentage of the Total Aluminum in Solution (from Araujo and Coelho, 1984).
2.5.1.3 Adsorption Species

Considerable debate exists in the scientific literature regarding the nature of the cationic species that cause charge reversal. It has variously been proposed that these specifically adsorbing species are:

(a) first hydrolysis species of cations
(b) cationic polynuclear complexes of discrete composition
or
(c) various complex polynuclear or hydrous oxide species of cations.

All metal cations appear able to cause charge reversal of negatively charged colloids. However, such charge reversals occur only above a particular pH characteristic of each cation. It is a well corroborated fact that no reversal of charge occurs in the pH region where only the free aquo cation exists in solution (Matijevic et al., 1961; O'Melia and Stumm, 1967; James and Healy, 1972b).

The pH values characteristic of charge reversal effects have been recognised as indicating the initial existence of charge reversal species inside the hydrodynamic shear plane of the electrical double layer. On this basis, correlations have been sought between the pH values of initial charge reversal and bulk solution thermodynamics. Such correlations have led to the conclusion that adsorption of specific hydrolysis species, such as the cation first hydrolysis species, is responsible for charge reversal (Fuerstenau, Elgillani and Miller, 1970; Fuerstenau, 1975; Fuerstenau and Palmer, 1976).

It is now well established that cation concentrations and pH values measured in bulk solution can be different significantly from those at a solid/liquid interface (Tewari and Lee, 1975; Ananthapadmanabhan and
Somasundaran, 1985, 1985a). Direct correlations between interfacial phenomena and bulk solution thermodynamic data consequently appear, at best, tenuous. This is exemplified in those systems where such correlations fail to exist (Figure 65). As shown by James and Healy (1972a), charge reversal phenomena and cation species adsorption can initiate at pH values significantly below that necessary for hydrolysis in bulk solution.

The hypothesis that various complex polynuclear or hydrous oxide species of cations are responsible for charge reversal has received considerable support. James and Healy (1972), in a major investigation of charge reversal phenomena in a variety of cation systems, concluded that the specifically adsorbing species were large, weakly solvated polynuclear or hydrous oxide species. This followed earlier suggestions by Hahn and Stumm (1968) and Stumm and Morgan (1970) that such species might be responsible for charge reversal.

![Figure 65 - Adsorption Isotherm for Co(II) Adsorption at 1.2 x 10^{-6} M on Silica at 25 °C. Computed hydrolysis data for this cation concentration are shown as the percentage of each aquo complex as a function of pH (from James and Healy, 1972a).](image-url)
There is currently considerable direct evidence for the specific adsorption of polynuclear or hydrous oxide species onto the surface of minerals. Early findings consistent with the presence of such species on mineral surfaces can be found in the autoradiographic studies of Pol'kin, Kuzkin and Golov (1955). In these studies, polished sections of cassiterite were treated with $\beta$-radioactivity labelled iron salt, dried, and then arranged on a $\beta$-sensitive photographic plate. After development, mosaic distributions of iron on the surfaces of the cassiterite sections were evident (Plate 1). It is generally considered that monolayer film coverages of the surfaces in the 'clear' areas would not be revealed by the autoradiographic technique (Allison, 1982). The finding of mosaic patterns is, therefore, significant in that it indicates both the non-uniform nature of the adsorbed iron films and that the films were many layers thick. The latter result is consistent with the adsorption of larger iron sol species. The heterogeneity of the cassiterite surface is the most frequently cited reason for the non-uniform adsorption (Klassen and Mokrousov, 1963).

Further substantial corroborating evidence for the existence of amorphous films on mineral surfaces contacted with ion solutions comes from electron microscopy. Langdon, Perrott and Wilson (1973) have shown, through such examinations, that mica surfaces treated with ferric chloride solution became covered with colloidal particles. These sols were found to collapse when dried in air suggesting that they were of high water content. Using freeze drying and carbon/platinum replication techniques, it was established that individual sols were up to 10 nm in diameter. On the mica surface, each individual sol was consequently considered to cover of the order of 50 negative surface sites.
Plate 1 - Distribution of Radioactive Iron (Dark Spots) on the Surface of a Polished Section of Cassiterite. The polished section was treated at a concentration of (a) 100 mg/l; (b) 200 mg/l (from Pol'kin, Kuzkin and Golov, 1955).

More recently, Iwasaki and coworkers (Heerema and Iwasaki, 1980; Iwasaki et al., 1980; Krishnan and Iwasaki, 1983) have used scanning electron microscopy (SEM) to examine the surfaces of quartz particles that had undergone charge reversal in the presence of magnesium and calcium ions. In both systems, the particle surfaces were found to have areas covered by fine amorphous precipitates of morphology corresponding to that of the cation hydrous oxide. The amorphous coatings were not uniform in distribution but were concentrated in certain surface locations. No differences in morphology were observed between samples prepared under surface nucleation and heterocoagulation conditions. However, surface precipitation samples did exhibit more dense coatings than those subject to heterocoagulation under otherwise identical pH and concentration conditions. Coating thicknesses were estimated to vary between 0.8 and 10 nm. Such estimates must, however, be considered questionable, given the possible collapse of sols and associated morphology changes attending direct SEM examinations.
The published SEM analyses of surfaces that have undergone charge reversal in the presence of cations strongly support the contention that polymeric hydrous oxide sols cause charge reversal. However, such studies are themselves not able to answer definitively all questions relating to the nature of the adsorption species. The only information provided by SEM is that pertaining to the adsorbed species morphology. However, SEM cannot be used for in-situ analyses thereby raising the issue of surface modification during sample preparation. The possibility of lower order hydrolysis species adsorbing also cannot be precluded entirely due to the limited resolving power of the electron microscope.

A surface analysis technique which does allow chemical analysis, although not on an in-situ basis, is that of X-ray photoelectron spectroscopy (XPS). The technique has not been applied widely in surface analysis of adsorbed inorganic ion species. This is presumably due to the perception that the high vacuum and temperature of analysis might cause significant surface modification. Tewari and Lee (1975) have argued that these effects are not critical, at least in cobalt species adsorption onto Al₂O₃ and ZrO₂. In these systems, they have asserted that XPS analyses confirm that the adsorbed cobalt species is the hydrous oxide.

A number of fundamental questions still remain with regard to the nature of the species that cause charge reversal. One such issue is that of at what pH cations capable of causing charge reversal first adsorb inside the Stern plane. Adsorption inside the Stern plane must be related intimately to charge reversal phenomena since it is the charge at the hydrodynamic shear plane (which is assumed to be near the Stern plane) that is physically measured in electrokinetic studies. As pointed out by James (1981), one of the most
challenging problems still to be answered is whether the amorphous coatings observed in SEM analyses are the result of:

(a) condensation of simple ionic species adsorbed inside the Stern plane.

(b) condensation of hydrolyzed species, including polycations, inside the Stern plane, or

(c) colloidal hydrous oxides forming in the diffuse region of the double layer or in bulk solution, and at some critical point adsorbing inside the Stern plane.

Most certainly the last mechanism is feasible as confirmed in SEM analyses of minerals undergoing charge reversals in heterocoagulation studies (Krishnan and Iwasaki, 1983). However, whether the same mechanism applies in surface nucleation and condensation studies remains to be resolved.

2.5.1.4 Adsorption Mechanisms

A number of detailed mechanisms have been proposed to explain the charge reversal effects of cations. As would be expected, these mechanisms have varied significantly depending on the perceived nature of the species responsible for charge reversal.

In early publications, Allen and Matijevic (1971) and Fuerstenau, Elgillani and Miller (1970) proposed that it was only the first hydroxy species of a metal cation that caused reversal of charge. These species were postulated to adsorb through direct reaction with an hydroxylated mineral surface to produce either water or hydronium ions. Schematically, the
proposed reactions can be represented as:

$$\text{SOH} + \text{M(OH)(H}_2\text{O)}_5^{2+} \leftrightarrow \text{SOM(OH)(H}_2\text{O)}_4^{+} + \text{H}_3\text{O}^+$$

$$\text{SOH} + \text{M(OH)(H}_2\text{O)}_5^{2+} \leftrightarrow \text{SOM(H}_2\text{O)}_5^{2+} + \text{H}_2\text{O}$$

These mechanisms were extensively criticized in the literature on the basis that for them to proceed, the cations had to become desolvated (at least in the direction of the surface) and lose their hydration sheaths (James and Healy, 1972a). This was considered unlikely. In subsequent publications, Fuerstenau and coworkers (Fuerstenau, 1975; Fuerstenau and Palmer, 1976) maintained that the first hydroxy species was the entity responsible for charge reversal but that adsorption might have been the result of increased hydrogen bonding. However, as concluded by James and Healy (1972a), hydrogen bonding would be similar between an hydroxylated mineral surface and either coordinated ion hydroxyls or water molecules. A simple hydrogen bonding mechanism, therefore, also seems implausible.

The most comprehensive model of charge reversal proposed to date is that of James and Healy (1972). This model has as one of its cornerstones, the tenet that charge reversal is caused by weakly solvated, polynuclear or hydrous oxide species adsorbing or being formed at a surface. On this basis, the charge reversal points CR.1, CR.2, and CR.3 are interpreted as follows:

CR.1 - is the isoelectric point (iep) of the oxide mineral
CR.2 - is the pH of nucleation of metal hydrous oxide
CR.3 - is the isoelectric point of the adsorbed metal hydrous oxide if sufficient metal ion is adsorbed to yield a complete mineral surface coating. Incomplete coating, due to lower concentration of metal ions or to higher concentrations of colloidal substrate particles,
reflects the dual surface of coated and uncoated areas. Thus CR.3 can occur at pH values at or below the isoelectric point of the metal hydrous oxide depending on the coverage achieved.

A number of fundamental issues are immediately raised on the basis of the James and Healy model of charge reversal. If CR.2 is the point of surface nucleation of the hydrous oxide, then the pH region between CR.2 and that of deviation of the electrophoretic mobility curve from the cation free system lacks physical interpretation. Furthermore, CR.2 itself occurs at pH values significantly below that necessary for bulk precipitation of the hydrous oxide. To explain this latter phenomenon, James and Healy proposed that adsorption was controlled by competition between free energy changes that favour adsorption i.e. coulombic and chemical energy changes and a solvation energy that opposes adsorption.

The possible role of solvation effects in specific adsorption had been recognised earlier by Hahn and Stumm (1968) and Stumm and Morgan (1970). However, James and Healy (1972b) proposed a more rigorous treatment based on differences in dielectric constant between an oxide mineral surface and a solvent. Using the Born charging equation, it was shown that differences in medium dielectric constant gave rise to an additional free energy term that opposes adsorption. However, as hydroxylation proceeds the ionic charge is lowered and the species become less strongly solvated such that the coulombic and chemical energy contributions dominate and adsorption is abruptly enhanced. Furthermore, the pH of this abrupt adsorption now logically corresponds to the formation of hydrous oxide in the interfacial region. The additional solvation energy term serves to reduce the total (negative) free
energy change for adsorption at the interface such that the interfacial solubility product of the hydrous oxide is less than that of the bulk solution value. This final result is a consequence of the fundamental relationship between stability constants and free energy of formation:

$$\Delta G = -RT \ln K.$$ 

The issue of whether there is a change in the intrinsic stability constants of cation hydroxy species in the interfacial region, as advocated by the James and Healy model, has been a controversial one. Tewari and Lee (1975), in measuring the pH dependence of Co(II) adsorption on TiO$_2$, ZrO$_2$ and NiFe$_2$O$_4$, claimed that the adsorption did not follow any trend of mineral dielectric constant. This was despite the dielectric constant of TiO$_2$ being in excess of 80, and that of ZrO$_2$ and NiFe$_2$O$_4$ being much lower. However, their own data is not conclusive as the specific area of the rutile used in the adsorption measurements was almost an order of magnitude less than that of the other two minerals.

More recently, Ananthapadmanabhan and Somasundaran (1985, 1985a) have proposed that it is not necessary to invoke a new thermodynamic constant for the interfacial region, provided that the pH and species concentrations at the interface are fully considered. These researchers performed a series of calculations showing that variations in pH and cation species concentrations between the interfacial region and bulk solution could account for the preferential precipitation of hydrous oxides at an interface. While it is not currently possible to measure pH and concentration at an interface, the necessary assumptions regarding double layer thickness, pH and concentration differences all appear physically realistic.
To date, no definitive test has been devised to evaluate the James and Healy concept of intrinsically different stability constants in the interfacial region. Furthermore, the recognition of concentration and pH differences between an interface and bulk solution does allow an equally plausible alternative explanation of all of the phenomena cited by James and Healy in support of their model. For example, reproduced in Figure 66 is the James and Healy data for cobalt adsorption on TiO\textsubscript{2} and SiO\textsubscript{2}. An abrupt increase in adsorption occurs on TiO\textsubscript{2} at a pH value measurably lower than that for SiO\textsubscript{2}. This phenomenon cannot be explained on the basis of either available surface area (the higher TiO\textsubscript{2} surface area is not sufficiently large to account for the adsorption differences) or electrostatic attraction (the SiO\textsubscript{2} has the more negative surface). James and Healy (1972a) consequently considered that the effect was due to the difference in the dielectric constants of the two minerals; the high dielectric constant of TiO\textsubscript{2} reducing the total free energy change of adsorption and lowering the stability constant of hydrous oxide formation at the interface. However, following the Ananthapadmanabhan and Somasundaran approach, it can equally well be argued that the more negative surface charge of the quartz will result in a greater concentration of H\textsuperscript{+} and Co\textsuperscript{2+} ions in the electrical double layer. The difference in cobalt species adsorption on the two mineral surfaces, therefore, might reflect differences in interfacial pH and ion concentrations and not fundamental changes in intrinsic thermodynamic stability constants.

The existence of a solvation energy opposing adsorption appears plausible on the basis of the theoretical development of the James and Healy model. Indeed, such an energy term must exist if the free aquated forms of multivalent cations do not specifically adsorb on mineral surfaces. The work
Figure 66 - Adsorption of Co(II) at $10^{-4}$ M on Silica ($\text{pH}_{\text{pzc}} = 2.0$) and Titania ($\text{pH}_{\text{pzc}} = 5.6$). The available surface areas were 75 and 115 m² litre⁻¹, respectively (from James and Healy, 1972a).

of Ananthapadmanabhan and Somasundaran, however, calls into question the magnitude of the solvation energy of hydrous oxide species with respect to the attractive forces of adsorption. If physically realistic estimates of differences in bulk and interfacial ion concentrations and pH values can account for observed pH values of charge reversal effects, this term might for such species be negligible.

A further issue raised on the basis of the James and Healy model is that of interpretation of charge reversal phenomena associated with CR.3. According to the model, the asymptoting of electrophoretic mobilities at high pH values back to those in the absence of ions is due to changes in the surface charge of the adsorbed species. For complete surface coverage, CR.3 is then considered to be the isoelectric point of the adsorbed hydrous metal oxide. The positive to negative charge reversal at high pH values might, however, reflect both the changing charge character of the adsorbed sols and
sol desorption. Both phenomena are undoubtedly intimately related since resolubilization of sols in the absence of minerals is known to occur in the presence of excess hydroxyl ions (Stol, van Helden and de Bruyn, 1976).

The forces of attraction between a mineral surface and a cationic hydroxy species are generally regarded as being those of electrostatic interaction and hydrogen bonding (Matijevic et al., 1961; Mackenzie, 1966). Most researchers have considered the electrostatic term as the dominant attractive force (Healy, 1969; James and Healy, 1972; Krishnan and Iwasaki, 1983) although some such as Critchley and Jewitt (1979) have proposed that hydrogen bonding might play a key role in adsorption. The realization that extensive hydrolysis produces large complex polycationic and hydrous oxide sols and the identification of such sols on the surface of minerals suggests that hydrogen bonding forces might be very important. While an individual hydrogen bond is relatively weak (3 - 10 kcal/mol), large polymeric sols would cover many surface sites and the total contribution of hydrogen bonding to adsorption might be appreciable. Such a conclusion is supported by the rather profound finding of Fuerstenau, Elgillani and Miller (1970) that ferric hydroxy species adsorb strongly on the surface of sapphire in an acidic pH environment (Figure 67). In the acidic pH range, both the sols and the sapphire surface would be charged positively.

Greater understanding of the forces responsible for cation species adsorption is still required. Such understanding will provide information on such critical issues as that of the selectivity of cation adsorption in multi-mineral flotation systems. At present, the general view is that adsorption is non-selective with cationic hydrous oxide coatings forming on all surfaces in proportion to their available surface area (Healy, 1969). However, such an
hypothesis does not take into account the potential role of the source of the dissolved metal ionic species. For example, ions derived from a particular mineral might preferentially form films on that mineral surface due to local concentration or kinetic effects. If such ions were to hydrolyze and adsorb on another mineral surface, transfer away from the source mineral interface and through the bulk solution must occur. Provided that thermodynamically both adsorption processes are equivalent, kinetic considerations would presumably favour adsorption on the mineral of the ions origin.

Other kinetic aspects of cationic species adsorption are also of importance in flotation. Hydroxylated metal ionic precipitates are known to be stable and removed with difficulty even at low pH. While no data are available on how rapidly the adsorbed sols are removed by simple pH decrease,
it is known that it is slow with a half-life of tens of minutes rather than seconds. In contrast, the kinetics of adsorption-nucleation of metal cationic species has been found to be of the order of seconds and is clearly a realistic reaction under flotation conditions (Healy, 1973; Weise and Healy, 1975).

2.5.1.5 Effects of Fluoride

Fluoride forms stable complexes with many cations. Particularly strong complexes are formed with aluminum and ferric ions at low pH. The presence of fluoride ions might, therefore, affect significantly the electrokinetic properties of cassiterite in ferric or aluminum ion solutions. Such a contention is strongly supported by the studies of Matijevic, Kratohvil and Stickels (1969) with silver halide sols. In low pH solutions (pH < 4.0), where aluminum fluoro-complexes were the predominant species, no coagulation was found to occur. Coagulation only took place at higher pH where hydrolyzed aluminum species formed in solution. These researchers concluded that aluminum fluoro-complexes were strongly hydrated and showed little or no tendency to polymerize in the manner of the hydroxy species. As such, they would not be expected to adsorb onto the surface of oxide minerals and cause charge reversal.

2.5.2 Fluoride Ion Adsorption on Cassiterite

Fluoride reagents are widely used in cassiterite flotation. However, at present their role is not well understood. As indicated above, the fluoride ion would be expected to interact under acidic conditions with ferric and aluminum cationic species in flotation pulps. It is also possible that the fluoride ion might itself adsorb specifically onto the cassiterite surface.
It is known that the stannic ion readily forms aqueous complexes with the fluoride ion (Jackson and Helgeson, 1985). Unfortunately, there is a general dearth of pertinent thermodynamic data on stannic fluoride complexes. Dissolution of cassiterite in highly concentrated fluoride solutions is also known to occur (Klintsova et al., 1975). In acidic solutions dissolution is considered to proceed primarily via the formation of neutral hydroxofluoride complexes:

\[
\text{SnO}_2(c) + HF + H_2O \rightleftharpoons \text{Sn(OH)}_3F(aq)
\]

\[
K = (8.0 \pm 1.6) \times 10^{-6}
\]

In alkaline solutions up to pH 10.6, SnO_2 is believed to dissolve according to the reaction:

\[
\text{SnO}_2(c) + F^- + H_2O \rightleftharpoons \text{Sn(OH)}_4F^-(aq)
\]

\[
K = (3.7 \pm 0.5) \times 10^{-6}
\]

On the basis of the measured stability constants (Klintsova et al., 1975), the solubility of cassiterite in fluoride solutions only exceeds that in pure water at fluoride concentrations higher than 1 x 10^{-1} M.

No investigations of the possible adsorption of the fluoride ion onto the cassiterite surface have been published. However, its ability to form complexes with the stannic ion and promote cassiterite dissolution at high concentrations supports the contention that specific adsorption might occur onto the mineral surface. In many other insoluble oxide systems, such adsorption has been established. Warren and Kitchener (1972) have shown that for concentrations less than 1 x 10^{-3} M, fluoride ion adsorption occurs on quartz below pH 4.5. At higher concentrations, chemical reaction of hydrofluoric acid with the silica was found to promote the dissolution of the
mineral. This latter finding was independently confirmed in leaching tests by Read and Manser (1975). Specific adsorption also has been established in the case of alumina (Warren and Kitchener, 1972) and gibbsite and goethite (Hingston, Posner and Quirk, 1972).

A number of mechanisms have been proposed for the specific adsorption of fluoride onto oxide minerals. Warren and Kitchener (1972) considered that adsorption of fluoride on silica was due to hydrogen bonding. In the case of alumina, an ion exchange mechanism with fluoride ions displacing coordinated hydroxyls from the mineral surface was thought to occur. A similar general mechanism has been proposed by Hingston, Posner and Quirk (1972) for all oxide minerals. According to these researchers, specific adsorption of fluoride involves the displacement of coordinated hydroxyls or water groups from an oxide surface with the subsequent coordination of the fluoride to a surface lattice cation. Furthermore, they consider that such a reaction is only possible when protons are present either on the oxide surface at pH values more acidic than the pzc or derived from dissociation of hydrofluoric acid. If this is the case, the specific adsorption of fluoride on cassiterite would be expected only in the acidic pH range since the pzc of the mineral is generally below pH 5.0 and the pK\textsubscript{a} value for hydrofluoric acid is 2.94 (Weast and Astle, 1983).

2.5.3 Phosphonic Acid Flotation Activation/Depression

Numerous effects on tin flotation performance have been ascribed to metal ionic species dissolved in flotation pulps. These have ranged from the precipitation of collectors to the activation of cassiterite and/or associated gangue species (Topfer, Gruner and Menzer, 1971; Arbiter, 1977). In phosphonic acid flotation, the general consensus is that ferric and aluminum
ions have pronounced deleterious effects (Collins, 1967; Wottgen and Topfer, 1976; Bulled, 1982; and Mosch and Becker, 1985).

Despite the generally accepted importance of dissolved metal ionic species, few fundamental studies of the effects of such ions on phosphonic acid cassiterite flotation have been made. At present, no comprehensive theory of the role of dissolved ions exists. However, a number of important scientific contributions have been made. Particularly significant with respect to phosphonic acid interactions with ions in solution are the early studies of Collins and coworkers (Collins, 1967; Collins and Jackson, 1967; Collins, Hollick and Joy, 1969). While such interactions are of importance, more recent advances in metal ion interfacial chemistry suggest that bulk solution effects are only one aspect of the complicated nature of metal ionic species interactions in cassiterite flotation.

2.5.3.1 Vacuum Flotation Studies

No microflotation data have been published for the phosphonic acid flotation of cassiterite in the presence of dissolved metal ions. However, vacuum flotation techniques have been used extensively by Collins and coworkers in investigating such effects (Collins 1967; Collins and Jackson, 1967; Collins, Hollick and Joy, 1969). Dissolved calcium and iron species in mill water supplies were believed by these researchers to produce fundamental changes in phosphonic acid flotation. Detailed vacuum flotation studies using heptyl and isohexyl phosphonic acids and cassiterites of different origins were conducted to confirm such effects. In all tests, collector solutions containing salts of the ions of interest were prepared prior to pH adjustment or conditioning of the mineral.
Figures 68 to 72 show the published data of Collins and coworkers. Depressant effects were found for all the ions examined. However, the extent of the flotation inhibition varied significantly depending on the type of cation, its concentration in solution and the pH. Slight differences in vacuum flotation response were also observed with different cassiterites. This was attributed to varying iron contents in the minerals. The addition of ferric salts to the collector solutions produced a most marked depressant effect for all the cassiterites (Figures 68 to 70). Total ferric iron concentrations of less than 25 mg/l were sufficient to produce complete depression at collector levels of less than 80 mg/l (Figure 70). Measurable inhibition of flotation occurred at cation concentrations as low as 1 mg/l (Figures 68 and 69). Ferrous iron salts produced significant decreases in the vacuum flotation response only at much higher concentrations. This depressant effect was particularly pronounced above pH 6.0 (Figure 70). Calcium ions could similarly be tolerated at higher concentrations but over a broader pH range. Very high concentrations (> 400 mg/l) of calcium ions were required to inhibit severely flotation with isoheptyl phosphonic acid (Figure 72). A minor anomaly occurred in the case of the heptyl phosphonic acid flotation of Mount Pleasant cassiterite (Figure 69) where activation was observed in the presence of 10 ppm Ca$^{2+}$. Such calcium ion activation was not found in other tests.

The data given in Figures 68 to 72 must be interpreted with due regard to experimental procedure. In particular, it is of importance that pH and potential control were not used during preparation of the cationic solutions. In the case of the ferric ion, it is therefore probable that the cation underwent significant hydroxylation prior to contacting with the collector. If
Figure 68 - Vacuum Flotation Response of South Crofty Cassiterite with Heptyl Phosphonic Acid in the Presence and Absence of Ferric and Calcium Ion Species (from Collins and Jackson, 1967).

Figure 69 - Vacuum Flotation Response of Mount Pleasant Cassiterite with Heptyl Phosphonic Acid in the Presence and Absence of Ferric and Calcium Ion Species (from Collins, 1967).
Figure 70 - The Effect of Ferric Ion Species on the Isoheptyl Phosphonic Acid Flotation of Cassiterite (from Collins, Hollick and Joy, 1969).

Figure 71 - The Effect of Ferrous Ion Species on the Isoheptyl Phosphonic Acid Flotation of Cassiterite (from Collins, Hollick and Joy, 1969).
Figure 72 - The Effect of Calcium Ion Species on the Isoheptyl Phosphonic Acid Flotation of Cassiterite (from Collins, Hollick and Joy, 1969).

Collector precipitation occurred, it was presumably the polymeric species of the ferric ion that were responsible. The chemistry of the ferrous ion solutions is similarly likely to have been complex. Depending on the solution potential, oxidation of the solvated ferrous ion might have occurred at higher pH values. Such oxidation, together was associated formation of ferric (-ferrous) polycationic species, might correspond to the enhanced depressant effect of the ferrous salt solutions observed above pH 6.0.

The results of Collins and associates represent some of the key fundamental data supporting the contention that phosphonic acid interactions with metal ionic species are of importance in cassiterite flotation. The affinity of the acids for iron species, such as the hydroxy species of the ferric ion, is clearly particularly strong. Calcium ions at low concentrations in flotation solutions are less able to modify flotation
response. While interactions between collectors and cations are, therefore, probable in industrial flotation systems, the solution chemistry of such pulps is far more complex than assumed in the Collins studies. Investigation of the role of ions using a test procedure where ion and collector solutions are contacted prior to the addition of the mineral for flotation implicitly assumes that the ionic species are present predominantly in solution. In the case of the calcium ion, this is a reasonable assumption, given the pH range characteristic of cassiterite flotation. However, the free aquated ferric ion is unlikely to exist under flotation conditions. At the Eh and pH levels typical of cassiterite flotation the ferrous ions and polymeric ferric (ferrous) polycations are the stable ion species (Figure 18). The free ferrous ion would be expected to be strongly solvated at low pH but to undergo oxidation and polymerization at higher pH. These highly polymerized sols might be adsorbed strongly onto the surfaces of minerals and, therefore, not present in solution at levels sufficient to precipitate collector in the bulk solution. The overall influence of dissolved metal ionic species is presumably a complex function of their interaction with phosphonic acids at both cassiterite and gangue mineral interfaces and their bulk solution effects.

The realisation that cations in solution resulted in a depressant effect in phosphonic acid flotation led Collins, Hollick and Joy (1969) to investigate the effects of complexing agents on flotation. Figure 73 shows the effects of sodium fluorosilicate additions on the vacuum flotation of cassiterite with isoheptyl phosphonic acid in the presence of various cations. In the pH range 2.0 to 6.0, a depressant effect occurred with the fluoride reagent addition. To explain this phenomenon, it was proposed by the
researchers that isoheptyl phosphonic acid floated cassiterite by virtue of iron in the mineral lattice or adsorbed onto its surface. The interaction of the fluoride ion with these iron species was thought to inhibit flotation by reducing collector adsorption. Interactions of the fluoride ion with iron species on the cassiterite surface certainly represent the most plausible explanation of the flotation depressant effect. Such species on the cassiterite surface might well interact strongly with the collector, given the affinity of phosphonic acids for iron species, and thereby activate flotation. However, the assertion that isoheptyl phosphonic acid is floating cassiterite solely by virtue of iron in the lattice or adsorbed on the surface is unjustified. Overwhelming evidence exists confirming the strong interaction of phosphonic acids with stannic ions and synthetic cassiterites containing no measurable iron content. The adsorption study and flotation data of Gruner
(1971) (Figures 36, 37 and 39) provide irrefutable support for such a conclusion.

2.5.3.2 Batch Flotation Studies

Topfer and coworkers have performed a series of batch flotation tests on cassiterite - quartz binary mixtures to investigate the influence of dissolved metal ionic species. Results from tests with supernatants from various common cassiterite gangue species and ferric chloride salts have been published (Topfer and Gruner, 1972; Topfer, Gruner and Bilsing, 1975). In all studies, n-heptyl phosphonic acid was used as collector.

Figure 74 shows the batch flotation results for tests in which cassiterite was floated in the presence of supernatants derived from quartz, tourmaline and apatite minerals. The flotation data for the quartz and tourmaline supernatants exhibit discernable depressant effects. Flotation in the presence of a supernatant derived from apatite was not measurably different from that in distilled water.

Despite the rather profound nature of their results, Topfer and Gruner (1972) offered no explanation of their data. Indeed, as published, their results are completely uninterpretable. Numerous key aspects of their experimental techniques are not reported in their publication. It is not stated, for example, whether supernatant solutions were contacted with collector solutions prior to cassiterite addition or vice versa. No test pH (or Eh) is specified and no analyses of the supernatants are given. Furthermore, the implication from associated electrokinetic studies is that the test pH was not controlled. Variations in flotation response might, therefore, reflect changing pH conditions.
Figure 74 – Batch Flotation Response of Cassiterite with n-heptyl Phosphonic Acid in the Presence and Absence of Supernatants from Other Minerals (from Topfer and Gruner, 1972).

Figure 75 shows similar batch flotation results for tests in which cassiterite was preconditioned in ferric chloride solution, extensively washed and then floated. A depressant effect can be seen in the data although it is highly collector concentration dependent. As for the earlier results, the pH and Eh of conditioning were not stated nor were the conditions of flotation specified. If, again, a constant pH was not maintained, the collector concentration dependence might reflect primarily a pH effect. Increasing concentrations of n-heptyl phosphonic acid would have moved the pH of flotation to more acidic values.

In associated infrared studies, Topfer, Gruner and Bilsing (1975) claimed that an identical ferric chloride pretreatment increased the intensity of the characteristic peaks of n-heptyl phosphonic acid adsorbate on cassiterite.
Figure 75 - The Effect of FeCl₃ Pretreatment on the Batch Flotation of Cassiterite from Binary Mixtures with Pure Quartz using n-heptyl Phosphonic Acid as Collector (from Topfer, Gruner and Bilsing, 1975).

Such a result, and its apparent incompatibility with the flotation data, was cited as one example of the role of dissolved ions that could not be explained or interpreted by existing flotation theory. Although in the absence of further experimental data a myriad of possibilities exists, the reported phenomena appear far less irreconcilable than stated by Topfer, Gruner and Bilsing. It should be borne in mind that the characteristic absorbance bands of ferric and stannic phosphonates are not readily distinguishable (Wottgen and Dietze, 1969) and that infrared spectroscopy is generally an ex-situ technique. The infrared spectra of Topfer, Gruner and Bilsing (1975), therefore, presumably indicate the presence of a ferric phosphonate species on the surface of the cassiterite. The nature of the association of this species with the surface, however, cannot be assumed to be the same as that for genuine phosphonic acid adsorption (as implied by Topfer, Gruner and Bilsing). The flotation results would suggest, that in an aqueous environment, these
ferric phosphonate species resolubilize producing a depressant effect. Furthermore, this resolubilization might be dependent significantly on pH in the acidic pH range and hence influenced by the collector concentration.

2.5.3.3 Adsorption Studies

As part of their research into the effects of dissolved metal ionic species, Topfer and coworkers (Topfer, Gruner and Menzer, 1971; Topfer, Bilsing and Gruner, 1972) performed a series of complex adsorption tests in which the adsorption of n-heptyl phosphonic acid on binary mineral mixtures, in the presence and absence of gangue mineral supernatants, was measured. Tests were conducted for a range of cassiterite/gangue mixtures and various supernatants. Gangue minerals used as sources of supernatant solutions and as components in the binary mixtures included quartz, hematite, fluorite, apatite and biotite. Adsorption density on each of the mineral components was determined by radiometric detection of P\textsuperscript{32} marked phosphonic acid.

Figure 76 shows the reported adsorption results for cassiterite and hematite binary mixtures at pH 6.0. Profound changes are evident in the adsorption density dependent upon the nature of the supernatant present. For example, the supernatant from the mineral apatite appears to promote the preferential adsorption of phosphonic acid onto the cassiterite surface. Other mineral supernatants produced significant, but less dramatic, enhancement of adsorption onto cassiterite relative to hematite. In the distilled water system, adsorption on hematite exceeded that on cassiterite by more than an order of magnitude.

Topfer, Gruner and Menzer (1971) offered no explanation of their results, other than to suggest that the effect of dissolved ions was due to changes in mineral surface properties and ion solution effects. Indeed, as is the case
Figure 76 - Adsorption Density at pH 6.0 of n-heptyl Phosphonic Acid on Cassiterite and Hematite in Binary Mixtures of the Minerals in the Presence and Absence of the Supernatants from Other Minerals (from Topfer, Gruner and Menzer, 1971).

for the related batch flotation studies of Topfer and coworkers, the results cannot be interpreted from their publication. No analyses of the supernatants were made, Eh values are not specified nor is the order of contacting of mineral, collector and supernatant solutions stated. While illustrating the importance of dissolved metal ionic species in cassiterite flotation, these adsorption data contribute little to a fundamental understanding of dissolved ion effects.

2.5.3.4 Electrokinetic Studies

Streaming potential measurements were conducted by Topfer and Gruner (1972) to complement their batch flotation data on the effects of gangue mineral supernatants. Zeta potentials of cassiterite in n-heptyl phosphonic
acid solutions were measured in the presence and absence of supernatants from quartz, tourmaline and apatite.

In distilled water containing no phosphonic acid, the zeta potential of cassiterite at pH 6.0 was reported to be $-80 \text{ mV}$. Figure 77 shows that in the presence of n-heptyl phosphonic acid alone the zeta potential of the mineral became slightly less negative. The effects of both collector and supernatant additions were far more pronounced and the potential varied significantly depending upon the type of mineral supernatant present. Tourmaline supernatant together with n-heptyl phosphonic acid gave much more negative cassiterite zeta potentials while, at similar phosphonic acid additions, apatite and quartz supernatants resulted in much less negative values.

![Graph showing the variations of cassiterite zeta potentials with increasing collector addition](image)

Figure 77 - The Variations of Cassiterite Zeta Potentials with Increasing Concentrations of n-heptyl Phosphonic Acid in the Presence and Absence of Supernatants from Other Minerals (from Topfer and Gruner, 1972).
Topfer and Gruner (1972) proposed that the ions of tourmaline greatly increased the adsorption of phosphonic acid onto the cassiterite surface thereby increasing the negative charge character of the mineral. However, it was not shown independently that the ions themselves could not account for the zeta potential change nor does it appear that the pH was maintained constant. Evidence for variations in pH in these studies can be seen in the distilled water data where increasing n-heptyl phosphonic acid additions were found to reduce the negative charge character of the cassiterite. Such a result is difficult to reconcile with the initial negative charge of the mineral and the anionic nature of phosphonic acids if the pH is constant. However, in the absence of pH control, increasing concentrations of phosphonic acid would move the pH to more acidic values and hence towards the iep of the mineral. The associated decrease in negative surface charge would account for the streaming potential data of the cassiterite in the presence of n-heptyl phosphonic acid alone.

The influence of quartz and apatite supernatants was attributed by Topfer and Gruner directly to the ions of these minerals. However, again this was not confirmed independently in the absence of collector and the effect might be largely pH related. As for all of the analyses of Topfer and coworkers, the electrokinetic studies do indicate that dissolved metal ionic species likely to be present in flotation pulps can have potentially profound effects on the phosphonic acid flotation of cassiterite. However, much crucial experimental information is lacking and, consequently, no rational interpretation of the mechanisms of these effects is possible.
2.5.3.5 Bench Scale Studies on Ores

Systematic studies of the role of dissolved metal ionic species in cassiterite flotation under controlled batch flotation conditions have not been performed. However, numerous researchers have ascribed aspects of batch flotation phenomena to dissolved metal ions and some results pertaining to the role of ferric ion species in solution do exist.

Virtually from the inception of phosphonic acid cassiterite flotation, it has been considered that certain metal ions might interfere significantly with the flotation process. This belief led Kirchberg and Wottgen (1965), in their pioneering studies of phosphonic acid batch flotation, to evaluate the effect of added ferric sulphate. The results of these tests with p-ethylphenylene phosphonic acid as collector are shown in Figure 78. At a low ferric sulphate addition, both recovery and grade were found to increase. At higher concentrations, where added ferric ion and collector levels in solution were similar, grade steadily decreased. Recovery was more erratic but did not diminish significantly.

The results of Figure 78 are rather striking in that the influence of the added ferric sulphate in the batch tests was not to depress flotation. However, considerable caution must be exercised in drawing definitive conclusions from the data. Kirchberg and Wottgen in their publication made reference to the use of tap-water with pH 6.9 in all flotation studies. However, they did not control the pH during their tests stating only that the pH of the pulps was generally between pH 6.4 and 7.2. As such, it would be expected that the ferric ion would have undergone extensive hydroxylation in the pulp and in so doing reduced the pulp pH toward the lower pH in this range (pH 6.4). Changing flotation response, such as the enhanced grade and
recovery at low ferric sulphate additions, therefore, might be related to some extent to pH. For many ores, it has been claimed that optimum phosphonic acid flotation occurs between pH 4.5 and 5.5 (Mosch and Becker, 1985; Lepetic, 1986).

It is to be expected that the influence of dissolved metal ionic species would be related intimately to pulp pH. Indeed, this is clearly evident in the frequently reported dramatic and often complete inhibition of flotation that occurs with phosphonic acids below pH 4.0. This phenomenon appears to be a characteristic of phosphonic acid flotation with many ores, both in laboratory testing and in actual plant flotation.

The profound effect of decreasing pH can be seen in the batch flotation data of Collins and Jackson (1967) for heptyl phosphonic acid flotation of...
South Crofty ore (Figure 79) and the phosphonic acid flotation of Altenberg and Rooiberg ores (Figures 80 and 81). All these data show that recovery decreases dramatically in strongly acidic solution. In the case of South Crofty ore, overall (cleaner) recovery decreased from 80 percent at pH 6.5 to less than 25 percent at pH 3.0. Compared to the vacuum flotation behaviour (Figure 68), the optimum conditions for heptyl phosphonic acid in batch testing exclude the acidic portion (pH < 5.0) of the corresponding vacuum flotation curve. Collins and Jackson attributed this to increasing ferric ion concentrations in solution at low pH and associated collector precipitation. Such a conclusion was supported by the finding that the residual collector concentration in solution decreased significantly below pH 5.0 (Figure 79). Higher surfactant adsorption on other minerals was thought unlikely on the basis of the reasonable selectivity achieved in the acidic pH range.

The inhibition of cassiterite flotation in batch testing at low pH is a striking result. In fundamental adsorption studies, the pH region below 4.0 is the region of maximum phosphonic acid adsorption on cassiterite (Figures 38 to 42). The most plausible explanation would appear to involve the interactions of phosphonic acids with dissolved metal ionic species adsorbed at mineral surfaces or present in flotation pulps. However, in many respects it is difficult to interpret the batch flotation data for ores where no systematic study of cation effects was performed. In such systems, interactions can occur between surfactants, minerals, size fractions of minerals, products derived from minerals, products derived from grinding and so on. Thus, for example, it is conceivable that the low pH depressant effect is associated with certain of the gangue species. In highly acidic solution, significant increases in phosphonic acid adsorption on particular gangue
Figure 79 - Data from the Batch Flotation of South Crofty Ore with Heptyl Phosphonic Acid (from Collins and Jackson, 1967).

Figure 80 - The pH Dependence of Cassiterite Recovery in Batch Flotation Tests with Phosphonic Acid for Two Different Altenberg Ore Types (from Wottgen and Luft, 1971).
Reference to several chemical pretreatment processes can be found in the phosphonic acid literature. The generally stated purpose of these treatments is the elimination of the adverse effects of dissolved metal ions in flotation. Such treatments have invariably involved the use of complexing reagents such as sodium fluorosilicate and oxalic acid.

In batch flotation tests, Collins (1967) found that improved tin grades could be achieved by conditioning rougher concentrates with hydrofluoric acid at pH 2.5 - 3.0, filtering, repulping and then floating at pH 6.5 with
residual phosphonic acid collector. Grades were reported to improve from 14.3 to 35.0 percent Sn with less than a one percent loss in recovery. A remarkably similar process was subsequently patented by Wottgen, Neuber and Luft (1974) for pretreatment of cassiterite flotation feed material. According to this process, the flotation feed is pretreated with large additions (1.0 - 4.0 kg/t) of sodium fluorosilicate or other complexing reagents such as oxalic acid. After dewatering and repulping with ion free water, the ore is floated with phosphonic acid. Substantial increases in grade and recovery are claimed with the process. Batch flotation data reported in the patent for sodium fluorosilicate pretreatment are reproduced in Table VII. Oxalic acid was stated to produce a similar but less dramatic effect. In an earlier patent, Schubert and Raatz (1972) also claimed that oxalic acid additions improved concentrate grades in laboratory tests with phosphonic acids. However, in this case the addition of the oxalic acid was directly to the mineral pulp prior to flotation and no solution replacement was specified.

The flotation literature concerning chemical pretreatment processes is particularly confused. Mechanisms claimed in patents generally lack any supporting technical data and are of such a broad nature as to provide little useful information. For example, the Wottgen, Neuber and Luft patent states that:

due to contamination or covering of the surface of the tin ore particles, the surface state thereof can be so changed that the tin ore particles no longer have the surface properties of tin ore. In this way, the normal interaction between collector and tin ore is destroyed, with the result that enrichment of the tin ore is too small .... pretreatment allows the removal of superficial impurities from the tin ores such that the tin ores are activated.
TABLE VII
BATCH FLOTATION OF A CASSITERITE ORE WITH AND WITHOUT SODIUM FLUOROSILICATE CHEMICAL PRETREATMENT
(from Wottgen, Neuber and Luft, 1974)

<table>
<thead>
<tr>
<th>Pretreatment of the Ore with Na₂SiF₆ (g/tonne)</th>
<th>Styryl Phosphonic Acid Addition (g/tonne)</th>
<th>Feed (%Sn)</th>
<th>Grade (%Sn)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>200</td>
<td>0.87</td>
<td>4.05</td>
<td>63.8</td>
</tr>
<tr>
<td>-</td>
<td>400</td>
<td>0.87</td>
<td>3.32</td>
<td>74.2</td>
</tr>
<tr>
<td>-</td>
<td>800</td>
<td>0.87</td>
<td>3.10</td>
<td>81.7</td>
</tr>
<tr>
<td>1000</td>
<td>400</td>
<td>0.87</td>
<td>3.20</td>
<td>74.0</td>
</tr>
<tr>
<td>1500</td>
<td>400</td>
<td>0.87</td>
<td>3.75</td>
<td>80.2</td>
</tr>
<tr>
<td>2000</td>
<td>400</td>
<td>0.87</td>
<td>4.30</td>
<td>92.0</td>
</tr>
<tr>
<td>4000</td>
<td>400</td>
<td>0.87</td>
<td>4.62</td>
<td>92.9</td>
</tr>
</tbody>
</table>

In the Schubert and Raatz patent (1972), it is stated that oxalic acid is not a complexing reagent but a reducing agent that keeps Fe(III) and its hydrolysis products at a minimum by converting them to Fe(II). Again, no supporting evidence is provided to support this claimed mechanism. Other apparent anomalies also exist. Thus the batch flotation data of Collins showing enhanced phosphonic acid flotation response in the presence of sodium fluorosilicate are difficult to reconcile with the same researcher's vacuum flotation data (Figure 73) showing a severe depressant effect with the reagent.

Sufficient data exist to indicate that dissolved metal ionic species in flotation pulps can have profound effects on the phosphonic acid flotation of cassiterite. It is, therefore, conceivable that the mechanisms of patented pretreatment processes are intimately connected with complexing of ionic species. For example, it is known that the concentration of ferric iron in a
centrifuged cassiterite ore pulp can increase markedly when sodium fluorosilicate is added (Evans, Ewers and Meadows, 1962). However, there is a dearth of reliable scientific information on which an unequivocal conclusion can be reached. The phenomena involved are undoubtedly complex and at present no comprehensive theory of the role of dissolved ions or their interactions with pretreatment reagents exists.

2.5.3.6 Plant Studies

Few references exist in the literature concerning plant flotation characteristics of cassiterite with phosphonic acids. However, information supplied from the Renison mine in Australia (Winby, 1985) indicates that there is generally a strong correspondence between the flotation of cassiterite in bench scale tests and plant behaviour. In particular, it can be confirmed that cassiterite in the Renison ore cannot be floated in acidic solutions below pH 4.0. Of further interest is that plant surveys of the Renison circuit have consistently shown that gangue species, such as quartz, are not recovered by genuine flotation (Figure 82). This is despite the pulp containing significant levels of dissolved iron, aluminum, magnesium and calcium ionic species (Table VI). Under plant conditions, the effect of dissolved metal ionic species is therefore not to activate inherently strongly hydrophilic gangue minerals.

Fluoride reagents are used extensively in the Renison cassiterite flotation circuit. The plant experience is that when direct additions of fluoride reagent are made to a flotation pulp small additions improve selectivity with minimal effect on recovery while large additions severely depress flotation. Similar effects have been reported at the Altenberg mine in the German Democratic Republic (Wottgen and Topfer, 1976). However, in
this circuit, pretreatment of flotation feed with relatively large quantities of fluoride with removal thereafter of solution, as claimed in the Wottgen, Neuber and Luft patent (1974), is reported to give remarkable increases in selectivity. No level of fluoride reagent addition directly to the flotation pulp apparently produces an equivalent effect. In the most recent published reference to the Altenberg pretreatment process (Mosch and Becker, 1985), it was claimed that the process produced 5 to 10 percent higher plant recovery and between 2 and 5 percent better grade.

Figure 82 - Size-by-Size Recovery Data for Cassiterite Flotation with Styryl Phosphonic Acid at the Renison Mine (from Cross, 1981).
2.5.4 Conclusions

1. The technique of electrophoresis measurements of cassiterite particles in the presence of cations is a powerful method for investigation of mineral-cation interactions. Due regard must, however, be paid to metal cation hydroxylation kinetics, the method of suspension preparation and the surface area available for adsorption. In the iron system, the suspension oxidation-reduction potential (Eh) is also of critical importance.

2. A number of analyses of the effects of metal cations on the electrokinetic properties of cassiterite have been published. These studies have established that calcium and magnesium ions do not cause charge reversal in the pH range of interest in cassiterite flotation. In contrast, clear evidence exists for the adsorption of ferric ion species at high Eh in the range pH 2.0 - 7.0. No similar data exist for tests performed under Eh conditions more typical of flotation environments. Other studies with ferrous ions are incomplete and difficult to interpret due to the absence of relevant electrochemical measurements. Few data are available pertaining to the interaction of aluminum ion species with the cassiterite surface. However, by analogy with electrokinetic effects observed in other oxide mineral systems and from detailed theories developed by researchers such as James and Healy, it might be expected that aluminum species will specifically adsorb in the pH region of interest in cassiterite flotation.

3. Adsorption measurements are difficult to conduct for systems where significant cation hydroxylation occurs and where polycationic and hydrous oxide species form in bulk solution. Nevertheless, calcium and ferric species adsorption isotherms for the cassiterite system have been
The results indicate that calcium species adsorb only in strongly alkaline solution above pH 8.0. In contrast, ferric species adsorb strongly between pH 2.0 and pH 5.0. Both the calcium and ferric ion adsorption isotherms are consistent with data obtained for other mineral substrates and with corresponding electrokinetic measurements.

4. The specifically adsorbing metal ionic species responsible for charge reversal are currently believed to be large, weakly solvated polynuclear or hydrous oxide species similar to the polymeric species of bulk solution precipitation. However, a number of fundamental aspects pertaining to the initial formation of these species inside the Stern plane remain unresolved.

5. The most comprehensive treatment of charge reversal phenomena proposed to date is that due to James and Healy. According to their model, the adsorption of metal ionic species responsible for charge reversal is controlled by competition between free energy changes that favour adsorption i.e. coulombic and chemical energy changes, and a solvation energy that opposes adsorption. A consequence of the existence of a solvation energy term is that the solubility product of cationic hydrous oxide species in the region of a solid interface is less than that in bulk solution.

6. The issue of whether there is a change in the intrinsic stability constants of cation hydroxy species in the interfacial region, as advocated by the James and Healy model, has been a controversial one. Other researchers have proposed that it is not necessary to invoke a new thermodynamic constant for the interfacial region, provided that the pH and species concentration at the interface are fully considered. However,
a solvation energy term must exist if free aquated forms of multivalent cations do not specifically adsorb inside the Stern plane at a solid/liquid interface. The magnitude of the solvation energy of hydrous oxide species with respect to the attractive forces of adsorption is a matter of debate.

7. At present, the general view is that specific adsorption of dissolved metal sols is nonselective with cationic hydrous oxide coatings forming on all surfaces in proportion to their available surface area. However, such an hypothesis does not take into account the potential role of the source of the dissolved metal ionic species. Ions derived from a particular mineral might preferentially form films on that mineral surface due to local concentration and kinetic effects.

8. Dissolved metal ionic sols are known to be stable and removed with difficulty from mineral surfaces even at low pH. While no data are available on how rapidly the adsorbed sols are removed by simple pH decrease, it is known that such removal is slow with a half-life of tens of minutes rather than seconds. In contrast, the half-life for adsorption-nucleation of metal ionic species has been found to be of the order of seconds and is clearly a realistic reaction under flotation conditions.

9. No microflotation data have been published for phosphonic acid flotation of cassiterite in the presence of dissolved metal ions.

10. Results from vacuum flotation studies confirm that phosphonic acids interact strongly with certain iron species such as the hydroxy species of the ferric ion. Significant interactions with calcium ions occur only at very high concentrations of the cation. While confirmation of such
effects is important, the solution chemistry in actual flotation systems is far more complex than assumed in published vacuum flotation studies. At the Eh and pH levels typical of cassiterite flotation, the ferrous ion and polymeric ferric polycations are most likely the stable iron species. The ferric ion and lower order hydroxy species are probably not the predominant iron species in solution. Furthermore, the polymeric iron sols would be expected to be adsorbed strongly onto the surfaces of minerals and, therefore, not present in solution at the levels assumed in the vacuum studies. The overall influence of dissolved metal ionic species is presumably a complex function of their interaction with phosphonic acids at both the cassiterite and gangue mineral interfaces and their bulk solution effects.

11. Reported binary mineral batch flotation, adsorption study and electrokinetic measurements for cassiterite and n-heptyl phosphonic acid, in the presence and absence of supernatants derived from various common cassiterite gangue species, clearly indicate the importance of dissolved metal ionic species in cassiterite flotation. However, the lack of clearly defined experimental conditions in these studies results in this significant volume of data contributing little to a fundamental understanding of the dissolved ion effects.

12. In laboratory testing and actual plant flotation of ores, a dramatic and often complete inhibition of flotation occurs with phosphonic acid collectors below 4.0. In fundamental adsorption studies, the pH region below 4.0 is the region of maximum phosphonic acid adsorption on cassiterite. The most plausible explanation of these apparently contradictory phenomena would appear to involve the interactions of
phosphonic acids with dissolved metal ionic species adsorbed at mineral surfaces or present in flotation pulps. The possible influence of gangue mineral species also cannot be precluded in the absence of further experimental data.

13. Detailed size-by-size analyses of an actual tin flotation circuit have consistently shown that gangue species, such as quartz, are not recovered by genuine flotation. This is despite the pulp containing significant levels of dissolved iron, aluminum, magnesium and calcium ionic species. Under plant conditions, the effect of dissolved metal ionic species is, therefore, not to activate inherently strongly hydrophilic gangue minerals.

14. In published vacuum flotation studies for cassiterite in the presence of calcium, ferric and ferrous ion species, the influence of fluoride reagent additions is to depress flotation. This is in striking comparison to reported laboratory and plant flotation behaviour where fluoride reagents are widely used to improve flotation selectivity.

15. Laboratory and plant experience with ores is that where direct additions of fluoride reagents are made to flotation pulps, small additions improve selectivity with minimal effect on recovery while large additions severely depress flotation. The use of fluoride reagents is also believed to be a key component of commercially successful chemical pretreatment processes. The generally accepted detrimental effects of dissolved metal ionic species in cassiterite flotation might be connected intimately with the use of fluoride reagents in plant circuits. The fluoride ion is well known to complex with certain metal cations under appropriate chemical conditions.
2.6 Concluding Remarks

Specific findings pertaining to the role of dissolved metal ionic species in the phosphonic acid flotation of cassiterite have been presented throughout this review. Sufficient data are available to confirm unequivocally that dissolved metal ionic species in flotation pulps can have profound effects on phosphonic acid cassiterite flotation. Furthermore, their influence most probably accounts for many of the otherwise difficult to explain observations that exist in cassiterite flotation and almost certainly provides a reason why single mineral flotation and adsorption study results, in distilled water systems, are seldom consistent with the behaviour of cassiterites in ores. However, it is equally clear that despite many important scientific contributions and over 20 years of research, no comprehensive theory of the role of dissolved metal ionic species currently exists.

Deficiencies in the available data on the role of dissolved ions are numerous. Significant apparent anomalies exist both with regard to studies in the presence and absence of such ionic species. Microflotation and vacuum flotation studies conducted in the absence of added ionic species showing various cassiterites to exhibit strikingly different pH flotation dependence with the same collector is a profound example of the latter case. The implication, although currently lacking experimental support, is that the different cassiterites varied significantly in their surface properties. Fundamental adsorption and electrokinetic data correlate strongly with the microflotation data. The vacuum flotation results, however, cannot be regarded as anomalous as they represent a large body of test work and correspond remarkably with actual laboratory and plant flotation of cassiterite in ores.
No microflotation data have been published for phosphonic acid flotation of cassiterite in the presence of dissolved metal ionic species. Nevertheless, it has been perceived widely that phosphonic acids interact strongly with dissolved metal ionic species present in aqueous solutions. Direct and independent confirmation of this hypothesis is, however, lacking. Furthermore, in the case of iron, many studies for which this conclusion has been reached indirectly have not been conducted under the pH and Eh conditions characteristic of flotation. That the Eh is such that the ferric ion and lower order ferric hydroxy species are not the predominant iron species in flotation pulps largely has been overlooked. This is also true of published electrokinetic and adsorption study results where many of the available data for the iron system bear little correspondence to the Eh and pH conditions existing under actual flotation conditions. For certain other ions of interest in cassiterite flotation, no electrokinetic or adsorption study data have been published.

One of the most striking apparent anomalies in flotation is that, in plant circuits, a complete cessation of the phosphonic acid flotation of cassiterite occurs in strongly acidic solution. At these same pH values, fundamental single mineral microflotation and adsorption study results indicate maximum surfactant adsorption and flotation response. Conversely, the industrial flotation response is optimal where adsorption isotherms indicate greatly diminished surfactant adsorption and single mineral microflotation recoveries are appreciably reduced. Almost equally difficult to reconcile, in the absence of dissolved ionic species effects, are the reported profound influences of fluoride pretreatment processes in the flotation of cassiterite ores. Such processes, particularly those that involve fluoride treatment
followed by solution replacement prior to flotation, are almost certainly intimately related to the role of dissolved metal ionic species.
A flotation system comprising a cassiterite mineral to be floated, an aqueous surfactant solution and an aqueous solution of ionic species can be considered as a ternary system in which all three components interact with each other to varying degrees. The overall effect of these interactions determines the flotation response of the cassiterite. As established in the literature review, the chemistry of the individual components and their fundamental interactions with each other are not completely understood. The experimental approach adopted in this research was, therefore, to consider the three components of the flotation system individually and then in combination.

3.1 Minerals and Reagents

3.1.1 Cassiterite Samples

The cassiterite used in the research was a high purity cassiterite supplied from the Renison Limited mine in Australia. The sample, as received, was a plant table concentrate that had been subjected to subsequent laboratory treatment to remove additional sulphides and silicates. An hand magnet had been used to remove the sulphides while the silicates had been discarded by retabling the sample using laboratory equipment.

Microscopic examinations of the cassiterite sample confirmed that it was of high purity. Principal gangue species were pyrrhotite and arsenopyrite in the form of free grains and as particle intergrowths.
Figure 83 gives the details of the method of cassiterite preparation. The objectives of the preparation scheme were as follows:

(a) the removal of free and locked pyrrhotite and arsenopyrite gangue particles

(b) the preparation of a colloidal cassiterite fraction suitable for microelectrophoresis studies

(c) the preparation of a minus four micron fraction for adsorption study test work

(d) the preparation of a -38 + 4 micron fraction for microflotation studies.

Removal of free and locked pyrrhotite and arsenopyrite particles was achieved on the basis of their high magnetic susceptibilities using a Franz Isodynamic separator (Model Kl). To minimize size effects during magnetic separation, the sample was first split into different size fractions by sieving. Each individual size fraction, with the exceptions of the -45 + 38 μm and -38 μm fractions, was then passed through the Franz separator. The two finest size fractions were not subjected to magnetic separation because:

(i) they contained few locked particles, and

(ii) the lower size limit for effective separation using a Franz Isodynamic separator is generally considered to be 50 microns (Hutchison, 1974).

Efficient removal of the pyrrhotite and arsenopyrite particles, as the magnetic fraction, was achieved with a Franz separator current of 17 Amperes, a side angle of 10 degrees and a forward angle of 13 degrees. Frequent product examinations, using an optical microscope, confirmed that the magnetic fraction contained only locked and free gangue particles.
HIGH GRADE RENISON CASSITERITE SAMPLE

SIEVING

+600µm
-600±425µm
-425±212µm
-212±150µm
-150±106µm
-106±45µm
-45±38µm

FRANZ ISODYNAMIC SEPARATOR

MAGNETIC 
REJECTS

NON-MAGNETICS

GRINDING IN A CERAMIC MILL

WET SCREENING 
AT 38µm

DECANTATION AFTER 24 HOUR SETTLING

DECANT 
SUPERNATANT

DECANT SEDIMENT

SPECTROSCOPIC 
and ELEMENTAL 
ANALYSES

DECANTATION

-4µm FRACTION
ELZONE SIZING
BET SURFACE AREA 
DETERMINATION

-3814µm FRACTION

ELZONE SIZING
FOR MICROFLotation

FOR ADSORPTION 
STUDIES

FOR ELECTROPHORESIS

DECANT 
SUPERNATANT

DECANT SEDIMENT

SPECTROSCOPIC 
and ELEMENTAL 
ANALYSES

DECANTATION

-4µm FRACTION
ELZONE SIZING
BET SURFACE AREA 
DETERMINATION

-3814µm FRACTION

ELZONE SIZING
FOR MICROFLotation

FOR ADSORPTION 
STUDIES

Figure 83 - Cassiterite Preparation Flowsheet.
Following magnetic separation, the non-magnetic Franz product was recombined with the -45 + 38 μm size fraction from the original sieve analysis and ground in a ceramic mill. A ceramic mill was used to avoid iron pick-up. To minimize overgrinding, the grind time was limited to 30 minutes and the undersize was removed by wet screening at 38 microns before returning the oversize for regrinding. The mineral charge was maintained at 500 g with a standard ball charge of 1200 g. Distilled water was used throughout the grinding and screening stages to avoid sample contamination.

At the completion of grinding and wet screening, the accumulated screen undersize was allowed to settle for 24 hours. The supernatant was then drawn off and stored for use in microelectrophoresis studies. The settled fraction was split into 100 g lots for beaker decantation sizing. A subsample was also cut for bulk chemical and surface analyses.

Beaker decantation conditions for a cut size at 4 microns were calculated from Stokes' Law. A cut size of 4 microns was selected on the basis that this is the nominal cut size in cassiterite flotation desliming circuits. The decantation procedure was as follows:

(i) A 100 g cassiterite sample was dispersed in 100 mls of distilled water at 22 °C using an ultrasonics bath.

(ii) The dispersed sample was transferred to a 4 litre beaker and distilled water at 22 °C added to bring the slurry to a predetermined level.

(iii) The suspension was agitated and then allowed to settle for 1 hour after which time particles with a Stokes diameter of greater than 4 microns would have settled 19.73 cm (Appendix C).
(iv) The suspension was decanted to a depth of 19.7 cm and the decant fraction retained for adsorption study test work.

(v) The procedure was repeated four times and the final settled fraction stored for microflotation test work.

At the outset of the research program, a conscious decision was made to work with cassiterite that had not been subjected to surface chemical pretreatment. Many researchers have advocated acid treatment of mineral surfaces before flotation test work is carried out. Methods that have been described in the literature range from washing in cold 10 percent hydrochloric acid to soxhlet extraction in boiling concentrated acids (Somasundaran, 1970). The 'minerals' so treated are then washed continually with water until all chloride ions have been removed. However, it is well known that even a mild acid treatment is sufficient to change the surface properties of many minerals to such an extent that the flotation response bears no relationship to that of the original mineral. This is almost certainly due to the differential solubility of surface impurities in the acid. Whilst it is fully appreciated that surface impurities can lead to significant changes in flotation behaviour, it is indisputable that such species are also present in actual industrial flotations systems. In terms of the research objectives of this dissertation, it was, therefore, considered appropriate to conduct test work primarily with unleached cassiterite samples. Where necessary to elucidate further the role of mineral surface species during the research program, both a leached cassiterite and a pure stannic dioxide were used as reference materials.

Preparation of a leached cassiterite sample was performed by subjecting a subsample of upgraded Renison cassiterite to hydrochloric acid treatment at pH
1.0. Replacement of the leach liquor was performed daily for a total of 19 days, after which time no detectable levels of iron (the principal impurity in the cassiterite) were found in solution. The resultant cassiterite was then repeatedly washed with distilled water until the conductivity of the wash water returned to that of the distilled water. Solution conductivities were measured with a Radiometer conductivity meter (Type CDM 2d).

The stannic dioxide reference material was an Aldrich "Gold Label" sample used without further treatment. Elemental analysis of the powder, provided by Aldrich, quoted an actual batch assay of 78.2% Sn and a calculated assay of 78.76% Sn. Theoretically, pure SnO₂ is 78.8% Sn. The results of a spectrographic trace element analysis of the sample are given in Table VIII. Other metallic elements, not listed in Table VIII, were sought but not detected in the spectrographic analysis.

**TABLE VIII**

<table>
<thead>
<tr>
<th>Element</th>
<th>ppm</th>
<th>Element</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.5-2.0</td>
<td>Fe</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;1</td>
<td>Al</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;1</td>
<td>Cu</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Si</td>
<td>&lt;1</td>
<td>Ti</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
3.1.2 Phosphonic Acids

Samples of five commercial phosphonic acids were examined in the research program. These reagents included all the known industrially successful phosphonic acid collectors for the selective flotation of complex lode tin ores. Details of each reagent are as follows:

1. PH-PEP: A commercial surfactant marketed by Plaistere and Hanger International Limited (U.K.). Supplied in powder form, this reagent was believed to be styryl phosphonic acid:

\[
\text{CH=CH-P<OH} \quad \text{OP-CH=CH-P<OH}
\]

A sample of the reagent was provided by Renison Limited (Australia).

2. Flotinor P-184: A commercially available collector manufactured by Hoechst. Described as an aromatic phosphonic acid of general formula:

\[
\text{R-P-OH} \quad \text{P-OH}
\]

\[ R = \text{Aromatic Hydrocarbon} \]

in the Hoechst reagent handbook (Anon, 1981), subsequent correspondence indicated it to have the chemical composition of styryl phosphonic acid (Edelmann, 1984). As supplied, the reagent was a free-flowing, non-hygroscopic colourless powder with a slight aromatic odour. According to Hoechst,
P-184 contains less than 1% of insoluble byproducts (Anon, 1981). Hoechst (Canada) provided a sample of the reagent for test work.

3. Flotino P-195: A Hoechst reagent described in their technical literature only as an aliphatic phosphonic acid (Anon, 1981). The reagent has a colourless gel-like appearance. A sample was supplied by Renison Limited (Australia).

4. BPA: A phosphonic acid collector manufactured by ICI (Australia). A sample of commercial grade reagent was supplied on request by ICI. As received, the chemical was in the form of a fine, white powder. Benzyl phosphonic acid has the structure:

\[
\text{CH}_3\text{CH}_2\text{PO(OH)}_2
\]

5. EPPA: A commercially available collector produced by Organophos Pty. Ltd. (S.A.) and widely used in South African tin flotation plants. The surfactant is described by the supplier as "ethyl phenyl" phosphonic acid presumably indicating that its hydrocarbon radical is:

\[
\text{CH}_3\text{CH}_2\text{C}_6\text{H}_4
\]

However, according to IUPAC convention the correct nomenclature for the radical is p-ethylphenylene (IUPAC Rule A 13.2). Further uncertainty existed as to the actual
composition of the hydrocarbon radical as Bulled (1982), in describing tin flotation operations in South Africa, stated that "ethyl phenyl" phosphonic acid was otherwise known as "styrene" (styryl) phosphonic acid. As received, the EPPA was in the form of small powder granules with slightly discoloured grey appearance. Renison Limited (Australia) supplied the reagent sample.

3.1.3 Other Reagents

During the course of the thesis research a large number of inorganic and organic reagents were used. Table IX lists all of these reagents together with their respective applications. All of the chemicals were of the highest purity. Inorganic reagents were used primarily as sources of dissolved metal ionic species, as indifferent electrolytes and for pH control. Organic reagents included carbon tetrachloride and ethanol which were used as a solvent and for glass cleaning, respectively. The surfactant 2-methyl-3-hydroxypentanol (MIBC) was employed as frother in microflotation studies. Distilled water from a Sybron Barnstead electrically heated still was used at all times in preparing both inorganic ion and surfactant solutions.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula (M.W)</th>
<th>Supplier (Grade)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Chloride</td>
<td>KCl (74.56)</td>
<td>Fisher (A.C.S. cert.)</td>
<td>Supporting electrolyte</td>
</tr>
<tr>
<td>Potassium Hydroxide</td>
<td>KOH (56.11)</td>
<td>Amachem (Reag. Grade)</td>
<td>pH modifier</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>HCl (36.46)</td>
<td>Amachem (Reag. Grade)</td>
<td>pH modifier</td>
</tr>
<tr>
<td>Ferrous Ammonium Sulphate</td>
<td>Fe(NH₄)₂(SO₄)₂ 6H₂O (392.15)</td>
<td>Fisher (A.C.S. cert.)</td>
<td>Eh standard (Light's solution)</td>
</tr>
<tr>
<td>Ferric Ammonium Sulphate</td>
<td>Fe(NH₄)(SO₄)₂ 12H₂O (482.19)</td>
<td>Fisher (A.C.S. cert.)</td>
<td>Eh standard (Light's solution)</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>HNO₃ (63.01)</td>
<td>Allied Chemical (A.C.S. cert.)</td>
<td>Cleaning of glassware</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>Na₂CO₃ (105.99)</td>
<td>Baker (A.C.S. cert.)</td>
<td>Source of carbonate ions</td>
</tr>
<tr>
<td>Sodium Bicarbonate</td>
<td>NaHCO₃ (84.01)</td>
<td>Baker (A.C.S. cert.)</td>
<td>Source of bicarbonate ions</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>CaCl₂ 2H₂O (147.02)</td>
<td>Fisher (A.C.S. cert.)</td>
<td>Source of Ca aqueous species</td>
</tr>
<tr>
<td>Magnesium Chloride</td>
<td>MgCl₂ 6H₂O (203.31)</td>
<td>Baker (A.C.S. cert.)</td>
<td>Source of Mg aqueous species</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>FeCl₃ (162.21)</td>
<td>Fisher (purified)</td>
<td>Source of Fe(III) aqueous species</td>
</tr>
<tr>
<td>Aluminum Chloride</td>
<td>AlCl₃ 6H₂O (241.43)</td>
<td>Baker (A.C.S. cert.)</td>
<td>Source of Al aqueous species</td>
</tr>
<tr>
<td>Sodium Fluoride</td>
<td>NaF (41.99)</td>
<td>Fisher (A.C.S. cert.)</td>
<td>Source of fluoride ions</td>
</tr>
</tbody>
</table>
TABLE IX (cont.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula (M.W)</th>
<th>Supplier (Grade)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIBC(2 methyl 3 hydroxypentanol)</td>
<td>C₆H₁₃OH (102.0)</td>
<td>- (purified)</td>
<td>Frother</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>CCl₄ (153.82)</td>
<td>Fisher (spectranalyzed)</td>
<td>I.R. test work</td>
</tr>
<tr>
<td>Potassium Bromide</td>
<td>KBr (119.01)</td>
<td>Fisher (I.R. grade)</td>
<td>I.R. pellets</td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH₃CH₂OH (50.07)</td>
<td>Fisher (A.C.S. cert.)</td>
<td>Cleaning of glassware</td>
</tr>
<tr>
<td>Buffers</td>
<td>—</td>
<td>Fisher (A.C.S. cert.)</td>
<td>pH meter standardization</td>
</tr>
<tr>
<td>Ferrous Chloride</td>
<td>FeCl₂ 4H₂O (198.83)</td>
<td>Fisher (A.C.S. cert.)</td>
<td>Source of Fe (II) aqueous species</td>
</tr>
<tr>
<td>Ferric Fluoride</td>
<td>FeF₃</td>
<td>Aldrich</td>
<td>Référence for XPS Analyses</td>
</tr>
</tbody>
</table>
3.2 Mineral Characterization

3.2.1 Light Microscopy

Reflected light microscopy was used to examine the original cassiterite sample and the products of separation from the Franz Isodynamic separator. Mineral grains were examined directly without resin mounting. Inclusions, intergrowths and compositional variations were noted. These observations served as a control in the magnetic separator upgrading of the cassiterite and ensured the optimal rejection of free and locked pyrrhotite and arsenopyrite particles.

After completion of sample upgrading, grinding and size separation, grains of -38 + 4 μm cassiterite were mounted in cold-setting resin, polished and examined in detail using a reflected light Zeiss microscope. A large number of grains were scanned and all compositional variations and inclusions noted. Photomicrographs were taken to record overall sizes and textures of grains in the resin mount and the alteration and compositional variations of individual grains.

3.2.2 Chemical Analysis

A wet chemical analysis of the cassiterite from Renison Limited was provided by the assay department of the mine. After sample upgrading, a portion of the -38 + 4 μm size fraction was split out by standard riffling techniques and resubmitted to Renison for further wet chemical tin analysis. Samples of similar size ranges of leached and unleached cassiterite were also sent to Can Test Ltd. (Vancouver) for trace element analyses. These trace analyses were performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with argon as the plasma gas. Digestion of the samples was by reaction with a combination of acids (HF/HCl/HNO₃/HClO₄). Resulting
solutions were then scanned for metals using a Jarrell Ash Model 973 Inductively Coupled Argon Plasma Spectrograph. Analyses of thirty trace elements were obtained at detection limits generally in the range 0.1 - 10.0 ppm.

Descriptions of the basic principles of ICP-AES are given in standard texts on analytical chemistry such as Harris (1982). More detailed treatments of the applications and limitations of ICP-AES can be found in reviews by Fassel (1982), Boumans (1982), Robin (1982) and Barnes (1984). From a practical standpoint, the inductively coupled plasma produces a type of flame that is more uniform in thermal profile and reaches much higher temperatures than ordinary combustion flames. This allows increased detection levels and eliminates many of the interferences and sources of error encountered with conventional flames.

3.2.3 **Infrared Spectroscopy**

Infrared (IR) spectra of natural and synthetic cassiterite samples were recorded using a Perkin-Elmer 283 B double beam, optical null spectrophotometer. Scanning time in all analyses was 12 minutes with the scanning range being from 4000 cm\(^{-1}\) to 255 cm\(^{-1}\). A normal slit program (setting 6) was used throughout. Spectral slit widths were 7 cm\(^{-1}\) at 4000 cm\(^{-1}\) and 2.8 cm\(^{-1}\) at 2000 cm\(^{-1}\). A wedge attenuator was used in the reference beam since the samples were all highly scattering. Spectra were recorded at the ambient temperature of the spectrophotometer which was constant at about 320 K. Prior to each analysis, the wavelength calibration of the spectrophotometer was checked by examining a standard polystyrene film, the spectral band positions of which were accurately known.
All samples were prepared using the KBr pellet method. Approximately 1 mg in weight of each sample was ground to a very fine powder using a Retsch automatic pulverizer and then thoroughly mixed with 300 mg of Mallinckrodt infrared grade KBr. The mixture was transferred to a die (Perkin-Elmer model 186-00251), evacuated for 2 minutes, and then pressed at approximately 3000 kPa for 30 seconds. After pressing, each pellet was examined and, if optically transparent, transferred to the spectrophotometer for analysis. Surgical gloves were worn at all times when handling pellets.

In all of the KBr pellet analyses, a Perkin-Elmer heatless dryer was used to maintain the relative humidity in the sample compartment of the IR spectrophotometer at levels less than 5 percent. This prevented water vapour attacking the KBr. When water is adsorbed on the surface of KBr there is a local dissolution of the salt so that the pellet becomes "fogged". A fogged pellet scatters the radiation passing through it; the scatter being more pronounced at shorter wavelength (Miller, 1965).

Spectra obtained from each infrared scan were manipulated using a Perkin-Elmer infrared data station interfaced to the 283 B spectrophotometer. The Perkin-Elmer PECDS applications program FLAT was used to achieve flat spectral baselines. This software program allowed the subtraction of a parabolic curve from the spectral data, according to three specified baseline points, to produce baseline flattening. Mathematical smoothing of data was performed by means of the PECDS program SMOOTH operating according to the method of Savitsky and Golay (1964). In this method, a "moving" polynomial smooth is applied to the actual ordinate values. Smoothing is accomplished by the best fit of a quadratic (cubic) polynomial through successive windows of data and the computation of the best fit point in the centre of the window. Operation
of the spectrophotometer and general data storage, retrieval and plotting were also performed at the data station.

3.2.4 X-Ray Diffraction

X-ray diffraction patterns were recorded by continuous scanning of mineral powders mounted in a Philips wide angle diffractometer (model pw 1050/65). The X-ray generator was a Philips type pw 1011/60 generator operated at 36 kV and a current of 20 mA. Filtered CuKα radiation (λ = 1.5405 Å) was used in all analyses. Reflections were collected for the diffraction angle 2θ range 4° to 105°. Scanning speed in all tests was 1° 2θ/min. The pulse output of the diffractometer detector was measured by a scaling unit and a ratemeter. A strip chart was used to record intensity variation as a function of the diffraction angle 2θ scan. Mounting of samples was in standard specimen holders consisting of rectangular aluminum plates 2 mm thick. The plates contained a rectangular window in which the powder was placed.

For detailed reviews of X-ray diffraction theory and practice, the reader is referred to standard references such as those of Mitchell (1970) and Klug and Alexander (1974).

3.2.5 Size Analysis

Particle size analyses of unleached, leached and synthetic cassiterite were performed using an Electrozone Celloscope (Particle Data Inc.). In all analyses, ASTM standard method C 690-71T was used to prepare the dilute, dispersed suspensions required for Celloscope sizing.

The Electrozone Celloscope is an electrical resistance zone counter similar in principle to a Coulter counter. Details of its operation have been discussed in depth by Karuhn and Berg (1982). More general reviews of
particle size analysis with electrical resistance zone counters are given in Lines (1973), Allen (1975) and Cheremisinoff (1981). The basis of the technique is that as particles dispersed in an electrolyte pass through a calibrated orifice they cause a change in electrical resistance proportional to the volume of the displaced liquid. In the Celloscope, two electrodes, positioned on either side of an orifice, detect such resistance changes and produce voltage pulses of magnitude proportional to particle volume. The resultant series of pulses are electronically amplified, scaled and counted. Data are recorded as number frequency against volume which are then used to determine a size distribution.

3.2.6 Surface Area Determinations

Surface area measurements were performed according to the multipoint BET (Brunauer, Emmett and Teller) technique. Data were obtained by the chromatographic dynamic desorption method using a Quantasorb manufactured by Quantachrome Corporation (Greenvale, N. Y.). Union Carbide 'medical grade' nitrogen, certified to better than 99.9% purity, was used as adsorbate gas. The carrier gas was helium. Calibration of desorption signals was accomplished by injecting pure adsorbate gas, through a septum, into the flow stream using a Hamilton gas-tight precision syringe (Hamilton Co., Reno, Nevada). In all surface area measurements, the relative pressure was maintained in the range 0.05 to 0.3. The highest precision in estimation of area using the BET isotherm is generally considered to occur in this range (Allen, 1975). All data were checked to confirm the linearity of the BET plots over the range of relative test pressures. The effective molecule area of nitrogen was assumed to be $16.2 \times 10^{-20}$ m$^2$ (Rhodin, 1950).

The determination of BET specific surface area by dynamic desorption
methods, such as used in the Quantasorb, is a standard technique. Assumptions, restrictions and applications of the BET theory are discussed in most texts on surface chemistry (Shaw, 1966; Allen, 1975; Hiemenz, 1977). Detailed treatments of the application of BET theory to surface area measurements have been published by numerous researchers such as Sing and coworkers (Sing, 1976; Gregg and Sing, 1976). Specific details on the operation of the Quantasorb can be found in publications by Quantachrome Corporation.

In standard dynamic desorption measurements of surface area, nitrogen is usually used as the adsorbate gas. However, for low surface area (< 1 m²/g) samples, thermal diffusion signals can occur with nitrogen. These signals merge with the adsorption and desorption signals and can result in significant errors in surface area determination (Salman and Robertson, 1965; Allen, 1975). The thermal diffusion signals, appearing as shoulders on the adsorption and desorption peaks, are caused by the separation of the adsorbate and carrier gases when the temperature gradient is changing. A detailed treatment of thermal diffusion effects in continuous flow gas chromatography has been published by Kourilova and Krejci (1972).

The problem of thermal diffusion in the Quantasorb can be overcome by using narrow bore, U-shaped sample tubes (Lowell and Karp, 1972). The use of a narrow bore U-tube, with no extra volume at its base, prevents gas separation since there exists no volume into which the heavier gas can accumulate. In addition, a high linear flow velocity at all points within the cell inhibits the separation process. An alternative solution is to use krypton as the adsorbate gas (Lowell, 1973). The low vapour pressure of krypton at liquid nitrogen temperatures results in its mole fraction in the
BET range of relative pressures being of the order of $10^{-4}$. At such low relative pressures, no obscuring thermal diffusion signals are generated when a sample cell is immersed in, or removed from, a liquid nitrogen bath.

To determine which of the above techniques was the most appropriate for the small surface area samples of this research, advice was sought from Quantachrome Corporation. After single point BET analysis of the lowest area cassiterite sample, it was recommended that a Quantachrome No 200 microcell be used for low surface area samples. For all other samples, a conventional No 100 cell was considered appropriate. The use of krypton was thought unnecessary, particularly given its high cost and the need for absolute determinations of premixed Kr/He gases. It was further indicated that the Quantachrome experience with krypton was that the appropriate cross-sectional area for use in the BET equation varied with the equation C-value (Seltzer, 1986).

In all surface area determinations conducted in this research, the powder was first dried in an oven at 75°C before being transferred to the sample cell. Outgassing was then performed according to the repetitive cycling method of Lopez-Gonzalez, Carpenter and Deitz (1955). This method involved repetitively adsorbing and desorbing the adsorbate at a relative pressure ($P/P_0$) of approximately 0.3 ($P$ = adsorbate partial pressure and $P_0$ = adsorbate saturated vapour pressure). Six cycles were generally found sufficient to produce a surface that allowed reproducible measurements of its area. However, when measuring low surface areas the number of cycles was increased to ten. The high filament currents and low attenuator settings required for the microcell, in such cases, made the Quantasorb extremely sensitive to impurities. For all area determinations, the cell weight with powder was
determined after outgassing and analysis to avoid weighing any impurities.

3.2.7 Scanning Electron Microscopy

Scanning electron microscopy was used to identify the chemical elements present in the lattice structure of unleached cassiterite grains. Analyses were performed with an Etec Autoscan (no. 26) scanning electron microscope (SEM) with energy dispersive X-ray (EDX) analyzer capabilities. The SEM was operated at an energy of 20 keV. The beam diameter was approximately 150 Å. The SEM X-ray detector was an energy dispersive Si(Li) solid-state detector recording simultaneously the full spectrum from 1 keV up to 20 keV. Counts were recorded and displayed using an Ortec 6200 multichannel analyzer. The cassiterite grains were mounted in resin, polished and carbon coated.

Technical details of scanning electron microscopy are described in many handbooks such as those of Oatley (1972) and Wells (1974). Publications by Lorimer and Cliff (1976) and Suter et al (1976) deal more specifically with the techniques of chemical analysis using energy dispersive X-ray detectors.

The mineralogical analyses were performed with the SEM/EDX by obtaining a full X-ray spectrum of individual grains. This allowed the identification of most of the elements present and, in turn, identified the nature of the mineral and its principal impurities. However, no information on grain surface characteristics were obtained as SEM/EDX spectra provide only a "bulk" chemical analysis. The X-rays generated by a primary SEM electron beam are from a bulbous volume the diameter of which is determined by the accelerating voltage of the primary beam and the nature of the sample material. The depth of emission of X-rays for minerals is generally of the order of a few microns (Blaschke, 1976).
3.2.8 **Electron Microprobe Analysis**

The distribution of elements in cassiterite grains was determined by electron microprobe microanalysis. Analyses were performed using a Joel JXA-3A electron probe X-ray microanalyzer with an accelerating voltage of 25 kV and a beam current of approximately $1 \times 10^{-7}$ amp. Peaks from the emission spectra were recorded by the wavelength dispersive (WDX) method. Detection limits were approximately 0.5% for light elements and 0.1% or less for heavier elements, depending on the crystal line used. Spatial resolution was of the order of a few microns with the emission depth being two to three microns. This signal volume varied depending on the element being analyzed but is known to be larger with lighter elements at the same kV (Brown and Thresh, 1970). All cassiterite grains analyzed were resin mounted, polished and carbon coated.

Data were recorded both in the form of elemental line analyses and characteristic X-ray images. In the line scans, the electron beam was moved across particular grains and the characteristic X-rays of an element mapped onto a cathode ray tube. Photographs were taken with an oscilloscope camera of two orthogonal line scans superimposed on the sample absorbed electron image. In the case of the characteristic X-ray images, the focused electron beam was swept across a grain surface in a raster pattern using the electron microprobe scanning coils. The X-ray image of the mineral grain surface was displayed on the cathode ray tube and photographed with the oscilloscope camera. Detailed information on the methods of X-ray imaging and the operation of the electron microprobe can be found in the text by Birks (1963), in various conference proceedings (Pattee, Cosslett, and Engstrom, 1963; McKinley, Heinrich and Wittry, 1966; Castaing, Descamps and Philibert, 1966),
and in several review articles (Castaing, 1960; Duncumb, 1967; Ogilvie, 1968; Poole and Martin, 1969).

3.2.9 Secondary Ionization Mass Spectroscopy

It is well recognized that the surface properties of a mineral can vary significantly from those of the bulk mineral lattice. Surface alteration can occur as a result of both grinding, which tends to create a disturbed surface layer, and through contact with both aqueous and gaseous phases. In the case of the cassiterite used in this study, these changes were expected to be significant. As received, the mineral had been ground under the highly reducing conditions of plant rod and ball milling, exposed to an aqueous phase containing appreciable concentrations of dissolved metal ionic species and then oven dried in contact with air.

Two spectrochemical analytical techniques were used to characterize the surface properties of cassiterite grains - secondary ionization mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS). In terms of the surface information they provide, these two techniques are largely complementary (Shepard et al, 1977). The SIMS technique is highly sensitive and can analyze fractions of monolayers (compared to XPS it is of the order of a thousand times more sensitive). It can be used to analyze both surface characteristics and to obtain depth profiles. The disadvantages of SIMS include large differences in sensitivities for different surface structures (Newbury, 1977) and the limited information it provides on the molecular structure of inorganic surface species (the most prevalent species in the secondary ion spectra are usually monoatomic ionic species). By comparison, binding energy shifts in XPS provide appreciable molecular structural information. A comparison of the two spectrochemical techniques, together
with relevant data pertaining to electron microprobe analysis, is given in Table X.

The basic physical phenomena involved in SIMS have been the subject of many reviews (McHugh, 1975; Blaise, 1976; Colton, 1981). In short, the impact of heavy metal ions (typically noble gas ions such as Ar⁺) on a solid surface produces a collision cascade of lattice atoms. The momentum of the primary ion is transferred to the lattice as the cascade propagates in random directions. Sputtering occurs when the recoiling atoms have an outward component of momentum which is sufficient to overcome the surface binding energy. The actual collisions which cause surface atoms to eject can be rather low in energy (tens of eV) compared to the initial beam energy. Most sputtered particles, therefore, originate from the uppermost surface layer and have an energy distribution which is peaked at relatively low energies (2-10 eV). Ion fractions are then formed through complex ionization and neutralization processes operative at or above the surface. Secondary positive and negative ion particles are the species analyzed for in SIMS.

In this research, secondary ionization mass spectroscopy was used to determine both the overall surface properties of a large number of cassiterite grains and the surface properties of individual grains. Analyses were performed in a SIMS instrument housed in a Vacuum Generators Microlab MkII Chamber with base pressure between 7.5 × 10⁻¹¹ and 3 × 10⁻¹¹ torr. Positive and negative ion SIMS spectra were recorded with a MM 12-12S quadrupole mass analyzer. Two primary ion guns were used. Multiple grain analyses were performed with an AG 61 "Argon" gun with a Wein filter operating at 5 kV. Beam diameter was 200 μm at 3 nA and 300 μm at 20 nA. The horizontal dimension of the area over which the beam was rastered varied between 400 and
TABLE X

COMPARISON OF SPECTROCHEMICAL ANALYTICAL TECHNIQUES
(from Cheremisinoff, 1981)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Primary Radiation</th>
<th>Secondary Radiation</th>
<th>Constituents</th>
<th>Lateral Resolution</th>
<th>Depth Resolution</th>
<th>Detection Limit</th>
<th>Typical Accuracy</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Microprobe</td>
<td>Electron</td>
<td>X-Ray</td>
<td>Elements</td>
<td>1μm</td>
<td>2-3μm</td>
<td>100ppm</td>
<td>1-5%</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Z &gt; 11 (WDX)</td>
<td></td>
<td></td>
<td>(WDX)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-Ray Photoelectron</td>
<td>X-Ray</td>
<td>Photoelectron</td>
<td>Elements</td>
<td>10μm</td>
<td>1nm</td>
<td>0.1%</td>
<td>5%</td>
<td>No</td>
</tr>
<tr>
<td>Spectroscopy (XPS)</td>
<td></td>
<td></td>
<td>Z &gt; 3</td>
<td></td>
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<tr>
<td>Secondary Ion Mass Spectrometry (SIMS)</td>
<td>Ion</td>
<td>Ion</td>
<td>All Elements</td>
<td>1μm</td>
<td>1nm</td>
<td>1ppm</td>
<td>20%</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Molecules
Beam fluences ranged from $3 \times 10^{-7} \, \text{A/cm}^2$ for static SIMS experiments to $14 \, \text{µA/cm}^2$ for rapid depth profiling. With the argon gun operating, the argon pressure in the analytical chamber was $7.5 \times 10^{-8} \, \text{torr}$ and $7.5 \times 10^{-6} \, \text{torr}$ in the preparation chamber. Analyses of individual grains were performed with a narrow beam (0.5 µm diameter) liquid metal ion (MIG 100) gun with Ga⁺ source. Operating voltage of the gun was 10 kV. Tests were conducted by rastering the beam over an area with a horizontal dimension of 20 µm. A constant fluence of 250 µA/cm² was used in all individual grain analyses.

Depth profiling for both multiple and individual grain mounts was achieved by continuous recording of metal ion isotope ($^{120}\text{Sn}^+$ and $^{56}\text{Fe}^+$) and $^{16}\text{O}^-$ counts. A major limitation of the experimental arrangement was, however, that only one single element spectrum could be obtained in one sputter. Moving to different surfaces after each individual sputtering, therefore, complicated the analyses, since it could not be assumed a priori that all surfaces were homogeneous in their composition. For the multiple grain analyses, a further complication was that different sputtering areas might have contained different numbers of mineral grains. To verify the depth profile results obtained by sputtering in different sample areas, tests were performed where tin and iron counts were recorded manually as a function of time from a series of consecutive scanning spectra. While providing information on the two elements for the same sputtering area, this technique was inferior to direct depth profiling methods. Considerable surface information was lost between scans, particularly at the onset of sputtering where counts changed rapidly, and noise effects complicated the depth profiles. The appearance of secondary ion oxygen particles predominantly in the negative spectrum precluded the simultaneous recording of oxygen counts by this method.
Samples for all SIMS analyses were prepared by imbedding the mineral grains in either silver or gallium foil. Grains were sprinkled onto a foil, which was then folded and hand pressed. Silver and gallium were selected as foil materials on the basis of their high purity, their malleability and the low concentrations of these elements in the mineral grains analyzed.

3.2.10 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) involves the measurement of the energies of electrons ejected from an atom when it is irradiated with photons. In such photoelectric processes, conservation of energy requires that the kinetic energy \( E_{\text{kin}} \) of the photoelectron be given by the equation:

\[
E_{\text{kin}} = E_{\text{X-ray}} - E_b - \phi_{\text{sp}}
\]

where

- \( E_{\text{X-ray}} \) = quantum energy of the X-ray photon
- \( E_b \) = binding energy of the electron
- \( \phi_{\text{sp}} \) = work function of the spectrometer.

In practice, the work function, \( \phi_{\text{sp}} \), can be eliminated from the energy balance by the use of a reference transition, usually the carbon 1s peak at 284 eV (Siegbahn et al, 1967).

The binding energies of core electrons are characteristic of a particular element. Accurate measurements of photoelectron kinetic energies at fixed irradiating X-ray energy therefore provide elemental identification. Information on the chemical environment also can be obtained since the binding energies of core electrons are affected by their chemical environment. These core electron environment effects give rise to chemical shifts of binding energy peak positions (Szalkowski, 1977; McGuire, 1982).
Both the elemental and chemical information provided by XPS pertain to the surface and near surface region of a solid. While bombarding X-rays can penetrate a solid and dislodge core electrons at significant depths, only emitted electrons close to the surface can escape from a solid. Dislodged electrons deeper in the solid are retarded by the material and are unable to escape. For metal oxides, typical XPS sampling depths (more explicitly defined as the electron mean free path) are in the range 15 to 40 Å (Riggs and Parker, 1975). The surface area sampled is normally of the order of several square millimeters, as defined by the solid acceptance angle of the electron optics (McIntyre, 1985). The ability to be able to provide information on the surface region of a large number of mineral grains makes XPS ideally suited to analysis of samples of geochemical and mineralogical interest (Bancroft, Brown and Fyfe, 1979; McIntyre, 1985; Cecile, 1984).

X-ray photoelectron spectroscopy was used in this research to study the surface properties of unleached, leached and synthetic cassiterite samples. Additional analyses were performed on two unleached samples subject to:

(a) grinding followed by controlled oxidation

(b) further chemical treatment.

The first of these two additional samples was prepared by dry grinding the cassiterite under an inert atmosphere. Grinding was performed in a Retsch RM-0 automatic mortar pulverizer mounted inside a Fisher Scientific Isolater-Lab glove box. High purity argon was used to continuously purge the glove box. The atmosphere inside the glove box was monitored by means of an oxygen meter (Yellow Springs Instrument Co., model 54) positioned next to the pulverizer. At all times during sample grinding, the O₂ level was less than 1.5 ppm. Final transfer to the spectrometer was conducted inside a nitrogen
purged glove bag which minimized the total exposure time of the ground mineral to air to less than 15 seconds. XPS spectra were recorded immediately and after timed exposure of the sample to air. For long exposure times, the ground sample was exposed to an highly oxidizing environment (97% relative humidity) inside a Vapor-Temp controlled temperature humidity chamber (Model VP-100 AT-1). Celloscope particle size analysis was used to confirm that grinding significantly reduced the mean particle size of the cassiterite and, therefore, created a large increase in new surface.

The effects on the surface properties of unleached cassiterite subjected to a strong acidic environment followed by partial solution neutralization were also investigated by XPS. Under highly acidic conditions, inorganic impurity elements on the cassiterite surface, such as iron, might be expected to be leached into solution. After the addition of a strong base, such species could form hydrous oxides and redeposit on the mineral surface. Evidence for such changes was sought in the XPS spectrum of cassiterite leached at pH 1.0 for one hour and then partially neutralized to pH 5.5.

Leaching was performed by agitating one gram of the mineral in 500 mls of distilled water acidified with hydrochloric acid. Potassium hydroxide was used for solution neutralization at the completion of the test. The pH and the Eh of the suspension were continuously monitored throughout the sample leaching. The pH was measured using a Fisher Accumat Model 230 pH/ion meter and a Fisher combination, polymer-body pH electrode (No. 13-639-97). Prior to use, the pH meter was standardized on two buffers (pH 4.01 and pH 10.4). All pH measurements were accurate to ± 0.05 pH units. The suspension potential (Eh) was measured with a polished platinum electrode (Corning electrode No. 476060) and a saturated calomel electrode (Fisher Scientific electrode No. 13-
639-51) connected to a Corning 150 ion analyzer set in mV mode. The potential was converted to the standard hydrogen electrode (SHE) scale by the addition of 0.245 volt. Calibration of the Eh electrodes was checked with respect to a standard ferrous-ferric (Light's) solution (Light, 1972). After solution neutralization, the settled cassiterite was transferred using a spatula to a beaker containing 2.5 litres of distilled water. Washing of the mineral to remove residual dissolved ions was then conducted by repeated decantation and supernatant replacement until the conductivity of the supernatant returned to that of the distilled water (1.7 uMHO). At the completion of washing, the supernatant was removed, the cassiterite transferred to a petri dish and dried in a vacuum desiccator.

X-ray photoelectron spectra of all cassiterite samples were recorded on a Varian IEE-15 spectrometer, using unmonochromatized MgKα radiation (1253.60 eV) at 280 watts and an operating pressure of 10^-7 Torr. The electron analyzer pass energy was 20 eV. Spectrometer instrumental resolution was 1.5 eV on the (4f)7/2 peak for pure gold. Each sample was lightly dusted onto 3M scotch tape covering a sample holder and introduced into the spectrometer on a rapid insertion probe. All binding energies were calibrated with reference to the carbon 1s peak (285.0 eV) of graphite. Binding energy shifts of greater than 0.5 eV were considered significant.

3.2.11 Leaching Tests

Leaching tests were performed to determine the extent of abstraction of trace metal species from the surface of cassiterite at low pH. Both thermodynamic and kinetic data were obtained on trace metal abstraction.

Leaching was conducted in glass vessels containing 2000 mls of distilled water and 5 grams of mineral. The pH was adjusted to the desired value by
means of hydrochloric acid addition. Both pH and Eh were monitored using the experimental arrangement described previously. During the course of leaching, the suspension was continuously agitated.

Trace metal analyses of leach liquors were performed by Atomic Absorption Spectrometry (AAS) after Millipore membrane filtration at 0.45 μm to remove suspended solids. A Perkin-Elmer model 306 Atomic Absorption Spectrophotometer with a conventional atomizer/burner system was used to analyze all solutions for Al, Fe, Mg and Ca. Acetylene-air and acetylene-nitrous oxide fuel-oxidizer combinations were used as appropriate. The calibration of the atomic absorption spectrophotometer was checked by means of standards with suitable matrix. These standards were prepared from "Matheson, Coleman and Bell" iron, aluminum, magnesium and calcium AAS reference solutions. Background trace element levels in laboratory distilled water were checked prior to all analyses.

Equilibrium data on trace metal abstraction were obtained from leaching tests conducted at constant pH for a total of 14 days. Such data were considered to correspond to equilibrium conditions as no measurable changes in ion concentrations were observed at longer time periods. Kinetic data were obtained from leaching tests performed for variable time periods at constant pH. The maximum extent to which trace metals associated with unleached cassiterite could be removed was established by leaching at pH 1.0 with daily replacement of the leach liquor. After a total of 19 days, no detectable levels of metals were found in solution. The resultant cassiterite, after repeated washing with distilled water, was assayed for iron (the major cassiterite impurity) by ICP-AES. An iron balance was calculated on the basis of the initial and final cassiterite iron levels and the total amount of iron
abstracted during leaching.

3.2.12 Electrokinetic Studies

The electrokinetic properties of cassiterite suspensions were determined by microelectrophoresis using a Zeta-Meter and a type II UVA electrophoresis cell, both from Zeta-Meter Inc. Measurements were made according to the procedure set out in the Zeta-Meter manual (Anon, 1975). A bright platinum electrode was used for low conductivity solutions where gassing was not a problem. For high conductivity solutions, a molybdenum electrode that removed gas as the metal oxide was used. An average of at least 20 electrophoretic mobility measurements were made at each test pH and the mean and standard deviation of the particle mobilities recorded. All results were reported directly as mobilities rather than as zeta-potentials to avoid uncertainties associated with commonly used conversion equations (Overbeek, 1950; Wiersema, Loeb and Overbeek, 1966; Ottewill and Shaw, 1972, O'Brien and White, 1978) or the necessity of allowing for retardation and relaxation effects (Henry, 1931; Overbeek, 1943; Booth, 1950; Lyklema and Overbeek, 1961; Hunter, 1966). Repeated measurements of the mobilities of cassiterite particles were reproducible to within ± 0.2 micron/sec. per volt/cm.

Microelectrophoresis measurements were used to compare the electrokinetic properties of unleached, leached and synthetic cassiterite samples. Additional tests were performed to determine the effects on unleached cassiterite electrokinetic properties of sample aging, chemical pretreatment and vacuum drying. For all cassiterite mineral tests, the following procedure was used to prepare suspensions for electrophoretic mobility measurements:

(1) A weighed amount of indifferent (KCl) electrolyte was transferred to a volumetric flask, 100 mls of mineral
suspension stock solution was added and the volume made up to 1000 mls with distilled water.

(2) The sample was conditioned for 30 minutes in a water bath set at 23.5 °C. The initial pH and Eh of the solution were measured and recorded.

(3) Samples of 100 mls in volume were transferred from the volumetric flask and the pH adjusted to the test value using HCl or KOH as appropriate.

(4) The electrophoresis cell was flushed with distilled water at 23.5 °C and the test solution added.

(5) At the completion of electrophoresis measurements, the solution pH was re-measured. The test pH was considered to be the average of the initial and final pH values.

Synthetic cassiterite suspensions were prepared as above except that stannic dioxide powder, hard ground with an agate mortar and pestle, was added directly to the 1 litre volumetric flask of step (1) in place of the mineral stock solution. In the aging tests, aqueous stock solutions of unleached cassiterite, stored for different time periods, were used. Chemical pretreatment tests involved the acidification of a 1 litre unleached cassiterite suspension (prepared according to step (1)) to pH 1.0 for 2 hours followed by partial neutralization to pH 5.5. Adjustment of the pH was by means of hydrochloric acid and potassium hydroxide addition. No solution replacement or sample washing was used. Electrophoretic mobilities of the suspended particles in the solution were recorded for different time periods after the chemical pretreatment according to steps (2) to (5). A portion of the 1 litre solution was also transferred to a vacuum dessicator and dried.
After re-dispersion of the dried sample, in a volume of distilled water identical to that removed by the vacuum drying, particle electrophoretic mobility measurements were repeated.
3.3 Surfactant Characterization

All of the commercial phosphonic acids obtained for this research program were subject to full elemental analyses. The molecular structures of the surfactants were further characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. On the basis of the established structures and purities, one surfactant (Hoechst P-184) was selected for subsequent test work. This selection was made with appropriate regard to the reagents preferred in industrial flotation practice and the desirability, in fundamental studies, to work with as pure a surfactant as possible. Ultraviolet (UV) spectral analyses, titrimetry, surface tension measurements, light scattering photometry and molecular modelling were conducted to complete the chemical characterization of Hoechst P-184.

3.3.1 Infrared Spectroscopy

Infrared analyses of phosphonic acid surfactants were performed using the Perkin-Elmer 283 B double beam, optical null spectrophotometer described previously with respect to mineral characterization. Scanning time for surfactant analyses was again 12 minutes with the scanning range being from 4000 cm\(^{-1}\) to 255 cm\(^{-1}\). All other operating conditions were identical to those for the mineral infrared spectral studies.

Phosphonic acid samples were prepared using the KBr pellet method. Approximately 1 mg in weight of each reagent was dried in a vacuum dessicator and then thoroughly mixed with 300 mg of Mallinckrodt infrared grade KBr. The mixture was transferred to a die (Perkin-Elmer model 186-00251), evacuated for 2 minutes, and then pressed at approximately 3000 kPa for 30 seconds. After pressing, each pellet was examined and, if optically transparent, transferred to the spectrophotometer for analysis. Surgical gloves were worn at all times.
when handling pellets.

Spectra obtained from each infrared scan were manipulated using a Perkin-Elmer infrared data station interfaced to the 283 B spectrophotometer. Operation of the spectrophotometer and general data storage, retrieval and plotting were also performed at the data station. Details of these operations are described in depth in the aforementioned section on infrared mineral characterization.

3.3.2 Nuclear Magnetic Resonance Spectroscopy

To identify the hydrocarbon skeletal features of the phosphonic acid surfactants, proton nuclear magnetic resonance (NMR) spectra of all the reagents were obtained. Analyses were performed using a Bruker WP-80 spectrometer operating at a constant radio frequency of 80 MHz. The magnetic field strength was systematically varied to bring each proton in a surfactant into resonance. Proton resonances were recorded in terms of chemical shifts $\delta$ (ppm of the spectrometer frequency), relative to the standard reference tetramethylsilane (TMS). Peak areas were electronically integrated to give the ratios of each type of hydrogen present in the surfactants.

Preparation of surfactants for NMR analysis was by initial drying in a vacuum dessicator followed by dissolution in 'MSD Isotopes' deuterium oxide (minimum isotopic purity 99.8 Atom % D). Repeated vacuum drying and deuterated solvent replacement was used to minimize residual water concentrations. Protons in residual water molecules gave rise to additional strong peaks which unnecessarily complicated the NMR spectra. Final deuterated surfactant solutions were transferred with disposable pipettes to Norell 507 NMR tubes and placed in the spectrometer.
3.3.3 Chemical Analysis

All phosphonic acid samples supplied for this research were subject to total carbon and phosphorus determinations together with full trace element analyses. The samples were digested "as received" using a combination of hydrofluoric, hydrochloric, nitric and perchloric acids. Resulting solutions were then scanned for metals using a Jarrell Ash Model No. 975 Inductively Coupled Argon Plasma Spectrograph (ICAP). Analyses of twenty-seven trace metal elements were obtained at detection limits generally in the range 0.1-10.0 ppm. In the case of phosphorus, all values were cross-checked using an approximately 0.1% water soluble dilution of the surfactants. The total carbons were determined using a Leco induction furnace. For all elements, results were recorded as either percent or micrograms per gram on an "as received" basis.

3.3.4 Ultraviolet Spectroscopy

Ultraviolet spectral scans were obtained with a Perkin-Elmer Lambda 3 double-beam spectrophotometer using a deuterium lamp source. The spectrophotometer was interfaced to a Perkin-Elmer R100 chart recorder for linear absorbance and wavelength presentation. Wavelengths were checked with a holmium glass standard and the absorbance was checked with acid potassium dichromate and potassium nitrate solutions according to the procedure of Edisbury (1966). Photometric accuracy and reproducibility at an absorbance (A) of 1.0 were ± 0.005 A and 0.002 A, respectively. Spectra were run over the range 190 - 310 cm with the absorbance range being 0.0 to 3.0 A. Scanning speed was 15 nm/min (2.0 second response). Quartz window cuvettes of 1 cm path length were used for all analyses. Background correction for the cuvette and solvent (distilled water) was achieved automatically using the
microprocessor driven zeroing facility of the spectrophotometer.

Ultraviolet spectral curves were recorded for $1 \times 10^{-4}$ M solutions of styryl phosphonic acid at different pH values. All peak position and intensity shifts, associated with changing pH, were noted. Absorbance at 256.2 nm was used as a measure of phosphonic acid concentration.

### 3.3.5 Titrimetry

The phosphonic acids are weak acids. Since the conjugate of a weak acid is always a weak base, the sodium salts of phosphonic acids are weak bases. When a weak base is titrated with a strong acid, sharp inflections occur in the titration curves at the equivalent points. Knowing the volume of the titrant added to reach the inflection points, the dissociation constants of the weak base can be determined from the titration curve. Pressman and Brown (1943) have successfully used this method of potentiometric titration to determine the dissociation constants of a range of arsionic acids.

Potentiometric titrations of a $1 \times 10^{-4}$ M styryl phosphonic acid solution were performed using a Metrohm automatic titrator in end-point titration mode. End-point values were set by means of a model 614 Impulsomat and the titrant volume addition was controlled through a Multi-Dosimat (Model 645). A Metrohm 620 pH-meter, connected to a Fisher combination, polymer-body pH electrode (No. 13-639-97), was used to measure pH values. Prior to all titrations, the pH meter was standardized on two buffers (pH 4.01 and pH 10.4). All pH measurements were accurate to ± 0.05 pH units.

The styryl phosphonic acid was prepared as its sodium salt in carbon dioxide-free distilled water and back titrated with a standardized solution of 0.1 N hydrochloric acid. Back titration of the sodium salt of the acid, rather than direct titration, was performed to avoid possible solubility
problems with the undissociated acid species. Actual additions of the acid to the surfactant solution were made in a sealed 100 ml cell continuously purged with argon to avoid carbon dioxide adsorption from the atmosphere. Volume changes on addition of the titrant were negligible. Acid solution standardization was against sodium carbonate according to the method of Swift and Butler (1972).

Titrations were performed for each of two surfactant solutions to confirm the reproducibility of the data. Each titration run consisted of a series of successive back-point titrations with the pH being reduced in increments not exceeding 0.2 pH units. Plots of solution pH against the volume of acid added were graphed after each titre to ensure sufficient data in the region of the equivalence point.

The equivalence points of the titration curves were determined by means of Gran plots (Gran, 1952). When a weak base B is titrated with a strong acid, the appropriate Gran function is:

\[ V_{H} \cdot 10^{\text{pH}} = \frac{1}{K_{A}} \frac{\gamma_{B}}{\gamma_{BH^{-}}} (V_{e} - V_{H}) \]

where \( V_{e} \) is the equivalence volume, \( V_{H} \) is the volume of strong acid added and \( K_{A} \) is the first dissociation constant of the base. A graph of \( V_{H} \cdot 10^{\text{pH}} \) versus \( V \) consequently gives a straight line with a slope of \( \frac{1}{K_{A}} \frac{\gamma_{B}}{\gamma_{BH^{-}}} \) and an intercept of \( V_{e} \) on the \( V_{H} \) axis. Thus, from the data near the titration curve inflection point, it is possible to find the equivalence volume \( V_{e} \). The pH values corresponding to the half neutralization points of the first and second
hydrogen ions (i.e. at 1/2 $V_e$ and 3/2 $V_e$) are the ionization constants of a diprotic acid. The method is considered accurate to within 0.1 pH units, limiting the dissociation constant uncertainty to ±15 percent. Details of the calculation of the Gran function are given in Appendix D.

3.3.6 Surface Tension Measurements

Surface tension measurements of styryl phosphonic acid solutions were made with a Cenco (model no. 70545) Du-Nouy ring tensiometer equipped with a 5.992 cm circumference platinum-iridium ring. A fixed 80 cm$^3$ volume of surfactant solution, held in a 70 x 50 mm cylindrical cell, was used for all measurements. The free surface of solution was 19.6 cm$^2$. Surfactant concentrations varied between $1 \times 10^{-3}$ M and $1 \times 10^{-2}$ M and, as such, the change in the surfactant volume concentration in the cell due to adsorption or evaporation was negligible. Establishment of an equilibrium surface tension was rapid and no equilibration time effects were noted.

For each test solution, a minimum of three surface tension measurements were made. Individual measurements were generally reproducible to within ±0.50 dyne/cm. The absolute calibration of the tensiometer was checked with Christian Becker precision weights and found to be accurate to within ±0.40 dyne/cm over the entire range of interest for the aqueous surfactant solutions. Contamination effects were minimized by washing the ring with distilled water after every measurement and then flaming it with a butane torch. As a further precaution, the ring and all glassware were periodically cleaned with a concentrated nitric acid-ethanol mixture. Zuidema and Waters (1941) correction factors were used to convert all apparent surface tensions into absolute values. The more rigorous method of Huh and Mason (1975) was considered but the difference was found to be insignificant for the R/r and
R³/V values used (where R is the radius of the ring, r is the radius of the wire and V is the volume of liquid raised above the level of the liquid surface).

3.3.7 Light Scattering Photometry

Light scattering tests were performed with a Brice Phoenix Model 2000 Universal light scattering photometer equipped with a high pressure (85 watt) mercury vapour lamp. A green filter combination was used and all data were obtained at the 546 nm wavelength of the mercury spectrum. Output from the photomultiplier of the photometer was continuously recorded using a Beckman Model 1005 chart recorder. Four neutral filters of accurately known transmittance, which could be placed in the primary beam, served as optical multipliers to adjust the intensity of the transmitted beam. This allowed the photomultiplier output for both the scattered and the transmitted beams to be measured on the chart recorder when both were nearly equal and approaching full scale. In this manner, variable phototube fatigue effects and nonlinearity of response were eliminated.

Turbidities of 50 ml aliquots of styryl phosphonic acid solutions were analyzed directly in the photometer using a 30 x 30 x 60 mm optical plate (melt number 2) sample cell with plane entrance and exit windows. (Brice Phoenix type T-101). Cleaning of the cell was performed after each analysis with a nitric acid-ethanol mixture followed by washing with copious amounts of distilled water. A minimum of five turbidity measurements were made for each solution and data showing deviations of more than three percent discarded. Individual turbidity values (τ) were calculated from the relative intensities of transmitted light (Gw) and light scattered through 90° (Gs) for each solution using the expression:
$$\tau = \frac{16 \text{TD}}{3(1.049)h} \left[ \frac{n^2 (R_w / R_c)}{a F (G_a / G_w)} \right]$$

where:

- $F$ was the product of the transmittances of the neutral filters used in determining the scattering ratio ($G_a / G_w$).
- $a$ was a constant relating the photometer working standard to an opal glass reference standard.
- $\text{TD}$ was the experimentally determined product of the diffuse transmittance of the opal glass reference standard and a correction factor which made the reference opal glass transmitting diffusor equivalent to a perfect reflecting diffusion.
- $h$ was the width of the photometer diaphragm which determined the depth of scattering solution viewed.
- $n$ was the refractive index of the solution which, for the surfactant solutions, was assumed to be that of the distilled water solvent at 25 °C ($n = 1.334$).
- $1.049$ was the overall correction for surface reflections from the scattering cell and for back reflection by the standard opal.
- $R_w/R_c$ was an experimentally determined correction for incomplete compensation for refraction effects.

The theoretical basis of this turbidity expression is the Rayleigh theory of light scattering, details of which have been discussed by Hiemenz (1977).

On the basis of the calculated turbidities, the solubility of styryl phosphonic acid in aqueous solution was found by the simple determination of the lowest concentration at which a turbidity increase for a surfactant solution, relative to the distilled water solvent, was detected.
3.3.8 Molecular Modelling

Molecular models of both trans and cis styryl phosphonic acid isomers were constructed using a Fisher-Hirschfelder-Taylor model set. Atoms in the models were represented by spheres sawed off at right angles to the direction of the bonds and equipped with snap locks that could be joined by fasteners. Individual atomic components were to scale with respect to both atomic and interatomic dimensions. The scale was 100,000,000 : 1 (1 Å = 1 cm) with sphere radius being 80 percent of the appropriate van der Waals radius. Apparent crowding was, therefore, somewhat less severe than in the actual molecules. This was to compensate for the fact that the bond angles in the models were rigid whereas bond angles in the actual molecules can be deformed relatively readily.

The modelling of styryl phosphonic acid allowed the determination of a number of key molecular parameters. The effective volume (defined as the volume encompassed by a sphere having a diameter equal to the length of the largest axis of a molecule) and the hydroxyl group separation in the polar head of the molecule were determined by direct measurement. The degree to which particular atoms in the molecule could approach each other and the strain in the molecules, due to overcrowding of certain atoms, were readily assessed. Accurate determination of the projected area of the trans isomer of styryl phosphonic acid was also made. The model of the molecule was positioned on a glass plate illuminated from beneath. Orientation of the molecule was such that the alkene group was in the plane of the aromatic ring and the polar group was orientated away from the ring. Concave mirrors were then used to focus the image of the model onto a screen from which an outline could be traced accurately. The area encompassed by the outline was
determined by use of a planimeter. The projected area of the molecule was found by calculation, after appropriate allowance for optical magnification and planimeter calibration.
3.4 Ion Solution Chemistry

A considerable volume of information on the chemistry of ionic species in aqueous solution has been published. Experimental findings and conclusions from the literature, relevant to the surface chemical studies of this dissertation, were presented in the review of Section 2.3. In general, most subject areas in ion solution chemistry have been investigated extensively and are relatively well understood. However, a complete absence of published data pertaining to certain solution chemical and electrochemical aspects of ion chemistry of relevance to cassiterite flotation was found to exist. In particular, the effects of fluoride ion additions to solutions containing aluminum or iron polycations and hydrous oxides had not been investigated. While, thermodynamically, fluoride complexes of aluminum and iron can form at low pH (and high Eh in the case of iron), it was not known if, kinetically, such reactions were realistic in the time frames typical of flotation.

To provide information on the ion solution chemistry of cassiterite flotation and, in particular, to clarify the role of the fluoride ion in aqueous solution chemistry, a series of plant water analyses, thermodynamic calculations and laboratory electrochemical experiments was performed. Overall results from the pulp analyses of the Renison flotation circuit have been presented previously as a private communication (Winby, 1985 – Table VI). These experimental results formed the necessary database for the calculations of the thermodynamic diagrams of the literature review. Experimental investigation of the effects of fluoride in the aluminum ion system were performed primarily by means of light scattering photometry. Ultraviolet spectroscopy and solution electrochemical measurements of Eh and pH were used to investigate iron species interactions with the fluoride ion.
3.4.1 **Plant Water Analyses**

To ascertain the nature and concentrations of metal cations present in industrial cassiterite flotation pulps, the management of the Renison Limited concentrator (Australia) agreed to perform, on behalf of this research, a series of water analyses around the tin flotation circuit of their plant. A survey program was mapped out whereby samples were collected at various points around the Renison circuit according to a prescribed procedure. Both the sampling and the analytical determination techniques of this procedure were selected to conform to the recommendations of the reference "Standard Methods for the Examination of Water and Wastewater" edited by Taras et al (1971).

The flowsheet details of the Renison flotation circuit together with the associated desliming circuit are shown in Figure 84. The configuration of the flotation circuit is conventional, consisting of a rougher-scavenger bank followed by three stages of cleaning. Prior to tin flotation, the feed is deslimed at a nominal cut size of 4 micron in a multi-cyclone desliming circuit. Interposed between the desliming circuit and the flotation circuit is a sulphide scavenger bank, the function of which is to remove residual sulphide minerals prior to cassiterite flotation. Sulphide minerals are well known to be floated effectively by cassiterite flotation collectors.

During the course of the plant water surveys, the Renison circuit was sampled at three different locations:

(a) the head of the desliming circuit (Sample Point 1, Figure 84).

(b) the head of the rougher flotation bank (Sample Point 2, Figure 84) and

(c) the third cleaner bank (Sample Point 3, Figure 84).
Figure 84 - Flowsheet of the Renison Cassiterite Flotation and Desliming Circuits. Pulp sampling points are marked in the figure.
Multiple samples were collected at each point during two sampling runs conducted on different dates. The pH and Eh values of all samples collected were measured immediately. The samples were then allowed to settle for an hour, filtered and the supernatant acidified and analyzed for Fe, Al, Cu, Ca and Mg by atomic absorption spectrophotometry (A.A.S.). The total alkalinity of each sample was also determined by standard wet chemical analysis. All ion concentrations were reported directly in parts per million. The alkalinity was expressed as µg/ml of CaCO₃.

3.4.2 Thermodynamic Calculations

The regions of thermodynamic stability of metal ionic species in aqueous solution can be illustrated graphically in a number of ways. The most informative graphical stability constructs are generally the distribution diagram (species fraction - pH), the equilibrium (log [metal] - pH) diagram and the Pourbaix (Eh-pH) diagram. During the course of this research, all three stability diagram types were utilized to determine the predominant ionic species in solutions of interest. Where necessary, the results from the Renison plant water analyses were used to delineate the range of total metal ionic species likely to be in solution. In the case of stability diagrams calculated for actual experimental analyses, the true concentrations of all ionic species in the tests were used.

Details of the methods of construction of thermodynamic stability diagrams are given in standard references such as Garrels and Christ (1965). Such calculations are generally straightforward. However, problems can arise in both distribution and Pourbaix diagram constructions if inconsistencies exist in the equilibrium constants used. For example, in Pourbaix diagram calculations, this problem manifests itself in line elimination difficulties
and the associated existence of phase regions where no stable species can be identified. To avoid problems of stability constant inconsistencies in this work, Gibbs free energy data were used to calculate all required thermodynamic constants. In this way, self consistency of all the stability constants was assured. The sources of these free energy data are discussed in detail in Appendix A.

Calculations necessary for the construction of all the thermodynamic diagrams used in this study are summarized in Appendix B. The distribution diagram compilations were performed by expressing the total metal ion concentration in solution in terms of the sum of all the component species concentrations. Component species concentrations were then related to free ion concentrations and pH by means of stability constants giving polynomial expressions in the free ion concentration. For a given pH and total metal ion concentration, solutions of the polynomial expressions were found using the UBC Computing Department program DZFUN. This program is designed to find the real zeros of a nonlinear function of one variable. Details and examples of these calculations are given in Appendix B.

Concentration - pH diagram calculations were less complicated. The concentration of each ionic species in the solution of interest was simply expressed in terms of the free ion, the hydronium ion and the hydrous oxide concentration. The activity of the precipitated hydrous oxide was then assumed to be unity, such that all equilibrium equations could be expressed in terms of only the concentration of the metal cationic species of interest and the pH. Details of such calculations are also given in Appendix B. In the case of the Pourbaix diagram calculations, the number of components of interest was sufficiently limited to allow the diagrams to be calculated
manually. Thermodynamic equations relating all species pairs were written (Appendix B) and line eliminations performed by comparing the relative stabilities of all possible species in the phase region of interest.

3.4.3 Light Scattering Photometry

Light scattering tests were used to investigate the effects of fluoride ion additions on the hydroxylation and dissociation of aluminum ion species. The utility of light scattering photometry for such test work existed in the technique's ability to allow the detection of the onset of polymeric aluminum sol formation in aqueous solution. In general, the degree of light scattering by such sols is a function of their size, size distribution, shape and concentration in solution. However, for dilute suspensions, solution turbidities, as measured by light scattering, can be considered as being directly proportional to the number of solute particles in the suspension (Meehan and Chiu, 1964). On this basis, a semi-quantitative determination of the extent of sol formation can be obtained by light scattering photometry. Furthermore, such solution turbidities, taken at different time periods after a suspension preparation, can provide kinetic data on the relative rates of sol formation and dissolution, under varying chemical conditions.

Light scattering measurements on aluminum chloride solutions were performed with the Brice Phoenix Model 2000 Universal light scattering photometer described previously. A green filter combination was again used and all data were obtained at the 546 nm wavelength of the mercury spectrum. Turbidities of 30 ml aliquots of aluminum suspensions, in the presence and absence of NaF addition, were determined directly in the photometer using a Brice Phoenix type T-101 cell. Cleaning of the cell was performed after each analysis with a nitric acid-ethanol mixture followed by washing with copious
amounts of distilled water. A minimum of five turbidity measurements were made for each solution and data showing deviations of more than a few percent were rejected. Individual turbidities were calculated from the relative intensities of transmitted light and light scattered through 90° using the Rayleigh light scattering equation presented in Section 3.3.7.

Aluminum chloride suspensions used in the light scattering tests were prepared according to a number of procedures to permit investigation of both the forward and reverse kinetics of hydroxylation. In studies concerning the formation of aluminum sols in the presence of the fluoride ion, aluminum chloride solutions containing various concentrations of sodium fluoride were prepared under slightly acidic conditions. An appropriate weight of AlCl₃ to form a 1 x 10⁻³ M solution was added to a volumetric flask together with the desired weight of NaF and 1 ml of dilute hydrochloric acid. The volume was made up to a total of 500 mls and allowed to equilibrate for 15 minutes. Aliquots of 30 mls were then withdrawn and the pH adjusted to the test pH. After a further equilibration period totalling 10 minutes, the turbidity of the suspension was measured. For each test pH, fresh aliquots were taken. In this manner, it was found possible to determine accurately the onset of measurable solution turbidity. However, at pH values appreciably above this precipitation boundary, significant turbidity variability became evident. This undoubtedly reflected the complex nature of aluminum polycation and hydrous oxide sol formation and the dependence of the degree of light scattering on the size, shape and size distribution of such sols, in addition to their concentration.

Test work concerning the dissociation and resolubilization of aluminum hydroxy sols was performed using a 2 litre stock solution of 1 x 10⁻³ M AlCl₃,
aged for 18 hours. Preparation of this solution involved weighing an appropriate amount of AlCl₃ into a beaker, adjusting the volume to slightly less than 2 litres and adding sufficient KOH to give an initial pH of 6.0. Upon transferring to a 2 litre volumetric flask, the total volume was made up to the correct level and the stock left to age for a total of 18 hours. During this time period, the pH of the stock decreased considerably (ultimately to pH 4.1) and visible solution turbidity was noted. Both solution changes were consistent with the extensive hydroxylation of the aluminum in the solution and the formation of polymeric sols.

To allow both the effects of fluoride ion addition and acidification on the dissociation of aluminum sols to be investigated, the aged stock solution was split into four equal volumes and the pH adjusted back to approximately 6.0. To three of these volumes were added differing quantities of NaF. The NaF was added as a dry powder washed into the suspension with a small aliquot withdrawn for the purpose. All four solutions were left to age for a further period of 15 minutes. During this time, the pH of the suspensions to which sodium fluoride had been added increased appreciably. The addition of the equivalent of 6 x 10⁻⁴ M NaF, for example, increased the pH from 5.90 to 8.05 indicating the release of measurable levels of hydroxyl ions. Furthermore, with all of the aged aluminum suspensions, considerable time dependent pH and turbidity variability was noted when the pH was subsequently lowered below the initial value. This variability was particularly pronounced for the suspensions containing fluoride. Significantly, for all solutions, the pH drift was toward more basic pH values. This indicated either hydronium ion consumption or hydroxyl ion release and was further consistent with continuing dissociation of hydrous aluminum oxide sols. Experimentally, given this
variability, it was found necessary to measure suspension turbidities a fixed time period after addition of acid. The procedure adopted was to withdraw 30 ml aliquots from each of the four suspensions in turn, adjust the pH to the required range during a total pH adjustment and equilibration time of 5 minutes and then to take five turbidity measurements in the next 10 minutes. For each subsequent test pH, fresh aliquots were withdrawn and the procedure repeated. The test pH was considered to be the average of the initial and final values. By use of this procedure, definite trends in turbidity were found to exist with acidification of the aluminum sol suspensions both in the presence and absence of the sodium fluoride additions.

3.4.4 Ultraviolet Spectroscopy

Solutions containing hydrolyzed ferric ion species are characteristically coloured. Such colouration results from absorption in the violet to violet-blue range of the visible spectrum (380-440 nm) and varies with the extent of hydroxylation and polymerization of the ferric ion species. Solutions containing low molecular weight Fe(III) compounds are typically yellow in colour. A more intense brown-red colouration results when colloidal hydrous ferric oxide sols are present (Harris, 1982). In a similar manner, such hydrolyzed ferric ion species absorb strongly in the ultraviolet (200-380 nm) range. Ultraviolet (UV) spectroscopy, therefore, can be used as a sensitive test for the detection of polymeric ferric species in solution and as a semi-quantitative indicator of the extent of polymerization of such sols.

The UV absorbance of iron solutions was determined with a Lambda 3 double beam spectrophotometer. A deuterium lamp source was used and absorbance measured at 297 nm. This wavelength was found to be the most appropriate as it represented a shoulder point in iron solution UV spectra where dA/dλ was
small and gave absorbance values typically between 0.2 and 1.0. Spectrophotometers characteristically exhibit their minimum error at such intermediate levels of absorbance (Harris, 1982). To check the wavelength calibration of the spectrophotometer, a holmium glass standard was used. The absorbance was checked with acid potassium dichromate and potassium nitrate solutions according to the procedure of Edisbury (1966). Photometric accuracy and reproducibility at an absorbance (A) of 1.0 were ± 0.005 A and 0.002 A, respectively. Quartz window cuvettes of 1 cm pathlength were used for all analyses. Background correction for the cuvette and solvent (distilled water) was achieved automatically using the microprocessor driven zeroing facility of the spectrophotometer. Between each measurement, the cuvette was acid cleaned, washed with distilled water and the zero checked. This ensured that no residual iron species were retained on the quartz windows between measurements.

Iron suspensions used in the ultraviolet spectroscopy studies were prepared according to a series of procedures that paralleled those used in the aluminum ion light scattering tests. Analyses were conducted to investigate the forward and the reverse kinetics of hydrous ferric oxide sol formation in the presence and absence of sodium fluoride. Hydrous ferric oxide suspensions were prepared from ferric and ferrous chloride salts to provide data on the polymerization and depolymerization processes involved in the transitions to and from both the free ferric ion and the free ferrous ion states.

In studies concerning the formation of hydrous ferric oxide sols from the ferric ion state in fluoride bearing solutions, ferric chloride solutions containing various concentrations of sodium fluoride were prepared under acidic conditions. An appropriate weight of FeCl₃ to form a 1 x 10⁻⁴ M
solution was added to a 2 litre pyrex reaction vessel, together with the desired amount of NaF and hydrochloric acid. The volume was made up to 500 mls and allowed to equilibrate for 15 minutes. The pH was then adjusted to the test pH using additional hydrochloric acid or potassium hydroxide. After a pH equilibration period totalling 10 minutes, both the Eh and the pH were recorded, a sample withdrawn from the reaction cell by means of a pipette and the absorbance measured. For each subsequent test pH, the procedure was repeated. Between measurements, the sampling pipette was acid cleaned and washed with distilled water to remove residual iron species.

Test work concerning the onset of formation of hydrous ferric oxide sols from solutions in which ferrous ion species were initially predominant was performed in a similar manner. However, to avoid extensive oxidation of the ferrous ion to the ferric state, at the pH of solution preparation, the pyrex reaction vessel was sealed and continuously purged with argon supplied through a glass bubbler. Purging of the cell was performed both before and during solution preparation. Ports in the top of the reaction vessel allowed electrodes to be mounted in the cell for both solution pH and Eh measurement. Transfer from the vessel to the quartz window cuvette for absorption measurement was again by means of a pipette. The cuvette was then sealed with a plastic stopper and the time to measurement kept at a minimum to limit any solution oxidation due to exposure to the atmosphere.

Analyses of the effects of fluoride ion additions and acidification on the resolubilization of aged ferric sol suspensions were performed in a slightly different manner to those of the aluminum ion studies. This was necessitated by the availability of only one sealed reaction vessel and the associated need for fresh stocks of sol suspensions for each test run. Sol suspensions were
prepared by dissolving the required amount of FeCl$_2$.4(H$_2$O) in argon purged distilled water, adding sufficient potassium hydroxide to give an initial pH of approximately 6.0, and then sealing the vessel for a period of 18 hours. During this time, the pH continuously decreased and the solution became intensely coloured. Both solution changes indicated the continued hydroxylation and polymerization of the ferric ion species in solution. At the end of the 18 hour period, the absorbance was measured to provide a reference point prior to the addition of NaF or acid. These reference absorbances were found to vary between 0.7 and 1.1 A for the four stock solutions used. These variations almost certainly reflected the difficulty of preparing two identical hydrous ferric oxide suspensions and the differing amounts of hydroxide added initially to each to achieve a pH of 6.0.

The effect of acidification alone on an aged sol suspension was examined by decreasing the pH to the desired test value, allowing the solution pH and Eh potential to equilibrate for 15 minutes, and then measuring the absorbance of an aliquot of solution withdrawn with a pipette. In this manner, the pH was stepped down to acidic values approaching pH 1.5 and absorbance measurements made at each intervening pH value. For analyses involving the fluoride ion, sodium fluoride was added immediately to a sol suspension after the 18 hour aging period and reference absorbance measurement. The pH was then stepped down in increments and the absorbance measured after 15 minute equilibration periods in a manner identical to that in the absence of fluoride. The selection of a 15 minute equilibration period was based on the experimental need to achieve reasonable solution pH and Eh stability for absorbance measurements and the desirability of obtaining data kinetically relevant to expected flotation time frames.
3.4.5 Solution Eh-pH Measurements

During all experiments conducted in the research concerning the effects of iron species in solution, both the Eh and the pH were continuously monitored. Suspension potential (Eh) values were measured with a polished platinum electrode (Corning electrode No. 476060) and a saturated calomel electrode (Fisher Scientific electrode No. 13-639-51) connected to a Corning 150 ion analyzer set in mV mode. The potential was converted to the standard hydrogen electrode (SHE) scale by the addition of 0.245 volt. Calibration of the Eh electrodes was with respect to a standard ferrous-ferric (Light's) solution (Light, 1972). In concentrated iron solutions, periodic cleaning of the surfaces of both the platinum and calomel electrodes was found necessary to remove adhering iron films. The presence of such films caused ion meter instability and anomalous Eh readings.

Solution pH values were measured using a Fisher Accumet Model 230 pH/ion meter and a Beckman 39520 glass refillable combination electrode. Epoxy body refillable combination electrodes were found to be unsuitable in concentrated and acidic ferric chloride/sodium fluoride solutions. After exposure to such solutions, pronounced memory effects were found to exist with epoxy body pH electrodes. These were not present with the more chemically resistant (Anon, 1980) glass electrodes. The pH values measured with the glass electrode are believed accurate to ± 0.05 pH units. During all experimental test work, the calibration of the pH meter and electrode was checked daily with respect to two standard buffers (pH 4.01 and pH 10.4).
3.5 Mineral-Surfactant Interactions

Interactions between phosphonic acids and cassiterite were examined by microflotation, adsorption study and electrokinetic analyses. The principal objective of this research was to identify the pH and concentration ranges of surfactant-mineral interactions that were of importance in the flotation of the mineral. A key subsidiary objective was to establish if fundamental differences existed in these interactions after acid leaching of the cassiterite. To this end, high purity Aldrich "Gold Label" stannic dioxide was used as a reference material in both the adsorption study and electrokinetic analyses. The very fine grain size of this powder precluded its use in microflotation testing.

3.5.1 Microflotation Studies

Flotation studies were conducted using a modified microflotation tube similar in design to that described by Siwek, Zembala and Pomianowski (1981). Design of the microflotation tube varied from that of more conventional Hallimond tube apparatus primarily by nature of its tall upper section and pinched neck (Plate 2). Both features were designed specifically to minimize mechanical carryover of fine cassiterite.

Initial testing indicated that flotation of the test cassiterite in orthodox microflotation cells, such as the Hallimond tube described by Fuerstenau, Metzger and Seele (1957) or the Partridge and Smith cell (Partridge and Smith, 1971), was subject to severe mechanical carryover problems. These largely reflected the fine (-38 + 4 micron) size of the cassiterite. Collectorless flotation tests with several such cells all gave recoveries in excess of 50 percent. However, there was no evidence for any self-induced floatability of the cassiterite. High purity quartz of similar
Plate 2 - The Microflotation Tube Used to Float -38 + 4 Micron Cassiterite. Features of the tube are its 37 cm tall body and the pinched neck leading to the concentrate receiver (top left).
size range, when tested in an identical manner, gave similar recoveries. In contrast, collectorless flotation of both the cassiterite and quartz in the modified tube gave recoveries of the order of only seven percent. These recoveries were believed due entirely to entrainment of the finest fractions of both minerals into the concentrate receiver of the modified tube.

Bubble generation in the microflotation tube was by passage of pure air (Linde Medical Air, breathing grade) through a medium grade glass frit of pore size < 5 micron. A Dwyer RMA 150 SSV air flowmeter was used to control the air flowrate. Agitation in the microflotation cell was by means of a Fisher (No. 14-511-62) octagonal stir bar. The speed of agitation was controlled by a Corning PC-351 hot plate stirrer positioned beneath the tube.

All microflotation tests were conducted according to a standard procedure. The key steps in the procedure were as follows:

1. a 250 ml solution of surfactant, at the desired concentration, was prepared and the pH adjusted to the test value.

2. the base of the microflotation tube was placed in a predetermined position on the Corning hot plate stirrer. The air lines were connected, purged and then pinched closed with a clamp. Purging was necessary to prevent collector solution entering the air line during conditioning.

3. 1 gram of cassiterite, previously weighed on a Mettler PC 440 top loading balance, was washed into the base of the tube using the collector solution and the volume made up to a level just below the top of the base. The stirring bar was added, stirring commenced and 5 µl of nett 2-methyl-3-
hydroxy pentanol (MIBC) injected using a Hamilton microliter (No. 705) precision syringe. In the absence of the frother, recovery was low. The cassiterite particles floated but the air bubbles collapsed at the neck of the microflotation tube where it joined the receiver.

(4) after MIBC addition, the mineral suspension was conditioned for five minutes. During this time, the top of the microflotation tube was assembled and filled with the remaining collector solution.

(5) at the completion of the conditioning period, the air line was unclamped and the air flowmeter set at 60 cc/min. The cassiterite was then floated for the desired period. Five minutes was adopted as the standard flotation time for all tests, other than those for which the flotation kinetics were of interest.

(6) after flotation, the concentrate was recovered by removing the plug on the receiver side arm and washing the contents into a beaker. The tailings were recovered by inverting the tube and washing out the unfloated fraction. The pH of the tailings was measured to give the final pH of flotation. The test pH was considered to be the mean of the initial and final pH values.

(7) products of the flotation were filtered using Whatman 934-AH glass microfibre filters (1.5 μm particle retention) and then oven dried at 70°C for 24 hours. Weights of floated and unfloated fractions were determined using a Mettler H20T
five figure analytical balance. The mass balance was then checked with respect to the initial 1 gram weight of sample. Recovery was calculated on the basis of the concentrate and tailing mass distribution.

After a number of initial difficulties, the modified microflotation tube worked remarkably well. A series of five identical tests designed to assess the reproducibility of the flotation gave recoveries that varied by less than 5 percent. To achieve such reproducibility, it was necessary, however, to pay considerable attention to a number of factors.

Preliminary test work indicated that key variables that could influence flotation recoveries were the positioning of the microflotation tube on the Corning stirrer, instability in the air flowrate, and the tendency for the glass frit to become blocked with colloidal cassiterite particles. Positioning of the tube influenced the stir bar motion in the tube. If not aligned correctly, portion of the cassiterite to be floated became trapped in a 'dead zone' at the base of the tube and not fully contacted with the air bubbles generated by the frit. This problem was accentuated by the tapered nature of the base of the microflotation tube (Plate 2) and the use of a frit slightly smaller in diameter than the upper tube body. Recovery decreased noticeably when the misalignment was severe. Resolution of the problem was achieved simply by the use of positioning markers on the top of the stirrer.

Minor fluctuations in air flowrate to the microflotation cell were found also to affect recoveries. The sensitivity of recovery to small variations in the aeration rate was undoubtedly due to the fine size range of the cassiterite being floated. To minimize such flowrate variations, the air flow to the microflotation tube was routed through a stopcock valve that allowed it
to be diverted to an auxiliary air line. This auxiliary line was pinched in such a manner that it provided a flow resistance similar to that of the microflotation tube. The use of this line allowed the air flowrate to be set with precision prior to flotation and then switched in at the conclusion of the conditioning period. In such a manner, flowrate instability, particularly during the critical initial period at the onset of flotation, was minimized.

The problems associated with the blockage of the glass frit by mineral fines were both the most difficult to identify and to deal with. Variations in flotation recoveries, due to frit blockage, only became significant after a considerable number of tests were performed. The effect was always to lower recoveries, presumably due to changes in the bubble size distribution. However, the longer term nature of the problem and the considerable difficulty in assessing the extent of the resultant recovery variations until after the completion of a large number of tests, made identification of the problem difficult. The solution adopted was to clean the glass frit with aqua regia. After every three tests, 40 mls of aqua regia was poured into the base of the microflotation tube and allowed to pass through the frit for a 24 hour period. At the conclusion of the cleaning, the base was thoroughly washed with distilled water until all traces of the acid were removed. A standard microflotation test was then performed to check the flotation reproducibility. The experimental tests were then conducted. In this manner, it was found possible to achieve excellent reproducibility over the course of the experimental program. However, the cleaning requirements greatly increased the time required for the flotation testing. Alternative cell designs were considered, but frit blockage is undoubtedly a problem with all microflotation cells that utilize glass frits for bubble generation when fine particles are
to be floated. A more satisfactory resolution of the problem would require an alternative means of bubble generation that gives appropriate bubble sizes and size distributions in as reproducible a manner as can be achieved with glass frits. As such, it was believed to be a more complex problem than reasonably could be dealt with in this research and the cleaning procedure was adopted.

3.5.2 Adsorption Studies

The adsorption of styryl phosphonic acid on both cassiterite and Aldrich "Gold Label" stannic dioxide was determined by measuring the surfactant concentration in solution before and after contacting with the samples. Equilibration of the surfactant solution with the adsorbents was performed in Wheaton '800' glass vials, shaken continuously in a Lab-Line Orbit Environ-Shaker at a constant 300 rpm and a controlled temperature of 25°C. After contacting, the solution was decanted into Corex (No. 8445) 30ml centrifuge tubes and centrifuged for 10 minutes in an International Equipment Co. HT Centrifuge operating at 12,000 rpm. The centrifuged supernatant was then decanted, the solution pH adjusted to pH 5.0 and analyses for residual phosphonic acid performed by UV spectroscopy. The characteristic phosphonic acid absorbance at 256.2 nm was used as a measure of surfactant concentration. At this wavelength, the Beer-Lambert Law was found to apply in the styryl phosphonic acid concentration range $1 \times 10^{-5}$ M to $1 \times 10^{-4}$ M. Further details of the experimental procedure are as follows:

1. For any one series of adsorption tests a 1 litre surfactant stock solution of desired concentration was prepared. This served as a common 'parent' for all individual test solutions. In such a manner, errors due to variations in
concentration between separately prepared solutions were eliminated.

2. The desired amount of adsorbent was weighed into a vial using a Mettler H20T five figure analytical balance. For tests with unleached cassiterite, one gram of the mineral was used. Half this weight was used in the case of the stannic dioxide, which was finer, and had a considerably higher surface area.

3. A 60 ml volume of the stock solution was transferred to a beaker and adjusted to the test pH. A pipette was then used to transfer a 25 ml aliquot of this solution to the vial containing the adsorbent. A further 25 ml aliquot was added to a vial containing no adsorbent. By running blanks (surfactant solutions without the adsorbent added) it was possible to correct for dilution effects due to pH adjustment, surfactant adsorption on glassware, centrifuge tubes, etc.

4. The procedure was repeated for each test pH and all vials, including the blanks, transferred to the Lab-Line shaker. In agreement with the published data of Wottgen (1969) and Yap (1975), the adsorption of styryl phosphonic acid on both adsorbents was very rapid. Equilibrium conditions were reached within one hour, with the majority of the uptake occurring in the first 10 minutes of contacting. However, given the finite time required for sample handling, centrifuging and analyses, all tests (except those for which
the kinetics were of interest) were conducted with a shaking period of 150 minutes. By using such a long equilibration period, the time lapse between analysis of the first and last samples in a test run had a negligible effect on the adsorption.

5. Absorbance measurements were made in the Perkin-Elmer Lambda 3 double-beam spectrophotometer described previously. The wavelength calibration of the spectrometer was again checked with a holmium glass standard. The absorbance was checked with acid potassium dichromate and potassium nitrate solutions according to the procedure of Edisbury (1966). Photometric accuracy and reproducibility at an absorbance (A) of 1.0 were ± 0.005 A and 0.002 A, respectively. A solution analysis pH of 5.0 was selected for the absorbance measurements. Styryl phosphonic acid solution absorbances within ± 0.5 pH units of pH 5.0 were found to vary negligibly. Quartz window cuvettes of 1 cm pathlength were used for all analyses.

A sample of unleached cassiterite of suitable size range for adsorption measurements was prepared by combining the -4 micron unleached cassiterite fraction from beaker decantation (Figure 83) with 100 grams of -38 + 4 micron cassiterite ground in a Retsch RM-0 automatic mortar pulveriser. In preparing this sample, considerable care was taken to ensure its homogeneity. The two components of the sample were thoroughly mixed by standard rolling and coning and quartering techniques. Details pertaining to the Aldrich "Gold Label" stannic dioxide have been described previously. As supplied, the stannic
dioxide was in the form of small (1 mm) aggregates of very fine powder. A 2-minute grinding time in the pulveriser was found sufficient to break down the aggregates to produce a uniform powder suitable for adsorption studies.

The calculation of the adsorption density of a surfactant on an adsorbent from the difference between its initial and final molar concentrations in solution is a standard technique. Nevertheless, it has a number of limitations. Specifically, it can only provide an indirect measurement of the adsorption. An assumption that all surfactant not present in bulk solution after contacting with the mineral is adsorbed is implicit in all adsorption density determinations made on the basis of solution concentration changes. In some instances, this is well recognised as being an unsubstantiated assumption. This is particularly the case where solution interference effects can occur. In this research, the latter limitation became strikingly evident in analyses with the unleached cassiterite. At low pH, solubilization of a surface impurity associated with the mineral was found to occur. The presence of this impurity, in solutions equilibrated at pH values below 3.0, resulted in the absorbance after contacting of the styryl phosphonic acid with the cassiterite, exceeding that of the initial surfactant solution. At less acidic pH values, a similar but smaller interference might have occurred. However, since the effect of such an interference was to increase the final solution absorbance, calculated adsorption density values were presumably only underestimated and never overestimated. As such, significant trends in phosphonic acid adsorption on unleached cassiterite could still be recognised. Important comparisons further could be made with the surfactant adsorption behaviour on the stannic dioxide, for which no evidence of interference was found. A number of striking solution colour changes were associated with the
interference effects. This allowed evidence for such effects to be recorded photographically.

3.5.3 Electrokinetic Studies

The technique of microelectrophoresis was used to investigate the specific adsorption of styryl phosphonic acid at both unleached cassiterite and stannic dioxide interfaces. The objectives of these electrokinetic studies were to:

(1) confirm the existence of specific chemical interactions between styryl phosphonic acid and cassiterite and stannic dioxide surfaces.

(2) establish whether significant differences in such interactions existed between pure stannic dioxide suspensions, prepared from powdered Aldrich "Gold Label" stannic oxide, and unleached cassiterite suspensions.

(3) correlate changes in measured electrophoretic mobilities in the presence of styryl phosphonic acid with adsorption isotherm data. Specifically, if the data reported by Yap (1975) for p-tolyl phosphonic acid adsorption on cassiterite (Figure 47) could be reproduced, substantial corroborating evidence would then be available supporting the hypothesis that neutral phosphonic acid species coadsorb at the cassiterite surface in acidic solutions.

The experimental arrangement and procedure adopted in the microelectrophoresis test work was essentially that used in the mineral characterization studies. Electrophoretic mobilities were again measured
using a Zeta-Meter with a type II - UVA cell. A bright platinum electrode was used for low conductivity suspensions where gas evolution was not a problem. For high conductivity suspensions, a molybdenum electrode, that removed gas as the metal oxide, was used. An average of at least 20 electrophoretic mobility measurements were made at each test pH and the mean and standard deviation of the particle mobilities recorded. All results were reported directly as mobilities, rather than zeta-potentials, to avoid uncertainties associated with commonly used conversion equations and the necessity of allowing for retardation and relaxation effects. Repeated measurements of the mobilities of cassiterite and stannic dioxide particles were reproducible to within ± 0.2 micron/sec. per volt/cm.

For all tests with unleached cassiterite particles, the procedure used to prepare suspensions for microelectrophoresis was as follows:

(a) A weighed amount of styryl phosphonic acid, sufficient to give the desired concentration, was transferred to a volumetric flask, 100 mls of mineral suspension stock solution was added and the volume made up to 1000 mls with distilled water. The final solids concentration in the suspension was 0.05 g litre\(^{-1}\).

(b) The suspension was conditioned for 30 minutes in a water bath set at 23.5 °C. The initial pH of the solution was measured and recorded.

(c) Samples of 100 mls in volume were transferred from the volumetric flask and the pH adjusted to the test value using HCl or KOH as appropriate. The suspension was equilibrated at the test pH for 30 minutes. During this time, further
acid or base was added as required.

(d) The electrophoresis cell was flushed with distilled water at 23.5 °C and the test suspension added.

(e) At the completion of the electrophoresis measurements, the pH was again measured. The test pH was considered to be the average of the initial and final pH values.

(f) Steps (c) through (e) were then repeated for each required test pH.

Synthetic cassiterite suspensions were prepared in a similar manner, except that stannic dioxide powder, ground for 30 minutes in an agate bowl Retsch RM-0 automatic mortar pulveriser, was added directly to the 1 litre volumetric flask of step (a), in place of the mineral stock solution. The final solids concentration of the stannic dioxide suspensions was 0.03 g litre⁻¹.
3.6 Mineral–Ion Interactions

The interactions between inorganic ionic species and an insoluble mineral surface, such as that of cassiterite, were investigated using microelectrophoresis. Tests were conducted for all of the ions previously identified as being present in substantial concentrations in industrial cassiterite flotation circuits. Where appropriate, microelectrophoresis measurements were made for mineral substrates in the presence of combinations of ions.

During the course of the experimental work, the role of certain iron and fluoride species was identified as being crucial in influencing the nature of the surface properties of cassiterite. Particular emphasis was consequently placed on elucidating all aspects of the interactions of these ions with the cassiterite surface. To this end, additional electrokinetic studies were performed with mineral substrates other than that of unleached cassiterite. X-ray photoelectron spectroscopy (XPS) analyses and leaching tests, to complement the findings of the microelectrophoresis studies, were also included, for this purpose, in the research program.

3.6.1 Microelectrophoresis Studies

Electrokinetic studies of mineral–ion interactions were conducted using a range of mineral substrates and inorganic reagents. Tests with all the ions were performed primarily with unleached cassiterite particles, in accordance with the stated objectives of the research. However, where necessary to elucidate further the role of mineral surface species and mineral–ion interactions, leached cassiterite, pure stannic dioxide or high purity quartz particles were used as test substrates. The leached cassiterite and the stannic dioxide served essentially as reference materials for the unleached
cassiterite. These reference materials allowed a number of striking surface properties of the unleached cassiterite to be identified. Tests with the high purity quartz particles were used, in the first instance, to confirm the general nature of certain charge reversal phenomena found to be associated with the cassiterite. Such tests also allowed more detailed investigations of the iron system to be performed. Under the experimental conditions of the research, the onset of transformation of ferric and ferrous ions to hydrous ferric oxide species was found to occur at pH values below pH 4.0. As such, CR. 1 was absent in testing with such ions for both the cassiterite and the stannic dioxide systems. However, in quartz suspensions, CR.1 could be distinguished readily, since no iep was found for the quartz, in the absence of added ions, down to pH 2.0. The use of the quartz provided a further advantage in that comparisons could be drawn readily with previously verified data published in the literature.

Descriptions of mineral and suspension preparations pertaining to both unleached and leached cassiterite samples and stannic dioxide have been given previously. Preparation of a quartz suspension, suitable for microelectrophoresis, was performed in a similar manner to that for the cassiterite. As supplied from the Department of Mines, Energy and Resources (Canada), the quartz used in the research was in the form of coarse crystals of very high purity. Multiple wet chemical analyses of the sample gave an average assay of 99.56% SiO₂. As such, no further upgrading was deemed necessary and the objective of the sample preparation was solely to produce a suitable quartz size fraction for microelectrophoresis. This was achieved by batch grinding, wet screening and finally sedimentation and decantation to recover a colloidal quartz size fraction (Figure 85).
HIGH PURITY QUARTZ
(DEPARTMENT OF MINES, ENERGY AND RESOURCES)

GRINDING IN A CERAMIC MILL

WET SCREENING AT 38 μm

DECANTING AFTER 24 HOUR SETTLING

DECANT SUPERNATANT

FOR ELECTROPHORESIS

Figure 85 - Flowsheet Showing the Method of Preparation of the Quartz Size Fraction Used in the Microelectrophoresis Studies.
Grinding of the quartz was performed in a ceramic mill to avoid iron contamination. Overgrinding was minimized by limiting the grind time to 30 minutes and by removing the undersize by wet screening at 38 microns before returning the oversize for regrinding. The mineral charge was maintained at 500 g with a standard ball charge of 1200 g. Distilled water was used throughout the grinding and screening stages to avoid sample contamination. At the completion of grinding and wet screening, the accumulated screen undersize was allowed to settle for 24 hours. The supernatant was then drawn off and stored in nalgene containers until required for the microelectrophoresis studies.

Measurements of the electrokinetic properties of the various mineral substrates were made in the presence of a wide range of metal ions. Inorganic reagents used included aluminum chloride, ferric chloride, ferrous chloride, magnesium and calcium chloride, potassium bicarbonate and sodium fluoride. The method of preparation of the mineral suspensions, containing the ions of interest, varied with both the nature of the ion and the objective of the experiment. However, with the exception of tests with ferrous chloride, preparation of most cassiterite and quartz suspensions was based on the procedures outlined previously for both the mineral characterization and mineral-surfactant interaction studies. The key steps in the procedure were as follows:

1. A weighed amount of indifferent (KCl) electrolyte, together with 100 mls of mineral suspension stock solution, was added to a beaker. If required, the suspension was acidified with hydrochloric acid. An appropriate weight of inorganic reagent was then added and the suspension thoroughly
dispersed in an ultrasonics bath. The total volume was transferred to a volumetric flask and made up to 1000 mls with distilled water. For unleached and leached cassiterite suspensions, the final solids concentrations were 0.05 and 0.02 g litre$^{-1}$, respectively. For quartz suspensions, the solids concentration was 0.16 g litre$^{-1}$.

(2) The suspension was conditioned for 30 minutes in a water bath set at 23.5 °C. The initial pH of the solution was measured and recorded.

(3) Samples of 60 mls in volume were transferred from the volumetric flask and the pH adjusted to the test value using HCl or KOH as appropriate. The suspension was equilibrated at the test pH for 15 minutes. During this time, further acid or base was added as required.

(4) The electrophoresis cell was flushed with distilled water at 23.5 °C and the test suspension added.

(5) At the completion of the electrophoresis measurements, the pH was again measured. The test pH was considered to be the average of the initial and final pH values.

(6) Steps (3) through (5) were then repeated for each required test pH.

In tests where stannic dioxide was the required mineral substrate, the preparation procedure described previously (Section 3.5.3) was used. The powder was added directly to the beaker of step (1), in place of the mineral stock solution. The final solids concentration of the stannic dioxide suspensions was 0.03 g litre$^{-1}$. 
Based on the above procedure, only minor procedural changes were required to allow both surface nucleation and surface condensation (type II) tests to be performed. In the surface condensation (type II) tests, the suspension acidification of step (1) was omitted. The initial pH values of the suspensions then represented the inherent pH levels of the mineral-ion systems when prepared in distilled water. As such, they varied with the concentration of the inorganic reagent added. For all surface nucleation tests and for certain tests with the sodium fluoride, the stock solutions were acidified prior to inorganic reagent addition. In the surface nucleation tests, the level of the acid addition varied with the nature of the cationic salt since the objective was to ensure that the initial pH was below that corresponding to the stability constant of the cation first hydroxy complex (pK₁). In the fluoride ion tests, only small acid additions were required. The initial pH values of these suspensions were generally not below pH 3.2.

The preparation procedure for suspensions containing ferrous chloride was considerably more complex than that used for other ions. This was dictated by the need to minimize the oxidation of the ferrous ion prior to electrophoretic mobility measurements. In preparing such suspensions, a sealed pyrex electrochemical cell was used. Prior to both substrate and inorganic ion additions, the cell was partially filled with distilled water acidified with HCl to pH 2.5. A 100 ml volume of mineral stock solution was then added and the suspension purged with high purity argon supplied through a gas bubbler. After a 30 minute purging period, the ferrous chloride was added and the volume made up to a total of 1 litre. During subsequent pH adjustments and sample transfer to the microelectrophoresis cell, purging was maintained. The pH and the Eh of the suspensions in the cell were also continuously monitored.
by means of electrodes mounted in ports in the top of the cell. As for all work with inorganic ions, solution pH and Eh measurements were made using the equipment and measurement procedures described in detail in Section 3.4.5.

Electrophoretic mobilities of substrate particles, in suspensions containing inorganic ions, were measured using the previously described Zeta-Meter and Type II - UVA cell. Either bright platinum or molybdenum electrodes were used as appropriate, depending on the suspension conductivity. For work with the ferrous ion, a Zeta-Meter Automatic Sample Transfer (AST-83) unit was used. This allowed the continuous circulation of suspensions containing ferrous species between the electrochemical cell in which they were prepared and the microelectrophoresis cell. When measurements were required, the pinch clamp of the AST was activated. After checking both the microelectrophoresis cell alignment and the absence of colloid movement prior to voltage application, electrophoretic mobility measurements were made according to standard Zeta-Meter practice. In tests both with and without the AST, an average of at least 20 measurements were made at each test pH. When using the AST, adjustment of the suspension pH was by KOH addition directly to the electrochemical cell. The pH was increased in increments from its initial low value and measurements made at successively higher pH values. Between each pH adjustment, the suspension was continuously circulated between the microelectrophoresis and the electrochemical cells.

In determining the appropriate experimental procedure to use for each ion system, a correspondence between test procedure and actual industrial flotation was sought. Due regard was also paid to the forward and reverse kinetics of hydroxylation of cations. Thus, interactions between magnesium and calcium ion species and the cassiterite surface were studied exclusively.
by means of surface nucleation tests. This ensured that, at the initial pH of suspension preparation, the ions were not hydroxylated. Such would be the case in a plant environment, since cassiterite flotation pulps are typically slightly acidic in nature. In studies with aluminum ions, a surface condensation (type II) procedure was used. This reflected the fact that in only mildly acidic pulps the aluminum ion would be expected to undergo measurable hydroxylation. The iron system was considerably more complex. As such, both ferric chloride surface nucleation and surface condensation (type II) tests were performed for several different mineral substrates. Such tests indicated the relative kinetics of hydrous ferric oxide formation and resolubilization from mineral surfaces. Surface nucleation studies conducted with ferrous chloride allowed investigation of the ferrous ion to hydrous ferric oxide transition in the presence of a mineral substrate. For iron entering solution under the acidic and highly reducing conditions of ball mill grinding, such a transition is of fundamental importance.

Tests to establish the effect of sample drying on the electrophoretic mobilities of minerals exposed to aluminum and iron bearing solutions were also included in the research program. Unleached cassiterite suspensions containing $1 \times 10^{-4}$ M $\text{AlCl}_3\cdot6\text{(H}_2\text{O)}$ and $5 \times 10^{-5}$ M $\text{FeCl}_3\cdot6\text{(H}_2\text{O)}$, respectively, were prepared according to a surface condensation (type II) procedure. One half of each solution was then withdrawn and particle electrophoretic mobilities measured. The remaining portions were thermally dried at 120 °C for 24 hours. At the end of this period, the dried samples were redispersed in volumes of distilled water identical to those removed by drying and the microelectrophoresis measurements repeated. The results from such tests were found to be of key importance in the interpretation of the surface properties
of the original unleached cassiterite particles. The findings are believed also to have profound implications for all ex-situ test work involving adsorption of metal ionic species on mineral surfaces.

3.6.2 X-Ray Photoelectron Spectroscopy

To elucidate in greater detail the interactions between hydrous ferric oxide species, the fluoride ion and the cassiterite surface, X-ray photoelectron spectra of a number of substrates that had been in contact with these ionic species were obtained. All analyses were performed with the previously described Varian IEE-15 spectrometer, using unmonochromatized MgKα radiation (1253.60 eV) at 280 watts and an operating pressure of 10⁻⁷ Torr. The electron analyzer pass energy was 20 eV. Spectrometer instrumental resolution was 1.5 eV on the (4f)⁷/₂ peak of pure gold. In an identical manner to previous XPS analyses, each sample was lightly dusted onto 3M scotch tape covering a sample holder and introduced into the spectrometer on a rapid insertion probe. All binding energies were calibrated with reference to the carbon 1s peak (284.0 eV) of graphite. As a general rule, binding energy shifts of greater than 0.5 eV were considered significant.

Two series of XPS spectral analyses were performed. Both were designed to complement the results of the microelectrophoresis research. As such, the samples analyzed by XPS were subjected to solution chemical treatments identical to those that gave rise to significant charge reversal phenomena in the electrokinetic studies.

The first series of tests examined the surface character of a leached cassiterite sample exposed to a solution containing iron, under conditions where hydrous ferric oxide species were known to absorb on the mineral surface. The mineral suspension was prepared using ferrous chloride according
to the surface nucleation procedure of the microelectrophoresis test work. A 500 ml volume of acidified distilled water (pH 3.8) was contacted with 1.5 grams of the leached cassiterite in a sealed electrochemical cell. The suspension was purged with high purity argon for 30 minutes. After purging, an appropriate weight of FeCl$_2$.4(H$_2$O) was added to give a concentration of $1 \times 10^{-3}$ M. Base (KOH) and acid (HCl) were then added to adjust the pH to 6.0. Mineral solution contacting was maintained for 1 hour, during which time the pH and Eh were continuously recorded. The cassiterite was subsequently recovered using a spatula and repeatedly washed with distilled water. Washing was performed by transferring the cassiterite between successive 2.5 litre volumes of distilled water. In each volume, the mineral was dispersed ultrasonically for 15 minutes to remove loosely adhering iron sols. At the completion of the fifth such washing, the conductivity of the supernatant was found to have returned to the level of the original distilled water (1.7 $\mu$MHO). The cassiterite was then recovered and transferred to a vacuum dessicator. When dry, tin (3p)$_{3/2}$ and iron (2p)$_{3/2}$ XPS spectra were obtained using the Varian spectrometer.

The second series of tests involved analyses of unleached and pure stannic dioxide samples that had been exposed to identical fluoride ion bearing solutions. Initial contacting of the substrates was with 5x10$^{-4}$ M NaF solutions acidified with hydrochloric acid to pH 3.3. Both suspensions were agitated continuously for 2 hours and their pH maintained constant by appropriate acid (HCl) and base (KOH) additions. The Eh and the pH were recorded at 5 minute intervals. After 2 hours, the pH was increased to 5.5 and maintained constant for a further 20 minutes. The substrates were then recovered, washed and dried in a manner identical to that described for the
iron test. XPS spectra were recorded for binding energy ranges covering the fluorine (1s)\(_{1/2}\), tin (3p)\(_{3/2}\), tin (3d)\(_{3/2}\), tin (3d)\(_{5/2}\), iron (2p)\(_{3/2}\) and oxygen (1s)\(_{1/2}\) peaks. To assist in identifying the chemical environments of the core electrons from the chemical shifts of their binding energy peak positions, two further samples were analyzed. Fluorine (1s)\(_{1/2}\) XPS spectra were obtained for a high purity Aldrich ferric fluoride (FeF\(_3\)) reagent and the Fisher (A.C.S. certified) sodium fluoride used as the fluoride ion source in the aqueous solution treatment. In the case of the ferric fluoride, an iron (2p)\(_{3/2}\) spectrum was also obtained.

3.6.3 Leaching Tests

Leaching tests were conducted to determine the extent of abstraction of trace metal species from the surface of cassiterite in acidic solutions containing fluoride ions. Both thermodynamic and kinetic data were obtained on trace metal abstraction. All tests were designed to parallel those performed in the mineral characterization studies. In this way, it was found possible to assess the role of the fluoride ion in promoting the solubilization of metal ionic species from the cassiterite surface.

As described previously, leaching tests were conducted in glass vessels containing 2000 mls of distilled water and 5 grams of cassiterite. The pH was adjusted to the desired value by means of hydrochloric acid addition. Fluoride was added in the form of sodium fluoride. Both the pH and the Eh were measured using the experimental arrangement described in Section 3.4.5. During the course of leaching, the suspension was continuously agitated.

Trace metal analyses of leach liquors were performed by Atomic Adsorption Spectrometry (AAS) after Millipore membrane filtration at 0.45 \(\mu\)m to remove suspended solids. A Perkin-Elmer model 306 Atomic Absorption
Spectrophotometer with a conventional atomizer/burner system was used to analyze all solutions for Al, Fe, Mg and Ca. Acetylene-air and acetylene-nitrous oxide fuel-oxidizer combinations were used as appropriate. The calibration of the atomic absorption spectrophotometer was checked by means of standards with suitable matrix. Background trace element levels in laboratory distilled water were checked prior to all analyses.

Equilibrium data on trace metal abstraction were obtained from leaching tests conducted at constant pH for a total of 14 days. Such data were considered to correspond to equilibrium conditions as no measurable changes in ion concentrations were observed at longer time periods. Kinetic data were obtained from leaching tests performed for variable time periods at constant pH.
3.7 Surfactant-Ion Interactions

Many metal ionic species precipitate surfactants in aqueous solution. One of the most sensitive and widely used techniques for studying such phenomena is light scattering photometry. The utility of the technique lies in its ability to detect sharp increases in solution turbidity associated with the onset of precipitation (Matijevic, Kratohvil and Stickels, 1969; Peacock and Matijevic, 1980).

In this research, light scattering photometry was used to study the interactions between styryl phosphonic acid (Hoechst reagent P-184) and various metal ionic species. The ionic species investigated were those previously identified as being present in significant concentrations in cassiterite flotation pulps. Where appropriate, tests were conducted using combinations of ions

3.7.1 Light Scattering Photometry

Light scattering measurements were performed with the Brice Phoenix Model 2000 Universal light scattering photometer described in detail in Section 3.3.7. A green filter combination was again used and all data were obtained at the 546 nm wavelength of the mercury spectrum. This avoided the need to correct light scattering ratios for solution colouration or absorption.

Turbidities of 30 ml aliquots of test solutions were determined directly in the photometer using a Brice Phoenix type T-101 cell. Cleaning of the cell was performed after each analysis with a nitric acid-ethanol mixture followed by washing with copious amounts of distilled water. A minimum of five turbidity measurements were made for each solution. Data showing deviations of more than a few percent were rejected. Individual turbidities were calculated from the relative intensities of transmitted light and light
scattered through 90° using the Rayleigh light scattering equation also presented in Section 3.3.7.

The inorganic reagents used as sources of metal cations in the light scattering studies were the chloride salts of the aluminum, ferric, ferrous, magnesium and calcium ions. Sodium fluoride was used as a source of the fluoride ion. For each of the metal ionic species, turbidity measurements were made for a range of concentrations at a fixed pH. Data were also obtained for different pH values at constant inorganic reagent concentrations.

The fixed pH value used in all the concentration dependence tests, except those with the ferrous ion, was pH 5.0. This value was selected on the basis that actual cassiterite flotation pulps are buffered frequently near this pH. For turbidity-concentration tests with the ferrous ion, the pH was maintained constant at pH 1.5. The highly acidic nature of these solutions minimized the extent of oxidation of the ferrous ion to the ferric ion state. Ferrous ion oxidation is well known to be kinetically very slow in acidic solutions (Leja, 1982). Dissolved metal ionic species concentrations, at the fixed pH values, were typically varied between 1x10^{-6} M and either 1x10^{-3} M or 1x10^{-2} M. The selection of the upper concentration level depended on the cation type. Aluminum and iron species tended to produce voluminous precipitates at pH 5.0 with correspondingly high solution turbidities. In contrast, magnesium and calcium chloride solutions, at concentrations as high as 1x10^{-2} M, frequently had turbidities not significantly greater than that of distilled water. In all tests, the preferred styryl phosphonic acid concentration was 1x10^{-4} M. The selection of this surfactant concentration was based on its correspondence with the attainment of maximum cassiterite recoveries in microflotation testing.
In the pH dependence tests, an inorganic ion concentration of $1 \times 10^{-4}$ M was used for the aluminum and ferric ion test work. A higher concentration of $1 \times 10^{-2}$ M was used for light scattering studies with magnesium and calcium chloride. Both ion species concentrations were chosen on the basis of their correspondence with plant water ion levels and the existence of measurable turbidities when $1 \times 10^{-4}$ M styryl phosphonic acid was added. In test work with the fluoride ion, a sodium fluoride concentration of $6 \times 10^{-4}$ M was used.

The solution preparation procedures for the concentration dependence tests differed from those used in the variable pH analyses. In the former case, a 2 litre solution, usually of $2 \times 10^{-2}$ M concentration with respect to its cation concentration, was used as a common parent stock solution. This solution was prepared by transferring distilled water to a 2 litre volumetric flask, adjusting the water pH to the test value, and then adding the required weight of metal ion salt. For each ion concentration of interest, appropriate aliquots of the stock were then pipetted into each of two 100 ml volumetric flasks. To one flask was added an appropriate volume of styryl phosphonic acid solution. Both flask volumes were then made up to a total of 100 mls with distilled water. These individual test solutions were subsequently transferred to beakers and the pH checked. Each solution was allowed to equilibrate for 30 minutes, during which time hydrochloric acid or potassium hydroxide was added as appropriate. Light scattering measurements were made immediately after the equilibration period. By using such a procedure, direct comparisons between the turbidities of ion solutions with and without styryl phosphonic acid could be made. All suspensions were prepared at one time, in an identical manner, from a common parent stock solution.

In the pH dependence tests, a 2 litre stock solution, acidified if
necessary, was prepared initially also. However, the concentration of this solution was only twice the desired test value. As such, for the AlCl₃·6(H₂O) and FeCl₃ test work, the stock concentration was only 2x10⁻⁴ M as opposed to 2x10⁻² M for the concentration dependence studies.

Preparation of solutions of constant ion concentration but differing pH involved withdrawing two 250 ml volumes from the original stock solution. To one volume was added surfactant. Both volumes were then made up to 500 ml and allowed to equilibrate for 30 minutes. After this period, the pH of each was recorded and denoted as the initial solution pH (pH₄). From each of the 500 ml volumes, 50 ml volumes were transferred to beakers using pipettes. Beaker solution pH values were then adjusted to each of the desired test values using hydrochloric acid or potassium hydroxide as appropriate. After a further 30 minute pH adjustment and equilibration period, solution turbidities were measured using the Brice Phoenix photometer. In this manner, it was again ensured that each of the different pH test solutions had a common parent solution. Furthermore, where solutions containing combinations of ions were required, the procedure was modified simply by adding both ion entities to the initial 2 litre stock solution.

The use of differing preparation procedures for the constant concentration and constant pH test solutions allowed light scattering analyses to be performed rapidly. It also ensured correspondence within individual data sets. However, during the course of the research, small variations were noted between the turbidities of identical ion concentration solutions prepared according to the different methods.

In the published literature, different methods of preparation of ion species solutions are well recognised as frequently giving rise to
intrinsically different solution physical properties (Sylva, 1972). In particular, the nature of polymeric hydrous oxide sols is known to be dependent on parameters such as the initial solution total ionic strength (Strahm, Patel and Matijevic 1979; Segal, 1984, 1984a) and the hydroxyl/cation ratio (Dousma and de Bruyn, 1978; de Hek, Stol and de Bruyn, 1978). In the surfactant-ion interaction research, both of these factors varied with the method of solution preparation. As such, the observed solution turbidity variations most probably reflected differences in the nature of sols present in solutions formed at different initial concentrations but subsequently diluted to the same concentration level.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Mineral Characterization

4.1.1 Mineralogical and Chemical Analyses

Plate 3 shows a photograph of mounted and polished cassiterite grains. The grains appear grey in colour against the mounting resin. Dark spots in the photograph represent pits in the resin surface produced during polishing. The cassiterite grains themselves also exhibit some colour zoning. This is believed to be characteristic of all cassiterite minerals. Uytenbogaardt and Burke (1971) state that cassiterite generally appears brownish grey in colour under a light microscope but can vary from deep red-brown to almost colourless. Darker cassiterite is generally associated with higher iron content.

No free grains, that could be unequivocally identified as impurity minerals, were evident in the polished sample. For a small number of grains, some particle intergrowths were noted. In plates 4 and 5, the cassiterite grains in the centre of the photographs show pyrrhotite and arsenopyrite occlusions. The pyrrhotite appears cream in colour with a faint pinkish-brown tint. The arsenopyrite is more intensely white with a faint pinkish tint. Under the light microscope, the arsenopyrite was readily identified by the absence of internal reflections. Detailed examinations of Plates 3 to 5 reveal other colour variations within grains. However, these could not be identified definitively as separate mineral phases as opposed to cassiterite grains exhibiting colour zoning.
Plate 3 - Photomicrograph of Cassiterite Grains Used in the Research.
(Magnification 160 X)
Plate 4 - Photomicrograph Showing a Cassiterite Grain with a Pyrrhotite Intergrowth. The grain is located in the centre of the plate. (Magnification 320 X)
Plate 5 - Photomicrograph Showing a Cassiterite Grain with an Arsenopyrite Intergrowth. The grain is located in the centre of the plate. (Magnification 320 X)
The photomicrographs shown in Plates 3 to 5 confirm the high purity of the cassiterite sample. Few grains exhibited definite particle intergrowths. In identifying the grains with occlusions that are shown in Plates 4 and 5, a considerable time period was spent scanning the polished specimen. It is estimated that particles containing distinct occlusions represented less than 1 in 10,000 of the total number of grains examined.

Considerable variation in cassiterite grain size is evident in all three of the micrographs presented. Based on the optical magnifications of 160 X and 320 X used, particle diameters ranged from 63 to 3 micron. The majority of particles tended to be in the 15 to 40 micron range. The particle intergrowths that were observed also varied considerably in size. The pyrrhotite intergrowth shown in Plate 4 is approximately 6 microns in diameter. In Plate 5, the arsenopyrite intergrowth is of the order of 16 microns.

The high purity of the cassiterite used in the research was further confirmed by chemical analyses (Table XI). As received, the sample assayed 75.0 % Sn. After upgrading, wet chemical analysis gave an assay of 75.8 % Sn. In pure stannic dioxide tin represents 78.8 percent by weight. The upgraded sample was therefore 96.2 % SnO₂, as determined by direct analytical tin determination.

The major impurity in the unleached cassiterite was iron. This element was present at the 0.75 % level. Numerous other elements were present in the cassiterite at less than the 0.2 % level. The most notable of these were titanium, calcium, tungsten, magnesium and bismuth. Based on the analytical determinations of all detectable impurity elements, the cassiterite was 98.7 percent SnO₂. The difference between this determination and the tin based
TABLE XI
CASSITERITE WET CHEMICAL AND INDUCTIVELY COUPLED ARGON PLASMA (ICAP) ANALYSES

<table>
<thead>
<tr>
<th>Wet Chemical</th>
<th>Inductively Controlled Argon Plasma Analyses <em>(ppm)</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin Analysis</td>
<td></td>
</tr>
<tr>
<td><strong>%Sn</strong></td>
<td><strong>Cu</strong>  <strong>Pb</strong>  <strong>Zn</strong>  <strong>Mn</strong>  <strong>As</strong>  <strong>Bi</strong>  <strong>La</strong>  <strong>B</strong>  <strong>W</strong>  <strong>Mg</strong>  <strong>Fe</strong>  <strong>Ca</strong>  <strong>P</strong>  <strong>Ti</strong>  <strong>Al</strong>  <strong>Na</strong>  <strong>K</strong></td>
</tr>
<tr>
<td>As-Received</td>
<td>75.0</td>
</tr>
<tr>
<td>Cassiterite</td>
<td></td>
</tr>
<tr>
<td>Up-Graded</td>
<td>75.8</td>
</tr>
<tr>
<td>Cassiterite</td>
<td>285  86  43  323  366  415  34  14  655  500  7500  800  500  1500  300  100  100</td>
</tr>
<tr>
<td>Leached</td>
<td></td>
</tr>
<tr>
<td>Up-Graded</td>
<td>—</td>
</tr>
<tr>
<td>Cassiterite</td>
<td>50  &lt;10  &lt;10  100  &lt;10  &lt;10  10  &lt;10  200  10  &lt;10  &lt;10  1000  10  &lt;10  &lt;10</td>
</tr>
</tbody>
</table>

*Mo, Ag, Ni, Co, U, Th, Sr, Cd, Sb, V, Cr and Ba were sought but were below the detection limit of 10 ppm.*
value reflects the errors inherent in analyzing high purity minerals.

After acid leaching, analyses of the cassiterite indicated a number of remarkable changes. As shown in Table XI, leaching reduced the concentrations of certain impurity elements to levels far below those in the unleached sample. The most notable decreases were for iron (7500 ppm to 10 ppm) and tungsten (655 to < 10 ppm). Other elements, such as calcium, arsenic, bismuth and magnesium, were reduced appreciably also. In contrast, the level of titanium associated with the cassiterite was diminished much less significantly.

Cassiterite is an extremely insoluble mineral. Presumably only the first few monolayers of the crystal structure are extensively disrupted and solubilized by acidic solutions. The metallic impurities extensively removed by leaching, therefore, both must have been exposed widely to the acidic solution and present in a form that was readily solubilized. Such might have been the case for impurities in the form of either exposed occlusions or surface impurities. Inclusion elements, randomly occupying sites in the cassiterite lattice normally occupied by tin ions, would be expected to have been far less susceptible to leaching. The inability of leaching to reduce the titanium levels in the cassiterite to the extent found for other metal ions is most likely due to the titanium being present primarily as an inclusive species. The stannic and titanium ions both have the same charge and are of similar size (Weast and Astle, 1983). Inclusions are well known to be more prevalent in a mineral when the impurity ion has a similar size and charge to a lattice ion (Harris, 1982).
4.1.2 Infrared and X-Ray Diffraction

Infrared spectra for Aldrich "Gold Label" stannic dioxide, leached and unleached cassiterite are shown in Figure 86. Band assignments for the major peaks in the spectra are given in Table XII. Comparison of the spectra indicates that the overall peak correlation is excellent. Furthermore, the major infrared bands observed correspond with band assignments reported in the literature for cassiterite (Table XII). The infrared analyses unequivocally confirm that the research mineral was cassiterite.

### TABLE XII

STANNIC DIOXIDE AND CASSITERITE INFRARED BANDS

<table>
<thead>
<tr>
<th>Band Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2^{2-}$ in-plane vibration</td>
<td>Farmer (1974)</td>
</tr>
<tr>
<td>SnO$_2^{2-}$ out-of-plane vibration</td>
<td>Farmer (1974)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Band</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1097</td>
<td>1089 w</td>
<td></td>
</tr>
<tr>
<td>670 sh</td>
<td>683 sh</td>
<td>683 sh</td>
</tr>
<tr>
<td>616 s,b</td>
<td>650 s,b</td>
<td>641 s,b</td>
</tr>
<tr>
<td>515 m,b,sh</td>
<td>513 m,b,sh</td>
<td>513 m,b,sh</td>
</tr>
<tr>
<td>296 m</td>
<td>295 m</td>
<td>300 m</td>
</tr>
</tbody>
</table>

s = strong, m = medium, w = weak
b = broad, sh = shoulder
Figure 86 - Infrared Spectra of Aldrich "Gold Label" Stannic Dioxide, Leached and Unleached Cassiterite.
All three of the tin oxide spectra shown in Figure 86 are dominated by a sharp peak near 300 cm\(^{-1}\) and a broad band extending from 550 to 700 cm\(^{-1}\). The peak at 300 cm\(^{-1}\) can be assigned to the out-of-plane \(O^2-\) vibration of the cassiterite lattice. The higher wavenumber band is due to the corresponding \(O^2-\) in-plane vibration (Farmer, 1974).

Associated with the broad \(O^2-\) in-plane vibrational band is a series of shoulder peaks. The most pronounced such peak is that at approximately 513 nm. In his compilation of mineral infrared spectra, Gadsden (1975) lists a medium intensity, very broad shoulder band at 512 nm as a characteristic cassiterite vibration but makes no assignment. Reference to the lattice vibration tabulations (Table II) of Katiyar et al (1971), indicate that a band at 513 cm\(^{-1}\) most closely corresponds to the \(B_{1u}\) vibrational mode at 505 cm\(^{-1}\). However, this mode is not known to interact directly with electromagnetic radiation (Summitt, 1968). While, therefore, presumably not a fundamental vibration, the band could be an overtone, combination or a difference band. Its appearance in all three spectra (but not in blank KBr pellets) and the reference to it by Gadsden is considered to preclude the possibility that the band is due to an impurity.

The other prominent peaks occurring in all three tin oxide spectra are the broad bands extending from 3150 to 3650 cm\(^{-1}\) and those near 1640 cm\(^{-1}\). These absorption bands are due to the oxide surface hydroxyl groups and molecular water. The O-H stretching vibrations of the water molecule produce a very broad and intense band near 3400 cm\(^{-1}\). The O-H stretching vibrations of surface OH groups lead to narrower bands in the same region but these are generally obscured by the more intense water bands (Thornton and Harrison, 1975). Absorption bands near 1640 cm\(^{-1}\) are due to the H-O-H bending...
vibrations of molecular water (Bellamy, 1962).

The wavelengths, relative intensities and shapes of absorption bands in the leached and unleached cassiterite spectra are essentially indistinguishable. In comparing these spectra with that of the stannic dioxide powder, a number of differences in the fine structure of some peaks can be identified. Notable in the stannic dioxide spectrum is that the out-of-plane $O^{2-}$ lattice vibration appears as a pair of peaks. In the mineral spectra only a single peak is observed. Similarly, the broad peak of the in-plane $O^{2-}$ vibrations differs in fine structure. However, this variation might be, to some degree, an artefact. The Perkin-Elmer 283 B spectrometer has a particularly pronounced grating change at 600 cm$^{-1}$. Scans of blank pellets invariably produce spectra that show small asymmetric peaks near this wavenumber. Interpretation of any fine peak structure in this range, therefore, appears at best tenuous. For example, the apparent shoulder peaks at 598 cm$^{-1}$ and 597 cm$^{-1}$ for the leached and unleached cassiterite and the maximum near 616 cm$^{-1}$ in the stannic dioxide spectrum might all be due to artifacts of the grating change.

The most significant difference between the stannic dioxide and the mineral spectra of Figure 86 is the existence in the latter of a very weak, broad peak centred around 1090 cm$^{-1}$. No reference to such a peak is made in publications on cassiterite spectra. However, this might be due simply to its weak nature. It is conceivable for a band near 1090 cm$^{-1}$ to be a weak overtone or combination band since it exists at approximately twice the frequency of the strong lattice fundamental vibrations. An alternative possibility is that the band is due to elemental inclusions in the lattice of the natural cassiterites. However, the absence of reported data for such
vibrations as Sn–O–Ti precludes a definitive assignment. Similarly, it is
difficult to assign such a band to the presence of contaminants since no other
extraneous peaks are evident. Specifically, the characteristic peaks of
hydrocarbons, such as those due to the strong C–H vibrations, are completely
absent. One inorganic species that could account for a band near 1090 cm\(^{-1}\) is
the sulphate ion \(\text{SO}_4^{2-}\). According to Socrates (1980) this ion has two
characteristic vibrations producing a strong broad band at 1130–1180 cm\(^{-1}\) and
a less intense band at 680 – 650 cm\(^{-1}\). This latter band would be expected to
be obscured by the strong in-plane \(\text{O}_2^–\)-cassiterite lattice vibration leaving
only the higher frequency band visible in the spectrum.

The absence of hydrocarbon peaks in the leached and unleached cassiterite
spectra is of significance since the as supplied sample had been subject to
grinding and sulphide flotation in the presence of xanthates. Within the
limits of the infrared detectability, it can be concluded that no adsorbed
hydrocarbon reagents were present on the surfaces of the samples. Similarly,
there is no evidence for the introduction of hydrocarbon contaminants during
sample preparation.

X-ray diffraction patterns for stannic dioxide, leached and unleached
cassiterite are presented in Figures 87 and 88. Interplanar spacings,
determined from the experimental data, are compared with published values in
Table XIII. For all three tin oxides, the only lines observed in the
diffraction patterns are those reported for cassiterite. No extraneous peaks
exist. All three samples were, therefore, of high purity. Occluded particles
were not present at levels that could be detected by X-ray diffraction.
Figure 87 - Diffraction Patterns of Stannic Dioxide, Leached and Unleached Cassiterite Particles for the Region $2\theta = 20^\circ - 60^\circ$. Numbers above peaks are $d$ values in Angstrom units.
Figure 88 - Diffraction Patterns of Stannic Dioxide, Leached and Unleached Cassiterite Particles for the Region $2\theta = 60^\circ - 100^\circ$. Numbers above peaks are d values in Angstrom units.
<table>
<thead>
<tr>
<th>Aldrich &quot;Gold Label&quot;</th>
<th>Leached</th>
<th>Unleached</th>
<th>Published Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stannic Dioxide</td>
<td>Cassiterite</td>
<td>Cassiterite</td>
<td>(Berry, 1974)</td>
</tr>
<tr>
<td>d (Å)</td>
<td>I/I₁</td>
<td>d (Å)</td>
<td>I/I₁</td>
</tr>
<tr>
<td>3.33</td>
<td>100</td>
<td>3.35</td>
<td>100</td>
</tr>
<tr>
<td>2.634</td>
<td>83</td>
<td>2.642</td>
<td>90</td>
</tr>
<tr>
<td>2.360</td>
<td>22</td>
<td>2.363</td>
<td>30</td>
</tr>
<tr>
<td>2.296</td>
<td>5</td>
<td>2.302</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.116</td>
<td>3</td>
</tr>
<tr>
<td>1.760</td>
<td>65</td>
<td>1.762</td>
<td>86</td>
</tr>
<tr>
<td>1.668</td>
<td>15</td>
<td>1.672</td>
<td>25</td>
</tr>
<tr>
<td>1.589</td>
<td>6</td>
<td>1.591</td>
<td>7</td>
</tr>
<tr>
<td>1.496</td>
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<tr>
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<tr>
<td>1.411</td>
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</tr>
<tr>
<td>1.319</td>
<td>6</td>
<td>1.320</td>
<td>12</td>
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<tr>
<td></td>
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<td>1.318</td>
</tr>
<tr>
<td>1.213</td>
<td>9</td>
<td>1.214</td>
<td>15</td>
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<td></td>
<td></td>
<td></td>
<td>1.212</td>
</tr>
<tr>
<td>1.181</td>
<td>3</td>
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<td></td>
<td>1.181</td>
<td>6</td>
</tr>
<tr>
<td>1.152</td>
<td>7</td>
<td>1.153</td>
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<td></td>
<td>1.151</td>
<td>4</td>
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<tr>
<td>1.116</td>
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<td>1.114</td>
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<td>7</td>
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<tr>
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<td>4</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>1.033</td>
<td>6</td>
</tr>
</tbody>
</table>
Detailed inspection of Table XIII shows that all the experimental interplanar spacings (d) and line intensities (I/I₀) are remarkably consistent with the published data. For the unleached cassiterite sample, all calculated d values are within ± 0.004 Å of the reported values. Intensity correlations are excellent. The diffraction pattern of leached cassiterite shows slightly higher interplanar spacing and intensity variations. High d values (d > 1.5 Å) in the pattern are within ± 0.007 Å of reported values. For lower d values, the difference is generally less than 0.002 Å. While overall intensity correlations are still good, some pronounced changes, relative to both the unleached cassiterite pattern and the data reported by Berry (1974), are evident. The line intensities corresponding to the (211) and (101) planes, in particular, are much stronger relative to the line of the (100) plane than reported by Berry or found in either the unleached cassiterite or stannic dioxide patterns. The change in peak intensities might reflect the effects of acid leaching on certain exposed crystal planes.

In the Aldrich "Gold Label" stannic dioxide diffraction pattern, interplanar spacings differ from the reported values more than observed for the natural cassiterite samples. These variations are most pronounced at higher d values but do not exceed 0.01 Å. For lower d values the variations are generally less than 0.002 Å. In comparison to the natural cassiterites, the stannic dioxide line intensities correlate with the literature values to a higher degree. The most notable variation is that the very weak line at 2.120 Å is missing.

Critical comparison of the actual diffraction patterns in Figures 87 and 88 reveals two further differences between the patterns of the stannic dioxide and the natural cassiterites. In the former, all lines are very broad. In
contrast, the lines in the latter patterns are considerably more sharp and, at higher interplanar spacings, show clear evidence of being split into pairs.

It is well documented that line broadening occurs with very small particle size, lattice distortions, or both (Klug and Alexander, 1974). The presence of poorly crystalline material can also give rise to broad diffraction lines. Fluctuations in diffractometer intensities, such as line splitting, are generally due to the presence of coarse crystalline particles. Particles above 20 micron in size can cause intensities to fluctuate sharply as a function of the orientation of the larger crystal grains (Klug and Alexander, 1974). The observed differences in the diffraction patterns, therefore, can be explained on the basis of the relative particle sizes of the stannic dioxide powder and the natural cassiterite grains. In the former sample, it is also possible that a higher degree of lattice distortion or more poorly crystalline material was present.

4.1.3 Size and Surface Area Analyses

The stannic dioxide used in the research was supplied by Aldrich in the form of aggregates of very fine powder. From an experimental perspective, such coarse particles were of little use as reference material for mineral characterization. They were both of a size too large for bulk chemical and surface analyses and too readily degraded during handling. To produce a powder of more suitable size, the aggregates were broken down by grinding.

Figure 89 shows the size distribution of ground Aldrich stannic dioxide. The distribution is characterized by its broad nature and its complex form. The latter property is believed due to the original sample being composed of aggregated fines. While these original aggregates were of the order of millimetres in size, individual crystallite grains were presumably of mean
size near four microns. The products of aggregate degradation were, therefore, smaller aggregate particles of approximately 40 microns top size and fine powder particles approaching the individual crystalline size. Such a mixture of particles would account for the broad nature of the size distribution in Figure 89, its strongly negatively skewed nature and the existence of some bimodal character.

The log mean size of the ground stannic dioxide, calculated from the distribution in Figure 89, is 10.68 micron. The mode and the median sizes are 18.15 and 11.99, respectively (Table XIV). Consistent with the fine nature of the sample, as indicated by these distribution parameters, the specific surface area of the sample, determined by the BET method, was found to be 31.59 m²/g (Appendix E).
### TABLE XIV

**STANNIC DIOXIDE AND CASSITERITE SIZE ANALYSIS AND SURFACE AREA DATA**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Log Mean Size (μm)</th>
<th>Mode Size (μm)</th>
<th>Median Size (μm)</th>
<th>Specific Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich &quot;Gold Label&quot; Stannic Dioxide</td>
<td>10.68</td>
<td>18.15</td>
<td>11.99</td>
<td>31.59</td>
</tr>
<tr>
<td>Leached Cassiterite</td>
<td>26.84</td>
<td>39.70</td>
<td>30.82</td>
<td>0.166</td>
</tr>
<tr>
<td>Unleached Cassiterite</td>
<td>24.48</td>
<td>34.58</td>
<td>30.12</td>
<td>0.192</td>
</tr>
<tr>
<td>Decantation Supernatant</td>
<td>2.56</td>
<td>3.01</td>
<td>2.68</td>
<td>—</td>
</tr>
</tbody>
</table>

In comparison to the stannic dioxide, the leached and unleached cassiterite samples were much coarser and more closely sized. The size distributions of these samples (Figures 89 and 90) are slightly negatively skewed and have maxima near 35 microns. A sharp cut-off exists at 38 microns which was the aperture size in the screening stage of sample preparation. The majority of particles in both samples had sizes between this upper limit and 10 microns. Less than 10 percent of all particles were smaller than 10 microns in size in the cassiterite samples.

Reference to the distribution parameters calculated from the cassiterite sizings (Table XIV), indicates that the leached cassiterite was coarser than the unleached cassiterite. Furthermore, the specific surface area of the leached sample was less than that of the unleached sample (Table XIV-Appendix E). Both of these changes were almost certainly due to the removal of colloidal cassiterite particles during the leach liquor replacement and sample washing stages of the leaching process. There is no evidence for any substantial chemical degradation of the cassiterite during leaching.
Figure 90 - Size Distributions of Leached and Unleached Cassiterite (Volume Basis).

During the preparation of the unleached cassiterite sample, beaker decantation was used to remove colloidal particles at a nominal cut-size of 4 microns. This lower cut size is not pronounced in Figure 90 due to the small percentage of fine particles in the sample and the use of exponential functions in Electrozone sizings to model the tails of size distributions. The success of the beaker decantation sizing, however, can be seen in the size distribution of the decant fraction (Figure 91). Clearly evident in this distribution is an upper cut size near 4 microns. On a volume size basis, more than 80 percent of the decant sample was less than 4 microns while less than 4 percent was greater than 7 microns. The log mean, mode and medium sizes calculated from the distribution in Figure 91 are 2.50, 3.01 and 2.68 microns, respectively.
4.1.4. Scanning Electron Microscopy and Microprobe Analyses

Figure 92 shows the scanning electron microscope EDX spectra of two individual unleached cassiterite grains. As expected, the characteristic X-ray emissions of tin dominate both spectra. In full scans from 1 keV to 20 keV, the only other elements found to be present were silicon and iron. The silicon counts for one grain were only just above background as shown in the upper spectrum of Figure 92. In the other, the counts were higher but not at a level where the silicon could be considered present above trace. In the case of iron, the relative peak intensities of the spectra in Figure 92 are consistent with the element being present at significantly above background but not exceeding two percent.
Figure 92 - SEM/EDX X-Ray Spectra of Typical Unleached Cassiterite Grains.
No information on the form of the iron or silicon associated with the cassiterite grains is available from the emission spectra. The information provided represents a bulk chemical analysis of the individual grains. The area scanned by the electron microscope covered the entire exposed surface of the grains and the depth of emission of the X-rays was of the order of microns. As such, it is impossible to conclude whether the impurities are localized in the cassiterite, uniformly distributed throughout the mineral lattice or present on the surface of the grains.

The X-ray spectra shown in Figure 92 are considered typical of the major portion of all those observed during electron microscope analyses. In most grains, no evidence for impurity elements, other than iron and silicon, was found. Scanning of numerous grains failed to indicate the presence of frequently reported lattice impurities, such as tantalum, at levels exceeding the background. Only in a very small number of grains were additional impurities found.

Figure 93 shows the X-ray spectrum of an unleached cassiterite grain containing a tungsten impurity. The characteristic X-ray emissions of tungsten are clearly evident at 8.42, 9.72, and 9.98 keV. Both iron and silicon peaks also appear in the spectrum. The relative peak heights of these elements indicates them to be present at levels higher than found in more typical cassiterite grains (Figure 93). In the case of iron, this is confirmed by the appearance of the additional Fe (Kα) peak at 7.04 keV. Under the scanning electron microscope no definite impurity phase, that could account for the elements observed in the spectrum, was visible. However, electron microprobe line scans and X-ray images (Plate 6) showed the presence of a small 3 micron iron-tungsten occlusion in the grain.
Figure 93 - SEM/EDX X-Ray Spectrum of an Unleached Cassiterite Grain Containing a Tungsten Impurity.

In Plate 6, tungsten line scans, shown superimposed on the cassiterite absorbed electron image, indicate a concentration of tungsten in the top left hand corner of the grain. Associated with the tungsten is a concentration of iron. This element is also present throughout the grain at a level appreciably above background. Presumably, the iron is present both in association with the tungsten as an occlusion and as a cassiterite lattice inclusion. As expected, the tin distribution is uniform. In microprobe elemental scans, silicon was found not to be present above background. The absorbed electron image of the grain itself shows no distinguishable impurity phase. The light areas on the image (Plate 6) are blebs of resin. The inability to detect any evidence of an occlusion in the absorbed electron image is consistent with the small size of the iron and tungsten
Plate 6 - Electron Microprobe Line Scans and X-Ray Images Showing the Distributions of Tin, Iron and Tungsten in an Unleached Cassiterite Grain. The tungsten line scans are superimposed on the absorbed electron image.
concentrations found in the X-ray elemental scans. It is also conceivable that the occlusion indicated in the latter was at depth and not exposed at the grain surface.

The SEM/EDX spectrum and microprobe X-ray images of the most mineralogically complex grain found in the leached cassiterite are shown in Figure 94 and Plate 7, respectively. In this grain, two distinct intergrowths were found. The first was that of an iron sulphide species approximately 14 microns in size. This occlusion produced the characteristic iron and sulphur X-ray emissions seen in the EDX spectrum. In the microprobe iron distribution image (Plate 7), the occlusion is evident as the area of very high concentration slightly to the left of centre. The second intergrowth was that of an iron silicate containing some aluminum. This phase is shown clearly in the upper right hand corners of the silicon and iron distribution mappings in Plate 7. The X-ray peaks corresponding to silicon, iron and aluminum can be distinguished readily in the EDX spectrum.

![Figure 94 - SEM/EDX X-Ray Spectrum of a Mineralogically Complex Unleached Cassiterite Grain.](Image)
Plate 7 - Electron Microprobe X-Ray Images Showing the Distributions of Tin, Iron, Aluminum and Silicon in a Mineralogically Complex Unleached Cassiterite Grain.
In addition to the elements shown by the microprobe to be associated with the two impurity phases in the complex cassiterite grain, the SEM/EDX analyses indicated the presence of arsenic and manganese (Figure 94). Both of these elements are believed associated with the two particle intergrowths. However, the nature of the associations could not be determined with the microprobe. If the arsenic was present in the iron sulphide phase, the occlusion was presumably arsenopyrite.

4.1.5. Surface Analyses

4.1.5.1 Secondary Ionization Mass Spectroscopy

Static SIMS spectra for Aldrich stannic dioxide, leached and unleached cassiterite are shown in Figures 95 to 98. All spectra are for an Ar$^+$ beam of 5 kV and an ion current density of $3 \times 10^{-7}$ A/cm$^2$. At this ion density, the mineral consumption was of the order of $10^{-3}$ monolayers per second (Blaise, 1976). The recording time for all spectra was 300 seconds. In the period of accumulation of counts, the mineral consumption was, therefore, equivalent to approximately one percent of a monolayer. The raster size for the Ar$^+$ beam static spectra was 800 microns. As such, it encompassed an area occupied by a large number of mineral grains.

The positive SIMS spectrum of Figure 95 confirms the very high purity of the Aldrich "Gold Label" stannic dioxide. The only surface impurities present in the static spectrum are lithium and sodium. The first of these elements was identified, during the course of the research, as an impurity in the indium foil used to mount the stannic dioxide. Lithium is not considered to have been present in the stannic dioxide at a detectable level. The sodium identified in Figure 95 was associated with the oxide but represents only a trace level. The sputtering yield of sodium is more than two orders of
Figure 95 - Positive SIMS Spectrum of Aldrich "Gold Label" Stannic Dioxide (Ar\(^+\) beam = 3 × 10\(^{-7}\) A/cm\(^2\) at 5 kV; raster size = 800 μm).

Figure 96 - Negative SIMS Spectrum of Aldrich "Gold Label" Stannic Dioxide (Ar\(^+\) beam = 3 × 10\(^{-7}\) A/cm\(^2\) at 5 kV; raster size = 800 μm).
Figure 97 - SIMS Spectrum of Leached Cassiterite (Ar⁺ beam = 3 x 10⁻⁷ A/cm² at 5 kV; raster size = 800 µm).

Figure 98 - SIMS Spectrum of Unleached Cassiterite (Ar⁺ beam = 3 x 10⁻⁷ A/cm² at 5 kV; raster size = 800 µm).
magnitude higher than for tin (Newbury, 1977). As such, its atomic concentration in the stannic dioxide is extremely low.

The principal ion fragments observed in the negative SIMS spectrum of Aldrich "Gold Label" stannic dioxide (Figure 96) are $^{16}\text{O}^-$ and $^{17}\text{OH}^-$. These ions were presumably from the cassiterite lattice oxide anions and chemisorbed water molecules on the oxide surface. Fluorine, sulphur and chlorine just can be detected in the spectrum. The levels of these species on the surface of the oxide is considered infinitesimal.

In comparison to the stannic dioxide spectrum, the positive SIMS spectra of unleached and leached cassiterite (Figures 97 and 98) indicate additional surface impurities to have been associated with the natural cassiterite. Iron, calcium, potassium and aluminum can be detected at various levels in the two spectra. Like sodium, aluminum and potassium have sputtering yields over two orders of magnitude higher than that of tin. Similarly, the sputtering ion yield of iron is of the order of 35 times that of tin (Newbury, 1977). The levels of sodium, aluminum and potassium surface contaminants in both cassiterites were, therefore, not high. The most prevalent surface impurity was the iron.

Direct comparisons of impurity element peak intensities in the SIMS spectra of leached and unleached cassiterite are not strictly possible. It cannot be assumed that the rastered areas over which counts were obtained for the different samples contained the same number of particles. However, an estimate of comparative impurity levels can be gained from the actual ion counts recorded during the static SIMS analyses. For both cassiterites, the $^{16}\text{O}^-$ and $^{120}\text{Sn}^+$ counts were of the same order of magnitude. However, the ratio of $^{56}\text{Fe}^+$ to $^{120}\text{Sn}^+$ was remarkably different. For the leached sample,
the ratio was 2.66:1 while that for the unleached sample was 14.52:1. The important implication is that the unleached cassiterite had a surface iron level considerably in excess of that present after acid leaching. Similarly the level of aluminum and calcium on the surface of the unleached sample greatly exceeded that after leaching.

Figure 99 shows the static SIMS spectrum of the same unleached cassiterite area as in Figure 98 after sputtering for 75 minutes with a 5 kV Ar⁺ beam at a 1.4 x 10⁻⁵ A/cm² ion current density. Under such conditions, the sputtering rate would have been of the order of 50 Å / min (McHugh, 1975). As such, the spectrum represents an analysis of bulk mineral lattices. Aluminum can be seen to have been present at depth in the grains although at an extremely low atomic concentration. Significantly, iron was still detected at appreciable levels. Sodium is ubiquitous in SIMS analyses, due to its high sputtering yield, and is considered unlikely to have been a lattice element.

Noticeable by their absence in the SIMS spectra of Figure 99 are silicon and titanium. Both these elements had been detected in previous chemical analyses (Table XI) and SEM EDX spectra (Figure 92) of cassiterite grains. The absence of distinguishable ²⁸ Si⁺ and ⁴⁰ Ti⁺ peaks in Figure 99 is almost certainly due to the small number of impurity element counts obtained. Such small count numbers were a consequence of maintaining constant experimental conditions in the Ar⁺ SIMS analyses for the purposes of data comparison. In metal ion gun static SIMS spectra of individual unleached and leached grains that had been extensively sputtered, counts were far higher and both elements could be detected readily (Figures 100 and 101). In these latter spectra, iron still can be confirmed as the most prevalent impurity. While the silicon and titanium counts are relatively high, both elements have sputtering yields
Figure 99 - SIMS Spectrum of Unleached Cassiterite (Ar⁺ beam = 3 x 10⁻⁷ A/cm²; raster size = 200 µm) after 75 Minute Sputtering with 1.4 x 10⁻⁵ A/cm² Ar⁺ beam at 5 kV.

Figure 100 - SIMS Spectrum of Unleached Cassiterite (Ga⁺ beam = 250 µA/cm²; raster size = 20 µm) after 15 Minute Sputtering with 250 µA/cm² Ga⁺ beam at 10 kV.
Figure 101 - SIMS Spectrum of Leached Cassiterite (Ga⁺ beam = 250 µA/cm²; raster size = 20 µm) after 15 Minute Sputtering with 250 µA/cm² Ga⁺ beam at 10 kV.

appreciably above that of iron (Newbury, 1977). The presence of a ⁶⁺Zn⁺ peak in Figure 100 is not considered significant. A number of the silver foils used for sample mounting were found to contain minute zinc impurities.

A crucial conclusion that can be reached from static SIMS analyses is that the level of surface iron on unleached cassiterite particles was not indicative of that of the bulk mineral lattice. More iron existed on the surface of unleached particles (Figure 98) than was characteristic of their bulk lattice (Figure 99). The implication is, therefore, that the difference in surface iron levels between unleached and leached grains was due primarily to the removal of excess surface iron from the unleached cassiterite during leaching. There is no evidence supportive of the alternative possibility that
leaching simply depleted the natural iron level of the cassiterite lattice in the vicinity of the surface.

To determine the variation of iron concentration with depth in cassiterite grains a series of \textit{Ar}$^+$ beam SIMS depth profiles were recorded. The standard beam fluence for profiling was 1.9 \textmu A/cm$^2$. Sputtering was, therefore, of the order of fractions of monolayers per minute. While relatively slow for depth profiling, such a sputtering rate allowed data to be accumulated pertaining to the outmost surface of the mineral grains. Such information was considered crucial in confirming the existence of any surface films.

The depth profiles obtained during the SIMS analyses are relatively complex. This complexity is believed due to differential sputtering effects. It has been reported previously that ion yields at the onset of sputtering can be proportional not only to the concentration of the element of interest present but also to sputtering rates (Turos et al, 1974; Wehner, 1975). Only at long sputtering times are steady state conditions reached where ion yields are proportional to bulk concentrations alone.

Zinner (1978) has shown that differential sputtering is a characteristic of ion microprobe depth profiles for a variety of minerals. Examples of elemental profiles published by this researcher for the mineral labradorite are reproduced in Figure 102. In all the profiles, count rates can be seen to be either initially enhanced or suppressed. At longer sputtering times, the counts asymptote to constant values. In a critical analysis of these and other data, Zinner ruled out other interference effects as the source of the variations in the count rates. It was concluded that preferential sputtering of certain elements occurred at the onset of sputtering producing transients that did not follow a simple mass dependence.
Figure 102 - Depth Profiles Measured in a Polished Section of Labradorite (from Zinner, 1978). The data indicate the presence of count rate transients for all elements at the onset of sputtering.

Figure 103 shows the tin-120 and oxygen-16 depth profiles for Aldrich stannic dioxide. The secondary ion tin counts can be seen to have increased in the first minute of sputtering and then decreased to a constant level at longer times. The data indicate that the $^{16}$O$^-$ counts followed the reverse trend.

The count rate variations of Figure 103 parallel those observed by Zinner. The only difference is that in the first minute of sputtering the tin counts increased and the oxygen counts decreased before both trends reversed and ion yields asymptoted to constant values at longer time periods. This difference is considered to reflect the hydroxylated nature of the stannic dioxide surface and the presence of absorbed water. At higher sputtering rates, such as used by Zinner, this outer hydroxy-oxide film would have been rapidly removed and not observed in the depth profiling.
Figure 103 - Tin-120 and Oxygen-16 SIMS Depth Profiles at Constant Fluences (Ar$^+$ beam = 1.9 μA/cm$^2$ at 5 kV; raster size = 200 μm) for Different Areas of Aldrich "Gold Label" Stannic Dioxide.

In addition to differential sputtering, other effects have been reported by various researchers as complicating SIMS depth profiles. These include ion migration, surface reduction, chemical effects and surface contamination.

Ion migration effects can result from the charging of a surface under ion bombardment (Hughes, Baxter and Phillips, 1972). However, in this research no evidence of sample charging was observed. Furthermore, such effects are unlikely since natural cassiterites are good conductors (Shuey, 1975).

Reduction of metal oxides to the metal with preferential sputtering of oxygen has been reported for a number of oxides including those of iron, copper, and lead (Yin, Ghose and Adler 1972; Kim, Baitinger and Winograd, 1976; Shepard et al, 1977). However, published studies with stannic dioxide subject to ion bombardment with 400 eV Ar$^+$ beams have shown no reduction to
the metal or to lower order oxides (Kim et al, 1974). This finding and the fact that tin, rather than oxygen, was preferentially sputtering from the Aldrich stannic dioxide precludes reduction effects as the cause of the transients in Figure 103.

Chemical effects arise from interactions between the target surface and the implanted primary ion. The most well known such effect is that of enhancement of positive ion yields when negative oxygen beams are used for sputtering. However, for oxide mineral containing lattice oxide anions chemical effects are known not to play a role ever for oxygen ion beams (Zinner, 1978). For positive ion beams of inert \( ^{16}\text{Ar}^+ \), chemical effects are extremely unlikely. It is highly improbable that an \( ^{16}\text{Ar}^+ \) ion beam could interact chemically with stannic ions so as to enhance \( ^{120}\text{Sn}^+ \) sputtering.

Surface contamination also can be ruled out as the source of the variations in the tin counts of Figure 103. This element existed in the matrix in much higher concentrations than conceivably could be expected in any surface contaminant.

Figures 104 and 105 show the tin-120, iron-56 and oxygen-16, SIMS depth profiles of leached and unleached cassiterite. For the tin and oxygen profiles of both cassiterites, differential sputtering effects can be observed. In comparison to the stannic dioxide (Figure 103), these effects are much more pronounced. Reference to the count rate ranges marked in Figures 103 to 105 indicates that the variations in \( ^{120}\text{Sn}^+ \) and \( ^{16}\text{O}^- \) ion counts, associated with differential sputtering transients, were several orders of magnitude higher for the cassiterite samples than for the stannic dioxide. This might have reflected a greater degree of surface disruption in the natural samples.
Figure 104 - Tin-120, Iron-56 and Oxygen-16 SIMS Depth Profiles at Constant Fluences (Ar⁺ beam = 1.9 μA/cm² at 5 kV; raster size = 200 μm) for Different Areas of Leached Cassiterite Samples.
Figure 105 - Tin-120, Iron-56 and Oxygen-16 SIMS Depth Profiles at Constant Fluences (Ar⁻ beam = 1.9 μA/cm² at 5 kV; raster size = 200 μm) for Different Areas of Unleached Cassiterite Samples.
It has been reported by numerous researchers that the surfaces of ground minerals are highly disordered (Klassen and Mokrousoy, 1963; Lin and Somasundaran, 1972; Lin, Nadiv and Grodzian, 1975; Somasundaran, 1984). For many minerals, this disturbed layer has been estimated to be of the order of tens of angstroms and as much as 300 Å in thickness in some cases (van Lier, de Bruyn and Overbeek, 1960; Somasundaran, 1970). Given the methods of sample preparation, it is probable that the surfaces of the cassiterite samples were highly disrupted. This is particularly the case for the leached cassiterite. Surface disturbance would be expected to have been far less severe for the stannic oxide. Consistent with these expectations, transient variations were most pronounced for SIMS sputtering of the leached cassiterite and much less pronounced for the stannic dioxide. It must be emphasized, however, that surface disruption cannot explain the existence of the transients. There is no apparent reason why surface disruption would result in preferential sputtering of $^{120}$Sn$^+$ ions relative to $^{16}$O$^-$ ions. On the contrary, if transients were due only to surface distortions, it would be expected that oxygen, with its high sputtering yield and high volatility (Yin, Ghose and Alder, 1972), would be more likely to escape the oxide than a heavy metal such as tin.

In Figures 104 and 105, the iron profiles for both the unleached and leached cassiterite samples are similar in form to the corresponding tin profiles. Both increase at the onset of sputtering and then asymptote down to constant values at longer sputtering times. In terms of identification of surface films, it is the initial 2 minutes of sputtering that is of most interest. It can be seen in Figures 104 and 105 that maximum $^{56}$Fe$^+$ ion counts were observed in this time period. While it is extremely difficult to
estimate depths, due to surface irregularities and distortion (both of which can produce changing ionization efficiencies in depth profiling), it is evident that the $^{56}\text{Fe}^+$ count maxima do correspond with the sputtering of the outermost grain surfaces. Maxima in the $^{56}\text{Fe}^+$ counts for both cassiterite samples occur at sputtering times associated with the removal of the outer hydroxy-oxide film. In contrast, $^{120}\text{Sn}^+$ counts reach their maxima at considerably longer sputtering times. It can be concluded, therefore, that the cassiterite SIMS depth profiles are consistent with the existence of surface iron films. However, the data are not unequivocal. The possibility that the form of the iron profiles is due entirely to differential sputtering cannot be precluded entirely. However, on the basis of the static SIMS analyses the latter appears less likely.

As discussed in experimental Section 3.2.9, a limitation of the Vacuum Generators SIMS was that depth profiles for two elements could not be recorded at the same time. In Figures 103 to 105, individual profiles, therefore, correspond to different target areas. To confirm that the form of the profiles was general and not a consequence of different sputtering areas, iron and tin counts were recorded manually at a fixed position on a series of grains. A plot of one set of such data is shown in Figure 106. It can be seen that the $^{56}\text{Fe}^+$ counts decreased rapidly with sputtering time while the tin counts increased, passed through a maximum, and then became relatively constant. Both responses are in qualitative agreement with the profiles of the elements shown in Figures 104 and 105. Some variations in the count rate changes with sputtering time are evident but these are a function of the reduced fluences used in the latter studies. Reduced sputtering rates were necessary to allow ease of manual recording of count rates. The other
Figure 106 - Iron-56 and Tin-120 SIMS Depth Profiles for Unleached Cassiterite Obtained by Recording $^{56}\text{Fe}^+$ and $^{120}\text{Sn}^+$ Count Rates as a Function of Time at One Fixed Sample Position ($\text{Ar}^+$ beam = $6.3 \times 10^{-7}$ A/cm$^2$ at 5 kV; raster size = 200 $\mu$m).

The observable difference is that no maximum in $^{56}\text{Fe}^+$ secondary ion counts is evident at the onset of sputtering in Figure 106. This is due almost certainly to the fact that only a single reading could be made for each element at the commencement of sputtering when count rates were changing rapidly.

The SIMS data presented in this section are supportive of a number of critical findings regarding the surface properties of the research cassiterite samples. Specifically, the data support the hypotheses that:

(a) the concentration of iron on the surface of unleached cassiterite greatly exceeded that which was characteristic of the mineral lattice
(b) leaching largely removed the surface iron contamination of unleached cassiterite, and
(c) the surface of the leached cassiterite still contained iron at a level which was at least comparable to that of the bulk mineral lattice.

However, the nature and limitations of SIMS analyses are such that the data cannot be considered as providing definitive proof of the hypotheses. For example, it might be argued that insufficient numbers of grains can be analyzed reasonably by SIMS to satisfy sampling statistical requirements or that data variations between grains cannot be precluded on a strictly statistical basis. However, it can be stated categorically that all of the SIMS data are consistent fully with the assertions and that no finding refutes any aspect of the hypotheses. In isolation the data are not definitive. In combination with other results the evidence is overwhelming.

4.1.5.2. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy confirmed that iron was the dominant surface impurity associated with unleached cassiterite. In a survey XPS scan of unleached cassiterite grains, covering the binding energy range from 0 to 800 eV, three iron peaks were observed (Figure 107). A low energy Fe (3p) peak was found at a binding energy of 58 eV while two high energy Fe (2p) peaks occurred at 711.8 eV and 726 eV, respectively. In addition to the expected tin and oxygen peaks, the only other peak in the spectrum was that due to carbon. This carbon Is peak resulted from vacuum oil contamination in the spectrometer.

Survey and more detailed scans of leached cassiterite similarly failed to indicate the presence of surface impurities other than iron. The absence of
detectable levels of other impurities verified the dominance of iron as the principal surface contaminant. On the basis of the SIMS analyses, other impurities were presumably present but at levels below detection by XPS. Newbury (1977) has reported that XPS is of the order of a thousand times less sensitive than SIMS.

In Figure 108 the oxygen (1s)_{1/2} peaks for unleached cassiterite, leached cassiterite and Aldrich "Gold Label" stannic dioxide are shown. All these oxygen peaks are relatively broad, symmetric in shape and centered at a binding energy of 532.0 eV. At the resolution possible with the Varian 1EE-15 spectrometer, hydroxyl oxygen could not be distinguished from lattice oxygen. However, the broad nature of the O (1s) peaks (\( \Delta_{1/2} \approx 3.4 \text{ eV} \)) is consistent with the presence of hydroxyl oxygen. Allen et al (1974) have reported that, for many oxides, the dissociative chemisorption of water can lead to a high
surface concentration of hydroxyl groups characterized by broadening of the oxygen 1s peak to the high binding energy side.

Studies with iron oxides (Kishi and Ikeda, 1973; Allen et al, 1974; McIntyre and Zetaruk, 1977) have shown three distinct binding energy regions for oxygen, namely 530, 531 to 532 and 533 eV. These regions were associated with oxide, hydroxide or chemisorbed oxygen species and physically adsorbed water, respectively. The absence of a 530 eV peak in Figure 108 suggests that the oxide anion core electrons of cassiterite either have a higher binding energy than is typical for iron oxides or that the surfaces of all three tin oxides were strongly hydroxylated. It is known that O (1s)_{1/2} spectra of many metal oxides become dominated by hydroxyl oxygen if exposed to an aqueous environment or moist air (Kishi and Ikeda, 1973; Allen et al, 1974).
Charging effects could conceivably explain the high binding energies of Figure 108. However, surface charging was not detected on any of the samples. The carbon reference C (1s) binding energy (285 ± 0.15 eV) was invariant while reproducibility of sample binding energies was better than ± 0.2 eV for at least three independently prepared specimens of each mineral sample. The symmetric nature of the O (1s) peaks is also consistent with the absence of charging. Riggs and Parker (1975) have reported that for irregular sample surfaces, such as in the case of grain mounts, charging typically occurs to varying extents on different grains. These so-called differential charging effects invariably produce broad asymmetric peaks.

The two strongest tin peaks in the survey spectrum of unleached cassiterite (Figure 107) were those due to Sn (3d) core electrons with binding energies in the 480 to 500 eV range. Standard tabulations of electron binding energies, such as those of Riggs and Parker (1975), report the Sn (3d)_{3/2} and Sn (3d)_{5/2} peaks at 494 eV and 485 eV, respectively. For the unleached cassiterite, a detailed tin (3d) spectrum (Figure 109) indicated both binding energies to be higher at 496.6 and 487.7 eV, respectively. These high binding energies are consistent with the bonding of stannic ions to either strongly electronegative (Pauling, 1948) oxide anions or surface hydroxyl groups. Strongly electronegative atoms withdraw electron density from the valence and bonding orbitals of atoms, thereby reducing the screening of the core electrons from the nuclear charge and increasing their binding energy (Riggs and Parker, 1975).

Tin possesses a number of other XPS peaks. Of considerable interest is the binding energy range between 705 and 725 eV which embraces both the Sn (3p)_{3/2} peak and that due to Fe (2p)_{3/2} electrons. Figure 110 shows the
Figure 109 - Tin \((3d)_{3/2}\) and \((3d)_{5/2}\) Spectrum for Unleached Cassiterite. Binding energies of the peaks are marked in the figure.

Figure 110 - Tin \((3p)_{3/2}\) and Iron \((2p)_{3/2}\) Spectra for Unleached Cassiterite, Leached Cassiterite and Aldrich "Gold Label" Stannic Dioxide (Synthetic Cassiterite).
Sn (3p)\textsubscript{3/2} and Fe (2p)\textsubscript{3/2} spectra for unleached cassiterite, leached cassiterite and Aldrich "Gold Label" stannic dioxide in this range. Clearly evident in the unleached cassiterite spectrum is a strong Fe (2p)\textsubscript{3/2} peak. In contrast, the iron peak was much less intense for leached cassiterite and not discernable at all in the case of the stannic dioxide.

The cassiterite XPS spectra of Figure 110 are relatively complex. Both the tin and the iron peaks are very broad and overlap appreciably. Diminished peak resolution in compounded by the broad rising background. This is a characteristic of the high binding energy range and results from the energy degradation of photoelectrons in transit to the surface.

In XPS spectra, Fe (2p)\textsubscript{3/2} electrons invariably exhibit broad peaks due to multiplet splitting and shake-up phenomena (Carver, Schweitzer and Carlson, 1972; Allen et al, 1974; Koppelman and Dillard, 1975). Multiplet splitting is caused by the presence of unpaired valence electrons resulting in exchange interactions which affect differently the remaining spin-up and spin-down electrons (Allen et al, 1974). Shake-up peaks are due to a process whereby the primary photoelectron, on leaving the atom, causes the excitation of a valence electron to an unfilled higher energy level, thus removing some energy from the photoelectron and making it appear at apparently higher binding energy in the spectrum. At least in the case of iron, the shake-up transition appears to involve promotion of an electron from a ligand orbital to an empty metal 3d orbital (Riggs and Parker, 1975).

Given the limited resolving power of the Varian 1EE-15 spectrometer and the broad band and overlapping nature of the Sn (3p)\textsubscript{3/2} and Fe (2p)\textsubscript{3/2} peaks, it is difficult to analyze in detail the spectra of the Figure 110. It can be concluded, however, that the iron peak in the unleached cassiterite was
centered at a binding energy of approximately 712.0 eV. In the leached cassiterite spectrum, the Fe (2p)\(3/2\) peak was less well defined and, although a small maximum did occur in the 710.5 to 711.5 range, it is considered impossible to define a value with the same accuracy accorded to the Fe (2p)\(3/2\) binding energy in unleached cassiterite.

In Table XV a compilation of reported binding energies of Fe (2p)\(3/2\) electrons in various compounds and minerals is given. Although there is some scatter in the values reported in the literature, the binding energies increase with increasing iron oxidation and ligand electronegativity. The high binding energy of the Fe (2p)\(3/2\) electrons in the unleached cassiterite spectrum of Figure 110 is consistent with iron being in the ferric state and either hydrated or complexed with strongly electronegative hydroxyl ions. The experimental binding energy of 712.0 eV correlates closely with the 711.9 eV value reported by Koppelman and Dillard (1975) for amorphous hydrous ferric oxide.

X-ray photoelectron spectroscopy is not an in-situ technique. As such, it must be emphasized that the form of the iron associated with the cassiterite surface might have undergone oxidation or dehydration when the sample was removed from solution and dried under vacuum. While the surface iron analyzed was almost certainly that of a hydrous ferric oxide species, significant differences might have existed between this species and that existing in the original aqueous flotation environment.

The binding energies of the tin (3p)\(3/2\) peaks in Figure 110 show excellent consistency. In all three spectra, the peaks are broad but clearly centered around a binding energy of 716.6 eV. As for the two Sn (3d) core electrons, this experimental binding energy is higher than the 715 eV value cited in the
literature (Riggs and Parker, 1975). The shift to higher binding energy is again considered to reflect the bonding of surface stannic ions to either lattice oxide anions or chemisorbed hydroxyl groups.

**TABLE XV**

**THE XPS BINDING ENERGIES OF IRON (2p)\textsubscript{3/2} ELECTRONS IN VARIOUS COMPOUNDS AND MINERALS**

(adapted from Brion, Hayer and Predali, 1980)

<table>
<thead>
<tr>
<th>Compounds and Materials</th>
<th>Binding Energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Fe(II)</td>
</tr>
<tr>
<td>Fe Metal</td>
<td>707.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>706.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>708.2</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td></td>
<td>710.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>709.5</td>
</tr>
<tr>
<td>FeF\textsubscript{2}</td>
<td></td>
<td>711.5</td>
</tr>
<tr>
<td>(\alpha) - FeOOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td></td>
<td>711.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>711.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>711.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>712.4</td>
</tr>
<tr>
<td>FeF\textsubscript{3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous Hydrous Ferric Oxide</td>
<td></td>
<td>711.9</td>
</tr>
</tbody>
</table>
The relative intensities of the unleached cassiterite Fe (2p)\textsubscript{3/2} and Sn (3p)\textsubscript{3/2} peaks in Figure 110, after correction with the appropriate photoelectron cross-sections (Riggs and Parker, 1975) was of the order of 1:2. This is much greater than the atom ratio for the mineral of 1:48 as determined by chemical analysis (Table XI). Such an high ratio confirms unequivocally the extensive iron contamination of the outermost cassiterite surface.

Confirmation of the existence of iron films on the surface of unleached cassiterite grains raises the crucial issue of the origin of such films. It is extremely unlikely that high surface iron concentrations represent the natural geological state of the cassiterite. While it is known that iron can exist in association with minerals as fossils of the solution from which they crystallized (Fander, 1985), iron rimming is relatively rare. In the case of Renison cassiterite, detailed mineralogical examinations of the mine orebody (Patterson, Ohmoto and Soloman, 1981) reference no such rimming and there appears no geological basis for its occurrence. The iron observed experimentally is both too concentrated at the surface and too prevalent for it conceivably to represent the natural state of the finely disseminated crystal grains.

The most probable source of the surface contamination of the unleached cassiterite is the aqueous pulps of the Renison plant. It has been established (Winby, 1985) that these pulps contain high levels of dissolved metal ionic species including iron (Table VI). Furthermore, the pH and the Eh are such that a significant and possibly predominant proportion of the iron would have been present in the form of hydrous ferris oxide sols (Figure 18). These sols are well known to adsorb strongly on mineral surfaces (Section 2.5.1).
Alternative mechanisms that might explain a surface iron concentration on cassiterite grains do exist. In the case of bornite, Buckley, Hamilton and Woods (1984) have postulated that iron can migrate out of the sulphide lattice on exposure of the mineral to air to form a surface iron oxide. These researchers observed that the intensities of bornite iron XPS peaks increased relative to those of copper with increasing exposure time of the mineral to air (Figure 111). Similarly, it might be argued that during grinding negative defects could be created on the cassiterite surface causing mobile lattice iron to migrate and concentrate at the surface.

To date, no evidence exists supporting the hypothesis that iron inclusions in the cassiterite lattice are highly mobile. Furthermore, the high levels of surface iron identified in the XPS analyses are extremely difficult to reconcile with a mechanism based on ion migration alone. However, the possibility that surface iron films were derived from lattice iron cannot be precluded definitively on this basis alone. Migration of inclusive iron at least appears plausible since the iron atom is smaller than the tin atom it replaces in the cassiterite lattice.

In Figure 112 the tin (3p)\textsuperscript{3/2} and iron (2p)\textsuperscript{3/2} spectrum of leached cassiterite exposed to moist air for 3 days is compared to that of unleached and leached cassiterite. It can be seen that no significant change occurred in the leached sample spectrum during the oxidation period. Specifically, the intensity of the iron peak did not change relative to that of tin on exposure to the highly oxidizing environment. The absence of peak intensity changes in the two leached cassiterite spectra indicates that no iron diffused from the bulk of the mineral to replace that dissolved from the surface by leaching.
Figure 111 - Copper (3p) and Iron (3p) Spectra for Bornite. Curve A, freshly cleaved surface; curve B, surface exposed to moist air for 17 minutes; curve C, exposed for 3 days (from Buckley, Hamilton and Woods, 1984).
A spectrum of the tin \(3p_{3/2}\) and iron \(2p_{3/2}\) binding energy region of unleached cassiterite ground under argon to reveal surfaces not previously exposed to air is shown in Figure 113. Remarkably, the iron peak all but disappeared after the inert atmosphere grinding. This finding provides striking and definitive evidence that the concentration of iron on the surface of the original unleached cassiterite greatly exceeded that which was characteristic of the mineral lattice. The effect of the agate mortar grinding was presumably to abrade the iron film from the old mineral surface and to expose new fracture planes not possessing high iron levels. Significant new surface was created during the grinding and the changing
Figure 113 - Comparison of the Tin \((3p)_{3/2}\) and Iron \((2p)_{3/2}\) Spectra for (A) Unleached Cassiterite, (B) Unleached Cassiterite after being Ground in an Inert Atmosphere and (C) Unleached Cassiterite after Inert Atmosphere Grinding and Exposure to Moist Air for 3 Days.

Surface atom ratio of tin to iron might have been the predominant factor accounting for the spectral changes in Figure 113. Electrozone sizing indicated the log mean particle size before and after grinding to be 24.48 and 4.66 microns, respectively.

Exposure of freshly cleaved cassiterite to moist air for varying periods produced spectra similar to that obtained for the unleached cassiterite ground under argon and analyzed immediately. As for the leached cassiterite, exposure to the oxidizing environment for periods of up to 3 days failed to alter measurably the tin to iron peak intensities (Figure 113).

On the basis of the XPS spectra of Figures 112 and 113, it can be
concluded that no evidence exists to support the contention that lattice iron can accumulate on the surface of cassiterite due to migration through the mineral lattice. Such migration cannot be demonstrated either through mineral grinding to create a fresh surface or through extensive exposure of the mineral to an highly oxidizing environment. Instead, all of the XPS data support the hypothesis that the iron film on the surface of unleached cassiterite was the result of previous adsorption of hydrous ferric oxide sols in the plant environment from which the mineral was sampled.

4.1.6 Leaching Tests

The degree to which metal species can be solubilized from the surface of unleached cassiterite at acidic pH is shown in Figures 114 to 116. All abstraction data are based on solution analyses after 14 days leaching. The data are considered to represent equilibrium conditions as no detectable changes in ion concentration were observed at longer time periods.

Measurable abstraction of metal species was not found above pH 5.0. Below this pH, abstraction of iron, aluminum, magnesium and calcium increased dramatically. In particular, iron levels in solution under the acidic conditions (Figure 114) were an order of magnitude greater than that for the other metal ions (Figures 115 and 116). This again confirmed that iron was the most prevalent surface impurity species associated with the cassiterite.

At all acidic pH values, the cation analyses of the leach liquors followed the concentration sequence of Fe > Ca > Mg > Al. This sequence is consistent with the results of the bulk chemical inductively coupled argon plasma elemental analyses of the cassiterite (Table XI). According to these analyses, the cassiterite contained 7500 ppm Fe, 800 ppm Ca, 500 ppm Mg and 300 ppm Al.
Figure 114 - The pH Dependence of Iron Abstraction from Unleached Cassiterite (milligrams Fe/gram cassiterite). Leaching time = 14 days.

Figure 115 - The pH Dependence of Aluminum Abstraction from Unleached Cassiterite (milligrams Al/gram cassiterite). Leaching time = 14 days.
Figure 116 - The pH Dependence of Magnesium and Calcium Abstraction from Unleached Cassiterite (milligrams/gram cassiterite). Leaching time = 14 days.

With respect to extraction kinetics, the rate of dissolution of iron from the cassiterite was relatively slow (Figure 117). In leaching tests at pH 3.5, solution iron levels were below the detection limit of 1 ppm for time periods of less than 60 minutes. At longer leaching times, measurable iron was detected in solution. After 3 hours, the amount of iron solubilized was found to be 22.5 μg per gram of cassiterite. This represented just over 5 percent of the total amount abstracted under identical conditions in a total of 14 days of leaching (Figure 114).

Tests conducted to establish the maximum extent to which iron associated with the cassiterite could be removed indicated extraordinarily high abstraction levels. Based on chemical analyses of the leach liquors, 6.64 mg of iron could be leached into solution at pH 1.0 for every gram of
Figure 117 - Kinetics of Iron Abstraction from Unleached Cassiterite at pH 3.5 (micrograms Fe/gram cassiterite).

cassiterite. Initial and final solids assays gave an iron abstraction of 7.5 mg/g. In the first instance, the percentage abstraction of total cassiterite iron was of the order of 88 percent. On the solids assay basis, extraction was essentially complete. The iron balance is considered acceptable given the number of analyses involved and the levels of iron assayed.

In the absence of any evidence supporting inclusive element mobility in the lattice, the finding that iron associated with the cassiterite could be solubilized readily is considered to confirm that the iron was predominantly a surface species.

4.1.7 Electrokinetic Studies

Electrophoretic mobility measurements of unleached cassiterite in KCl electrolyte solutions (Figure 118) indicated that the iep of the mineral was at pH 4.0. This value is in excellent agreement with the iep and pzc values reported for cassiterite by other researchers (Table III). Changes in the
The Electrophoretic Mobility of Unleached Cassiterite as a Function of pH in the Presence of Increasing Concentrations of KCl Electrolyte.

The concentration of KCl did not alter the iep of the cassiterite confirming that KCl was an indifferent electrolyte. As expected, the magnitudes of the measured electrophoretic mobilities decreased slightly with increasing electrolyte concentrations due to the compression of the electrical double layer.

Strong acid leaching followed by extensive washing with distilled water was found not to affect the cassiterite iep. However, such treatment increased the magnitude of the mineral electrophoretic mobilities at pH values above and below the iep (Figure 119). The implication from this finding is that leaching either removed indifferent ions compressing the double layer or created more surface hydroxyl sites. The surface charge of cassiterite is considered to be due to the adsorption-dissociation of H+ from surface hydroxyls (Section 2.1.6).
Numerous effects on mineral surface properties have been ascribed in the literature to acid leaching. These include contamination of the surface with the acid anion, differential solubility of ions from the surface and surface disruption (Somassundaran, 1970). In the case of the hydrochloric acid leaching of this research, it is difficult to envisage that adsorbed chloride ions could increase the positive mineral surface charge below the iep. Furthermore, this ion was found to be indifferent (Figure 118) and negative SIMS spectral analyses indicated no significant chloride ion surface contamination. Surface disruption is possible, although the magnitude of the electrophoretic mobility increases (0.8 micron/sec. per volt/cm. at higher pH values) cannot be reconciled readily with the degree to which surface
disruption could create new hydroxyl sites. Leaching undoubtedly modified the surface of the cassiterite by removing adsorbed iron hydrous oxide films. This was confirmed by both SIMS and XPS to be the most significant surface change associated with leaching.

The electrophoretic mobility curve of the leached cassiterite was essentially indistinguishable from that of the Aldrich "Gold Label" stannic dioxide used as a reference material (Figure 119). Both oxides had an iep of 4.0. Houchin and Warren (1984) have reported an iep for Aldrich stannic dioxide of 4.3. An iep difference of 0.3 is considered acceptable for different researchers working with different batches of the reagent.

During the course of the research, a number of distinct changes were noted with prolonged aging of the cassiterite in aqueous solution. Specifically, the negative electrophoretic mobilities of the particles in the slightly acidic to alkaline range decreased in magnitude (Figure 120). Over almost a two year period, the magnitude of the electrophoretic mobilities at higher pH values decreased by as much as 1.0 micron/sec. per volt/cm. These decreases in negative charge character and less pronounced decreases in positive character below the iep correlated with increased solution conductivities and the release of magnesium and calcium ions into solution (Table XVI). Chemical analyses of the aqueous phase recovered from the aging suspensions indicated magnesium and calcium levels as high as 3.65 ppm and 2.2 ppm, respectively. Iron and aluminum were analyzed for but at all times were below the detection limit of 0.1 ppm. Presumably, the source of magnesium and calcium was the mineral particles. However, contamination from the nalgene containers, in which the suspensions were stored, cannot be precluded entirely. The similarity of the aging effects to the difference between leached and
Figure 120 - The Effect of Aging Time in Aqueous Solution on the Electrophoretic Mobility of Unleached Cassiterite. The dates of measurements are shown in the figure. All mobility determinations were made in the presence of $1 \times 10^{-4}$ M KCl.

### TABLE XVI

ATOMIC ABSORPTION SPECTROSCOPIC ANALYSES OF SOLUTION RECOVERED FROM UNLEACHED CASSITERITE SUSPENSIONS AGED FOR DIFFERENT TIME PERIODS

<table>
<thead>
<tr>
<th>Analysis Date</th>
<th>Fe</th>
<th>Al</th>
<th>Mg</th>
<th>Ca</th>
<th>Conductivity (mho)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Dec 1984</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>26 July 1985</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>0.5</td>
<td>85</td>
</tr>
<tr>
<td>03 Aug 1986</td>
<td>-</td>
<td>-</td>
<td>3.65</td>
<td>2.2</td>
<td>145</td>
</tr>
</tbody>
</table>
unleached cassiterite electrophoretic mobilities suggests that the latter also were due to double layer compression resulting from calcium and magnesium ions solubilized from the surface of the unleached cassiterite.

Slow dissolution of surface impurities is the most commonly cited consequence of aging in water (Somasundaran, 1970). However, more dramatic effects have been reported. For simple oxides, Smith and Trivedi (1974) have claimed that iep's can move to more basic pH values with prolonged aging in aqueous solution. It was postulated that this phenomenon was due to dissolution of disturbed surface layers from the mineral accompanied by later readsorption of metal hydroxy species back onto these surfaces. The readsorption was thought to take place after the solution became supersaturated with respect to some crystalline phase. In this research, no evidence for any such changes in the iep values of unleached and leached cassiterite was found.

The most extraordinary aspect of all the data presented to date on the electrokinetic properties of unleached cassiterite is that charge reversal phenomena, normally associated with adsorbed hydrous iron oxide species, were completely absent. This is despite the fact that a very significant portion of the unleached mineral surface was known to be covered with such iron species. The intriguing question as to the nature of the surface iron films is thereby raised.

In published test work concerning charge reversal of oxide minerals, experimental procedures invariably are such that the electrokinetic measurements were made in the presence of freshly precipitated hydrolyzed metal ion species. For the unleached cassiterite of this research, this was not the case. The sample had been both aged in solution for an extensive
period and dried prior to redispersal in distilled water for the electrokinetic studies.

Figure 121 provides a comparison of the electrophoretic mobilities of an unleached cassiterite suspension initially acidified to pH 1.0 for 2 hours with data for the same suspension with an initial pH of 5.8. Remarkably, charge reversal phenomena were present after the initial acidification.

On the basis of leaching test results (Figure 114), there appears no doubt that iron would have been solubilized extensively from the unleached cassiterite surface at pH 1.0. The data of Figure 121, therefore, confirm that appreciable iron was present on the surface of the unleached cassiterite in the suspensions used for electrokinetic studies. More importantly, the data establish that when solubilized and allowed to readsorb, this iron did cause charge reversal in the manner typical of that reported in the literature.

In aqueous solutions, hydrous oxide sols of metal ions are known to undergo complex aging processes. Associated with such aging are changes in the degree of hydration and the extent of olation and oxolation bonding in the hydrous oxides. The degree of hydration generally diminishes with time while oxolation reactions increase at the expense of olation. These changes tend to diminish the positive charge character of the sols as the number of coordinated hydroxyl ions in the polymer is reduced (Section 2.3.13). It is not unreasonable to assume that hydrous metal oxide sols adsorbed at a mineral surface might undergo similar aging.

Figure 122 shows the electrophoretic mobilities of an unleached cassiterite suspension initially acidified to pH 1.0 for 2 hours and then partially neutralized to pH 5.5. When measured immediately after
Figure 121 - Electrophoretic Mobilities of an Unleached Cassiterite Suspension Initially Acidified to pH 1.0 for 2 hours. Also shown are data for the same suspension with an initial pH (pH\_i) of 5.8.

Figure 122 - Electrophoretic Mobilities of an Unleached Cassiterite Suspension Initially Acidified to pH 1.0 for 2 Hours and Partially Neutralized to pH 5.5 for Different Time Periods. The aging times before each series of electrophoretic mobility measurements are marked in the figure.
neutralization, the electrophoretic mobilities were positive up to pH 6.7. This clearly indicated the adsorption of positively charged sol species onto the cassiterite surface. With increased aging time at pH 5.5, prior to electrokinetic measurements, the positive mobilities below pH 6.7 decreased in magnitude. Above pH 6.7, the magnitude of the negative mobilities increased slightly. However, even after 14 days of suspension aging the original negative cassiterite surface character between pH 4.0 and 6.7 was not restored. While electrophoretic mobility changes consistent with predicted adsorbed sol aging were therefore observed, the kinetics of such processes was extremely slow. In the time frames of interest in flotation, adsorbed sol aging would not be expected to be a significant factor in influencing mineral charge character.

As supplied from Renison Limited, the research cassiterite had been oven dried. The other possibility for the altered charge character of the adsorbed hydrous ferric oxide species was, consequently, that drying had dehydrated the sols. To establish the effect of drying, a portion of the acid pretreated suspension used in the experiments of Figure 122 was vacuum dried. After drying, charge reversal was found to have disappeared completely (Figure 123). The mineral so treated had electrophoretic mobilities that closely resembled those prior to any acid treatment.

The extraordinary results of Figure 123 confirm unequivocally that drying can remove completely the characteristic charge reversal effects of adsorbed hydrous metal oxides. Such a finding has not been reported previously in the literature despite innumerable studies pertaining to the adsorption of metal sols on oxide mineral surfaces. The most plausible explanation of such an effect is that drying reduces the degree of hydration of adsorbed surface
Figure 123 - Electrophoretic Mobilities of an Acid Pretreated, Unleached Cassiterite Suspension Before and After Vacuum Drying. Acid pretreatment involved initial suspension acidification to pH 1.0 for 2 hours followed by partial neutralization to pH 5.5. Also included for comparison in the figure are data for the same suspension prior to acid treatment.

sols. It is coordinated and chemisorbed water molecules and hydroxyl groups of such sols that produce their charge character.

Detailed studies of the morphology changes associated with drying of metal ionic sols would be inherently complex and, as such, were beyond the scope of this research. The most daunting experimental aspect of such analyses is that, at least initially, the sols must be examined in-situ. With the exception of certain infrared techniques, spectroscopic and microscopic methods of analysis require sample drying. On the basis of the findings of this research, such drying almost certainly causes a change in the character of any adsorbed sols. The species examined, therefore, in all probability, are not those that actually existed in the aqueous solution.
In Figure 124 the tin (3p)$_{3/2}$ and iron (2p)$_{3/2}$ XPS spectrum of the original unleached cassiterite is compared to that of portion of the same sample that had been acid pretreated and then vacuum dried. Within the limits of resolution provided by the Varian IEE-15 spectrometer, the two spectra were identical. From electrokinetic measurements indicating charge reversal (Figure 123), it was known that hydrous ferric oxide sols were adsorbed on the acid pretreated sample prior to vacuum drying. The absence of spectral differences, therefore, confirms that the original unleached cassiterite spectrum is consistent with one of cassiterite on which hydrous ferric oxide sols had adsorbed but that drying associated with the XPS analyses almost certainly caused fundamental structural changes in these sols.

![Figure 124 - Comparison of the Tin (3p)$_{3/2}$ and Iron (2p)$_{3/2}$ Spectra for (A) Unleached Cassiterite and (B) Unleached Cassiterite Acid Pretreated and then Vacuum Dried. Acid pretreatment involved placing the cassiterite in distilled water at pH 1.0 for 1 hour and then partially neutralizing the solution to pH 5.5.](image-url)
Somasundaran (1970) has cited the effects of drying on mineral surface properties as those of:

(a) contamination of the surface by impurities introduced during evacuation,
(b) reduced surface hydration, and
(c) changes in crystal stoichiometry at high temperatures.

In the vacuum drying analyses of this research, no evidence for the introduction of contaminant species was found in the XPS surface analyses. Furthermore, the observed electrokinetic changes, if due solely to contaminants, would be virtually impossible to reconcile with anything less than massive contamination.

Changes in crystal stoichiometry with heating can be discounted since the vacuum drying was conducted at room temperature. Reduced surface hydration of the cassiterite is possible, although alone cannot explain the disappearance of charge reversal effects associated with adsorbed hydrous oxide sols. The close correspondence of the electrophoretic mobilities of vacuum dried, acid pretreated cassiterite and those of the same cassiterite prior to such treatment, suggests that changes in the surface structure of the cassiterite itself, caused by drying, were minimal.

The most important aspect of sample drying established in this research, is that dehydration and dehydroxylation of adsorbed metal ionic sols can occur. In terms of electrokinetic analyses, this makes the presence of such sols on mineral surfaces extremely difficult to identify. Furthermore, there is no evidence to suggest that, once such changes in sol morphology have occurred, the process is reversible. While stored for almost 2 years in an aqueous solution, no evidence for extensive sol rehydroxylation was found in
the case of the unleached cassiterite. The charge reversal phenomena associated with the formation of freshly precipitated hydrous iron oxides on the mineral (Figure 121) did not reappear with aging time in solution after thermal drying (Figure 120). Such a result is not unexpected since highly charged amorphous polymeric sols are known to be thermodynamically unstable. In aqueous solution, such sols age to produce more distinctly crystalline phases (Section 2.3.1.3). Drying and heating both are known to promote transformations to the more crystalline phases (Dousma and de Bruyn, 1976; Rubio and Matijevic, 1979; Strahm, Patel and Matijevic, 1979; van der Woude, Verhees and de Bruyn, 1983).

4.1.8 **Principal Findings and Conclusions**

1. Surface iron films existed on cassiterite grains recovered from the tin concentrator of the Renison plant. The level of iron contamination on the surface, as indicated by SIMS, XPS and chemical abstraction analysis, was far in excess of that characteristic of the bulk mineral lattice.

2. Other impurity elements such as aluminum, magnesium and calcium were present on the cassiterite surface. However, the levels of these contaminants were more than an order of magnitude less than that of the iron.

3. Hydrochloric acid leaching substantially removed the surface iron contamination of the Renison cassiterite. However, the surface of the leached cassiterite still contained iron at a level which was at least comparable to that of the bulk mineral lattice.

4. No evidence was found in XPS analyses to support the
contention that the surface iron films represented lattice iron that had accumulated on the cassiterite surface due to migration through the lattice, as has been suggested to be the case for bornite.

(5) The binding energies of iron (2p)\(^{3/2}\) electrons associated with the iron films correlated with those reported in the literature for amorphous hydrous ferric oxide.

(6) After grinding of Renison cassiterite in an agate mortar, the iron peak in the XPS spectrum of the unleached mineral virtually disappeared.

(7) All impurity elements associated with the cassiterite, including the iron, could be solubilized readily in acidic solutions. The extent of abstraction increased significantly with decreasing pH below pH 4.0.

(8) The aqueous pulps of the Renison plant are the most probable source of the cassiterite surface iron contamination. It has been established that these pulps contain high levels of dissolved metal ionic species including iron. The pH and Eh of these pulps are such that a significant portion of the iron would have been present in the form of hydrous ferric oxide sols. These sols are well known to adsorb strongly on mineral surfaces.

(9) The hydrous ferric oxide sols adsorbed on the cassiterite underwent fundamental structural changes when the mineral was dried. As a result, the presence of an iron film did not change significantly the electrokinetic properties of
the cassiterite as is known to be the case for other insoluble oxide minerals in the presence of freshly precipitated hydrolyzed metal ionic species.

(10) When solubilized and readorsorbed, the iron associated with the cassiterite did cause charge reversal in a manner typical of that reported in literature.

(11) Vacuum drying of the cassiterite grains, on which hydrous ferric oxide sols were known to have adsorbed, was shown independently to cause the charge reversal phenomena related to the metal ion adsorption to disappear. Such charge reversal was not re-established when the dried cassiterite was placed in distilled water and aged for periods of up to two years.

(12) Sample drying changed the charge character of adsorbed sols presumably by reducing the degree of hydration and hydroxylation of the sols. True analyses of such sols, therefore, cannot be made by any ex-situ spectroscopic or microscopic technique that requires sample drying.

(13) Aging of adsorbed hydrous ferric oxide sols in aqueous solution is kinetically very slow. In the time frames of interest in flotation, adsorbed sol aging would not be expected to be a significant factor in influencing mineral charge character.

(14) The isoelectric points of both unleached and leached Renison cassiterite occurred at pH 4.0. An identical isoelectric point was found for Aldrich "Gold Label" stannic dioxide.
4.2 Surfactant Characterization

4.2.1 Infrared Spectroscopy

Infrared spectra of the five commercial cassiterite flotation collectors examined in this research are presented in Figures 125 to 127. Band assignments for the major peaks in each spectra are given in Table XVII. On the basis of these assignments, it can be concluded unequivocally that all of the surfactants were phosphonic acids.

The phosphonic acid polar group possesses a number of characteristic vibrations. In the infrared spectrum, the most distinctive such bands are those due to the O-H, P-O, P=O and P-C vibrations.

The two P-OH groups of phosphonic acids give rise to broad bands of weak to medium intensity in the regions 2900-2800 cm\(^{-1}\) and 2500-2200 cm\(^{-1}\). Both bands are due to O-H stretching vibrations (Socrates, 1980). However, as their band positions indicate, they occur at much lower wavenumbers than is generally typical of hydroxyl group stretching. This is due to the presence of the pentavalent phosphorous and associated strong hydrogen bonding effects (Daasch and Smith, 1951). Dietze (1971) has assigned the lower frequency O-H stretching vibration specifically to interactions between the two hydroxyls of the phosphonic acid group. However, Socrates (1980) has reported both bands to be present in pentavalent phosphorous compounds containing a P=O bond and a single P-OH group.

The existence of two broad O-H stretching vibrations in the 2900-2800 cm\(^{-1}\) and 2500-2200 cm\(^{-1}\) ranges can be considered as essentially a fingerprint for the P-OH group. Few compounds, including other phosphorus species, absorb in this range (Ross, 1974). In the ICI BPA spectrum of Figure 126 and the three spectra of Figure 127, these vibrations can be identified readily. In the
Figure 125 - Infrared Spectrum of Hoemochlor Ragent P-195.

Wavenumber (cm⁻¹)

Transmittance (%)
Figure 126 - Infrared Spectrum of ICI Reagent BPA.
Figure 127 - Comparison of the Infrared Spectra of the Tin Flotation Collectors Hoechst P-184, Plaistere and Hanger PH-PEP and Organophos EPPA.
<table>
<thead>
<tr>
<th>P-184</th>
<th>PH-PEP</th>
<th>EPPA</th>
<th>BPA</th>
<th>P-195</th>
<th>Band Assignments</th>
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<td>3400m</td>
<td>3401s</td>
<td>3401w</td>
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<td></td>
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<td>2924s</td>
<td>2800s</td>
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<td>1615m</td>
<td>1612m</td>
<td>1600w</td>
<td></td>
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<td>1123vs</td>
<td>1122vs</td>
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<td>992vs</td>
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<td>956vs</td>
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Hoechst P-195 spectrum (Figure 125), CH$_3$ and CH$_2$ vibrations of the hydrocarbon radical are superimposed on the higher frequency band but the lower band is clearly evident near 2326 cm$^{-1}$.

Socrates (1980) has reported that weak broad bands in the 1740-1600 cm$^{-1}$ range are also produced by phosphonic acid group hydroxyls. Such bands are due to OH deformation vibrations. In the Hoechst P-195 spectrum (Figure 125), these bands can be distinguished at 1699 cm$^{-1}$, 1651 cm$^{-1}$ and 1625 cm$^{-1}$ in association with the broad H-O-H bending vibration of water (1640 cm$^{-1}$). In the spectra of the other phosphonic acids, the bands cannot be resolved from the background. With the possible exception of the Organophos EPPA, the free water in these phosphonic acids was appreciably less than for the P-195. This can be seen from the relative intensities of the O-H stretching vibration of water present in all spectra near 3400 cm$^{-1}$.

Two other characteristic vibrations of the phosphonic acid group are the P-O and P=O vibrations. The former produces a strong broad band in the 1040-910 cm$^{-1}$ range due to P-O stretching. The band due to the stretching vibration of the P=O group is also strong and occurs in the region 1350-1150 cm$^{-1}$ (Socrates, 1980). In phosphonic acids, the existence of two P-OH groups and interactions with oxygen bonded to the phosphorus can result in a series of P-O and P=O bands in the infrared spectrum.

Reference to the spectra of Figures 125 to 127 indicates that all of the reagents produced a pair of strong bands near 995 cm$^{-1}$ and 946 cm$^{-1}$. These bands have been assigned as P-O vibrations (Table XVII) on the basis of their small variability and their existence within the appropriate range cited by Socrates (1980). The absence of appreciable shifts in the band positions is considered to preclude the possibility that they are hydrocarbon radical
vibrations.

In the Hoechst P-195 spectrum (Figure 125), the most pronounced band in the range cited for P=0 vibrations was a medium intensity doublet with peaks at 1157 cm\(^{-1}\) and 1135 cm\(^{-1}\). Given the reported strong nature of P=0 bands and the absence of other strong hydrocarbon radical or polar group bands in this range, the doublet has been assigned to P=0 stretching vibrations (Table XVII). Socrates (1980) has referenced that the P=0 stretching band can sometimes appear as a doublet.

In the case of the other four phosphonic acids (Figures 126 and 127), the infrared spectra in the region of interest for the P=0 vibration were more complex. The ICI BPA surfactant produced four bands in the range 1265 to 1065 cm\(^{-1}\). The other three reagents gave identical three peak patterns. Qualitative similarity was evident between all the spectra. In particular, the lowest frequency peak in the range was particularly strong and broad for all the surfactants such that the adjacent higher frequency band occurred as a shoulder peak.

Definitive assignment of P=0 vibrations in the spectra of Figures 126 and 127 is difficult due to the number of peaks present. In Table XVII, the two higher frequency peaks have been assigned tentatively to P=0 stretching vibrations as they fall most clearly within the range reported in the literature (Daasch and Smith, 1951; Socrates, 1980). The other peaks are possibly hydrocarbon radical vibrations. It is known that aromatic hydrocarbon radicals have a number of C-H in-plane deformation bands in the region 1290-1000 cm\(^{-1}\). These bands are sharp but usually only of weak-to-medium intensity (Socrates, 1980). Impurities are a further possibility. However, the excellent peak correlations between all the spectra suggests
that, if present, the impurities must have been identical for all of the surfactants. That all of the peaks in the 1265 to 1065 cm$^{-1}$ range were due to the P=O vibration also cannot be precluded entirely. However, for this to have been the case, the different hydrocarbon radicals of the surfactants must have interacted strongly with the P=O group to have produced the appreciably different spectra observed.

For aliphatic phosphonic acids, two vibrations involving stretching of P-C bonds are typically found near 750 cm$^{-1}$ and 650 cm$^{-1}$ (Daasch and Smith, 1951). Both of these bands are referenced as being relatively weak and their positions are reported to vary appreciably with the size and structure of the alkyl group. In Figure 125, a weak doublet with peaks at 777 cm$^{-1}$ and 763 cm$^{-1}$ and a stronger peak near 609 cm$^{-1}$ are evident. The latter peak appears somewhat distorted due to the 600 cm$^{-1}$ grating change of the Perkin-Elmer 283B spectrometer. In the absence of other possible band assignments in this range, both bands have been assigned tentatively to P-C vibrations.

A number of important conclusions regarding the nature of the hydrocarbon radicals of the commercial phosphonic acids can be reached on the basis of the spectra in Figures 125 to 127.

Examination of the infrared spectrum of Hoechst reagent P-195 (Figure 125) confirms that the reagent is an aliphatic rather than an aromatic phosphonic acid. No aromatic carbon skeletal vibrations are evident in the spectrum. Instead, the very characteristic CH$_3$ and CH$_2$ asymmetric and symmetric stretching vibrations are present in the high wavenumber 2960-2850 cm$^{-1}$ range. Sharp aliphatic C-C skeletal vibrations can be seen at 518, 499 and 443 cm$^{-1}$ (Table XVII). The presence of CH$_2$ groups further can be confirmed from the strong scissor vibration at 1462 cm$^{-1}$.
While the aliphatic nature of the hydrocarbon radical of P-195 is clearly evident in Figure 125, the detail in the infrared spectrum is insufficient to characterize fully the length and the branch structure of the radical.

The spectrum of the ICI reagent BPA (Figure 126) indicates the reagent to contain a monosubstituted phenyl ring. Peaks at 862, 779 and 691 cm$^{-1}$ are consistent with C-H out-of-plane bending and deformation vibrations in such a ring. The four C=C skeletal in-plane vibrations of the ring were evident in the 1600-1398 cm$^{-1}$ range. Whether the ring is bonded directly to the phosphorus of the polar group or to a methylene group cannot be determined unequivocally from the spectrum. However, the absence of a strong band in the range 1440-1420 cm$^{-1}$ supports the view that the reagent is not phenyl phosphonic acid. The Aldrich Handbook of Infrared Spectra (Pouchert, 1975) gives the spectrum of phenyl phosphonic acid. Comparison of this spectrum with that of BPA indicates a number of differences. In phenyl phosphonic acid, an unusually sharp and relatively strong band due to the phenyl-phosphorus bond occurs at 1450-1430 cm$^{-1}$ (Socrates, 1980). Clearly evident in the Aldrich spectrum of phenyl phosphonic acid, it is absent in that for BPA.

As shown in Figure 127, the infrared spectra of the reagents P-184, PH-PEP and EPPA were found to exhibit a remarkable correspondence with regard to both their hydrocarbon radical and their phosphonic acid group vibrations. The invariant nature of almost all the peak positions and intensities strongly suggests that the three reagents were the same. Given the exceptional correlations of their spectra, differences in chemical composition of the surfactants could exist only in the nature of trace components. This might be the case for impurities not well defined in the infrared spectra or present at very low concentrations.
Peaks in the range 745 to 680 cm\(^{-1}\) and near 814 cm\(^{-1}\) confirm the presence of mono-substituted phenyl ring vibrations in all three of the surfactant spectra of Figure 127. The former bands are those of C-H out-of-plane deformations in a mono-substituted phenyl radical. The latter represent the corresponding bending vibrations. The pair of ring out-of-plane vibrations near 606 and 572 cm\(^{-1}\) and the four C=C skeletal in-plane phenyl ring vibrations in the 1615-1440 cm\(^{-1}\) range are also consistent with the conjugation of an alkene group with the phenyl ring and with the structure of the styryl radical (Bellamy, 1962). The absorption peak at 1573 cm\(^{-1}\) is of particular significance as Randall et al (1949) regard a band in the range 1587-1575 cm\(^{-1}\) as a positive indicator of an alkene conjugated with an aromatic ring. While the 1573 cm\(^{-1}\) peak for P-184 is 2 cm\(^{-1}\) outside this range, the precision of the Perkin-Elmer 283 B Spectrophotometer, on a polystyrene standard in the 2000 to 400 cm\(^{-1}\) range, is ±4 cm\(^{-1}\) (Hanah and Swinehart, 1974).

The infrared spectra of P-184, PH-PEP and EPPA support the contention that all three reagents are styryl phosphonic acid with the structure:

\[
\text{CH} = \text{CH} - \text{P}\left< \text{OH} \right> \text{OH}
\]

The data are not consistent with any of the reagents being p-ethylphenylene phosphonic acid. Specifically, the C-H in-plane deformation vibrations observed were not those of a para di-substituted phenyl ring.
4.2.2 **Nuclear Magnetic Resonance Spectroscopy**

In agreement with the findings of the infrared studies, proton nuclear magnetic resonance (NMR) analyses of the reagents P-184, PH-PEP and EPPA confirmed conclusively that the hydrocarbon radicals of all three surfactants were the same. Furthermore, the peak patterns of the reagents were unambiguously that of styryl phosphonic acid:

\[ \text{\includegraphics[width=0.3\textwidth]{styryl_phosphonic_acid.png}} \]

The spectra of the three phosphonic acids P-184, PH-PEP and EPPA (Figures 128 to 130) all show a complex peak pattern centered at a chemical shift (\(\delta\)) of approximately 7.4. This peak position is a fingerprint resonance for phenyl ring protons (Kemp and Vellaccio, 1980). The detailed peak splitting resulted from coupling of the ring protons with the protons of the substituted alkene (\(-\text{CH}=\text{CH}-\)) group. The alkene group of the radical itself produced six peaks lying in the chemical shift range 6.1 \(\delta\) to 7.2 \(\delta\). Proton NMR spectra of alkene groups typically show a quartet of peaks (referred to as an AB quartet) in this range (Kemp and Vellaccio, 1980). However, the presence of the directly coupled phosphorus atom caused the doublet of the chemically most shielded alkene protons to split into a pair of doublets. The coupling interaction of the phosphorus with the deshielded alkene protons was presumably too weak to cause observable peak splitting and the six peak pattern resulted. Such splitting is possible since the phosphorus nucleus, like the proton, has spin quantum numbers of \(\pm 1/2\). The splitting of the AB quartet is shown schematically below:
Figure 128 - Proton Nuclear Magnetic Resonance Spectrum of Hoechst Reagent P-184.

Figure 129 - Proton Nuclear Magnetic Resonance Spectrum of Plaistere and Hanger Reagent PH-PEP.
Figure 130 - Proton Nuclear Magnetic Resonance Spectrum of Organophos Reagent EPPA.

The series of peaks in the chemical shift 8.0 to 6.0 range of Figures 128 to 130 can be considered as a fingerprint not only for the presence of a styryl radical but for such a radical bonded to a phosphorus atom. There was no evidence that any of the reagents were p-ethylphenylene phosphonic acid. If present, the ethyl group of this radical would have produced a series of large peaks in the chemical shift range 1.5 \( \delta \) to 2.5 \( \delta \). Furthermore, a 4 proton para-disubstituted aromatic ring would have given a distinctly
different peak pattern at $7.4 \delta$ (Silversteen, Bassler and Morrill, 1974). All such peaks were clearly absent.

The only peaks in the spectra of Figures 128 to 130 not attributable directly to a styryl radical were the series of three peaks between $4.5 \delta$ and $5.5 \delta$. These peaks were due to the hydroxyl group protons of the phosphonic acids and structurally bound water in the reagents. Water and hydroxyl group protons characteristically produce a large peak at $4.85 \delta$ and small side bands at $5.4 \delta$ and $4.2 \delta$ (Kemp and Vellaccio, 1980).

Peak integration performed on the P-184, PH-PEP and EPPA NMR spectra indicated that the aromatic ring to alkene group proton ratio for all three phosphonic acids was approximately 5 : 1.5. Strictly, for the styryl radical, the rate should have been 5 : 2. The difference between the observed and expected ratios is considered to be due to:

1. the post-delay period in the NMR phosphonic acid scans being too short to allow full proton relaxation in all groups.
2. the accuracy of digital integration being greater for broad peaks than for sharp narrow peaks. This probably led to significant integration errors between the broad ring peaks and the sharp alkene peaks.

The proton NMR spectrum of the ICI reagent BPA (Figure 131) shows a single peak at $7.38 \delta$ and a doublet centered at $2.75 \delta$. The single resonance at $7.38 \delta$ is characteristic of a mono-substituted phenyl ring in which the substituent is neither a strongly electron-withdrawing nor a strongly electron-donating group (Kemp and Vellaccio, 1980). The doublet at $2.75 \delta$ was the result of splitting of the methylene group resonance by the attached phosphorus atom. The NMR spectrum is unambiguously that of the hydrocarbon radical of benzyl
phosphonic acid:

\[
\text{O} - \text{CH}_2 - \text{P(OH)_2}
\]

Figure 131 - Proton Nuclear Magnetic Resonance Spectrum of ICI Reagent BPA.

Only two hydrocarbon radical proton resonances were found in the NMR spectrum of Hoechst P-195. Both resonances produced broad peaks; one extending from 1.5 \( \delta \) to 1.0 \( \delta \) and the other from 0.9 \( \delta \) to 0.6 \( \delta \) (Figure 132). These peaks are characteristic of a straight chain hydrocarbon radical. The methylenes in the radical appeared as the large unresolved peak at the higher chemical shift. The terminal methyl group of the chain was clearly evident by the fact that it appeared upfield from the methylene protons. The methyl group was split by the methylene group next to it into a crude triplet and was distorted and broadened by virtual coupling (Kemp and Vellaccio, 1980). The ratio of the NMR peak areas was found to be 4:1. Since a methyl group
contains 3 protons, the hydrocarbon radical contained 6 methylene groups (12 protons). The surfactant Hoechst P-195 is, therefore, heptyl phosphonic acid with the structure:

\[
\text{CH}_3-(\text{CH}_2)_5-\text{CH}_2-P\ \text{OH}
\]

Figure 132 - Proton Nuclear Magnetic Resonance Spectrum of Hoechst Reagent P-195.

Examination of all the phosphonic acid NMR spectra indicates that no significant hydrocarbon impurities were present in the surfactants. However, in comparison to the other spectra, that of Organophos EPPA (Figure 130) is considerably more noisy. This is believed due to insoluble impurities associated with the reagent. Dissolution of EPPA in D_2O invariably produced more turbid solutions than was characteristic of the other commercial phosphonic acids.
4.2.3 Chemical Analyses

Chemical analyses of the commercial phosphonic acids indicated the reagents to vary considerably both with regard to their absolute purities and the nature of their trace level contaminants. Compositional variations were particularly pronounced among the three styryl phosphonic acids.

Table XVIII summarizes the results of total carbon, total phosphorus and trace metal ICAP analyses of all five reagents. From the results, it is possible to calculate phosphonic acid percentage purities based on actual to theoretical carbon and phosphorus levels or by difference based on the trace elements detected. Table XIX compares purity levels calculated according to each of these three methods.

The ICI BPA reagent was of relatively high purity. On a total carbon, total phosphorus and trace metals difference basis, weight percent benzyl phosphonic acid in BPA was calculated as 92.1, 97.8 and 99.9 percent, respectively. The principal inorganic contaminants were sodium (537 ppm) and calcium (250 ppm). At these levels, the reagent could have contained only negligible concentrations of phosphonic acid salt species. If the reagent had been disodium or dicalcium benzyl phosphonate, the sodium and calcium assays would have been 21.3% Na or 32.0% Ca; respectively. Appreciable levels of heavy metals were detected also in the reagent. Most significant amongst these were aluminum, titanium, iron, zinc and molybdenum.

In comparison to the BPA, trace metal levels in both of the Hoechst reagents were particularly low. The dominant contaminant was again sodium. Reagent P-184 contained 173 ppm of this element while 85 ppm was found in P-195. Of importance in terms of the research, the concentrations of aluminum, iron and magnesium were low. For the styryl phosphonic acid P-184,
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>BPA</th>
<th>P-195</th>
<th>PH-PEP</th>
<th>P-184</th>
<th>EPPA</th>
<th>DETECTION LIMIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Carbon</td>
<td>TC</td>
<td>45.0%</td>
<td>46.5%</td>
<td>46.3%</td>
<td>45.5%</td>
<td>45.2%</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>78.4</td>
<td>L</td>
<td>L</td>
<td>L</td>
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<tr>
<td>Antimony</td>
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<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>38.9</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>38.9</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>6.2</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>7.1</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>0.6</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>100.</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>16.1</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>16.1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
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<tr>
<td>Calcium</td>
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<td>21.7</td>
<td>68.9</td>
<td>31.2</td>
<td>81.4</td>
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<tr>
<td>Chromium</td>
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<tr>
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<td>L</td>
<td>L</td>
<td>L</td>
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</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>18.1</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>19.5</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>44.4</td>
<td>9.9</td>
<td>20.2</td>
<td>L</td>
<td>875.</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
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<td>L</td>
<td>L</td>
<td>L</td>
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<td>Magnesium</td>
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<td>Manganese</td>
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<tr>
<td>Molybdenum</td>
<td>Mo</td>
<td>34.0</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>19.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>7.40</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>107.</td>
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<tr>
<td>Phosphorus</td>
<td>P</td>
<td>17.6%</td>
<td>17.4%</td>
<td>17.1%</td>
<td>16.6%</td>
<td>17.6%</td>
</tr>
<tr>
<td>Potassium</td>
<td>K</td>
<td>4.9</td>
<td>4.0</td>
<td>7.9</td>
<td>17.5</td>
<td>7.1</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>537.</td>
<td>85.0</td>
<td>136.</td>
<td>173.</td>
<td>147.</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr</td>
<td>5.4</td>
<td>L</td>
<td>0.7</td>
<td>L</td>
<td>0.5</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>49.3</td>
<td>L</td>
<td>43.</td>
<td>21.5</td>
<td>69.1</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
<td>9.9</td>
<td>31.6</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>44.3</td>
<td>11.9</td>
<td>13.7</td>
<td>9.7</td>
<td>140.</td>
</tr>
</tbody>
</table>

All results expressed in parts per million
L = less than
TABLE XIX
CALCULATED PURITIES OF COMMERCIAL PHOSPHONIC ACID REAGENTS

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Assays</th>
<th>Actual Assays</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%C</td>
<td>%P</td>
<td>%C</td>
</tr>
<tr>
<td>BPA</td>
<td>48.85</td>
<td>18.00</td>
<td>45.0</td>
</tr>
<tr>
<td>P-195</td>
<td>46.6</td>
<td>17.19</td>
<td>46.5</td>
</tr>
<tr>
<td>PH-PEP</td>
<td>52.18</td>
<td>16.82</td>
<td>46.3</td>
</tr>
<tr>
<td>P-184</td>
<td>52.18</td>
<td>16.82</td>
<td>45.5</td>
</tr>
<tr>
<td>EPPA</td>
<td>52.18</td>
<td>16.82</td>
<td>45.2</td>
</tr>
</tbody>
</table>

the levels of aluminum and iron were below detection. In the case of P-195, evidence was found to suggest that residual phosphorus species were present. Actual phosphorus assays for the reagent exceeded that theoretically present in n-heptyl phosphonic acid. Excess phosphorus most probably is indicative of residual levels of phosphorus reactants from the surfactant synthesis.

In terms of contaminants, the Plaistere and Hanger styryl phosphonic acid contained only slightly higher heavy metal levels than P-184. However, it did contain detectable iron (20.2 ppm) and higher magnesium (29.5 ppm) and calcium (68.9 ppm) concentrations than P-184. As for Hoechst P-195, the phosphorus assays indicated the possible presence of residual phosphorus species.

Organophos EPPA was the most impure of the commercial phosphonic acids. The spectrographic assays indicated it to contain numerous heavy metal elements at high trace levels. These included iron (875 ppm), chromium (283 ppm), zinc (140 ppm) and nickel (107 ppm). Calcium and sodium levels at 81.4 ppm and 147 ppm, respectively, were also appreciable. The 17.6 percent actual
phosphorus assay, relative to the theoretical 16.82 percent of pure styryl phosphonic acid, further suggested the reagent to contain significant phosphorus byproduct.

The infrared and NMR analyses of this research have revealed, rather surprisingly, that the reagents Hoechst P-184, Plaistere and Hanger PH-PEP and Organophos EPPA are identical in terms of the nature of their phosphonic acid components. All industrial concentrators that float cassiterite with phosphonic acids are, therefore, using reagents that have structurally similar hydrocarbon radicals. These preferred commercial reagents differ chemically only in the nature of their purity and trace element compositions.

In endeavouring to correlate the results of this fundamental research with industrial practice, it was desirable that one of the styryl phosphonic acid reagents should be used for the detailed solution chemical test work. The Hoechst P-184 reagent was selected on the basis of its high purity and the absence of residual phosphorus. While containing only slightly lower total contaminant levels than PH-PEP (Table XIII), it did not contain detectable iron or aluminum and its magnesium and calcium concentrations were lower. The ionic species of these metals were the key elements under investigation in the solution chemical studies of the research.

4.2.4 Styryl Phosphonic Acid Dissociation Constants

Figure 133 shows experimental data for the back titration of a sodium salt solution of styryl phosphonic acid (Hoechst P-184). Data are given for titrations with two different concentrations of titrant (HCl). Both curves possess a single sharp inflection at just below pH 5.0. Gran plot calculations (Appendix D), performed for one data set, gave an equivalence volume of 9.65 mls of HCl (Figure 134). Based on this equivalence point, the
Figure 133 - Experimental Back Titration Curves for the Sodium Salt of Styryl Phosphonic Acid (Hoechst P-184). Data are given for two separate titrations of a $1 \times 10^{-4}$ M solution.

Figure 134 - Gran Plot for the Titration Curves of the Sodium Salt of Styryl Phosphonic Acid (Hoechst P-184). The HCl equivalence volume is 9.65 mls of HCl.
associated half-neutralization points of the titration curve indicated the pK values of styryl phosphonic acid to be 2.60 and 7.60, respectively (Figure 133). Calculations for the other data set gave similar values.

Theoretically, the titration curve for a diprotic acid should show two endpoints. In Figure 133, the lower endpoint is blurred and only the higher pH inflection is clearly evident. Such endpoint blurring is not uncommon (Harris, 1982). It results from the fact that the dissociated acid species is too strong (or equivalently that the partially neutralized species is too weak a base) for it to exist partially dissociated with substantial free H⁺.

Chavane (1949) has reported the dissociation constants of styryl phosphonic acid to be pK₁ = 2.00 and pK₂ = 7.10. The disparity between these values and those of this research are greater than might be expected on the basis of the accuracy of the potentiometric titration technique. A possible contributing factor might be that Chavane did not use carbon dioxide-free distilled water in preparation of his analyte and titrant. No reference to such can be found in his publication.

Carbon dioxide is widely recognized as a serious source of error in titrations. Absorbed from the atmosphere, it can react with alkaline solutions to form bicarbonate species. These, in turn, reduce the pH of the solution and increase the level of acid required for reaction near the endpoint in the titration.

A fractional composition diagram, calculated from the experimental dissociation constants of the Hoechst styryl phosphonic acid (Appendix F), is shown in Figure 135. In cassiterite flotation circuits, where phosphonic acid collectors are used, the pH range of flotation is typically between pH 4.5 and 5.5. Reference to the compositional diagram, indicates that, in this pH
range, styryl phosphonic acid is predominantly present as the partially dissociated species.

Figure 135 - Styryl Phosphonic Acid Fractional Composition Diagram.

4.2.5 Ultraviolet Absorbance of Styryl Phosphonic Acid

Ultraviolet spectra have been reported for a large number of phosphonic acids (Jaffé and Freedman, 1952; Banks and Davis, 1955; Polestak and Zimmerman, 1956). However, no such data for styryl phosphonic acid exist in the published literature.

Spectroscopic analyses conducted in this test work have shown that the ultraviolet spectra of slightly acidic and alkaline solutions of styryl phosphonic acid essentially corresponded to that of benzene. No electronic transitions of the ethylene group of the styryl radical were observed for such solutions. This finding is consistent with the reported 175 nm wavelength of
these ethylene group transitions (Jaffé and Orchin, 1962) and have hence their existence in the far ultraviolet region of the electromagnetic spectrum.

In highly acidic solutions, profound changes in the UV spectrum of styryl phosphonic acid were found. The observed spectral differences were consistent with a pronounced bathochromic shift of either the allowed benzene ring $^1E_u \leftarrow ^1A_{1u}$ transition or the ethylene group transition such that a strong band became visible in the UV spectrum near a wavelength of 195 nm.

At pH 5.0, the ultraviolet spectrum of styryl phosphonic acid (P-184) was dominated by two bands (Figure 136). The first band was centered near 202 nm and exhibited a degree of fine structure. Such a band corresponds with the forbidden $^1B_{1u} \leftarrow ^1A_{1u}$ transition of the benzene ring. Jaffé and Orchin (1962) have reported that this transition normally produces a broad band near 200 nm. The second band was centered near 256 nm and was a secondary benzene ring band resulting from the symmetry-forbidden $^1B_{2u} \leftarrow ^1A_{1u}$ transition. This secondary band lacked fine structure presumably since the spectrum was determined in water. In a polar solvent, such as water, solute-solvent complexes can be formed due to hydrogen bonding and fine structure can disappear. The allowed $^1E_{2u} \leftarrow ^1A_{1u}$ transition of the benzene ring was not observed in the styryl phosphonic acid spectrum at pH 5.0. This band has been reported (Jaffé and Orchin, 1962) normally to exist in the far ultraviolet at 180 nm.

Increasing the alkalinity of the styryl phosphonic acid solution to pH 10.0 produced a very slight hyperchromic shift of the 256 nm peak and a significant such shift in that of the forbidden $^1B_{1u} \leftarrow ^1A_{1u}$ transition. In the latter case, there was also some evidence for a small hypsochromic shift (Figure 136). In contrast, acidifying the solution to pH 1.0 produced a
Figure 136 - Ultraviolet Spectra of a $1 \times 10^{-4}$ M Styryl Phosphonic Acid (P-184) Solution at Three Different pH Values.

A moderate hypochromic and a small bathochromic shift in the 256 nm peak and fundamentally altered the spectrum below a wavelength of 220 nm (Figure 136). These low wavelength changes were consistent with a hypochromic shift of the $^1B_{1u} \leftarrow ^1A_{1g}$ peak and an associated overlapping of this peak with a new peak centered near 195 nm. This new peak could have been that of the allowed benzene ring $^1E_{2u} \leftarrow ^1A_{1g}$ transition or the electronic transitions of the ethylene group of the styryl radical, or both. Irrespective of which was the case, the bathochromic shift caused by substitution was significant.

Reference to the fractional composition diagram of styryl phosphonic acid (Figure 135) indicates that at pH 5.0 the phosphonic acid exists as the partially neutralized species. At pH 10.0, the diprotic acid is completely dissociated while at pH 1.0 undissociated phosphonic acid molecules
predominate. It can be concluded, therefore, that the P(O)(OH)O\(^-\) and P(O)(O\(^-\))\(_2\) groups, in aqueous solution, cause no profound change in the spectrum of the parent styryl hydrocarbon compound. However, the P(O)(OH)\(_2\) group has a more pronounced effect. Such findings are in accordance with those of studies with other phosphonic acids (Jaffe and Freedman, 1952; Banks and Davis, 1955, Polestak and Zimmerman, 1956). It has been proposed that weak resonance interactions can exist between the P(O)(OH)\(_2\) group and a phenyl ring (Freedman and Doak, 1957; Hudson, 1965) such that aryl phosphonic acids typically show bathochromic shifts of the order of 10 nm relative to that of the parent hydrocarbon. For styryl phosphonic acid, the bathochromic shift was clearly greater than this at pH 1.0 but the characteristic higher wavelength peaks of the benzene ring were still easily recognizable.

For styryl phosphonic acid concentration determinations in aqueous solution, an ultraviolet band was sought for which the absorbance was both relatively pH independent and followed the Beer-Lambert Law. The logical choice was the benzene ring symmetry-forbidden \(^1B_{2u} \leftarrow ^1A_{1g}\) transition band at 256.2 nm. Absorbance of a 1 x 10\(^{-4}\) M surfactant solution was found to be relatively constant at this wavelength for at least one pH unit either side of pH 5.0 (Figure 137). Furthermore, the Beer-Lambert Law was confirmed as applying at pH 5.0 in the styryl phosphonic acid concentration range 1x10\(^{-5}\) M to 1 x 10\(^{-4}\) M (Figure 138). The 256.2 nm ultraviolet absorbance of solutions adjusted to pH 5.0 was consequently adopted for phosphonic acid concentration determinations in all adsorption test work.
Figure 137 - The pH Dependence of the 256.2 nm Ultraviolet Absorbance of a $1 \times 10^{-4}$ M Styryl Phosphonic Acid (P-184) Solution.

Figure 138 - The Concentration Dependence of the 256.2 nm Ultraviolet Absorbance of Styryl Phosphonic Acid (P-184) Solution at pH 5.0.
4.2.6 Styryl Phosphonic Acid Surface Tensions

Styryl phosphonic acid was found to have significant surface tension lowering effects in acidic aqueous solutions (Figure 139). For surfactant concentrations of $1 \times 10^{-3}$ M and $3 \times 10^{-3}$ M, pronounced decreases were measured in the acidic range below pH 4.0 and pH 7.0, respectively. Higher phosphonic acid concentrations similarly produced maximum surface tension lowering in highly acidic solutions although definite decreases were also observed at higher pH values.

The surface tension measurements with styryl phosphonic acid confirmed unequivocally that the undissociated acid possessed an high degree of inherent surface activity. The same finding has been made by Kamienski and Krauss (1965) for the chemically similar arsonic acids (Figure 140).

The dependence of the surface activity of phosphonic and arsonic acids on pH can be explained readily on the basis of the degree of ionization of the molecules. In increasingly acidic solutions, protonation of these surfactants occurs (Figure 135). This reduces the overall polar character of the molecules and increases the tendency for them to escape the polar aqueous phase. By orientating at the air-liquid interface, with their hydrocarbon chains exposed to the air and their polar groups in the aqueous phase, the undissociated acid molecules can reduce their overall free energy. Such orientations produce the decreases in surface free energy at low pH observed in the surface tension measurements. At higher surfactant concentrations, it is evident (Figures 139 and 140) that sufficient partially and completely dissociated species can exist at the air/liquid interface to cause also some lowering of the surface tension.
Figure 139 - Surface Tensions of Styryl Phosphonic Acid Solutions. Data are shown for a range of concentrations. The initial pH (pH$_i$) values of the surfactant solutions are marked in the figure.

Figure 140 - Surface Tension of 0.1 M KCl in the Presence of (1) 0.04 M Phenyl; (2) 0.02 M o-tolyl; and (3) 0.04 M p-tolyl Arsonic Acids (from Kamienski and Krauss, 1965).
The styryl phosphonic acid concentrations required to achieve significant surface tension lowering (Figure 139) were higher than is typical in surfactant studies. This was a consequence of the relatively insoluble nature of the surfactant and the short length of its styryl radical. For most surfactants, surface tension lowering usually is observed only with relatively long chain (> C₁₀) homologues (Fuerstenau, 1982; Leja, 1982). It is generally considered that the presence of a phenyl ring in a hydrocarbon radical is equivalent to between 3.2 (Dick, Fuerstenau and Healy, 1971) and 3.5 methylene groups (Shinoda et al, 1963; Rekker, 1977). On this basis, the styryl radical would be equivalent to only a C₅ or C₆ chain length alkyl radical.

A striking feature of the surface tension data in Figure 139 is that three of the curves show minima. As recently pointed out by Healy (1986), such minima must indicate the formation of a second phase either in bulk solution or at the air/liquid interface. This is a consequence of the fundamental relationship between the Gibbs free energy and surface tension (Hiemenz, 1977).

The formation of a second phase in acidic solutions and the association of styryl phosphonic acid molecules that it implies, are particularly interesting phenomena given the short nature of the styryl radical. Van der Waals interactions between styryl groups would not be expected to be particularly strong since the standard free energy change for removing CH₂ groups from water though association is only of the order of 2.5 kJ/mole (Wakamatsu and Fuerstenau, 1968). It is possible, therefore, that the driving force for association is not primarily the tendency for the hydrocarbon radicals to associate (as usually is considered the case in surfactant solution chemistry) but the ability of the polar groups to hydrogen bond. Kosolapoff (1952), in
his pioneering publication on phosphonic acid chemistry, was of the view that, at very low pH, hydrogen bonding might persist in aqueous solution. However, Freedman and Doak (1956), criticised the hypothesis on the basis that the weak energy of the hydrogen bond would result in rapid dissolution of such associations in a polar solvent such as water.

It is evident from this research, that indeed some form of association does exist in strongly acidic solutions and that this association is uncharacteristically strong for such a short chain surfactant. Furthermore, in the solid state and in certain non-polar solvents the phosphonic acids do associate in long chains through molecular hydrogen bonding. The existence of these bonds has been demonstrated clearly by molecular weight studies, infrared spectroscopy and X-ray diffraction (Kosolapoff and Powell, 1950; Freedman, Doak and Ezzell, 1971).

Both the surface tension lowering effect and the existence of minima indicating a phase change are of importance in terms of phosphonic acid adsorption at the cassiterite/aqueous solution interface. The phenomena confirm that, at low pH, undissociated phosphonic acid molecules have sufficient non-polar character that they can lower their free energy by adsorbing at an interface and that associations between such adsorbed molecules can occur. While the surfactant concentrations in the surface tension studies where these phenomena were observed were orders of magnitude higher than reasonably might be expected in the aqueous phase of a flotation pulp, they are not necessarily unrepresentative of that existing at a cassiterite aqueous solution interface. Due to the affinity of phosphonic acids for the cassiterite surface, concentrations at the interface would be expected to greatly exceed that existing in the bulk.
4.2.7 **Styryl Phosphonic Acid Solution Turbidities**

Light scattering analyses confirmed that concentrated styryl phosphonic acid solutions possessed measurable turbidities. At pH 5.0, turbidity increases above that of the distilled water solvent were observed at concentrations as low as $5 \times 10^{-5}$ M. At higher concentrations, an approximately linear relationship between turbidity and log molar styryl phosphonic acid concentration was found (Figure 141).

When a solution becomes supersaturated, it no longer represents a homogeneous system but forms a colloidal or non-colloidal in size dispersion of an insoluble surfactant phase in a saturated solution of surfactant. For styryl phosphonic acid solutions at pH 5.0, it is evident that supersaturation can occur at the relatively low concentration of $5 \times 10^{-5}$ M. This confirms that the commercially important styryl phosphonic acid is only sparingly soluble in water and explains why the surfactant is prepared industrially for flotation circuits as the sodium salt (Anon, 1981).

The degree of solubility of styryl phosphonic acid in aqueous solution, as measured by light scattering, was found not to change significantly over the pH 1.0 to 10.0 range (Figure 142). Only moderate increases in solubility occurred at higher pH for more concentrated solutions. This solubility increase undoubtedly reflected the more polar nature of completely dissociated styryl phosphonic acid molecules that are the predominant species in alkaline solutions (Figure 135).

It was evident from the light scattering studies that solution supersaturation must have existed during the surface tension measurements of Figure 139. This presumably explains the absence of any correlation between the pH dependence of the surface activity of styryl phosphonic acid and its
Figure 141 - The Concentration Dependence of Styryl Phosphonic Acid Solution Turbidities at pH 5.0.

Figure 142 - The pH Dependence of Styryl Phosphonic Acid Solution Turbidities. Data are shown for four surfactant concentrations.
bulk solution turbidity. At the pH of solution preparation, unassociated molecules would have been the predominant species adsorbing at the air/liquid interface. Inherently more stable colloidal aggregates would have remained in solution. The former species, therefore, determined the surface activity while the latter were responsible for the turbidity. It is well known that light scattering is only sensitive to colloidal size aggregates and not free molecules or very small surfactant associations (Hiemenz, 1977). On adjustment of the pH, the number of molecules adsorbed at the interface either increased or decreased, as evidenced by the surface tension changes in Figure 139, but the extent of the change clearly was not sufficient to reduce the concentration of the larger molecular associations in solution.

4.2.8 Molecular Modelling

Styryl phosphonic acid molecules can exhibit stereoisomerism due to the presence of the alkene group in the styryl radical. The $\pi$ bond of this alkene group (formed between the sp$^2$-hybridized carbon atoms) prevents rotation about the double bond. This results in the phenyl ring and phosphonic acid polar group of the surfactant either being at a definite angle, forming a nonlinear configuration (the cis form at the molecule), or in a nearly linear configuration (the trans form). While both isomers can exist, the trans form invariably predominates since it is inherently more stable (Butler and Berlin, 1972).

Plate 8 shows molecular models of cis and trans styryl phosphonic acid. Evident from the models is that the cis isomer is less "planar" and much more constrained stereochemically. In the trans isomer, the alkene group and phosphonic acid group are free to rotate with respect to the phenyl ring. Consequently, it is possible for the alkene group to be in the plane of the
THE QUALITY OF THIS MICROFICHE IS HEAVILY DEPENDENT UPON THE QUALITY OF THE THESIS SUBMITTED FOR MICROFILMING.

UNFORTUNATELY THE COLOURED ILLUSTRATIONS OF THIS THESIS CAN ONLY YIELD DIFFERENT TONES OF GREY.

LA QUALITE DE CETTE MICROFICHE DEPEND GRANDEMENT DE LA QUALITE DE LA THESES SOUMISE AU MICROFILMAGE.

MALHEUREUSEMENT, LES DIFFERENTES ILLUSTRATIONS EN COULEURS DE CETTE THESES NE PEUVENT DONNER QUE DES TEINTES DE GRIS.
Plate 8 - Molecular Models of the Trans and Cis Isomers of Styryl Phosphonic Acid. The model colour coding is: carbon - black; hydrogen - orange; oxygen - blue; phosphorus - magenta.

Aromatic ring. In the case of the cis isomer, this is not possible due to steric hindrance between the polar group and the ring.

The constrained nature of cis styryl phosphonic acid is reflected in the effective volume of the molecule. For the trans isomer, the effective volume is 776.1 Å³ while for the cis form it is only 492.5 Å³. The maximum length of the trans form is also greater at 12 angstroms.

Considerable molecular compatibility exists between styryl phosphonic acid and the surface of cassiterite. With the two hydroxyls of the phosphonic acid polar group orientated away from the hydrocarbon radical, but in the same direction, the minimum and maximum separation of these hydroxyls is 2.5 Å and 3.5 Å, respectively. For the (110) cleavage plane of the cassiterite lattice,
hydroxyl ions completing the coordination number of exposed stannic ions would be expected to have ionic separations similar to that of the oxygen atoms of the bulk mineral lattice (Figure 3). Published crystallographic data for cassiterite (Shuey, 1975) give this separation as 2.58 Å. It, therefore, is possible sterically for the hydroxyls of the phosphonic acid polar group to replace two adjacent coordinated hydroxyls from the surface of the (110) plane of cassiterite. Similar compatibility reasonably might be expected to exist on certain other cleavage planes.

Examination of the molecular model of the trans isomer of styryl phosphonic acid (Plate 8) indicates that the breadth of the hydrocarbon radical, rather than that of the polar group, is the steric parameter that will affect predominantly the conformations of these molecules absorbed at an interface. As is evident in Plate 9, the physical structure of the styryl radical is such that styryl phosphonic acid molecules can pack in a condensed state. Such a packing arrangement is favourable obviously to strong van der Waals bonding between the non-polar groups.

The projected area of the trans styryl phosphonic acid molecule, orientated in the manner of Plate 9, was determined from the molecular models to be 35.2 Å². This is considerably larger than the value of 25 Å² assumed in the adsorption study calculations of Section 2.4.5. While the styryl radical is of greater cross-sectional area than that of the heptyl radical, a projected area of 25 Å² most definitely is conservatively small even for the latter radical.
Plate 9 - Arrangement of Molecular Models Showing the Ability of Styryl Phosphonic Acid Molecules (trans-form) to Pack in a Condensed State. The model colour coding is: carbon – black; hydrogen – orange; oxygen – blue; phosphorus – magenta.
4.2.9 **Principal Findings and Conclusions**

(1) Infrared and nuclear magnetic resonance spectroscopy have confirmed unequivocally that the reagents Plaistere and Hanger PH-PEP, Hoechst P-184 and Organophos EPPA are identical in terms of the nature of their phosphonic acid components. The three reagents are styryl phosphonic acid. All major industrial concentrators that float cassiterite with phosphonic acids are, therefore, using styryl phosphonic acid.

(2) The commercial styryl phosphonic acid reagents differ chemically only in terms of their purity and trace element compositions. Both the Hoechst and Plaistere and Hanger styryl phosphonic acids are relatively pure. In contrast, Organophos EPPA contains numerous heavy metals elements at high trace levels.

(3) Hoechst P-184 styryl phosphonic acid was selected for use in the detailed solution chemical test work of this thesis. The basis of this selection was the surfactant's high purity and the absence of residual phosphorus. While containing only slightly lower total contaminant levels than PH-PEP, P-184 did not contain detectable iron or aluminum and its magnesium and calcium concentrations were lower. The ionic species of these metals were the key elements under investigation in the solution chemical studies of this research.
(4) Hoechst reagent P-195 is n-heptyl phosphonic acid while ICI BPA is benzyl phosphonic acid. Both reagents are of high purity.

(5) The dissociation constants of styryl phosphonic acid, as determined by potentiometric titration of Hoechst P-184, are $pK_1 = 2.60$ and $pK_2 = 7.60$. The predominant species in the pH range characteristic of industrial cassiterite floatation (pH 4.5 - 7.0) is, therefore, the partially dissociated acid species.

(6) The ultraviolet spectrum of styryl phosphonic acid corresponds essentially to that of the hydrocarbon radical benzene ring. In slightly acidic and basic solutions, the $P(0)(OH)O^-$ and $P(0)(O^-)_2$ groups cause no marked change in the aromatic ring spectrum. In highly acidic solutions, the $P(0)(OH)_2$ group produces a more significant change consistent with a resonance interaction between the polar group and the phenyl ring of the radical.

(7) The 256.2 nm ultraviolet absorbance of styryl phosphonic acid solutions at pH 5.0 is both relatively insensitive to small pH variations and follows the Beer-Lambert Law over the concentration range $1 \times 10^{-5} \text{ M}$ to $1 \times 10^{-4} \text{ M}$. This absorbance, at a solution pH of 5.0, consequently was adopted as the standard for phosphonic acid concentration determinations in all adsorption test work.
Styryl phosphonic acid has significant surface tension lowering effects in acidic aqueous solutions. Furthermore, surface tension curves at low pH can exhibit minima indicating the formation of a second phase. These phenomena confirm that, at low pH, undissociated phosphonic acid molecules have sufficient non-polar character that they can lower their free energy by adsorbing at an interface and that associations between such adsorbed molecules can occur.

Supersaturation of styryl phosphonic acid solutions occurs at concentrations as low as $5 \times 10^{-5}$ M. This confirms the sparingly soluble nature of the surfactant in water.

The solubility of styryl phosphonic acid in aqueous solution, as measured by light scattering, was found not to change significantly over the range pH 1.0 to 10.0. A $1 \times 10^{-4}$ M solution of the surfactant has a relatively constant turbidity of approximately $1.3 \times 10^{-4}$.

The cis form of styryl phosphonic acid is less "planar" and much more constrained stereochemically than the trans isomer.

Molecular compatibility exists between styryl phosphonic acid and the surface of cassiterite. It is possible sterically for the hydroxyls of the phosphonic acid polar group to replace two adjacent coordinated hydroxyls on certain cassiterite cleavage planes such as the (110) plane.

The physical structure of trans styryl phosphonic acid molecules is such that they can pack in a condensed state
with both hydroxyls of their polar groups orientated away from the ring and in the same direction. The projected area of individual molecules orientated in such a manner is $35.2\AA^2$. 
4.3 Ion Solution Chemistry

4.3.1 Plant Water Analyses

The results of Renison cassiterite floatation pulp water analyses have been summarized previously in the literature review (Table VI). In Table XX a complete data set is given. Included in this table are the sampling run and the positions in the circuit where the samples were taken. The latter are referenced with respect to the circuit diagram of Figure 84.

The analyses of the Renison pulps confirmed that extraordinarily high levels of ions can exist in tin flotation pulps. In particular, the data indicating dissolved iron levels of the order of 50 to 60 ppm are remarkable. Such iron assays are strongly supportive of the hypothesis that iron films observed on the surfaces of cassiterite grains recovered from the Renison circuit are due to iron species adsorbed from the aqueous phase.

The assay data of Table XX show considerable variability both with regard to sampling time (run number) and position. In the case of iron, very high (60 ppm) levels were found at the head of the rougher bank in the first run while assays from the other two sampling points were more than an order of magnitude lower. In the second sampling run, the trend was reversed. Similar variability existed in the aluminum assays. For calcium and magnesium assays, a definite decreasing trend through the floatation circuit was noted.

To a significant degree, the variability in the pulp assays between runs probably reflects the dynamic nature of the cassiterite flotation circuit. It is considered that steady-state conditions are rarely, if ever, established in the Renison tin flotation plant (Sutherland, 1983). Furthermore, the dissolved ion levels most probably vary appreciably with the mineralogical composition of the ore, the nature of the return water and the performance of
### TABLE XX

**RENISON CASSITERITE FLOTATION PULP WATER ANALYSES**

<table>
<thead>
<tr>
<th>Sampling Run</th>
<th>Sample Location</th>
<th>Sample Number</th>
<th>pH  (mV)</th>
<th>Eh</th>
<th>AAS Analyses (ppm)</th>
<th>Total Alkalinity (ppm CaCO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe     Al   Cu   Ca   Mg</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>&lt;0.5</td>
<td></td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>60</td>
<td>21</td>
<td></td>
<td></td>
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<tr>
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<td>2</td>
<td>62</td>
<td></td>
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<td></td>
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<tr>
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<td>3</td>
<td>61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>&lt;0.5</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|               | 1               | 6.25          | -22     | 52.4 | 1.3    0.04 | 470 200 24 |
| 2            | 1               | 6.27          | -21     | 50.0 | 0.6    0.04 | 440 200 27 |
| 2            | 2               | 6.28          | -22     | 49.7 | 0.7    0.03 | 450 198 24 |
| 3            | 1               | 7.31          | -13     | 0.4  | 0.9    0.02 | 510 280 40 |
| 3            | 2               | 7.30          | -10     | 0.1  | 0.1    0.04 | 520 300 38 |
| 3            | 3               | 7.31          | -7      | 0.3  | <0.1   0.02 | 510 290 40 |
| 2            | 1               | 5.21          | 44      | 17.0 | 4.8    0.03 | 164 66  3  |
| 2            | 2               | 5.24          | 39      | 17.3 | 4.2    0.01 | 160 65 <3 |
| 2            | 3               | 5.21          | 41      | 18.2 | 3.8    0.04 | 160 60 <3 |

up-stream unit operations. However, within the time frame of an individual sampling run, such changes would normally not be expected to be as pronounced as those observed. In the case of the iron assays, which showed the greatest variability, there logically might be a correspondence between the assays and the pulp pH and Eh. These pulp parameters must necessarily be indicative of the form of the iron species in the aqueous phase.

In Figure 143, the Pourbaix diagram for the Fe–H₂O system at 25°C, 1 atmosphere total pressure and total iron species activities of 10⁻³ and 10⁻⁶
Figure 143 - Pourbaix Diagram for the Fe - H₂O System at 25 °C, 1 Atmosphere Total Pressure and Total Iron Species Activities of 10⁻³ and 10⁻⁶. The shaded area represents the range of Eh and pH values believed typical of actual tin flotation pulps.
is given. Renison plant measurements are marked on the figure. It is evident that the higher pulp water iron assays of Table XX correspond to Eh and pH conditions where a greater proportion of the iron reasonably might be expected to have been in the soluble ferrous ion state. The lower assays correlate with conditions where iron is more likely thermodynamically to have been predominantly in the form of hydrous ferric oxide sols. Such sols would be expected to have been adsorbed strongly on mineral surfaces and not present to an appreciable extent in the aqueous phase. Furthermore, solubilization of such sols by simple acidification is known to be slow kinetically (Section 2.3.2).

A number of probable sources of the high levels of dissolved metal cations in the Renison circuit can be identified. Communications with the mine (Winby, 1985) have indicated that the high calcium and magnesium levels are consistent with the hardness of the plant water supplies. The principal source of the copper ions is considered to be plant CuSO₄ additions. This copper salt is used in the sulphide flotation circuits of the plant as a sulphide mineral activator. The sources of the aluminum ions are somewhat less certain but probably include the dissolution of alumino-silicate minerals, such as tourmaline, which are present in the Renison ore. This might, in part, correlate with the frequently reported interfering effect of tourmaline in cassiterite flotation (Topfer and Gruner, 1972; Topfer, Gruner and Bilsing, 1975; Bulled, 1982).

There are potentially a number of origins for the high iron levels found in the plant waters. Corrosion of grinding media in the Renison comminution circuits is undoubtedly one source. Leaching of siderite and oxidation of sulphide minerals, such as pyrite and pyrrhotite, are others. The solution
chemistry of these minerals is such that they all can release iron into solution. In particular, electrochemical studies by Hamilton and Woods (1981) have shown that hydrous ferric oxide species are thermodynamically favoured products of pyrite and pyrrhotite oxidation. These researchers considered that the oxidation of pyrrhotite can be represented ideally by the equations:

\[
\text{FeS} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + \text{S} + 3\text{H}^- + 3\text{e} \quad (E^o = + 0.395 \text{ V})
\]

and

\[
\text{FeS} + 7\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + \text{SO}_4^{2-} + 11 \text{H}^+ + 9\text{e} \quad (E^o = + 0.370 \text{ V})
\]

The oxidation of pyrite was interpreted in terms of the reactions:

\[
\text{FeS}_2 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 2\text{S} + 3\text{H}^- + 3\text{e} \quad (E^o = + 0.579 \text{ V})
\]

and

\[
\text{FeS}_2 + 11\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 19\text{H}^+ + 15\text{e} \quad (E^o = + 0.402 \text{ V})
\]

4.3.2 Ferric and Ferrous Ion Hydrolysis

Hydrolyzed ferric ion species characteristically are intensely coloured. Such species also absorb strongly in the ultraviolet (200–380 nm) range as shown in the ultraviolet-visible scanning spectrum of Figure 144. Clearly evident in this spectrum is a very high absorbance at wavenumbers below 270 and a broad peak centered between 290 and 300 nm. This latter peak overlaps the high energy absorbance and extends well into the visible range on the high wavenumber side. Based on the detailed studies of Sherman and Waite (1985), the high energy features at wavelengths below 270 nm can be assigned to ligand-to-metal charge-transfer transitions. The broad absorption band near 290–310 nm corresponds to ligand field transitions of Fe$^{3+}$. 
In contrast to hydrous ferric oxide species, the free aquated ferric and ferrous ions absorb far less strongly in the ultraviolet. This was confirmed experimentally for initially strongly acidified (pH 1.0 - 2.0) solutions of both ferric and ferrous chloride (Figure 145). It was only when the pH of these solutions was raised to levels where appreciable concentrations of polymerized ferric species were formed in solution that absorbances increased significantly.

It is well established that the formation of ferric-hydroxy polycations is rapid while resolubilization, even in the presence of excess acid, is very slow (Lamb and Jacques, 1938; Segal, 1984a). Such variations in the kinetics of the transitions to and from both the free ferric ion and ferrous ion states were observed in this research. The absorbances of ferric and ferrous chloride solutions initially at pH 3.7 were found not to decrease
significantly when the solutions were acidified. Absorbances after acidification were invariably much higher than those for solutions of the same concentration and final pH but initially strongly acidified (Figure 145). In contrast, when appreciable base was added to the initially highly acidic solutions, absorbances similar to those of solutions prepared at high pH were found. These results confirmed that in the 10 minute time periods of the pH adjustment and UV absorbance measurements, hydroxylation of iron species proceeded extensively when base was added. Conversely, resolubilization of hydroxy sols was kinetically very slow even when solutions were strongly acidified. The important implication for flotation is that resolubilization of hydrous ferric oxide sols adsorbed on mineral surfaces might also not proceed to a significant extent upon acidification of a pulp unless long conditioning times are involved.
The results of Figure 145 establish that ultraviolet spectral changes can be used as a qualitative indicator of the extent of hydroxylation of ferric ions in aqueous solution. As such, the spectral changes are subject, theoretically, to qualitative interpretation with respect to solution composition on the basis of known Nernst potentials, if equilibrium conditions reasonably can be assumed to prevail.

In Figure 146, measured Eh and pH values are shown for the solutions used in the ultraviolet absorbance analyses of Figure 145. These data are plotted on a Pourbaix diagram for the Fe-H₂O system at 25°C, 1 atmosphere total pressure and total activities of dissolved iron species of 10⁻³ and 10⁻⁴. For the initially strongly acidified ferric and ferrous chloride solutions (pH₄ = 1.0 - 2.0) the thermodynamically stable species were the respective free ions.

Figure 146 - The Eh - pH Dependence for FeCl₃ and FeCl₂.₄(H₂O) Solutions Prepared at Various Initial pH (pH₄) Values. The data are shown plotted on a Pourbaix diagram for the Fe - H₂O system at 25°C, 1 atmosphere total pressure and total activities of dissolved iron species of 10⁻³ and 10⁻⁴.
The low initial absorbances of these solutions (Figure 145) confirms that these species did not absorb strongly in the ultraviolet. When base was added to these solutions, pronounced absorbance increases occurred. It is evident (Figure 146) that such absorbance changes corresponded to the thermodynamic transitions between either the free ion or lower order hydroxy species state and that of the hydrous ferric oxide. The close correspondence between the experimental absorbance measurements and the thermodynamic data again verifies that the kinetics of hydroxylation were rapid.

The experimental and thermodynamic data of Figure 146 confirm that the degree to which ferric and ferrous chloride solutions prepared at pH 3.7 were acidified during the UV studies was sufficient for the formation of the respective free ions. It is equally evident from the absorbance measurements (Figure 145) that the transitions did not proceed kinetically to any significant extent.

4.3.2.1 Effect of Fluoride on Hydroxylation

As discussed in detail in the literature review (Section 2.3.2.4), various complexing agents have been shown to affect appreciably the polymerization processes of ferric ion hydrolysis. However, no data pertaining to iron hydrolysis in the presence of the fluoride ion have been published. In the ultraviolet spectral analyses of this research, it has been established that the presence of fluoride can modify profoundly the onset of hydrous ferric oxide formation in both ferrous and ferric chloride solutions.

The pH dependence of the UV absorbance of $1 \times 10^{-3}$ M ferrous chloride solutions is shown in Figure 147 as a function of the initial pH and sodium fluoride addition. This latter reagent was added during solution preparation and not after aging of the iron solutions. The corresponding absorbance data
Figure 147 - The pH Dependence of the UV Absorbance at 297 nm for $1 \times 10^{-3}$ M FeCl$_2$.4(H$_2$O) Solutions as a Function of Initial pH ($\text{pH}_i$) and NaF Addition. Addition of the NaF was during solution preparation.

For $1 \times 10^{-4}$ M ferric chloride solutions are shown in Figure 148. For both iron chlorides, the effect of increasing fluoride additions was to suppress the formation of hydrous ferric oxide species. In the absence of fluoride, solutions of both ferric and ferrous chlorides, whether initially acidified or not, had measurable absorbances between pH 2.0 and pH 3.5. In contrast, no absorbances were evident in this acidic pH range for the iron solutions containing fluoride. However, above a slightly higher critical pH, the absorbances increased rapidly to levels more indicative of that of iron solutions containing no fluoride. This critical pH of absorbance increase moved to less acidic values the greater the amount of fluoride reagent added.
FeCl₃ Solutions as a Function of Initial pH ($pH_A$) and NaF Addition. Addition of the NaF was during solution preparation.

The absorbance variations of the iron-fluoride solutions can be interpreted successfully on the basis of known system equilibria and measured solution pH and Eh. For the ferrous chloride solutions containing $6 \times 10^{-4}$ M NaF the thermodynamically stable species at the pH of solution preparation ($pH_A = 2.8$) were the fluoro complexes of the ferric ion (Figure 149). At lower pH values and for less acidic solutions up to pH 3.9, these species remained the most thermodynamically stable entities. In this pH range, solution absorbances were negligible (Figure 147). Such data indicate that ferric fluoro complexes, like ferrous and ferric ions, do not absorb appreciably in the ultraviolet. Above pH 3.9, a transition occurred such that hydrous ferric oxide sols became the thermodynamically stable species.

Figure 148 - The pH Dependence of the UV Absorbance at 297 nm for $1 \times 10^{-4}$ M FeCl₃ Solutions as a Function of Initial pH ($pH_A$) and NaF Addition. Addition of the NaF was during solution preparation.
Associated with this transition were sharp increases in solution absorbance (Figure 147). The correspondence of the pH of the measured absorbance increase and that for the thermodynamic transition to the hydrous ferric oxide state confirmed that kinetically the transition was rapid. Similar correlations between thermodynamic data and absorbance increases were found for ferric chloride solutions containing fluoride (Figures 148 and 150). The onset of absorbance increase invariably corresponded remarkably with the thermodynamically expected pH of hydrous ferrous oxide formation.

Figure 149 – The Eh–pH Dependence for 1 x 10⁻³ M FeCl₂·4(H₂O) Solutions as a Function of Initial pH (pHᵢ) and NaF Addition. The data are shown plotted on a Pourbaix diagram for the Fe–F–H₂O system at 25°C, 1 atmosphere total pressure, a total activity of dissolved iron species of 10⁻³ and fluoride species activities of 6 x 10⁻³ and 6 x 10⁻⁴.
Figure 150 - The Eh - pH Dependence for 1 x 10^{-4} M FeCl₃ Solutions as a Function of Initial pH (pH₀) and NaF Addition. The data are shown plotted on a Pourbaix diagram for the Fe - F - H₂O system at 25°C, 1 atmosphere total pressure, a total activity of dissolved iron species of 10^{-4} and fluoride species activities of 6 x 10^{-3} and 6 x 10^{-4}.

It is evident from all the experimental data pertaining to iron solution chemistry that the Eh and pH of such solutions are not independently variable. The Eh is determined by the electrochemical equilibria between the system components including dissolved oxygen. The pH reflects the equilibria between the free ferrous and ferric ions and their various hydroxylation states. Additions of fluoride obviously affects both parameters.

In Figure 149, the experimental Eh and pH data indicate that in the presence of 6 x 10^{-3} M NaF the Eh of the ferrous chloride solution was sufficiently low that the ferrous ion was still the thermodynamically stable species at the pH of solution preparation. The lack of attainment of complete
Equilibria is evident from the divergence between the plotted thermodynamic boundaries and the experimental data. Increasing the pH further lowered the Eh consistent with hydroxylation of ferric ion species and the formation of hydrous ferric oxide sols. As for all previous data, the thermodynamic transition to the hydrous ferric oxide state was accompanied by a rapid increase in the solution ultraviolet absorbance.

The experimental absorbance data of Figures 147 and 148 confirm definitively that, in acidic solutions, the fluoride ion can compete successfully with the hydroxyl ion for coordinative positions around the aqueous ferric ion. The strong affinity between the ions presumably results in the fluoride ion occupying many of the coordinative sites of the ferric ion thereby suppressing polymerization. At higher pH values, ferric hydroxy species become more stable thermodynamically and polymeric ferric oxide sols are formed in solution. While the latter are insoluble and absorb in the UV, the fluoro complexes of the ferric ion are completely soluble and have no absorbance in this region of the electromagnetic spectrum.

4.3.2.2 Effect of Fluoride on Hydrous Ferric Oxide Solubilization

Ferrous chloride solutions prepared at pH 6.0 were found to become intensely coloured when allowed to age for extended periods. Associated with these increases in colouration were steady downward drifts in pH. Both changes were indicative of the oxidative hydroxylation of the ferrous ion and the formation of hydrous ferric oxide sols. Ultimately these sols grew to sizes sufficient for them to be visible in solution.

It was reported previously that resolubilization of hydrous ferric oxide sols was kinetically very slow even for sols formed under appreciably acidic solutions (and hence in the presence of fewer coordinating ligands) and not
extensively aged. As expected, virtually no evidence for resolubilization was found in ultraviolet absorbance measurements of aged ferrous chloride solutions even after strong acidification (Figure 151). This was despite the fact that at the low pH values the Eh was such that the free ferrous ion was the thermodynamically stable species (Figure 152). The kinetics of depolymerization and solubilization of the aged sols was extremely slow and clearly did not proceed to any significant extent even in the total 90 minute period used for pH adjustments and absorbance measurements in the UV studies.

Figure 151 - The pH Dependence of the UV Absorbance at 297 nm for $1 \times 10^{-3}$ M FeCl$_2$.4(H$_2$O) Solutions Aged between pH 6.0 and pH 4.5 for 18 Hours Followed by Subsequent NaF Addition and/or Acidification with Hydrochloric Acid. The single point (△) shows the absorbance and pH of an aged FeCl$_2$.4(H$_2$O) stock solution prior to addition of either the $6 \times 10^{-3}$ M NaF or acid.
In remarkable contrast to the data obtained for acidified solutions of aged sols, the addition of fluoride ion produced rapid and marked decreases in absorbance (Figure 151). Upon addition of the fluoride, the immediate effect observed was an increase in the pH. This presumably reflected the ability of the fluoride ion to displace coordinated hydroxyls from the hydrous ferric oxide sols. For high fluoride additions (6 x 10^{-3} M NaF), these pH changes were significant and were accompanied by measurable decreases in absorbance (Figure 151 - open and closed triangles). These absorbance decreases occurred in time frames of less than five minutes. When solutions were acidified
subsequently, the absorbance further decreased dramatically. After the $6 \times 10^{-3}$ M NaF addition, subsequent strong acidification to pH 3.5 and below reduced solution absorbances to negligible levels within an hour (Figure 151).

The striking decreases in absorbance accompanying fluoride ion additions were consistent with the depolymerization of hydrous ferric oxide sols and the associated formation of soluble ferric fluoro complexes. That this was the case was confirmed by solution pH and Eh measurements. These data indicated that the combination of acidification and fluoride ion addition produced conditions where ferric fluoro complexes were thermodynamically the most stable species (Figure 153). The remarkable aspect was that such transitions were very rapid in comparison to those observed in the absence of fluoride under otherwise identical experimental conditions. While clearly evident in the absorbance measurements themselves, the close correlations between the actual pH and Eh measurements and those expected thermodynamically are further indicative of the attainment of almost equilibrium conditions.

The finding that the fluoride ion can promote dramatically the kinetics of solubilization of hydrous ferric oxide sols in acidic solutions is considered to be of fundamental importance in terms of understanding of the role of this ion in cassiterite flotation. Additions of fluoride reagents to acidic flotation pulps reasonably might be expected to result in appreciable solubilization of hydrous ferric oxide sols in time frames of relevance to flotation processes. Furthermore, there is no a priori reason to assume that solubilization will not proceed for all such hydrous oxide sols whether present in the aqueous phase or adsorbed on the surfaces of minerals. In the absence of fluoride, solubilization of such sols would not be expected to proceed kinetically to any measurable extent.
4.3.3 Effect of Fluoride on Aluminum Ion Hydrolysis

In a manner analogous to the iron system, aluminum ions can hydrolyze and form polymeric hydrous oxides in slightly acidic to basic solutions. The onset of the formation of such sols can be detected readily by light scattering photometry.

Turbidity measurements performed in this research indicated that 1x10⁻³ M aluminum chloride solutions prepared at pH 4.1 produced negligible light scattering. Solution turbidities were essentially those of distilled water. Lowering the pH resulted in no detectable turbidity change. In contrast, the
addition of base produced a sharp turbidity increase above pH 4.5 (Figure 154). This increase was characterized both by its occurrence over a very narrow pH range and its large magnitude.

Detailed thermodynamic analyses of the aluminum system have been presented previously in the literature review (Section 2.3.1.4). Specifically, these data indicated that the free aquated aluminum ion and lower order hydroxy species exist in the more strongly acidic pH range. At higher pH values, aluminum ion solutions become supersaturated with respect to hydrous aluminum oxide precipitates (Figure 12).

The pH of supersaturation of aluminum ion solutions is a function of the total concentration of the cation present. Thermodynamic calculations, analogous to those performed in the construction of Figure 12, indicate that, for a $1 \times 10^{-3}$ M aluminum chloride solution, supersaturation should occur at pH 4.23 (Appendix B). The strong correlation between this calculated value and that observed experimentally (pH 4.5) confirms that the formation of hydrous aluminum oxide sols was kinetically rapid.

Evident from the magnitude of the turbidity increases in Figure 154 is that once supersaturation occurs, hydrous aluminum oxide sols grow rapidly to appreciable sizes and become highly insoluble. This is in contrast to the free aquated aluminum ion and lower order hydroxy species which do not polymerize and are highly soluble. That the latter are strongly solvated is clearly indicated by the absence of measurable turbidities in the pH range where they predominate in solution.

The characteristic pH dependence of turbidity increases associated with aluminum ion hydrolysis was found to undergo extensive change when the solutions were prepared in the presence of fluoride. Specifically, the
The critical pH of turbidity increase moved to progressively higher pH values with increasing concentrations of fluoride (Figure 154). Such changes were consistent with the well established ability of the fluoride ion to form stable fluoro complexes with aluminum in acidic solutions. The suppression of aluminum sol formation was presumably due to fluoride ions occupying many of the coordinative sites around the aluminum ion and thereby restricting the extent of polymerization.

The data of Figure 154 indicate that, in the pH range where aluminum fluoro complexes were the predominant species in solution, measured turbidities were essentially those of distilled water. This confirms that
such complexes are strongly solvated and have little or no tendency to polymerize in the manner of the hydrous aluminum oxide. A similar conclusion has been reached previously by Matijevic, Kratohvil and Stickels (1969). The inability of aluminum fluoro complexes to polymerize is almost certainly due to the high electronegativity of fluorine. As a result of its high electronegativity, this element has little tendency to increase its coordination number by donating electrons (Porterfield, 1984).

Aging of aluminum chloride solutions under slightly acidic conditions (pH 6.0) produced very stable dispersions of colloidal hydrous aluminum oxides. Such sols were found not to be readily solubilized even when subject to strong acid treatment. Turbidities of these solutions, while exhibiting some decrease, remained at high levels down to pH 1.5 (Figure 155). In the acidic range below pH 4.5, the turbidities were at least an order of magnitude greater than for equivalent solutions formed under initially low pH conditions (Figure 154).

Some evidence of resolubilization of aged aluminum sols in acidic solutions was found during the course of the research. In particular, considerable time dependent pH and turbidity instability was noted when the pH was lowered. Significantly, the pH drift was always upward indicating hydroxyl ion release and presumably depolymerization of hydrous aluminum oxide sols. However, as shown by the light scattering measurements, the kinetics of depolymerization were extremely slow. Stol, van Helden, and de Bruyn (1976) have similarly reported that the breakdown of polymeric aluminum species is very slow.

The addition of sodium fluoride to aged aluminum sol solutions was found to produce remarkable changes in both solution pH and turbidity. In the
absence of any pH manipulation, the addition of the equivalent of 6 $\times$ 10$^{-4}$ M NaF to a 1 $\times$ 10$^{-3}$ aluminum chloride solution increased the pH from 5.90 to 8.05. Presumably, this pH increase was the result of coordinated hydroxyl groups being displaced from aluminum hydrous oxides. Similar pH shifts toward the alkaline range were observed for higher fluoride additions. Subsequent acidification of all these fluoride bearing solutions produced turbidities lower than those measured under otherwise identical conditions in the absence of fluoride (Figure 155). The effect of the fluoride clearly was to promote markedly the kinetics of depolymerization and solubilization of the sols in acidic solutions.

Figure 155 - The pH Dependence of 1 $\times$ 10$^{-3}$ M AlCl$_3$·6(H$_2$O) Solution Turbidities After Solution Aging at pH 5.9 for 18 Hours Followed by Subsequent NaF Addition.
4.3.4 Principal Findings and Conclusions

(1) Dissolved iron levels in the flotation pulps of the Renison concentrator can range up to 60 ppm. The identification of such high concentrations is strongly supportive of the hypothesis that iron films, identified on the surfaces of cassiterite grains recovered from the plant, were due to adsorption of iron species from the aqueous phase.

(2) The possible sources of iron species in Renison flotation pulps include corrosion of grinding media, leaching of siderite and oxidation of major gangue sulphide minerals such as pyrite and pyrrhotite.

(3) Calcium and magnesium ions are present at appreciable levels in the Renison circuit. Concentrations as high as 520 ppm calcium and 300 ppm magnesium were found in analyses of tin flotation pulps. These ions are believed to have been derived from the plant water supplies. Aluminum was detected at lower but not insignificant levels. The most probable source of this latter metal was the dissolution of alumino-silicate minerals, such as tourmaline, which are present in the Renison ore.

(4) The formation of hydrous ferric oxide sols from both ferrous and ferric ion solutions is kinetically very rapid. Conversely, depolymerization and resolubilization of such sols is extremely slow. Such resolubilization would not be expected to proceed to any significant extent in the time frames characteristic of flotation even in the presence of
excess acid.

(5) The free aquo ferric and ferrous ions and the fluoro complexes of the ferric ion are strongly solvated species and have little or no tendency to polymerize in the manner of ferric hydroxy species.

(6) The presence of fluoride in acidic iron solutions can result in significant increases in the pH corresponding to the onset of hydrous ferric oxide formation when base is added. In the acidic range, the fluoride ion can compete successfully with the hydroxyl ion for coordinative positions around aqueous ferric ions thereby suppressing polymerization.

(7) The addition of fluoride ions to solutions of aged ferric hydroxy sols produces dramatic increases in the kinetics of solubilization of such sols when the pH is lowered. This presumably reflects the ability of the fluoride ion to displace coordinated hydroxyls from the ferric ions of the hydrous oxide sols.

(8) Additions of fluoride reagents to acidic flotation pulps would be expected to result in appreciable solubilization of hydrous ferric oxides in time frames of relevance to flotation processes. Furthermore, there is no a priori reason to assume that solubilization will not proceed for all such hydrous oxide sols whether present in the aqueous phase or adsorbed on the surfaces of minerals. In the absence of fluoride, solubilization of such sols would not
be expected to proceed kinetically to any measurable extent.

(9) The formation of hydrous aluminum oxide sols is kinetically very rapid. Such sols polymerize extensively and are highly insoluble. In contrast, the fluoro complexes of aluminum do not polymerize and are strongly solvated.

(10) The critical pH of hydrous aluminum oxide formation moves to progressively higher pH values when increasing concentrations of fluoride are present in solution. Such effects are consistent with the well established ability of the fluoride ion to form stable fluoro complexes with aluminum in acidic solutions.

(11) Aging of aluminum solutions under slightly acidic conditions (pH 6.0) produces very stable dispersions of colloidal hydrous aluminum oxides. Such sols are not solubilized readily even when subjected to strong acid treatment.

(12) Fluoride additions to solutions of aged aluminum hydroxy sols markedly promotes the kinetics of depolymerization and solubilization of such sols in acidic solutions.
4.4 Mineral - Surfactant Interactions

4.4.1 Styryl Phosphonic Acid Adsorption

4.4.1.1 Stannic Dioxide Substrate

Styryl phosphonic acid was found to adsorb rapidly on Aldrich "Gold Label" stannic dioxide. Equilibrium conditions were reached within one hour, with the majority of uptake occurring in the first 10 minutes of contacting. Such rapid adsorption behaviour is consistent with the published data of Wottgen (1969) and Yap (1975) for adsorption of other various chain length phosphonic acids onto cassiterite.

Adsorption measurements, conducted for long equilibration times (150 minutes), indicated styryl phosphonic acid adsorption onto the stannic dioxide to reach significant levels over the range pH 1.0 to 7.0. The adsorption isotherms (Figure 156) were broad but displayed distinct maxima near pH 3.0. This pH of maximum adsorption correlates with that established by Gruner (1971) for adsorption of n-heptyl phosphonic acid on various doped and undoped stannic dioxides (Figures 39 and 40). However, it is one pH unit higher than that reported by Wottgen, Luft and Neuber (1971) for styryl phosphonic acid adsorption on a natural cassiterite. Such a pH shift logically might represent the accumulated effects of measurement errors and drifts in pH during test work rather than a fundamental change in adsorption character with the nature of substrate.

In comparison to the data of other researchers (Figures 38 to 42), the adsorption maxima in the isotherms of Figure 156 are much less pronounced. The adsorption densities were found to decrease measurably at pH values above and below the maximum but not to the extent reported by researchers such as Wottgen, Luft, and Neuber (1971). Adsorption in the pH range between 4.0 and
Figure 156 - The Adsorption Density of Styryl Phosphonic Acid on Aldrich "Gold Label" Stannic Dioxide as a Function of pH. Data are shown for initial surfactant concentrations of $1 \times 10^{-4} \text{ M}$ and $5 \times 10^{-5} \text{ M}$. The equilibration time in all tests was 150 minutes.

6.0 was, for example, still appreciable with respect to that at pH 3.0. In the Wottgen, Luft and Neuber data, adsorption in this higher pH range was diminished much more substantially relative to that at the adsorption maximum (Figure 41).

The apparent broader form of the isotherms of this research can be attributed to the different ratios of adsorbate concentration to substrate surface area used. While Wottgen, Luft and Neuber (1971) did not cite the styryl phosphonic acid concentration used in their research, it is evident from their reported adsorption densities that the ratio of adsorbate to adsorbent surface area greatly exceeded that in this research. Assuming the
area occupied by a styryl phosphonic acid molecule to be $35.2 \, \text{Å}^2$ (Section 4.2.8), the maximum surface area coverage in Figure 156 is 3.2 percent. Similar calculations indicate the adsorption density maximum at pH 2.0 in the Wottgen, Luft and Neuber data to represent a 58.3 percent surface coverage.

It was established by Wottgen (1969) that the concentration dependence of phosphonic acid adsorption densities varies critically with the pH of adsorption (Figure 44). That this is the case for styryl phosphonic acid adsorption on stannic dioxide was confirmed in this research (Figure 157). At pH 5.0, the adsorption density was found to asymptote to a plateau value at equilibrium surfactant concentrations above 40 µmole l$^{-1}$. In contrast, adsorption at lower pH values was substantially higher and showed no tendency towards attaining a saturation level over the range of surfactant concentrations tested. It is evident, therefore, that the adsorption maximum near pH 3.0 will increase at higher initial surfactant concentrations while the level of adsorption in less acidic solutions above pH 5.0 will not. Clear indications of this trend can be seen in the data of Figure 156. Ultimately, at very high surfactant concentrations, such an adsorption - concentration dependence must result in much less broad isotherms with very pronounced maxima, as indeed reported by Wottgen, Neuber and Luft (1971).

The adsorption data of Figures 156 and 157 confirm that the extent of styryl phosphonic acid adsorption on stannic dioxide is similar in magnitude to that of other shorter chain length phosphonic acids. Specifically, the dependence of the adsorption density on surfactant concentration at pH 3.0 (Figure 157) correlates strongly with that found by Yap for p-tolyl phosphonic acid adsorption on cassiterite (Figure 43). However, this adsorption character is clearly dependent critically on the aqueous solution pH.
Figure 157 - The Adsorption Density of Styryl Phosphonic Acid on Aldrich "Gold Label" Stannic Dioxide as a Function of the Surfactant Equilibrium Concentration. The equilibration time in all tests was 150 minutes.

The implication from this research and other published adsorption data is that a fundamental change in the interactions between phosphonic acids and stannic dioxide substrates occurs in the more strongly acidic range below pH 4.0. This change is responsible for the pronounced increases in adsorption density observed in all such systems at more strongly acidic pH values. Coadsorption of undissociated phosphonic acid molecules (Fuerstenau and Healy, 1972) or increased electrostatic attraction between partially dissociated surfactant molecules and the substrate surface below the iep (Wottgen, 1969; Gruner, 1971) have both been suggested as the mechanisms responsible for the profound increase in the adsorption levels. However, on the basis of adsorption data alone it is impossible to determine which of these two
mechanisms is the more plausible. Indeed, it is conceivable that both might contribute to increased adsorption in more acidic solutions.

It has been concluded by virtually all researchers working in the field of phosphonic acid flotation that adsorption of the surfactants on stannic dioxide substrates involves a chemisorption component (Section 2.4). The measurable levels of styryl phosphonic acid adsorption above pH 4.0, indicated by the data of Figures 156 and 157, support such a conclusion. In this slightly acidic range, the surfactant essentially is completely in the form of partially dissociated species (Figure 135). Furthermore, the mineral has a negative charge character since its iep is at pH 4.0. Adsorption therefore occurs despite electrostatic repulsion between the anionic surfactant molecules and the negatively charged mineral surface.

4.4.1.2 Unleached Cassiterite Substrate

A series of adsorption tests was performed on a sample of unleached Renison cassiterite. The method of preparation of this mineral substrate has been described previously (Section 3.5.2). Electrozone celloscope sizing of the sample indicated it to have a log mean size of 9.09 microns. The surface area, determined by the multipoint BET method, was 2.304 m²/g (Appendix E).

Adsorption of styryl phosphonic acid onto the unleached cassiterite was found to be particularly rapid. Irrespective of the pH of adsorption, uptake from a 1 x 10⁻⁴ M surfactant solution reached equilibrium levels within 60 minutes (Figure 158). The greater portion of this adsorption occurred in the first 10 minutes of mineral surfactant contacting.

The adsorption density of styryl phosphonic acid on the unleached cassiterite exhibited a critical dependence on both the surfactant concentration and the pH of contacting. Adsorption at pH 3.0 was
Figure 158 - The Time Dependence of Styryl Phosphonic Acid Adsorption on Unleached Cassiterite at Three Different pH Values. In all three series of tests, the initial surfactant concentration was $1 \times 10^{-4}$ M.

substantially higher than that at pH 4.0 or 5.0. (Figure 159). This trend of increasing adsorption density with decreasing pH below pH 5.0 was similar to that observed for the stannic dioxide substrate (Figure 157). However, the percentage surface coverage achieved in the unleached cassiterite case greatly exceeded that with the synthetic dioxide.

The higher adsorption densities associated with the unleached cassiterite were due in large part to the smaller surface area of this substrate. Even allowing for the different substrate weights used, the available surface area of unleached cassiterite at a fixed surfactant concentration was 2.304 m² compared to an area of 15.8 m² for the stannic dioxide. Such differences in area available for adsorption undoubtedly are reflected in the higher adsorption densities determined for the cassiterite.
Figure 159 - The Adsorption Density of Styryl Phosphonic Acid on Unleached Cassiterite as a Function of the Surfactant Equilibrium Concentration. The equilibration time in all tests was 150 minutes.

Examination of the adsorption isotherms shown in Figure 159 indicates that there was no evidence for adsorption saturation at pH 5.0 for equilibrium styryl phosphonic acid concentrations up to 85 μmole l\(^{-1}\). This is in striking contrast to the corresponding data for adsorption on the stannic dioxide. These latter data indicated clearly that the adsorption density asymptoted to a plateau at equilibrium concentrations above 40 μmole l\(^{-1}\). Furthermore, this saturation concentration was of the order of 0.08 μmole/m\(^2\) (Figure 157). At the same pH, considerably higher adsorption densities were measured on the unleached cassiterite. The implication, therefore, is that adsorption on the unleached cassiterite at pH 5.0 was enhanced to a level greater than that which can be explained on the basis of different substrate surface areas alone.
Figure 160 shows the pH dependence of styryl phosphonic acid adsorption on unleached cassiterite. Measurable adsorption densities were found between pH 3.0 and 10.0. In agreement with the published data of all other researchers (Figures 38 to 42), adsorption increased remarkably below pH 4.0. At higher pH values, the adsorption was lower and corresponded to less than a 5 percent surface coverage. These data confirm that a fundamental change in the nature of styryl phosphonic acid adsorption on unleached cassiterite occurs below pH 4.0.

In Figure 160, adsorption data are shown only down to pH 3.0. At pH values below 3.0, solubilization of a surface impurity associated with the unleached cassiterite was found to interfere seriously with the determinations of residual styryl phosphonic acid in aqueous solution. The presence of this impurity resulted in the absorbance, after contacting of the styryl phosphonic acid with cassiterite, exceeding that of the initial surfactant solution. At less acidic pH values, a similar but smaller interference most probably also occurred. However, since the effect of such an interference was to increase the final solution absorbance, calculated adsorption densities were presumably only underestimated and never overestimated. As such, the significant adsorption trends of Figure 160 represent real phenomena although the magnitudes of the actual adsorption densities at the lower pH values are presumably increasingly conservative.

The most probable interfering element on the basis of established surface and solution chemical properties of the unleached cassiterite was iron. This element was known to be present as a surface film on the unleached cassiterite (Section 4.1) and has been shown to be solubilized readily in acidic solutions (Figures 114 and 117). Furthermore, hydrolyzed iron species absorb strongly
Figure 160 - The Adsorption Density of Styryl Phosphonic Acid on Unleached Cassiterite as a Function of pH. Data are shown for initial surfactant concentrations of $1 \times 10^{-4}$ M and $5 \times 10^{-5}$ M. The equilibration time in all tests was 150 minutes.

in the ultraviolet range (Figure 144) and hence their presence would increase solution absorbances as was observed experimentally. That iron was indeed the interfering element was confirmed by chemical analyses. The styryl phosphonic acid supernatants recovered from adsorption tests at pH 1.0 and 2.0 were found to assay 270 ppm and 125 ppm iron, respectively.

The degree to which iron was solubilized from the surface of the unleached cassiterite in the 150 minute equilibration period of the adsorption studies was remarkable. Such high abstraction rates were found to be attributable partly to the small particle size of the unleached cassiterite used in the adsorption studies. However, the presence of styryl phosphonic acid in solution contributed significantly to the level of solubilization. In experiments conducted in an identical manner to the adsorption tests but with
distilled water replacing the surfactant solutions, measured iron levels were much lower. The supernatants recovered from such tests at pH 1.0 and 2.0 assayed only 173 and 86 ppm. The important conclusion, therefore, was that styryl phosphonic acid promoted the solubilization of iron from the surface of the unleached cassiterite in acidic solutions.

Associated with the solubilization of iron from the surface of unleached cassiterite during the adsorption study tests were a number of striking solution colour changes. These changes were not evident in the adsorption study supernatants at the pH of contacting with the unleached cassiterite but became clearly visible when the pH of the supernatants was adjusted. Styryl phosphonic acid solutions are characteristically colourless. Similarly, the supernatants recovered after contacting of the surfactant with the unleached cassiterite showed no evidence of colouration. However, when acidified strongly all these solutions turned a characteristic green colour. Even more dramatic was that, when partially neutralized with potassium hydroxide, the more acidic supernatants gave rise to voluminous yellow-brown precipitates (Plates 10 and 11).

The initial absence of precipitates in the acidic supernatants recovered from the adsorption tests and the colour changes associated with further supernatant acidification suggest strongly that the iron was associated with the styryl phosphonic acid in the form of a solvated complex. Such a conclusion is obviously supported by the solution chemical assays which show styryl phosphonic acid to promote the solubilization of iron from the surface of unleached cassiterite in acidic solution.
Plate 10 - Styryl Phosphonic Acid Solutions Before and After Contacting with Unleached Cassiterite. The test tube solutions were:

1. \(1 \times 10^{-4}\) M styryl phosphonic acid at pH 5.0.
2. \(5 \times 10^{-5}\) M ferric chloride at pH 5.0.
3. \(1 \times 10^{-4}\) M styryl phosphonic acid/\(5 \times 10^{-5}\) M ferric chloride at pH 5.0.
4. Supernatant at pH 1.0 from a \(1 \times 10^{-4}\) M styryl phosphonic acid/ unleached cassiterite suspension equilibrated at pH 1.0.
5. Supernatant at pH 5.0 from a \(1 \times 10^{-4}\) M styryl phosphonic acid/ unleached cassiterite suspension equilibrated at pH 1.0.
6. Supernatant at pH 2.0 from a \(1 \times 10^{-4}\) M styryl phosphonic acid/ unleached cassiterite suspension equilibrated at pH 2.0.
7. Supernatant at pH 5.0 from a \(1 \times 10^{-4}\) M styryl phosphonic acid/ unleached cassiterite suspension equilibrated at pH 2.0.

The photographs were taken one hour after the preparation of the solutions.
Plate 11 - Styryl Phosphonic Acid Solutions Before and After Contacting with Unleached Cassiterite. The test tube solutions were:

1. $1 \times 10^{-4}$ M styryl phosphonic acid at pH 5.0.
2. $5 \times 10^{-5}$ M ferric chloride at pH 5.0.
3. $1 \times 10^{-4}$ M styryl phosphonic acid/ $5 \times 10^{-5}$ M ferric chloride at pH 5.0.
4. Supernatant at pH 1.0 from a $1 \times 10^{-4}$ M styryl phosphonic acid/unleached cassiterite suspension equilibrated at pH 1.0.
5. Supernatant at pH 5.0 from a $1 \times 10^{-4}$ M styryl phosphonic acid/unleached cassiterite suspension equilibrated at pH 1.0.
6. Supernatant at pH 2.0 from a $1 \times 10^{-4}$ M styryl phosphonic acid/unleached cassiterite suspension equilibrated at pH 2.0.
7. Supernatant at pH 5.0 from a $1 \times 10^{-4}$ M styryl phosphonic acid/unleached cassiterite suspension equilibrated at pH 2.0.

The photographs were taken 14 hours after the preparation of the solutions.
When ferric chloride is added to styryl phosphonic acid in only slightly acidic solutions, an insoluble precipitate is formed. Such a precipitate was observed when the equivalent of $5 \times 10^{-5}$ M ferric chloride was added to a $1 \times 10^{-4}$ M styryl phosphonic acid solution at pH 5.0. A very fine, white colloidal precipitate was formed which, while evident visually, was unfortunately difficult to discern in photographs taken of the solution (Plates 10 and 11 - Test Tube 3). Such precipitates were not observed in solutions of either the styryl phosphonic acid or the ferric chloride alone (Plates 10 and 11 - Test Tubes 1 and 2).

In contrast to the very fine nature of the colloidal precipitates observed on contacting styryl phosphonic acid with ferric chloride, the precipitates formed on adding base to the supernatants recovered from the adsorption tests at pH 1.0 and 2.0 were voluminous and intensely coloured (Plates 10 and 11-Test Tubes 5 and 7). Such massive precipitation undoubtedly reflected the very high concentrations of iron that were in these solutions. However, on the basis of other studies, it is not unreasonable to assume that phosphonic acid molecules might have been incorporated into the growing hydrous ferric oxide sols formed when the base was added. This has been shown to be the case for other complexing agents when present in ferric ion solutions that were hydrolyzed subsequently (Gustafson and Martell, 1963; Aasa et al, 1964; Spiro, Bates and Saltman, 1967; Schugar et al, 1967).

It was established earlier that strong evidence existed for enhanced adsorption of styryl phosphonic acid onto unleached cassiterite at pH 5.0. Given the clear affinity of the surfactant for ferric ion and its hydroxy complexes, it is probable that this enhanced adsorption was due to the presence of iron on the cassiterite surface. Iron species adsorbed on the
surface of cassiterite, therefore, apparently promoted the adsorption of styryl phosphonic acid onto the mineral in the slightly acidic to basic pH range where solubilization of the iron was negligible. In strongly acidic solutions, stable iron phosphonate complexes were formed and the solubilization of the surface iron film was increased appreciably. In this latter case, it is implicit that the extent of phosphonic adsorption onto the cassiterite diminished since a significant proportion of the surfactant was presumably complexed with the iron in solution.

4.4.2 Electrokinetic Studies

4.4.2.1 Stannic Dioxide

In the presence of styryl phosphonic acid, the positive electrophoretic mobilities of stannic dioxide were found to be reduced at low surfactant concentrations and to reverse in sign at high concentrations. Significantly, more negative electrophoretic mobilities were found also at pH values above the oxide iep (Figure 161). Such data are analogous to those reported by Yap (1975) for cassiterite in the presence of p-tolyl phosphonic acid (Figure 45).

The observed decreases in electrophoretic mobility above the stannic dioxide iep confirm that adsorption of anionic phosphonic acid species must have occurred onto the negatively charged oxide surface. Such adsorption is indicative clearly of a strong chemical interaction between the surfactant and the stannic dioxide. It is generally considered that adsorption of an anionic surfactant above a mineral iep is definitive evidence for chemisorption (Han, Healy and Fuerstenau, 1973).

In systems involving long chain surfactants, it is recognized that van der Waals interactions between the surfactant hydrocarbon radicals can contribute to a lowering of the free energy of adsorption (Fuerstenau, 1982; Leja, 1982).
Figure 161 - The pH Dependence of the Electrophoretic Mobilities of Stannic Dioxide Particles in Suspensions Containing Various Concentrations of Styryl Phosphonic Acid. The stannic dioxide particles were prepared as a powdered form of the Aldrich "Gold Label" reagent stannic oxide.

These so called hydrophobic bonding contributions typically produce a positive-to-negative charge reversal below the mineral iep in electrokinetic studies involving anionic surfactants. The general form of such electrokinetic effects has been characterized schematically by Han, Healy and Fuerstenau (1973) for the case of both physically and chemisorbing surfactants (Figure 162). An electrophoretic mobility curve inflection below the mineral iep and a subsequent positive-to-negative charge reversal were considered by these researchers to be indicative of the onset of hydrophobic bonding interactions and ultimately the formation of hemi-micelles.
Figure 162 - Schematic Representation of Zeta-Potential - pH Curves for (1) a Simple Inorganic Electrolyte, (2) Surfactants Exhibiting Simple Physisorption Plus Hydrophobic Effects and (3) Surfactants Exhibiting Coulombic, Hydrophobic and Specific Chemisorption. Point A is the mineral iep. Points D and D' represent the onset of hemi-micelle formation. Points E and E' are the charge reversal points due to hydrophobic adsorption effects (from Han, Healy and Fuerstenau, 1973).

Examination of the electrokinetic data of Figure 161 indicates that inflections were completely absent in all the electrokinetic mobility curves over the range of pH 2.0 to 8.0. No evidence consequently existed for hemi-micelle formation over this pH range for styryl phosphonic acid concentrations as high as $2 \times 10^{-3}$ M. Such data verify the previous assertion of the surface tension analyses (Section 4.2.6) that van der Waals interactions between styryl radicals would not be strong.

The absence of any significant hydrophobic bonding interactions in the styryl phosphonic acid system is consistent with the short nature of the surfactant radical. As discussed previously (Section 4.2.6), the styryl radical would be equivalent to only a $C_5$ or $C_6$ chain length alkyl group.
Surfactants with such short hydrocarbon chains typically do not form hemi-micelles. This has been verified for innumerable surfactant systems. Amines (Somасundaran, Healy and Fuerstenau, 1964), sulphonates (Wakamatsu and Fuerstenau, 1968) and hydroxamates (Han, Healy and Fuerstenau, 1973) have all been shown not to form hemi-micelles when their chain lengths are shorter than Cₐ.

Figure 163 shows the pH dependence of the decrease in the electrophoretic mobility of stannic dioxide particles in the presence of increasing concentrations of styryl phosphonic acid. The data indicate that, for all the surfactant concentrations tested, the decreases in the electrophoretic mobilities were greatest in the acidic range between pH 2.0 and 3.0. With increasing pH, these electrophoretic mobility changes became progressively less pronounced. Only at high (2 x 10⁻³ M) styryl phosphonic acid concentrations were distinct mobility decreases found in the slightly acidic to alkaline range above pH 5.0.

The electrokinetic data of Figure 163 correlate remarkably with the adsorption data obtained for stannic dioxide in the presence of styryl phosphonic acid (Figure 156). In the pH 4.0 – 8.0 range, the adsorption density increases observed in the isotherms were paralleled by increasing changes (decreases) in the electrophoretic mobilities. These data are consistent and indicate that negatively charged surfactant species adsorbed inside the inner Helmholtz plane of the stannic dioxide electrical double layer. Below pH 4.0, the changes in the electrophoretic mobilities were indicative of a substantial increase in the adsorption of such negatively charged species. That styryl phosphonic acid adsorption increased appreciably below pH 4.0 was confirmed by the adsorption isotherm data. In the very
Figure 163 - The pH Dependence of the Decrease in Electrophoretic Mobility of Stannic Dioxide Particles in the Presence of Increasing Concentrations of Styryl Phosphonic Acid. The stannic dioxide particles were prepared as a powdered form of the Aldrich "Gold Label" reagent stannic oxide.

acidic range between pH 3.0 and 2.0, a minor anomaly existed in that the electrophoretic mobilities indicated continued adsorption while the adsorption isotherms showed evidence of maxima and small adsorption decreases. However, these opposing trends can be reconciled readily on the basis that appreciable compression of the electrical double layer almost certainly occurred in this pH range. Such double layer compression would have decreased the magnitude of the stannic dioxide electrophoretic mobilities, particularly at higher surfactant concentrations. These decreases, presumably, were superimposed on those due directly to surfactant adsorption, thereby producing the continued trend of decreasing electrophoretic mobilities with pH in the very acidic range.
In similar analyses of the published adsorption study and electrophoretic mobility data of Yap (1975) strikingly different results to those of Figures 156 and 163 were obtained. Yap's data indicated that over the range pH 2.5 to 4.0 an almost three-fold increase in p-tolyl phosphonic acid adsorption occurred with no corresponding change in the electrophoretic mobility (Figure 47). It was argued (Section 2.4.5) that such findings were reconcilable only if adsorption in this pH range was due to fundamentally different species, or species having a different adsorption mechanism to those that produced charge reversal at higher pH. The possibility was raised that this might be the case for coadsorption of neutral phosphonic acid molecules.

The inability to reproduce the results of Yap in the styryl phosphonic system seriously questions the consistency of this researcher's adsorption study and electrokinetic measurements. Indeed, Yap attributed perceived inconsistencies in the data to "the unreliable nature of electrophoresis measurements of minerals in the presence of surfactants". For the styryl phosphonic acid system, the results of this research have established that complete consistency does exist between adsorption and electrokinetic data. There is no fundamental change in the charge reversal character associated with styryl phosphonic acid adsorption on stannic dioxide in the acidic pH range.

The correspondence of appreciable increases in charge reversal (Figure 163) with abrupt increases in styryl phosphonic acid adsorption on stannic dioxide below pH 4.0 (Figure 156) confirms that negatively charged species are at least partially responsible for the adsorption increase. Such a finding supports the Wottgen (1969) and Gruner (1971) hypothesis that the adsorption increase is due to enhanced electrostatic attraction between partially
dissociated phosphonic acid molecules and the substrate below the latter's iep. Conversely, such data provide no evidence supporting the alternative Fuerstenau and Healy (1972) hypothesis that coadsorption of undissociated phosphonic acid molecules is responsible for the increase. However, the possibility that both, in fact, might be occurring cannot be eliminated. On the basis of the adsorption and electrokinetic data alone, an unequivocal interpretation of the mechanism of the adsorption increase is not possible.

4.4.2.2 Unleached Cassiterite

In the presence of styryl phosphonic acid, the electrophoretic mobilities of unleached cassiterite particles became significantly more negative over the entire pH range from 2.0 to 8.0 (Figure 164). Remarkably, at higher surfactant concentrations, mobility decreases above the mineral iep were not dissimilar in magnitude to those at pH values below the iep. Such findings were in contrast to the corresponding data for stannic dioxide. In the latter case, decreases in electrophoretic mobilities above the iep were much less substantial than those in the pH range where the oxide surface was positively charged.

The appreciable decrease in unleached cassiterite electrophoretic mobility above the mineral iep is indicative clearly of a much stronger chemical interaction between the phosphonic acid and the mineral surface. Such a conclusion is consistent with the earlier adsorption study finding of enhanced surfactant adsorption on unleached cassiterite, relative to that of stannic dioxide, in the slightly acidic to alkaline pH range. This enhanced adsorption was attributed to the presence of a surface iron film on the unleached cassiterite.
Figure 164 - The pH Dependence of the Electrophoretic Mobilities of Unleached Cassiterite Particles in Suspensions Containing Various Concentrations of Styryl Phosphonic Acid.

In agreement with the stannic dioxide data, the electrophoretic mobility curves of Figure 164 do not exhibit marked inflections or charge reversals at pH values below the mineral iep. As for the stannic dioxide, no evidence consequently exists for the formation of hemi-micelles in the styryl phosphonic acid system.

Calculations of the change in electrophoretic mobilities with surfactant adsorption indicate a complex relationship between mobility decrease, pH and styryl phosphonic acid concentration (Figure 165). In the presence of $1 \times 10^{-4}$ M phosphonic acid, the electrophoretic mobilities exhibited only a small decrease above pH 5.0. Below pH 5.0, the magnitude of this decrease became substantially greater before passing through a maximum between pH 3.5 and 4.0 and diminishing slowly in the very acidic range. At higher surfactant concentrations, the form of the mobility changes below pH 4.5 was not altered.
Figure 165 - The pH Dependence of the Decrease in Electrophoretic Mobility of Unleached Cassiterite Particles in the Presence of Increasing Concentrations of Styryl Phosphonic Acid.

to any significant extent. The magnitude of the maximum, however, did increase and become more distinct near pH 3.5. In contrast to the behaviour at lower surfactant concentrations, the charge reversal behaviour above pH 4.5 changed dramatically. At higher phosphonic acid levels, much larger decreases in electrophoretic mobility occurred in the less acidic solutions. These decreases were relatively constant in the near neutral pH range but exhibited clear minima near pH 5.0.

As proposed in the adsorption study analyses (Section 4.4.1.2), the adsorption of styryl phosphonic acid on unleached cassiterite is a complex function of both the surfactants genuine affinity for the cassiterite surface and its strong interaction with iron species. The former effect reasonably might be expected to exhibit an analogous concentration and pH dependence to
that for adsorption on stannic dioxide. The interaction between iron and the phosphonic acid appears strong over the entire pH range of interest but is complicated by the tendency for the iron to be solubilized in acidic solutions. Furthermore, strong evidence exists that styryl phosphonic acid promotes this abstraction in the acidic pH range through the formation of strongly solvated iron phosphonate complexes.

In the slightly acidic to alkaline pH range (≥ pH 6.0), solubilization of surface iron would be expected to be negligible. The presence of such a surface contaminant, therefore, would enhance adsorption in this pH range. The data of Figure 165 clearly show this to be the case. The implication from the data below pH 6.0 is that solubilization of surface iron occurs. Such solubilization appears particularly pronounced in more concentrated surfactant solutions. At high phosphonic acid levels, this effect apparently dominates the tendency for genuine adsorption above the mineral iep. The net result is a minimum in the electrophoretic mobility decrease before the characteristically strong genuine adsorption of the phosphonic acid onto cassiterite becomes dominant below the oxides iep (pH 4.0). In very acidic solutions below pH 3.5, there is evidence that surfactant complexation, associated with massive solubilization of surface iron, again becomes a significant factor. Such a conclusion is supported both by the reduced mobility decreases in this pH range and the tendency for the maximum mobility decrease to move to more acidic pH values with increasing surfactant concentration. The latter is almost certainly a consequence of the amount of iron in the system being essentially invariant. At higher surfactant concentrations, the proportion of surfactant complexed with such iron must, therefore, have diminished. This in turn would have left more surfactant
available to adsorb on the mineral surface at a fixed pH and conversely required lower pH values to solubilize sufficient iron to affect appreciable surfactant complexing.

In comparing the unleached cassiterite adsorption isotherms (Figure 160) with the corresponding electrophoretic mobility data (Figure 165), it is evident that strong correspondence exists between the two for the $1 \times 10^{-4}$ M surfactant concentration which is common to both data sets. A small variance exists in terms of adsorption magnitudes between pH 4.0 and 3.0 at this concentration, but is explicable readily on the basis that the cassiterite samples used were not of the same size fraction and hence the solids concentrations and iron levels were almost certainly different. Most importantly, the rapid adsorption increase below pH 4.0 again can be seen to be associated with a substantial increase in charge reversal. No evidence consequently exists for a fundamental change in the styryl phosphonic acid adsorption mechanism in this pH range.

A number of limitations were associated with the use of ultraviolet absorbance measurements to determine residual surfactant concentrations in solution. Most obvious was that solubilized iron interfered seriously with the analyses. A further limitation of the adsorption study technique was that the analysis range was constrained to lower surfactant concentrations by the maximum absorbance that could be measured with the ultraviolet spectrometer. Due to both of these factors, it was found impossible to obtain adsorption isotherms for unleached cassiterite substrates at styryl phosphonic acid concentrations exceeding $1 \times 10^{-6}$ M. As such, the question of whether such high concentration isotherms would have shown the complex form of the corresponding electrophoretic mobility data (Figure 165) remains one of
conjecture. That iron was solubilized significantly at these high phosphonic acid concentrations, in only moderately acidic solutions (pH 4.0 - 6.0), was confirmed, however, by colour changes observed in the adsorption study supernatants.

4.4.3 Microflotation

4.4.3.1 Leached Cassiterite

Microflotation testing of leached Renison cassiterite indicated the mineral to exhibit optimal flotation response with styryl phosphonic acid in the strongly acidic range between pH 2.0 and 3.0 (Figure 166). For surfactant concentrations below $6 \times 10^{-5}$ M, particularly pronounced recovery maxima were found in this pH range. In more acidic solutions, recoveries dropped rapidly and invariably reached negligible levels by pH 1.0. Above pH 3.0, flotation response similarly diminished appreciably over a narrow pH range. However, recoveries higher than those that could be attributed solely to entrainment were found up to pH 8.0.

The effect of higher collector concentrations on the flotation of the leached cassiterite was to enhance markedly the response in the less acidic pH range (Figure 166). With a styryl phosphonic acid concentration of $1 \times 10^{-3}$ M, high recoveries were found to exist between pH 2.0 and 6.0. Associated with this broadening of the flotation region was a slight shift in the flotation recovery maximum to lower pH values. Presumably, this shift reflected the diminishing influence of solubilization of residual surface iron from the cassiterite. With increasing collector concentration, the ability of iron solubilized in strongly acidic solutions to complex a significant proportion of the surfactant and thereby affect the flotation response, obviously diminished. As such, the pH of maximum recovery moved to lower values. That
small levels of residual iron were present on the surface of the leached cassiterite was confirmed previously in both SIMS (Figure 97) and XPS analyses (Figure 110).

Figure 166 - The pH Dependence of Cassiterite Flotation Recovery after Acid Leaching of the Mineral. Data are shown for three different styryl phosphonic acid concentrations.

A most important aspect of the observed styryl phosphonic acid flotation of leached cassiterite is that the pH dependence of the response is analogous completely to that reported by Wottgen and Luft (1971) and Raatz and Schubert (1971) for cassiterite flotation with n-heptyl phosphonic acid (Figures 30 and 32). The results of Figure 166 are further consistent with the description given by Balachandran (1982) for styryl phosphonic acid flotation of a synthetic cassiterite. In all of these data, maximum recoveries were reported in strongly acidic solutions (pH 2.0 - 3.0) while the flotation response in the less acidic range was diminished appreciably. With regard to the broad pH
range of strong flotation response observed in this research at high (1x10^{-3} M) phosphonic acid concentrations, it is probable that surfactant adsorption was still greater below pH 4.0. This can be confirmed by the presence of a small maximum between pH 2.0 and 3.0. However, at higher pH values extending to pH 6.0, it is evident that the styryl phosphonic acid adsorption density on the cassiterite was sufficient to impart a very strong floatability to the mineral. It is well recognized that there frequently exists a level of surfactant surface overage that is sufficient for complete flotation of a mineral. Higher adsorption densities, while possibly influencing the flotation rate, do not produce measurably greater overall recoveries at longer flotation times.

In addition to correlating with data reported by other researchers, the microflotation response of the leached cassiterite corresponds remarkably with the previously presented stannic dioxide adsorption study and electrokinetic data. Specifically, the pH values of strongest flotation response in Figure 166 are essentially those of maximum styryl phosphonic acid adsorption (Figure 156) and charge reversal (Figure 163) found with the dioxide. Furthermore, it is clear from Figure 166 that a definite flotation response occurred at pH values above the cassiterite iep even at low phosphonic acid concentrations. This confirms the finding of the adsorption and electrokinetic studies that the interaction between styryl phosphonic acid and tin oxide involves a significant chemisorption component.

Results of potentiometric titrations of styryl phosphonic acid presented in Section 4.2.4 established that the pK values of the acid occur at pH 2.6 and 7.6, respectively. Examination of the data of Figure 166 indicates that there exists a definite relationship between the region of strongest
microflotation response and the pH region between \( pK_1 \) and \( pK_2 \) of the acid. This relationship exists for all three surfactant concentrations tested but is most marked at the highest (1 x 10\(^{-3} \) M) collector level. The general trend is that below \( pK_1 \) and above \( pK_2 \) recovery drops dramatically. Implicit in such a trend is that the partially dissociated styryl phosphonic acid species is responsible primarily for adsorption on the cassiterite surface. Such a conclusion is supported strongly by the stannic dioxide electrokinetic data of Figure 163 which show the negative charge character at the shear plane of the oxide double layer to increase proportionately with surfactant adsorption.

Intuitively, there appears to be some basis for the partially dissociated species of styryl phosphonic acid adsorbing most strongly onto the cassiterite surface. For undissociated phosphonic acid molecules to bond chemically, both of the surfactants hydroxy protons presumably must dissociate. In strongly acidic solutions, where these undissociated molecules predominate, such deprotonation is energetically unfavourable since there already exists an excess of protons. Conversely, above \( pK_2 \), where completely dissociated molecules are the predominant phosphonic acid species, there exists increased electrostatic repulsion between the divalent anionic molecules and the negatively charged cassiterite surface.

In final reference to the data of Figure 166, it should be noted that in all of the microflotation testing of this research, the maximum recovery that could be achieved was of the order of 90 percent. The inability to recover the remaining 10 percent of the cassiterite is believed attributable to the accumulation of a small proportion of coarser cassiterite in a 'dead zone' at the base of the microflotation tube during testing. Once trapped in this zone, the cassiterite was not fully contacted with the air bubbles generated
by the frit. Electrozone celloscope sizing of the products of several flotation tests confirmed that it was invariably the coarser fraction of cassiterite that remained unfloted (Figure 167). Finer particles were presumably more readily swept out by turbulence resulting from agitation in the cell. The existence of such a 'dead zone' was a function of the microflotation tube design. Specifically, it resulted from the tapered nature of the tube base and the use of a glass frit slightly smaller in diameter than the upper tube body.

Figure 167 - Size Distribution of Cassiterite Microflotation Feed and Tail (Volume Basis).
4.4.3.2 Unleached Cassiterite

In the presence of styryl phosphonic acid, unleached Renison cassiterite exhibited a profoundly different microflotation response to that of the corresponding leached sample. At low ($\leq 2 \times 10^{-5}$ M) collector concentrations, optimal floatability of the unleached sample occurred only in the slightly acidic to alkaline range between pH 4.0 and 7.5 (Figure 168). Outside of this pH range, recovery decreased dramatically. No evidence of any appreciable floatability was observed in strongly acidic solutions (pH 2.0 - 3.0). Such a microflotation pH dependence was almost the complete reverse of that observed with leached Renison cassiterite (Figures 166 and 169).

The effect of greater collector additions on the microflotation response of unleached cassiterite was to increase markedly both the pH range of flotation and the associated recoveries (Figure 168). In the presence of $1 \times 10^{-4}$ M styryl phosphonic acid, strong flotation response occurred over a broad range and the flotation behaviour bore a more closer resemblance to that of leached cassiterite with a surfactant concentration of $1 \times 10^{-3}$ M (Figure 170). However, even at these respective concentrations, there still remained clear evidence for enhanced unleached cassiterite flotation in the more alkaline range and a corresponding depressant effect in very acidic solutions.

It is dramatically clear from the data of Figures 168 to 170 that the effect of the iron film on the surface of the unleached cassiterite was to activate flotation at higher pH values and to interfere seriously with that in acidic pH solutions. The former effect was most clearly demonstrated by unleached cassiterite recoveries above pH 4.0 typically exceeding those of leached cassiterite at an order of magnitude lower styryl phosphonic acid concentration (Figure 170).
Figure 168 - The pH Dependence of Unleached Cassiterite Flotation Recovery. Data are shown for three different styryl phosphonic acid concentrations.

Figure 169 - Comparison of Cassiterite Flotation Response in the Presence of 2 \times 10^{-5} \text{ M} Styryl Phosphonic Acid Before and After Leaching of the Mineral.
Figure 170 - Comparison of Cassiterite Flotation Response in the Presence of Styryl Phosphonic Acid Before and After Leaching of the Mineral. The surfactant concentration in the case of the unleached cassiterite was $1 \times 10^{-4}$ M while that for the same cassiterite after leaching was $1 \times 10^{-3}$ M. The pK values shown are for styryl phosphonic acid.

On the basis of previous findings concerning the role of surface iron in adsorption studies and electrokinetic analyses, it can be concluded unequivocally that the flotation activation and depressant effects were related intimately to the pH range over which the unleached cassiterite surface iron was solubilized. In the slightly acidic to alkaline range above pH 5.0, the iron clearly must have remained predominantly on the surface and thereby strongly activated the cassiterite flotation through increased surfactant adsorption. It has been demonstrated consistently in direct leaching tests (Figure 114), adsorption measurements (Section 4.4.1.2) and electrokinetic studies (Figure 165) that the surface iron associated with unleached cassiterite is most readily solubilized in strongly acidic
solutions. The data of Figure 168 suggest that the onset of such solubilization occurred near pH 5.0 in agreement with the corresponding unleached cassiterite electrokinetic data (Figure 165). Below pH 4.0, solubilization demonstrably was of such a magnitude that it caused complete inhibition of flotation at low (8 x 10^{-6} M) collector concentrations. Increased collector additions allowed this interfering iron effect to be overcome since the amount of iron associated with the unleached cassiterite was presumably relatively constant from one test sample to another. At higher collector concentrations, it was possible to float the unleached cassiterite in the acidic range below pH 4.0.

In an attempt to gain a quantitative estimate of the amount of iron solubilized in the 10 minute total time of flotation testing (5 minutes conditioning + 5 minutes flotation), a collectorless test was performed at pH 2.0 and the solution analyzed for iron. Atomic absorption spectroscopy indicated the soluble iron level after contacting with the unleached cassiterite to be 0.15 mg/1 (2.7 x 10^{-6} M) Fe. While this concentration of iron is low, it is not insignificant. Furthermore, it must be emphasized that strong evidence exists from the adsorption study analyses (Section 4.4.1.2) that the amount of iron solubilized from the surface of unleached cassiterite in the presence of styryl phosphonic acid can greatly exceed that in distilled water alone. Such enhanced solubilization is almost certainly a consequence of the strong affinity of phosphonic acids for ferric species and their ability to form soluble iron complexes in more acidic solutions.

In comparing the 1 x 10^{-6} M styryl phosphonic acid microflotation response of unleached cassiterite with the corresponding adsorption density (Figure 160) and electrokinetic data (Figure 165), it is evident that strong internal
consistency exists. It is equally clear, however, that the different cassiterite size fractions used in these three tests varied appreciably with respect to their surface iron levels.

On the basis of the electrokinetic data, it might have been expected that recoveries with $1 \times 10^{-4}$ M phosphonic acid have been a maximum near pH 4.0 and decreased less dramatically at lower pH values than in the more neutral pH range. That the recovery maximum at pH 4.0 was not pronounced and flotation response decreased slightly more rapidly in the more acidic solutions, can be attributed to higher total iron levels in the flotation system. The solids concentration of 5 g/litre (1 g/200 mls) in the microflotation tests clearly substantially exceeded that in the electrophoresis suspensions. The latter suspension was determined experimentally to have a solids concentration of only 0.46 g/litre. However, the surface areas were presumably at least similar, if not greater, for the electrophoresis suspension due to its smaller solids particle size (log mean size 2.56 microns) relative to that of the flotation samples (log mean size 24.48 microns) (Table XIV).

In comparison to the adsorption study samples, it is clear that total iron levels in the microflotation test work were also appreciably greater. Such a result is not unexpected since the sample used in the adsorption studies was composed primarily of ground -38 + 4 micron cassiterite. X-ray photoelectron spectroscopic analyses of this ground cassiterite showed that the iron level was diminished substantially (Figure 113). This was due almost certainly to abrasion of the iron film from the mineral surface during grinding (Section 4.1.5.2). A further contributing factor in the different pH dependencies of the adsorption and microflotation study data, presumably, was that the adsorption study cassiterite had a substantially higher surface area (2.304
m²/g compared to 0.192 m²/g for the microflotation sample - Appendix E). Logically, at a fixed collector concentration below that corresponding to adsorption saturation, higher adsorption densities would have existed on the microflotation sample. As such, the surface coverage at higher pH values might have been sufficient to produce strong floatability despite being lower than in more acidic solutions. Phosphonic acid adsorption densities higher than expected solely on the basis of the surfactants interaction with the exposed cassiterite surface must obviously also have occurred due to the acids affinity for the surface iron film.

That the overall recovery dependence on pH shown in Figure 168 represented the net effect of surface iron interference and genuine phosphonic acid adsorption onto the unleached cassiterite was further demonstrated in both kinetic and surfactant concentration tests with the mineral. In these microflotation tests, recovery was found to be a complex function of surfactant concentration, pH and flotation rate.

Figure 171 shows the dependence of unleached cassiterite microflotation recovery on styryl phosphonic acid concentration for three different pH values. These pH values span the range over which solubilization of surface iron was first initiated and encompass the region of interest in actual industrial circuits. The data show clearly that recoveries were greatest in neutral (pH 7.0) solutions at low surfactant levels, but that at higher concentrations the trend reversed and more cassiterite floated under acidic conditions. The remarkable nature of the data in Figure 171 is completely consistent with iron producing either an activating or depressant effect on the phosphonic acid flotation of the cassiterite depending on the extent to which it is solubilized.
It has been established that, in the absence of surface iron, cassiterite exhibits its strongest flotation response with phosphonic acids in the range pH 2.0 - 3.0. However, such acidic pH values are conducive to extensive iron solubilization. Consequently, at low surfactant concentrations, complexing of collector with solubilized iron severely depressed flotation relative to that at higher pH values. Ultimately, in the presence of excess collector, the interfering iron effect was offset and recoveries at pH 3.0 exceeded those at higher pH values (pH 7.0) where genuine surfactant interaction with the mineral was weaker. As expected, the flotation response at pH 5.0 exhibited a concentration dependence intermediate in character to that at pH 3.0 and 7.0.
The influence of a surface iron activation or depressant effect was observed also in flotation rate analyses of the unleached cassiterite. While total recoveries in five minutes of flotation were not appreciably different over the range pH 3.0 to 7.0 in the presence of $1 \times 10^{-4}$ M styryl phosphonic acid (Figure 168), the corresponding rate data (Figure 172) exhibited subtle variations. Specifically, maximum recovery was reached most rapidly at pH 5.0 indicating genuine surfactant adsorption at this pH to exceed that at pH 7.0. Recoveries at pH 3.0 were found to be initially lower than at pH 7.0 but ultimately reached higher levels at longer flotation times. The strong initial depressant effect was presumably due to the onset of extensive iron solubilization and the formation of soluble iron phosphonate complexes in the more acidic solution. This evidently interfered with the kinetics of phosphonic acid adsorption on the cassiterite and delayed the formation of a surfactant surface coverage sufficient for strong floatability.

Figure 172 - The Flotation Recovery - Time Dependence of Unleached Cassiterite at Three Different pH Values in the Presence of $1 \times 10^{-4}$ M Styryl Phosphonic Acid.
One of the most extraordinary aspects of the microflotation response of unleached cassiterite at low styryl phosphonic acid concentrations is that it corresponds remarkably to the vacuum flotation data published by Collins and coworkers (Collins, 1967; Collins and Jackson, 1967; Collins, Hollick and Joy, 1969) for a range of natural cassiterites (Figure 35). In these vacuum flotation studies, it was established similarly that optimum flotation response at low phosphonic acid concentrations occurred between pH 5.0 and 6.0. Appreciably greater concentrations of phosphonic acid were found to be required for vacuum flotation at both more acidic and alkaline pH values. On the basis of the correlations established in this research, it is hereby proposed that the presence of an iron film on the surface of various test cassiterites is the factor responsible for the two distinctly different flotation responses that have been reported for cassiterite in fundamental test work with phosphonic acids.

The presence of iron films on the surface of cassiterite in both batch and plant flotation of the mineral can also explain why flotation and adsorption study results for single purified minerals in distilled water systems are seldom consistent with the flotation behaviour of cassiterite in ores. In this regard, it should be emphasized that the low concentration styryl phosphonic acid flotation response of Figure 168 bears a striking relationship to the actual flotation behaviour observed in the Renison plant from which the sample was taken. In particular, it is known that a dramatic and complete cessation in Renison cassiterite flotation occurs below pH 4.0. The critical examination of the literature performed in Section 2.5.3.5 further revealed that such a recovery decrease in acidic solutions was a characteristic feature of the phosphonic acid flotation of most natural cassiterites in both batch
testing and plant scale processing of ores (Figures 79 to 81).

It must be emphasized that in the treatment of ores other factors exist which make an unequivocal assessment of the validity of the proposed hypothesis difficult. However, the mechanism whereby surface iron produces an activating or depressant effect, dependent on the pH influenced extent of its solubilization, can explain all key aspects of known plant flotation behaviour. With regard to other possible hypotheses, this is either known not to be the case or has never been demonstrated definitively. A case in point is that despite innumerable studies on the influence of cassiterite lattice dopants, no flotation response has ever been reported that even remotely approximates that actually observed in the plant flotation of ores (Sections 2.4.1, 2.5.3.5 and 2.5.3.6).

4.4.4 Principal Findings and Conclusions

(1) Styryl phosphonic acid adsorbs rapidly on both stannic dioxide and unleached Renison cassiterite. Equilibrium is reached within one hour, with the majority of uptake occurring in the first 10 minutes of contacting.

(2) Maximum adsorption of styryl phosphonic acid on stannic dioxide occurs in the acidic range between pH 2.0 and 3.0. In less acidic solutions, adsorption decreases rapidly to pH 4.0 and then more slowly at higher pH values. Such adsorption behaviour is analogous entirely to that reported independently by several different research groups for a range of phosphonic acids and natural cassiterites.

(3) Measurable levels of adsorption above pH 4.0 confirm that the styryl phosphonic acid interaction with stannic dioxide
involves a chemisorption component. In this pH range, the surfactant is dissociated and the stannic dioxide has a negative charge character. Strong interaction therefore occurs despite electrostatic repulsion between the anionic surfactant molecules and the negatively charged mineral surface.

(4) Changes in the electrophoretic mobilities of stannic dioxide particles in the presence of styryl phosphonic acid are consistent in all respects to the corresponding adsorption data. In particular, maximum charge reversal occurs in the pH range 2.0 to 3.0. No evidence exists for extensive surfactant adsorption without an associated change in electrokinetic properties of the oxide as analyses of published data suggest the case to be for p-tolyl phosphonic acid.

(5) Stannic dioxide electrophoretic mobilities in styryl phosphonic acid solutions exhibit a pH dependence generally considered characteristic of a chemisorbing surfactant. Decreases in electrophoretic mobilities above the stannic dioxide iep confirm that anionic phosphonic acid species can adsorb onto the negatively charged oxide surface. No evidence exists for hemi-micelle formation even at phosphonic acid concentrations as high as $2 \times 10^{-3}$ M.

(6) The absence of any significant hydrophobic bonding interactions in the styryl phosphonic acid system is consistent with the short nature of the surfactant radical.
It has been verified in innumerable surfactant systems that hemi-micelles do not form when hydrocarbon chain lengths are shorter than Cₘ.

(7) Markedly higher charge reversals, associated with abrupt increases in styryl phosphonic acid adsorption on stannic dioxide below pH 4.0, confirm that adsorption of negatively charged species is at least partially responsible for the adsorption increase. Such a finding supports the Wottgen (1969) and Gruner (1971) hypothesis that the adsorption increase is due to enhanced electrostatic attraction between partially dissociated phosphonic acid molecules and the substrate below the latter's iep. Conversely, such data provide no evidence supporting the alternative Fuerstenau and Healy (1972) hypothesis that coadsorption of undissociated phosphonic acid molecules is responsible for the increase. However, the possibility that both might be occurring cannot be precluded unequivocally.

(8) In microflotation testing, leached Renison cassiterite exhibits optimal flotation response with styryl phosphonic acid in the strongly acidic range between pH 2.0 and 3.0. Above pH 3.0, flotation response at low surfactant concentrations diminishes appreciably over a narrow pH range. Such flotation behaviour is analogous completely to that reported by other researchers for both synthetic and natural cassiterites. It further correlates remarkably with all aspects of the stannic dioxide adsorption study and
Recoveries of leached Renison cassiterite higher than could be attributed solely to entrainment were found above the mineral's iep even at very low surfactant concentrations. This confirms the finding of the stannic dioxide adsorption and electrokinetic studies that the interaction between styryl phosphonic acid and tin oxide involves a significant chemisorption component.

A distinct relationship exists between the pH region of optimum leached cassiterite flotation response and that between $pK_1$ and $pK_2$ of the acid. Implicit in such a relationship is that the partially dissociated styryl phosphonic acid species is responsible primarily for adsorption on the cassiterite surface. Such a conclusion is supported strongly by stannic dioxide electrokinetic data which show the negative charge character at the shear plane of the oxide double layer to increase proportionately with surfactant adsorption.

The presence of an iron film on the surface of unleached Renison cassiterite profoundly influences the microflotation, adsorption and surface charge character of the mineral in solutions containing styryl phosphonic acid. In the slightly acidic to neutral pH range ($pH > 5.0$), such iron results in increased styryl phosphonic acid adsorption onto the cassiterite thereby increasing the negative charge character of the mineral and strongly promoting its...
floatability. Conversely, in strongly acidic solutions the iron is solubilized and forms aqueous complexes with the phosphonic acid. Adsorption and charge reversal are consequently diminished in such solutions. If sufficient iron is present, associated mineral floatability can be inhibited entirely at these low pH values.

(12) Solution chemical assays have established that styryl phosphonic acid promotes the solubilization of iron from the surface of unleached cassiterite in acidic solutions. Styryl phosphonic acid supernatants recovered from adsorption tests at pH 1.0 and 2.0 were found to assay 270 ppm and 125 ppm iron, respectively. Corresponding distilled water supernatants assayed only 175 and 86 ppm.

(13) Evidence for the formation of strongly solvated iron phosphonate complexes in acidic solutions exists in the striking colour changes associated with the addition of acid or base to supernatants recovered from low pH suspensions of unleached cassiterite and styryl phosphonic acid.

(14) The microflotation response of unleached Renison cassiterite at low styryl phosphonic acid concentrations corresponds remarkably with published vacuum flotation data for a range of natural cassiterites. In these data, it was established that optimum flotation response at low phosphonic acid levels occurred between pH 5.0 and 6.0. Appreciably greater concentrations of phosphonic acid were found to be required for vacuum flotation at both more acidic and alkaline pH
(15) On this basis of the correlations established in this research, it is proposed that the presence of an iron film on the surface of various test cassiterites is the factor responsible for the two distinctly different flotation responses that have been reported for cassiterite in fundamental test work with phosphonic acids.

(16) A mechanism whereby surface iron produces an activating or depressant effect on phosphonic acid adsorption, dependent on the pH influenced extent of its solubilization, can explain why flotation behaviour in both batch testing and actual industrial circuits invariably bears little resemblance to that observed in fundamental flotation and adsorption tests with single purified minerals and iron free solutions. In particular, the low pH solubilization of such surface films can account for the dramatic and complete cessation of cassiterite flotation that typically occurs below pH 4.0 in the processing of ores.
4.5 Mineral - Ion Interactions

4.5.1 Microelectrophoresis Studies

4.5.1.1 Surface Charge of Cassiterite in Aluminum Ion Solutions

The electrophoretic mobilities of unleached cassiterite particles in the presence of various concentrations of aluminum chloride are shown in Figure 173. All test suspensions were prepared according to a surface condensation (type II) procedure. Initial pH values of the cassiterite suspensions are marked in the figure.

The electrokinetic data of Figure 173 show clearly that, at the pH of preparation of the test suspensions, the presence of aluminum chloride produced substantial charge reversal effects. Such charge reversals were indicative of the strong adsorption of positively charged aluminum species onto the surface of unleached cassiterite. Reference to Figure 12 confirms that, for all tests, the initial pH values of the suspensions corresponded to the region of stability of aluminum hydroxy species. In the tests conducted at aluminum chloride concentrations of $5 \times 10^{-5}$ M and $1 \times 10^{-4}$ M, it was possible to observe colloidal aluminum hydroxy sols directly in solution.

Increasing the pH of the initial suspensions produced electrophoretic mobility changes consistent with those proposed by James and Healy (1972a) for the general case of insoluble minerals in the presence of hydrolyzable cations (Figure 52). The mobilities initially increased, passed through a maximum and then underwent a subsequent positive-to-negative reversal. In more strongly alkaline solutions, the mobilities approached those of the mineral in the absence of aluminum chloride. As expected, the (CR.3) positive-to-negative charge reversal point varied with the aluminum addition but for all test concentrations was between pH 7.2 and 8.6.
Figure 173 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in the Presence and Absence of Various Concentrations of AlCl₃·6(H₂O). The initial pH (pHᵢ) values of the cassiterite suspensions are shown in the figure. All suspensions were prepared according to a surface condensation (type II) procedure.

In solutions more acidic than those initially, the surface charge of the unleached cassiterite remained positive. The absence of charge reversal points CR.1 and CR.2 can be attributed to the thermodynamic stability of the adsorbing aluminum species down to pH values approaching the mineral iep (pH 4.0) and the slow kinetics of their resolubilization. The latter factor was clearly important at higher aluminum concentrations were electrophoretic mobilities remained considerably greater than in the absence of aluminum down to pH 2.0. At such low pH values, the free aquo ion was the thermodynamically stable aluminum species. This strongly solvated species would not be expected to adsorb inside the hydrodynamic shear plane so as to cause an increase in the positive charge of the cassiterite.
An almost complete absence of published data on electrophoretic mobilities of cassiterite in aluminum ion systems exists. However, the results of Figure 173 are consistent with those from tests with aluminum using other mineral substrates (Figure 53). They further correlate with a single reported measurement for cassiterite at pH 6.0 in the presence of 60 mg/l AlCl₃ (Figure 56).

In Section 4.1.7, electrokinetic data were presented establishing that drying under vacuum could remove completely the characteristic charge reversal effects of adsorbed hydrous iron oxide sols. To confirm that thermal drying produced the same effect in the aluminum system, electrophoretic mobilities of an unleached cassiterite suspension containing 1 x 10⁻⁶ M aluminum chloride were measured before and after such drying (Section 3.6.1). Remarkably, the charge reversal effects associated with adsorption of the aluminum species all but disappeared (Figure 174). As proposed previously, the most plausible explanation of such an effect is that drying reduced the degree of hydration of the adsorbed sols. It is the coordinated and chemisorbed water molecules and hydroxyl groups of such sols that produce their charge character.

The ability of drying to cause the disappearance of charge reversal effects normally associated with the adsorption of hydrolyzed metal ionic species is a significant finding. The importance of the result is that metal ionic species can exist on a mineral surface after drying but cannot be detected readily by microelectrophoresis. It is, therefore, highly conceivable that many mineral samples used previously for surface chemical test work by other researchers and considered to be of high purity were contaminated by a surface metal film. Such could have been the case for minerals exposed to solutions containing hydrolyzed metal ionic species and
Figure 174 - The Effect of Thermal Drying on the Electrophoretic Mobility of Cassiterite Particles Prepared in the Presence of 1 x 10^-4 M AlCl₃·6(H₂O). Data are shown for the same mineral suspension before and after thermal drying at 120°C for 24 hours. The initial suspension pH was 4.65. After drying and redispersal in distilled water for 1 hour the pH was 5.25. Data are given also for an identical suspension in the absence of AlCl₃·6(H₂O) addition.

then subsequently dried. On a more fundamental level, the disappearance of such charge reversal effects raises the issue of the morphology changes associated with drying. It further emphasizes that only in-situ surface analytical techniques can provide information concerning adsorbed hydrous oxide sols that pertains directly to the aqueous environment.

4.5.1.2 Surface Charge of Cassiterite in Ferric Ion Solutions

In the presence of ferric chloride, unleached cassiterite particles were found to undergo pronounced charge reversal effects. For suspensions prepared according to a surface condensation (type II) procedure, these electrophoretic mobility changes (Figure 175) were similar to those observed in the cassiterite-aluminum system (Figure 173).
Figure 175 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in the Presence and Absence of Various Concentrations of FeCl<sub>3</sub>. The initial pH (pH<sub>i</sub>) values of the cassiterite suspensions are shown in the figure. All suspensions were prepared according to a surface condensation (type II) procedure.

Examination of the data of Figure 175 shows that, at the pH of preparation of the ferric chloride bearing cassiterite suspensions, the electrophoretic mobilities of the mineral reversed in sign and became highly positive. On increasing the pH, the mobilities initially passed through a maximum and then decreased and became negative. The CR.3 point of zero cassiterite mobility associated with these charge reversals moved from pH 5.8 to 8.3 with increasing concentration. In solutions more acidic than at the point of suspension preparation, the electrophoretic mobilities remained positive and of a magnitude significantly higher than in the absence of the ferric chloride. As for the aluminum chloride system, charge reversal points CR.1 and CR.2 were found to be absent.
The observed electrokinetic behaviour of the cassiterite in ferric chloride solutions is consistent with the finding of Gaudin and Sun (1946) that an initially negatively charged cassiterite became highly positively charged in the presence of 125 mg/l FeCl$_3$.6(H$_2$O) at pH 5.0 (Figure 56). The data further correlate with the finding of Bellot (1970) that the pzc of cassiterite moved from pH 4.0 to 6.0 in the presence of 5.7 x 10$^{-6}$ M ferric chloride. In this research, a concentration of 5 x 10$^{-6}$ M ferric chloride moved the point of zero electrophoretic mobility to pH 5.8.

In Figures 176 and 177, the measured Eh and pH values of the cassiterite suspensions containing 5 x 10$^{-6}$ M and 5 x 10$^{-5}$ M ferric chloride are shown. The data are plotted on Pourbaix diagrams for the Fe-H$_2$O system at 25°C, 1 atmosphere total pressure and the appropriate activity of dissolved iron species. It is clearly evident that all of the measured pH and Eh values corresponded to conditions where hydrous ferric oxide would have been the thermodynamically stable iron species in the absence of cassiterite.

In most cases, the pH of dissolved metal ion solutions is known to be insensitive to the presence of an insoluble mineral. However, it is generally considered that for conducting minerals, such as sulphides, the Eh can adopt a potential that represents both the ion solution chemistry and the potential of the conducting solid components in the pulp (Heyes and Trahar, 1977). Since cassiterite is a conductor (Section 2.1.2), it is possible that the Eh values of the cassiterite suspensions also might have represented mixed potentials arising from bulk solution and mineral-solution interfacial redox reactions. However, at the relative levels of solids to ferric ion concentrations in the microelectrophoresis studies, no evidence was found that the presence of the mineral substrate altered the Eh and the pH to any significant extent. Both
solution chemical parameters appeared to be controlled predominantly by the ferric ion solution chemistry.

![Eh-pH Dependence for the Cassiterite Suspension Containing 5 x 10^{-6} M FeCl₃](image)

Figure 176 - The Eh - pH Dependence for the Cassiterite Suspension Containing 5 x 10^{-6} M FeCl₃ Used in the Electrophoretic Mobility Determinations. The initial pH and Eh of the suspension were 5.00 and 517 mV (SHE), respectively. The data are shown plotted on a Pourbaix diagram for the Fe - H₂O system at 25°C, 1 atmosphere total pressure and a total activity of dissolved iron species of 5 x 10^{-6}.

The key conclusion from the data of Figures 175 to 177 is that under solution chemical conditions where hydrous ferric oxide sols were thermodynamically stable, strong adsorption of positively charged ferric species occurred on the cassiterite surface. All aspects of the associated charge reversal phenomena were consistent with these hydrous ferric oxide sols being the adsorbing species as proposed in the James and Healy model (Section 2.5.1.3). Given the iron levels and solution chemical conditions known to
exist in the Renison plant (Section 4.3.1), appreciable adsorption of such species would have been expected. The hypothesis that the aqueous flotation pulps of the Renison concentrator were the source of the observed iron films on cassiterite recovered from the plant is, therefore, highly plausible.

Figure 177 - The Eh – pH Dependence for the Cassiterite Suspension Containing $5 \times 10^{-5}$ M FeCl$_3$ Used in the Electrophoretic Mobility Determinations. The initial pH and Eh of the suspension were 3.85 and 659.8 mV (SHE), respectively. The data are shown plotted on a Pourbaix diagram for the Fe – H$_2$O system at 25°C, 1 atmosphere total pressure and a total activity of dissolved iron species of $5 \times 10^{-5}$.

A feature of the electrophoretic mobility curves in Figure 175 is that, even at low ($5 \times 10^{-6}$ M) ferric chloride concentrations, electrophoretic mobilities at pH 3.0 were substantially higher than in the absence of the ferric salt. Acidification of the suspensions to this pH obviously did not cause measurable solubilization of the absorbed hydrous ferric oxide sols. Such a finding is consistent with both the thermodynamic stability of these
sols down to the more strongly acidic range (Figures 176 and 177) and the slow kinetics of their depolymerization.

In the literature review pertaining to electrokinetic effects associated with ion-mineral interactions (Section 2.5.1.1), it was established that the method of mineral-cation suspension preparation could influence significantly the form of electrophoretic mobility curves. These variations were concluded to be a consequence of differences in the kinetics of polymerization and depolymerization of hydroxy cationic sols and the complicated nature of their aging processes. During the course of the investigations into the interactions between ferric ion species and mineral substrates, a number of instances of such variations were observed.

In Figure 178, electrokinetic data are given for unleached cassiterite suspensions containing $1 \times 10^{-5}$ M FeCl$_3$, prepared according to a surface condensation (type II) and a surface nucleation procedure. It is evident, in this system, that the cassiterite electrokinetic behaviour differed only slightly with the method of suspension preparation. The most noticeable change was that charge reversal in the surface nucleation tests was less pronounced at pH 3.0 but exhibited a more distinct maximum near pH 4.0. Significantly, these latter data correlate more closely with those published by Schubert, Baldauf and Raatz (1969) for cassiterite surface nucleation tests with ferric chloride (Figure 58). The absence of complete coincidence of the data in Figure 178 does confirm, however, that the hydrolysis of ferric species and their associated adsorption on the cassiterite surface was neither entirely reversible nor kinetically rapid. Had this been the case, the two electrophoretic mobility curves would have been indistinguishable.
Thermodynamically, it would have been expected that the onset of hydrous ferric oxide formation in the surface nucleation tests would have occurred near pH 2.8 (Figure 179). Experimentally, it was found impossible in the cassiterite system to determine the pH of electrophoretic mobility increase associated with hydrolyzed ferric ion adsorption. This was a consequence of the difficulty in measuring cassiterite mobilities at such low pH values and the fact that the mineral itself was highly positively charged in this pH range. However, on the basis of tests conducted with high purity quartz suspensions, it was found possible to elucidate further the role of pH in the onset of ferric species adsorption on mineral substrates and the effect of acidification on resolubilization of such charge reversal species.
Figure 179 - The Eh - pH Dependence for the Cassiterite Suspensions Containing 1 x 10^{-5} M FeCl_3 Used in the Electrophoretic Mobility Determinations. The initial pH values (pH_i) of the two suspensions were 2.14 and 4.70, respectively. The data are shown plotted on a Pourbaix diagram for the Fe - H_2O system at 25°C, 1 atmosphere total pressure and a total activity of dissolved iron species of 10^{-5}.

In Figure 180, electrophoretic mobility data are given for quartz suspensions containing 1 x 10^{-5} M ferric chloride prepared according to surface condensation (type II) and surface nucleation procedures. Remarkably, the method of suspension preparation produced profound differences in the quartz mobilities. This was despite the Eh and pH of the two suspensions being very similar in magnitude and following almost identical trends during the course of all measurements (Figure 181).

A remarkable aspect of the data in Figure 180 is that the surface nucleation procedure produced an electrokinetic response of a form expected on the basis of the James and Healy model while the electrokinetic properties of
quartz prepared according to the surface condensation (type II) procedure were
totally different. In particular, charge reversal points CR.2 and CR.3 were
clearly evident in the surface nucleation data while only a single reversal
point was found in the surface condensation tests. In this latter case, the
charge character of the quartz surface became increasingly more positive in
the strongly acidic range. Somewhat extraordinarily, the highest positive
electrophoretic mobility was observed at pH 2.0 where free aquo ferric ions
thermodynamically should have been the most stable species (Figure 181).

![Graph showing electrophoretic mobilities of pure quartz particles in the presence and absence of FeCl₃.](image)

**Figure 180** - The Electrophoretic Mobilities of Pure Quartz Particles in the Presence and Absence of 1 x 10⁻⁵ M FeCl₃. Data are shown for suspensions containing FeCl₃ prepared according to a surface condensation (type II) procedure (pH₄ = 5.1) and a surface nucleation procedure (pH₄ = 2.2). Also included in the figure are the data of Mackenzie (1966) for a quartz suspension containing 5.7 x 10⁻⁵ M ferric chloride prepared according to a surface nucleation procedure (pH₄ = 2.0).
Figure 181 - The Eh - pH Dependence for the Quartz Suspensions Containing 1x10^{-5} M FeCl_3, Used in the Electrophoretic Mobility Determinations. The initial pH values (pH_i) of the two suspensions were 2.2 and 5.1, respectively. The data are shown plotted on a Pourbaix diagram for the Fe - H_2O system at 25°C, 1 atmosphere total pressure and a total activity of dissolved iron species of 10^{-5}.

The results of Figure 180 confirm that the nature of iron hydrolysis species present in a suspension, prior to adjustment of the pH, fundamentally influences the electrokinetic character of the mineral. In the surface condensation tests, the initial pH and Eh were such that hydrous ferric oxide sols were stable thermodynamically. These species clearly adsorbed on the quartz surface. Changes in the pH then caused the charge character of the adsorbed sols to vary, thereby altering the overall electrophoretic mobilities of the substrate particles. The implication is that the adsorbed sols became more positively charged in acidic solutions and more negatively charged at higher pH values. Such a trend is consistent with the protonation and
deprotonation of the hydroxy groups of the sols in a manner analogous to that of insoluble oxide minerals (Section 2.1.6). There was no evidence to suggest that measurable solubilization of the adsorbed sols occurred even in acidic solutions near pH 2.0. This is despite the thermodynamic instability of hydrous ferric oxide at such low pH values (Figure 181). As established in Section 4.3.2 of this research, the depolymerization and resolubilization of ferric-hydroxy polycations in aqueous solutions is kinetically very slow even in the presence of excess acid. The same is clearly true for such sols adsorbed on mineral surfaces.

In the surface nucleation tests, the free aquo form of the ferric ion was the thermodynamically stable species at the pH of suspension preparation. In accord with the postulates of the James and Healy model, no charge reversal occurred at this pH. This implies that the free aquo ferric ion did not adsorb specifically so as to cause charge reversal. However, as the pH was increased and the iron hydrolyzed, adsorption on the quartz surface did occur. Ultimately, the quartz became positively charged in the pH region 3.5 to 6.6. The implication from these data is that the onset of specific adsorption occurred just above pH 2.0 as evidenced by the rapid decrease in the negative quartz surface charge in slightly less acidic solutions. Such a pH is marginally below that expected thermodynamically for the ferric ion to hydrous ferric oxide transition (Figure 181). However, such a finding is qualitatively similar to results published by James and Healy (1972a) for other mineral systems showing charge reversal phenomena and cationic species adsorption to initiate at pH values significantly below that necessary for hydrolysis in bulk solution (Section 2.5.1.3).
In Figure 180, published data from Mackenzie (1966) for quartz suspensions initially at pH 2.0, prior to $5.7 \times 10^{-5}$ M FeCl$_3$ addition, have been included for comparison. These data can be seen to correspond remarkably to the surface nucleation data of this research given that different quartz samples and ferric chloride concentrations were used.

The different form of the surface condensation electrophoretic mobility curve in Figure 180 is striking when compared to both the surface nucleation data of this research and those of Mackenzie. However, the trend was completely general as confirmed in a series of surface condensation (type II) tests at successively increasing ferric chloride concentrations (Figure 182). For all these suspensions, only one charge reversal point existed and the maximum positive charge character of the quartz invariably occurred in the most acidic solution. This was despite the measured Eh and pH values of these acidic solutions lying outside the stability region of hydrous ferric oxide (Figures 183 and 184).

It is evident in the data of Figure 182 that a strong tendency existed for the initial pH of the surface condensation suspensions to decrease with increasing ferric chloride concentration. Similar trends can be noted in the corresponding data for cassiterite in the presence of aluminum and ferric chloride (Figures 173 and 175). Such decreases in initial suspension pH were almost certainly indicative of greater proportions of hydroxyl ions being consumed in ion hydrolysis reactions at higher cation concentrations.

In a manner analogous entirely to that observed in the aluminum ion system, the charge reversal effects associated with the adsorption of hydrous ferric oxide sols onto the cassiterite surface disappeared completely when the sample was dried (Figure 185). Such a finding is a crucial result. It
supports strongly the key tenet of this research that the surface iron film found on Renison cassiterite was the result of previous adsorption of hydrous ferric oxide sols from the plant pulps. As supplied from Renison, the cassiterite sample was known to have been dried thermally. The absence of any charge reversal character associated with the cassiterite iron films, therefore, is totally consistent with such adsorption given that thermal drying can cause the charge reversal phenomena related to hydrolyzed metal ion adsorption to disappear.

Figure 182 - The Electrophoretic Mobilities of Pure Quartz Particles in the Presence and Absence of Various Concentrations of FeCl$_3$. The initial pH ($pH_i$) values of the quartz suspensions are shown in the figure. All suspensions were prepared according to a surface condensation (type II) procedure.
Figure 183 - The Eh - pH Dependence for the Quartz Suspension Containing 5 x 10^{-6} M FeCl₃ Used in the Electrophoretic Mobility Determinations. The initial pH and Eh of the suspension were 5.45 and 553.8 mV (SHE), respectively. The data are shown plotted on a Pourbaix diagram for the Fe - H₂O system at 25°C, 1 atmosphere total pressure and a total activity of dissolved iron species of 5 x 10^{-6}.

Figure 184 - The Eh - pH Dependence for the Quartz Suspension Containing 5 x 10^{-5} M FeCl₃ Used in the Electrophoretic Mobility Determinations. The initial pH and Eh of the suspension were 4.00 and 728.8 mV (SHE), respectively. The data are shown plotted on a Pourbaix diagram for the Fe - H₂O system at 25°C, 1 atmosphere total pressure and a total activity of dissolved iron species of 5 x 10^{-5}.
Figure 185 - The Effect of Thermal Drying on the Electrophoretic Mobility of Cassiterite Particles Prepared in the Presence of \(5 \times 10^{-5}\) M FeCl\(_3\). Data are shown for the same mineral suspension before and after thermal drying at 120 °C for 24 hours. The initial suspension pH and Eh were 3.85 and 679 mV, respectively. After drying and redispersal in distilled water for 1 hour the pH was 5.00 and the Eh 490.7 mV. Data are given also for an identical suspension in the absence of FeCl\(_3\).6(H\(_2\)O) addition.

Despite solution chemical conditions after drying corresponding to the stability region of hydrous ferric oxide (Figure 186), it is obvious that the changes produced by thermal drying were not reversible. Once removed by drying, the characteristic charge reversal phenomena associated with the formation of freshly precipitated hydrous iron oxides were not re-established on subsequent exposure to an aqueous environment. Drying presumably gave rise to a more stable hydrous ferric oxide entity than the highly charged, amorphous sols of initial precipitation. Freshly precipitated sols, even in aqueous solution, are known to be unstable thermodynamically and to age slowly to more distinctly crystalline phases (Section 2.3.1.3).
Figure 186 - The Eh – pH Dependence of the Unleached Cassiterite Suspensions Containing $5 \times 10^{-5}$ M FeCl$_3$, Used in the Determinations of the Effects of Thermal Drying on Particle Electrophoretic Mobilities. The data are shown plotted on a Pourbaix diagram for the Fe – H$_2$O system at 25°C, 1 atmosphere total pressure and a total activity of dissolved iron species of $5 \times 10^{-5}$.

4.5.1.3 Surface Charge of Cassiterite in Ferrous Ion Solutions

It was established in the literature review (Section 2.3.2.7) and in solution chemical analyses around the Renison circuit (Section 4.3.1) that the free aquo ferrous ion and hydrous ferric oxide were most likely the predominant iron species in the plant pulps. Conditions were found to be neither sufficiently oxidizing for the existence of the free ferric ion or lower order ferric hydroxy species nor sufficiently reducing for the existence of significant concentrations of ferrous hydroxide (Figure 143). The key iron solution transition, therefore, was that between the ferrous ion and the hydrous ferric oxide stability regimes which occurred at low Eh and slightly acidic pH values.
Figure 187 shows the electrophoretic mobilities of unleached cassiterite particles in the presence and absence of ferrous chloride. Preparation of the test suspensions was according to a surface nucleation procedure. Solution chemical measurements associated with the electrophoretic mobility determinations (Figures 188 and 189) indicated the free aquo ferrous ion to be the thermodynamically stable species at the pH of suspension preparation.

The electrophoretic mobility curves of Figure 187 follow the general form proposed by James and Healy (1972a) for colloidal systems in the presence of hydrolyzable metal ions. Charge reversal points CR.1 and CR.2 were absent but this was clearly a consequence of the onset of specific adsorption at pH values below the mineral iep. Most importantly, no evidence of specific adsorption was found at pH 3.0 even at the higher (5 x 10^-6 M) ferrous chloride concentration. The absence of any change in cassiterite charge character at pH 3.0 indicated that the free aquo ferrous ion did not specifically adsorb. At this pH, the measured Eh values were such that the free aquo ion would have been the thermodynamically stable species in solution.

In Figure 187, divergence between the electrophoretic mobility curves of unleached cassiterite particles in the presence and absence of ferrous chloride can be seen to have initiated in the range pH 3.0 to 4.0. These points of divergence correlate closely with the corresponding ferrous ion to hydrous ferric oxide thermodynamic transitions (Figures 188 and 189). Specifically, the electrophoretic mobility curve for the 1 x 10^-6 M ferric chloride suspension deviated from that in the absence of the salt at approximately pH 3.7. In the presence of 5 x 10^-6 M ferric chloride, the point of deviation was less readily discernable but occurred near pH 3.2.
Figure 187 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in the Presence and Absence of FeCl$_2$.4(H$_2$O). Data are given for FeCl$_2$.4(H$_2$O) concentrations of $1 \times 10^{-6}$ M and $5 \times 10^{-6}$ M. Both suspensions were prepared according to a surface nucleation procedure. The initial pH ($pH_i$) values of the suspensions are shown in the figure.

Figure 188 - The Eh - pH Dependence for the Cassiterite Suspension Containing $1 \times 10^{-6}$ M FeCl$_2$.4(H$_2$O) Used in the Electrophoretic Mobility Determinations. The initial pH of the suspension was 2.95. The data are shown plotted on a Pourbaix diagram for the Fe - H$_2$O system at 25°C, 1 atmosphere total pressure and a total activity of dissolved iron species of $10^{-6}$. 
Interpolation between measured Eh and pH data points in Figures 188 and 189 indicates that the onset of hydrous ferric oxide formation, thermodynamically, should have occurred at pH 3.9 and 3.8 for the two respective ferric chloride concentrations. Evidence exists, therefore, for initiation of cationic species adsorption and charge reversal phenomena at pH values below that necessary for hydrous ferric oxide formation in bulk solution in accord with previous findings by James and Healy (1972a). However, the data cannot be considered entirely definitive since the measured Eh values strictly represented mixed potentials and not the potentials of iron solution redox reactions alone.
Ferrous chloride surface nucleation tests with quartz substrates produced results (Figure 190) remarkably similar to those with unleached cassiterite. At the low pH levels of preparation of these quartz suspensions, the free aquo ferrous ion was the thermodynamically stable species (Figures 191 and 192). No measurable increases in the charge character of the quartz were observed at these pH values. However, subsequent additions of base caused substantial charge reversal effects. As observed in the cassiterite system, the pH values corresponding to these changes in electrokinetic character varied appreciably with the ferrous chloride concentration. For suspensions containing $1 \times 10^{-6}$ M FeCl$_2$.4(H$_2$O), initial decreases in quartz surface charge character, relative to that in a distilled water system, were observed between pH 3.0 and 3.4. At the higher ferrous chloride concentration of $5 \times 10^{-6}$ M, measurably lower electrophoretic mobilities were found in acidic solutions above pH 2.4.

The electrophoretic mobility curves of Figure 190 follow the general trends predicted on the basis of the James and Healy model. The free aquo ferrous ion clearly does not adsorb specifically. However, positively charged species formed at higher pH values have a very strong affinity for adsorption on the quartz surface. Adsorption of these species ultimately caused the quartz to attain a net positive charge.

Solution chemical parameters measured during the electrokinetic studies (Figures 191 and 192) confirm unequivocally that the charge reversals were related to the onset of hydrous ferric oxide formation. However, as for the cassiterite system, the onset of charge reversal initiated at slightly lower pH values than would have been predicted on the basis of thermodynamic data. Such a finding supports the hypothesis that adsorption of hydrous ferric oxide on mineral surfaces occurs at pH values slightly below that necessary for bulk
solution precipitation. Standard references such as Shuey (1975) do not list quartz as a semiconducting mineral. As such, the Eh potentials measured in the electrophoresis suspensions presumably were determined uniquely by the iron solution redox reactions. Differences between the electrokinetic and thermodynamic data, therefore, cannot be attributed to the presence of the mineral substrate, as was a possibility in the case of cassiterite.

Figure 190 - The Electrophoretic Mobilities of Pure Quartz Particles in the Presence and Absence of FeCl$_2$$\cdot$4(H$_2$O). Data are given for FeCl$_2$$\cdot$4(H$_2$O) concentrations of $1 \times 10^{-6}$ M and $5 \times 10^{-6}$ M. Both suspensions were prepared according to a surface nucleation procedure. The initial pH ($pH_i$) values of the suspensions are shown in the figure.
Figure 191 - The Eh – pH Dependence for the Quartz Suspension Containing 1 x $10^{-6}$ M FeCl$_2$.4(H$_2$O) Used in the Electrophoretic Mobility Determinations. The initial pH of the suspension was 2.40. The data are shown plotted on a Pourbaix diagram for the Fe – H$_2$O system at 25 °C, 1 atmosphere total pressure and a total activity of dissolved iron species of $10^{-6}$.

Figure 192 - The Eh – pH Dependence for the Quartz Suspension Containing 5 x $10^{-6}$ M FeCl$_2$.4(H$_2$O) Used in the Electrophoretic Mobility Determinations. The initial pH of the suspension was 2.4. The data are shown plotted on a Pourbaix diagram for the Fe – H$_2$O system at 25 °C, 1 atmosphere total pressure and a total activity of dissolved iron species of $5 \times 10^{-6}$. 
In common with all published microelectrophoresis data, it is impossible from the results of Figures 190 to 192 to determine unequivocally the mechanism responsible for hydrous oxide species adsorption on quartz at pH values below that necessary for bulk precipitation. No definitive test has been devised to evaluate the James and Healy concept of intrinsically different stability constants in the interfacial region nor to show that concentration and pH variations between an interface and bulk solution provides the definitive answer (Section 2.5.1.4).

During the course of the electrokinetic studies with quartz, a series of striking potential changes were noted. At pH values just above those corresponding to the onset of charge reversal and thermodynamic stability of hydrous ferric oxide, very pronounced decreases in Eh occurred (Figures 191 and 192). These decreases, while clearly evident in the quartz system, were absent in that of cassiterite (Figures 188 and 189).

The pH range of the rapid Eh decreases in the ferrous chloride bearing quartz suspensions suggests they were related intimately to adsorption of hydrous ferric oxide species onto the mineral surface. Presumably, this adsorption left the bulk solution depleted in ferric species such that the potential became significantly lower. It was the redox reactions between the ferrous ion and the various ferric species of its oxidative hydroxylation that determined the solution potential. On the basis of the fundamental Nernst equation, a depletion of ferric species relative to ferrous species would have been expected to lower the bulk solution Eh.

The absence of similar pronounced Eh decreases associated with hydrous ferric oxide adsorption on cassiterite most probably was a consequence of the much lower solids concentrations used in these tests. Cassiterite
Electrophoresis suspensions were found experimentally to contain 0.458 g/litre solids while the solids concentration in the quartz suspensions was 1.63 g/litre. Increased substrate surface area presumably resulted in greater adsorption from bulk solution. An alternative, although somewhat less plausible explanation, is that the different forms of the Eh-pH curves reflected the fact that cassiterite was a semiconductor while quartz was not. Eh measurements in the cassiterite system, therefore, strictly might have been mixed potentials arising from both bulk solution and mineral-solution interfacial redox reactions. The manner in which such interfacial redox reactions could have influenced the measured Eh potentials is, however, one of conjecture.

4.5.1.4 Surface Charge of Cassiterite in Magnesium and Calcium Ion Solutions

Figures 193 and 194 show the effects of calcium and magnesium chloride on the electrokinetic properties of unleached cassiterite. All test suspensions were prepared according to a surface nucleation procedure. The slightly acidic nature of these suspensions confirmed that no significant hydrolysis of magnesium and calcium ions occurred during their preparation.

At the pH of preparation of the test suspensions, cassiterite electrophoretic mobilities were found to have decreased in magnitude relative to those in KCl electrolyte alone. However, they did not undergo charge sign reversal even at very high (> 1 x 10^-3 M) magnesium and calcium concentrations (Figures 193 and 194). When hydrochloric acid was added, the surface charge character remained less negative down to the cassiterite iep. Significantly, the iep of the cassiterite at pH 4.0 was unchanged over the entire range of magnesium and calcium chloride concentrations tested.
Figure 193 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in the Presence and Absence of Various Concentrations of MgCl$_2$.6(H$_2$O). The initial pH ($pH_\text{i}$) values of the cassiterite suspensions are shown in the figure. All suspensions were prepared according to a surface nucleation procedure.

Figure 194 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in the Presence and Absence of Various Concentrations of CaCl$_2$.2(H$_2$O). The initial pH ($pH_\text{i}$) values of the cassiterite suspensions are shown in the figure. All suspensions were prepared according to a surface nucleation procedure.
The addition of base to the magnesium and calcium bearing suspensions similarly produced electrophoretic mobilities that were initially negative in sign although of a reduced magnitude compared to those in only KCl electrolyte. At higher pH values above 9.0, charge reversals (negative to positive) were observed for magnesium chloride concentrations above $2.5 \times 10^{-4}$ M. The points of zero mobility associated with the charge reversals were at pH values of 10.7, 10.3 and 9.3 for magnesium chloride concentrations of $2.5 \times 10^{-4}$ M, $5 \times 10^{-4}$ M and $2 \times 10^{-3}$ M, respectively. In the case of calcium, a charge reversal occurred only at a very high ($3 \times 10^{-3}$ M) concentration. The associated point of zero electrophoretic mobility was at pH 10.9. Reference to Figures 19 through 21 indicates that the reversals in charge sign of the cassiterite occurred only in the pH region of stability of hydroxy magnesium and calcium species.

The electrophoretic mobility data of Figures 193 and 194 confirm conclusively that free aquo magnesium and calcium ions do not adsorb specifically inside the inner Helmholtz plane of the electrical double layer and cannot reverse the surface charge of cassiterite. The indifferent nature of these ions is evident further from the unchanged isoelectric point of cassiterite in magnesium and calcium chloride solutions. The reduced charge character at high concentrations of these ions, below pH 8.0, can be attributed to their non-specific adsorption and the associated compression of the electrical double layer. As for all previous analyses, the charge reversal effects at higher pH values are consistent with the adsorption of hydrous oxide sols of the cations.

The results of Figures 193 and 194 are consistent fully with a large body of data pertaining both to cassiterite and other mineral systems. It is well
established in all such systems that only extensively hydroxylated calcium and magnesium ions adsorb on mineral substrates (Figures 59 to 62). As such, adsorption occurs only in strongly alkaline solutions and hence outside the pH range of interest in cassiterite flotation. Under the slightly acidic conditions typical of cassiterite flotation pulps, the free aquo cations of these elements predominate in solution. These cations are indifferent and cannot cause charge reversal as shown both in this research and in previous publications by Gaudin and Sun (1946) and Raatz and Schubert (1971a) (Figures 56 and 57).

4.5.1.5 Surface Charge of Cassiterite in Bicarbonate Solutions

During the analyses of the Renison flotation pulps, low but not insignificant levels of carbonate species were detected (Table XX). Such species were considered unlikely to influence the surface properties of cassiterite but, for completeness, a series of cassiterite electrophoretic mobility measurements in the presence of potassium bicarbonate was made. As expected, the electrophoretic mobilities of the mineral were unaltered by such additions over the entire pH range from 2.5 to 11.0 (Figure 195).

According to the data of Garrels and Christ (1965), the dissociation constants of carbonic acid are $pK_1 = 6.4$ and $pK_2 = 10.3$. Therefore, at pH 10.3 the carbonate and bicarbonate ion concentrations are equal while the bicarbonate and carbonic acid concentrations are the same at pH 6.4 (Figure 22). The unchanged electrophoretic mobilities of cassiterite shown in Figure 195 indicate that carbonic acid and bicarbonate and carbonate ions were all indifferent with respect to cassiterite at concentrations of up to $5 \times 10^{-4}$ M.

Carbonato species are well known to act readily as ligands for magnesium and calcium ions in alkaline solutions (Figures 24 and 25). However, it was
found in this research that additions of up to $5 \times 10^{-6}$ M potassium bicarbonate to cassiterite suspensions containing magnesium and calcium chloride produced no discernable effect on the mineral electrophoretic mobilities (Figures 196 and 197). These mobilities were essentially the same as those in the cation solutions alone. In the pH range of interest in cassiterite flotation, carbonic acid and bicarbonate ions clearly exert no influence on the charge character of cassiterite. Carbonate ions further appear not to affect the charge character of adsorbing calcium and magnesium hydroxy species in strongly alkaline solutions.

Figure 195 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in the Presence and Absence of Various Concentrations of KHCO₃. Data points are shown for KHCO₃ concentrations of $5 \times 10^{-6}$ M and $5 \times 10^{-4}$ M. The solid line indicates the electrophoretic mobility in the absence of potassium bicarbonate.
Figure 196 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in the Presence and Absence of Both MgCl\(_2\).6(H\(_2\)O) and KHC\(_3\). Data are given for suspensions containing 5 x 10\(^{-4}\) M and 2 x 10\(^{-3}\) M MgCl\(_2\).6(H\(_2\)O) together with 5 x 10\(^{-4}\) M KHC\(_3\). The initial pH values of these two suspensions were 7.30 and 7.45, respectively. Also included in the figure are data for two suspensions containing 5 x 10\(^{-4}\) M and 2 x 10\(^{-3}\) M MgCl\(_2\).6(H\(_2\)O) (pH\(_4\) = 6.2 and 6.4, respectively) but no KHC\(_3\).

Figure 197 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in the Presence and Absence of Both CaCl\(_2\).2(H\(_2\)O) and KHC\(_3\). Data are given for suspensions containing 5 x 10\(^{-4}\) M and 3 x 10\(^{-3}\) M CaCl\(_2\).2(H\(_2\)O) together with 5 x 10\(^{-4}\) M KHC\(_3\). The initial pH values of these two suspensions were 7.2 and 7.4, respectively. Also included in the figure are data for two suspensions containing 5 x 10\(^{-4}\) M and 3 x 10\(^{-3}\) M CaCl\(_2\).2(H\(_2\)O) (both with pH\(_4\) = 6.2) but no KHC\(_3\).
4.5.1.6 Surface Charge of Cassiterite in Fluoride Solutions

Fluoride, added in its various forms (HF, Na$_2$SiF$_6$ and NaF), is used extensively as a modifying agent in cassiterite flotation (Sections 2.5.3.5 and 2.5.3.6). At low pH values, the fluoride ion is well known to form stable complexes with ferric iron (Figure 28). Electrokinetic studies performed in this research have established that profound changes in the surface charge of unleached Renison cassiterite can occur when sodium fluoride is added to acidic suspensions of the mineral.

Figure 198 shows the electrophoretic mobilities of unleached cassiterite particles in the presence and absence of sodium fluoride. The initial pH values of these suspensions are shown in the figure. These pH values were those immediately after addition of the fluoride and prior to any addition of acid or base. The immediate effect of the sodium fluoride was to increase slightly the pH of the suspensions indicating reduced hydronium ion concentrations in solution. At higher concentrations of the fluoride ion, a small but definite decrease in the electrophoretic mobility of the cassiterite was noted. This slightly more negative mineral charge character persisted at higher pH values when base was added. However, the difference, relative to the mobilities of unleached cassiterite particles in the absence of NaF, diminished with increasing pH.

The addition of hydrochloric acid to the fluoride ion bearing cassiterite suspensions resulted in an appreciably more negatively charged mineral character. Significantly, the point of zero electrophoretic mobility of the mineral moved to lower pH values in such solutions. The negatively charged fluoride ion clearly adsorbed specifically on the surface of unleached cassiterite. Such a finding is consistent with the strong affinity of the
anion in acidic solutions for both ferric ion species (Figure 28) and the stannic ion (Section 2.5.2). The tendency for cassiterite suspensions to become less acidic upon addition of fluoride ion further correlates with the Hingston, Posner and Quirk (1972) proposal that adsorption of fluoride ion on insoluble oxide minerals involves an ion exchange mechanism whereby the anion displaces coordinated surface hydroxyls.

Figure 198 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in the Presence and Absence of NaF. Data are given for NaF concentrations of $5 \times 10^{-5}$ M and $5 \times 10^{-4}$ M. The initial pH ($\mathrm{pH}_i$) values of all suspensions are shown in the figure.

The data of Figure 198 show some indication of a small decrease in the electrophoretic mobility of unleached cassiterite in the presence of $5 \times 10^{-5}$ M sodium fluoride when sufficient acid was added to lower the pH to 5.0. In initially acidified suspensions, such negative-to-positive charge reversals reached quite extraordinary levels.
In Figure 199, electrophoretic mobility data are given for unleached cassiterite suspensions that were acidified prior to sodium fluoride addition. At the initial pH levels of these suspensions, the cassiterite electrophoretic mobilities were significantly more negative than in the absence of NaF. However, increasing the pH produced a dramatic decrease in charge character and for $3 \times 10^{-4}$ M NaF, a charge reversal occurred such that between pH 4.5 and 6.5, the surface of the cassiterite was positively charged. Remarkably, with increasing concentrations of sodium fluoride, this charge reversal effect diminished. At high fluoride ion levels and pH values above 7.0, the electrophoretic mobilities of the cassiterite were more negative than in the absence of the fluoride. Similarly, in solutions more acidic than those at suspension preparation, the sodium fluoride significantly increased the negative charge character of the cassiterite. At concentrations above $3 \times 10^{-4}$ M, no isoelectric point was observed in measurements down to pH 2.5.

The interaction of the fluoride ion with unleached cassiterite in acidic solutions is complex. However, immediately apparent from the data of Figure 199 is that the fluoride ion specifically adsorbs very strongly onto the cassiterite in acidic solutions. This was evident from the marked changes in the pH of zero electrophoretic mobility of the mineral. Equally clear is that the changes produced by variations in the initial pH are not readily reversible. At identical sodium fluoride concentrations and final pH values, it was found possible for cassiterite electrophoretic mobilities in the slightly acidic range (pH 4.5 to 6.5) to be different both in magnitude and sign depending on the initial suspension pH (Figure 200). The implication from such data is that the interfacial chemistry and the form of the resulting electrophoretic mobility curves varied critically with the nature of the
species existing in solution at the time of preparation of the solutions.

Figure 199 - The Electrophoretic Mobilities of Unleached Cassiterite Particles in Initially Acidified Suspensions Containing NaF. Data are given for a range of NaF concentrations. The initial pH (pH±) values of all suspensions are shown in the figure. Included for comparison are the electrophoretic mobilities of the same cassiterite in the absence of the sodium fluoride.

The adsorption of a positively charged species on the cassiterite surface in the pH range 4.5 to 6.0, after sodium fluoride addition to acidic suspensions of the mineral, is a profound result. In this pH range, the cassiterite is normally negatively charged (Figure 118). Furthermore, the dissolution of sodium fluoride produces no product that can account for adsorption of a positively charged species on the cassiterite surface. This implies that the fluoride ion, under acidic conditions, interacted chemically with the unleached Renison cassiterite surface.
Figure 200 - The Effect of Initial pH on the Electrophoretic Mobilities of Unleached Cassiterite Particles in Suspensions Containing NaF. Data are given for an NaF concentration of $5 \times 10^{-4}$ M and initial suspension pH ($p_{H_4}$) values of 3.3 and 6.2. Included in the figure for comparison are the electrophoretic mobilities of the same cassiterite in the absence of sodium fluoride.

The thermodynamic data of Figure 28 show that fluoride can complex strongly with ferric ions under acidic conditions. At high Eh, ferric fluoro complexes are stable with respect to ferric hydroxy species up to pH values in the range 3.5 to 5.0, depending on the total ferric iron concentration in solution. Furthermore, it has been established (Sections 4.3.2.1 and 4.3.2.2) that ferric fluoro complexes are strongly solvated. As such, they would have little or no tendency to adsorb on mineral surfaces. Consequently, it is proposed that under acidic conditions the fluoride ion promotes the abstraction into solution of ferric iron present on the surface of unleached cassiterite. At pH values above 4.0, this ferric iron hydrolyzes and then re-adsorbs onto the cassiterite surface as positively charged hydrous ferric oxide sols. The conclusion that these sols are the positively charged species that adsorb on the surface of cassiterite in the pH range 3.5 to 7.0 is
supported by the observations that:

(1) the pH range of the charge reversals is characteristic of that of hydrous iron oxide species (Figures 178 and 180)

(2) an iron film is known to exist on the surface of unleached cassiterite (Sections 4.1.5 to 4.1.7)

(3) a similar charge reversal effect is barely discernable in the case of quartz (Figure 201) where it is known that iron is present at near negligible levels. The absence of a significant charge reversal effect in the quartz-sodium fluoride system indicates that the sodium fluoride itself is not responsible for charge reversal.

The proposed mechanism of fluoride interaction with unleached cassiterite is further strongly supported by previous findings from the ion solution chemical analyses (Section 4.3.2.2). In this research, it was established that adding fluoride to solutions of aged ferric hydroxy sols produced dramatic increases in the kinetics of solubilization of such sols when the pH was lowered (Figure 151). Furthermore, it has been shown that unleached Renison cassiterite, when leached in hydrochloric acid solution for 2 hours, exhibits charge reversal effects (Figure 121). The presence of the fluoride ion is not necessary specifically for charge reversal to occur. However, the fluoride ion clearly accelerates greatly the kinetics of solubilization of iron from the mineral surface and moves the pH of charge reversal to higher pH values. These findings strongly support the previous conclusions that the charge reversal species is a polymeric ferric hydroxy species, such as the hydrous oxide, and that ferric-fluoro complexes are strongly solvated and do not adsorb.
Figure 201 - The Electrophoretic Mobilities of Pure Quartz Particles in the Presence and Absence of NaF. Data are given for NaF concentrations of $3 \times 10^{-4}$ M and $3 \times 10^{-3}$ M. The initial pH ($pH_i$) values of all suspensions are shown in the figure.

The experimental finding that charge reversal effects occurred only when the unleached Renison cassiterite suspension was conditioned in the presence of fluoride below pH 4.0 and not above (Figure 200) can be interpreted readily on the basis of the proposed mechanism. It is clear that a necessary condition for charge reversal is the solubilization of the surface iron associated with the unleached cassiterite. Since this only occurs in acidic solution (Figure 114), the initial pH must be low to allow iron concentrations in solution to reach levels where hydroxylation at higher pH can produce measurable levels of hydrous ferric oxide sols. It is the re-adsorption of these sols at high pH values that causes the charge reversal. If the order of pH adjustment is reversed, no freshly precipitated hydrous ferric oxide sols
exist on the mineral surface in the slightly acidic range and no charge reversal occurs. While iron abstraction presumably proceeds when the pH is lowered subsequently, this solubilized iron is in the form of strongly solvated fluoro complexes and has no tendency to readsorb.

A striking feature of the data of Figure 199 is that the charge reversal effects associated with the sodium fluoride additions diminished with increasing concentrations of the fluoride reagent. There are a number of possible mechanisms which might explain this trend. The most plausible would appear to be:

1. increased levels of fluoride ions in solution gave rise to more stable iron fluoro complexes which reduced the extent of iron hydrolysis

2. the fluoride ion was incorporated into the structure of growing hydrous ferric oxide sols at higher pH values such that the sols were less negatively charged.

3. the iron available for abstraction from the cassiterite was finite. At higher fluoride ion concentrations, the increased specific adsorption of the negatively charged fluoride ion progressively offset the charge reversal effects of the positively charged hydrous iron oxide sols. The measured electrophoretic mobilities represented the overall surface charge and hence the net effect of specific adsorption of positively and negatively charged species.

On the basis of the electrophoretic mobility data alone, it is not possible to offer a definitive assessment of which of these mechanisms was
responsible primarily for the reduced charge reversal effects at the higher sodium fluoride concentrations.

In distinct contrast to the data obtained with unleached Renison cassiterite, the corresponding leached cassiterite did not exhibit charge reversal phenomena in the presence of sodium fluoride (Figure 202). Such a finding is considered to confirm unequivocally that the iron film on the unleached cassiterite surface was involved fundamentally in the reversal of charge sign of the unleached mineral. It has been established that the principal difference between the surface of leached and unleached cassiterite was the presence of an iron film on the latter (Sections 4.1.5 to 4.1.7).

![Figure 202 - The Electrophoretic Mobilities of Leached Cassiterite Particles in an Initially Acidified Suspension Containing 3 x 10^{-4} M NaF. Also included are data for leached and unleached cassiterite in the absence of NaF. The initial pH (pH_{i}) values of all suspensions are shown in the figure.](image-url)
The electrophoretic mobility data of leached cassiterite particles in an initially acidified suspension containing sodium fluoride (Figure 202) indicates clearly that the fluoride ion can adsorb specifically onto the cassiterite surface in the acidic range below pH 4.5. A distinct shift in the point of zero electrophoretic mobility of the leached cassiterite was found in this range. Given the very low level of surface iron contamination of unleached cassiterite (Figures 97 and 110 and Table XI) and the tendency for such iron to be solubilized at low pH, it is extremely unlikely that the shift in the cassiterite iep was due to interactions between fluoride anions and leached cassiterite surface iron.

The charge reversal effects of unleached Renison cassiterite were found to be reproduced remarkably by the addition of both ferric chloride and sodium fluoride to suspensions of the leached mineral (Figure 203). Significantly, increasing the fluoride to ferric ion ratio in such tests caused the magnitude of the charge reversal phenomena to decrease exactly as observed in the unleached cassiterite–fluoride ion case (Figure 199).

The data of Figure 203 compare strikingly to those of Figures 175 and 182 which show the electrokinetic behaviour of cassiterite and quartz in suspensions containing ferric chloride alone. In these electrokinetic studies without fluoride, appreciably more positively charged surface character occurred even in strongly acidic solutions (pH 2.0 - 4.0). This is in contrast to the results of Figure 203, where electrophoretic mobilities below pH 3.5 were invariably lower than in the absence of the fluoride and iron additions. Such differences cannot be attributed to initial pH variations as the suspensions containing high (5 x 10⁻⁴ M) ferric chloride additions in both Figures 175 and 182 were initially at pH 3.5. This pH represents almost the
mid-point of the initial pH values in Figure 203. Instead, the differences
serve to illustrate conclusively the ability of the fluoride ion to form
fluoro complexes with ferric iron under low pH conditions. These ferric
fluoro complexes clearly were solvated strongly and did not adsorb onto the
surface of cassiterite so as to increase the positive charge character of the
mineral in the strongly acidic pH range. The electrophoretic mobility
decreases at these low pH values were almost certainly due to specific
adsorption of the fluoride ion on the cassiterite surface.

Figure 203 - The Electrophoretic Mobilities of Leached Cassiterite Particles
in Initially Acidified Suspensions Containing \(1 \times 10^{-4}\) M FeCl₃
and Increasing Concentrations of NaF. The initial pH (\(pH_i\))
values of all suspensions are shown in the figure.
In Sections 4.1.7 and 4.5.1.2, it was established that mineral charge reversal effects associated with the adsorption of hydrous ferric oxide sols disappeared when the sample was dried. As such, iron films can exist on a mineral surface after drying but not be detected readily by microelectrophoresis measurements of the mineral in indifferent electrolyte alone. It is possible, therefore, that many minerals used by surface chemistry researchers and considered to be of high purity were not as pure as believed. As shown in this research, bulk assays of minerals can be misleading. Total iron levels of the unleached Renison cassiterite were relatively low (0.75%) but the iron was predominantly on the surface and exerted a profound influence on the mineral surface chemical properties. An important consequence of the fluoride ion research is, therefore, that such treatment can provide a rapid and sensitive test for the detection of iron films. If such surface contamination is present, initial acidification of the mineral suspension, followed by sodium fluoride addition and electrophoretic mobility measurements in the range pH 4.5 to 5.5, will result in the reappearance of the characteristic charge reversal effects of hydrous ferric oxide sols. For more soluble minerals, the test might not be definitive but its use for insoluble oxide minerals would appear general.

The fluoride ion is well known to form stable complexes with aluminum (Section 2.3.5). In a similar manner to ferric fluoro complexes, the fluoro complexes of aluminum predominate in solution only under acidic conditions. In weakly acidic or neutral conditions, the hydroxy species and hydrous oxides of aluminum are present at significantly higher concentrations (Figure 27). As expected, the actual pH of transition between the stability regions of the fluoro and hydroxy species of aluminum depends critically on the relative
concentrations of fluoride and aluminum present in solution (Figure 154).

In electrokinetic studies with stannic dioxide suspensions containing both aluminum chloride and sodium fluoride, it was found that pronounced charge reversal effects occurred (Figure 204). These changes in substrate charge character followed either one of two forms. The relative levels of fluoride to aluminum in the suspensions was identified as the factor that controlled which form of electrokinetic behaviour occurred. The principal influence of the ion ratio was to determine whether aluminum fluoro or hydrous oxide sols were the stable species at the pH of formation of the suspensions.

Figure 204 - The Electrophoretic Mobilities of 'Synthetic' Cassiterite Particles in Suspensions Containing 1 x 10^{-4} M AlCl_3.6(H_2O) and Increasing Concentrations of NaF. The initial pH (pH_i) values of all suspensions are shown in the figure. The 'synthetic' cassiterite was prepared from Aldrich "Gold Label" stannic oxide.
Reference to Figure 204 indicates that at low concentrations of sodium fluoride (≤ 1 x 10^{-4} M) the electrokinetic properties of the stannic dioxide were similar to those of unleached cassiterite in aluminum chloride bearing suspensions alone (Figure 173). Specifically, the lower pH (pH < 5.0) mobilities of the substrate showed clear evidence of the adsorption of positively charged hydrous oxide sols. Such changes in charge character strongly indicated that, at the pH of formation of the suspensions, appreciable levels of hydrous aluminum oxide sols were present. These species adsorbed onto the stannic dioxide and caused its charge character to change from negative to positive. Subsequent acidification of the suspensions at these low fluoride levels did not result in appreciable solubilization of the sols at least down to pH 2.0.

In contrast to the effects of low fluoride additions, concentrations of 3 x 10^{-4} M and 6 x 10^{-4} M NaF produced stannic dioxide electrophoretic mobility curves strikingly similar to those of initially acidified leached cassiterite suspensions containing ferric and fluoride ions (Figure 203). In particular, cassiterite electrophoretic mobilities below pH 4.5 were more negative in character than those in the absence of the aluminum and fluoride additions. However, at higher pH values strong positive charge reversals were noted (Figure 204). Significantly, the positive charge reversal with 3 x 10^{-4} M NaF was greater than at the higher concentration of 6 x 10^{-4} M.

It is evident from the data of Figure 204 that the ion solution chemistry at the pH of preparation of the high fluoride concentration suspensions was such that aluminum-fluoro complexes were the stable species. These complexes have been shown previously to be solvated strongly (Section 4.3.3) and consequently had little tendency to adsorb. The more negatively charged
character of the stannic dioxide below pH 4.5 was due almost certainly to the specific adsorption of the fluoride ion as was the case in the studies with leached cassiterite and sodium fluoride (Figure 202). The strong negative-to-positive charge reversals at pH values above those at suspension preparation were indicative undoubtedly of the onset of formation of hydrous aluminum oxide sols. These sols adsorbed strongly and produced the charge reversal effects. As for the unleached cassiterite case, three possible mechanisms exist that can explain the tendency for the charge reversal effects associated with sol adsorption to diminish with increasing fluoride concentrations. However, there is no information available on the basis of the electrokinetic data alone to test the relative validities of the proposed mechanisms.

Evidence of the changing solution chemical character of the stannic dioxide suspensions of Figure 204 with increases in fluoride ion concentration can be seen in the initial pH values of the suspensions (Figure 204). Stannic dioxide suspensions containing only indifferent electrolyte typically had a pH of 5.0. This was the pH of the distilled water used in the research. In the presence of $1 \times 10^{-4}$ M $\text{AlCl}_3\cdot6(\text{H}_2\text{O})$ and for NaF additions below $2 \times 10^{-4}$ M, the pH was slightly lower. This indicated consumption of hydroxyls and was consistent with the hydroxylation of the aluminum ion in such solutions. Conversely, the high fluoride ion concentration suspensions had pH values higher than that of the distilled water. These more alkaline solutions were indicative of an absence of aluminum ion hydrolysis. This supports the conclusion that aluminum fluoro complexes were the stable species initially present in these suspensions.

The significance of the results of Figure 204, in terms of cassiterite flotation surface chemistry, is that hydrous aluminum oxide sols adsorbed on
the surface of minerals would be expected to be solubilized extensively under conditions of high fluoride ion concentration and low pH. The manner of this solubilization essentially would be identical to that shown to be the case for hydrous ferric oxide sols.

4.5.2 X-ray Photoelectron Spectroscopy

A fundamental tenet of this research is that the iron films observed on the surface of Renison cassiterite were the result of previous adsorption of hydrous ferric oxide sols in the plant flotation environment. In the electrokinetic studies of Section 4.5.1, it was established that such sols adsorbed strongly on the surface of cassiterite. Furthermore, drying was shown to cause charge reversal phenomena related to hydrolyzed metal ion adsorption to disappear. This explained the absence of charge reversal effects associated with iron films on the cassiterite recovered from the Renison plant. The sample supplied from the mine was known to have been dried thermally. It also has been verified previously (Section 4.3.1) that sufficient iron existed in the Renison pulps for the proposed mechanism to be feasible and that the pH and Eh of the pulps were such that hydrous ferric oxide sols were thermodynamically stable species. As a final test of the hypothesis, a series of surface analyses of leached cassiterite exposed to solutions containing hydrous ferric oxide sols was performed. The X-ray photoelectron spectra of these samples were found to compare remarkably with those of the unleached cassiterite recovered from the Renison plant.

Contacting of leached cassiterite with ferrous chloride bearing solution was performed according to the procedure described in Section 3.6.2. Solution chemical conditions were manipulated to give Eh and pH values that correlated as closely as possible with those existing in the Renison circuit. During the
greater proportion of the 60 minute contacting period, the Eh was in the range 190 ± 25 mV (SHE) while the pH was relatively constant near pH 6.0 (Figure 205). Reference to the thermodynamic data of Figure 28 indicates that such Eh and pH values are just within the upper limit of the range considered typical of actual tin flotation pulps. They further represent solution chemical conditions where hydrous ferric oxide sols would be expected to form in solution in the absence of a mineral substrate.

![Graph showing the variation of suspension Eh with contacting time and pH during the preparation of the iron treated, leached cassiterite XPS sample.](image)

**Figure 205** - The Variation of Suspension Eh with Contacting Time and pH During the Preparation of the Iron Treated, Leached Cassiterite XPS Sample. The suspension was acidified initially to pH 3.8 prior to the addition of $1 \times 10^{-3}$ M FeCl$_2$.4(H$_2$O). Base (KOH) and acid (HCl) were added subsequently to maintain a pH near 6.0. Measured pH values are marked in parentheses in the figure.
In the X-ray photoelectron spectroscopic analyses of Section 4.1.5.2, it was shown that the XPS spectrum of Renison cassiterite was characterized by a very pronounced Fe (2p)\(3/2\) peak centered at a binding energy of 712.0 eV. The high binding energy of this peak indicated the iron to be in the ferric state and either hydrated or complexed with strongly electronegative hydroxyl ions. The experimental binding energy further correlated closely with a value of 711.9 eV reported by Koppelman and Dillard (1975) for amorphous hydrous ferric oxide. While the peak was very pronounced in the XPS spectrum of unleached cassiterite, it was just barely discernable in that of the same cassiterite after leaching (Figure 110).

In Figure 206, an XPS spectrum covering the binding energy range 707 to 726 eV is shown for leached cassiterite after contacting of the mineral with ferrous chloride solution. The spectrum embraces the binding energy range of both the Sn (3p)\(3/2\) peak of cassiterite and that due to Fe (2p)\(3/2\) electrons. Included in the figure are the corresponding XPS spectra of unleached and leached cassiterite prior to the test work. Comparison of the two leached cassiterite spectra shows conclusively that exposing the mineral to iron solutions of Eh and pH similar to those in the Renison plant results in the appearance of an iron (2p)\(3/2\) peak. Furthermore, this iron peak is of the same form and is centered at the same binding energy as that of the Fe (2p)\(3/2\) peak in unleached cassiterite. As such, it almost certainly corresponds to that of iron in hydrous ferric oxide sols.

X-ray photoelectron spectroscopy is not an in-situ technique. It is possible, therefore, that the form of the iron adsorbed on the leached cassiterite after exposure to the iron solution might have undergone oxidation or dehydration when the sample was removed from solution and dried under
vacuum. That significant such changes can occur has been demonstrated clearly in the profound effects of drying on the electrokinetic properties of cassiterite exposed to ferric chloride solutions (Figure 185). However, the remarkable correspondence of the binding energy of the surface iron analyzed to that of iron in hydrous ferric oxide is supportive strongly of the contention that this hydrous oxide was the adsorbing species.

![Graph showing XPS spectra](image)

Figure 206 - Tin (3p)$^{3/2}$ and Iron (2p)$^{3/2}$ XPS Spectra for Leached Cassiterite, Iron Treated Leached Cassiterite and Unleached Cassiterite.
In the electrokinetic studies of Section 4.5.1.6 it was shown that solubilization of the surface iron film of unleached Renison cassiterite occurred in low pH and high fluoride concentration solutions. Subsequent increases in pH produced negative-to-positive charge reversals in the electrophoretic mobilities of the mineral due to hydroxylation of the abstracted iron and readsorption of hydrous ferric oxide species. However, these charge reversal effects diminished with increasing concentrations of fluoride ion in solution (Figure 199). This indicated that the anion either altered the extent or nature of the ferric ion hydroxylation or itself adsorbed specifically onto the cassiterite surface in the slightly acidic (pH 4.5 to 5.5) range. To test the validity of these alternative hypotheses, suspensions of stannic dioxide and unleached cassiterite particles containing sodium fluoride were prepared. The suspensions were maintained at pH 3.3 for two hours and then partially neutralized to pH 5.5 by the addition of base (Figure 207). Substrate particles subsequently were recovered, repeatedly washed and analyzed by X-ray photoelectron spectroscopy (Section 3.6.2).

Figure 208 shows the 676 to 696 eV binding energy range XPS spectra of the sodium fluoride treated stannic dioxide and unleached cassiterite samples. In the spectrum of the unleached cassiterite, a strong peak was visible at a binding energy of 691.2 eV. This peak was not present in the mineral spectrum prior to sodium fluoride treatment (Figure 107). Remarkably, it also was absent for the stannic dioxide substrate treated in an identical manner to that of the unleached cassiterite.

Standard tabulations of electron binding energies, such as those of Riggs and Parker (1975), quote a binding energy of 686 eV for the (1s) \_1/2 peak of fluorine. The peak in the cassiterite XPS spectrum of Figure 208 is almost
certainly due to F (1s)_{1/2} electrons. However, its occurrence at a binding energy of 691.2 eV indicates that the chemical environment of the fluorine was such that a significant shift to higher binding energies occurred.

Figure 207 - The Variation of Suspension Eh with Contacting Time and pH during the Preparation of the Unleached Cassiterite and Aldrich "Gold Label" Stannic Dioxide XPS Samples. Both suspensions were acidified to pH 3.3 prior to the addition of 5 x 10^{-4} M NaF. Base (KOH) and acid (HCl) were added subsequently to maintain the pH at 3.3. After 2 hours, the suspension was partially neutralised to pH 5.5 with KOH. Measured pH values are marked in parentheses in the figure.
Figure 208 - Fluorine \((1s)_{1/2}\) XPS Spectra for NaF Treated Unleached Cassiterite, NaF Treated Stannic Dioxide, Sodium Fluoride (NaF) and Ferric Fluoride (FeF\(_3\)). Binding energies of the F \((1s)_{1/2}\) peaks in each spectrum are marked in the figure.
The complete absence of any fluorine peak in the XPS spectrum of stannic dioxide is significant in that it suggests there was no measurable adsorption of fluoride ion onto this substrate under the conditions of contracting. There is consequently no evidence to indicate that fluoride interacted with the exposed surface of cassiterite under similar conditions. However, it is possible that fluoride ions were associated with the hydrous ferric oxide species that redesorbed onto the unleached cassiterite surface. Given the strong electronegativity of the fluoride ion (Pauling, 1948) and its affinity for the ferric ion, it would not totally be unexpected that the anion would be incorporated into the structure of such sols. It is well known that certain chelating agents, which form strongly bonded complexes with ferric ions, can occupy many of the coordination sites in polymeric hydrous ferric oxides (Gustafson and Martell, 1963; Aasa et al, 1964; Spiro, Bates and Saltman, 1967; Schugar et al, 1967).

A feature of the NaF treated unleached cassiterite F (1s)\textsuperscript{1/2} peak in Figure 208 is its high binding energy. Whether fluoride coordinated into the structure of hydrous ferric oxide sols would have such a high binding energy is a matter of conjecture. Unfortunately, no reference XPS data exist for fluorine in such species. However, XPS analyses of a high purity ferric fluoride reagent performed in this research indicated the fluorine (1s)\textsuperscript{1/2} peak of coordinated fluoride in this compound to have a binding energy of only 685.6 eV (Figure 208). This confirmed that the fluoride associated with the unleached cassiterite was not in the form of a lower order ferric fluoro complex such as FeF\textsubscript{3}.

An alternative explanation for the existence of a fluorine peak in the unleached cassiterite spectrum is that residual fluoride species remained in
solution after washing of the mineral. Any fluoride species not removed during washing would have been expected to have re-deposited on the mineral surface during vacuum drying. However, there is no apparent reason why an identical washing procedure should have been efficient in removing residual fluoride in the case of stannic dioxide but not for unleached cassiterite. Furthermore, it can be confirmed unequivocally that the unleached cassiterite fluorine peak in Figure 208 is not that of the fluorine ion in sodium fluoride. The F (1s)_{1/2} electrons of the NaF used in the research were found to have a binding energy of 688.5 eV (Figure 208). This was 2.7 eV below that of the peak in the NaF treated unleached cassiterite spectrum.

In agreement with the conclusion that fluoride was not bonded to cassiterite or stannic dioxide surface stannic ions, no significant shifts in the XPS tin (3d)_{3/2} and (3d)_{5/2} peaks of these substrates after contacting with sodium fluoride were found. XPS spectra of the 480 to 500 eV binding energy range showed small variation in the positions of these two strongest tin peaks (Figure 209) but none that could be considered experimentally significant. Given that the electronegativity of fluorine is higher than that of oxygen (Pauling, 1948), it might have been expected that coordination of fluoride ions to stannic ions on the exposed surface of cassiterite or stannic dioxide would have produced higher Sn (3d) core electron binding energies. It is well known that strongly electronegative atoms withdraw electron density from the valence and bonding orbitals of atoms, thereby reducing the screening of the core electrons from the nuclear charge and increasing their binding energy (Riggs and Parker, 1975). The absence of any observable such shifts in the spectra of Figure 209 is supportive of the conclusion that no significant fluoride ion adsorption occurred under the conditions of contacting of the two
tin oxide substrates with fluoride ions. It therefore appears highly unlikely that the diminished charge reversal effects found in Figures 199 and 203 at higher fluoride ion concentrations can be attributed to increased specific adsorption of negatively charged fluoride ion offsetting the charge reversal effects of the positively charged hydrous ferric oxide sols.

Figure 209 - Tin (3d)_{3/2} and (3d)_{5/2} XPS Spectra. Curve A, NaF treated unleached cassiterite. Curve B, NaF treated stannic dioxide. Curve C, unleached cassiterite not subjected to NaF treatment. Binding energies of the Sn peaks in each spectrum are marked in the figure.
Examination of the other characteristic peaks in the stannic dioxide and unleached cassiterite spectra similarly indicated no changes in peak binding energies after fluoride ion treatment. As expected, the oxygen \((1s)_{1/2}\) spectra were completely unchanged (Figure 210). In the case of the unleached cassiterite, no observable change existed in the Sn \((3p)_{3/2}\) and Fe \((2p)_{1/2}\) spectral region (Figure 211). It might have been expected that bonding of fluorine to ferric ions in hydrous ferric oxide sols would have produced changes in the binding energy of these Fe \((2p)_{3/2}\) electrons.

Figure 210 - Oxygen \((1s)_{1/2}\) XPS Spectra. Curve A, NaF treated unleached cassiterite. Curve B, NaF treated stannic dioxide. Curve C, unleached cassiterite not subjected to NaF treatment. Curve D, stannic dioxide not subjected to NaF treatment.
Figure 211 - Tin (3p)\textsubscript{3/2} and Iron (2p)\textsubscript{3/2} XPS Spectra. Curve A, NaF treated unleached cassiterite. Curve B, unleached cassiterite not subjected to NaF treatment. Curve C, ferric fluoride (FeF\textsubscript{3}). Binding energies of peaks in each spectrum are marked in the figure.

The inability to detect spectral differences in the Fe (2p)\textsubscript{3/2} binding energy range of unleached cassiterite after contacting with fluoride ions cannot be considered as definitive evidence against the presence of fluoride ion in the structure of adsorbed hydrous ferric oxide sols. As discussed in depth previously (Section 4.1.5.2), Fe (2p)\textsubscript{3/2} electrons invariably exhibit broad peaks due to multiplet splitting and shake-up phenomena. Furthermore, in the case of unleached cassiterite, the Fe (2p)\textsubscript{3/2} peak overlaps appreciably with the broad Sn (3p)\textsubscript{3/2} peak. Given the limited resolving power of the Varian IEE-15 spectrometer and the broad and overlapping nature of the Sn
(3p)_{3/2} and Fe (2p)_{3/2} peaks, it is possible that spectral changes could have occurred but not been detected. This is particularly the case since any bonding to the highly electronegative fluorine would almost certainly have increased the binding energy of Fe (2p)_{3/2} electrons and hence caused greater overlap with the Sn (3p)_{3/2} peak. This is shown clearly in Figure 211 for the case of ferric fluoride. The Fe(2p)_{3/2} peak of this reagent was found to have a binding energy of 715.5 eV and consequently would have overlapped appreciably with the broad Sn(3p)_{3/2} peak of cassiterite. These Sn (3p)_{3/2} electrons characteristically produced a peak centered at a binding energy near 716.5 eV.

The form of the cassiterite electrophoretic mobility curves in Figures 199 and 203 indicated clearly that increasing levels of fluoride in solution fundamentally altered the nature of the charge reversal effects associated with adsorption of hydrous ferric oxide sols. The XPS analyses suggest that these changes were related to the nature of the ferric ion hydrolysis species themselves rather than to an interaction between the fluoride ion and the cassiterite surface. The possibilities therefore exist that high levels of fluoride either gave rise to more stable iron fluoro complexes which reduced the extent of iron hydroxylation or resulted in fluoride ions being incorporated into the structure of the adsorbing hydrous ferric oxide sols such that they were less negatively charged. The presence of the fluorine peak in the spectrum of unleached cassiterite after fluoride treatment is strongly supportive of the latter hypothesis. However, no unequivocal conclusion can be reached since no reference binding energy data exist for fluorine in such sols and no definitive evidence was found for associated Fe (2p)_{3/2} electron binding energy changes.
4.5.3 Leaching Tests

In the solution chemical analyses of Section 4.3.2.2, it was established that the addition of fluoride ions to solutions of aged ferric and aluminum hydroxy sols produced dramatic increases in the kinetics of solubilization of such sols at low pH (Figures 151 and 155). During the course of the electrokinetic studies, considerable evidence was obtained that acidic fluoride solutions strongly promoted the resolubilization of the surface iron film associated with unleached Renison cassiterite. Direct confirmation that this latter effect was general for all surface impurities of the unleached cassiterite was sought and obtained in a series of leaching tests that paralleled those performed in the mineral characterization studies of Section 4.1.6.

Figures 212 to 214 show the extent of dissolution of metal ionic species from Renison cassiterite in the presence and absence of sodium fluoride after 14 days of leaching. The data are considered to represent equilibrium conditions as no detectable changes in ion concentrations were observed at longer time periods.

The solution chemical analyses of Figures 212 to 214 indicate that, irrespective of the presence of sodium fluoride, extraction of iron, aluminum, magnesium and calcium was negligible above pH 5.0. However, below this pH value, abstraction increased rapidly with decreasing pH. In these more strongly acidic solutions, the levels of solubilized iron were typically an order of magnitude greater than those of other metals. This was consistent with iron being the principal contaminant of the cassiterite surface.
Figure 212 - The pH Dependence of Iron Abstraction from Renison Cassiterite (milligrams Fe/gram cassiterite) in the Presence and Absence of $6 \times 10^{-4}$ M NaF. Leaching time = 14 days.

Figure 213 - The pH Dependence of Aluminum Abstraction from Renison Cassiterite (milligrams Al/gram cassiterite) in the Presence and Absence of $6 \times 10^{-4}$ M NaF. Leaching time = 14 days.
The presence of sodium fluoride during leaching in the more acidic solutions increased significantly the extent of abstraction of all impurity metal ions from the Renison cassiterite. This effect was most pronounced for iron and aluminum. Such a result is consistent with the strong tendency for the fluoride ion to form complexes with ferric and aluminum cations at low pH (Section 2.3.5). Increased solubilization of these species presumably was due to the formation of the strongly solvated fluoro complexes of these metal ions.

With respect to abstraction kinetics, the presence of fluoride ions in solution greatly increased the rate of dissolution of iron from the surface of the Renison cassiterite (Figure 215). In leaching tests at pH 3.5, soluble iron levels were below the detection limit of 1 ppm for time periods of less
than 60 minutes in the absence of fluoride reagents. In contrast, iron levels of over 10 ppm were detected in solution in less than 10 minutes when $6 \times 10^{-4}$ M sodium fluoride was present in solution. Iron dissolution kinetics of the order indicated in the low pH fluoride leaching tests are clearly of significance in terms of the time periods characteristic of flotation processes.

Figure 215 - Kinetics of Iron Abstraction from Renison Cassiterite at pH 3.5 in the Presence and Absence of $6 \times 10^{-4}$ M NaF.
4.5.4 **Principal Findings and Conclusions**

(1) Positively charged aluminum and ferric iron species adsorb strongly on the surface of cassiterite under the pH and Eh conditions that prevail in cassiterite flotation. In microelectrophoresis studies, a series of characteristic charge reversals is associated with the adsorption of such species.

(2) All of the electrokinetic and solution chemical data of this research are consistent with the hydrous oxide sols of metal ions being the adsorbing species that cause charge reversal. This is in agreement with the proposals of the James and Healy model.

(3) The adsorption of hydrous ferric oxide sols onto the cassiterite surface, under solution chemical conditions known to exist in the Renison plant, is strongly supportive of the hypothesis that the aqueous pulps of the concentrator were the source of the observed iron films on this cassiterite.

(4) The form of the charge reversal effects accompanying adsorption of hydrous metal oxide sols on cassiterite and quartz conform to those of the James and Healy model when suspensions are prepared according to a surface nucleation procedure. Distinctly different electrophoretic mobility curves can be obtained for iron bearing suspensions prepared according to a surface condensation (type II) procedure. These differences reflect the very slow kinetics of
resolubilization of adsorbed hydrous ferric oxide sols even in highly acidic solutions.

(5) Evidence was found in surface nucleation electrokinetic studies with cassiterite and quartz suspensions containing ferrous chloride that onset of charge reversal initiated at slightly lower pH values than would have been predicted for hydrous ferric oxide formation on the basis of known thermodynamic data. Such a finding supports the hypothesis that adsorption of hydrous ferric oxide on mineral surfaces occurs at pH values slightly below that necessary for bulk precipitation as proposed in the James and Healy model.

(6) Thermal drying can remove completely the characteristic charge reversal effects of hydrous metal oxide adsorption on minerals. The most plausible explanation of such an effect is that drying reduces the degree of hydration of these adsorbed sols. It is the coordinated and chemisorbed water molecules and hydroxyl groups of such sols that produce their charge character.

(7) The ability of drying to cause the disappearance of charge reversal effects associated with the adsorption of hydrous metal oxides represents key evidence supporting the fundamental tenet of this research that the surface iron film on Renison cassiterite was the result of previous adsorption of hydrous ferric oxide sols from the plant pulps. As supplied from Renison, the cassiterite sample was known to have been dried thermally. The absence of any
charge reversal character associated with Renison cassiterite iron films, therefore, is consistent totally with the adsorption of such sols prior to sample drying.

(8) The changes in adsorbed sol charge character produced by drying are not reversible. Once removed by drying, the characteristic charge reversal phenomena associated with the adsorption of freshly precipitated hydrous metal oxide sols are not re-established on subsequent exposure of the dried substrate to an aqueous environment.

(9) The X-ray photoelectron spectrum of leached cassiterite exposed to a solution containing hydrous ferric oxide sols, under Eh and pH conditions closely approaching those in the Renison circuit, was found to be similar remarkably to that of unleached cassiterite recovered from the plant. Specifically, exposure to such a solution resulted in the appearance of an iron \( (2p)_{3/2} \) peak of the same form and centered at the same binding energy as that of the Fe \( (2p)_{3/2} \) peak in unleached Renison cassiterite. Prior to solution contracting, this peak was barely discernable in the leached cassiterite spectrum.

The binding energy of the Fe\( (2p)_{3/2} \) peak indicated that it almost certainly was that of iron in hydrous ferric oxide sols. While X-ray photoelectron spectroscopy is not an in-situ technique, such a finding is supportive strongly of the contention that this hydrous oxide was the specifically adsorbing species.
(10) The free aquo ions of aluminum, magnesium, calcium and ferric and ferrous iron do not adsorb specifically on the surface of cassiterite.

(11) Carbonic acid and bicarbonate and carbonate ions are all indifferent with respect to cassiterite at least up to concentrations of $5 \times 10^{-4}$ M. The presence of similar levels of carbonate species in cassiterite suspensions containing magnesium and calcium chloride further fails to produce discernable effects on mineral electrophoretic mobilities.

(12) The fluoride ion adsorbs specifically on the surface of leached cassiterite in strongly acidic solutions below pH 4.0. Associated solution pH changes are consistent with the Hingston, Posner and Quirk proposal that adsorption of fluoride ion on insoluble oxide minerals involves an ion exchange mechanism whereby the anion displaces coordinated surface hydroxyls.

(13) The addition of sodium fluoride to strongly acidic (pH < 4.0) suspensions of unleached Renison cassiterite results in the appearance of striking negative-to-positive charge reversals in the range pH 4.5 to 6.5 when base subsequently is added. All aspects of these charge reversal effects are consistent with the solubilization of the iron film associated with the unleached cassiterite surface under acidic conditions followed by re-adsorption of freshly precipitated hydrous ferric oxide sols at higher pH values.
In accord with the electrokinetic data, leaching tests confirm independently that the presence of fluoride in acidic suspensions enhances significantly the kinetics of solubilization of contaminant surface iron from unleached cassiterite.

(14) The negative-to-positive charge reversal effects associated with sodium fluoride additions to acidic unleached cassiterite suspensions were found to diminish with increasing concentrations of the fluoride reagent. XPS analyses of the mineral substrate after such charge reversal indicated this decrease to be related directly to the nature of the ferric ion hydrolysis species rather than to interactions between the fluoride ion and the cassiterite surface. The presence of a strong fluorine peak in the XPS spectrum of unleached cassiterite after fluoride treatment, but not in the spectrum of similarly treated stannic dioxide, further was supportive strongly of the hypothesis that fluoride ions were incorporated into the structure of the adsorbing hydrous ferric oxides. This presumably reduced their charge character. However, interpretation of the XPS results cannot be considered definitive due to the absence of reference binding energy data for fluorine in hydrous oxide sols and an inability to detect associated Fe (2p)\(^{3/2}\) electron binding energy changes.

(15) Additions of sodium fluoride to strongly acidic suspensions of leached Renison cassiterite, followed by subsequent
increases in pH, did not produce negative-to-positive charge reversals as observed for unleached cassiterite. However, such charge reversal phenomena could be reproduced remarkably by suitable additions of both ferric chloride and sodium fluoride to leached cassiterite suspensions. This finding confirmed unequivocally that the surface iron film of unleached cassiterite was responsible for the charge reversal effects of the mineral in the moderate to slightly acidic range pH 4.5 to 6.5.

(16) Electrokinetic studies with stannic dioxide suspensions containing aluminum chloride and sodium fluoride indicate strongly that hydrous aluminum oxide sols adsorbed on the surface of minerals would be solubilized extensively under conditions of high fluoride ion concentration and low pH. The manner of this solubilization essentially would be identical to that for hydrous ferric oxide sols.

(17) The fluoro complexes of the aluminum and ferric ions are strongly solvated and have no tendency to adsorb on mineral surfaces.

(18) The addition of fluoride ions to acidic suspensions of minerals, with subsequent electrophoretic mobility measurements at higher pH values, provides a rapid and sensitive test for the detection of iron films on the surface of insoluble minerals. If surface contamination is present, such treatment results in the re-appearance of the characteristic charge reversal effects of hydrous ferric
(19) The presence of sodium fluoride during acid leaching of Renison cassiterite significantly increases the extent of solubilization of aluminum, iron, magnesium and calcium surface impurities from the mineral. The effect is most marked for aluminum and iron which form particularly strong complexes with the fluoride ion.
4.6 Surfactant – Ion Interactions

It has been presupposed, in much of the cassiterite flotation literature, that phosphonic acids interact and form insoluble precipitates with many cations. Ferric ions, in particular, have been reported frequently as precipitating phosphonic acids (Collins and Jackson, 1967; Anon, 1981; Iriarte, 1985). Calcium ions also have been reported as interacting but much less strongly than ferric ions (Collins, 1967; Wottgen and Topfer, 1976; Iriarte, 1985). Despite the importance in cassiterite flotation of such effects, no noteworthy studies pertaining directly to the interactions of phosphonic acids with cations of interest in flotation have been published (Section 2.2.4). Conclusions regarding the ability, or otherwise, of certain cations to precipitate phosphonic acids invariably have been reached by implication from other flotation related research (Section 2.5.3.1). Furthermore, in these studies distinctions rarely have been made between interactions with the free ions of metals and their corresponding hydroxy and hydrous oxide species.

In this research, direct evidence that styryl phosphonic acid formed insoluble complexes with the aquo metal ions and hydroxy metal ionic species typically present in cassiterite flotation pulps was sought in light scattering measurements. The measurement of light scattered from an incident beam focused on a solution is an extremely sensitive technique for the detection of insoluble precipitates in the solution.

4.6.1 Aluminum Solutions

Figure 216 shows the light scattering behaviour of aluminum chloride solutions as a function of concentration at pH 5.0. At low concentrations of this reagent, solution turbidities were essentially those of distilled water.
However, above a concentration of $1 \times 10^{-4}$ M, turbidities increased dramatically. This rapid increase in turbidity undoubtedly reflected the onset of formation of appreciable levels of aluminum polycationic and hydrous oxide species in solution. Reference to the thermodynamic data of Figure 12 indicates that a $2 \times 10^{-4}$ M aluminum chloride solution is oversaturated with respect to hydrous aluminum oxide at pH 5.0. As such, precipitation of aluminum polycations and hydrous oxide sols would be appreciable at this and higher concentrations.

Figure 216 - Turbidities of Aluminum Chloride Solutions as a Function of Concentration at pH 5.0 in the Presence and Absence of $1 \times 10^{-4}$ M Styryl Phosphonic Acid (SPA). The dashed line indicates the measured turbidity of the styryl phosphonic acid in distilled water alone.

In the surfactant light scattering studies of Section 4.2.7, solutions of $1 \times 10^{-4}$ M styryl phosphonic acid were found to have low turbidities of the order of $1 \times 10^{-4}$ over the entire pH range from pH 1.0 to 10.0 (Figure 142). However, when the equivalent of $1 \times 10^{-4}$ M styryl phosphonic acid was added to
solutions containing aluminum chloride at concentrations higher than $4 \times 10^{-5}$ M, the measured turbidities exceeded those of either component alone (Figure 216). This finding confirmed directly that aluminum polycationic and hydrous oxide species present in high concentration aluminum solutions at pH 5.0 interacted with styryl phosphonic acid to form insoluble precipitates.

In Figure 217, data indicating the pH dependence of aluminum solution turbidities in the presence and absence of $1 \times 10^{-4}$ M styryl phosphonic acid are given. The initial pH values of the respective stock solutions are marked in the figure.

As prepared, the $1 \times 10^{-4}$ M aluminum chloride solution containing no phosphonic acid was moderately acidic in character with a pH of 4.65. The lack of measurable turbidity indicated this solution not to contain appreciable levels of aluminum sols. The stable species in solution were presumably the lower order hydroxy species of the aluminum ion and the free aquo aluminum ion itself (Figure 12). It has been established previously (Section 4.3.3) that these aluminum species are strongly solvated and have little tendency to polymerize. As such, they do not give rise to measurable solution turbidities.

Lowering the pH of the surfactant free aluminum chloride solution resulted in no detectable turbidity change. In contrast, the addition of base produced a sharp turbidity increase above pH 5.0. On the basis of the thermodynamic data of Appendix B, it would be expected that a $1 \times 10^{-4}$ M aluminum chloride solution would become supersaturated with respect to hydrous aluminum oxide at pH 4.6. The turbidity increase in Figure 217 was, therefore, clearly due to the formation of appreciable levels of such sols in solution.
The addition of the equivalent of $1 \times 10^{-4}$ M styryl phosphonic acid produced a significant decrease in the pH of the aluminum solution and a marked increase in turbidity. The latter solution change confirmed that styryl phosphonic acid interacted with either the free ion or the lower order hydroxy species of aluminum to form insoluble precipitates. The persistence of these high turbidities at lower pH values further indicated that the complexes were not dissociated in acidic solutions down to pH 2.0. Consistent with the data of Figure 216, solution turbidities increased appreciably in the less acidic range above pH 5.0 where polymeric aluminum species would have been stable thermodynamically in the absence of the surfactant. This again verified that a strong interaction existed between styryl phosphonic acid and hydrous aluminum oxide sols.
As established in the solution chemical analyses of Section 4.3.3, the presence of fluoride ions in acidic solutions of aluminum chloride suppresses the onset of hydrous aluminum oxide formation. In light scattering measurements of $1 \times 10^{-6}$ M aluminum chloride solutions containing $6 \times 10^{-6}$ M NaF, no measurable turbidity was found below pH 6.5 (Figure 218). The same concentration aluminum solution containing no fluoride exhibited a sharp rise in turbidity at pH 5.0 (Figure 217). Such a solution chemical change was consistent with the well established ability of the fluoride ion to form stable fluoro complexes with aluminum in acidic solutions. The fluoro complexes of aluminum ions that predominate in low pH solution have been shown consistently in this report to be solvated very strongly (Sections 4.3.3, 4.5.1.6 and 4.5.3).

![Figure 218 - The pH Dependence of the Turbidities of Solutions Containing both $1 \times 10^{-4}$ M AlCl$_3$.6(H$_2$O) and $6 \times 10^{-6}$ M NaF in the Presence and Absence of $1 \times 10^{-4}$ M Styryl Phosphonic Acid. The dashed line indicates the measured turbidity of styryl phosphonic acid in distilled water alone.](image-url)
In Figure 217, it was established that styryl phosphonic acid addition to an aluminum chloride solution, in which the free ion and lower order hydroxy species were the predominant species, produced a significant turbidity increase. In contrast, no turbidity increase was found when an equivalent surfactant addition was made to the same concentration aluminum solution containing fluoride (Figure 218). In the presence of the fluoride, light scattering indicated a low turbidity, equivalent essentially to that of the styryl phosphonic acid solution alone. The turbidity remained unchanged when the solution was acidified. At higher pH values, turbidities were essentially those of aluminum solutions containing fluoride and no surfactant. Such data are considered to indicate conclusively that styryl phosphonic acid does not form insoluble precipitates with aluminum fluoro complexes. The obvious further implication is that the ability of phosphonic acids to form complexes with aluminum ions is not as strong as that of fluoride ions. It is well known that aluminum fluoro complexes are particularly stable in acidic solutions (Section 2.3.5).

4.6.2 Iron Solutions

In a manner analogous to that in the aluminum system, ferric chloride solutions at pH 5.0 were found to have low turbidities at dilute concentrations but to possess very high turbidities at more concentrated levels. As shown in Figure 219, a concentration of $1 \times 10^{-5}$ M was found to represent the point above which turbidities of ferric chloride suspensions increased appreciably. Consistent with the tendency of ferric iron to hydrolyze and form hydrous oxide sols at lower pH values, this concentration was an order of magnitude below that observed in the aluminum system.
It is evident from the data of Figure 219 that ferric chloride solutions possessed measurable turbidities at pH 5.0 down to concentrations below $1 \times 10^{-6} \text{M}$. The distilled water used for all solution preparations typically had a turbidity of $4 \times 10^{-5}$. This was markedly lower than the $1.3 \times 10^{-4}$ level found for the $1 \times 10^{-6}$ ferric chloride solution. Such experimental findings correlate with published thermodynamic data for the ferric iron system. Reference to the equilibrium diagram of Figure 16 indicates that, at pH 5.0, ferric iron solutions are supersaturated with respect to hydrous ferric oxide at concentrations above approximately $1 \times 10^{-8} \text{M}$.

During the course of styryl phosphonic acid adsorption, electrokinetic and microflotation studies conducted in this research with unleached cassiterite
(Sections 4.4.1.2, 4.4.2.2 and 4.3.2.2), clear evidence was found that the surfactant interacted very strongly with iron species over a broad pH range. The data of Figure 219 confirm directly that hydrous ferric oxide sols interact with styryl phosphonic acid at pH 5.0. At this pH, very pronounced turbidity increases were found when the equivalent of $1 \times 10^{-6}$ M styryl phosphonic acid was added to ferric chloride solutions of concentration above $1 \times 10^{-6}$ M. These turbidities exceeded significantly those of either component alone.

The interaction between hydrous ferric oxide species and phosphonic acids is clearly particularly strong. This is evident from the marked increases in solution turbidity found at ferric chloride concentrations as low as $2 \times 10^{-5}$ M when the phosphonic acid was added. Such a strong interaction is consistent with the microflotation data of Figure 168. In these studies, it was established that iron present on the surface of unleached cassiterite was able to cause a strong flotation activation effect in the slightly acidic to alkaline range above pH 4.0.

In Figure 220, the pH dependence of ferric chloride solution turbidities in the presence and absence of styryl phosphonic acid is shown. Data are given for ferric solutions prepared according to two different procedures. Details of these two methods of preparation have been discussed previously in Section 3.7.1. Initial pH values of all the stock solutions are marked in the figure.

Light scattering measurements of a $1 \times 10^{-4}$ M ferric chloride solution prepared at pH 3.8 indicated the solution to have appreciable turbidity in the absence of surfactant. This clearly indicated that extensive polymerization of ferric species had occurred at this pH. Supersaturation with respect to
hydrous ferric oxide also would have been expected in a $1 \times 10^{-4}$ M ferric chloride solution at pH 3.8 on the basis of known thermodynamic data (Figure 16).

![Figure 220](image)

**Figure 220** – The pH Dependence of $1 \times 10^{-4}$ M FeCl$_3$ Solution Turbidities in the Presence and Absence of $1 \times 10^{-4}$ M Styryl Phosphonic Acid. Data are given for solution initial pH values of (a) pH$_4$ = 1.0 and (b) pH$_4$ = 3.8. The dashed line indicates the measured turbidity of styryl phosphonic acid in distilled water alone.

In the absence of styryl phosphonic acid, decreasing the pH of the ferric solution from pH 3.8 produced lower solution turbidities presumably indicating some sol depolymerization. However, these turbidities were considerably larger than those of ferric solutions at the same final pH but initially strongly acidified (pH = 1.0). In this latter case, the free aquo ferric ion was the predominant ferric species initially in solution (Figures 16 and 17). This finding was consistent with the previously established slow kinetics of
hydrous ferric oxide depolymerization (Section 4.3.2). Increasing the pH above the initial value of 3.8 resulted in higher solution turbidities. At pH values above 6.0, some time dependent fluctuations in light scattering were observed. These are believed to have reflected the complex nature of the growth of hydrous ferric oxide sols in the presence of increasing hydroxyl ion concentrations.

Measured turbidities of initially acidified ferric solutions (Figure 220) were found to be essentially those of distilled water up to approximately pH 4.0. Above pH 4.0, turbidities increased appreciably and, by pH 6.0, were not measurably different from those of ferric solutions initially prepared at pH 3.8 and upwardly pH adjusted. The sharp increase in turbidity at pH 4.0 undoubtedly reflected the onset of extensive ferric hydroxy species polymerization and hydrous oxide formation.

The addition of styryl phosphonic acid to solutions containing polymeric hydroxy sols produced profound increases in turbidities below pH 6.0. In this acidic pH range, turbidities of iron-surfactant solutions prepared at pH 3.8 were almost an order of magnitude greater than those of the corresponding component systems (Figure 220). This confirmed that significant interaction between polymeric ferric hydroxy species and phosphonic acids occurred over the entire pH range of interest in cassiterite flotation. Such a result provides independent confirmation of the plausibility of the mechanism whereby a surface iron film on cassiterite can produce an activating or depressant effect on phosphonic acid adsorption, dependent on the pH influenced extent of its solubilization. This mechanism was found previously to explain all aspects of the observed differences between the microflotation response of cassiterite before and after leaching of the mineral (Section 4.4.3.2).
When neutralized to above pH 6.0, the ferric chloride-surfactant solution prepared at pH 3.8 possessed turbidities that approached those of the corresponding ferric chloride solution alone. As shown in Figure 220, the tendency for the turbidities to approach similar values was the result of both decreases in the turbidity of the combined system and an increase in the ferric chloride solution turbidity. The existence of these opposing trends, in the same pH region, is an intriguing phenomenon. However, on the basis of light scattering measurements alone it is not possible to attempt a fundamental interpretation. In solutions containing sols, the degree of light scattered is a complex function of sol size, size distribution, shape and concentration in solution. Changes in any one of these parameters might have caused the opposing trends in the turbidity data.

The light scattering results of Figure 220 confirmed that styryl phosphonic acid also interacted strongly with lower order ferric hydroxy species such as Fe(OH)$_2^+$, Fe(OH)$_3^+$, et cetera. In ferric solutions where these species predominated (lower pH ferric chloride solutions upwardly pH adjusted to between pH 2.0 and 4.0), the addition of styryl phosphonic acid increased solution turbidities to levels more than an order of magnitude greater than those of either of the component systems. However, at very low pH (pH < 1.5), where only free aquo ferric ions were present in solution prior to surfactant addition, turbidity increases were much lower (Figure 220). The implication is that, in these very low pH solutions, the free ferric ion either did not interact strongly with the phosphonic acid or the complexes formed were relatively soluble. The existence of a small turbidity increase and the previously established ability of styryl phosphonic acid to promote the solubilization of the surface iron film from unleached cassiterite at pH
1.0 (Section 4.4.1.2) both suggest that the latter was the case.

The very strong interaction between styryl phosphonic acid and both hydrous ferric oxide sols and lower order ferric hydroxy species, indicated by the light scattering studies, correlates with the results of vacuum flotation test work published by Collins and coworkers (Figures 68 to 70). In these vacuum flotation studies, the addition of ferric salts to heptyl and isoheptyl phosphonic acid solutions, prior to contacting with the mineral, produced severe flotation depressant effects. Total ferric ion concentrations of less than 25 mg/l were found to produce a complete cessation of flotation at collector levels of less than 80 mg/l. Measurable inhibition of flotation, over the pH range 2.0 to 8.0, occurred at cation concentrations as low as 1 mg/l. While the order of pH adjustment and ferric iron additions used in the preparation of these phosphonic acid solutions is not entirely unambiguous from the information published, it would appear almost certain that the principal iron species in solution were the lower order ferric hydroxy species or the hydrous ferric oxide.

As discussed in detail in a preceding section of this research (Section 2.3.2.7), conditions in industrial cassiterite flotation circuits are unlikely to be either sufficiently oxidizing for the existence of the free ferric ion or lower order ferric hydroxy species nor sufficiently reducing for the existence of significant concentrations of ferrous hydroxide. The two predominant iron species in such pulps are almost certainly the ferrous ion and hydrous ferric oxide (Figure 23).

In Figure 221, turbidity data are given for ferrous chloride solutions as a function of concentration at pH 1.5. Under such highly acidic conditions, the oxidation of the ferrous ion is well known to be very slow kinetically
(Leja, 1982). While the free aquo ferrous ion was presumably the predominant species in these solutions, light scattering indicated the solutions to have measurable turbidities. Furthermore, these turbidities increased appreciably with the concentration of added ferrous chloride.

Figure 221 - Turbidities of Ferrous Chloride Solutions as a Function of Concentration at pH 1.5 in the Presence and Absence of 1 x 10^-4 M Styryl Phosphonic Acid. The dashed line indicates the measured turbidity of the styryl phosphonic acid in distilled water alone.

Standard chemical references such as Dean (1979) indicate that ferrous chloride is highly soluble. Seidell's tabulations of inorganic compound solubilities (Seidell, 1919) quote the solubility of FeCl₂·4(H₂O) as being equivalent to 39.82 grams FeCl₂ per 100 grams of solution. As such, it would have been expected that ferrous chloride would have dissolved completely over the concentration range shown in Figure 221. However, consistent with the turbidity measurements, considerable difficulty existed in dissolving the reagent. Even following extensive ultrasonic treatment, a minute but finite
proportion of undissolved reagent remained visible in solution. While it was possible that this residue was an impurity, this was not probable. The ferrous chloride used was a Fisher A.C.S. certified reagent with an analytically determined negligible insolubles component. It was considered equally unlikely that the observed turbidity was due to products of ferrous ion hydrolysis or oxidation given the reagent concentrations used and the very low pH of the solution (Figure 18). The most probably cause of the ferrous chloride turbidities exceeding that of distilled water, therefore, was incomplete solubility of the reagent under the acidic conditions of solution preparation. While this appears contrary to the reported solubilities of FeCl$_2$.4(H$_2$O), no reference to pH exists in the published literature. Experimentally, it was found that ferrous chloride dissolved almost instantaneously in less acidic solutions. This suggests that the published solubility data pertain more to the slightly acidic and alkaline ranges than to very acidic conditions.

The addition of the equivalent of 1 x 10$^{-4}$ M styryl phosphonic acid to ferrous chloride solutions at pH 1.5 produced no measurable turbidity change at concentrations of the inorganic reagent below 3 x 10$^{-5}$ M. At higher concentrations, increases in turbidity were noted. As for the free ferric ion case, the data suggest that the free aquo ferrous ion either interacts only weakly with styryl phosphonic acid or forms more soluble complexes with the surfactant. Strongly solvated complexes that have no tendency to polymerize do not give rise to measurable solution turbidities. A case in point is that of the fluoro complexes of the aluminum ion (Figure 218). On the basis of the light scattering data alone, it was not possible to evaluate the two alternative hypotheses regarding the absence of turbidity increase at low
ferrous chloride concentrations. However, the increase in turbidity at higher concentrations (Figure 221) was strongly supportive of the hypothesis that the surfactant did interact with the free ferrous ion.

In vacuum flotation studies, Collins, Hollick and Joy (1969) found that ferrous salt additions to isoheptyl phosphonic acid solutions, prior to contacting with cassiterite, produced severe flotation depressant effects above pH 3.0. Consistent with a weak interaction with the free ferrous ion, no inhibition of flotation occurred at lower pH values even for ferrous salt additions up to 500 mg/l (Figure 71). As discussed previously (Section 2.5.3.1), it is most probable that, in the absence of solution potential control, the free ferrous ion would have oxidised and hydroxylated in the less acidic range. Consequently, the enhanced depressant effect observed by Collins, Hollick and Joy above pH 4.0 is more likely to have reflected the interaction of isoheptyl phosphonic acid with hydrous ferric oxide sols than with free aquo ferrous ions.

In the aluminum ion system, it was established that the addition of sodium fluoride inhibited completely the otherwise strong tendency for styryl phosphonic acid to form insoluble precipitates with aluminum species in acidic solutions (Figure 218). It is known that the ferric ion also forms strong fluoro complexes in acidic solutions (Section 2.3.5). Furthermore, these complexes have been shown consistently in this research to be solvated very strongly (Sections 4.3.2.1, 4.3.2.2, 4.5.1.6 and 4.5.3). It was, consequently, of interest to investigate the nature of interactions, if any, between ferric fluoro species and styryl phosphonic acid.

As prepared, solutions containing $1 \times 10^{-4}$ M FeCl$_3$ and $6 \times 10^{-4}$ M NaF had a pH of 3.7. This was almost identical to the pH 3.8 value of $1 \times 10^{-4}$ M
FeCl₃ solutions containing no fluoride. However, the turbidities of the solutions were remarkably different. At all pH values below 4.0, the turbidities of the ferric-fluoro solutions were essentially equal to that of distilled water. Above pH 4.0, the turbidity increased dramatically (Figure 222).

![Figure 222](image)

**Figure 222** - The pH Dependence of the Turbidities of Solutions Containing $1 \times 10^{-4}$ M FeCl₃ and/or $6 \times 10^{-4}$ M NaF in the Presence and Absence of $1 \times 10^{-4}$ M Styryl Phosphonic Acid (SPA). Data are given for the solutions (a) $1 \times 10^{-4}$ M SPA + $6 \times 10^{-4}$ M NaF (b) $1 \times 10^{-4}$ M FeCl₃ + $6 \times 10^{-4}$ M NaF (pHₐ = 3.7) (c) $1 \times 10^{-4}$ M FeCl₃ + $6 \times 10^{-4}$ M NaF + $1 \times 10^{-4}$ M SPA (pHₐ = 3.7) and (d) $1 \times 10^{-4}$ M SPA + $1 \times 10^{-4}$ M FeCl₃ (pHₐ = 3.8).

The data of Figure 222 correspond remarkably with the UV absorbance results of Section 4.3.2.2. As concluded in this previous research, fluoro complexes of the ferric ion were the stable species in the acidic pH range. At higher pH, ferric polycations and hydrous ferric oxide became increasingly
more stable. The onset of rapid growth of these sols undoubtedly produced the order of magnitude increase in turbidity observed between pH 4.0 and 6.0.

The light scattering measurements shown in Figure 222 provided direct evidence that ferric fluoro complexes interacted with phosphonic acid. The addition of styryl phosphonic acid produced substantial increases in ferric-fluoro solution turbidities in the acidic pH range. The implication from these results was that styryl phosphonic acid molecules were stronger coordinating molecules for ferric ion species than the fluoride ion. Comparison of solution turbidities in the presence and absence of fluoride ions (Figure 222), however, suggests that ferric-fluoro complexes either interacted with the phosphonic acid appreciably less strongly than polymeric ferric sols and lower order hydroxy species or produced less insoluble precipitates. Furthermore, the level of this interaction or degree of insolubility diminished significantly with decreasing pH.

Comparison of the data of Figures 218 and 222 provides an interesting contrast. The fluoro complexes of the aluminum ion are well known to be stronger than those of the ferric ion (Sillén and Martell, 1964). It is evident from the light scattering data that styryl phosphonic acid has a much greater ability to form insoluble precipitates when added to acidic solutions containing ferric fluoro complexes than when added to solutions of aluminum fluoro complexes of similar pH.

4.6.3 Magnesium and Calcium Solutions

In dissolved ion analyses of Renison plant waters (Section 4.3.1), it was established that very high magnesium and calcium levels can exist in cassiterite flotation pulps. In this circuit, magnesium was found to be present at levels up to 300 ppm while calcium concentrations were as high as
520 ppm (Table XX). Bulled (1982) has reported that plant waters at the Rooiberg mine are similarly characterized by high levels of magnesium and calcium ions.

Industrial flotation of cassiterite is typically conducted under slightly acidic conditions (pH 4.5 - 6.0). As such, the predominant species of both magnesium and calcium in such pulps are the free aquo ions of the metals (Figures 19 to 21).

Light scattering measurements of magnesium and calcium chloride solutions at pH 5.0 indicated the solutions to have negligible turbidities (Figures 223 and 224). The turbidity of the calcium solution was that of distilled water for concentrations of the reagent up to $2 \times 10^{-2}$ M. In the case of magnesium, a small increase in turbidity was noted only at concentrations above $1 \times 10^{-2}$ M. This small turbidity increase at high concentration was presumably due to solution saturation.

The absence of measurable turbidities in magnesium and calcium chloride solutions at pH 5.0 was consistent with the free ions of these metals being the stable aqueous species. These free ions are well known to be solvated strongly. As such, they have no tendency to form insoluble precipitates except in saturated solutions and hence only at concentrations well above those of interest in cassiterite flotation.

The addition of the equivalent of $1 \times 10^{-3}$ M styryl phosphonic acid to magnesium and calcium chloride solutions prepared at pH 5.0 produced measurable turbidity increases only at high concentrations of the inorganic reagents. At magnesium and calcium chloride concentrations below $4 \times 10^{-4}$ and $1 \times 10^{-3}$ M, respectively, turbidities of these ion-surfactant solutions were found to correspond to that of the surfactant alone (Figures 223 and 224). At
higher inorganic reagent concentrations, turbidities did increase, but only slightly. This was in striking contrast to the order of magnitude increases in turbidity found in the corresponding test work with aluminum and ferric chloride (Figures 216 and 219).

Figure 223 - Turbidities of Magnesium Chloride Solutions as a Function of Concentration at pH 5.0 in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid. The dashed line indicates the measured turbidity of the styryl phosphonic acid in distilled water alone.

Figure 224 - Turbidities of Calcium Chloride Solutions as a Function of Concentration at pH 5.0 in the Presence and Absence of 1 x 10^{-4} M Styryl Phosphonic Acid. The dashed line indicates the measured turbidity of the styryl phosphonic acid in distilled water alone.
As expected, turbidities of $1 \times 10^{-2}$ M magnesium and calcium chloride solutions remained unchanged over the entire acidic to moderately basic pH range (Figures 225 and 226). In more strongly alkaline solutions above pH 8.0, small turbidity increases were noted. These almost certainly represented the onset of hydroxylation of the ions and the formation of hydrous oxide species. It is well established that magnesium and calcium ions undergoolation and oxolation reactions only in concentrated solutions and at high pH (Section 2.3.3).

The addition of styryl phosphonic acid to magnesium and calcium solutions similarly caused no turbidity changes in acidic and moderately basic solutions (Figures 225 and 226). At higher pH values, solution turbidities increased only slightly above that of the surfactant alone. These increases were not pronounced and turbidities of the combined system did not measurably exceed that of the sum of the component systems.

![Figure 225 - The pH Dependence of $1 \times 10^{-2}$ M MgCl₂.6(H₂O) Solution Turbidities in the Presence and Absence of $1 \times 10^{-6}$ M Styryl Phosphonic Acid.](image-url)
The data of Figures 223 to 226 indicate definitively that free aquo magnesium and calcium ions have little tendency to form insoluble precipitates with styryl phosphonic acid. While it is conceivable that soluble complexes are formed, the finding that industrial flotation is performed successfully in the presence of several hundred parts per million of these ions suggests that there is negligible or only weak interaction between the ions and the surfactant. In the case of calcium, such a conclusion is supported by the results of vacuum flotation studies with heptyl and isoheptyl phosphonic acids (Figures 68, 69 and 72). In these studies, it was found that calcium salt additions to the collector solutions, prior to contacting with the mineral, could be tolerated at high levels over a broad pH range without affecting flotation. With these surfactants, a flotation depressant effect occurred only at very high calcium ion concentrations ( > 400 mg/l).
The interactions between styryl phosphonic acid, the cassiterite surface and the hydrous oxides of aluminum and ferric iron clearly are much stronger than those between the surfactant and calcium and magnesium ions. As such, the amount of collector available for interaction with magnesium and calcium ions in a flotation pulp would appear negligible, even if weak complexes with these ions were stable in such pulps.

4.6.4 Principal Findings and Conclusions

(1) Aluminum polycationic and hydrous oxide species interact strongly with styryl phosphonic acid to form insoluble precipitates in the slightly acidic to alkaline pH range above 5.0.

(2) In more strongly acidic solutions below pH 5.0, styryl phosphonic acid interacts with either the free ion or lower order hydroxy species of aluminum to form insoluble precipitates. These insoluble precipitates persist in solution at least down to pH 2.0.

(3) The addition of sodium fluoride can inhibit completely the otherwise strong tendency for styryl phosphonic acid to form insoluble precipitates with aluminum species in acidic solutions. The implication is that the fluoride ion forms more stable complexes with the aluminum ion in acidic solutions than does the phosphonic acid. Aluminum fluoro complexes are well known to be strongly solvated and to have no tendency to polymerize and form insoluble precipitates.

(4) Hydrous ferric oxide sols interact particularly strongly with styryl phosphonic acid and cause massive collector
precipitation. These precipitates remain highly stable over the entire acidic pH range.

(5) Styryl phosphonic acid interacts and forms insoluble precipitates with lower order ferric hydroxy species such as Fe(OH)$_{2}^{+}$, Fe(OH)$_{3}^{+}$, et cetera.

(6) In strongly acidic (pH < 1.5) solutions, where the free ferric ion is the predominant species, formation of insoluble precipitates following the addition of styryl phosphonic acid is not pronounced. On the basis of light scattering data alone, it is not possible to determine unequivocally whether the free ion interacts only weakly with the surfactant or simply forms more strongly solvated complexes. However, the existence of a small turbidity increase and previous data showing styryl phosphonic acid to promote the solubilization of iron from the surface of unleached cassiterite at pH 1.0 both strongly support the latter postulate.

(7) The very strong interaction between styryl phosphonic acid and ferric hydroxy species, including hydrous ferric oxide, provides direct evidence supporting the hypothesis that such iron species, whether adsorbed onto the cassiterite surface or present in the aqueous phase, can influence the flotation of the mineral significantly. Such a strong interaction is a necessary prerequisite if the effects of the iron species are to be pronounced.
(8) Under highly acidic (pH = 1.5) conditions, there is no evidence that styryl phosphonic acid forms insoluble precipitates when added to solutions containing low concentrations of free aquo ferrous ions. At higher ferrous ion concentrations, an increase in turbidity of such solutions occurs. As for the free ferric ion, such findings suggest that the free aquo ferrous ion either interacts only weakly with styryl phosphonic acid or forms relatively soluble complexes with the surfactant.

(9) Ferric fluoro complexes interact and form insoluble precipitates with styryl phosphonic acid. The implication is that styryl phosphonic acid molecules can compete successfully with the fluoride ion for coordinative positions around the ferric ion.

(10) The tendency for ferric fluoro complexes to form insoluble precipitates with styryl phosphonic acid is either appreciably weaker than that of polymeric ferric sols and lower order ferric hydroxy species or the precipitates are markedly more soluble. Furthermore, the degree of interaction or level of insolubility diminishes significantly with decreasing pH.

(11) The free aquo magnesium and calcium ions have little tendency to form insoluble precipitates with styryl phosphonic acid. Such a conclusion is consistent with the finding that industrial flotation is performed successfully
in the presence of several hundred parts per million of these ions.

(12) There is no evidence to suggest that magnesium and calcium ions interfere seriously in the flotation of cassiterite with phosphonic acids. Even if weak soluble complexes are formed between these cations and the surfactant, the much stronger tendency for phosphonic acid to adsorb on the cassiterite surface and complex with aluminum and ferric hydrous oxide sols presumably would leave negligible levels of surfactant available for such interactions. On the other hand, there is every evidence that iron species, particularly hydrous ferric oxide sols, have a profound effect on phosphonic acid cassiterite flotation.
CHAPTER 5

IMPLICATIONS OF THE RESEARCH FINDINGS

During the course of this dissertation an appreciable number of research findings and conclusions have been presented. In addition, a number of hypotheses, with important implications for both fundamental and industrially related cassiterite flotation research, have been advanced. The following represents an attempt to collate these many results and to assess the overall implications of the research findings.

5.1 The Fundamental Nature of Phosphonic Acid Adsorption on Cassiterite

Adsorption measurements conducted in this research with very high purity stannic dioxide have established conclusively that maximum adsorption of styryl phosphonic acid on the stannic dioxide substrate occurs in the acidic range between pH 2.0 and 3.0 (Figure 156). In less acidic solutions, adsorption decreases rapidly to pH 4.0 and then more slowly at higher pH values. Such adsorption behaviour is analogous entirely to that reported independently by several different research groups for a range of phosphonic acids and high purity natural cassiterites (Figures 38 to 42). It is postulated that, in the absence of mineral surface contaminants, styryl phosphonic acid adsorption on all natural cassiterites is characterized by such a fundamental pH independence.

Changes in the electrophoretic mobility of stannic dioxide particles in the presence of styryl phosphonic acid (Figures 162 and 163) are consistent in all respects with the corresponding adsorption data. In particular, maximum charge reversal occurs in the pH range 2.0 to 3.0. No evidence exists for extensive surfactant adsorption without an associated change in electrokinetic
properties of the oxide as other published data would suggest the case to be for p-tolyl phosphonic acid (Section 2.4.5). Similarly, leached cassiterite, known to have negligible surface contamination, exhibits a microflotation response in the presence of styryl phosphonic acid that correlates remarkably with all aspects of stannic dioxide adsorption and electrokinetic behaviour in solutions of the surfactant. In particular, optimal flotation response occurs in the acidic range between pH 2.0 and 3.0 (Figure 166). Above pH 3.0, flotation response at low phosphonic acid concentrations diminishes appreciably over a narrow pH range. Flotation response is unequivocally a direct function of the level of surfactant adsorption. There is no complex relationship whereby the pH region of maximum phosphonic acid adsorption is a region of poor floatability and vice versa as might be concluded by direct comparison of published adsorption isotherms (Figures 38 to 42) with vacuum flotation results (Figure 35). The latter data indicate optimum flotation response for a range of different cassiterites and phosphonic acids to be in the slightly acidic range pH 5.0 - 6.0.

In accord with Balachandran's and Gruner's findings that styryl phosphonic acid floats undoped synthetic cassiterite, the microflotation response of leached cassiterite (Figure 166) strongly indicates that the surfactant genuinely floats cassiterite. Flotation in these systems cannot logically be attributed to lattice or surface impurities.

The adsorption, electrokinetic and microflotation data of this research (Section 4.4) confirm that a substantial increase in styryl phosphonic adsorption on cassiterite occurs in the more acidic range below approximately pH 4.0. The onset of this adsorption increase correlates with fundamental changes in both surfactant solution chemistry and mineral surface properties.
A pH value of 4.0 corresponds closely to that of formation of undissociated styryl phosphonic acid molecules in aqueous solution (Figure 135). It also corresponds to the iep of cassiterite and hence is the charge reversal point of the mineral. These observations have led to two fundamentally different interpretations being offered for the adsorption increase in the acidic pH range. Wottgen (1969) and Gruner (1971) interpreted the enhanced adsorption as being due to increased electrostatic attraction between partially dissociated phosphonic acid molecules and the positively charged mineral surface below the latter's iep. Fuerstenau and Healy (1972) proposed that coadsorption of undissociated phosphonic acid molecules was the mechanism responsible for the increase in adsorption.

The finding in this research that markedly higher charge reversals were associated with the abrupt increase in styryl phosphonic acid adsorption on stannic dioxide below pH 4.0 confirms that adsorption of negatively charged species is at least partially responsible for the adsorption increase. Such a finding supports the Wottgen and Gruner hypothesis. Conversely, such data provide no evidence supporting the alternative Fuerstenau and Healy hypothesis of coadsorption of undissociated phosphonic acid molecules. However, the possibility that both might be occurring cannot be precluded entirely.

Strong evidence for some coadsorption of undissociated molecules in the case of heptyl phosphonic acid can be found in the published adsorption data of Wottgen (1969). These adsorption isotherms (Figure 44) show that monolayer adsorption was exceeded at pH 2.0 and very closely approached at pH 1.0 even assuming the extreme ease of uniform surfactant adsorption and only 25 Å² as the area occupied by an heptyl phosphonic acid molecule on the cassiterite surface. The existence of an excess of adsorbed phosphonic acid over that
necessary for monolayer adsorption clearly indicates that coadsorption of phosphonic acid species must have occurred in this system at low pH values. Any chemical adsorption character obviously cannot be maintained for more than one layer of adsorbate on one layer of underlying adsorbent. However, whether similar coadsorption exists at lower phosphonic acid concentrations, such as those in this research where abrupt increases in adsorption also were found below pH 4.0, is a matter of conjecture.

During the course of the surface tension measurements of Section 4.2.6, it was established that styryl phosphonic acid has significant surface tension lowering effects in acidic aqueous solutions. Furthermore, surface tension curves at low pH were found to exhibit minima indicating the formation of a second phase (Figure 139). These phenomena confirm that, at low pH, undissociated phosphonic acid molecules have sufficient non-polar character that they can lower their free energy by adsorbing at an interface and that associations between such adsorbed molecules can occur. Molecular modelling (Plate 9) has also verified that the physical structure of trans styryl phosphonic acid molecules is such that they can pack in a condensed state with both hydroxyls of their polar groups orientated away from the ring and in the same direction. These results provide strong circumstantial evidence supporting the hypothesis that undissociated phosphonic acid molecules might coadsorb in acidic solutions. However, definitive resolution of whether such coadsorption is associated with the increase in styryl phosphonic acid below pH 4.0 appears possible only through detailed in-situ spectroscopic analyses such as might be provided by reflection-absorption infrared spectrophotometric techniques.

Considerable evidence exists supporting the hypothesis of a significant
chemical component in styryl phosphonic acid adsorption on cassiterite. The microflotation (Figure 166), adsorption (Figure 156) and electrokinetic studies (Figure 161) of this research all indicate that appreciable styryl phosphonic acid adsorption can occur above the iep of high purity stannic dioxide and leached cassiterite. In this pH range, the surfactant is dissociated and the oxide substrates have a negative charge character. Strong interaction, therefore, occurs despite electrostatic repulsion between the anionic surfactant molecules and the negatively charged substrate surfaces. Published data for other phosphonic acids (Sections 2.4.1 to 2.4.5) further suggest that the ability to adsorb above the iep of cassiterite is a characteristic of all phosphonic acids.

The adsorption of styryl phosphonic acid above the iep of stannic dioxide and leached cassiterite can be considered as definitive evidence for chemisorption of the surfactant. No data exist supporting the alternative hypothesis that hydrophobic bonding contributions can account for such adsorption. Stannic dioxide electrophoretic mobilities in styryl phosphonic acid solutions do not exhibit the characteristic charge reversals normally associated with hemi-micelle formation even at surfactant concentrations as high as $2 \times 10^{-3}$ M. The absence of any significant hydrophobic bonding interaction in the styryl phosphonic acid system is further consistent with the short nature of the surfactant radical. It has been verified in innumerable surfactant systems that hemi-micelles do not form when hydrocarbon chain lengths are shorter than $C_a$.

The ability of styryl phosphonic acid to chemisorb onto the surface of uncontaminated cassiterite in slightly acidic solutions is critically important in terms of industrial cassiterite flotation. In commercial
operations, the preferred pH range of flotation is invariably between pH 4.0 and 6.0.

Investigation of the mechanism of styryl phosphonic acid chemisorption on cassiterite was beyond the scope of this research. However, the molecular modelling performed indicates that molecular compatibility does exist between styryl phosphonic acid and the surface of cassiterite. It can be verified that it is possible sterically for the hydroxyls of the phosphonic acid polar group to replace two adjacent coordinated hydroxyls on certain cassiterite cleavage planes such as the (110) plane. Such compatibility must exist if styryl phosphonic acid is to adsorb chemically according to a chelation mechanism in which the phosphonic acid acts as a bidentate 1:1 chelating molecule. Infrared spectral data obtained by Wottgen and Dietze (Wottgen, 1969; Wottgen and Dietze, 1969) have been interpreted by these and other researchers as indicating the formation of bidentate stannic phosphonate chelate species on the cassiterite surface (Sections 2.4.6 and 2.4.7).

None of the results of this research can be considered as proof of a mechanism whereby styryl phosphonic acid chemisorbs to surface stannic ions of cassiterite through the formation of bidentate chelates. However, the electrokinetic study data showing the charge character of stannic dioxide to become more negative above the oxide iep is consistent with such a mechanism. The strongest supportive evidence for the chelation mechanism is still its inherent plausibility, the infrared spectral changes observed by Wottgen and Dietze and the implication from Mossbauer analyses (Pietzsch, Fritzsch and Braun, 1981) that stannic ions form bidentate chelates with phosphonic acids. More highly sensitive in-situ infrared analyses are required to provide the necessary spectral detail to resolve unequivocally that this is the mechanism
of chemisorption. Currently, the lack of spectral detail associated with the poor signal to noise ratio in the Wottgen and Dietze infrared analyses (Figures 49 to 51) does not allow completely unambiguous confirmation of the nature of the adsorbed species.

The adsorption of styryl phosphonic acid onto cassiterite above pH 4.0 can be considered as definitive evidence that the partially dissociated form of the surfactant chemisorbs onto the mineral. Between pH 4.5 and 5.5, this is essentially the only species present in solution (Figure 135). Evident also in the leached cassiterite microflotation data obtained in this research is that the pH region of optimum flotation response corresponds to that between pK₁ and pK₂ of styryl phosphonic acid. Implicit in such a relationship is that the partially dissociated species is responsible primarily for adsorption onto the cassiterite surface over the entire pH range of interaction.

Intuitively, there appears to be a sound basis for the partially dissociated species of styryl phosphonic acid adsorbing most strongly onto the cassiterite surface. For undissociated phosphonic acid molecules to bond chemically, the surfactants hydroxyl protons presumably must dissociate. In strongly acidic solutions, where these undissociated molecules predominate, such deprotonation is energetically unfavourable since there already exists an excess of protons. Conversely, above pK₂, where completely dissociated molecules are the predominant phosphonic acid species, there exists increased electrostatic repulsion between the divalent anionic molecules and the negatively charged cassiterite surface.
5.2 The Role of Surface Iron Films in Fundamental Research

It was shown during the course of the literature review of this dissertation that a large body of published vacuum flotation data existed indicating optimum cassiterite flotation with phosphonic acids to occur between pH 5.0 and 6.0 (Figure 35). In these studies, appreciably greater concentrations of phosphonic acid were found necessary to achieve vacuum flotation at both more acidic and basic pH values. Such fundamental data were strikingly different to other published adsorption, microflotation and electrokinetic results, all of which indicated maximum phosphonic acid adsorption to be in the strongly acidic pH 2.0 - 3.0 range. These vacuum flotation results, however, could not be regarded as anomalous as they represented a large body of test work and corresponded remarkably with actual laboratory and plant flotation of cassiterite in ores.

In this research, it has been established that the presence of an iron film on the surface of cassiterite can influence profoundly the microflotation response of the mineral. Specifically, in the slightly acidic to neutral pH range (pH > 5.0), such iron results in increased styryl phosphonic acid adsorption onto cassiterite thereby strongly promoting its floatability. Conversely, in more highly acidic solutions, the iron is solubilized and forms aqueous complexes with the phosphonic acid. If sufficient iron is present, associated mineral floatability can be inhibited entirely at low pH values.

The overall effect of iron contamination on the surface of Renison cassiterite was to move the optimum microflotation response of the mineral at low styryl phosphonic acid concentrations from more acidic values around pH 2.0 to between pH 5.0 and 6.0 (Figure 168). As such, the microflotation response of the unleached cassiterite corresponded remarkably with the vacuum
flotation results published in the literature. On the basis of this correlation, the hypothesis was advanced that iron films on the surfaces of the various test cassiterites used in the vacuum flotation studies were responsible for the fundamentally different flotation response observed in this test work.

In Table XXI a compilation is given of all published cassiterite flotation research involving phosphonic acids for which reasonable sample description and preparation information exist. It is evident from this summary that where high purity natural cassiterite, synthetic cassiterite containing no dopants, or acid leached cassiterite was used as the test mineral, optimum surfactant adsorption and flotation of the sample with phosphonic acids occurred in the pH range 2.0 to 3.0. Adsorption and flotation behaviour in all these tests were essentially the same, irrespective of small variations in the nature of the substrate, the type of phosphonic acid hydrocarbon radical and the experimental technique used. In every aspect, these finding correlate with the results of this research for leached cassiterite and styryl phosphonic acid.

The information summarized in Table XXI indicates that for the vacuum flotation analyses, in which optimum flotation response occurred under only slightly acidic conditions, sample preparation was distinctly different to that in other test work. The cassiterites used in these vacuum flotation studies were upgraded from ore samples. Grinding, flotation with xanthates to remove the sulphides and subsequent gravity concentration, superpanning and magnetic separation were used to produce an enriched cassiterite. Most importantly, no acid leaching of the samples was performed. In a manner analogous entirely to that of the cassiterite recovered from the Renison
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<td>No Dopants</td>
<td>n-heptyl</td>
<td>Batch flotation from binary mixtures with SiO₂</td>
<td>Floated between pH 5.0 and 7.0. No data for lower pH.</td>
</tr>
</tbody>
</table>
TABLE XXI (cont.)

SAMPLE PREPARATION METHODS, EXPERIMENTAL TECHNIQUES AND PRINCIPAL FINDINGS PERTAINING TO PUBLISHED FUNDAMENTAL CASSITERITE FLOTATION RESEARCH INVOLVING PHOSPHONIC ACIDS

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Sample Preparation</th>
<th>Phosphonic Acid</th>
<th>Technique</th>
<th>Principal Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gruner (1971)</td>
<td>Stannic Dioxide</td>
<td>n-heptyl</td>
<td>Adsorption studies using P&lt;sup&gt;32&lt;/sup&gt; marked surfactant.</td>
<td>Maximum adsorption at pH 3.0. Much lower adsorption at higher pH.</td>
</tr>
<tr>
<td>Wottgen, Luft &amp; Neuber (1971)</td>
<td>Cassiterite described as pure mineral.</td>
<td>styryl</td>
<td>Adsorption studies using P&lt;sup&gt;32&lt;/sup&gt; marked surfactant.</td>
<td>Maximum adsorption at pH 2.0. Much lower adsorption at higher pH.</td>
</tr>
<tr>
<td>Yap (1975)</td>
<td>Acid Cleaned</td>
<td>p-tolyl</td>
<td>Adsorption studies using UV analysis of residual surfactant levels</td>
<td>Maximum adsorption at pH 2.2. Much lower adsorption at higher pH.</td>
</tr>
</tbody>
</table>

* * Upgraded from ore samples. Upgrading was by grinding, flotation with xanthates to remove the sulphides and subsequent gravity concentration, superpanning and magnetic separation to produce an enriched cassiterite. No acid leaching was performed.
plant, there was every opportunity for hydrous ferric oxide sols to have adsorbed on these mineral surfaces. Such iron species could have been derived from ball mill grinding or from associated gangue minerals, particularly the sulphides, as is believed to be the case for Renison cassiterite. Precisely as observed in this research for unleached cassiterite contaminated with surface iron, flotation response was strongest in the slightly acidic range between pH 5.0 and 6.0.

Prior to the work of this dissertation, no experimentally supported mechanism existed explaining the different pH ranges of optimum cassiterite flotation response cited in published microflotation and vacuum flotation studies. The hypothesis advanced here that such differences were due to surface iron films derived from aqueous mineral pulps is supported experimentally by a large body of data. As demonstrated above, it further correlates with all that is known about the methods of preparation of the samples used in the respective test work.

It has been recognized by many researchers working in the field of cassiterite flotation that a significant number of apparent anomalies exist in the published literature. The most frequently cited reasons for these discrepancies have invariably related to either the effects of crystal lattice impurities on the surface properties of cassiterite or to the role of dissolved metal ionic species present in industrial flotation pulps. The latter effect has, to date, generally only been considered of significance when attempting to correlate the results of laboratory studies to plant observations. As shown unequivocally in this research, dissolved hydrous ferric oxide sols can change dramatically the nature of samples used for fundamental research if contacted with the cassiterite during sample
The perception that differences in published fundamental data were due to changes in cassiterite lattice properties has resulted in considerable research being conducted in this field. Numerous papers and at least two major dissertations (Gruner, 1969; Balachandran, 1982) pertaining directly to the effects of cassiterite lattice dopants on the mineral surface properties exist. However, even at the fundamental level, major inconsistencies are evident in such work. For example, the iep values reported by Gruner and Balachandran for both undoped and doped stannic dioxide crystals differ by approximately two pH units. Furthermore, the reported effects of iron doping, for which a direct comparison is possible between the published data of these researchers, shows opposing trends. The Gruner data indicate that iron doping moves the iep to more acidic pH values (Figure 5) while the Balachandran data (Figure 6) indicate an higher iep value with iron doping. As discussed previously (Section 2.1.6), these disparities in electrokinetic properties between different synthetic stannic dioxides and between synthetic and natural crystals presumably reflect variations in the conditions of formation of the crystals. The conditions of synthesis used by Gruner (1971) (growth of crystals from stannic dioxide powder vaporised at 1300°C and allowed to condense) and Balachandran (firing of pressed stannic dioxide pellets at 1400°C in air for 4 hours) are both far removed from those in geological environments.

With regard to flotation behaviour, none of the work on the effects of cassiterite crystal dopants has produced a flotation response even remotely similar to that observed in published vacuum flotation studies or in actual industrial flotation (Section 2.4.1). Irrespective of the type or level of
dopants used, maximum phosphonic acid adsorption and flotation recoveries invariably have been found in very acidic solutions with pH near 2.0 (Sections 2.4.1 and 2.4.4).

The hypothesis that cassiterite surface iron contamination is responsible for observed differences in reported fundamental phosphonic acid flotation behaviour is completely consistent with a large body of experimental data. Conversely, no evidence exists supporting the alternative possibility that marked changes in the pH range of flotation are due to cassiterite lattice impurities.

5.3 The Role of Dissolved Metal Ionic Species in Industrial Flotation

As clearly demonstrated in the literature review of this dissertation, the flotation of cassiterite in industrial operations bears little or no resemblance to that which one would expect on the basis of fundamental single mineral adsorption, electrokinetic or microflotation studies with purified cassiterite samples. All published data pertaining to phosphonic acid flotation of cassiterite in ores are typified by a dramatic and generally complete inhibition of flotation in highly acidic conditions below pH 4.0. This phenomenon appears to be a characteristic of phosphonic acid flotation, both in laboratory testing and in actual plant flotation of ores (Figures 79 to 81). No flotation consequently occurs in the pH region of maximum phosphonic acid adsorption in fundamental studies. Conversely, high recoveries and acceptable selectivities are achieved in the pH region where fundamental studies would suggest collector adsorption to be diminished considerably. In the following sections, the degree to which the results of this research can reconcile and explain these observations is appraised.
5.3.1 Iron Species

Pulp solution analyses have confirmed that total iron concentrations in cassiterite flotation pulps can reach appreciable levels. In the Renison circuit, analyses of pulp supernatants performed during the course of this research indicated iron to be present at concentrations as high as 62 ppm.

Dissolved iron species in flotation pulps can exist theoretically in a variety of forms. However, on the basis of Eh and pH measurements of Renison flotation pulps, the predominant iron species in industrial flotation circuits are almost certainly the free ferrous ion and hydrous ferric oxide sols. Conditions seem neither sufficiently oxidizing for the existence of the free ferric ion or lower order ferric hydroxy species nor sufficiently reducing for the existence of significant concentrations of hydrous ferrous oxide.

In aqueous suspensions, hydrous ferric oxide sols adsorb strongly on the surface of minerals. In this research, it has been demonstrated unequivocally that such sols adsorb onto cassiterite and quartz surfaces under solution chemical conditions that reasonably might be expected in an industrial flotation plant (Figures 187 to 189). No similar evidence was found that the free aquo ferrous ion specifically adsorbed. This ion is strongly solvated and would exist predominantly in the aqueous phase of a cassiterite flotation pulp.

Surface analyses of cassiterite grains recovered from the Renison plant have shown definitively that iron films exist on the surface of the mineral. The level of surface iron of these grains, as indicated by SIMS, XPS and chemical abstraction analysis, was far in excess of that characteristic of the bulk mineral lattice. All aspects of the nature of this surface iron contamination were consistent with the iron being the result of previous
adsorption of hydrous ferric oxide sols onto the cassiterite surface in the plant environment. In particular, the binding energies of iron \( (2p)_{3/2} \) electrons associated with the iron films correlated with those reported in the literature for amorphous hydrous ferric oxide. Furthermore, it was verified by X-ray photoelectron spectroscopy that exposing a pure leached cassiterite to a solution containing hydrous ferric oxide sols, under \( \text{Eh} \) and \( \text{pH} \) conditions approaching those in the Renison circuit, resulted in the appearance of iron peaks in the XPS spectrum identical to those observed for cassiterite recovered from the plant. No evidence was found in the XPS analyses to support the contention that the surface iron represented lattice iron that had accumulated on the surface due to migration through the lattice. The latter has been suggested to be the case for certain sulphide minerals.

Light scattering analyses (Section 4.6.2) have confirmed that hydrous ferric oxide sols interact particularly strongly with styryl phosphonic acid. The insoluble precipitates formed by interaction remain highly stable over the entire acidic \( \text{pH} \) range. Conversely, free aquo ferrous ions either interact only weakly with styryl phosphonic acid or form relatively soluble complexes with the surfactant. Given that the free ferrous ion and any complexes it might form with styryl phosphonic acid are strongly solvated, it is evident that the cation does not interfere seriously with flotation under industrial conditions. If the levels of ferrous ions were very high or aqueous solution interactions with collector pronounced, it is unlikely that high recoveries could be achieved industrially at all. However, there is every evidence that hydrous ferric oxide sols adsorbed onto the surface of minerals profoundly influence the industrial cassiterite flotation process.

The picture that emerges on the basis of this research is that, in a
flotation pulp, all of the minerals are, to some degree, coated by adsorbed hydrous ferric oxide sols. As indicated by autoradiographic studies (Plate 1) and electron microscopy (Langdon, Perrott and Wilson, 1973) these coatings are probably not uniform in distribution but are concentrated in certain locations on the surfaces of the minerals. It is generally accepted that mineral surfaces, on a molecular scale, are highly non-uniform and can possess a wide range of high to low energy sites (Kitchener, 1965; Scamehorn, Schechter and Wade, 1982). Furthermore, in a tin flotation circuit where total available surface area is very large, the percentage coverage of minerals might not be high. While the amount of surface iron associated with the Renison cassiterite of this research was clearly appreciable, it was impossible to assess the degree of surface coverage it represented. However, the high selectivity that can be achieved in industrial cassiterite flotation (enrichment ratios up to 30) suggests that the surface coverages are not approaching saturation levels. If all minerals were completely covered by such sols they would all have the same surface properties and there would be no flotation selectivity. This is obviously not the case.

The conclusion that only a portion of all mineral surfaces, in a flotation circuit, are covered by adsorbed hydrous oxide sols suggests that mineral charge reversal effects associated with the adsorption of the sols might themselves not be of great importance. In the very dilute suspensions of microelectrophoresis, ferric ion concentrations typical of the Renison plant do cause charge reversal. However, in the present of orders of magnitude greater surface area, the same ion concentrations might not produce a sufficient coverage of available surface to reverse the charge of individual cassiterite particles.
In a single mineral system, it is indisputable that an iron film on the surface of cassiterite promotes the adsorption of styryl phosphonic acid in the slightly acidic to alkaline pH range where the iron film is not solubilized. As shown in this research, iron contaminated cassiterite floats most strongly between pH 4.0 and 7.5. As such, it exhibits a flotation response that corresponds remarkably to that in the Renison plant from which the sample was recovered. However, this link between single and multi-mineral systems is far more complex than such a cursory analysis would suggest.

If hydrous ferric oxide sols are adsorbed on all minerals in a cassiterite flotation pulp, then it reasonably might be expected that styryl phosphonic acid adsorption will be enhanced on all gangue species in the pulp. As such, any activation of cassiterite flotation will tend to be offset by depletion of collector available for adsorption on cassiterite. Such must be the case, given that the total amount of iron adsorbed as sols on the surface of cassiterite grains is orders of magnitude less than that adsorbed on the surfaces of all gangue species combined (cassiterite usually represents of the order of 1 percent by weight of a tin flotation feed and presumably less in terms of total surface area, given its high density). However, at least in the Renison circuit, size-by-size analyses (Figure 82) have indicated consistently that gangue species such as quartz are not recovered by genuine flotation. The adsorption of styryl phosphonic acid onto such gangue, due to hydrous ferric oxide activation, therefore, is not detrimental in the sense that the extent of adsorption is sufficient to impart an high degree of hydrophobicity to these minerals.

The fact that gangue minerals, such as quartz, do not float when presumably covered by levels of hydrous oxide sols similar to those that
remarkably enhance the flotation of cassiterite raises a number of fundamental issues. These pertain to the selectivity of adsorption of hydrous ferric oxide sols onto minerals, the selectivity of styryl phosphonic acid interaction with such sols and the influence of the substrate on both genuine and adsorbed sol surfactant adsorption.

It has been assumed tacitly in the analysis to date that the adsorption of hydrous ferric oxide sols is not selective for one mineral surface as opposed to another. While no definitive experiment has ever been devised to test unequivocally that this is the case, conventional wisdom is that adsorption of all hydrous metal oxide sols is non-selective. This conclusion is supported by innumerable single mineral test results, such as those of this research, which show strong adsorption of hydrous metal oxide sols to occur over a certain characteristic pH range irrespective of the substrate. It further has been shown (Fuerstenau, Elgillani and Miller, 1970) that hydrous ferric oxide sols even adsorb strongly on the surface of sapphire in an acidic environment (Figure 67). In the acidic pH range, both the sols and the sapphire surface would be charged positively. Such adsorption consequently can occur despite electrostatic repulsion between the adsorbing sols and the substrate.

It was concluded in the literature review of this dissertation (Section 2.5.1.4) that the balance of evidence suggested adsorption of hydrous oxide sols to be due predominantly to hydrogen bonding. As such, there is no fundamental basis for expecting any selectivity. The only exceptions would appear to be for those minerals that constituted the original source of the metal ions. It is conceivable that ions derived from a particular mineral might preferentially form films on that mineral surface due to local concentration or kinetic effects. If such ions were to hydrolyze and adsorb
on another mineral surface, transfer away from the source mineral interface and through the bulk solution must occur. Provided that thermodynamically both adsorption processes were equivalent, kinetic considerations would presumably favour adsorption onto the mineral of the ions origin. Thus, if pyrite is a major source of dissolved iron in the Renison circuit, the percentage surface coverage of this mineral by hydrous ferric oxide sols might exceed that of other minerals such as quartz. However, the levels of such sols on cassiterite and quartz should not be different significantly.

Proceeding from the postulate that hydrous ferric oxide adsorption is non-selective, at least for species such as cassiterite and quartz, the strong activation of the former mineral and absence of floatability of the latter in the Renison circuit simply might reflect low total surface coverages of these minerals by adsorbed sols and the use of very high styryl phosphonic acid concentrations. If the percentage surface coverage of the quartz by adsorbed hydrous ferric oxide sols is below the threshold level required to achieve activated flotation, then no level of surfactant addition will induce flotation. However, the same is not true for cassiterite where genuine adsorption will increase up to a maximum level with higher phosphonic acid additions. Under this scenario, the principal effect of the adsorbed hydrous oxide sols in plant pulps is to deplete surfactant levels necessitating increased additions of the very expensive styryl phosphonic acid collector to achieve high cassiterite recoveries. This, in turn, might reduce overall flotation selectivity since styryl phosphonic acid is well known to float gangue species such as tourmaline, siderite, pyrrhotite, topaz, et cetera, but at rates slower than that of cassiterite. Higher collector additions and hydrous ferric oxide activation of these minerals might increase significantly
their flotation rates.

The difficulty with the preceding analysis is that it cannot be reconciled readily in the first instance with the iron levels that were found associated with the cassiterite recovered from the Renison plant and in the second to the level of activation that this iron produced in the microflotation studies. As established in Section 4.1.6, it was found possible to solubilize the equivalent of 6.64 mg of iron from the surface of a single gram of cassiterite recovered from the Renison circuit. Furthermore, in the pH range above 4.0, this iron resulted in cassiterite microflotation recoveries, in the presence of $1 \times 10^{-4}$ M styryl phosphonic acid, exceeding those after leaching even when the equivalent of $1 \times 10^{-3}$ M surfactant was added (Figure 170). The level of surface iron contamination was clearly substantial and profoundly affected the flotation of the cassiterite.

There is no doubt that some genuine adsorption of styryl phosphonic acid must occur on uncontaminated portions of cassiterite grains in the pH range typical of industrial flotation. This conclusion is supported by the adsorption, electrokinetic and microflotation work of this research, all of which indicate the surfactant to adsorb on leached cassiterite at measurable levels up to slightly alkaline pH values near pH 8.0. It further correlates with the finding of Gruner (1971) that n-heptyl phosphonic acid could float undoped stannic dioxide from quartz in the range pH 5.0 - 7.0 under batch flotation conditions. It is conceivable, therefore, that genuine surfactant adsorption produces a synergistic effect either with regard to the tendency of styryl phosphonic acid to associate with ferric oxide sols or with respect to the level of floatability that such association produces.

Given that any two hydrous ferric oxide sols are unlikely to be different,
the probability of a styryl phosphonic acid molecule attaching to either sol should be the same. However, if the surfactant can also chemisorb with the substrate on which one sol is adsorbed, the ability of the surfactant molecules to condense and form a close packed layer logically might be enhanced. Whether cooperative bonding effects would actually increase the amount of adsorption of styryl phosphonic acid onto hydrous ferric oxide sols on the cassiterite surface relative to those on a gangue species, such as quartz, is a matter of speculation. However, cooperative bonding might tend to immobilize surfactant adsorbed through iron sol activation on the cassiterite surface. In the case of quartz, no similar cooperative bonding would occur since chemisorption is negligible. Surfactant bonded to hydrous ferric oxide sols on this mineral surface, therefore, might be sheared easily from the mineral in the turbulent environment of a flotation cell. Given that hydrogen bonding is the most probably mechanism of attachment of hydrous oxide sols to mineral surfaces, there is a reasonable probability that such shearing might occur after surfactant adsorption.

In phosphonic acid flotation, the general consensus is that the presence of ferric ion species produces pronounced deleterious effects (Collins, 1967; Wottgen and Topfer, 1976; Bulled, 1982; Mosch and Becker, 1985). However, the weight of evidence in this research suggests that there might exist an optimum surface iron coverage of minerals for which the flotation of cassiterite is improved with respect to gangue minerals such as quartz. At higher iron levels, the effect of hydrous ferric oxide sols adsorbed on mineral surfaces is undoubtedly deleterious. Increased collector additions almost certainly are required to compensate for surfactant adsorption onto iron sols attached to gangue minerals. This, in combination with activation of the more
floatable gangue, would reduce overall flotation selectivity. In the Renison circuit, all indications are that the level of iron is such that the deleterious effects of iron species adsorption are pronounced. Considerable incentive consequently exists to reduce the total iron concentrations in the circuit.

It is frequently cited that high phosphonic acid reagent consumptions, together with low selectivity with respect to certain gangue species, are the two major problems encountered in industrial cassiterite flotation. Considerable evidence exists that these problems are intimately related to the presence of hydrous ferric oxide sols in industrial flotation pulps.

The complete inability to float cassiterite industrially in acidic solutions below pH 4.0 undoubtedly represents one of the more remarkable differences between fundamental and actual plant flotation behaviour. During the single mineral microflotation studies of this dissertation an analogous depressant effect was observed for iron contaminated cassiterite. This effect was shown unequivocally to be due to the solubilization of surface iron species in the acidic pH range and the strong interaction between these solubilized iron species and styryl phosphonic acid. It appears logical, therefore, that the cessation of flotation in industrial cassiterite flotation operations, including the Renison plant, is a dramatic manifestation of the same phenomenon. Given that such is the case, the levels of iron contamination in industrial plants is clearly extraordinarily high. Furthermore, the flotation of the cassiterite at higher pH must be dependent critically on this iron activation as it is inhibited completely in its absence.

A mechanism whereby cessation of flotation in industrial flotation
circuits at low pH is due to resolubilization of hydrous ferric oxide sols from the surface of minerals is supported by the entire body of data obtained in this experimental research. It further correlates with the finding of Collins and Jackson (1967) that the inhibition of heptyl phosphonic acid flotation of cassiterite in South Crofty ore was associated with a significant decrease in residual collector concentration in solution. On the basis of the research of this dissertation, this might be attributed logically to complexing of phosphonic acid by ions in the aqueous solution.

Due to the complexity of industrial flotation pulps, other possibilities exist that potentially might explain the inability to float cassiterite industrially in acidic solutions. Wottgen and Luft (1971) have argued that the flotation depressant effect is due to significant increases in phosphonic acid adsorption on particular gangue species in strongly acidic solutions which thereby depletes the collector available for adsorption on cassiterite. However, given that in the absence of iron contamination genuine adsorption on cassiterite also increases markedly in acidic solution and that cassiterite floats more strongly at higher pH values than other gangue, such a mechanism appears at best improbable.

An alternative possibility is that the cessation of flotation is due to the onset of dissolution of gangue species, such as siderite, at low pH. The released ions from such dissolution might logically cause pronounced collector precipitation. While more feasible than the Wottgen and Luft proposal, it has never been demonstrated that the rate of dissolution of such minerals could explain the almost instantaneous depressant effect observed industrially. Conversely, the kinetics of resolubilization of hydrous ferric oxide sols from mineral surfaces have been shown in this research to be extremely rapid in the
presence of fluoride ions and collector. Such resolubilization can clearly proceed extensively in the time frames characteristic of cassiterite flotation processes.

There seems little doubt that the dramatic and complete cessation of flotation in industrial circuits at low pH is due to resolubilization of hydrous ferric oxide sols and associated collector precipitation in bulk solution. Whether low pH induced dissolution of gangue minerals contributes to this effect remains to be resolved.

5.3.2 Aluminum Species

In the pH range typical of cassiterite flotation circuits (pH 4.5 to 7.0) aluminum exists predominantly in the form of hydrous oxide sols. It has been demonstrated in this research (Section 4.5.1.1), that such sols adsorb strongly onto the surface of cassiterite. On the basis of other studies and general theories pertaining to metal ion species adsorption, such as the James and Healy model, there is every likelihood that such sols will also adsorb strongly onto other minerals.

In an analogous manner to the corresponding ferric ion species, hydrous aluminum oxide and lower order hydroxy species of the metal interact with styryl phosphonic acid and form insoluble precipitates (Figures 216 and 217). There is consequently every indication that hydrous aluminum oxide sols can influence cassiterite flotation in a manner similar to that of hydrous oxide sols of the ferric ion.

While aluminum sols potentially can play a role as significant as that of hydrous ferric oxide sols in industrial cassiterite flotation, the pulp water and mineral surface analyses of this research indicate that, in the Renison circuit, the total concentration of aluminum species is far below that of
iron. Total aluminum concentrations in supernatants recovered from the plant pulps were generally less than 5 ppm and often below 1 ppm (Table XX). Similarly, aluminum was not detected on the surface of cassiterite in XPS analyses of grains recovered from the plant (Figure 107). SIMS analyses confirmed that aluminum was present only as a trace surface impurity on the cassiterite (Figure 98).

It is conceivable that dissolved aluminum ion species might assume a more important role in the flotation of cassiterite from ores with a different gangue composition to that of the Renison mine. Such might be the case for ores containing high levels of more soluble alumino-silicate minerals such as tourmaline. High concentrations of aluminum ions dissolved from alumino-silicate minerals might correlate with the frequently cited interfering effect of such gangue species. However, given the more ubiquitous nature of iron in industrial flotation pulps, it is difficult to envisage a mineralogical composition for which hydrous aluminum oxide species might influence cassiterite flotation response to a degree exceeding that of hydrous ferric oxide sols.

5.3.3 Calcium and Magnesium Species

Industrial cassiterite flotation pulps can contain very high levels of both calcium and magnesium ions. Analyses of pulp supernatants recovered from the Renison plant during the course of this research indicated total calcium and magnesium concentrations to be in the ranges 160 to 520 ppm and 300 to 600 ppm, respectively.

Under the pH conditions of cassiterite flotation, the aquo magnesium and calcium ions are the predominant species of these metals in solution. The concentrations of these free aquo ions in tin flotation pulps are many orders
of magnitude greater than those of the possible hydroxy and carbonato complexes of the cations.

Light scattering analyses performed in this research have shown unequivocally that the free aquo magnesium and calcium ions have little tendency to form insoluble precipitates with styryl phosphonic acid. Given the weak nature of any such interactions, it would be expected that magnesium and calcium ions would have a negligible effect on cassiterite flotation. Styryl phosphonic acid would adsorb far more strongly on the cassiterite surface and on aluminum and ferric hydrous oxide sols present in the flotation system. The conclusion that calcium and magnesium ions do not interfere in cassiterite flotation is strongly supported by the finding that industrial flotation is performed successfully in the presence of several hundred parts per million of these ions.

5.4 Mechanisms of Chemical Pretreatment Processes

Reference to several chemical pretreatment processes involving fluoride reagents can be found in the phosphonic acid flotation literature. Invariably these processes involve pretreating flotation feed with large additions (1.0–4.0 kg/t) of sodium fluorosilicate or other complexing reagents such as oxalic acid. After dewatering and repulping in ion free water, the ore is floated with phosphonic acid. Substantial increases in grade and recovery are claimed with these processes (Sections 2.5.3.5 and 2.5.3.6).

In the Renison cassiterite flotation circuit, fluoride reagents are used extensively. The plant experience is that, when direct additions of fluoride reagent are made to the flotation pulp, small additions improve selectivity with minimal effect on recovery, while large additions severely depress flotation. Similar effects have been reported at the Altenberg mine in the
German Democratic Republic (Wottgen and Topfer, 1976). However, in this circuit, pretreatment of flotation feed with relatively large quantities of fluoride with removal thereafter of solution, as claimed in the Wottgen, Neuber and Luft patent (1974), is reported to give remarkable increases in selectivity. No level of fluoride reagent addition directly to the flotation pulp evidently produces an equivalent effect. In the most recent published reference to the Altenberg pretreatment process (Mosch and Becker, 1985), it was claimed that the process produced 5 to 10 percent higher plant recovery and between 2 and 5 percent better grade.

It is apparent that in most cassiterite flotation circuits iron levels are such that the deleterious effects of excessive hydrous ferric oxide adsorption on mineral surfaces are pronounced. Considerable incentive consequently exists to reduce the total iron concentrations in these circuits. Technically, the simplest way to remove adsorbed sols from mineral surfaces, prior to cassiterite flotation, is to resolubilize them and then make a bulk solution rejection. This latter stage can be accomplished most easily in the cyclone desliming circuit that usually precedes tin flotation.

During the course of this research, it has been demonstrated that the resolubilization of hydrous ferric oxide sols adsorbed on mineral surfaces by direct suspension acidification is kinetically very slow (Figures 175 and 215). Significantly, it has been shown in both electrokinetic studies and leaching tests that the presence of fluoride in acidic suspensions enhances remarkably the kinetics of solubilization of contaminant surface iron from unleached cassiterite. It is hereby proposed that industrial pretreatment processes involve the solubilization under acidic conditions of adsorbed hydrous ferric oxide sols from the surfaces of minerals prior to cassiterite
flotation. Appreciable levels of fluoride bearing reagents are added during this solubilization stage to promote both the extent and kinetics of iron abstraction in the characteristic residence times of industrial flotation plants. A bulk rejection of this abstracted iron, in the form of strongly solvated ferric fluoro complexes, is then made in the water split of the desliming circuit that precedes flotation.

The solution chemical evidence supporting the proposed mechanism of pretreatment is considerable and no finding, in this work or elsewhere, refutes it. While it is acknowledged that the fluoride ion can adsorb specifically on many minerals, including cassiterite, no selective depressant mechanism can be correlated logically with the fundamental requirement of pretreatment processes that solution replacement be performed. Conversely, the finding of this research that strongly solvated ferric fluoro complexes interact and form insoluble precipitates with styryl phosphonic acid explains why this step is crucial in the pretreatment process. If fluoride reagents are added immediately prior to, or during flotation, the resulting solubilized iron will precipitate the collector. The well documented complete cessation of flotation in both the Renison and Altenberg circuits when large direct additions of fluoride are made is undoubtedly due to collector precipitation by ferric fluoro species. The small increases in selectivity achieved at low fluoride reagent additions presumably reflect the fact that such low concentrations are insufficient to cause significant resolubilization of hydrous ferric oxide sols but rather result in fluoride ions adsorbing on the sols and inhibiting the activating influence they exert on the flotation of certain gangue species.
It has been recognised almost from the inception of cassiterite flotation that fluoride reagent additions to mineral flotation pulps can increase soluble iron levels. Thus, as early as 1962, it was reported (Evans, Ewers and Meadows, 1962) that the concentration of ferric iron in a centrifuged cassiterite ore pulp increased remarkably when sodium fluorosilicate was added. However, it appears less well recognised that this abstracted iron was derived principally from hydrous ferric oxide sols adsorbed on mineral surfaces. Given this to be the case, the advantage of making the fluoride reagent additions to the desliming circuits of tin flotation plants is that the abstracted iron is rejected in the form of aqueous complexes to the slime tail due to the water split in the circuit. The pulp then re-equilibrates prior to phosphonic acid addition and flotation at conditions under which the iron and fluoride species are greatly diminished. The depressant effects which might otherwise be caused by collector precipitation with solubilized iron-fluoro complexes are thereby avoided.
CHAPTER 6

CONCLUSIONS

A significant number of conclusions have been reached on the basis of the research findings of this dissertation. These have been detailed in the closing sections of the Literature Review and at the end of each Results and Discussion section. The following represents a compilation of the most important conclusions as they pertain specifically to the surface properties of cassiterite in industrial flotation environments and the role of dissolved metal ions in the phosphonic acid flotation of the mineral.

(1) Iron films on the surface of cassiterite can profoundly influence the flotation of the mineral in the presence of styryl phosphonic acid. Most notably, such iron contaminated cassiterite exhibits a maximum microflotation response between pH 4.0 and 7.5. This response is strikingly different to that of purified cassiterite which floats most strongly between pH 2.0 and 3.0 and much less strongly in the slightly acidic to alkaline range.

(2) All aspects of the microflotation response of iron contaminated cassiterite and associated adsorption and electrokinetic behaviour are consistent with a mechanism whereby cassiterite surface iron produces an activating or depressant effect on flotation depending on the extent to which it is solubilized. In the slightly acidic to neutral pH range (pH > 5.0), such iron results in increased styryl phosphonic acid adsorption onto cassiterite thereby increasing the negative charge character of the mineral and strongly promoting its floatability. Conversely, in strongly acidic solutions the iron is solubilized and
forms aqueous complexes with the phosphonic acid. Adsorption and charge reversal are consequently diminished in such solutions. If sufficient iron is present, associated mineral floatability can be inhibited entirely at these low pH values. That there exists a very strong interaction between the hydroxy species of iron and styryl phosphonic acid has been verified independently in this research by light scattering measurements.

(3) The microflotation response of iron contaminated cassiterite at low styryl phosphonic acid concentrations corresponds remarkably with published vacuum flotation data for a range of natural cassiterites. In these data, it was established that optimum flotation response at low phosphonic acid levels occurred between pH 5.0 and 6.0. Conversely, the microflotation response of cassiterite, after leaching to remove the iron films, exhibits remarkable consistency with a large body of published data for which it was known that the cassiterite used was either an high purity sample not exposed to solutions containing dissolved metal ionic species or had been acid cleaned prior to test work. On the basis of these correlations, the hypothesis is advanced that the presence of surface iron films on certain test cassiterites is responsible for the two distinctly different flotation responses that have been reported in the fundamental literature on phosphonic acid cassiterite flotation. This hypothesis is strongly supported by a critical examination of the methods of sample preparation used by researchers reporting these two different flotation behaviours.

(4) Industrial cassiterite flotation pulps can contain high levels of dissolved metal ionic species including iron. Furthermore, the Eh and
pH of these pulps are typically such that a significant portion of this iron would be present in the form of hydrous ferric oxide sols. It has been demonstrated in this research that such sols adsorb strongly onto the surface of cassiterite. On the basis of these findings, it is proposed that hydrous ferric oxide adsorption on the surface of minerals is responsible for cassiterite flotation from ores, both in batch testing and actual industrial circuits, exhibiting little resemblance to that predicted on the basis of fundamental flotation and adsorption tests with single purified minerals and iron free solutions. In the slightly acidic pH range, the evidence is that these sols activate the flotation of cassiterite but deplete collector levels and increase gangue mineral recoveries. At low total iron levels an overall improvement in the flotation of cassiterite with respect to gangue minerals might occur. However, at higher iron levels, the effect is undoubtedly deleterious. Increased collector additions are required to compensate for surfactant adsorption onto iron sols attached to gangue minerals. This, in combination with activation of the more floatable gangue, reduces overall flotation selectivity. At low pH, the resolubilization of hydrous ferric oxide sols and associated collector precipitation in bulk solution most probably causes the dramatic and complete cessation of flotation frequently reported in industrial circuits.

Surface analyses of cassiterite grains recovered from the tin concentrator of the Renison mine have confirmed the presence of iron films consistent in every respect with the previous adsorption of hydrous ferric oxide sols onto the mineral surface in the plant.
environment. The changes in the XPS spectrum of uncontaminated cassiterite, produced by sol adsorption, were independently shown to correlate completely with the spectral features of the cassiterite recovered from the Renison plant.

(6) The presence of iron films on cassiterite recovered from the Renison plant was found not to change significantly the electrokinetic properties of the cassiterite, as is known to be the case for other insoluble oxide minerals in the presence of freshly precipitated hydrolyzed metal ionic species. This was established to be a direct consequence of the drying of the cassiterite.

(7) The addition of sodium fluoride to strongly acidic (pH < 4.0) suspensions of unleached Renison cassiterite resulted in the appearance of striking negative-to-positive charge reversals in the range pH 4.5 to 6.5 when base subsequently was added. All aspects of these charge reversal effects were consistent with the solubilization of the iron films associated with the unleached cassiterite surface under acidic conditions followed by re-adsorption of freshly precipitated hydrous ferric oxide sols at higher pH values. In accord with the electrokinetic data, leaching tests confirmed independently that the presence of fluoride in acidic suspensions enhances significantly the kinetics of solubilization of contaminant surface iron from unleached cassiterite.

(8) Based on the finding that the fluoride ion significantly promotes the solubilization of surface iron entities under acidic conditions, the hypothesis is advanced that industrially successful pretreatment processes involve the solubilization, under acidic conditions, of
adsorbed hydrous ferric oxide sols from the surface of minerals prior to cassiterite flotation. Appreciable levels of fluoride bearing reagents are added during this solubilization stage to promote both the extent and kinetics of iron abstraction in the residence times characteristic of industrial flotation plants. A bulk rejection of this abstracted iron, in the form of strongly solvated ferric fluoro complexes, is then made in the water split of the desliming circuit that precedes flotation. The solution chemical evidence obtained supporting such a mechanism is considerable and no finding, in this work or elsewhere, refutes any aspect of its formulation.

In the pH range typical of commercial cassiterite flotation (pH 4.5 to 7.0), aluminum exists predominantly in the form of hydrous oxide sols. These sols adsorb strongly onto the surface of cassiterite and form particularly stable complexes with styryl phosphonic acid. As such, they can potentially influence the flotation of cassiterite with this surfactant in a similar manner to the hydrous oxide sols of the ferric ion.

Under the pH conditions of cassiterite flotation, the aquo magnesium and calcium ions are the predominant species of these metals in solution. While industrial cassiterite flotation pulps can contain very high levels of both of these ions, they have little tendency to form insoluble precipitates with styryl phosphonic acid. The evidence is that they do not interfere seriously with the flotation of cassiterite with phosphonic acids.
CHAPTER 7

RECOMMENDATIONS FOR FURTHER RESEARCH

A myriad of possibilities for further research into cassiterite flotation exist. However, on the basis of the findings of this dissertation it is considered that additional studies principally are required to elucidate further:

(i) the mechanism of styryl phosphonic acid chemisorption onto cassiterite, and

(ii) the role of hydrous ferric oxide sol adsorption in the flotation of cassiterite from multi-mineral systems under the turbulent conditions of industrial flotation.

Since the publications of Wottgen and Dietze, enormous progress has been made in the field of infrared spectrophotometry. Highly sensitive reflection-absorption techniques have been developed that allow in-situ analyses to be performed. The advent of Fourier Transform infrared has further allowed peak resolutions to be achieved that were not possible previously. Given these advances, there is considerable likelihood that an unambiguous identification of the nature of styryl phosphonic acid species that adsorb on cassiterite surfaces in aqueous solutions can be made. Furthermore, it might be possible to determine the nature of the pronounced increase in adsorption that occurs in acidic solutions below pH 4.0. Specifically, it would be of interest to establish if neutral molecule coadsorption occurs in this pH range.

In previous discussions on the implications of this research, it was emphasized that flotation in multi-mineral systems is far more complex than in single mineral studies. The analyses presented at that time led unavoidably
to the conclusion that there might exist an optimum surface iron coverage of minerals for which the flotation of cassiterite is improved with respect to certain gangue species such as quartz. To test the validity of this hypothesis, it is recommended that phosphonic acid batch flotation tests on binary mixtures of pure cassiterite and quartz, in the presence and absence of ferric ion additions, be conducted. Ideally, these tests should be performed using the batch flotation techniques developed and used so successfully by Trahar and associates (Heyes and Trahar, 1977; Heyes and Trahar, 1979; Heyes and Trahar, 1984; Trahar, 1984; Guy and Trahar, 1984; Shannon and Trahar, 1986) in elucidating the fundamental nature of sulphide mineral flotation. If selective activation can be verified, the test work logically can be extended to establish the underlying mechanisms of the activation phenomenon and to assess its importance with regard to other mineral mixtures and ores.
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APPENDIX A

GIBBS FREE ENERGY DATA
Stability constants for aqueous polyvalent cationic species and their complexes have been reported by numerous researchers. However, in many cases conflicting data exist or the data lack internal consistency (Sillén and Martell, 1971). Such data inconsistencies can lead to problems in distribution and Pourbaix diagram construction. In the case of Pourbaix diagrams, the problem manifests itself in terms of difficulties in 'line eliminations' and the existence of phase regions in which the stable species cannot be identified.

The problems associated with stability constant inconsistencies can be avoided by the use of Gibbs free energy data to calculate required thermodynamic constants. Gibbs free energy of formation for many of the species of importance in cassiterite flotation pulps are tabulated in standard references (Sylva, 1972; Weast and Astle, 1983). However, data for other species are not available.

Table XXII presents a compilation of Gibbs free energy of formation data for all species of interest in cassiterite flotation, for which reliable thermodynamic data exist. The values of Sylva and Weast and Astle are reported directly. Values for other species have been calculated from reported stability constants and stability products. Data from critical reviews of thermodynamic constants, such as those of Baes and Mesmer (1976) and Snoeyink and Jenkins (1980), have been used wherever possible.
TABLE XXII
VALUES OF GIBBS FREE ENERGY OF FORMATION FOR SPECIES OF IMPORTANCE IN CASSITERITE FLOTATION PULPS

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta G^\circ_f ) (kJ/mol)</th>
<th>Reference</th>
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<tr>
<td>( \text{H}_2\text{O} )</td>
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<td>Weast and Astle (1983)</td>
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<td>( \text{OH}^- )</td>
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TABLE XXII (cont.)

VALUES OF GIBBS FREE ENERGY OF FORMATION FOR SPECIES
OF IMPORTANCE IN CASSITERITE FLOTATION PULPS

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APPENDIX B

THERMODYNAMIC CALCULATIONS
B.1 Concentration - pH Stability Equations

(A) Aluminum Hydrolysis

The stable hydrolysis species of Al(III) are the mononuclear species Al(OH)\(^{2+}\), Al(OH)\(^{2-}\), Al(OH)\(_{3(aq)}\), Al(OH)\(^{-}\) and the polynuclear species Al\(_2\)(OH)\(_{2}\)(aq), Al\(_3\)(OH)\(_5^+\) and Al\(_{13}\)O\(_4\)(OH)\(_{24}\)^{7+} (Baes and Mesmer, 1976). The relative stabilities of each of these species can be illustrated conveniently by using a concentration - pH diagram. To plot such a diagram requires that the concentration of each species be expressed in terms of Al(III), H\(^+\) and Al(OH)\(_{3(aq)}\) concentrations. The activity of the solid Al(OH)\(_{3(aq)}\) is assumed to be unity so that the equilibrium constant is then in terms of only Al(III) and H\(^+\). For example,

\[\text{Al}^{3+} + 3\text{OH}^- \rightleftharpoons \text{Al(OH)}_{3(aq)} \quad \text{K} = 10^{-32.3}\]

\[
\begin{align*}
\log [\text{Al}^{3+}] & - 3 \log [\text{OH}^-] = -32.3 \\
\log [\text{Al}^{3+}] & + 3(\text{pH} - 14) = -32.3 \\
\log [\text{Al}^{3+}] & = -3\text{pH} + 9.7
\end{align*}
\]

Similarly,

\[
\begin{align*}
\text{Al}^{3+} + \text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}^{2-} + \text{H}^+ \\
\log [\text{Al(OH)}^{2-}] & = -2\text{pH} + 4.73 \\
\text{Al}^{3+} + 2\text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}^{2+} + 2\text{H}^+ \\
\log [\text{Al(OH)}^{2+}] & = -\text{pH} + 0.4 \\
\text{Al}^{3+} + 3\text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}_3 + 3\text{H}^+ \\
\log [\text{Al(OH)}_3] & = -5.3 \\
\text{Al}^{3+} + 4\text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}^{-} + 4\text{H}^- \\
\log [\text{Al(OH)}^{-}] & = \text{pH} - 13.3 \\
2\text{Al}^{3+} + 2\text{H}_2\text{O} & \rightleftharpoons \text{Al}_2\text{(OH)}^{2+} + 2\text{H}^+ \\
\log [\text{Al}_2\text{(OH)}^{2+}] & = -4\text{pH} + 11.7 \\
3\text{Al}^{3+} + 4\text{H}_2\text{O} & \rightleftharpoons \text{Al}_3\text{(OH)}^{5+} + 4\text{H}^- \\
\log [\text{Al}_3\text{(OH)}^{5+}] & = -5\text{pH} + 15.2 \\
13\text{Al}^{3+} + 28\text{H}_2\text{O} & \rightleftharpoons \text{Al}_{13}\text{O}_4\text{(OH)}^{24\text{7+}} + 32\text{H}^- \\
\log [\text{Al}_{13}\text{O}_4\text{(OH)}^{24\text{7+}}] & = -7\text{pH} + 27.4.
\end{align*}
\]
(B) **Ferric Iron Hydrolysis**

\[
\begin{align*}
\text{Fe(OH)}_3^{(aq)} & \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^- \\
\log [\text{Fe}^{3+}] &= -3\text{pH} + 3.5 \\
\text{Fe(OH)}_3^{(aq)} & \rightleftharpoons \text{Fe(OH)}^2+ + 2\text{OH}^- \\
\log [\text{Fe(OH)}^2+] &= -2\text{pH} + 0.5 \\
\text{Fe(OH)}_3^{(aq)} & \rightleftharpoons \text{Fe(OH)}^2+ + \text{OH}^- \\
\log [\text{Fe(OH)}^2+] &= -\text{pH} - 2.9 \\
\text{Fe(OH)}_3^{(aq)} + \text{OH}^- & \rightleftharpoons \text{Fe(OH)}_4^- \\
\log [\text{Fe(OH)}_4^-] &= \text{pH} - 19.9 \\
2\text{Fe}^{3+} + 2\text{H}_2\text{O} & \rightleftharpoons \text{Fe}_2\text{(OH)}_2^{4+} + 2\text{H}^+ \\
\log [\text{Fe}_2\text{(OH)}_2^{4+}] &= -4\text{pH} + 4.1 \\
3\text{Fe}^{3+} + 4\text{H}_2\text{O} & \rightleftharpoons \text{Fe}_3\text{(OH)}_5^{5+} + 4\text{H}^+ \\
\log [\text{Fe}_3\text{(OH)}_5^{5+}] &= -5\text{pH} + 4.7
\end{align*}
\]

(C) **Magnesium Hydrolysis**

\[
\begin{align*}
\text{Mg(OH)}_2^{(aq)} & \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \\
\log [\text{Mg}^{2+}] &= -2\text{pH} + 16.9 \\
\text{Mg}^{2+} + \text{H}_2\text{O} & \rightleftharpoons \text{Mg(OH)}^+ + \text{H}^+ \\
\log [\text{Mg(OH)}^+] &= -\text{pH} + 4.90 \\
4\text{Mg}^{2+} + 4\text{H}_2\text{O} & \rightleftharpoons \text{Mg}_4\text{(OH)}_4^{4+} + 4\text{H}^+ \\
\log [\text{Mg}_4\text{(OH)}_4^{4+}] &= -4\text{pH} + 27.7
\end{align*}
\]

(D) **Calcium Hydrolysis**

\[
\begin{align*}
\text{Ca(OH)}_2^{(aq)} & \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^- \\
\log [\text{Ca}^{2+}] &= -2\text{pH} + 22.8 \\
\text{Ca}^{2+} + \text{H}_2\text{O} & \rightleftharpoons \text{Ca(OH)}^+ + \text{H}^+ \\
\log [\text{Ca(OH)}^+] &= -\text{pH} + 10.1
\end{align*}
\]

(E) **Magnesium Carbonato Complexes**

\[
\begin{align*}
\text{MgCO}_3^{(aq)} & \rightleftharpoons \text{Mg}^{2+} + \text{CO}_3^{2-} \\
\log [\text{CO}_3^{2-}] &= 2\text{pH} - 22.0 \\
\text{MgCO}_3^{(aq)} & \rightleftharpoons \text{Mg}^{2+} + \text{CO}_3^{2-} \\
\log [\text{MgCO}_3^{(aq)}] &= -1.70 \\
\text{Mg(HCO}_3)^+ & \rightleftharpoons \text{Mg}^{2+} + \text{HCO}_3^- \\
\log [\text{Mg(HCO}_3)^+] &= -\text{pH} + 6.36 \\
\text{Mg}^{2+} + 2\text{HCO}_3^- & \rightleftharpoons \text{Mg(HCO}_3)_2^{(aq)} \\
\log [\text{Mg(HCO}_3)_2^{(aq)}] &= -5.44
\end{align*}
\]
(F) **Calcium Carbonato Complexes**

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}
\]
\[
\log [\text{CO}_3^{2-}] = 2\text{pH} - 31.16
\]

\[
\text{CaCO}_3(aq) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}
\]
\[
\log [\text{CaCO}_3(aq)] = -8.3
\]

\[
\text{Ca(HCO}_3\text{)}^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-
\]
\[
\log [\text{Ca(HCO}_3\text{)}^+] = -\text{pH} + 3.20
\]

(G) **Fluoro Complexes**

\[
\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-
\]
\[
\log [\text{F}^-] = \text{pH} - 16.60
\]

\[
\text{Ca}^{2+} + \text{F}^- \rightleftharpoons \text{CaF}^+
\]
\[
\log [\text{CaF}^+] = -\text{pH} + 7.20
\]
B.2 Distribution Diagrams

(A) Aluminum Hydrolysis

The stable hydrolysis species of Al(III) are the mononuclear species Al(OH)$_2^+$, Al(OH)$_2^+$, Al(OH)$_3^{aq}$, and Al(OH)$_4^-$ and the polynuclear species Al$_3$(OH)$_2^+$, Al$_3$(OH)$_4^{5-}$ and Al$_{13}$O$_4$(OH)$_{24}^{7-}$ (Baes and Mesmer, 1976). Therefore,

$$[\text{Al(III)}]_T = [\text{Al}^3^+] + [\text{Al(OH)}^2^+] + [\text{Al(OH)}^2^+] + [\text{Al(OH)}^3^+] + [\text{Al(OH)}^4^-] + 2[\text{Al}_2(\text{OH})^4^+] + 3[\text{Al}_3(\text{OH})^4^{5-}] + 13[\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7-}]$$

or, in terms of reaction stability constants:

$$[\text{Al(III)}]_T = [\text{Al}^3^+] (1 + \frac{^*K_1}{[\text{H}^+]^1} + \frac{^*K_2}{[\text{H}^+]^2} + \frac{^*K_3}{[\text{H}^+]^3} + \frac{^*K_4}{[\text{H}^+]^4} + 2 \frac{^*K_{22}}{[\text{H}^+]^2} \cdot [\text{Al}]^3^+ + 3 \frac{^*K_{23}}{[\text{H}^+]^3} \cdot [\text{Al}^3^+]^2 + 13 \frac{^*K_{28,13}}{[\text{H}^+]^{32}} \cdot [\text{Al}^3^+]^{12})$$

$$= [\text{Al}^3^+] (1 + 10^{(\text{pH} - 4.97)} + 10^{(2\text{pH} - 9.3)} + 10^{(3\text{pH} - 15.0)} + 10^{(4\text{pH} - 23.0)} + 2\{10^{(2\text{pH} - 7.7)}\} [\text{Al}^3^+] + 3\{10^{(4\text{pH} - 13.9)}\} [\text{Al}^3^+]^2 + 13\{10^{(32\text{pH} - 98.7)}\} [\text{Al}^3^+]^{12})$$

For any pH and $[\text{Al(III)}]_T$, the equilibrium concentration for all participating Al(III) species can be computed. The quantitative evaluation of the equations that determine the equilibrium concentrations of a solution constitutes a purely mathematical problem that is subject to exact and mathematical treatment.

Table XXIII shows the percentages of each Al(III) species present in the range pH 1.0 - 6.0 for total Al(III) concentrations of 5 X 10$^{-6}$ M and 2 X 10$^{-4}$ M. These aluminum ion concentrations represent the limits of the range of concentrations found in an analysis of Renison cassiterite flotation waters.
Solutions of the polynomial equation in $[\text{Al}^{3+}]$ were obtained using the U.B.C. Computing Department program DZFUN which is designed to find the real zeros of a nonlinear function of one variable.

**TABLE XXIII**

**DISTRIBUTION OF ALUMINUM ION HYDROLYSIS SPECIES**

<table>
<thead>
<tr>
<th>$[\text{Al(III)}]_T$</th>
<th>pH</th>
<th>Mole Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{Al}^{3+}$</td>
</tr>
<tr>
<td>5x10$^{-6}$ M (0.1 ppm)</td>
<td>1.0</td>
<td>99.98</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>99.97</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>99.89</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>99.66</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>98.89</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>96.25</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>86.33</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>53.43</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>12.37</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.07</td>
</tr>
<tr>
<td>2x10$^{-4}$ M (5.4 ppm)</td>
<td>1.0</td>
<td>99.99</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>99.97</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>99.89</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>99.66</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>98.89</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>96.25</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>86.32</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>53.40</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>12.37</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.07</td>
</tr>
</tbody>
</table>
(B) Ferric Iron Hydrolysis

\[
[\text{Fe(III)}]_T = [\text{Fe}^{3+}] + [\text{Fe(OH)}^{2+}] + [\text{Fe(OH)}_{2}^{-}] + [\text{Fe(OH)}_{3}] + [\text{Fe(OH)}_{4}^{-}] + 2[\text{Fe}_2(\text{OH})_{2}^{4+}] + 3[\text{Fe(OH)}_{5}^{-}]
\]

\[
= [\text{Fe}^{3+}] \left( 1 + \frac{\beta_1}{[H^+]} + \frac{\beta_2}{[H^+]^2} + \frac{\beta_3}{[H^+]^3} + \frac{\beta_4}{[H^+]^4} + 2 \frac{\beta_{22}}{[H^+]^2} [\text{Fe}^{3+}] + 3 \frac{\beta_{34}}{[H^+]^4} [\text{Fe}^{3+}]^2 \right)
\]

\[
= [\text{Fe}^{3+}] \left( 1 + 10^{(\text{pH} - 3.0)} + 10^{(2\text{pH} - 6.3)} + 10^{(3\text{pH} - 11.4)} + 10^{(4\text{pH} - 23.3)} + 2(10^{(2\text{pH} - 2.9)}) [\text{Fe}^{3+}] + 3(10^{(4\text{pH} - 5.8)}) [\text{Fe}^{3+}]^2 \right)
\]

Solutions of the cubic polynomial equation in \([\text{Fe}^{3+}]\) are given in Table XXIV.

(C) Magnesium Hydrolysis

\[
[\text{Mg(II)}]_T = [\text{Mg}^{2+}] + [\text{Mg(OH)}^{-}] + [\text{Mg}_4(\text{OH})_{4}^{4-}]
\]

\[
= [\text{Mg}^{2+}] \left( 1 + \frac{\beta_1}{[H^+]} + 4 \frac{\beta_{24}}{[H^+]^4} [\text{Mg}^{2+}]^3 \right)
\]

\[
= [\text{Mg}^{2+}] \left( 1 + 10^{(\text{pH} - 12.0)} + 4(10^{(4\text{pH} - 39.7)}) [\text{Mg}^{2+}]^3 \right)
\]

Table XXV shows the percentages of each Mg(II) species present in the range pH 1.0 - 6.0 for total Mg(II) concentrations of 2 X 10^{-3} M and 2 x 10^{-2} M.
Table XXIV

DISTRIBUTION OF FERRIC ION HYDROLYSIS SPECIES

<table>
<thead>
<tr>
<th>[Fe(III)]_T</th>
<th>pH</th>
<th>Mole Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe³⁺</td>
</tr>
<tr>
<td>5x10⁻⁶ M</td>
<td>1.0</td>
<td>99.01</td>
</tr>
<tr>
<td>(0.3 ppm)</td>
<td>1.5</td>
<td>96.89</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>90.50</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>73.13</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>39.84</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>10.74</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.01</td>
</tr>
<tr>
<td>1x10⁻³ M</td>
<td>1.0</td>
<td>98.98</td>
</tr>
<tr>
<td>(55.9 ppm)</td>
<td>1.5</td>
<td>96.66</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>88.68</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>64.56</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>27.94</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>7.31</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg(II)(_T)</td>
<td>pH</td>
<td>Mole Percent</td>
</tr>
<tr>
<td>----------</td>
<td>----</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg(^{2+})</td>
</tr>
<tr>
<td>2x10(^{-3}) M</td>
<td>1.0</td>
<td>100.00</td>
</tr>
<tr>
<td>(48.6 ppm)</td>
<td>2.0</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>99.99</td>
</tr>
<tr>
<td></td>
<td>9.0</td>
<td>99.90</td>
</tr>
<tr>
<td></td>
<td>9.5</td>
<td>99.68</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>99.01</td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td>96.93</td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>90.91</td>
</tr>
</tbody>
</table>

| 2x10\(^{-2}\) M | 1.0 | 100.00 | - | - |
| (486.2 ppm) | 2.0 | 100.00 | - | - |
|          | 3.0 | 100.00 | - | - |
|          | 4.0 | 100.00 | - | - |
|          | 5.0 | 100.00 | - | - |
|          | 6.0 | 100.00 | - | - |
|          | 7.0 | 100.00 | - | - |
|          | 8.0 | 99.99 | 0.01 | - |
|          | 9.0 | 99.90 | 0.10 | - |
|          | 9.5 | 99.69 | 0.32 | - |
|          | 10.0 | 99.01 | 0.99 | - |
|          | 10.5 | 96.93 | 3.07 | - |
|          | 11.0 | 90.87 | 9.09 | - |
(D) **Stannic Ion Hydrolysis**

\[
[\text{Sn(IV)}]_T = [\text{Sn}^{4+}] + [\text{Sn(OH)}^3_] + [\text{Sn(OH)}_2^{2+}] + [\text{Sn(OH)}_3^+] + [\text{Sn(OH)}_4] \\
= [\text{Sn}^{4+}] \left(1 + \frac{K_1}{[\text{H}^+]} + \frac{K_2}{[\text{H}^+]^2} + \frac{K_3}{[\text{H}^+]^3} + \frac{K_4}{[\text{H}^+]^4}\right) \\
= [\text{Sn}^{4+}] \left(1 + 10^{(\text{pH}-0.3)} + 10^{(2\text{pH}-1.1)} + 10^{(3\text{pH}-0.4)} + 10^{4\text{pH}}\right)
\]

Table XXVI shows the percentages of each Sn(IV) species present in the range pH -1.5 to 3.5 for a total Sn(IV) concentration of \(4 \times 10^{-7}\) M. This concentration represents the solubility limit of cassiterite as measured by Barsukov and Klintsova (1970).

### TABLE XXVI

**DISTRIBUTION OF STANNIC ION HYDROLYSIS SPECIES**

<table>
<thead>
<tr>
<th>Sn(IV)(_T)</th>
<th>pH</th>
<th>Sn(^{4+})</th>
<th>Sn(OH(^3+)</th>
<th>Sn(OH(^2+)</th>
<th>Sn(OH(^3+)</th>
<th>Sn(OH(^4+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4 \times 10^{-7}) M</td>
<td>-1.5</td>
<td>98.4</td>
<td>1.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.0</td>
<td>95.1</td>
<td>4.8</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-0.5</td>
<td>84.1</td>
<td>13.3</td>
<td>0.7</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>33.6</td>
<td>16.8</td>
<td>2.7</td>
<td>13.4</td>
<td>33.6</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.9</td>
<td>1.4</td>
<td>0.7</td>
<td>10.9</td>
<td>86.2</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>3.8</td>
<td>96.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>99.6</td>
</tr>
</tbody>
</table>
(E) Carbonate System

The chemical species that make up the carbonate system are gaseous \( \text{CO}_2 \), \( \text{CO}_2(g) \); aqueous or dissolved \( \text{CO}_2 \), \( \text{CO}_2(aq) \); carbonic acid, \( \text{H}_2\text{CO}_3 \); bicarbonate, \( \text{HCO}_3^- \) and carbonate, \( \text{CO}_3^{2-} \).

Assuming a closed system, i.e. only solution equilibria:

\[
\begin{align*}
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

\[
K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \implies [\text{HCO}_3^-] = \frac{[\text{H}_2\text{CO}_3]}{[\text{H}^+]} K_1
\]

\[
K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \implies [\text{CO}_3^{2-}] = [\text{HCO}_3^-] \frac{K_2}{[\text{H}^+]} = [\text{H}_2\text{CO}_3] \frac{K_1 K_2}{[\text{H}^+]^2}
\]

Mass balance:

\[
F = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]
\]

\[
= [\text{H}_2\text{CO}_3] \left(1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2}\right)
\]

The fraction of carbonate species in the form \( \text{H}_2\text{CO}_3 \) can be described as \( \alpha_0 \), the fraction in the form \( \text{HCO}_3^- \) as \( \alpha_1 \) and the fraction in the form \( \text{CO}_3^{2-} \) as \( \alpha_2 \). From the definition of \( \alpha_0 \):

\[
\alpha_0 = \frac{[\text{H}_2\text{CO}_3]}{F} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2}
\]

Similarly,

\[
\alpha_1 = \frac{[\text{HCO}_3^-]}{F} = \frac{K_1[\text{H}^+]}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2}
\]

\[
\alpha_2 = \frac{[\text{CO}_3^{2-}]}{F} = \frac{K_1 K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2}
\]

Calculation of the stability constants \( K_1 \) and \( K_2 \) consequently allows the fraction of each species to be determined for any given pH.
B.3 Pourbaix (Eh – pH) Diagrams

(A) Fe – H₂O System

The stability (or instability) of dissolved iron species in aqueous solution of selected composition can be summarized by means of an Eh – pH diagram. The following equations are the contours in the Eh – pH diagram for the Fe – H₂O system at 25°C and 1 atmosphere total pressure.

\[ \text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+} \]

Reaction quotient \( Q = \frac{\{\text{Fe}^{2+}\}}{\{\text{Fe}^{3+}\}e^-} \)

\[ \log Q = \log \{\text{Fe}^{2+}\} - \log \{\text{Fe}^{3+}\} - \log e^- \]

At equilibrium, \( \log Q = \log K \)

\[ \log K = \log \{\text{Fe}^{2+}\} - \log \{\text{Fe}^{3+}\} + pE \]

\[ pE = \frac{Eh}{0.059} = \log K + \log \frac{\{\text{Fe}^{3+}\}}{\{\text{Fe}^{2+}\}} \]

\[ Eh = 0.768 + 0.059 \log \frac{\{\text{Fe}^{3+}\}}{\{\text{Fe}^{2+}\}} \quad [1] \]

Similarly,

\[ \text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}^{2+} + \text{H}^+ \]

\[ \text{pH} = 3.01 + \log \frac{\{\text{Fe(OH)}^{2+}\}}{\{\text{Fe}^{3+}\}} \quad [2] \]

\[ 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+ \]

\[ \text{pH} = 0.73 + 0.5 \log \frac{\{\text{Fe}_2(\text{OH})_2^{4+}\}}{\{\text{Fe}^{3+}\}^2} \quad [3] \]

\[ \text{Fe(OH)}^{2+} + \text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_2^{4+} + \text{H}^+ \]

\[ \text{pH} = 0.09 + \log \frac{\{\text{Fe}_2(\text{OH})_2^{4+}\}}{\{\text{Fe}^{3+}\}\{\text{Fe}^{2+}\}} \quad [4] \]

\[ \text{Fe(OH)}^{2+} + e^- + \text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2\text{O} \]

\[ Eh = 0.950 - 0.059 \text{ pH} + 0.059 \log \frac{\{\text{Fe(OH)}^{2+}\}}{\{\text{Fe}^{2+}\}} \quad [5] \]
\[
\begin{align*}
\text{Fe(OH)}^{2+} + H_2O & \rightleftharpoons \text{Fe(OH)}_2^{-} + H^+ \\
\text{pH} &= 3.29 + \log \frac{[\text{Fe(OH)}_2^-]}{[\text{Fe(OH)}^{2+}]} \quad [6] \\
\text{Fe(OH)}^{2+} + 2H_2O & \rightleftharpoons \text{Fe(OH)}_3(aq) + 2H^+ \\
\text{pH} &= 0.21 - 0.5 \log [\text{Fe(OH)}^{2+}] \quad [7] \\
\text{Fe(OH)}_2^+ + H_2O & \rightleftharpoons \text{Fe(OH)}_3(aq) + H^+ \\
\text{pH} &= -2.87 - \log [\text{Fe(OH)}_2^+] \quad [8] \\
\text{Fe(OH)}_3(aq) + 3H^+ & \rightarrow \text{Fe}^{3+} + 3H_2O \\
\text{pH} &= 1.143 - 0.333 \log [\text{Fe}^{3+}] \quad [9] \\
\text{Fe}^{2+} + H_2O & \rightarrow \text{Fe(OH)}^+ + H^+ \\
\text{pH} &= 8.6 - \log \frac{[\text{Fe(OH)}^+]}{[\text{Fe}^{2+}]} \quad [10] \\
\text{Fe(OH)}^+ + H_2O & \rightleftharpoons \text{Fe(OH)}_2(aq) + H^+ \\
\text{pH} &= 3.0 - \log [\text{Fe(OH)}^+] \quad [11] \\
\text{Fe}^{2+} + 2H_2O & \rightleftharpoons \text{Fe(OH)}_2(aq) + 2H^+ \\
\text{pH} &= 5.815 - 0.5 \log [\text{Fe}^{2+}] \quad [12] \\
\text{Fe(OH)}^+ + 2H_2O & \rightleftharpoons \text{Fe(OH)}_3(aq) + 2H^+ + e^- \\
\text{Eh} &= 0.814 - 0.118 \text{ pH} \quad [13] \\
\text{Fe(OH)}_2(aq) + H_2O & \rightleftharpoons \text{Fe(OH)}_3(aq) + H^+ + e^- \\
\text{Eh} &= 0.284 - 0.059 \text{ pH} \quad [14] \\
\text{Fe}^{2+} + 3H_2O & \rightleftharpoons \text{Fe(OH)}_3(aq) + 3H^+ + e^- \\
\text{Eh} &= 0.971 - 0.177 \text{ pH} - 0.059 \log [\text{Fe}^{2+}] \quad [15]
\end{align*}
\]
(B) \textbf{Fe} - \textbf{CO}_3 - \textbf{H}_2\text{O} \text{ System}

In addition to the \textbf{Fe} - \textbf{H}_2\text{O} system equilibria set out above, the following reactions also must be considered in the \textbf{Fe} - \textbf{CO}_3 - \textbf{H}_2\text{O} system:

\begin{align*}
\text{HCO}_3^- + H^+ & \rightleftharpoons H_2\text{CO}_3 \\
pH &= 6.36 \quad [16] \\
\text{FeCO}_3^{(aq)} + 2H^+ & \rightleftharpoons \text{Fe}^{2+} + H_2\text{CO}_3 \\
pH &= 3.12 - 0.5 \log \{\text{Fe}^{2+}\}\{H_2\text{CO}_3\} \quad [17] \\
\text{FeCO}_3^{(aq)} + H^+ & \rightleftharpoons \text{Fe}^{2+} + \text{HCO}_3^- \\
pH &= -0.12 - \log \{\text{Fe}^{2+}\}\{\text{HCO}_3^-\} \quad [18] \\
\text{Fe(OH)}_3^{(aq)} + \text{H}_2\text{CO}_3 + H^+ + e^- & \rightleftharpoons \text{FeCO}_3^{(aq)} + 3\text{H}_2\text{O} \\
Eh &= 0.603 - 0.059pH + 0.059 \log \{\text{H}_2\text{CO}_3\} \quad [19] \\
\text{Fe(OH)}_3^{(aq)} + \text{HCO}_3^- + 2H^+ + e^- & \rightleftharpoons \text{FeCO}_3^{(aq)} + 3\text{H}_2\text{O} \\
Eh &= 0.978 - 0.118pH + 0.059 \log \{\text{HCO}_3^-\} \quad [20]
\end{align*}

(C) \textbf{Fe} - \textbf{F} - \textbf{H}_2\text{O} \text{ System}

\begin{align*}
H^+ + F^- & \rightleftharpoons HF \\
pH &= 2.94 \quad [21] \\
\text{Fe}^{3+} + HF & \rightleftharpoons \text{FeF}^{2+} + H^+ \\
pH &= -2.26 + \log \frac{\{\text{FeF}^{2+}\}}{\{\text{Fe}^{3+}\}\{HF\}} \quad [22] \\
\text{FeF}^{2+} + HF & \rightleftharpoons \text{FeF}_2^{2+} + H^+ \\
pH &= -1.00 + \log \frac{\{\text{FeF}_2^{2+}\}}{\{\text{FeF}^{2+}\}\{HF\}} \quad [23] \\
\text{FeF}^{2+} + \text{H}_2\text{O} & \rightleftharpoons \text{Fe(OH)}^{2+} + H^+ + F^- \\
pH &= 8.22 + \log \frac{\{\text{Fe(OH)}^{2+}\}\{F^-\}}{\{\text{FeF}^{2+}\}} \quad [24]
\end{align*}
\[
\text{FeF}_2^\text{+} + \text{HF} \rightleftharpoons \text{FeF}_3 + \text{H}^+
\]

\[
\text{pH} = 0.11 + \log \frac{[\text{FeF}_3]}{[\text{FeF}_2^\text{+}] \cdot [\text{HF}]}
\]  \[25\]

\[
\text{FeF}_2^\text{+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}^2\text{+} + \text{H}^+ + 2\text{F}^-
\]

\[
\text{pH} = 12.16 + \log \frac{[\text{Fe(OH)}^2\text{+}] \cdot [\text{F}^-]^2}{[\text{FeF}_2^\text{+}]}
\]  \[26\]

\[
\text{FeF}^2\text{+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 3\text{H}^+ + \text{F}^-
\]

\[
\text{pH} = 2.88 + 0.333 \log \frac{[\text{F}^-]}{[\text{FeF}^2\text{+}]}
\]  \[27\]

\[
\text{FeF}_2^\text{+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 3\text{H}^+ + 2\text{F}^-
\]

\[
\text{pH} = 4.19 + 0.333 \log \frac{[\text{F}^-]^2}{[\text{FeF}_2^\text{+}]}
\]  \[28\]

\[
\text{FeF}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}^2\text{+} + \text{H}^+ + 3\text{F}^-
\]

\[
\text{pH} = 15.00 + \log \frac{[\text{Fe(OH)}^2\text{+}] \cdot [\text{F}^-]^3}{[\text{FeF}_3]}
\]  \[29\]

\[
\text{FeF}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 3\text{H}^+ + 3\text{F}^-
\]

\[
\text{pH} = 5.14 + 0.333 \log \frac{[\text{F}^-]^3}{[\text{FeF}_3]}
\]  \[30\]

\[
\text{FeF}^2\text{+} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}^{2\text{+}} + \text{HF}
\]

\[
\text{Eh} = 0.63 - 0.059\text{pH} - 0.059 \log \frac{[\text{Fe}^{2\text{+}}] \cdot [\text{HF}]}{[\text{FeF}^2\text{+}]}
\]  \[31\]

\[
\text{FeF}_2^\text{+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}^{2\text{+}} + 2\text{HF}
\]

\[
\text{Eh} = 0.576 - 0.118\text{pH} - 0.059 \log \frac{[\text{Fe}^{2\text{+}}]^2 \cdot [\text{HF}]}{[\text{FeF}_2^\text{+}]}
\]  \[32\]

\[
\text{FeF}_2^\text{+} + \text{e}^- \rightleftharpoons \text{Fe}^{2\text{+}} + 2\text{F}^-
\]

\[
\text{Eh} = 0.228 + 0.059 \log \frac{[\text{FeF}^2\text{+}]}{[\text{Fe}^{2\text{+}}] \cdot [\text{F}^-]^2}
\]  \[33\]

\[
\text{FeF}_3 + 3\text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}^{2\text{+}} + 3\text{HF}
\]

\[
\text{Eh} = 0.582 - 0.177\text{pH} - 0.059 \log \frac{[\text{Fe}^{2\text{+}}]^3 \cdot [\text{HF}]}{[\text{FeF}_3]}
\]  \[34\]
\[ \text{FeF}_3 + e^- \rightleftharpoons \text{Fe}^{2+} + 3\text{F}^- \]

\[ \text{Eh} = 0.061 - 0.059 \log \frac{\left[\text{Fe}^{2+}\right] \left[\text{F}^-\right]^3}{[\text{FeF}_3]} \]  

\[\text{[35]}\]

\(\text{(D) Al - F - H}_2\text{O System}\)

\[ \text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}^{2+} + \text{H}^+ \]

\[ \text{pH} = 4.97 + \log \frac{[\text{Al(OH)}^{2+}]}{[\text{Al}^{3+}]} \]  

\[\text{[36]}\]

\[ \text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_2^{2+} + 2\text{H}^+ \]

\[ \text{pH} = 4.65 + 0.5 \log \frac{[\text{Al(OH)}_2^{2+}]}{[\text{Al}^{3+}]} \]  

\[\text{[37]}\]

\[ \text{Al}^{3+} + 3\text{OH}^- \rightleftharpoons \text{Al(OH)}_3^{3-} \]

\[ \text{pH} = 3.233 - 0.333 \log \{\text{Al}^{3+}\} \]  

\[\text{[38]}\]

\[ \text{Al(OH)}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_2^{2+} + \text{H}^+ \]

\[ \text{pH} = 4.3 + \log \frac{[\text{Al(OH)}_2^{2+}]}{[\text{Al(OH)}^{2+}]} \]  

\[\text{[39]}\]

\[ \text{Al(OH)}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3^{3-} + 2\text{H}^+ \]

\[ \text{pH} = 2.35 - 0.5 \log \{\text{Al(OH)}^{2+}\} \]  

\[\text{[40]}\]

\[ \text{Al(OH)}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3^{3-} + \text{H}^+ \]

\[ \text{pH} = 0.3 - \log \{\text{Al(OH)}_2^{2+}\} \]  

\[\text{[41]}\]

\[ \text{Al(OH)}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3^{3-} + \text{H}^+ \]

\[ \text{pH} = 5.7 + \log \frac{[\text{Al(OH)}_3^{3-}]}{[\text{Al(OH)}_2^{2+}]} \]  

\[\text{[42]}\]

\[ \text{Al}^{3+} + \text{HF} \rightleftharpoons \text{AlF}^{2+} \text{aq} + \text{H}^+ \]

\[ \text{pH} = -3.7 + \log \frac{[\text{AlF}^{2+}]}{[\text{Al}^{3+}][\text{HF}]} \]  

\[\text{[43]}\]

\[ \text{AlF}^{2+} + \text{HF} \rightleftharpoons \text{AlF}_2^{3+} + \text{H}^+ \]

\[ \text{pH} = -2.4 + \log \frac{[\text{AlF}_2^{3+}]}{[\text{AlF}^{2+}][\text{HF}]} \]  

\[\text{[44]}\]
\[ \text{AlF}_2^+ + \text{HF} \rightleftharpoons \text{AlF}_3^- + \text{H}^+ \]

\[ \text{pH} = -1.1 + \log \frac{[\text{AlF}_3^-]}{[\text{AlF}_2^+][\text{HF}]} \]  \hspace{1cm} [45]

\[ \text{AlF}_3^- + \text{HF} \rightleftharpoons \text{AlF}_4^- + \text{H}^+ \]

\[ \text{pH} = 0.3 + \log \frac{[\text{AlF}_4^-]}{[\text{AlF}_3^-][\text{HF}]} \]  \hspace{1cm} [46]

\[ \text{AlF}_3^- + 3\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3^- + 3\text{H}^+ + 3\text{F}^- \]

\[ \text{pH} = 8.567 + 0.333 \log \frac{[\text{F}^-]^3}{[\text{AlF}_3^-]} \]  \hspace{1cm} [47]

\[ \text{AlF}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}^{2-} + \text{H}^+ + 3\text{F}^- \]

\[ \text{pH} = 21.0 + \log \frac{[\text{Al(OH)}^{2-}][\text{F}^-]^3}{[\text{AlF}_3]} \]  \hspace{1cm} [48]

\[ \text{AlF}_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_2^- + 2\text{H}^+ + 3\text{F}^- \]

\[ \text{pH} = 8.11 + 0.5 \log \frac{[\text{Al(OH)}_2^-][\text{F}^-]^3}{[\text{AlF}_3]} \]  \hspace{1cm} [49]
APPENDIX C

BEAKER DECANTATION STOKES LAW CALCULATION
In beaker decantation sizing, the material to be sized is dispersed in a fluid and allowed to settle under carefully controlled conditions. Separation is achieved on the basis of resistance to motion in a fluid. This resistance to motion determines the terminal velocity which a particle attains as it is allowed to fall in a fluid under the influence of gravity.

For particles within the sub-sieve range, the terminal velocity is given by the equation derived by Stokes (1891), namely:

\[ v = \frac{d^2 g (D_p - D_f)}{18 \eta} \]

where \( v \) is the terminal velocity of the particle (ms\(^{-1}\)), \( d \) is the particle diameter (m), \( g \) is the acceleration due to gravity (ms\(^{-2}\)), \( D_p \) is the particle density (kgm\(^{-3}\)), \( D_f \) is the fluid density (kgm\(^{-3}\)), and \( \eta \) is the fluid viscosity (Nsm\(^{-2}\)), \( \eta = 0.001 \text{ Nsm}^{-2} \) for water.

Stoke's law is derived for spherical particles: non-spherical particles will attain a terminal velocity, but this velocity will be influenced by the shape of the particles. Nevertheless, this velocity can be substituted in the Stoke's equation to give a value of \( d \), which can be used to characterize the particle. This value of \( d \) is referred to as the "Stokes equivalent spherical diameter". It is also known as the "Stokes diameter" or the "sedimentation diameter".

Stoke's law is only valid in the region of viscous flow, which sets an upper size limit to the particles which can be sized by sedimentation in a given liquid. The limit is determined by the Reynold's number, a dimensionless quantity defined by:

\[ R = \frac{vd D_f}{\eta} \]
The Reynold's number should not exceed 0.2 if the error in using Stoke's law is not to exceed 5 percent (British Standard 3406, 1963). In general, Stoke's law holds for all particles below 40 micron. The lower size limit is generally around 1 micron, below which the settling times are too long and also the effects of unintentional disturbances, such as can be caused by convection currents, are far more likely to produce serious error.

**Settling Velocity for a Cassiterite Particle with a Stoke's Diameter of 4 Microns**

\[ v = \frac{d^2 g (D_\infty - D_\varepsilon)}{18 \eta} \]

- \( d = 4 \times 10^{-6} \) m
- \( g = 9.81 \text{ ms}^{-1} \)
- \( D_\infty = 7,000 \text{ kgm}^{-3} \)
- \( D_\varepsilon = 1,000 \text{ kgm}^{-3} \)
- \( \eta = 0.0009548 \text{ Nsm}^{-2} \)

\[ v = \frac{16 \times 10^{-12} \times 9.81 \times 6000}{18 \times 0.0009548} \]

\[ v = 0.055 \times 10^{-3} \text{ ms}^{-1} \]

\[ v = 0.055 \times 3600 \times 100 \times 10^{-3} \text{ cmhr}^{-1} \]

\[ v = 19.73 \text{ cmhr}^{-1} \]
The titration of a weak base, B, with a strong acid proceeds according to the reaction:

\[ B + H^+ \rightleftharpoons BH^+ \]

At any point between the initial point and the endpoint of the titration, it is a good approximation that each mole of HCl converts one mole of B into one mole of BH\(^+\). If \( V_b \) ml of B, with formal concentration \( F_b \), is titrated with \( V_H \) ml of HCl with formal concentration \( F_H \), then:

\[
[BH^+] = \frac{\text{Moles of } H^+ \text{ delivered}}{\text{Total Volume}} = \frac{V_H F_H}{V_H + V_b} \tag{1}
\]

\[
[B] = \frac{\text{Original moles of } B - \text{Moles of } H^+}{\text{Total Volume}} = \frac{V_b F_b - V_H F_H}{V_b + V_H} \tag{2}
\]

The acid dissociation constant can be written as follows:

\[
K_a = \frac{[B][H^+][H^-]}{[BH^+]} \tag{3}
\]

Substituting the values of \([BH^+]\) and \([B]\) from Equations \([1]\) and \([2]\) into Equation \([3]\) gives:

\[
K_a = \frac{(V_b F_b - V_H F_H) \gamma_b [H^+] \gamma_{H^+}}{V_H F_H \gamma_{BH^+}}
\]

Rearranging,

\[
V_H [H^+]^{-1} (\gamma_{H^+})^{-1} = \left( \frac{1}{K_a} \frac{\gamma_b}{\gamma_{BH^+}} \right) \left( \frac{V_b F_b}{F_H} - V_H \right)
\]

since \( V_b F_b = V_e F_H \implies V_e = \frac{V_b F_b}{F_H} \)

and

\[
V_H 10^{pH} = \left( \frac{1}{K_a} \frac{\gamma_b}{\gamma_{BH^+}} \right) (V_e - V_H)
\]

A graph of \( V_H 10^{pH} \) versus \( V_H \) is, therefore, a straight line with a slope of \(-\frac{\gamma_b}{K_a \gamma_{BH^+}}\) and an intercept of \( V_e \) on the \( V_H \) axis.

The Gran function, \( V_H 10^{pH} \), does not actually go to zero, because \( 10^{pH} \) is never zero. The curve must be extrapolated to find \( V_e \). The function does not
reach zero because the approximation that every mole of $H^+$ generates one mole of $BH^+$ breaks down as $V_H$ approaches $V_m$. The Gran plot can also exhibit curvature with large changes in ionic strength due to variation in $\frac{\gamma_B}{\gamma_{BH^+}}$. However, data near $V_m$ gives a straight line because the ratio $\frac{\gamma_B}{\gamma_{BH^+}}$ is relatively constant in this range.
APPENDIX E

B.E.T. CALCULATIONS
During the course of the research, surface area measurements of a range of samples were made according to the multipoint B.E.T. method. The results of such analyses are shown in Figures 227 to 230 in the form of B.E.T. plots. Examination of the figures indicates that all B.E.T. curves are linear over the range of relative test pressures \( \frac{P}{P_0} \) used.

According to the B.E.T. equation, the actual weight of a gas adsorbed onto a substrate surface \( X \) is related to the relative pressure \( \frac{P}{P_0} \) and the monolayer coverage \( X_m \) by the expression:

\[
\frac{P}{X(P_0 - P)} = \frac{1}{X_mC} + \frac{C-1}{X_mC} \frac{P}{P_0}
\]

If a plot of \( \frac{1}{X[(P_0/P)-1]} \) versus \( \frac{P}{P_0} \) is a straight line, the intercept is equal to \( \frac{1}{X_mC} \) and the slope is \( \frac{(C-1)}{X_mC} \). Determinations of the intercept and slope then allow both \( X_m \) and \( C \) to be evaluated. Knowing the weight of gas \( X_m \) required for a monolayer surface coverage, the total substrate surface area can be calculated from the expression:

\[
\text{Total Surface Area (} S_t \text{)} = \frac{X_m(6.023\times10^{23})A_{cs}}{M_a}
\]

where,

\( A_{cs} = \) adsorbate cross sectional area

\( = 16\times10^{-20} \text{ m}^2 \text{ for nitrogen} \)

\( M_a = \) molecular weight of the adsorbate

\( = 28.01 \text{ g for nitrogen} \).

The specific surface area is then given simply by dividing the total surface area in \( \text{m}^2 \) by the substrate weight in grams.

Surface area calculations for the experimental B.E.T. plots of Figures 227 to 230, performed on such a basis, are given in Table XXVII.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Weight (g)</th>
<th>BET Plot Intercept</th>
<th>BET Plot Slope</th>
<th>Xₘ (g)</th>
<th>Total Surface Area (m²)</th>
<th>Specific Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich &quot;Gold Label&quot; Stannic Dioxide</td>
<td>1.54432</td>
<td>-0.335</td>
<td>70.816</td>
<td>0.014</td>
<td>48.79</td>
<td>31.59</td>
</tr>
<tr>
<td>Leached Cassiterite</td>
<td>0.22322</td>
<td>2907.458</td>
<td>88999.204</td>
<td>1.088 \times 10^{-5}</td>
<td>0.037</td>
<td>0.166</td>
</tr>
<tr>
<td>Unleached Cassiterite</td>
<td>0.29861</td>
<td>1684.884</td>
<td>58178.358</td>
<td>1.670 \times 10^{-5}</td>
<td>0.057</td>
<td>0.192</td>
</tr>
<tr>
<td>Ground Unleached Cassiterite</td>
<td>1.81715</td>
<td>19.281</td>
<td>801.992</td>
<td>1.218 \times 10^{-3}</td>
<td>4.187</td>
<td>2.304</td>
</tr>
</tbody>
</table>
Figure 227 - B.E.T. Plot of Nitrogen Adsorbed on 1.54432 Grams of Aldrich "Gold Label" Stannic Dioxide. The plot correlation coefficient is 1.000.

Figure 228 - B.E.T. Plot of Nitrogen Adsorbed on 0.22322 Grams of Leached Cassiterite. The plot correlation coefficient is 0.999.
Figure 229 – B.E.T. Plot of Nitrogen Adsorbed on 0.29861 Grams of Unleached Cassiterite. The plot correlation coefficient is 0.991.

Figure 230 – B.E.T. Plot of Nitrogen Adsorbed on 1.8172 Grams of the Ground Unleached Cassiterite Used for Adsorption Study Measurements. The plot correlation coefficient is 0.999.
APPENDIX F

CALCULATION OF FRACTIONAL COMPOSITION DIAGRAMS
Consider a solution of diprotic acid with formal concentration F.

\[
\begin{align*}
\text{H}_2\text{A} & \rightleftharpoons H^+ + \text{HA}^- \\
\text{HA}^- & \rightleftharpoons H^+ + A^{2-}
\end{align*}
\]

\[
K_1 = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} \implies [\text{HA}^-] = [\text{H}_2\text{A}] \frac{K_1}{[\text{H}^+]}
\]

\[
K_2 = \frac{[\text{H}^+][A^{2-}]}{[\text{HA}^-]} \implies [A^{2-}] = [\text{HA}^-] \frac{K_2}{[\text{H}^+]} = [\text{H}_2\text{A}] \frac{K_1K_2}{[\text{H}^+]^2}
\]

**Mass balance:** \( F = [\text{H}_2\text{A}] + [\text{HA}^-] + [A^{2-}] \)

\[
F = [\text{H}_2\text{A}] + \frac{K_1}{[\text{H}^+]} [\text{H}_2\text{A}] + \frac{K_1K_2}{[\text{H}^+]^2} [\text{H}_2\text{A}]
\]

\[
F = [\text{H}_2\text{A}] \left(1 + \frac{K_1}{[\text{H}^+]^2} + \frac{K_1K_2}{[\text{H}^+]^3}\right)
\]

For a diprotic system, the fraction of the acid in the form \( \text{H}_2\text{A} \) can be described as \( \alpha_0 \), the fraction in the form \( \text{HA}^- \) as \( \alpha_1 \), and the fraction in the form \( A^{2-} \) as \( \alpha_2 \). From the definition of \( \alpha_0 \):

\[
\alpha_0 \equiv \frac{[\text{H}_2\text{A}]}{F} = \frac{[\text{H}^-]^2}{[\text{H}^+]^2 + K_1[H^+] + K_1K_2}
\]

Similarly,

\[
\alpha_1 \equiv \frac{[\text{HA}^-]}{F} = \frac{K_1[H^+]}{[\text{H}^+]^2 + [\text{H}^+] K_1 + K_1K_2}
\]

\[
\alpha_2 \equiv \frac{[A^{2-}]}{F} = \frac{K_1K_2}{[\text{H}^+]^2 + [\text{H}^+] K_1 + K_1K_2}
\]

Knowing \( K_1 \) and \( K_2 \) consequently allows the fraction of acid present in each possible form to be calculated at a given pH. Fractional composition diagrams are simply plots of \( \alpha_0, \alpha_1 \), and \( \alpha_2 \) as a function of pH calculated from the above expressions.