ADSORPTION OF DEXTRIN ONTO SULPHIDE MINERALS AND ITS EFFECT ON THE
DIFFERENTIAL FLOTATION OF THE INCO MATTE

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES
Department of Mining and Mineral Process Engineering

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Dated: 9 March, 1993
Abstract

The major constituents of the Inco matte, chalcocite (Cu$_2$S) and heazlewoodite (Ni$_3$S$_2$), are separated by differential flotation with diphenylguanidine as collector. To select an effective organic depressant, many dextrins were tested and tapioca dextrin 12 was found to have an exceptional affinity towards heazlewoodite surface at a particular pH of the mineral suspension.

A new reagent system, involving the use of this dextrin as a modifying agent which provides better selectivity, has been studied. Adsorption tests revealed that while dextrin exhibits high affinity towards heazlewoodite, especially in alkaline solutions, the adsorption isotherm shape for dextrin on chalcocite showed weak affinity. The adsorption density of dextrin on Ni$_3$S$_2$ was found to vary with pH, with the maximum adsorption occurring around pH 11.7, which was established to be the i.e.p. of nickel hydroxide. For Cu$_2$S, the adsorption was much lower and did not exhibit any pH dependence.

Electrokinetic and co-precipitation measurements confirm such observations. While the zeta potential-pH curves for Ni$_3$S$_2$ and freshly precipitated Ni(OH)$_2$ were practically identical in alkaline solutions and revealed the presence of a nickel hydroxide layer on Ni$_3$S$_2$, such a correlation was absent for the Cu$_2$S and Cu(OH)$_2$ curves. The zeta potential-pH curves for Ni$_3$S$_2$ and Ni(OH)$_2$, and for Cu$_2$S and Cu(OH)$_2$ in the presence of dextrin, exhibited quite different trends. While the results indicate strong interactions and flat orientation of dextrin macromolecules onto nickel hydroxide and heazlewoodite, weak interactions between dextrin and chalcocite (and copper hydroxide) seem to result in an extended adsorption layer that drives the shear plane further away from the interface.

Conductometric and ATR-FTIR tests confirm that dextrin interacts strongly with Ni$_3$S$_2$ most likely through chemical bonding, while its interaction with chalcocite is physical in nature.

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1This is a brand name for the tapioca dextrin sample obtained from Staley Mfg. Co.
Based on the adsorption studies, batch differential flotation tests of Inco matte using diphenyl guanidine (DPG) and potassium amyl xanthate (KAX) as collectors and tapioca dextrin as a depressant were carried out. A single stage cleaner flotation using DPG collector in the presence of tapioca dextrin yielded a high grade copper concentrate. As compared to the cleaner flotation in the absence of tapioca dextrin, this resulted in about 70% reduction in the Ni content in the concentrate. Although amyl xanthate exhibited poor selectivity, the presence of tapioca dextrin dramatically improved its performance in the selective separation of the chalcocite from the heazlewoodite. This makes amyl xanthate a very attractive alternative to the currently utilized DPG collector.

On the basis of this research, it has been possible to provide a rational interpretation of all data pertaining to chalcocite-heazlewoodite differential flotation and to improve the selectivity of such separation with the use of dextrin as Ni$_3$S$_2$ depressant in the alkaline pH range.

A significant link has been established between the results of fundamental analyses and industrially related observations. In particular, it was shown how electrokinetic measurements can be utilized along with FTIR and adsorption measurements to study the interactions of macromolecular modifiers with sulphide minerals.

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ψ_o Potential at Stern plane
ψ_v Surface potential
F Faraday constant
z Valence of potential determining ion (PDI)
a^*_{pz} Activity of potential determining ion at the point of zero charge (pzc)
κ Inverse Debye length
E h Redox potential
ΔG_{ads} Standard free energy of adsorption
τ Shearing force per unit area
M_n Number-average molecular weight
M_v Viscosity-average molecular weight
M_w Weight-average molecular weight
M_i Molecular weight of species i
n_i Number proportion of molecular species i
\gamma_i Weight fraction of molecular species i
\Pi Osmotic pressure
R Universal gas constant
A_2 Second virial coefficient
A_3 Third virial coefficient
T Absolute temperature
N_0 Avogadro's number
n_o Refractive index of solvent
\eta_o Dynamic viscosity of pure solvent
\eta_{sp} Specific viscosity
\eta_R Relative viscosity
\eta Viscosity of polymer solution
Γ  Adsorption density
χ, χs  Energy parameters describing the interaction of a solvent and polymer segments, respectively, with a surface.
zs  Co-ordination number in a two-dimensional surface layer
zs  Co-ordination number in a three-dimensional surface layer
φi  Polymer volume fraction in the layer i
φ  Polymer volume fraction in the bulk solution
φs  Solvent volume fraction in the bulk solution
Ve  Elution volume
Vo  Void volume of the chromatographic column
Vi  Volume of solvent in gel
Kd  Distribution coefficient
P  The weight of flotation product i
λ  Assays for flotation product i
Ri  Percent recovery of fraction i
γn  Percent yield for flotation product n
α  Flotation feed assay
I wish to express my sincere thanks to Professor Janusz S. Laskowski for his indefatigable guidance and assistance as supervisor in the course of this work. Many thanks also go to all committee members for their constructive criticisms and comments. I will therefore take this opportunity to convey my appreciation to Professor Andy L. Mular, and Dr. George W. Poling (Mining and Mineral Process Eng., UBC), Dr. B D. Bowen (Department of Chemical Engineering, UBC) and Professor R.H Yoon of Virginia Polytechnic Institute and State University.

My thanks are also due to the technicians in my department, especially to Mrs. Sally Finora, for her assistance in the surface chemistry research laboratory; Mr. Pius Liu, for his help during the many batch flotation tests on the copper-nickel matte at the Centre for Coal and Mineral Processing; Mr. Peter Kempe, for the chemical analysis of the copper and nickel samples; and last, but not the least, Mr. Frank Schmidtiger for the general technical assistance.

Many useful discussions in the course of this work with Dr. Sankaran Subramanian, from the Indian Institute of Science, Bangalore (who was on his sabbatical leave at UBC) and Dr. Dai Qi, who is now a Research Engineer at Syncrude Edmonton Research Centre, are acknowledged.

For her constant spiritual and moral support, understanding and caring, my wife Catherine, deserves praise. For her untiring encouragement she made a dream come true.

This work was supported in part by the International Nickel Company of Canada (INCO) through financial and material means. In this regard, I wish to express my indebtedness for their sponsorship and more especially, to Dr. Richard Stratton-Crawley of INCO for his help and useful discussions.

Lastly, I render my biggest thanks and praises to the Almighty God who has led me in all ways throughout my pursuit of academic honours and has given me the power to produce this piece as a contribution towards the development of science.
Chapter 1

INTRODUCTION

Although the use of starches as depressants in flotation processes has been practised for a long time (Lange, 1931; Kitchener, 1978), investigations on the mode of action of dextrins have been rather limited. The properties of native starches, such as insolubility, high molecular weight and sensitivity to break down, limit their usefulness as mineral depressants (Würzburg, 1989). Conversely, pyrodextrins, being one of the end products of modified starches, serve as more effective depressants due to their lower molecular weight, highly-branched structure and high hydroxyl content, which renders the mineral surface hydrophilic when such a macromolecule is adsorbed onto the mineral surface.

The effective separation of polymetallic sulphide ores in most cases involves differential flotation with the use of thio-collectors such as xanthates. Since these collectors are active towards a whole range of sulphide minerals, selectivity becomes a problem in such systems. Inorganic modifiers (dichromates, cyanides, ferrocyanides and hypochlorites) have been used under such conditions to make the action of the collector more specific, and to improve separation efficiency (Finkelstein and Allison, 1976). These inorganic depressants are, however, toxic and their use is being increasingly restricted because of environmental concerns.

Several industrial applications of dextrins in the differential flotation of sulphide minerals include the bulk Cu-Ni concentrate separation at Outokumpu Oy, Kotalahti mine in Finland (Lukkarinen, 1968) which was reportedly carried out with dextrin in the presence of lime as a
depressant for nickel minerals at around pH 12.0, Cu-Pb sulphide separation circuit at Brunswick mines concentrator, using dextrin and SO₂ to selectively depress PbS (Neumann and Schnarr, 1971), and depression of galena using dextrin in a Cu/Pb separation circuit at Boliden (Bolin and Laskowski, 1990).

Various studies have been carried out to investigate the interaction between dextrin and mineral surfaces (Haung and Miller 1978; Haung, et al., 1978; Miller et al., 1988), and different interaction mechanisms have been reported. Qi Liu and Laskowski (1989) have recently proposed the idea of complex formation when dextrin interacts with metal hydroxides. They observed that dextrin adsorption was more pronounced in the pH ranges in which metallic species were hydroxylated. It was, therefore, suggested that the presence of hydroxylated metallic adsorption centres is the primary reason for the high affinity of dextrin towards mineral surfaces. Formation of insoluble complexes of metal hydroxides (e.g. Hydrous titanium(IV) oxide) with branched polysaccharides was also reported by other researchers (Kennedy et al., 1977).

Any advances in the effective use of polysaccharides in such applications will, however, depend on the understanding of the interaction mechanism.
Chapter 2

SCOPE AND SIGNIFICANCE OF THIS INVESTIGATION

This thesis intends to investigate the nature of the interaction mechanism between dextrin and the two mineral components of the Inco matte, chalcocite (Cu$_2$S) and heazlewoodite (Ni$_3$S$_2$), and the conditions under which dextrin could serve as an effective depressant in the selective flotation of the Inco matte.

In flotation processes, the primary purpose of a depressant is to improve the selectivity of separation by preventing the flotation of unwanted minerals. The inception of flotation in the early 1900s brought into its fold the wide use of inorganic modifiers to enhance selectivity. In 1980, it was estimated by Copper (1981) that the United States alone used over 500 million kg of such modifiers in the flotation of sulphide ores. Since many of these reagents are highly toxic, flotation technologies have become more of an environmental nuisance. Organic modifying agents such as dextrins could serve as substitutes. Such organic agents are bio-degradable and less harmful to the environment.

Sulphide ores are the largest group of minerals treated by the flotation process, and as the world has gradually been depleting its high-grade ore deposits, the head grade to this separation process has been diminishing, and low-grade complex sulphide ores are becoming a more important source of base metals.

Because of the problems associated with the differential flotation of pentlandite and chalcopyrite, Inco is switching its flotation process into a bulk flotation of both minerals. The
two minerals are finally separated as chalcocite and heazlewoodite which appear in the Inco matte. A collector used in this process, diphenyl guanidine (DPG), is highly carcinogenic, and since it is also water-insoluble its handling creates some problems. Dextrin was recently successfully tested as a depressant in the differential flotation of the galena-chalcopyrite bulk concentrate (Bolin and Laskowski, 1990) and was previously reported to be used in the selective flotation of a bulk concentrate of chalcopyrite and pentlandite (Lukkarinen, 1968). A better understanding of its interaction with chalcocite and heazlewoodite is essential to improved flotation separation of these two minerals in the differential flotation of the Inco matte and should lead to the replacement of DPG with xanthates that are much easier to handle. An understanding of the interaction mechanism between sulphide minerals and organic polymeric depressants will broaden applications of non-toxic polysaccharides in selective flotation of sulphide ores.

2.0 SCOPE AND SIGNIFICANCE OF THIS INVESTIGATION
Chapter 3

LITERATURE SURVEY

3.1 PRODUCTION OF COPPER-NICKEL SULPHIDE AT INCO

The International Nickel Company (INCO) of Canada is the leading producer of nickel and a substantial producer of copper, precious metals and cobalt in the world (Inco report, 1986). In addition to nickel and copper, INCO produces 13 other elements, primarily from its Canadian ores, the major ones being platinum, gold, palladium and silver. In addition, Inco is a major producer of sulphuric acid and liquid sulphur dioxide.

Nickel demand in the western world was estimated at 0.55 million metric-tons in 1985 and demand for the metal has been stable up till now. In 1986, it was estimated that Inco's proven and probable ore reserves in Canada were 415 million tonnes, containing 6.1 million tonnes of nickel and 3.7 million tonnes of copper.

3.1.1 Processing of Copper-Nickel Ores

Inco has three sulphide producing areas, the most important one being the nickel-copper-iron sulphide ores of the Sudbury basin. This region is one of the world's principal nickel sources and is the major nickel producing area for Inco, with an annual capacity of around 0.1 million metric-tons of nickel. Somewhat different ores with different mineral compositions from various mines in this area are blended together and processed at mills located at Clarabelle, Frood-Stobie and Copper Cliff. These mills are primary concentrators and produce chalcopyrite and nickel as well as bulk concentrates, with the rejection of pyrrhotite.
The other two nickel producing areas are in Thompson, Manitoba and Shebandowan, north western Ontario. At Thompson, the ore has a high nickel content with a lower copper grade as compared to that of the Sudbury basin. The nickel concentrate produced at the Thompson concentrator is smelted in electric furnaces on the same location and a copper concentrate is smelted into a copper-nickel matte that is sent to Copper Cliff for the final separation. A high grade nickel concentrate is also produced and marketed to Sherrit-Gordon, Ltd. Depending on the magnesia content, concentrate from Shebandowan is smelted either at Sudbury or Thompson. High magnesia content is more detrimental to the reverberatory furnaces at Sudbury than the electric furnaces at Thompson. Approximate average ore compositions from the three mining areas are given in Table 3.1. It should be noted that differences in mineralogical composition of these ores affect both the primary concentrating technique and the rejection of pyrrhotite.

Table 3.1 - Approximate Ore Compositions (%) from the Three Mining Areas
(after Agar, 1990)

<table>
<thead>
<tr>
<th></th>
<th>Sudbury</th>
<th>Thompson</th>
<th>Shebandowan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentlandite</td>
<td>3.0</td>
<td>7.1</td>
<td>5.0</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>3.7</td>
<td>0.5</td>
<td>2.3</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>20</td>
<td>23</td>
<td>20</td>
</tr>
<tr>
<td>Quartz</td>
<td>16</td>
<td>28</td>
<td>6</td>
</tr>
<tr>
<td>Feldspar</td>
<td>14</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>Chlorite</td>
<td>21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Biotite</td>
<td>11</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>Amphibole</td>
<td>10</td>
<td>6</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Carbonates</td>
<td>2</td>
<td>&lt;5</td>
<td>10</td>
</tr>
<tr>
<td>Tremolite</td>
<td>-</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>Talc</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
</tbody>
</table>
The control of pyrrhotite at various stages of processing is essential for the following reasons:

- Optimum amount of pyrrhotite rejection in the concentrators is needed to reduce the emission of sulphur dioxide from the smelters,
- pyrrhotite easily undergoes oxidation to generate acidic tailing ponds which must be treated with lime to neutralize the water for recycling purposes and also to control the level of the dissolved metal ions.

At the Copper Cliff mill, separation of chalcopyrite from pentlandite is enhanced by further addition of lime to near saturated levels. The use of sodium carbonate as a modifier in the Thompson and Shebandowan mills has been found to promote better flotation rates for both pentlandite and chalcopyrite. Better rejection of pyrrhotite under these conditions is also achieved due to its slow flotation rate. In some cases, further pyrrhotite rejection is through regrind and magnetic separation.

In the primary separation, an amyl xanthate collector and Dowfroth 1263 (a frother) are the flotation reagents used to produce a bulk concentrate of chalcopyrite, pentlandite and pyrrhotite. In addition, carboxymethylcellulose (CMC) is used in the Shebandowan mill to depress talc and other rock minerals. Concentrates from various mills are pumped to the Copper Cliff mill for the secondary separation with a feed assay of about 12% Cu, 10% Ni, 28% pyrrhotite and 10% rock. Lime, sodium cyanide and steam are used at this stage to produce a high grade chalcopyrite concentrate, assaying more than 29% Cu with less than 1% Ni (Agar, 1991). The remaining product becomes part of the nickel concentrate. It is worth mentioning that low levels of nickel in the copper concentrate are essential to the efficient operation of the subsequent copper smelting process.
3.1.2. Matte Separation and Smelting

For many years, the separation of copper from nickel was a major problem until an improved separation process was developed by Inco. This was based on a combination of metallurgical and mineral processing methods of flotation and magnetic separation (Sproule et al., 1960). A general flowsheet of Inco's Copper Cliff smelter complex is shown in Figure 3.1. In the smelting-converting process of the nickel concentrate, iron sulphide and other gangue materials are rejected.

During the slow cooling of the molten matte, discrete phases of nickel sulphide (heazlewoodite, \( \text{Ni}_3\text{S}_2 \)), copper sulphide (chalcolite, \( \text{Cu}_2\text{S} \)), and a copper-nickel alloy appear; a metallic alloy

Figure 3.1 - Flowsheet for the Copper Cliff Smelter
results from a deficiency in sulphur for the sulphides in the matte. The resulting matte has an approximate composition of 50% Ni, 25% Cu and 22% S (Wilson et al., 1989) and the coarse grain size of the various phases makes the matte amenable to a physical separation process.

A simplified flowsheet of the matte separation process is shown in Figure 3.1. The separation of the matte constituents is effected by crushing, grinding in rod and ball mills to 65% passing 44 μm and flotation. The precious metal-bearing metallic constituent with a composition of about 65% Ni and 15% Cu is removed by multiple magnetic separation and serves as a major component of the feed to the Copper Cliff nickel refinery. The non-magnetic fraction of the matte serves as a feed to the flotation circuit where chalcocite is selectively floated from heazlewoodite in the presence of lime at pH 12.4 and using diphenylguanidine (Tippman et al., 1976).

The final copper concentrate assays about 75% Cu, 3.5% Ni, and 21% S, and is achieved through a circuit consisting of rougher-regrind-two-stage cleaner flotation. The second stage cleaner incorporates a 1.8 m diameter flotation column, installed in 1987, to replace second and third mechanical cleaner banks of cells (Feeley et al., 1987). Two product streams are obtained in the nickel circuit; in the first stream, rougher tails are reground and the residual Cu₂S scavenged to produce a high grade nickel sulphide assaying approximately 70% Ni, 0.8% Cu and 26% S. The second nickel stream contains the middlings flotation circuit with its feed consisting of a combination of first cleaner tails from the copper circuit and scavenger concentrate from the nickel circuit. Rougher tails from the middlings circuit contain approximately 65% Ni, 5.5% Cu and 25% S which, after roasting, goes to the Copper Cliff and Clydach refineries for further processing.
Figure 3.2 - Flowsheet for the Separation of Inco matte

One special feature of this process is that unlike a conventional milling circuit, the matte separation flowsheet does not have a true tailings stream since all tails are products with strict assay specifications. A good separation efficiency of the unit operations is therefore of utmost importance. The high grade products maintained at present operation levels have been due to the
relentless efforts of Inco to keep on improving their metallurgical performance. Notwithstanding these successful strategies, tests are still being conducted to improve the separation of chalcocite from heazlewoodite in the light of a sulphur dioxide abatement project currently underway at the Copper Cliff smelter and which is to come into effect in 1993 (Wilson et al., 1989). Under this programme, the smelter will be processing bulk copper-nickel concentrate instead of the separate concentrates it has been processing for many years. At present, the matte has a Ni:Cu ratio of about 2, but in the bulk scenario, a Ni:Cu ratio of 1 is expected, and this calls for further improvement in flotation selectivity. Inco is presently conducting a series of tests on flotation columns for improved metallurgical performance.

In this project, attention is focused on the application of an organic modifying agent, dextrin, in the differential flotation of the matte. Dextrin is inexpensive and easy to handle. It is also bio-degradable and non-toxic and does not pose any harm to the environment. In order to achieve optimum results, however, a thorough understanding of the interaction of this modifier with sulphide minerals (especially, Cu$_2$S and Ni$_3$S$_2$) is needed.
3.2 SULPHIDE MINERALS

Froth flotation is presently the most widely used economic process in concentrating metal sulphide ores and it has been a major factor in the rapid expansion of the supply of such base metals as copper, nickel, lead and zinc. Based on extrapolated data from the U.S. Bureau of Mines (1980), it has been estimated that about 1.6 billion tonnes of sulphide ores were treated worldwide (excluding eastern-bloc countries) through this process in 1980 (Aplan and Chander, 1988; Klimpel, 1988).

With the grade of metal sulphide ores deteriorating due to the depletion of high grade ores, there is a strong need to improve upon the existing technology in order to meet the ever-increasing base metal demands. Thus, new reagents such as collectors and modifiers are constantly being tested for specific applications as the challenge for improved flotation performance intensifies.

3.2.1 Solution Chemistry

The chemistry of sulphide mineral suspensions is considered in terms of a surface where oxidation is taking place through a continuum of metal deficient sulphides of decreasing metal content through to elemental sulphur (Hayes et al., 1987). Peters (1977) further pointed out that such processes are anodic in character and lead to the formation of reaction products whose molar volumes are likely to differ from the underlying lattice.

The electric potential difference at the mineral-solution interface has been found to be one of the most important factors controlling surface reactions, since it determines which reactions may occur and the rate at which they occur. The effect of such a potential can be studied through the technique of linear sweep voltammetry (Chander and Fuerstenau, 1974; Hamilton and Woods, 1981; Fuerstenau and Hanson, 1990; Chander and Pang, 1991). The utilization of potential control in industrial flotation practice, however, has not achieved much
success since the potential of each sulphide particle in the system can be controlled only by chemical means.

Various studies have been carried out on common minerals like galena (Gardner and Woods, 1979), chalcopyrite (Gardner and Woods, 1979), chalcocite (Sato, 1960; Walker et al., 1983), pyrite (Janetski et al., 1977), and pyrrhotite (Hamilton and Woods, 1981). The following reactions were suggested to describe the processes taking place on the surface of sulphide particles. In an acidic environment simple sulphides oxidize as:

\[ M_2S \rightarrow zM^{z+} + S^0 + zne \]  
\[ \text{(3.1.1)} \]

and in neutral and alkaline medium the oxidation proceeds according to the reaction:

\[ M_2S + znH_2O = zM(OH)_n + S^0 + znH^+ + zne \]  
\[ \text{(3.1.2)} \]

However, under extreme oxidation conditions at high pH, sulphur may undergo further oxidation to produce oxy-sulphur species:

\[ xM_2S + (zn + y)H_2O = zxM(OH)_n + SzO_{2y}^z + (2y + zn - 2)e \]  
\[ \text{(3.1.3)} \]

Guy and Trahar, (1985) pointed out that reaction 3.1.3 is the most thermodynamically favourable but for most sulphides the kinetics of the oxidation process are very slow after the production of sulphur. For other sulphides, Peters (1977) and Pritzker (1985) claim that the formation of thiosulphate and sulphate by the last reaction may proceed at reasonable rates only at over-potentials of varying magnitudes. The metal hydroxide species from the above oxidation reactions may remain at the mineral-solution boundary if they are formed in situ. However, if the hydroxide formation is through a soluble intermediate, it would tend to precipitate in the solution rather than at the mineral surface (Walker et al., 1984; Grano et al., 1990; Smart, 1991; Senior and Trahar, 1991).

It is worth noting that under dynamic conditions, soluble oxidation products (e.g. \( S_xO_{2y}^{z-} \)) will be removed from the mineral-solution boundary and any subsequent reduction will result in the appearance of free metal on the mineral surface (Woods, 1972), according to the reaction:

\[ M(OH)_n + nH^+ + ne = M + nH_2O \]  
\[ \text{(3.1.4)} \]

3.2 SULPHIDE MINERALS
In a series of papers, Buckley and Woods (1983, 1984, 1985, 1991) and Buckley and Walker (1988), using X-ray photoelectron spectroscopic (XPS) techniques, have claimed that the theory of elemental sulphur formation on sulphide surfaces during oxidation is incorrect. In their studies they obtained the S(2p) photoelectron spectra for some fractured oxidized metal sulphides surfaces at 150 K (loss of S° to the spectrometer is minimized at this low temperature) and found that the spectra were not consistent with that of elemental sulphur. It was therefore proposed that, in air, the metal atoms migrate to the surface to form an overlayer of metal hydroxide or hydrated metal oxide, that covers the resultant metal-deficient sulphide lattice. This proposition is supported by the fact that moderately oxidized surfaces can be reformed electrochemically by reduction, since the metal atoms can retreat to the sulphide lattice. This would have been impossible if the elemental sulphur had been the oxidation product on the surface.

For galena and chalcopyrite, the following oxidation reactions prevail:

\[
\begin{align*}
CuFeS_2 & \rightarrow CuFe_{1-x}S_2 + xFe^{3+} + 3xe \\
PbS & \rightarrow Pb_{1-x}S + xPb^{2+} + 2xe
\end{align*}
\]  
(3.1.5)  
(3.1.6)

with \(x = 1\) for the outermost layers. In the case of galena, for example, there was a clear evidence for the presence of lead-oxygen species in the Pb(4f) spectra on the surface. Collectorless flotation becomes feasible when the hydrophilic metal-oxygen species on the surface are removed by the turbulent conditions and attrition in a flotation environment.

### 3.2.2 Flotation Chemistry of Chalcocite

The presence of dissolved oxygen is an important factor in sulphide flotation processes. Some level of surface oxidation is necessary for effective flotation separation, but under intensive oxidation conditions, unsatisfactory flotation with thiol collectors results. Plante (1949) stated that the formation of oxidation products may have a depressant or activating effect. The likely products of sulphide oxidation were set forth by Majima and Peters (1966).
Although elemental sulphur has been identified as a predominant oxidation product for sulphides in acidic medium, copper sulphide systems do not show such a behaviour. Figure 3.3 shows the $E_h$-pH stability diagrams in the absence of sulphur-oxy ions. The $E_h$-pH responses of a platinum and chalcocite electrodes in oxygenated aqueous solution of their respective ions have also been superimposed. For the Cu$_2$S electrode, the horizontal portion of the $E_h$-pH response in the acid pH range has been attributed to the corrosion region where the mineral electrode is responding to the concentration of Cu ions in solution (Natarajan and Iwasaki, 1972).

Under alkaline conditions, a passivated mineral surface is formed due to the presence of oxides or hydroxides and may thus, act similarly to an inert electrode. This explains the close $E_h$-pH responses of the Cu$_2$S and Pt electrodes. An important deduction can therefore be made of the surface product of chalcocite in oxygenated suspension under any specific redox condition. From Figure 3.3, it can be observed that, under alkaline conditions, the surface products of chalcocite is composed of various non-stoichiometric copper sulphide-oxide mixtures without the formation of a hydroxide. This is verified from the region where chalcocite and platinum electrodes overlap the $E_h$-pH diagrams for chalcocite.

Under acidic conditions and high $E_h$, chalcocite becomes soluble, which is the basis for oxidative leaching processes. Two different reaction stages have been proposed (Chander, 1985; Walker et al., 1984) as:

$$Cu_2S \rightarrow 2Cu^{2+} + S^0 + 4e \quad (3.1.7)$$

or through a reaction involving covellite as an intermediate (Sato, 1960):

$$Cu_2S \rightarrow Cu^{2+} + CuS + 2e \quad (3.1.8)$$

$$CuS \rightarrow Cu^{2+} + S^0 + 2e \quad (3.1.9)$$

From Eqns. 3.1.7 and 3.1.9, the surface of chalcocite is expected to be enriched with elemental sulphur which imparts surface hydrophobicity. In spite of that, chalcocite is not susceptible to collectorless flotation. Therefore, it becomes obvious that the absence of self-
induced floatability is related to the absence of any extensive sulphur enrichment on the surface. The most reasonable mechanism was proposed by Sato (1960), and Koch and McIntyre (1976):

\[ Cu_2S \rightarrow Cu^{2+} + CuS + 2e \]  

(3.1.10)

Sato (1960) pointed out that Covellite may be oxidized to sulphur according to eqn. 3.1.9, but the kinetics are very slow. It is known that such a reaction is feasible only in the absence of chalcocite since \( Cu_2S, CuS \) and \( S \) are not simultaneously stable (Garrels and Christ, 1965).

In an aqueous solution, the predominant copper-containing species in equilibrium with \( CuO \) are \( Cu^{++}, HCuO^- \) and \( CuO_2^- \) (Attia, 1975). Figure 3.4 shows the equilibrium relations of copper species in aqueous equilibrium with \( CuO \). The isoelectric point (IEP) of the dissolved copper species can be located around pH 9.0 and the point at which \( Cu^{++} \) and \( CuO_2^- \) are electrically equivalent (EP) is at pH 10.0. In Figure 3.5, \( Cu(OH)_2 \) establishes equilibrium with \( Cu^{++}, Cu(OH)_3^-, Cu(OH)_4^{2-} \) and \( Cu_2(OH)_2^{2+} \).

The IEP of the dissolved copper species is again around pH 9.0, and the EP for any ionic pair can be determined from the intersection of their equilibrium lines. Any of these ionic constituents in equilibrium with \( CuO \) and \( Cu(OH)_2 \) can be present on the surface of chalcocite depending on the pH of the aqueous medium (Parks and deBruyn, 1962). Thus, these ionic constituents together with \( OH^- \) and \( H^+ \) can be potential-determining ions for chalcocite.

Generally, surface oxidation of chalcocite has been known to be a relatively slow process and the following mechanism involved in charging the surface has been proposed by Oestreicher and McGlashan (1972):

\[ Cu(OH)_2(surface) + 2H^+ \rightarrow Cu^{2+}(surface) + H_2O \]  

(3.1.11)

\[ Cu(OH)_{2(surface)} + 2OH^- \rightarrow Cu(OH)_3^- \]  

(3.1.12)

The potential-determining ions can therefore be identified as \( Cu^{++}, Cu(OH)_3^-, H^+, OH^- \), and sulphur containing ions.

3.2 SULPHIDE MINERALS
Figure 3.3 - Eh-pH diagram for chalcocite. The response of platinum and chalcocite electrodes in oxygenated water has been superimposed. (Extracted from Young et al., 1988 and Natarajan and Iwasaki, 1972).
Figure 3.4 - Concentration of Various Cu(II)-Bearing Species in Aqueous Solution in Equilibrium with CuO (After Attia, 1975).

Figure 3.5 - Concentration of Various Cu(II)-Bearing Species in Aqueous Solution in Equilibrium with Freshly Precipitated Cu(OH)$_2$ (After Attia, 1975).
3.2.3 Flotation Chemistry of Heazlewoodite

Reports on the flotation chemistry of heazlewoodite are limited. Attempts have been made to float \( \text{Ni}_3\text{S}_2 \) with butyl and ethyl xanthates (Critchley and Straker, 1981; Critchley and Hunter, 1987). Voltammetric and surface capacitance measurements showed that dixanthogen forms on both oxidized and non-oxidized surfaces, both at low or high pH. However, the mechanical stability of dixanthogen on the \( \text{Ni}_3\text{S}_2 \) surface has been found to be weak (Heimala, 1985) and in dynamic flotation systems, loss of selectivity and recovery could be encountered. The most reasonable step for the concentration of heazlewoodite has therefore been through its selective depression.

The oxidation of heazlewoodite in aqueous environment follows a similar mechanism as presented in section 3.1.2. XPS and voltammetric analysis of \( \text{Ni}_3\text{S}_2 \) by Buckley and Woods (1991) indicates that, in basic solutions, the initial oxidation of heazlewoodite follows the reaction:

\[
\text{Ni}_3\text{S}_2 + 2x\text{H}_2\text{O} \rightarrow \text{Ni}_{3-x}\text{S}_2 + x\text{Ni(OH)}_2 + 2x\text{H}^+ + 2xe
\]  

(3.1.13)

Thus, the surface layer of the metal-deficient sulphide is composed of nickel hydroxide which is formed from the nickel ions that migrate from the sulphide lattice to the surface.

Under acidic conditions, the initial oxidation reaction is the removal of nickel from the sulphide lattice, resulting in the formation of the sulphide with lower nickel content and a subsequent production of NiS:

\[
\text{Ni}_3\text{S}_2 \rightarrow \text{Ni}_{3-x}\text{S}_2 + x\text{Ni}^{2+} + 2xe
\]  

(3.1.14)

\[
\text{Ni}_3\text{S}_2 \rightarrow 2\text{NiS} + \text{Ni}^{2+} + 2e
\]  

(3.1.15)
Figure 3.6 - Eh-pH diagram for heazlewoodite-water system at a total ionic species activity of 1E-04 M (Oxidation of sulphur is assumed to be complete). The response of a platinum electrode in oxygenated water has been superimposed. (Extracted from Critchley and Hunter, 1987 and Natarajan and Iwasaki, 1974).
An interesting aspect of heazlewoodite oxidation is that, even under acidic conditions, there is a high tendency for it to form a hydroxide (or hydrated oxide) which inhibits further oxidation of NiS. However, it was pointed out that NiS can undergo further oxidation to produce elemental sulphur according to the reaction (Buckley and Woods, 1991):

\[ \text{NiS} \rightarrow \text{Ni}^{2+} + S^0 + 2e \]  

(3.1.16)

The \( E_h\)-pH stability diagrams for the \( \text{Ni}_3\text{S}_2\cdot\text{H}_2\text{O} \) system is presented in Figure 3.6 with the potentials of \( \text{H}^+\cdot\text{H}_2 \) and \( \text{O}_2\cdot\text{H}_2\text{O} \) equilibria. Also shown on this diagram is the \( E_h\)-pH response of Pt electrode in oxygenated aqueous phase. As explained in section 3.2.2, the formation of oxides or hydroxides on mineral surfaces for the sulphide mineral-water-oxygen systems results in a passive layer formation which makes these surfaces behave similarly to inert electrodes. It can therefore be deduced that if heazlewoodite is to behave in a like manner to the platinum electrode under alkaline conditions then the surface product is likely going to be nickel hydroxide. This can be verified from \( E_h\)-pH response line of Pt, which overlaps the stability region of \( \text{Ni(OH)}_2 \) under alkaline conditions. At low pH, metal rich \( \text{Ni}_3\text{S}_2 \) will oxidize to produce \( \text{Ni}^{2+} \) and a sulphur-rich surface, and may account for self-induced floatability of nickel sulphide minerals at acidic pH (Heiskanen, 1990).

3.2 SULPHIDE MINERALS
3.3 ELECTROKINETICS

3.3.1 The Electrical Double Layer at Mineral-Water Interface

Most mineral particles develop a surface charge when brought into contact with a polar medium (e.g. water). The charge species will then move across the mineral-water interface until equilibrium conditions are established. The result is the formation of a region of electrical inhomogeneity in which excess charge fixed at the mineral surface is balanced by a diffuse region of equal but opposite charge on the liquid side, forming an electrical double layer.

Since the proposal of the first model of the double layer (Helmholtz, 1879), there have been various modifications to it. The latest refinement to the model was that by Grahame (Bockris et al., 1963, 1970), who replaced the Stern layer by the inner Helmholtz plane - the locus of electrical centres of dehydrated specifically adsorbing ions, and the outer Helmholtz plane - the locus of electrical centres of hydrated ions in contact with the surface (held only by electrostatic forces). A schematic presentation of the model as proposed by Grahame with a possible potential distribution at the interface is shown in Figure 3.7. From this model separate contributions to the diffuse layer charge made by cations and anions can be evaluated.

The potential-determining ions (PDIs), being the ionic species that give rise to the surface charge, influence the nature of the double layer and are unique to each kind of mineral. By developing a surface charge, the mineral surface acquires a potential with respect to the liquid phase. For ionic solids, the surface potential, \( \psi_0 \), is determined by the activity of the potential-determining ions as:

\[
\psi_0 = \frac{RT}{zF} \ln \left( \frac{a^+}{a^+_{pzc}} \right)
\]

(3.2.1)
Figure 3.7 - Grahame Model of the Electrical Double Layer

3.3 ELECTROKINETICS
where $F$ is Faraday constant, $z$ is the valence of the PDI ion, $a^+$ is the activity of the PDI ion in solution and $a^+_{pzc}$ is its activity at the point of zero charge (pzc). The pzc of a mineral is considered to be the single most important parameter that describes electrical double layer phenomena, since the sign of the surface charge has a major influence on the adsorption of all ions, and in particular, counter-ions (Fuerstenau and Urbina, 1988). The potential at the Stern plane, $\psi_b$, decreases with distance, $x$, and it drops to zero as $x \to \infty$. The potential, $\psi$, at any distance, $x$, from the surface, for small $\psi_o$, can be approximated as:

$$\psi = \psi_o \exp(-\kappa x)$$

(3.2.2)

where $\kappa^{-1}$ is the thickness of the double layer.

There is a large drop in potential between the solid surface and the Stern plane, $\psi_o - \psi_b$, that depends on the ionic strength of the solution. Some counter ions adsorb only electrostatically in the outer Helmholtz plane (OHP) and can reduce the value of $\psi_b$ to zero. Other ions may adsorb specifically in the inner Helmholtz plane (IHP). Under such conditions, the charge of ions adsorbed at the IHP may exceed the surface charge and therefore, may reverse the sign of $\psi_b$.

Table 3.2 shows various minerals and the corresponding potential determining ions. It can be seen that for ionic solids and oxide minerals, the PDIs can easily be predicted from the type of solid system. For oxides, hydrogen and hydroxyl ion are considered to be the PDIs (Wood, 1946; Verwey, 1950), while for ionic solids (e.g. AgI, Ag$_2$S, CaF$_2$), PDIs are simple lattice cations and anions. For ionic solids such as calcite (CaCO$_3$), the PDIs are considered to be Ca$^{2+}$ and CO$_3^{2-}$, but also H$^+$, OH$^-$ and HCO$_3^-$, since these determine the concentration of Ca$^{2+}$ and CO$_3^{2-}$ (Fuerstenau, 1971).

Theoretically, most sulphides are in reversible equilibrium with aqueous metal and sulphide ions, according to a definite solubility product ($K_{sp}$). In practice, however, the solubility is so low that other processes become more significant.

3.3 ELECTROKINETICS
Table 3.2 - Potential-Determining Ions of Various Solids

<table>
<thead>
<tr>
<th>TYPE OF SOLID</th>
<th>POTENTIAL-DETERMINING IONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic solids:</td>
<td></td>
</tr>
<tr>
<td>e.g. AgI, BaSO₄, CaF₂</td>
<td>AgI → Ag⁺, I⁻</td>
</tr>
<tr>
<td></td>
<td>BaSO₄ → Ba²⁺, SO₄⁻² → CaF₂ → Ca²⁺, F⁻ and Hydrolysis products of these ions</td>
</tr>
<tr>
<td>Oxides:</td>
<td></td>
</tr>
<tr>
<td>e.g. SiO₂, Fe₂O₃</td>
<td>SiO₂ → H⁺, OH⁻ and hydroxylated lattice ions</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphides:</td>
<td></td>
</tr>
<tr>
<td>CuFeS₂, Cu₂S, Ni₃S₂, PbS</td>
<td>Hydroxylated metal ions</td>
</tr>
<tr>
<td></td>
<td>Oxy-sulphur species</td>
</tr>
<tr>
<td></td>
<td>Sulphur and metal ions</td>
</tr>
</tbody>
</table>

For galena, Kₛₚ = 10⁻²⁸ (mol·l⁻¹)², which makes it practically an inert ionic solid. Depending on the redox potential (Eₗ), it may undergo superficial oxidation to thiosulphates and sulphates, which are relatively soluble. For sulphide minerals, therefore, the PDIs are not well defined due to the formation of variable surface oxidation products depending not only on the solution pH but also on the Eₗ.

3.3.2 Electrokinetic Phenomena

The physical chemistry of flotation systems is well understood through the concept of the electrical double layer, which is generally used in the interpretation of flotation phenomena (Aplan and Fuerstenau, 1962).

Electrokinetic phenomena are the phenomena which arise when the mobile part of the electrical double layer is sheared off from a charged surface. The shearing force causes a relative motion between the charged surface and the ions in the mobile part of the double layer. This provides a means for estimating the potential developed at the slipping plane. The exact position of the shear plane which is at the border with the diffuse part of the EDL is not known, but it is
assumed that slippage occurs not far from the OHP. This is due to the fact that a layer of water about one molecule thick may be bound to the surface by charge-dipole interaction (James, 1979). Electrokinetic results are generally expressed in terms of ζ-potential which is a measure of the potential at the slipping plane. But it is usually assumed that the ζ-potential and the δ (Stern)-potential are equivalent (Overbeek, 1952).

Various electrokinetic effects have been used to evaluate the zeta potential on a mineral surface for a given set of conditions, but the most widely used method is electrophoresis due to its practical applicability.

Electrophoresis involves the movement of charged colloidal particles relative to a stationary liquid under the effect of an applied potential gradient. The electrophoretic mobility, \( v_E \) (velocity per unit potential gradient), of charged colloidal particles suspended in an electrolyte is measured at an applied potential gradient. An increase in the electrolyte concentration results in the lowering of the ζ-potential due to the compression of the EDL.

### 3.3.3 Effect of Hydrolyzed Metal Ions Adsorption on ζ-Potential

The adsorption or precipitation of hydrolyzed metal ions may reverse the electrical charge on a solid surface. At the oxide-solution interface, the following observations have been made in terms of hydrolyzed metal ions adsorption as a function of pH (Stryker and Matijevic, 1966; Healy et al., 1968; Murray et al., 1968; Matijevic, 1976; Schindler and Stumm, 1987):

- For each metal ion there is a characteristic critical pH range over which the adsorption increases to a maximum.
- The adsorption behaviour is influenced by the charge on the surface of the substrate.
- When the solid surface is saturated, the adsorption density is equivalent to a layer of ions which has acquired at least one hydration sheath.
- Provided the adsorbate concentration is high enough, the adsorption at an interface can reverse the ζ-potential on the solid surface. The resulting surface shows another point of
ζ-potential reversal at still higher pH, corresponding closely to the i.e.p of the hydroxide of the adsorbed metal.

One interesting observation made by James and Healy (1972) was that even for a negatively charged surface, the adsorption of a positive multivalent ion (e.g. Fe\(^{3+}\), or Ni\(^{2+}\)) is not spontaneous until a certain pH level is reached when lower charged hydroxylated species, M(OH)\(^{(n-1)+}\), begin to appear. This phenomenon was explained by considering a model involving the hydration energy of the adsorbing species. For the highly charged ion, the energy used in removing the secondary hydration sheath to allow the ion to penetrate the IHP is large enough to make the overall value of \(\Delta G^0\) positive. However, when charge is reduced by hydroxylation, the net free energy of adsorption is negative and the process becomes spontaneous.

The same phenomenon is probably involved in an interfacial precipitation of the metal hydroxide, occurring at a pH lower than the bulk value. This model gives an interpretation of the points of zeta potential reversal. In Figure 3.8, the first charge reversal (prz1) is the i.e.p. or p.z.c.\(^2\) of the substrate oxide. The second charge reversal (prz2) corresponds to that of the metal hydroxide, and, depending on the available surface area and the metal ion concentration in solution, this layer may be incomplete.

For a complete layer, the prz2 occurs at a lower pH and the surface is more positive. The final charge reversal, prz3, usually appears at pH values below the i.e.p. (or p.z.c.) of the metal hydroxide and shifts upwards as the precipitation increases. The behaviour of such a surface is electrokinetically indistinguishable from that of the bulk hydroxide after several layers have been formed. It is not clear why more surface layers have to appear before the precipitated surface becomes electrokinetically identical to the pure hydroxide. However, factors such as surface roughness and imperfections in the crystal structure of the initial hydroxide nuclei could all have a modifying effect (Hunter, 1981).

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\(^2\) Strickly speaking, according to the IUPAC terminology, the term i.e.p. is equal to the negative log [PDI] when \(\xi\) is equal to zero. The term, p.z.c., stands for the negative log of the PDI concentration at which the charge is equal to zero. These two, however, are identical when there is no specific adsorption.

3.3 ELECTROKINETICS
Figure 3.8 - A model of charge reversal by adsorption of hydrolyzed metal ions onto silica. (after James and Healy, 1972)
It is worth mentioning that the above analysis does not hold universally and that there may be other influencing factors. Murray et al., (1968) found the behaviour of Co(II) on hydrous manganese oxide to be different from that of Ni(II) and Cu(II) and attributed it to the catalytic properties of the manganese.

### 3.3.4 Effect of Polymer Adsorption on \( \zeta \)-Potential

The adsorption of polymer molecules in the Stern layer and its influence on the zeta potential has been discussed by many researchers. In almost all cases, two main effects of the polymer adsorption can be identified:

- It influences the adsorption behaviour of the ions at the interface, including the potential determining ions,
- It may, under certain conditions, alter the position of the shear plane at the solid-liquid interface.

In a AgI system, Koopal and Lyklema (1975) observed the direct effect of the polymer adsorption on PDI ions adsorption and also on the position of the shear plane. At lower concentrations of the polymer, they observed that there was a gradual shift of the i.e.p. to more positive values as the polymer dosage increased. However, the maximum value of the zeta potential remained constant at these low concentrations and this phenomenon was explained in terms of the polymer orientation in a horizontal configuration.

It was also observed that the increased adsorption at higher polymer concentrations resulted in pronounced loops formation, which forced the shear plane out from the surface. From these results, they concluded that the shift of the shear plane and the consequent change in \( \zeta \)-potential was basically dependent on the fractional surface coverage of the surface by the polymer molecules.

A model of the interfacial region in the presence of neutral polymers adopted after Brooks (1973) is shown in Figure 3.9. The relative zeta potential, the thickness of the adsorbed
polymer layer, the position of the shear plane and the bulk ionic strength were discussed in a series of papers (Brooks and Seaman, 1973; Brooks, 1973). In this model, Brooks considered some possible cases of zeta potential change with respect to the magnitude to which adsorbed polymer molecules affect the position of the shear plane.

- The position of the plane of shear is not affected by the presence of the adsorbed polymer molecules, and \( x = d_s \).
- The shear plane moves to a position within the adsorbed polymer, and \( 0 < d_f < d \).
- The shear plane extends to a location where \( x = d \).

The shear plane is supposed to lie at a point \( x = d_s \) within the adsorbed layer \( 0 < d_s < d \) and \( d_f \) is the thickness of the adsorbed layer within which the fluid velocity is non-zero during electrokinetic measurement.

Generally, from the treatment given by Brooks (1973), the zeta potential of a surface in the presence of adsorbed neutral polymer molecules will increase under the following conditions:

- when the adsorbed layer is free draining\(^3\) to a certain extent and
- when the charge density of the surface is not affected by the presence of the adsorbed polymer molecules.

The zeta potential could also decrease with adsorbed polymer molecules under the following conditions:

- when there is a decrease in charge density,
- when there is a shift in the position of the shear plane.

Evidence for the shift in the location of the shear plane which, according to this model, results in zeta potential decrease was observed by Brooks and Seaman (1973), for the dextran - polysaccharide/erythrocyte-red blood cells system and Lyklema (1976), for the AgI-polyvinyl alcohol system.

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\(^3\) This means that in the double layer region \( 0 < x < d \), the water is not immobilized.
Figure 3.9 - Model of the interfacial region in the presence of an adsorbed layer of neutral polymer. (Adopted after Brooks, 1973).
The zeta potential change in the presence of adsorbed polymer has also been observed by other researchers. Wie and Fuerstenau (1974) found that the adsorption of dextrin macromolecules affected the zeta potential of molybdenite. The reduction of the zeta potential in absolute magnitude at all pH conditions was interpreted in terms of the effect of the large polymer molecules shifting the shear plane farther from the surface.

A decrease in the electrophoretic mobility on adsorption of a nonionic polymer at an interface was observed by Garvey et al., (1976) under conditions in which the presence of the polymer does not affect the following double layer parameters:

- the surface charge density
- the specific ion adsorption in the Stern plane and
- the charge distribution in the diffuse part of the double layer.

In this way, the decrease in ζ-potential can be attributed directly to a change in the location of the shear plane.

A decrease in the ζ-potential with the addition of an anionic polymer to hematite fines was reported by Sresty and Somansundaran (1980) and was ascribed to a change in the position of the shear plane. They, however, suggested that the measured ζ-potential could be that of the adsorbed polymer rather than that of the solid surface. This was because a constant zeta potential value was obtained over a wide concentration range.

There are other physical factors, independent of the solid surface, which may affect the electrophoretic mobility measurements in the presence of a polymer. A typical example is a non-Newtonian viscosity effect. For a Newtonian fluid, a parabolic velocity profile is established across the electrophoresis cell during measurement. Electrophoretic mobilities can therefore be measured at the position where the fluid velocity is zero, i.e. at the stationary level. Polymer solutions may, however, exhibit non-Newtonian viscosity characteristics, and in this case, the velocity profile could be blunted. The mobility at the location of what used to be the stationary

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4 Viscosity is described as Newtonian when the shearing force per unit area τ between two parallel planes of liquid in relative motion is proportional to the velocity gradient between the planes.
value in the Newtonian fluid would become non-zero. The measured particle mobility will therefore carry some level of error. For the dextran solutions, Brooks and Seaman (1973) measured the viscosities of dextran solutions as a function of shear rate and found that no non-Newtonian behaviour was present.

### 3.3.5 Electrokinetic Behaviour of Metal Sulphide Suspensions

Various attempts have been made, using electrokinetic studies, to explain the surface chemical behaviour of sulphide minerals (Hukki et al., 1952; Healy and Moignard, 1976), and in most cases, problems like surface oxidation and precipitation presented differing surface behaviour, even for the same metal sulphide system, depending on the conditions under which the experiment was carried out.

An early attempt to find a correlation between the ζ-potential and flotation properties of minerals was made by Gaudin and Sun (1946). As part of their work, they considered the effect of added ions (Cu$^{2+}$ and Fe$^{3+}$) on the ζ-potential of sphalerite at pH 6.0 and observed a change. Hukki et al., (1952) also studied the ZnS-Cu$^{2+}$-ethyl xanthate system and observed a large change in the ζ-potential with the addition of Cu$^{2+}$ ions and subsequent charge reversals which is possibly due to specific adsorption of Cu$^{2+}$ at low pH values, and hydroxide precipitation in alkaline environment.

In both studies, the equilibration time was approximated as the flotation time (i.e. 2 - 3 minutes), and factors such as conditioning time, percent solids of the suspension, pre-equilibration pH and chemical composition of the mineral were not considered. Further electrokinetic studies on sphalerite were done by McGlashan et al., (1968), Huber and Weigl (1969), Fuerstenau et al., (1974) and Fuerstenau et al., (1990). In all cases, however, the i.e.p. for ZnS was found to be different. Similar observations were made on other metal sulphide systems.
A more fundamental study by Moignard et al. (1977) indicated that the i.e.p. of sulphide minerals, unlike oxides, depends on conditions that promote or minimize sulphur-rich surfaces and other oxidation product coverages. Fuerstenau et al. (1990), showed that in the virtual absence of oxygen, the i.e.p. of pyrite is located at pH 4.0. In the presence of air, however, the zeta potential reversals occur and i.e.ps are established at pHs 2.6, 4.8 and 6.9.

The effect of pre-equilibration pH at fixed percent solids is shown in Figure 3.10, where the electrokinetic curves for elemental sulphur and zinc oxide-hydroxide have been given for comparison. It can be observed that as the pre-equilibration pH increases from 3.0 to 8.5, the pH$_{\text{iep}}$ shifts systematically to lower values. The unusual trend of the curve at pre-equilibration pH 9.8 has been interpreted in terms of the presence of metastable polynuclear Zn(II) species.

Figure 3.11 shows the effect of percent solids of sulphide suspensions on electrokinetic behaviour. At a fixed pH 3.0, the pH$_{\text{iep}}$ shifts to more alkaline as the concentration of the suspension is increased from 0.1 g/l to 2.0 g/l solids. Another finding in this work was the dependence of i.e.p. on conditioning time.

It is worth noting from this work that the pH$_{\text{iep}}$ of ZnS, more so than other sulphides, is not a unique value but depends on the conditions employed in bringing the surface to equilibrium. Generally, at low pH and especially at low percent solids, the i.e.p. shifts to approximate that of sulphur. The presence of a sulphur-rich surface can be represented by the following general metal sulphide reaction:

$$MS + \frac{1}{2}O_2 + 2H^+ \rightarrow M_{1-x}S + xM^{n+} + H_2O + xne$$

(3.2.3)

Thus, the formation of the surface products is also dependent on the redox potential ($E_h$) of the reaction. The formation of a sulphur-rich surface and the consequent inherent floatability of many sulphide minerals in acid circuits was observed by Clifford and Miller (1974).
Figure 3.10- Effect of Pre-equilibration pH on the Electrophoretic Mobility-pH Behaviour of ZnS (After Moignard et al, 1977).

Figure 3.11- Electrophoretic Curves for ZnS Suspensions Pre-equilibrated at pH 3.0 and at Various % Solids (After Moignard et al, 1977).
Equilibration at higher pH values leads to hydrolysis and metal hydroxide coatings on the mineral surface. This is corroborated by the shift of the pH$_{iep}$ towards Zn(OH)$_2$-ZnO i.e.p., as seen in Figure 3.10. Similar observations were made by James and Healy (1972) and Girczys et al., (1972) for nickel and copper systems, respectively.

In the discussion of electrokinetic results, the oxidation products formed on the surface of sulphide minerals can, under controlled conditions, be predicted from $E_h$ - pH diagrams to corroborate some observed trends. It can be seen from Figure 3.6 that for an aerated system, Ni(OH)$_2$ will be the most dominant surface product for heazlewoodite around the pH$_{iep}$, taking into consideration the position of the oxygen potential line. In much the same way, it can be deduced from Figure 3.3 that the formation of a hydroxide layer on the surface of chalcocite is thermodynamically non-existent under all alkaline conditions.
3.4 POLYSACCHARIDES IN FLOTATION

Polysaccharides occur universally in almost all plants. These are polymers of high molecular weight based on simple monosaccharide units (Aspinall, 1970), which are joined to each other by glycosidic linkages. Three main types of polysaccharides which are of importance to the mineral processing industry are cellulose, guar gum and starch. The main structural differences between these polysaccharides is the location of the hydroxyl groups in their anhydroglucose units. Galactomannan, which is the major constituent of guar gums has its two neighbouring OH groups of the D-mannose ring in a cis-configuration, while the OH groups of the D-glucose ring of starch and cellulose are in a trans-configuration. Again, the spatial configuration of the glucose ring is such that, for amylose, the OH groups on C-1 and C-2 are on the same side of the ring (alpha-glucose) while for cellulose, the OH groups are on opposite sides of the ring (beta-glucose). Figure 3.12 shows the basic structural differences between them and between their monomers. A brief review of these polysaccharides in connection with their use in the mineral industry is given in the section below.

Cellulose

Cellulose is by far the most abundant of all polysaccharides and also of all naturally occurring organic substances, being found as the principal cell-wall constituent of higher plants. It exists in almost pure form in cotton fibres where it is present up to about 98% on a dry-weight basis.

Cellulose is assumed to be isomeric with starch since it undergoes hydrolysis to yield glucose. With a D-glucose basic unit, its empirical formula can be written as C₆H₁₀O₅. Structurally, it is a linear polymer of D-glucopyranose units connected uniformly by ß-1,4 links (Figure 3.12). Such a structure is supported by the kinetics of the hydrolysis of cellulose in sulphuric acid which showed that at least 99% of the bonds are of the same type (Aspinall, 1970). Due to their size and the strong bonding forces holding the molecules together, cellulose
is insoluble in most solvents and the molecular weight is estimated to be over a million (Whistler and Smart, 1953).

Swelling and dissolution of cellulose is an important factor for any kind of interaction with mineral surfaces and therefore needs to be understood. Cellulose has a strong affinity for water and most reactions start when it is in the fibrous state. The fibrous nature imparts to it a large surface area which makes it easy for sorption on many substances. Apart from reactions of a sorptive nature, most cellulose interactions can be achieved by making all portions of the fibre available. Such a condition is possible if the fibre is highly swollen before or during the reaction. In the case of a complex formation with ions, the osmotic pressure of the opposite ions and the electrostatic repulsion between chains increase the swelling forces. Due to the existence of these strong forces, cellulose is only soluble in liquids which can break the associative forces between the chains and, at the same time, combine with the chains to prevent their reassociation.

Carboxymethyl cellulose (CMC), being an anionic derivative of cellulose, has been mostly used to depress talc (Edwards, 1980; Baker, 1982), and minerals which can be floated with fatty acids (Lin and Burdick, 1988), and also extensively tested in the flotation of sulphides to depress silicates (Bakinov et al., 1964; Gorlovsy, 1965; Rhodes, 1981; Steenberg and Harris, 1981; Jin et al., 1987). In the work by Bakinov et al., (1964), it was observed that the nickel content of the flotation concentrate could be markedly improved when the silicate gangue is depressed with a CMC having a high degree of polymerization and a low level of substitution. A more extensive investigation was carried out by Rhodes (1981), who utilized CMC to depress magnesia bearing minerals present in Australian nickel ores, with much success. It was also realized that the magnesia bearing tailings tended to flocculate with a higher molecular weight CMC product (degree of polymerization > 1000). The use of CMC to depress silicates in copper/nickel flotation was reported in the former U.S.S.R. in the 1950s (Vaneev, 1957).
**Galactomannan**

Galactomannans are present in the endosperms of most leguminous seeds, especially in alfalfa. They are most abundant in seeds of guar and the locust bean gum from locust trees which together serve as the primary present-day source of industrial production (Seaman, 1980; Aspinall, 1970; Whistler and Smart, 1953). They are soluble in water and form thick, highly viscous solutions.

Galactomannans are branched polymers composed of the sugars D-galactose and D-mannose. In most cases, the percentage of the D-mannose units is about 60-80 while that of the D-galactose is of the order of 40-20%. Guaran, the galactomannan of the guar seed endosperm, is the most extensively investigated and contains the highest proportion of D-galactose in relation to D-mannose, the ratio being around 1:3 (Heyne and Whistler, 1948). The ratio for the locust bean gum, on the other hand, is 1:4, while that of the alfalfa seed is known to contain an unusual D-galactose:D-mannose ratio of 2:1 (Smith, 1948). The galactomannan structure consists of linear chains of β-D-mannopyranosyl units linked together by (1→4) bonds with side branches of α-D-galactopyranosyl units joined to the main chain by (1→6) linkages.

Galactomannans dissolve in either hot or cold water to form very viscous solutions. This high viscosity is attributed to their branched structures, which make it difficult for such molecules to pack in close association. Strong interactions with solutions of inorganic cations have been observed (Seaman, 1980). Generally, it reacts with polyvalent cations under alkaline conditions through the adjacent hydroxyl groups in the cis-position, to produce an extensive cross linking. In most cases, these reactions lead to insolubilization or precipitation. Lin and Burdick (1988) observed that galactomannans can serve as more effective depressants than starches and dextrins due their cis-hydroxyl configuration.

Galactomannan and its derivatives are widely used as flocculants in liquid-solid separation in unit operations like filtration, settling and clarification of mineral slurries. It is worth mentioning that the flocculation process involves the adsorption of galactomannan on
only hydrated mineral surfaces through hydrogen bonding. When applied in low dosages, it serves as a depressant of talcose minerals and other gangue materials during the flotation of pentlandite (Seaman, 1980; Makarinsky, 1975).

**Starch**

The use of starch in mineral processing can be traced back to the early thirties when Lange (1931) patented it as a depressant in the selective separation of quartz from phosphate ores. Typically, corn and wheat grains and selected roots or tubers such as potato, cassava, and tapioca are the raw materials from which starch can be obtained (Evans and Würzbury, 1967; Rutenburg, 1980).

Starch is a carbohydrate containing units of anhydroglucose (d-glucose) joined together primarily through d-α-(1→4) bonds. The basic unit structure of starch, d-glucose (dextrose) is shown in Figure 3.12 with the carbon atoms numbered in the conventional IUPAC format. The molecular formula can be represented as $(C_6H_{10}O_5)_n$, where $n$ may be any integral number of up to 1000 or more (Schulz and Cooke, 1953).

Irrespective of the source, starch contains two major fractions: a water-soluble amylose and a water-insoluble amylopectin (Whistler and Pascall, 1965). The proportion of these two polysaccharide components varies between different plants, but the majority of starches contain between 15% and 30% of amylose, while the amylopectin content is 74 to 78% (Greenwood and Thomson, 1962; Banks and Greenwood, 1975). Amylose has a linear structure with the d-glucose units joined by d-α-(1→4) bonds, the molecular weights varying from 40,000 to 650,000, depending on the type of starch. Amylopectin, is a branched polymer having both (1→4) and (1→6)-α-d bonds, the latter occurring at every 25 to 27 glucose units. The molecular weight of amylopectin has been estimated to be as high as 1 to 6 million (Johnson, 1979).

The large number of hydroxyl groups in the amylose molecule imparts hydrophilic properties to the polymer, giving it a high degree of dispersibility in water. However, amylose
macromolecules, with their linearity, mobility, and abundant hydroxyl groups have a tendency to orient themselves in a parallel fashion and approach each other closely enough to permit hydrogen bonding between hydroxyl groups on adjacent polymers, and this can result in the reduced affinity of the polymer for water (Würzburg, 1989). On the other hand, the large size and branched structure of amylopectin reduces the mobility of the polymers and therefore interferes with any tendency for them to be oriented closely enough to form hydrogen bonds. As a result, amylopectin is quite insoluble in water.

Due to the high molecular weights of starches, their use in mineral separation has basically been restricted to the area of flocculation (Lin and Burdick, 1988), where most research studies have been carried out on the concentration of iron ores (Iwasaki et al., 1969, Balajee and Iwasaki, 1969; Colombo and Frommer, 1976; Iwasaki, 1979, 1983; Jacobs and Colombo, 1980; Colombo, 1980 and Termes and Wilfong, 1984). A selective flocculation process, in which starch is used, can be found at Tilden Mine, Michigan, U.S.A.

3.4.1 Dextrins

Some properties of native starches such as lack of free-flowing or water repellency of the starch granules, insolubility, sensitivity of cooked starches to breakdown when exposed to shear or to low pHs, etc., limit their usefulness (Würzburg, 1989). Modified starches were therefore developed which do not exhibit these deficiencies. Modifications can be carried out in a wide variety of ways, such as roasting, cooking, oxidation, hydrolysis, etc., and are designed to alter starch characteristics such as hydrophilicity, gelatinization, ionic character and molecular weight (Rutenburg, 1980; Colonna et al., 1987).

Dextrins are one of the end products of modified starches and are usually classified into four main groups, depending on the method of preparation:

• Those produced through the hydrolysis of starch by the action of liquifying enzymes such as amylases, (Dextrans),

3.4 POLYSACCHARIDES IN MINERAL FLOTATION
Figure 3.12 - Structural Differences Between Some Common Polysaccharides.
• Degradation products produced by acid hydrolysis of starch in aqueous media,
• The cyclic Schardinger dextrins formed by the action of Bacillus macerans on starch,
• The pyrodextrins, which are obtained by the action of heat, or both heat and acid on starch.

Pyrodextrins are commonly used in the mineral industry and are being investigated or utilized as depressants in the separation of a wide range of sulphide minerals (Hemlund, 1961; Merill and Pennington, 1964; Last and Ribotto, 1964; Wie and Fuerstenau, 1974;). Depending on their method of preparation, pyrodextrins may be classified as white, yellow (canary) or British gums, with white dextrins and British gums having solubilities between 10 - 95%, while yellow dextrins have solubilities between 95 and 100% (Colonna et al., 1987). British gums are prepared by the action of heat only in the range of 180 - 210 °C, while white and yellow dextrins are obtained by the action of a combination of heat and acid. The relationship existing between these pyrodextrins is shown in Figure 3.13.

Figure 3.13 - Relationship between various pyrodextrins obtained from starch degradation (after Evans and Würzburg, 1967).
The dextrinization of starch involves complex chemical changes which are not fully understood. Three major reaction steps can, however, be identified during this chemical transformation, the relative role of which depends on the type of dextrin being produced. These reactions are discussed below:

1. **Hydrolysis**

   This is the predominant reaction for the preparation of less converted white dextrins at low temperatures. In the presence of acid and moisture, scission of α-D-(1→4) and in some cases α-D-(1→6) glucosidic bonds in the starch occur in the initial stages of the dextrinization process. Such degradation results in increased reducing end groups due to the formation of aldehydic end groups, a decrease in molecular weight and a decrease in viscosity of the dispersed product in water.

2. **Transglucosidation**

   This is a rearrangement process involving the rupture of α-D-(1→4) linkages followed by a recombination of the fragments with nearby free hydroxyl groups to form α-D-(1→6) branched structures, under conditions of high temperature and low moisture content (Thompson and Wolf from, 1958; Kerr and Cleveland, 1953; Brimhall, 1944). Thus, this kind of transformation is predominant during the production of British gums.

3. **Repolymerization**

   This type of transformation usually occurs in yellow dextrins. Under acid-catalyzed conditions and at high temperatures, the hydrolyzed fragments undergo repolymerization to form larger, highly branched molecules (Colonna et al., 1987; Mora et al., 1958). This results in a drop of the reducing sugar content, and an increase in viscosity.
**Use of Dextrins in Sulphide Flotation**

Many important discoveries involving the use of polysaccharides to selectively treat ores that contain inherently hydrophobic minerals have been cited in the literature. A patent by Brown (1937) described the depression of molybdenite in the flotation of Mo-Cu ore with the aid of starch. Later work in the depression of sulphides, however, revealed that crossed-linked starches and dextrins were more effective depressants in terms of selectivity and the reagent dosage (Lim and Goodman, 1982). Booth (1939) claimed that corn dextrin was very effective in depressing carbonaceous materials in precious metal ores and was quite selective in its action. Since then, dextrins and other polysaccharides have been known to be good depressants for flotation of inherently hydrophobic minerals as molybdenite (Wie and Fuerstenau, 1973), talc (Steenburg and Harris, 1984), graphite (Afenya, 1982) and coal (Klassen, 1963; Huang et al., 1978). In the flotation of Cu-Mo sulphide ores, dextrin can be used to depress inherently hydrophobic molybdenite while floating copper sulphides with thio-collectors (Hernlund, 1961). At the Copper Concentrator of Mount Isa Mines, it has been reported (Grano et al., 1991) that a large proportion of pyrite is covered by carbonaceous matter approaching a graphite structure which imparts moderate hydrophobicity and causes the pyrite to report to the copper concentrate. To overcome this problem, an organic depressant that contains dextrin is used to inhibit pyrite flotation.

It is interesting to observe, however, that recent studies revealed that dextrins do not adsorb onto solid surfaces via hydrophobic interactions as postulated by some researchers (Wie and Fuerstenau, 1973; Huang et al., 1979), but through specific interactions with hydroxylated metallic adsorption centers (Qi Liu and Laskowski, 1989; Nyamekye and Laskowski, 1991; Subramanian and Laskowski, 1992). Further purification of graphite by leaching with acids that reduces the level of trace impurities in graphite makes it even more hydrophobic and was found to significantly decrease dextrin adsorption (Subramanian and Laskowski, 1992). In the papers by Kennedy and Kay (1976) and Kennedy et al. (1977) it was reported that branched
polysaccharides form insoluble complexes with freshly precipitated metal hydroxides and this is entirely in line with Qi Liu and Laskowski's observations.

In polymetallic sulphide flotation systems, dextrins have been used as depressants due to their low molecular weight, highly branched structure and high hydroxyl content which renders the mineral surface hydrophilic when it is adsorbed. Known industrial applications include depression of pentlandite at pH 11 - 12 in the differential flotation of Cu-Ni bulk concentrate at Outokumpu Oy, Kotalahti mine in Finland (Lukkarinen, 1968), and depression of galena in the Cu-Pb separation at Brunswick Mines using dextrin and SO$_2$ (Neumann and Schnarr, 1971).

These applications are based on experimental results and there is lack of understanding of the underlying mechanism of interaction of dextrin with the mineral surface which has retarded the wider application of the reagent as a selective depressant. A review of the different conflicting interaction mechanisms is given in section 3.5.4. In view of these misunderstandings, an investigation into the mode of dextrin depression action on sulphide mineral surfaces needs to be conducted.

3.4.2. Molecular Weight Characterization

The success of utilizing an organic polymer as a depressant in mineral processing depends to a large extent on its molecular weight. It is well known that high molecular weight polymers are usually used in the flocculation of fines while low molecular weight polymers serve as effective dispersants and depressants. The characterization of polysaccharides in terms of their molecular weight is therefore necessary in the development of good organic depressants.

The molecular weight of polysaccharides can be determined by employing either absolute (primary) methods which are capable of making determinations from first principles or using secondary methods which require calibration with known molecular weight standards. The most common primary methods involve:
(a) colligative property measurements to determine $\bar{M}_n$, of which osmotic pressure is the only one offering the required sensitivity for high molecular weight polymers, and

(b) light scattering techniques to determine $\bar{M}_w$.

Amongst the secondary methods, the most common techniques are:

(c) solution viscosity measurements, and

(d) gel permeation chromatography, a method which is gaining popularity and was used in this work to determine the molecular weight of tapioca dextrin.

(a) Colligative Properties

The properties of a solution at infinite dilution depend on the number of independent kinetic units in the solution and hence on the number of solute molecules. Such properties, known as the colligative properties, include lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. For the purpose of this work, only measurements involving osmotic pressure will be discussed since the other colligative properties are only suitable for low molecular weight materials (Campbell and White, 1989).

Successful application of the osmotic pressure method lies in the availability of a suitable membrane for the polymer to be studied. Various osmometers have been employed using the following relationship:

$$\Pi = \frac{RTc}{\bar{M}_n} + A_2 c^2 + A_3 c^3 + \cdots$$  \hspace{1cm} (3.5.1)

In the above expression, $c$ is the concentration, $\Pi$ the osmotic pressure and $R$ the gas constant. The second, third and higher power terms on the right hand side express the departure from ideality of polymer solutions. $A_2$ and $A_3$ are the second and third virial coefficients, respectively. In most applications the third and higher virial coefficients are negligible. A plot of $\Pi/c$ versus $c$ therefore yields an intercept of $RT/\bar{M}_n$ from which is readily obtained the molecular weight and a slope $A_2$ which accounts for the polymer-solvent interaction. The so-called theta-solvent
condition arise when $A_2 = 0$ and corresponds to a situation when an infinitely high molecular weight polymer just swells but does not dissolve in the solvent. In this case, a plot of $\Pi/c$ versus $c$ will have a zero slope.

Membrane osmometry is capable of measuring absolute molecular weight averages up to about one million. However, accuracy diminishes for higher molecular weights. For low molecular weight polymers, there is again a limitation due to the diffusion of low molecular weight molecules through the membrane. This experimental technique gives the number average molecular weight, which is based on the number of macromolecules, $n_i$, and the weight fraction, $g_i$, of molecules with molecular weight $M_i$:

$$\bar{M} = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum g_i}{\sum n_i}$$ (3.5.2)

The consequence of this averaging procedure is that the result is weighted equally for small and large molecules. The resultant average molecular weights are, therefore, strongly influenced by low molecular weight impurities.

**(b) Light Scattering**

This is a more reliable means of measuring the absolute molecular weight average of macromolecules and has been used extensively (Bender, 1952; Arond and Frank, 1954; Barry and Halsey, 1963). When light is transmitted through a liquid, a small part of it is scattered elastically (Rayleigh scattering) due to optical discontinuities arising from the liquid molecules. In the presence of polymer molecules, additional scattering is observed and has been shown to be a function of polymer size, shape and concentration of the molecules, $c$. Measurements of the differences in intensity of scattered light between the solvent and a series of dilute polymer solutions can therefore be used to determine the molecular weight. By using the light scattering photometer, the turbidity, $\tau$, can be determined and is related to the molecular weight, $\bar{M}_w$, by (Debye, 1947):
\[
\frac{H c}{\tau} = \frac{1}{M_w} + 2A_2 c
\]  
(3.5.3)

where

\[
H = \frac{32\pi^3}{3N_0} \left( \frac{dn}{dc} \right)^2 \frac{n_0^2}{\lambda^2}
\]  
(3.5.4)

\(A_2\) is the second virial coefficient which vanishes in an ideal solution, \(n_0\) is the refractive index of the solvent, \(dn/dc\) is the concentration dependence of the refractive index of the polymer solution (a constant), \(N_0\) is Avogadro's number and \(\lambda\) is the wavelength of incident light in air.

The differential refractive index \(dn/dc\) is determined by using the differential refractometer and scattered light intensity is measured at angles of incidence 0° and 90°. A plot of \(Hc/\tau\) versus \(c\) yields an intercept, \(1/M_w\), and so the molecular weight average can be obtained. Light scattering photometers involving laser light sources are now in use and because of their much higher light intensity, it is possible to detect light scattered at small angles.

Light scattering determines a weight average molecular weight; thus, averaging on the basis of the weight fractions \((g_i)\) of molecules of given mass \((M_i)\):

\[
\bar{M}_w = \frac{\sum g_i M_i}{\sum g_i}
\]  
(3.5.5)

In this case, the weighted average of each molecule is proportional to its molecular weight. Due to this weighting method, the resultant molecular weight is highly sensitive to traces of large contaminants, such as dust and molecular aggregates, which contribute to the overall scattering intensity. A good clarification technique is therefore needed in the preparation of the sample solutions.

(c) Solution Viscometry

Measurement of intrinsic viscosity of polymer solutions provides a means of determining the molecular weights of polysaccharides. The intrinsic viscosity \([\eta]\), is defined by:
where \( \eta_R \) is the relative viscosity, \( \eta_{sp} \) the specific viscosity, and \( \eta_o \) and \( \eta_i \) the viscosity of the pure solvent and the polymer solution, respectively, at concentration \( c \). The intrinsic viscosity is related to the viscosity average molecular weight \( \bar{M}_v \) through the Mark-Houwink equation (Greenwood, 1964):

\[
[\eta] = K \cdot \bar{M}_v^\alpha
\]  

(3.5.7)

where \( K \) and \( \alpha \) are empirical parameters associated with a particular polymer-solvent system. Although solution viscosities depend in part on the size of the polymer, it should be noted that the effective size of the polymer molecules also depends on the extent of interactions with the solvent. For good solvents, the molecules assume extended conformations, and as the solvent becomes poorer, there is a high tendency for intramolecular interactions. For theta solvents, the molecular chains assume their unperturbed dimensions. It is therefore apparent that solution viscosity will show different dependence on molecular weight in different solvents.

By applying the Huggins eqn.

\[
\frac{\eta_{sp}}{c} = [\eta] + k' [\eta]^2 c
\]

(3.5.8)

the intrinsic viscosity \([\eta]\) can be obtained by plotting \( \eta_{sp}/c \) versus \( c \) and extrapolating to zero concentration (Seymour and Carraher, 1981). In this equation \( k' \) is a positive constant. Experimentally, the intrinsic viscosity is determined by measuring the flow times of the solvent, \( t_o \), and of a series of dilute polymer solutions of known concentrations, \( t_c \), in a standard capillary viscometer and then applying the eqn. (3.5.9):

\[
\eta_{sp} = \frac{\eta_c - \eta_o}{\eta_o} = \frac{t_c - t_o}{t_o}
\]

(3.5.9)
The constants $K$ and $\alpha$ can be determined experimentally by measuring $[\eta]$ for various polymer samples of known molecular weights which themselves have been determined by one of the absolute methods. The viscosity average molecular weight is defined as:

$$\overline{M_v} = \left( \frac{\sum n_i M_i^{1+\alpha}}{\sum n_i M_i} \right)^{1/\alpha}$$  \hspace{1cm} (3.5.10)

Generally, $\overline{M_n} < \overline{M_v} < \overline{M_w}$ and $\overline{M_v} = \overline{M_w}$ when $\alpha = 1$.

\(d)\ Gel\ Permeation\ Chromatography\)

Gel permeation chromatography (GPC) or size exclusion chromatography, a secondary method for molecular weight determination, has developed into one of the most useful techniques for routine determination of average molecular weights and molecular weight distribution of polymers. GPC is a type of liquid chromatography based on the decreasing permeability of a swollen gel to molecules of increasing size. Utilization of the GPC method to determine the molecular weight of dextrin is described in section 4.3.2.
3.5 POLYMER ADSORPTION AT SOLID-LIQUID INTERFACES

Organic polymeric macromolecules consist of many segments which behave as random coils when in solution. The adsorption of such macromolecules at a solid-liquid interface results in a change of the molecular conformation, depending on the balance between the internal entropy (conformational entropy) and the adsorption energy, under a given set of conditions (Fleer, 1988). For instance, at low polymer concentrations and high adsorption energies, adsorbed chains usually lie flat on the surface, whereas at finite solution concentrations, the adsorbed layer becomes very thick, with the chains extending far into the solution. Thus, in contrast to the adsorption of simple molecules or ions, simple adsorption models like the Langmuir model cannot be applied to polymer systems.

Common polymers are frequently polydisperse mixtures of compounds of variable molecular-weight. Unlike a homopolymer (molecular weight is an average over the distribution), polydisperse polymers tend to show preferential adsorption of the long chains over the short ones. The average molecular weight of the adsorbed molecule of such a system is quite different from that of the solution and can affect the interpretation of experimental data. For polyelectrolytes the adsorption models are even more complicated than the models for neutral macromolecules due to the presence of long-range electrostatic interactions (Sato and Ruch, 1980; Papenhuijzen et al., 1985; Koopal, 1992).

The adsorption of organic macromolecules, taking into account the conformation at the interface, the mechanism of interaction and the nature of adsorption isotherms encountered, will be discussed in the following section, with emphasis on the self consistent field lattice theory for adsorption (SCFA) of chain molecules (Scheutjens and Fleer, 1979; 1980; 1982). This theory can be used to explain the behaviour of adsorbed polymers under different conditions.

In discussing the arrangement of polymer molecules at an interface, a distinction has to be made between the terms configuration and conformation, which are usually used interchangeably. According to Schulz (1974), configuration describes the internal structural
arrangement of the polymer chain while conformation applies to the physical outline of the polymer molecules at the surface. According to Sato and Ruch (1980), the possible number of conformations increases with the length of polymer chain. Moreover, the configuration of the adsorbed polymer chains depends on the following factors:

- the number of active sites on the solid surface,
- the number of the adsorbable functional groups in the polymer molecules,
- competitive intermolecular interactions with the solvent and with other polymer molecules,
- the adsorbability of solvent molecules,
- the position of the functional groups in the molecule.

### 3.5.1 Free Energy of Polymer Adsorption

Modern theories on polymer adsorption take into account various factors which contribute to the free energy change when flexible-chain molecules adsorb onto a surface. The possible contributing factors are (Fleer and Scheutjens, 1982; Fleer, 1988):

1. The adsorption energy due to contacts of the segments with the surface;
2. The conformational entropy of the chains;
3. The entropy of mixing of chains and solvent;
4. The polymer-solvent nearest-neighbour interactions.

The adsorption energy is the driving force of the process and adsorption occurs when the energy of a segment-surface contact is higher than that of a solvent-surface contact. The net effect of replacing the solvent molecule on the surface with a segment from the bulk solution is expressed as \(-\chi_s kT\) (\(\chi_s\) is the energy parameter describing the interaction of segments with the surface).

The conformational entropy of the chains accounts for the reduction in the internal degrees of freedom within the adsorbed chains and is equivalent to \(k \ln \frac{Z_a}{Z_s}\) per bond (\(Z_a\) and
$Z_*$ are the co-ordination numbers in the two-dimensional surface layer and three-dimensional solution, respectively.

The entropy of the mixing of chains and solvents is related to the configurational entropy loss which occurs when the polymer solution is separated into a polymer-rich surface phase and a solution enriched with respect to the solvent. The entropy loss for the polymer is given by $\Delta S^o = k \ln \phi_i/\phi_*$ per chain and that of the solvent is $k \ln \phi_i^*/\phi_*^*$ per solvent molecule, where $\phi_i$ and $\phi_*$ are the polymer volume fractions in the layer $i$ and in the bulk solution, respectively. Factors (2) and (3) serve as the opposing force to the adsorption process since they contribute to entropy loss.

For poor solvents, segments attract each other and thus enhance adsorption, while in a good solvent (athermal), segment accumulation is not favoured, resulting in less adsorption. The free energy contribution of this polymer-solvent nearest-neighbour interaction can be approximated as:

$$2\chi kT(\phi_i^* - \phi_*^*) \text{ per segment} \quad (3.6.1)$$

$\chi$ is the Flory-Huggins parameter, describing the interaction energy of segments with the solvent, and it is zero in athermal solvents and 0.5 in theta solvents (theta solvency corresponds to an ideal state where the solvent-solvent and segment-solvent interactions are equally preferred as opposed to athermal solvency ) (Flory, 1953).

From the free-energy contributions it is estimated that under equilibrium conditions, the adsorption process moves toward an optimal compromise, resulting in low energy (many adsorbed segments) and small entropy loss. The resultant structure of the adsorbed layer is that in which the polymer chains lie with several stretches of segments in the surface layer as trains (sequences in actual contact with the surface), with the parts connecting the trains sticking out in the solution as loops (stretches of segments in the solution of which both ends are on the surface). At the chain ends, freely dangling tails (chain with only one side fixed on the surface) are found.

3.5 POLYMER ADSORPTION AT SOLID-LIQUID INTERFACE
3.5.2 The SCFA Theory for Polymer Adsorption

The self consistent field lattice theory for adsorption (SCFA) of chain molecules, developed by Scheutjens and Fleer (1979, 1980) accounts for all possible chain conformations for interacting chain molecules near an adsorbing interface. Many theories on polymer adsorption (Simha et al., 1953; Frisch and Simha, 1954; Silberberg, 1962; Roe, 1974; Helfand, 1975) consider the case of an isolated chain on a surface and therefore neglect the interaction of segments. Other theories (Silberberg, 1968; Hoeve, 1970), which account for the segments, tend to neglect the effect of loops and tails. For other models (Silberberg, 1962; DiMarzio, 1965; Rubin, 1965; Motomura and Matuura, 1969), exact results have only been obtained for systems that are so dilute that the interaction of segments with each other and with solvent molecules is negligible.

In order to describe all the possible conformations, the SCFA theory considers a model of a quasicrystalline lattice with lattice layers parallel to the surface. Each macromolecule is seen as a sequence of segments equal in size to a solvent molecule which are placed in a lattice to facilitate the counting of the conformations. A lattice layer \( i \) runs from \( i = 1 \) (the surface layer) to \( i = M \) (a layer in the homogeneous bulk solution). A lattice site in layer \( z \) has a given number of neighbours of which, a fraction \( \lambda_0 \) are in the same layer and a fraction \( \lambda_1 \) in the adjacent layers.

**Conformation Probability**

The probability of finding any lattice site in layer \( i \) occupied by a segment is assumed to be equal to the volume fraction \( \phi_i \) of the segments in this layer. Chain conformations in the lattice are defined by specifying the lattice numbers where each of the segments of a chain are found. Figure 3.14a shows the conformation of an adsorbed chain in a lattice model. In Figure 3.14b, two conformations of a hexamer are presented, one in solution (B; \( i = 5, 6, 6, 7, 7, 7 \)) and one adsorbed (C; \( i = 2, 1, 1, 1, 2, 2 \)). The conformational probabilities and the free energy of mixing are calculated by assuming random mixing within each layer. The energy for any segment
is determined by the layer number, and each segment is assigned a weighting factor (Boltzmann factor) $P_i$, which depends only on the layer number. In general, for a chain of $r$ segments and $r-1$ bonds, if the conformation $n$ is characterized by $r_1$ segments in layer 1, $r_2$ in 2, \ldots $r_i$ in $i$, and $q$ bonds parallel to the surface, the probability for this conformation $n$ is given as:

$$P(n) = \lambda^q \lambda^{-r-1-q} P_1^{r_1} P_2^{r_2} \cdots P_i^{r_i} \cdots P_M^{r_M}$$ (3.6.2)

**Concentration Profile**

The relative weight of all the possible chain conformations can be evaluated if the segmental weighting factors $P_1$, $P_2$, \ldots, $P_M$ are known. From this the segment concentration profile in the adsorbed layer and the adsorbed amount can be determined.

In summary, the SCFA theory predicts the structure of the adsorbed layer for interacting polymers as follows:

- for isolated chains near an adsorbing surface, the conformation is flat, at least if $\chi_s$ is not too low. Most of the segments are in trains, loops are short and tails are negligible.
- for very small equilibrium concentrations, the competition between the adsorbing molecules becomes so strong that only a small fraction of the segments can attach to the surface and a substantial part is accommodated in loops and tails. The segment concentration in the outer regions of the adsorbed layer is largely due to these tails. Thus, the tails determine, to a large extent the average layer thickness.
- Molecules in contact with the surface consist of three parts of roughly equal size: two long tails and a middle part in which very short trains and longer loops alternate.
Figure 3.14a - Conformation of an adsorbed polymer chain on a cubic lattice. (After Papenhuijzen, 1985).

Figure 3.14b - Schematic illustration of the lattice model, with two possible conformations for a hexamer (After Fleer and Scheutjens, 1982).
3.5.3 Adsorption Isotherms of Polymers

A clear insight into the behaviour of various polymer adsorption isotherms can easily be obtained from the SCFA theory. The theory shows that monomers hardly adsorb and oligomers have Langmuir type isotherms of low affinity due to low adsorption energy. The longer the chains, the more prevalent the higher affinity character, with an increase in the amount adsorbed ($\theta$). For $r > 5$ and $\chi = 0$, the isotherms are linear in the range $0.05 < \phi_* > 1$, with a slope which increases with chain length. In poor solvents ($\chi = 0.5$), there is a deviation from this behaviour due to mutual attraction between the segments. The phenomenon of negative adsorption can occur in systems where the affinity of solvent for the solid is very high and the solvent molecules are preferentially adsorbed onto the surface, thereby forming a thick solvation layer. Under such conditions there is an increase in the concentration of the polymer in the bulk of the solution (Kipling, 1965; Parfitt and Willis, 1964). It is, however, not a common phenomenon.

For long chains, the adsorbed amount ($\theta$) from a bulk polymer ($\phi_* = 1$) is, for $r \geq 5$, proportional to the square root of the chain length and is related to the Gaussian behaviour of free and adsorbed chains in a bulk polymer (De Santis and Zachmann, 1977). The properties of the adsorbed layer at very high $\phi_*$ are independent of the energy parameters $\chi$ and $\chi_s$ since the transfer of a segment from the bulk solution to the surface does not change the energy system. Under this condition, adsorption is completely governed by the entropy, which depends on chain length.

The effect of solvent quality on adsorption is important only if the average segment concentration in the adsorbed layer is appreciably different in the surface region and in the bulk of the solution, which is the case when the solution is dilute. In this way, the total surface coverage becomes higher with decreasing solvent quality, especially for longer chains.

For macromolecules, the SCFA theory proposes the adsorption isotherm model which has a typical shape as exhibited experimentally for most non-polydisperse polymers, with a very
steep initial rise followed by an approximately horizontal pseudo-plateau. In this latter region, the amount adsorbed depends only weakly on $\phi_\ast$. In dilute solutions, the amount adsorbed from theta solvents increases with increasing chain length, whereas in athermal solvents $\theta$ is much lower, levels off for higher polymer chains, and is essentially independent of molecular weight.

The concentration of the polymer solution is usually low in many practical systems and in the dilute region ($\phi_\ast < .01$), the amount adsorbed in theta solvents increases linearly with the log $r$. This relationship differs considerably from the empirical function $\Gamma = KM^n$ used by other researchers (Howard and McConnel, 1967; Schmidt and Eirich, 1962; Silberberg, 1962; Stromberg et al., 1965) to explain the adsorption of polymers. It is worth-noting that there is no theoretical justification for this latter power law of adsorption.

Polymer systems are commonly polydisperse with a wide molecular weight distribution which has a profound effect on the adsorption behaviour (Felter and Ray, 1970; Koopal, 1981). The Scheutjens-Fleer theory indicates that the affinity for the surface and the adsorbed amount increase with increasing chain length, especially in theta solvents. Consequently, from a polydisperse system, preferential adsorption of the higher molecular species over the lower molecular weight species becomes dominant and has an effect on the shape of the resultant adsorption isotherm (Hlady et al., 1982; Fleer and Lyklema, 1983). Unlike monodisperse polymers, polydisperse polymers display rounded isotherms which gradually increase with polymer concentration.

Models for the adsorption of polyelectrolytes have been developed through the extension of the SCFA theory for uncharged polymer by incorporating the effect of electrostatic free energy (Hesselink, 1977; van der Schee and Lyklema, 1984; Papenhuijzen et al., 1985; Böhmer, 1990). A marked feature of polyelectrolyte adsorption, as compared to a non-ionic polymer adsorption, is the low level of adsorption. For an uncharged surface at high ionic strength and for a high positive charged surface at an intermediate ionic strength, polyelectrolyte adsorption
in both instances is much smaller than that of the uncharged polymer. By way of explanation the charges on the polyelectrolyte groups let water behave as an athermal solvent.

The effect of temperature on adsorption is used in some cases to evaluate the nature of polymer adsorption on a surface. Both an increase and a decrease in the amount of polymer adsorbed have been reported (Perkel and Ullman, 1961; Gilliland and Gutoff, 1960). The temperature dependence of adsorption is a function of the heat of adsorption and from the Clausius-Clapeyron equation, the enthalpy change on adsorption, $\Delta H_{\text{ads}}$, is related to the temperature by the relation:

$$\frac{\Delta H_{\text{ads}}}{R} = \frac{d \ln C}{d \left[ \frac{1}{T} \right]} \quad (3.6.3)$$

where $\Delta H$ can be obtained from the slope of the plot of $\ln C$ versus $1/T$. When the adsorption process is exothermic, the adsorption decreases with a rise in temperature. Khosla et al. (1983), however, pointed out that the Clausius-Clapeyron equation is applicable only in cases where the adsorption process is reversible (i.e. physical adsorption).

### 3.5.4 Mechanism of Polymer Adsorption

The mechanism of organic macromolecules adsorption on solids has been extensively reviewed in the literature by many researchers, including Siberberg (1962), Fleer and Lyklema (1983), Clunie and Ingram (1983), Hesselink (1983), Krishnan and Attia (1988), Laskowski et al., (1990) and Koopal (1992). Various interaction mechanisms have been enumerated in explaining the mode of adsorption of organic polymers on mineral surfaces. This is not surprising since there are different controlling factors in the surface reactions of minerals in aqueous environment. The most significant ones are hydration, dissolution, hydrolysis of dissolved species, and surface ionization which result in the formation of an electrical double
layer. The effect of these factors on how the mineral provides adsorption sites for polymer attachment will therefore depend on the mineral surface chemistry.

In all instances of polymer adsorption onto mineral surfaces, the process is thought to involve the interaction of particular functional groups on the polymer with adsorption centers on the solid surface. The interaction may involve either chemical or physical forces, or a combination of both.

The most significant chemical forces involved in polymer-solid interaction are:

- Chemical bonding
- Coordination bonding
- Hydrogen bonding

The physical forces can be summarized as follows:

- Electrostatic (coulombic) forces
- Hydrophobic association

It should be pointed out here that the adsorption of polymer molecules onto solid surfaces by chemical forces in the presence of electrostatic repulsion can be achieved only when the macromolecules closely approach the surface by some other intermediate mechanism, like London-van der Waals forces.

A chemical bond formation can occur when there is chelation or complexation between the mineral surface and the adsorbed macromolecules. Interactions involving this kind of bonding are also known to be characterized by high affinity-type adsorption isotherms. In the adsorption of corn starch on hematite and quartz, studied by Balajee and Iwasaki (1969), and also reviewed by Armando de Araujo (1988), it was shown that the adsorption process was caused by interactions of a chemical nature, of which hydrogen bonding was assumed to be the most important. From their analysis, it was shown that the starch sample was negatively charged under alkaline conditions and was more strongly adsorbed on the less electronegative hematite than on quartz. The adsorption of starch onto hematite at pH around 7.0 was also comparatively

3.5 POLYMER ADSORPTION AT SOLID-LIQUID INTERFACE
high and could not be accounted for by any charge mechanism (i.e., of Fe₂O₃ is closer to pH 7.0). It was also evident that the isotherms were of the high affinity type.

In a study by Solari et al. (1986), it was observed that carboxymethyl cellulose adsorbed strongly onto graphite which contained impurities like Ca²⁺, Mg²⁺ or Fe³⁺ with a resultant high affinity-type adsorption isotherm at low CMC concentrations. However, when the same graphite sample was purified by leaching, the adsorption isotherms revert to that of a low affinity. This gave an indication that the mechanism of interaction involved some sort of chemical interaction and the metallic impurities served as adsorption centres for the macromolecules anchorage. As shown in Figure 3.15, the adsorption test was conducted at a fixed pH of around 5.5. The effect of hydroxylation of these metallic centres under alkaline conditions remained unknown at that time.

Samygin et al. (1986) studied the adsorption of starch on the surface of sphalerite, chalcopyrite, bornite and chalcocite and mentioned improved flotation selectivity. A mechanism of adsorption involving the interaction of the hydroxyl groups of starch molecules and metal cations (Cu or Zn) was suggested. The mechanism of starch adsorption onto calcite was reported by Somasundaran (1969) to be a combination of complex formation between starch and calcium ions at the surface and the electrostatic attraction between the negatively charged starch and the positive sites on calcite. The adsorption was pH dependent and the isotherms were of the high affinity type around the pH of maximum adsorption. Specific chemical interactions between starch constituents and metallic ions such as Fe³⁺ and Ca²⁺ have also been suggested by other researchers (Kholsa et al., 1984; Kholsa and Biswas, 1984; Subramanian and Natarajan, 1988).

3.5 POLYMER ADSORPTION AT SOLID-LIQUID INTERFACE
Figure 3.15 - Relationship between adsorption density and concentration of CMC on Ceylon graphite before and after leaching. (After Solari et al., 1986).
A more detailed investigation on the adsorption mechanism between polymers and solid surfaces was conducted by Liu and Laskowski (1989). In the adsorption of dextrin onto hydrophilic quartz and methylated hydrophobic quartz (Figures 3.16 and 3.17), it was observed that adsorption density was very low and did not depend on surface wettability. The introduction of lead-ionic centres on quartz, however, resulted in a drastic increase in adsorption which also became pH dependent. Moreover, adsorption was observed to be pronounced in the pH range in which the metallic species were hydroxylated. It was, therefore, suggested that the presence of hydroxylated metallic adsorption centres (not just metallic ions) was the primary reason for the high affinity of dextrin towards the solid surface. Complex formation was found to occur at the pH closer to the i.e.p. of the metal hydroxide, where the number of undissociated OH groups on the solid surface is maximum. From Figure 3.17, it can be seen that the isotherms for the lead coated quartz is of the high affinity-type and a secondary factor which seems to further enhance the adsorption process is the surface hydrophobicity.

The complex formation between polysaccharides and metallic ions has been widely investigated and in almost all cases, the complexation reaction is observed to take place under alkaline conditions, where there is hydroxylation of the metallic species. A neutral copper (II) solution, containing Cu$_2$(OH)$_2$$^{++}$ complexes, forms an insoluble precipitate with mannans and galactans. Under alkaline environment the copper (II) solution predominantly containing the anions Cu(OH)$_4$$^{2-}$ has been found to form a complex with many gums (Rao, 1959). Iron (III) dextran complexes and complexation products of iron and dextrin have been used in the pharmaceutical industry (Takeda, 1962; Synowiedzki, 1962). Zaida et al., (1962), formed a complex between cobalt (III) hydroxide and dextrin at alkaline pH, and found that the complex consisted of 1:5 ratio of sodium hydroxide to dextrin per gram of cobalt.
Figure 3.16 - Effect of pH on the Adsorption of Dextrin onto Various Solids (After Qi Liu and Laskowski, 1988).

Figure 3.17 - Adsorption Isotherms of Dextrin on Different Quartz Samples (After Qi Liu and Laskowski, 1988).
In a series of studies carried out by Kennedy et al., (1976, 1977), it was observed that branched polysaccharides could effectively form complexes with metal hydroxides. An interesting aspect of this work was that while some metal hydroxides could strongly bind polysaccharides, others had just marginal binding power, and in some cases, no binding could be achieved. Such differences in the interaction properties of metal hydroxides with polysaccharides could have far reaching implications on the selective depression in the differential flotation of sulphides.

Hydrogen bonds can form between the hydrogen atoms of a polymer molecule and the oxygen atoms on the surface of a mineral and may be present in many polymer-oxide surface interactions. However, it may not be the primary mechanism of adsorption. In the study of the starch-hematite system by Balajee and Iwasaki (1969), strong arguments were advanced in favour of hydrogen bonding as the mode of adsorption mechanism, the strongest O-H...O bonds occurring at the primary alcohol groups at carbon C_6. Huang et al. (1978) showed that dextrin and amylose, when adsorbed onto a medium volatile bituminous coal, had a free energy of adsorption of -5 kCal/mol of dextrose monomer and a heat of adsorption of 0.5 - 3 kCal/mol. Such low energies of interaction are indicative of physical interaction, with hydrogen or hydrophobic bonding as the most obvious mechanism. Im and Aplan (1981) made similar claims for the adsorption of dextrin and various starch products on coal.

Hydrophobic bonding is known to arise when nonpolar groups tend to adhere to one another in a polar aqueous medium (micellisation), and so avoid the environment by presenting a lower number of chain components to the aqueous phase (Tanford, 1980). The attraction of nonpolar groups for each other is, however, very small and this is supposed to play a minor role in many adsorption processes (Parsegian and Ninham, 1971). The hydrophobic bonding mechanism was postulated by Wie and Fuerstenau (1979) in their studies on dextrin, amylose and starch on hydrophobic surfaces.
From the isosteric heat of adsorption, free energy of adsorption and thermochemical measurements, Miller et al. (1982, 1983) proposed a hydrophobic bonding mechanism for the adsorption of dextrin onto coal. In the adsorption of dextrin by natural and demineralized coal it was observed that the removal of hydrophilic mineral matter by demineralization caused an increase in dextrin adsorption, while an increase in the oxygen functional groups on the coal surface produced lower dextrin adsorption densities. The level of inorganic impurities in the adsorbent was, however, never recorded.

Wie and Fuerstenau (1974) compared the adsorption of dextrin onto molybdenite with that of dextrin onto quartz. It was suggested that since the dextrin-molybdenite adsorption density was far greater than that for the dextrin-quartz system (which is supposed to involve hydrogen bonding) some other kind of mechanism, possibly hydrophobic association, was involved in the interaction. It has been argued that, in general, dextrin adsorption by inherently hydrophobic solids like coal (hydrocarbon), molybdenite (sulphide), and talc (silicate) is independent of the solid's chemical composition.

The hydrophobic bonding mechanism has been supported by comparing the adsorption density of dextrin on crystal pyrite in the presence and absence of amyl xanthate. In the absence of xanthate, the low adsorption density of dextrin was thought to occur through hydrogen bonding. An increase in dextrin adsorption density in the presence of xanthate was considered to be the result of the formation of the hydrophobic dixanthogen at the pyrite surface (Haung and Miller, 1978).
Chapter 4

EXPERIMENTAL PROGRAM

4.1 REAGENTS

Three main reagents used in this study were diphenylguanidine (DPG), potassium amyl xanthate (KAX) and various dextrins, tapioca dextrin 12 being used in most cases because of its superior depressant properties. DPG and KAX served as collectors for chalcocite.

4.1.1 Diphenylguanidine

Commercial grade DPG \(\text{C}_{13}\text{H}_{13}\text{N}_3\), a white powder, was supplied by Inco and is the same collector used in the flotation of chalcocite in the processing of their matte. DPG is a member of the diaryl guanidines group, and is produced by the reaction of cyanogen chloride and aniline. It has a molecular weight of 211.3 and its chemical structure is shown in Figure 4.1.

![Figure 4.1 - Structure of diphenylguanidine](image)

The following physico-chemical properties have been reported in the literature for DPG (Cyanamid, 1950; Heilbron and Bunbury, 1943): It has a melting point of about 150 °C, is soluble in acetone, ethyl alcohol, benzene, chloroform and dilute hydrochloric acid. It is slightly
soluble in water and decomposes at 170 °C. The acid-base equilibrium is given as (Tipman et al., 1976):

\[ DPG + H_2O \leftrightarrow DPGH^+ + OH^- \]  \hspace{1cm} (4.1.1)

and the equilibrium constant \( K_b \) is given by:

\[ K_b = \frac{[DPGH^+] \cdot [OH^-]}{[DPG]} \]  \hspace{1cm} (4.1.2)

with a dissociation constant, \( pK_a \) of 9.8 (which is not very different from the \( pK_a \) for primary aliphatic amines). The solubilities of DPG in aqueous solution after agitation for periods of 1 to 10 days at specific pH values are given in Table 1.

<table>
<thead>
<tr>
<th>pH</th>
<th>DPG (mol/l)</th>
<th>DPG (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5</td>
<td>1.75 x 10^-3</td>
<td>370</td>
</tr>
<tr>
<td>10.5</td>
<td>1.37 x 10^-3</td>
<td>290</td>
</tr>
<tr>
<td>11.7</td>
<td>0.95 x 10^-3</td>
<td>200</td>
</tr>
<tr>
<td>12.4</td>
<td>0.80 x 10^-3</td>
<td>170</td>
</tr>
</tbody>
</table>

Chemically, DPG does not react with a broad range of reagents, from strongly oxidizing to strongly reducing, indicating its high stability. Under acid conditions, the hydrogen form of DPG (DPGH+) gives a yellow ion-pair complex with bromophenol blue and this reaction is the basis for the colorimetric determination of DPG in solutions (for details see chapter 4.3.4).

For the adsorption test, the commercial grade DPG was purified twice by first dissolving it in acetone. The resultant solution was then filtered using a Watman 934-AH glass micro-fibre filter. The DPG was recrystallized from solution using diethyl ether and then recovered by filtration. This product was washed several times with the organic solvent to remove any
contamination. DPG solutions were made by dissolving a known amount in a 10^{-2} M NaCl solution at pH 3.0. At this pH, turbidity tests with a light scattering photometer indicated that DPG was completely dissolved. Some degree of insolubility was, however, observed at higher pH values, as can be deduced from Table 4.1. In the batch flotation experiments, DPG was used as supplied by adding it to the rod mill during grinding. This is in line with INCO's industrial practice.

4.1.2 Amyl Xanthate

Literature on the properties and use of xanthates for the flotation of metal sulphides is rather extensive (Rao, 1971; Poling, 1976; Leja, 1982). Commercial xanthates are usually only 60 - 90% pure and they normally contain residual alkali hydroxide or metal carbonate, intentionally added to slow down decomposition of the product during storage.

Samples of commercial grade potassium amyl xanthate and sodium ethyl xanthate, obtained from Van Waters and Rogers Ltd., were purified by dissolving them in acetone, and recrystallizing them with anhydrous diethyl ether. The purified products were washed several times with distilled water to remove any residual organic contaminant used in the purification process. They were then stored in a dessicator.

In all adsorption studies with amyl xanthate, a fresh 1% stock solution was made and diluted to the necessary concentrations. For batch flotation tests, fresh 1% solutions of the commercial grade xanthates were utilized.

4.1.3 Dextrins

Dextrins are modified starch products of a lower molecular weight and a highly branched structure. Their structure, properties and methods of preparation have been elaborated upon in section 3.4.1. Four different samples of dextrins, all being the canary type, were used in this study. These were tapioca dextrin - obtained from A.E. Staley Mfg. Co., Decatur, corn dextrin -
purchased from Johns Scientific, Inc. (J.T. Baker product G193-7), and wheat and yellow-corn
dextrins - supplied by Van Waters and Rogers (Canada) Ltd. The molecular weight of the J.T.
Baker product was reported by Wie and Fuerstenau (1974) as 7,800 but the method for the
determination was not given. Characterization of the tapioca dextrin by gel permeation
chromatography yielded a molecular weight of 56,000. Other dextrins were not characterized,
since they were rejected in the initial stages of this work.

Dextrin solutions were made by dispersing a known amount in about 5 ml of cold
distilled water and ensuring that all particles were wetted. About 100 ml of 10^{-2} M NaCl solution
was brought to boil and then added to the dispersion to obtain a clear dextrin solution. After
cooling, it was transferred into a one litre flask and brought up to the mark with more of the
cold NaCl solution to maintain a constant ionic strength. Fresh dextrin solutions were made each
day before the tests.

**4.1.4 Other Chemical Reagents**

*Sephadex G-100* was obtained from Pharmacia Fine Chemicals, Sweden, and used for
the gel permeation chromatography (GPC) characterization of tapioca dextrin. It has a particle
size of 40 - 120 μm and a bed volume per g dry gel of 15 - 20 ml. It is a bed-formed gel,
prepared by cross-linking dextran with epichlorohydrin with a large number of hydroxyl groups
that render the gel extremely hydrophilic. This gel is insoluble in all solvents and it is stable in
water, salt solutions, organic solvents, alkaline and weakly acidic solutions. The molecular
weight range over which dextrin molecules can be fractionated by Sephadex G-100 is 1,000 -
100,000. Sephadex was supplied as a dry powder and the gel was prepared by allowing it to
swell in excess distilled water for 24 hours prior to loading it into the column.

*Dextran* was supplied by Polysciences, Inc., U.S.A., and it is the product of
polysaccharide transformation through the action of enzymes. It was used as a standard for the
calibration of the GPC column. The molecular weights employed were 10,000, 30,000, 40,000,
and 70,000. Dextran is 100% soluble in cold water and samples were prepared by making 1% solutions.

*Phenol* was a BDH laboratory reagent. It is soluble in water and has a molecular weight of 94.11 (C₆H₅OH). It was used in the colorimetric determination of dextrin concentrations in aqueous solutions. *Bromophenol Blue* was purchased from BDH Chemicals in a powdered form. Its aqueous solutions have pH 2.8 - 4.6. It was used in the colorimetric determination of DPG concentrations in solution. A 0.1% solution was prepared in distilled water for the tests.

Sodium hydroxide, sodium chloride, potassium nitrate, hydrochloric acid and sulphuric acid were BDH Chemicals, all of analytical reagent grade.

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4.2 REAGENTS
4.2 MINERAL SAMPLES

4.2.1 Chalcocite and Heazlewoodite

Samples of chalcocite and heazlewoodite were obtained from Inco’s J. Roy Gordon Research Laboratory in Mississauga. The chemical analyses for these were provided by Inco, as follows:

Table 4.2 - Elemental Analysis of Cu$_2$S and Ni$_3$S$_2$ Samples

<table>
<thead>
<tr>
<th></th>
<th>% Cu</th>
<th>% Ni</th>
<th>% S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcocite</td>
<td>79.6</td>
<td>-</td>
<td>20 - 22</td>
</tr>
<tr>
<td>Heazlewoodite</td>
<td>-</td>
<td>73.2</td>
<td>26.7</td>
</tr>
</tbody>
</table>

For the adsorption tests and zeta potential measurements, both samples were dry ground in an agate mortar and sieved to obtain the -38 μm fractions. The specific surface areas of these samples, determined with a Quantasorb sorption system using the BET adsorption method and nitrogen were in the range of 0.782 - 0.815 m$^2$g$^{-1}$ and 0.608 - 0.654 m$^2$g$^{-1}$ for chalcocite and heazlewoodite, respectively. Samples prepared for Hallimond Tube flotation were ground for a shorter time to obtain a coarser size fraction of +38 - 90 μm. In all cases, the test samples were stored under nitrogen in a dessicator and fresh samples were prepared at the end of every week. This measure was taken to eliminate the effect of surface oxidation of the sulphide minerals which influences their surface properties. The specific surface areas obtained from the BET adsorption were used to convert the adsorption units into moles or grams per unit surface area.

4.2.2 Inco Matte

A sample of the copper-nickel matte in the form of large chunks was received from Inco’s Copper Cliff smelter complex. The chemical analysis of the matte was kindly provided by Inco, with an approximate composition of 50% Ni, 25% Cu and 22% S. Samples of the matte for batch flotation tests were prepared by crushing below 2.38 mm, utilizing two cone crushers.
of different discharge settings. A 1.5 kg sample of the minus 2.38 mm matte was then charged into a rod mill and ground at 80% solids for an optimum time of 45 minutes. This time was established by conducting a series of tests in which the grinding time was varied, with a set product target of 75% passing 44 μm.

The pulp at this stage consists of grains of copper sulphide, nickel sulphide and a liberated magnetic copper-nickel alloy. The magnetic component was separated from the non-magnetic sulphides by means of a hand magnet. This was achieved by diluting the pulp to about 40% solids and stirring continuously to keep the particles in suspension.

4.2.3 Other Samples of Copper and Nickel

Cupric nitrate (Cu(NO$_3$)$_2$.3H$_2$O) and nickel nitrate (Ni(NO$_3$)$_2$.3H$_2$O) crystals were Baker and Adamson product of Allied Chemical and both assayed at 99.5% purity. Nickel hydroxide powder was supplied by Aldrich Chemical Co. Inc., USA, with a 97% purity and a Ni content of 61%. Copper hydroxide powder was also obtained from the same company.

Fresh nickel hydroxide (Ni(OH)$_2$) was prepared by precipitating it from an aqueous solution of Ni(NO$_3$)$_2$ with the addition of sodium hydroxide. The precipitate was washed several times by centrifugation and decantation. Fresh copper hydroxide was prepared in the same manner as Ni(OH)$_2$, by precipitating it from an aqueous solution of Cu(NO$_3$)$_2$. These fresh precipitates were used in the microelectrophoresis experiments.

Tenorite (melaconite) was of specimen grade and obtained from the Geological Sciences Museum, the University of British Columbia, Vancouver, and originated from Hesse-Nassau, Germany. A fine fraction of this sample was prepared by grinding in the agate mortar to a size suitable for microelectrophoretic studies. The fraction used for the adsorption test had a surface area of 4.28 m$^2$g$^{-1}$.
4.3 EQUIPMENT AND TECHNIQUES

4.3.1 Sizing

Samples for the adsorption, microelectrophoresis, and Hallimond tube flotation were sized by dry screening, using micro-sieves and a Rotap screen shaker. The sieves had aperture sizes of 38 μm, 90 μm and 150 μm. The screening time in each case was 5 minutes. Bulk sizing of the minus 2.38 mm fraction was performed by dry screening the crushed products from the cone crushers, using the Gilson vibratory screening system.

Wet sieving was deemed appropriate for the size analysis of the flotation feed, since it was wet ground. A 45-minute ground matte product, which had been demagnetized, was washed successively through a nest of vibrating sieves, ranging from 250 μm to 37 μm, to effect size separation.

4.3.2 Release Analysis

The state of liberation of chalcocite in the sample of Inco matte, as prepared for batch flotation tests (section 4.3.1), was studied through a release analysis technique, which is based on the premise that flotation rate is a measure of liberation. The metal values in any pulp can therefore be categorized as either fast floating, slow floating or non-floating, depending upon the degree of liberation. The procedure adopted in this test was based on the original method as described by Dell (1953), and Dell et al. (1972).

A plot of cumulative recovery against cumulative weight or cumulative grade of concentrate is a technique which has been applied by many flotation researchers in measuring the accuracy of a flotation separation by expressing, graphically, the state of liberation of an ore sample through a release curve (Dell, 1961; Khangaonkar and Satyanarayana, 1981). This same technique was used in determining the degree of liberation of chalcocite in the ground Inco matte by measuring its floatability for different grinding times, using potassium amyl xanthate as collector.
In this test, 45, 35, or 25-minute ground sample, which had been demagnetized, was placed in a 2-litre capacity Denver flotation cell. An excess collector dosage of 250 g/t potassium amyl xanthate was added to the pulp and no more collector additions were made throughout the test. The feed was then conditioned for 10 minutes at pH 11.0. Dowfroth 250 was used as a frother and measured quantities were added to the cell in the course of the float test to generate a stable froth. Flotation was carried out according to the flowsheet given in Figure 4.2. Such a procedure was followed to ensure that the maximum possible recovery of the valuable mineral was achieved without compromising the grade.

Three sets of float tests were performed before the final flotation products were obtained. In the first stage of flotation, a series of four concentrates were collected at timed intervals of \( \frac{1}{2} \) minute, 1 minute, 2 minutes and 4 minutes, respectively. The material remaining in the cell was saved as tailing (T1). In the second set of flotation tests, the \( \frac{1}{2} \) minute concentrate was placed in a 1-litre Denver cell and brought up to the mark with tap water. The first concentrate was collected for a \( \frac{1}{4} \) minute and the 1 minute concentrate from the first set of float
tests was then added to the cell and flotation was continued for another ¼ minute. A new pan was used to collect the second concentrate for ½ minute after which the 2 minute concentrate from the previous set of float tests was added to the cell and flotation continued for another ½ minute. This was followed by a collection of the third concentrate over a period of 1 minute and then adding the 4 minute concentrate to the cell and continuing the float for a further 1 minute before the collection of the fourth concentrate. Concentrate 4 was collected for a 4 minutes period and the tailing (T2) remaining in the cell was combined with the previous one. In the last set of flotation tests, the same procedure was followed, only that for each concentrate, flotation was carried out for ¾ of the initial time before the next concentrate was added to the cell. The resulting 4 concentrates and the tailings were dried overnight in an oven. From the weights of the products and the copper assays, a material balance was prepared from which a release analysis curve of the grade-gradient type was plotted.

4.3.3 Surface Area Determination

The Quanta-Sorb sorption system was used to measure the specific surface area of all the samples. In this system, nitrogen is adsorbed from a flowing nitrogen-helium gas mixture.

The surface area is determined by the process of adsorption and desorption of the nitrogen molecules which is monitored by measuring the change in thermal conductivity of the gas mixture. For a reading to be taken, an adsorbate to carrier gas ratio is established and a recorder base line is allowed to become constant. Adsorption is then initiated by immersing the sample, which is contained in a glass cell, in liquid nitrogen. The adsorption peak is produced by the change in the thermal conductivity of the gas mixture, resulting from the decrease in adsorbate concentration due to adsorption of nitrogen molecules on the powdered sample surface. A desorption peak, which is usually used in the surface area calculation, is obtained by withdrawing the sample from the liquid nitrogen. In the desorption process, gas molecules leaving the sample cell are richer in adsorbate and so the signal is opposite in polarity to that of
the adsorption. At the end of the desorption curve, a known amount of the adsorbate is injected into the flow stream in order to calibrate the desorption signal.

In this work, the powdered samples were prepared for surface area analysis by drying them overnight in an oven at 90 °C, together with the sample cells. A known weight of the sample is then introduced into the glass cell to fill it to about three-quarters way up in the cylindrical bottom. Since the surface areas for the heazlewoodite and chalcocite samples were very low, a capillary type of cell was used. This alleviated the effect of signal irregularities caused by thermal diffusion (separation of adsorbate and carrier gas due to the temperature gradient in the sample cell).

The multipoint B.E.T. method (Brunaur, Emmett and Teller, 1938), involving four different ratios of adsorbate to carrier gas flow ratios, were employed. The specific surface area was obtained by using the B.E.T. equation given as:

\[ \frac{1}{X(\frac{P_o}{P} - 1)} = \frac{C-1}{X_m C} \frac{P}{P_o} + \frac{1}{X_m C} \]  

(4.3.1)

where;

- \( X \) = weight of adsorbate adsorbed at a pressure \( P \)
- \( P \) = partial pressure of adsorbate
- \( P_o \) = saturated vapour pressure of adsorbate
- \( X_m \) = weight of adsorbate adsorbed at a coverage of one monolayer
- \( C \) = a constant which is a function of the heat of the adsorbate condensation and heat of adsorption

The B.E.T. equation is valid in the range where \( P/P_o \) is between 0.05 to 0.39 (Gregg, 1961). The flow ratios of the adsorbate to carrier, in this test, were therefore chosen in such a way that the \( P/P_o \) ratios were within this valid range. Since many surface area determinations were done, a very simple program in Basic language, involving regression analysis, was written.
to give an instant computation of the surface area, after obtaining the necessary parameters from the Quanta-Sorb sorption system. The program is given in Appendix 4. Surface areas determined for Cu$_2$S was in the range 0.85 - 1.17 m$^2$g$^{-1}$ and that for Ni$_3$S$_2$ was 0.53 - 0.75 m$^2$g$^{-1}$.

4.3.4 Gel Permeation Chromatography

The principle of gel permeation chromatography (GPC) (or molecular-sieve chromatography) is based on the decreasing permeability of a three-dimensional network of a swollen gel to molecules of increasing size. If a solution containing a mixture of compounds of different molecular sizes is made to flow down a column packed with a suitable gel, the large molecules will never enter the stationary phase and will therefore move through the chromatographic bed faster. The smaller molecules which can penetrate the gel pores will have a longer retention time, since a large proportion of their time will be spent in the stationary phase. Consequently, molecules are eluted in order of their decreasing molecular size. This technique, therefore, affords a rapid, relatively simple method for determining the molecular weight of polymers, such as polysaccharides. An extensive review on the theory and application of GPC techniques to carbohydrates has been provided by Fisher (1969), Churms (1970), Nilsson and Nilsson (1974) and Fleet and Manners (1976).

The theory behind this technique will be discussed in order to fully understand the method used in this work. GPC results are usually displayed in the form of an elution diagram which shows the variation of solute concentration in the eluent with the volume of eluent passed through the column. From this diagram, the elution volume, $V_e$, of a particular solute can be determined. When the volume of the applied sample is small enough to be negligible as compared to the bed volume, then the position of the peak maximum in the elution diagram is taken as $V_e$. The elution volume is therefore defined as the volume of solvent required for eluting the solute from the column at maximum concentration.

4.3 EQUIPMENT AND TECHNIQUES
In a packed bed of swollen gel, two solvent phases can be identified, a stationary phase (one within the gel) and a mobile phase (the other outside the gel). The volume of solvent in the gel, $V_i$, is the internal volume and the volume of solvent outside the gel particles, $V_o$, is the void volume of the column. A solute will distribute itself in the two phases according to the distribution coefficient, $K_d$, where:

$$K_d = \frac{V_e - V_o}{V_i}$$  \hspace{1cm} (4.3.2)

When solute molecules are very large, they are completely excluded from the gel, and from eqn. 4.3.2., $K_d = 0$ and $V_e = V_o$. Thus, the solute passes through the column entirely in the mobile phase. For very small molecules that can freely penetrate the gel pores, $K_d$ is unity and $V_e = V_o + V_i$. Between these limiting values lie all molecules that can penetrate the gel to various degrees. $K_d$ greater than unity indicates some kind of interaction between the gel and the solute and $K_d$ less than zero indicates channeling in the bed that may require repacking of the column.

The resolution of the elution diagram depends on the efficiency of the column and it must be high if the narrow peaks necessary for good resolution are to be achieved. Eluent composition does not directly influence the resolution of the elution diagram. However, in the GPC of substances carrying charged groups, an eluent containing a buffer, like sodium phosphate or sodium chloride, is used to counteract the possible effect of ionic interactions with the gel matrix.

Several different relationships have been proposed for the dependence of elution volumes and $K_d$ on the molecular weight, $M$, of the solute (Laurent and Killander, 1964; Granath and Kvist, 1967). The most commonly used relation is that developed by Anderson and Stoddart (1966), and it involves a correlation between $V_e$ and $\log M$ as:

$$V_e = -b' \log M + c'$$  \hspace{1cm} (4.3.3)

where $b'$ and $c'$ are constants. Thus, a plot of $V_e$ versus $\log M$ gives a linear relationship.
In practice, a series of similar solutes of known molecular weights are chromatographed under identical conditions on a column loaded with a gel of appropriate fractionation range. To obtain the calibration curve for the column, the elution volumes of these samples are plotted against log M. This should give a linear plot over a range of molecular weights coinciding with the fractionation range of the gel. The sample whose molecular weight is to be determined is then eluted on the same column, and under the same conditions as were used for the calibration. The molecular weight is interpolated from the calibration curve using the elution volume. An important consideration in this test is that the polymers used for the calibration must be structurally identical to the sample under examination. The calibration is valid only when the relationship between the Stokes radius and the molecular weight are similar, e.g., in the determination of the molecular weight of polysaccharides, well-characterized fractions of dextran are used for calibration.

In the determination of the molecular weight of the tapioca dextrin, used in this work, a GPC column of 70 cm by 1.6 cm provided by Pharmacia Fine Chemicals AB (Uppsala, Sweden) was used. This was loaded with Sephadex-G100 gel which has a molecular weight fractionation range of 1,000 - 100,000 for dextrans. The eluent was made up of 10^{-2} M sodium chloride solution and was fed by gravity. Before running any sample the column was eluted for 24 hours.

To obtain a calibration curve for the column, 0.1% solutions of various molecular weight fractions of dextran ranging from 15,000 - 70,000 were prepared and 1 ml of each was fed to the top of the column, making sure that the top layer of the gel was undisturbed. The flow rate was adjusted to 0.5 ml/min and equal fractions (3 ml) of effluent volumes were collected. The concentration of dextran in each fraction was determined, using the phenol-sulphuric acid method (section 4.3.5). The elution diagram for each dextran sample was plotted and the elution volumes, \( V_e \), for each sample were obtained. For tapioca dextrin, the same solution volume and concentration was applied to the column and eluted under the same conditions as the calibration stage. The dextrin content in each fraction was determined using the same method as above and the elution volume was obtained from the elution diagram.

4.3 EQUIPMENT AND TECHNIQUES
4.3.5 Microelectrophoresis

In electrophoretic measurements, the observed mobilities are usually converted into the electrokinetic potential (\( \zeta \)) and this depends on the dimensionless quantity \( \kappa a \). The radius of the particle, \( a \), is assumed to be spherical and \( \kappa \) is estimated by eqn. 4.3.4 for an aqueous solution of symmetrical electrolyte at a concentration of \( c \, \text{mol} \cdot \text{l}^{-1} \) at 25 °C (Shaw, 1966):

\[
\kappa = 0.328 \times 10^{10} \left( \frac{cz^2}{\text{mol} \cdot \text{dm}^{-3}} \right)^{\frac{1}{2}} \text{m}^{-1} \tag{4.3.4}
\]

The zeta potential is related to the electrophoretic mobility, \( \nu_E \), expressed in cm·s\(^{-1}\)/V·cm\(^{-1}\) by the Henry equation according to:

\[
\nu_E = \frac{\varepsilon \zeta}{6\pi \eta} f(\kappa a) \tag{4.3.5}
\]

where \( \varepsilon \) and \( \eta \) are the permittivity and dynamic viscosity of the electrolyte medium, respectively, and \( \kappa a \) is the ratio of particle radius to the double layer thickness. The Smoluchowski form of the Henry equation becomes operative for \( \kappa a > 1.0 \). This approximation is valid under moderate to high electrolyte concentration. Thus:

\[
\nu_E = \frac{\varepsilon \zeta}{4\pi \eta} \tag{4.3.6}
\]

In aqueous medium at 25 °C, Smoluchowski's equation reduces to:

\[
\zeta = 12 \cdot 83 \nu_E \, \text{mV} \tag{4.3.7}
\]

In most instances, the size of particles normally observed in microelectrophoresis is between 0.2 - 10 \( \mu \text{m} \) and with electrolyte concentrations usually employed, the Smoluchowski equation is found to be adequate.

Microelectrophoretic measurements for all samples were expressed in terms of the zeta potential, using equation 4.3.7 and a Zeta-Meter (Zeta-Meter Inc., N.Y.) with a standard plexiglas type II UVA cell was used. In all of the tests, the Zeta-Meter cell, with bright molybdenum and platinum electrodes was utilized in conjunction with the automatic sample
transfer assembly. Molybdenum was selected as the anode since the specific conductance of the suspension was greater than 1,000 µΩ, in all cases. In this way, gasification (evolution of oxygen and hydrogen at the anode and cathode, respectively), which influences the mobility of colloidal particles, was limited in the system. The temperature of the system was maintained at 25 ± 0.3 °C.

In order to study the electrokinetic behaviour of sulphide minerals in aqueous solutions, a 1 g/l suspension was made by dispersing 0.5 g of the sample in 500 ml of 10⁻² M NaCl solution and conditioning it at a fixed alkaline or acidic pH for 1 hour. Equilibration of the sulphide was done either in oxygen or under nitrogen gas in a closed vessel. Measurements were also taken for chalcocite suspensions in the presence of 10 mg/g dextrin and also 20 mg/g dextrin for tests involving heazlewoodite. A time interval of at least 30 minutes was allowed for surface equilibration, whenever the pH of the suspension was adjusted to a new value, before taking a reading. A lower dextrin dosage was used in the chalcocite system since higher concentrations made it impossible to track any of the mineral particles. In the case of copper and nickel hydroxides, freshly prepared samples were equilibrated at alkaline pH and the zeta potential was measured in the absence and presence of dextrin. The concentrations of dextrin were 10 mg/g, 20 mg/g and 40 mg/g. To compare the product of oxidation on the surface of chalcocite, the zeta potential of tenorite was also examined under the same experimental conditions. To verify the charge characteristics of the tapioca dextrin in aqueous environment, a 1000 ppm suspension was made in distilled water and subjected to electrophoresis at pHs varying from 2 to 12.

The pH was adjusted by using either HCl or NaOH and a period of 15 minutes was allowed for equilibration before proceeding with each electrokinetic measurement. To minimize the effect of polarization, the timing of particles was done in opposite directions by reversing the polarity of the electrodes. The particles selected for tracking were those moving at near average velocity and the faster and slower ones were avoided as much as possible. In most instances the mean velocity was calculated by timing 10 particles in both directions. The mobility and the zeta potential were determined from tables based on the Smoluchowski formula.

4.3 EQUIPMENT AND TECHNIQUES
4.3.6. Adsorption Tests

A comprehensive adsorption test program involving the reagents, dextrin, DPG, and amyl xanthate was conducted with pure samples of chalcocite and heazlewoodite and copper and nickel nitrates. The procedures used in each case are elaborated below.

**Adsorption of Dextrin onto Cu$_2$S, Ni$_3$S$_2$**

1.0 g powdered samples of either chalcocite or heazlewoodite were weighed into several test bottles and 25 ml of $10^{-2}$ M NaCl solution at a known pH was used to wet the particles. 25 ml of freshly prepared dextrin solution of identical pH and known concentration was then added to each bottle. The pH of the resultant suspensions was adjusted where necessary. The sample was conditioned in a Lab-Line Orbit Environ shaker at 300 r.p.m. for one hour at 25 °C. The final pH values of the various suspensions were measured and taken as the conditioning pH values. To obtain a clear solution for the subsequent analysis of residual dextrin concentration, the suspensions were centrifuged at 7,000 r.p.m. for 3 minutes in an IEC model HT centrifuge. A measured volume of the supernatant was analyzed for dextrin concentration with the aid of a Perkin-Elmer Lambda 3 UV-VIS spectrophotometer, at a wavelength of 490 nm. The phenol-sulphuric acid method described by Dubois et al. (1956) was utilized in developing the colour for absorbance measurement. The amount of dextrin adsorbed was determined from the difference between the initial and final dextrin concentrations.

The following series of experiments were performed to test:

- The effect of pH on adsorption of various types of dextrins on Cu$_2$S and Ni$_3$S$_2$ surfaces over the pH range 6.0 to 13.0;
- The rate of dextrin adsorption on chalcocite and heazlewoodite;
- Comparison of the tapioca dextrin adsorption onto chalcocite with that of heazlewoodite at varying pH levels.
- The adsorption isotherms of tapioca dextrin onto Ni$_3$S$_2$ and Cu$_2$S for different pH values between 8.0 to 12.0.
• Adsorption and desorption isotherms of tapioca dextrin on chalcocite and heazlewoodite versus temperature. This was done by conducting the adsorption test at temperatures of 25 °C and 50 °C.

• Adsorption and desorption isotherms of tapioca dextrin on Cu$_2$S and Ni$_3$S$_2$ by reagent dilution. This was carried out by first conditioning the mineral sample with a predetermined concentration of dextrin and then diluting the suspension and conditioning again for a set period.

**Adsorption of DPG onto Chalcocite and Heazlewoodite**

Experiments involving the adsorption of DPG onto chalcocite and heazlewoodite were carried out under similar conditions as that of dextrin above. Various tests were designed to study the following:

• Adsorption rates for DPG on chalcocite at pH 12.4 at various reagent concentrations;
• Adsorption isotherms of DPG on Chalcocite in the pH range from 10.9 to 12.4.
• Adsorption isotherms of DPG on heazlewoodite over the pH range from 7.0 to 13.0.

**Co-adsorption of DPG and Dextrin on Chalcocite and Heazlewoodite**

Various tests were conducted with solutions containing equal amounts of DPG (100 mg/l) and varying concentrations of dextrin 12 (20 - 250 mg/l). In each test, 10 ml of 10$^{-2}$ M NaCl solution at a specified pH was added to the sample to wet particles, followed by the addition of 20 ml of DPG and then tapioca dextrin at the same pH, to make up a 50 ml slurry. The concentrations of the reagents were made up in such a way that in a 50 ml volume, the required reagent levels could be achieved. The order of reagent addition was also tested to study its effect on adsorption. The following adsorption tests were carried out:

• Adsorption of DPG and tapioca dextrin onto Ni$_3$S$_2$; in these tests the pulp was conditioned with DPG for 30 minutes prior to the addition of dextrin and then conditioned for a further 30 minutes. The order of reagent addition was reversed in the subsequent series of tests.
Adsorption of DPG and dextrin reagents onto chalcocite sample. Test conditions were similar to the heazlewoodite system above.

Adsorption of DPG and tapioca dextrin onto chalcocite where 20 ml each of both reagents were simultaneously added to a $10^{-2}$ M NaCl mineral suspension and conditioned for an hour at a specified pH.

**Adsorption of Amyl Xanthate and Tapioca Dextrin on Cu$_2$S and Ni$_3$S$_2$**

The experimental technique used for this system followed the same pattern as that described for DPG and dextrin. The conditioned suspension was filtered through a Whatman 934-AH glass microfibre filter to obtain a clear solution for reagent concentration analysis. Centrifugation was, however, used in cases where the filtered solution was still turbid. The residual xanthate in solution was analyzed with a Perkin-Elmer Lambda 3 UV-VIS spectrophotometer at a wavelength of 301 nm.

Coadsorption of amyl xanthate and dextrin 12 was done with solutions containing 40 and 100 ppm amyl xanthate and varying concentrations of dextrin (10 - 200 ppm). In each case, the order of the conditioning was reversed. A set of experiments was performed to study the following:

- Effect of pH on the adsorption of amyl xanthate onto chalcocite and heazlewoodite at various reagent concentrations.
- The influence of amyl xanthate on the adsorption of dextrin 12 onto Ni$_3$S$_2$ and Cu$_2$S and vice versa.

**4.3.7 UV-VIS Spectroscopy**

Quantitative determination of reagent concentration in solution was performed applying colorimetric techniques and using a Perkin-Elmer Lambda 3 spectrophotometer. This is a double beam UV-visible unit, capable of scanning from 900 to 190 nm wavelength, and equipped with a recorder which can give a plot of the intensity-wavelength spectrum of samples. A deuterium
lamp provides the source for the Ultra-Violet radiation (wavelength 314 - 190 nm), while a tungsten-bromide lamp and a set of filters yield the wavelength range of 900 - 315 nm which is in the visible section of the electromagnetic spectrum.

For the samples handled in this work, only the visible part of the spectrum was utilized and the spectrophotometer was used in all the quantitative determination of DPG, dextrin and amyl xanthate in solution. In each case, the sample solution was scanned for the whole wavelength range to locate the position of maximum intensity and all determinations were made at such wavelength. The procedures adopted for the spectroscopic techniques for the various reagents are elaborated on below.

**Determination of Tapioca Dextrin Concentration**

In this modified procedure of the phenol-Sulphuric acid by Liu (1988), the amount of dextrin in solution was measured by obtaining a clear solution of the sample by means of centrifugation. A 2 ml of 5% phenol aqueous solution (weight-weight) was mixed with 4 ml of the dextrin solution and 10 ml of concentrated H$_2$SO$_4$. The resulting solution was allowed to cool in air for 10 minutes during which time a coloured complex developed. The solution was then transferred to a water bath and allowed to equilibrate at 27 °C for 20 minutes. The measurement of absorbance was conducted immediately after this time.

The blank solution for the calibration curve was made up of 10^{-2} M NaCl and fresh phenol solutions were prepared every day. For each stock solution of dextrin, a new calibration curve had to be prepared. A typical calibration curve for tapioca dextrin 12 used in this work is shown in Appendix 1.

**Determination of DPG Concentration**

Residual DPG in solution after adsorption was analyzed by adapting the colorimetric method used for the determination of amines by Metcalfe (1960), Mukerjee and Mukerjee (1962) and Culp and Caruso (1969). In this technique, the pH of a 25 ml DPG solution was adjusted to 2.0 with HCl and three drops of 64 ppm of bromophenol blue (BPB) solution was
added to form a yellow complex. This complex was extracted with 10 ml of chloroform by
repeated shaking. The resultant emulsion was set aside for a few minutes for the chloroform
layer to clear and the yellow complex was separated from the aqueous phase by means of a
separatory funnel. The absorbance was measured at a wavelength of 418 nm.

To obtain a calibration curve, a reference solution, made up of 10⁻² M NaCl solution at
pH 2.0, was extracted into chloroform after the addition of BPB. The absorbance of varying
concentrations of DPG solutions were also determined and a plot of absorbance versus
concentration obeyed Beer’s law up to a concentration of 10 ppm. The molar absorptivity (ε) of
the DPG-BPB complex was found to be 4.84 x 10⁴ l.mol⁻¹.cm⁻¹ and this was used for the
analysis of the DPG solution. For sensitive spectrophotometric methods, the molar absorptivity
is within the range

\[-1.5 \times 10^5 > \varepsilon > 1.0 \times 10^4 \text{ l.mol}^{-1}\text{cm}^{-1}\]

The effect of possible soluble ions, like Cu²⁺, SO₄²⁻ and Ni²⁺ in the suspensions in this
colorimetric method, were tested and found to have negligible interference up to a concentration
of 10⁻² M. The calibration curve for DPG solution is given in Appendix 2.

**Determination of Concentrations in DPG-Dextrin and KAX-Dextrin Solutions**

In all DPG-dextrin systems, the solution was always diluted to at least 10 times its initial
concentration, in order to obtain a DPG concentration which falls within the range in which
Beer's law is obeyed. The highest concentration of dextrin, used in the coadsorption test, was
250 mg/l and, when diluted to such a low level after adsorption, gave a negligible absorbance at
418 nm (wavelength for DPG analysis). The maximum concentration of DPG in the
coadsorption test was 100 ppm, and at 490 nm (wavelength for dextrin analysis), the absorbance
of 100 mg/l DPG solution was 0.025. Consequently, the reference solution for dextrin
determination in such a system was made up of 100 mg/l DPG to obviate the absorbance effect
of DPG in solution. The reference solution for DPG determination was 10⁻² M NaCl. The error
involved in the dilution of DPG solutions was found to be negligible.
To determine xanthate and dextrin concentrations from the same solution, the following procedure was utilized: Preliminary UV spectrophotometric measurements of the absorbance of tapioca dextrin solutions at 301 nm (wavelength for xanthate peak) indicated that for dextrin concentrations ranging from 20 to 200 ppm, the absorbance increased from 0.002 to 0.03. Therefore, for dextrin concentrations greater than 20 ppm, the solution was diluted to eliminate the effect of dextrin absorbance. In the determination of tapioca dextrin in solution it was found that the effect of xanthate absorbance up to 200 ppm was negligible (at a wavelength of 490 nm). Spectrophotometric measurement of xanthate concentration in solution was based the method described by Pomianowski and Leja (1963).

4.3.8 Conductivity Tests

The conductance of a solution depends on the concentration of ions present and the nature of the ions. A current $i$ passing through a given body of an electrolytic solution is proportional to the potential difference, $E$, where:

$$\frac{E}{i} = R$$

(4.3.8)

and

$$\frac{1}{R} = \frac{\kappa A}{\ell}$$

(4.3.9)

$R$ is the resistance of the solution in ohm and the reciprocal of $R$ is the conductance in ohm$^{-1}$. The conductance is therefore proportional to the cross-sectional areas of the cell, $A$, and inversely proportional to the effective length, $\ell$, of the conducting solution. The specific conductance or the conductivity, $K$, is in ohm$^{-1}$-cm$^{-1}$ or Siemen/cm (S·cm$^{-1}$). From eqn. 4.3.9:

$$K = \frac{1}{R} \frac{\ell}{A} = \frac{k}{R}$$

(4.3.10)

Thus the specific conductance of a solution in a cell of arbitrary design and dimensions can be obtained by first determining the cell constant, $k$, (the effective value of $\ell/A$) by measuring the resistance of a solution of known specific conductance. Usually, a standard solution of $2 \times 10^{-2}$
M KCl with a conductivity of 0.002768 Ω⁻¹·cm⁻¹ at 25 °C is employed (Shoemaker and Garland, 1962).

The principle of electrolytic conductance of ionic solutions was applied in this test to determine the changes in electrical conductivity when solutions of different reagents are brought together. This gave a measure of the degree of interaction between various ionic species and, therefore, allowed prediction of the nature of the interaction to be made. According to Kohlrausch's law of independent migration of ions (Moore, 1962), when dilute solutions of, say, two electrolytes WX and YZ are mixed at a fixed volume, the overall solution conductivity will be the sum of the individual conductances of various ionic species, provided that there are no ionic interactions. Thus for WX and YZ:

\[ \Lambda(WX) + \Lambda(YZ) = \lambda_w^+ + \lambda_x^- + \lambda_y^+ + \lambda_z^- \]  \hspace{1cm} (4.3.11)

Thus, when the net conductance of a mixture of solutions cannot be accounted for on the basis of the mobilities of the individual ions, then this is a manifestation of an ion-ion interaction or a complex formation.

Measurements of solution conductivities in this test were done by employing the 660 Conductometer manufactured by Metrohm Ltd., Switzerland. This is a highly automated instrument with a conductivity cell, which has a built-in Pt 100 temperature probe. The cell constant, \( k \), was 0.8 cm⁻¹ and was configured to the instrument by manually setting it on the panel. Although, the cell constant was set by the manufacturer, it was re-calibrated using a Metrohm KCl calibration solution standard. Conductivity measurements were taken by inserting the well-rinsed cell into the solution and recording the reading on a display panel. For low conductivities, the values were given in μS·cm⁻¹ and the instrument automatically switched to mS·cm⁻¹ when there was an increase in conductivity as indicated by the appropriate light diode. The measured conductivity was always corrected automatically by the instrument to a reference temperature of 20 °C. The measuring frequency was set at 2 kHz, as recommended for K

4.3 EQUIPMENT AND TECHNIQUES
between the range of 100 μS·cm\(^{-1}\) and 1999 mS·cm\(^{-1}\) (Anon., Metrohm Series 01). The measuring error of this instrument was within 1% of the final value at room temperature.

Conductometric measurements were made on aqueous solutions of copper nitrate, nickel nitrate and tapioca dextrin. These solutions were prepared using conductivity water (conductance being 1.5 - 1.7 μΩ\(^{-1} \cdot \text{cm} \)\(^{-1}\)). The concentration of the dextrin solution was fixed at 50 ppm and Ni\(^{2+}\) and Cu\(^{2+}\) concentrations were varied from 0 to 200 ppm. In order to ascertain the changes in conductivity for various metal ions-dextrin systems at different pH levels, the following tests were pursued:

- Measurement of conductivity for dextrin solutions at the following pH levels: 6.0, 8.9, 11.5 and 11.7.
- Determination of the conductivity for various concentrations of aqueous Cu\(^{2+}\) solutions at pHs 6.5, 8.9 and 11.5.
- Measurement of the conductivity of the Cu\(^{2+}\)-dextrin solution at a fixed volume and under the same conditions as in the previous test.
- Verification of the conductivity of the Cu\(^{2+}\)-dextrin system by summing up the individual conductivities of dextrin and Cu\(^{2+}\) solutions, measured at the same pH.
- The same procedures were followed for the Ni\(^{2+}\) solution at pH 6.0 and 11.7.

4.3.9 Co-precipitation Test

The co-precipitation experiments were performed to examine the interaction of dextrin with metallic ion species in aqueous solution at pHs ranging from 2 to 12. In each test, a 100 ml solution made up of either 1.7 x 10\(^{-3}\) mol·dm\(^{-3}\) of Ni\(^{2+}\) or Cu\(^{2+}\) ions, 50 ppm dextrin or a combination of both were conditioned for 15 minutes at a specified pH. The solution was left to stand for 5 minutes and then centrifuged at 8,000 rpm for 3 minutes in an IEC model HT centrifuge.
To assay for the concentration of metal ions left in solution, samples of the supernatant were collected and digested immediately, with a known volume of concentrated HCl at about 70°C for 5 minutes. The assay method involved the use of atomic absorption spectroscopy. The concentration of dextrin in the metal ions-dextrin solutions was determined by the colorimetric method described in section 4.3.7.

The following test conditions were examined for both aqueous copper and nickel ion systems:

- The abstraction of either Cu$^{2+}$ or Ni$^{2+}$ ions from a 100 ml solution at pH 2 - 12. The initial ionic concentration of 1.7 x 10^{-3} \text{ mol dm}^{-3} was obtained by taking 50 ml of the stock solution and diluting it twice with distilled water.

- The abstraction of dextrin from a dextrin solution with a change in pH from 2 to 12. 100 ml of 50 ppm dextrin was prepared by diluting twice 50 ml of the stock solution.

- The abstraction of Cu$^{2+}$ or Ni$^{2+}$ from a 100 ml solution consisting of 1.7 x 10^{-3} \text{ mol dm}^{-3} and 50 ppm dextrin. This solution was obtained by mixing 50 ml of aqueous metal ion stock solution and 50 ml of the dextrin stock solution. By using the same molar concentration for the two ionic systems, in 50 ppm dextrin solution, the level of abstraction could easily be compared.

4.3.10 ATR-FTIR Spectroscopy

The most common method of obtaining the infrared spectra of the surfactant adsorbed onto mineral surfaces has been through a transmission technique, in which the dried powdered mineral sample is mixed with KBr and pressed into a disk. A transmission spectrum of the sample is then obtained by means of a dispersive spectrophotometer. Phase changes induced by temperature and pressure in the sample preparation are possible and may cause a modification of the actual spectrum (Allison and Finkelstein, 1971).
Internal reflection spectroscopy (IRS), usually referred to as attenuated total reflection (ATR) multiple internal reflection or frustrated multiple internal reflection, allows in-situ measurements in aqueous solutions and as such, circumvents the problems inherent in the traditional infrared spectroscopy (Strojek et al., 1983; Miller and Kellar, 1988; Leppinen et al., 1989; Ishida and Griffiths, 1990; Cases and De Donato, 1991). It is therefore a more effective tool for studying flotation surface chemistry.

In this technique, the sample beam of a spectrometer is directed into one end of a thin crystal of a high refractive index (internal reflection element - IRE), usually made of germanium or ZnSe, and on which mineral particles are pressed. At an incident angle greater than the critical angle, the beam undergoes total internal reflection at the interface and an exponentially decaying evanescent wave is set up in the outer phase (sample) which propagates a short distance, about 8 to 10 \( \mu \text{m} \), away from the IRE (Perkin, 1987). At frequencies at which the sample does not absorb infrared radiation, the beam passes through the accessory essentially undiminished. But at those frequencies at which the sample exhibits infrared absorption bands, there is an interaction between the beam and sample at each reflection along the crystal-sample interface and the intensity of the internally reflected beam is attenuated (Figure 4.3).

![Figure 4.3 - Schematic diagram of a light beam undergoing multiple internal reflections in an internal reflection element (IRE).](image)

The depth of penetration, \( d_p \), is defined to be the distance from the IRE where the electric field intensity drops to \( e^{-1} \) of its value at the interface and is given by (Harrick, 1979):
\[ d_p = \frac{\lambda}{2\pi n_i \left[ \sin^2 \theta - \left( \frac{n_2}{n_1} \right)^2 \right]^{\frac{1}{2}}} \] 

(4.3.12)

where, \( \lambda \) = wavelength of light

\( n_1, n_2 \) = refractive indices of the IRE and sample, respectively

\( \theta \) = incident angle of light beam.

For a total internal reflection to occur in the IRE, two basic conditions must be met. First, the sample must be optically rarer, that is, have a lower refractive index than the IRE \((n_1 > n_2)\) and secondly, the incident angle of the light beam on the IRE must be greater than a critical angle \( \theta_c \), where,

\[ \theta_c = \sin^{-1} \left( \frac{n_2}{n_1} \right) \] 

(4.3.13)

Eqn. 4.3.12 shows that as the wavelength of light increases, the penetration becomes larger and this points out the major spectral difference between samples measured by transmittance and ATR. For the ATR technique, intensities of higher frequency bands are lower than for the transmittance, while lower frequency bands are stronger when measured by the ATR method.

The Fourier transform infrared (FTIR) spectrometer is preferable when there is an energy limitation and when there is a need for an increased signal-to-noise ratio. The availability of the FTIR technique has made it possible to work with aqueous solutions which had to be avoided in the past. Water has very strong absorption bands at about 3400 cm\(^{-1}\) (OH stretch) and 1640 cm\(^{-1}\) (OH bend) and is completely opaque below about 800 cm\(^{-1}\). FTIR spectroscopy cannot solve the problem of limited spectral range. However, the extremely high signal-to-noise ratios obtained so readily by the FTIR technique makes spectral subtraction and subsequent ordinate expansion of the difference spectrum quite feasible, even over the region of the 1640 cm\(^{-1}\) O—H bending mode. Thus, in the aqueous phase, absorption bands of the sample which lie in the same range as that of water can easily be obtained without significant interference.
FTIR instruments utilize interferometers in which the signal is collected in the time domain and then converted to an energy scale (expressed in frequency or wave numbers) via a Fourier transform using appropriate computer software.

ATR-FTIR spectra were recorded with a Nicolet Model 710SX FTIR spectrometer which incorporated a Deuterated Tri-Glycine Sulphate (DGTS) detector in a G series optical bench. Typical spectral measurements consisted of 512 scans at a resolution of 4 cm\(^{-1}\) and the bench was purged with nitrogen. Spectra for the wet mineral samples were taken with a solid sampling plate containing a germanium-IRE with a spectral window down to 600 cm\(^{-1}\) and an ATR optical system, obtained from Harrick Scientific Inc., U.S.A. In each scan, the dewatered precipitate (or mineral sample) was evenly spread over the surface of the germanium internal reflection element and a pressure plate was firmly applied in order to improve the contact between the sample and the IRE. Tapioca dextrin was prepared for IR scanning by contacting the IRE surface with an aqueous sample of the dextrin. Whenever the ATR system was installed in the bench for spectral measurements, an alignment procedure was first carried out to ensure that the energy throughput was at least 20% of the open beam energy intensity since this is very critical to the sensitivity of the absorption bands. Spectra of the adsorbed dextrin were obtained by subtracting a distilled water spectrum from the spectrum of the adsorbed system, both of which had been ratioed against the same IRE background.

Prior to each experiment, the IRE was alternatively cleaned with distilled water and acetone. Heazlewoodite and chalcocite samples were prepared for scanning by placing 1.0 g of -38 μm fraction in a beaker and conditioning it with 50 ml of 100 ppm dextrin solution at pH 11.7 and 8.7, respectively. The resultant suspension was then filtered to obtain the wet sulphide particles for scanning. Samples of the freshly precipitated copper and nickel hydroxides and that of the co-precipitated dextrin-hydroxide mixtures were prepared following the method described in section 4.3.9. Since adsorption and desorption studies indicated strong dextrin-Ni(OH)\(_2\) and weak dextrin-Cu(OH)\(_2\) interactions, it was decided to perform desorption tests to confirm the nature of the interactions between dextrin and the precipitates. The desorption procedure
consisted of reslurrying the co-precipitated sample and then dewatering it by centrifugation and decantation.

**4.3.11 Microflotation Tests**

Different kinds of small-scale flotation devices are employed in preliminary flotation research to elucidate the role played by parameters as particle size, pH, type of collector and dosage, choice of depressant, etc., under well-controlled conditions. Some common experimental designs, used in small-scale flotation studies, are bubble pickup, vacuum flotation and Hallimond tube flotation. Pure mineral samples are usually used in the studies and the results are very reproducible. It should, however, be stressed that in no way do these experimental techniques substitute the conventional batch flotation tests or continuous flotation cells.

Unlike the vacuum flotation and bubble pickup techniques, which are essentially static, Hallimond tube tests are dynamic, and as such, the most commonly used method. Some advantages offered by the latter technique are:

- The response of a mineral to pure reagents can be examined by eliminating the interference of gangue materials. Under such conditions, clear interpretation of flotation results can be achieved.

- In sulphide flotation systems, where surface oxidation is a critical factor, nitrogen or other pure gases can be used to study the effect of oxygen.

- Since tests are carried out in the absence of a frother, the behaviour of pure minerals can be tested under varying conditions with no complications of frother-collector interaction.

The drawback to this technique is mostly particle entrainment which is the effect of such factors as gas flowrate, height of Hallimond tube column, particle size range and in the case of sulphide minerals, self-induced floatability.

To examine the influence of tapioca dextrin depressant on the floatability of heazlewoodite and chalcocite, a Hallimond tube was used in a series of small scale flotation
tests. A medical gas grade nitrogen, supplied by Linde Union Carbide, was used as the source of gas for the flotation and the flowrate of nitrogen to the flotation tube was controlled by a Dwyer flow meter.

In a typical flotation test, approximately 1.5 g of a +38 -90 μm size fraction of either chalcocite or heazlewoodite was conditioned with a 130 ml solution of $10^{-2}$ M NaCl at a given pH in a beaker. The conditioning time was 10 minutes for all tests. Following decantation of the supernatant (conditioning solution), the sample was transferred into the flotation tube, using the supernatant to rinse all of the material from the beaker. The top section of the flotation tube was then fitted and the remaining conditioning solution was used to fill up the cell. A magnetic stirrer, which was set to the same level in all tests, maintained the particles in suspension. The nitrogen flowrate was set at 40 ml/min when the collector or depressant was used and 100 ml/min in the absence of a reagent. Flotation was carried out for 3 minutes in all cases and the floatability was determined from the ratio of the dry weights of particles that floated and those which remained in the cell. For the artificial mixture, recoveries were calculated from the assays of copper and nickel in the concentrate and tailing. The pH of flotation was always assumed to be the final pH of the suspension measured after flotation. The following factors were considered and tested in this work:

- Floatability of Cu$_2$S and Ni$_3$S$_2$ in the presence of amyl xanthate at varying pH;
- Flotation response of Cu$_2$S and Ni$_3$S$_2$ in the presence of amyl xanthate and tapioca dextrin at pH 11.6;
- Effect of the order of reagent addition on the floatability of chalcocite and heazlewoodite at pH 11.7.
4.3.12 Batch Flotation Tests

Feed for the batch flotation tests with the use of the Inco matte was prepared in accordance with the procedure described in section 4.2.2. Rougher flotation was performed by feeding the pulp which had been subjected to magnetic separation into a Denver laboratory flotation machine with a cell capacity of 1.5 litres at a pulp density of 38% solids. The air flowrate was maintained at 4 litres/minute with an impeller speed of 1,200 r.p.m.

In batch tests involving DPG, the collector and a measured quantity of lime were charged into the rod mill during grinding to produce a pulp pH of 12.4 at 38% solids. DPG is self-frothing and, therefore, there was no need for a frother during the initial stages of flotation. Dowfroth 250 was, however, added to the pulp after 3 minutes of flotation to maintain a stable froth. Flotation concentrates were collected over a period of 8 minutes at incremental time intervals. For tests involving the addition of tapioca dextrin, the pH of the pulp was maintained at 11.7 and conditioned for 10 minutes before flotation commenced.

The tests were also carried out with amyl xanthate, ethyl xanthate or aerofloat 208 (a dithiophosphate - ethyl and sec. butyl), as collectors. In these cases, a 10% stock solution of the collector was prepared. Prior to the flotation, a measured quantity of the aqueous solution was added to the cell and conditioned for 5 minutes at pH 11.0, followed by a further pH adjustment to 11.7 and the addition of a measured volume of freshly prepared 1% dextrin solution. Dowfroth 250 was used as frother in the initial stages of the flotation and pH was adjusted using lime.

Both rougher and cleaner batch tests were performed using DPG and xanthate in the absence and presence of dextrin. The copper and nickel contents in the flotation products were determined by atomic absorption spectroscopy, using the facility provided at the department's Cy Emerald assay laboratory. Sets of different performed tests are outlined below.

- The blank flotation test was conducted with DPG at pH 12.4 in the absence of a depressant to serve as a reference for evaluating the efficiency of separation when
dextrin is introduced into the test. This was done both at the roughing and cleaning stages. Collector dosages ranging from 100 g/t to 300 g/t were examined.

- The batch tests were carried out with DPG at a concentration of 200 g/t in the presence of tapioca dextrin. Dextrin dosages were varied from 100 g/t to 450 g/t and the pulp pH was fixed at 11.7 in both the rougher and cleaner flotations, using lime as pH regulator. Two different cleaning steps were adopted, one involving the addition of dextrin in both rougher and cleaner stages and the other with dextrin being added only at the cleaning stage.

- Flotation of chalcocite was performed with aerofloat 208, amyl and ethyl xanthate in the absence of dextrin at pH 11.0 at dosages 175 g/t, 250 g/t and 200 g/t, respectively. These were again used as references for evaluating the performance of tapioca dextrin as a depressant.

- Dextrin dosages of 100 g/t to 400 g/t were tested, using amyl and ethyl xanthates and aerofloat 208 in both the rougher and cleaner flotation. The pulp was first conditioned for 5 minutes at pH 11.0 and then adjusted to pH 11.7 before dextrin was introduced. A further 10 minutes conditioning was pursued before commencing flotation.
Chapter 5

RESULTS AND DISCUSSION

5.1 CHARACTERIZATION OF DEXTRIN AND INCO MATTE

5.1.1 Molecular Weight of Tapioca Dextrin

The elution curves for the various dextran samples of varying molecular weights employed in this work are shown in Figure 5.1, with the corresponding selectivity curve in Figure 5.2. The use of dextrans as calibration samples is quite appropriate since they are highly soluble in water and have similar structural features as tapioca dextrin, the only difference being the mode of their production. This makes it possible to compare the elution characteristics of the dextrin with that of the dextrans.

As seen from Figure 5.1, the elution volume distribution is a function of the molecular size (or weight) which is related to the mechanism of the separation. For higher molecular weight dextrans, the elution time (volume) is shorter as compared to the lower molecular weight dextrans. As explained in section 4.3.4, the smaller molecules penetrate farther into the gel pores than do the larger ones and are therefore retained for a longer period in the column (or have larger elution volumes). Thus, in the mixture of dextran samples, the 70,000 molecular weight dextran will be the first to elute while the 15,000 molecular weight dextran will be eluted last. The position of the elution volume for tapioca dextrin on the elution diagram indicates its comparatively high molecular weight.
Figure 5.1 - Elution Curves for Various Dextran Standards of Fixed Molecular Weights.

Figure 5.2 - Relationship Between Molecular Weight and Elution Volume.

5.1 CHARACTERIZATION OF DEXTRIN AND MATTE
The elution volume, $V_e$, for each sample was taken to be the mid-point of the normally distributed curve. In Figure 5.2, a plot of the various molecular weights versus the elution volumes gives a linear relationship. The molecular weight of the tapioca dextrin, with an elution volume of 53 ml, can therefore be estimated from this plot to be 56,000. This is an indication that tapioca dextrin is a high molecular weight dextrin since in general, the molecular weight of dextrins varies from 800 to 79,000 (Pigman and Goepp, 1948).

5.1.2 Sizing of the Inco Matte

The screen analysis of the Inco matte flotation feed, which has been subjected to a 45-minute grinding time, is presented in Table 5.1. The size distribution for this grinding time indicates about 77% passing 44 $\mu$m. Although the current flotation practice at Inco utilizes a nominal feed size of 60 - 65% passing 44 $\mu$m, the matte for the laboratory flotation test was ground finer. Such a procedure was adopted after obtaining additional information from the Process Development Engineer at Inco on the current liberation studies on the matte, which revealed that a considerable portion of unliberated metal sulphide values existed at the nominal flotation feed size. Grinding to 77% passing 44 $\mu$m, therefore, served as a means of solving the liberation problem, but at the same time a comparatively higher proportion of ultrafine material was produced. It was difficult to simulate the size distribution of the laboratory test feed to that of the plant, since the grinding characteristics of the small laboratory mill are different from that at the processing plant.

As pointed out in section 4.3.1, the matte has a magnetic component with a yield of 16% by weight. It was observed in the sieve analysis that most of the magnetic particles always occurred in the coarse size fractions within any specific grinding time and it was very difficult to reduce the size of such particles, even after long grinding times. This is not surprising, since these are basically in the form of metallics which are ductile and therefore, resistible to breakage. All particles retained on the 250 $\mu$m sieve actually reported to the magnetic product.
About 95% of the flotation feed was below 74 µm and 70% was passing 37 µm. From the size distribution (Table 5.1), it can be inferred that if fine grinding is a major criterion for the assessment of liberation characteristics for the matte, then a high degree of liberation was achieved after 45 minutes grinding time.

**Table 5.1 - Particle Size Distribution of the Batch Flotation Feed**

<table>
<thead>
<tr>
<th>Size Fraction (µm)</th>
<th>Wt. Retained (g)</th>
<th>Wt. Retained (%)</th>
<th>Cum. Oversize (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 250</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>+ 149</td>
<td>4.2</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>+ 105</td>
<td>14.8</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>+ 74</td>
<td>44.4</td>
<td>3.6</td>
<td>5.1</td>
</tr>
<tr>
<td>+ 63</td>
<td>90.0</td>
<td>7.4</td>
<td>12.5</td>
</tr>
<tr>
<td>+ 44</td>
<td>124.2</td>
<td>10.2</td>
<td>22.7</td>
</tr>
<tr>
<td>+ 37</td>
<td>90.9</td>
<td>7.5</td>
<td>30.2</td>
</tr>
<tr>
<td>- 37</td>
<td>850.9</td>
<td>69.8</td>
<td>100.0</td>
</tr>
<tr>
<td>Flotation Feed</td>
<td>1219.4</td>
<td>84.4% of matte</td>
<td>-</td>
</tr>
<tr>
<td>Magnetic Fraction</td>
<td>225.6</td>
<td>15.6% of matte</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1445.0</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.1.3 Release Analysis Studies on the Inco Matte

Table 5.2 shows the numerical calculations performed in order to generate parameters for plotting the release curve for the sample ground for 45 minutes. The only measured values were the weights of the flotation fractions and their assays (columns 1 and 2). Using the figures in columns 5 and 7, the effect of grinding time on the liberation of copper has been presented in Figure 5.3 for 25, 35 and 45 minutes grinding. For this type of plot, a steep slope implies a high
copper concentrate grade, whereas a tailing nickel fraction with a low copper content will be almost horizontal. The shape of the curves for the first two shorter grinding times suggests an incomplete liberation. Longer grinding time improves the liberation of copper, as shown by the curve for the 45-minute grinding.

Going beyond this time could further increase the degree of liberation but will also have a detrimental effect on the flotation process, since more fines will be generated. In actual plant practice, the shapes of the 25 and 35 minute grind curves could be shifted up by embarking on regrinding of the middlings. This could eliminate the problems of fines generation and moreover reduce the circuit load and power consumption.

### Table 5.2 - Numerical Calculation of the Release Curve for Chalcocite

<table>
<thead>
<tr>
<th>Sample Fraction</th>
<th>(1) Wt (g)</th>
<th>(2) % Cu</th>
<th>(3) Wt of Cu (P/100)</th>
<th>(4) $\sum R$</th>
<th>(5) $\frac{100\gamma_n}{\alpha}$</th>
<th>(6) $\frac{100\sum\gamma_n}{\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc 1</td>
<td>80.2</td>
<td>75.6</td>
<td>60.6</td>
<td>24.7</td>
<td>24.7</td>
<td>32.7</td>
</tr>
<tr>
<td>Conc 2</td>
<td>108.5</td>
<td>71.2</td>
<td>77.3</td>
<td>31.5</td>
<td>56.2</td>
<td>44.2</td>
</tr>
<tr>
<td>Conc 3</td>
<td>67.0</td>
<td>66.8</td>
<td>44.8</td>
<td>18.3</td>
<td>74.5</td>
<td>27.3</td>
</tr>
<tr>
<td>Conc 4</td>
<td>51.0</td>
<td>52.2</td>
<td>26.6</td>
<td>10.8</td>
<td>85.3</td>
<td>20.8</td>
</tr>
<tr>
<td>Tailing</td>
<td>766.8</td>
<td>4.7</td>
<td>36.0</td>
<td>14.7</td>
<td>100.0</td>
<td>312.6</td>
</tr>
<tr>
<td>Total</td>
<td>1073.5</td>
<td>22.9</td>
<td>245.3</td>
<td>100.0</td>
<td>437.6</td>
<td>$= 10^4/\alpha$</td>
</tr>
</tbody>
</table>

Going beyond this time could further increase the degree of liberation but will also have a detrimental effect on the flotation process, since more fines will be generated. In actual plant practice, the shapes of the 25 and 35 minute grind curves could be shifted up by embarking on regrinding of the middlings. This could eliminate the problems of fines generation and moreover reduce the circuit load and power consumption.

5.1 CHARACTERIZATION OF DEXTRIN AND MATTE
Figure 5.3 - Effect of grinding time on the liberation of chalcocite.
All batch flotation tests (section 5.8) were performed after grinding for 45 minutes. The feed grade for the matte can be determined from the slope of the line OA to be 22.9 %Cu. If the matte had been perfectly liberated and perfectly separated, the grade of the copper concentrate would have been represented by the gradient of the line 0B. The grade of copper in the tailings would then be the slope of line BA, which is zero percent. Since perfect liberation is practically impossible, the optimum liberation characteristics for the 45 minute grinding time can be calculated from the release curve presented in Figure 5.3. The shape of the curve indicates that the middlings fraction is minimal in the flotation product. Assuming an efficient separation with amyl xanthate in this test, a 90% copper recovery could be achieved at a grade of 72.6%. If the recovery is increased to 95%, the grade of copper drops to 66%. The sharp drop in the grade for the 5% recovery increment is suggestive of a reasonable proportion of middlings fraction which constitutes the slowly floating part of the material.
5.2 ADSORPTION STUDIES

5.2.1 Adsorption of DPG onto Chalcocite and Heazlewoodite

The kinetics of DPG adsorption onto chalcocite at pH 12.4, depicted in Figure 5.4, indicates a rapid uptake of DPG with time and equilibrium is virtually attained within the first 10 minutes of the process at all levels of DPG concentration.

The effect of pH on the adsorption of DPG onto chalcocite and heazlewoodite is presented in Figure 5.5. For heazlewoodite, DPG adsorption remains fairly constant throughout the tested pH range of 7.0 to 13.0, with an adsorption density of around 2.2x10^{-6} mol·m^{-2}. The adsorption of DPG onto chalcocite is, however, pH dependent and it increases from pH 7.0 up to a maximum of around pH 12.4, beyond which there is a rapid drop in adsorption. It is therefore not surprising that in plant practice, Inco conducts the differential flotation of chalcocite at pH 12.4, the pH of saturated lime, where the difference in adsorption density for Ni_3S_2 and Cu_2S is maximum. At the pH of maximum DPG uptake, the adsorption density on chalcocite can be estimated to be about 6.5 x 10^{-6} mol·m^{-2}. The relationship between the adsorption densities of DPG on the two minerals at this pH can be expressed as:

\[ \Gamma_{Cu_2S} \approx 3 \cdot 0 \Gamma_{Ni_3S_2} \]  

(5.2.1)

where \( \Gamma \) is the adsorption density of DPG, mol·m^{-2}. This is an indication that DPG has a strong affinity for the chalcocite surface and in the flotation pulp system consisting of Cu_2S and Ni_3S_2 particles, it adsorbs predominantly onto chalcocite.

The adsorption isotherms for DPG on chalcocite at alkaline pHs 10.9, 11.7 and 12.4 are shown in Figure 5.6. The trends in DPG adsorption are similar for all the three pH levels studied, and they depict a Langmuirian type of behaviour up to a concentration of 8.5x10^{-4} mol/l. Above this point the isotherms depart from the Langmuir behaviour with a rapid uptake of DPG which becomes more pronounced with further increase in pH.
**Figure 5.4 - Kinetics of DPG adsorption onto chalcocite at pH 12.4.**

**Figure 5.5 - Effect of pH on the adsorption of DPG on chalcocite and heazlewoodite**
From the DPG adsorption isotherms, a Langmuir plot has been constructed in Figure 5.8 to indicate the trends in DPG adsorption on chalcocite at pH 11.7 and 12.4. The Langmuir equation expressed in the following form was used:

\[
\frac{C}{\Gamma} = \frac{C}{\Gamma_{\text{max}}} + \frac{1}{k\Gamma_{\text{max}}} \tag{5.2.2}
\]

where
- \( C \) is the equilibrium concentration of solute, mol/l
- \( \Gamma \) is the amount of solute adsorbed, mol/g
- \( \Gamma_{\text{max}} \) is the amount of solute at a monolayer coverage, and
- \( k \) is constant depending on temperature.

In Figure 5.7, a plot of \( C/\Gamma \) versus \( C \), illustrates two different adsorption regions for the system. It can be seen that Langmuirian behaviour is obeyed up to an equilibrium concentration of about 6.0 x 10\(^{-4}\) mol/l (probably lower for pH 12.4), beyond which there is a break in the curves. This is likely to due to the beginning of DPG precipitation. It may be inferred that when the solution reaches saturation any unadsorbed DPG in solution will undergo precipitation onto the mineral surface. This type of behaviour is manifested by the vertical portion of the adsorption isotherms in Figure 5.6 and it is more pronounced at pH 12.4. It can also be observed that for pHs 11.7 and 12.4, any DPG concentration greater than 10x10\(^{-4}\) mol/l and 9x10\(^{-4}\) mol/l, respectively, leads to complete precipitation.

From Figure 5.7, the slopes of the lines at the lower DPG concentrations where Langmuirian behaviour is obeyed, were calculated using regression analysis. The amount of DPG required to form a monolayer, \( \Gamma_{\text{max}} \), is estimated from the slopes as 6.25x10\(^{-6}\) mol/g and 6.17x10\(^{-6}\) mol/g for pHs 12.4 and 11.7, respectively. The fraction of the adsorption sites, \( \theta \), on the surface of chalcocite which is occupied by the DPG molecules can be expressed as:

\[
\theta = \frac{N_A \sigma \Gamma_{\text{max}}}{A_{ad}} \tag{5.2.3}
\]
5.2 ADSORPTION STUDIES
where \( N_A \) is Avogadro's number, \( 6.023 \times 10^{23} \text{ mol}^{-1} \)
\( \sigma_o \) is the area occupied per DPG molecule, and
\( A_{ad} \) is the specific surface area of chalcocite, \( \text{m}^2/\text{g} \).

At maximum adsorption, \( \theta \) is unity and the area occupied by each DPG molecule is given as:

\[
\sigma_o = \frac{A_{ad}}{N_A \Gamma_{\text{max}}} \tag{5.2.4}
\]

For a chalcocite surface area of 0.782 \( \text{m}^2/\text{g} \), the area occupied per DPG molecule is estimated to be 21 \( \text{Å}^2 \) which is comparable to 30 \( \text{Å}^2 \) (area of DPG molecule calculated by Tipman et al., 1976).

### 5.2.2 Adsorption of Dextrin onto Chalcocite and Heazlewoodite

The trend in the adsorption of various dextrins (wheat, yellow corn and tapioca) onto heazlewoodite as a function of pH is shown in Figure 5.8. In all cases, the maximum adsorption density is exhibited around pH 11.5 - 11.8. The magnitude of the adsorption density of tapioca dextrin within this pH range is about twice that of the other dextrins. The superior nature of tapioca dextrin as an organic depressant in subsequent batch flotation tests is due to this exceptionally high adsorption affinity (Nyamekye and Laskowski, 1991). All tests carried out in this work, therefore, involved the use of tapioca dextrin as the most effective depressant. The adsorption maxima in Figure 5.8 for all the tested dextrins indicate that there is a relationship between dextrin adsorption and the pH at which nickel hydroxide is formed (i.e.p. of Ni(OH)\(_2\) is located around pH 11.5). This result is consistent with the findings of Liu and Laskowski (1989).

The kinetics of tapioca dextrin adsorption in Figure 5.9 indicate that for both chalcocite and heazlewoodite there is a rapid interaction of dextrin in the first 10 - 15 minutes and
equilibrium is attained after 60 minutes at all studied pH values. While dextrin interaction with heazlewoodite is pH dependent, the adsorption of dextrin on chalcocite is approximately constant at the two pH levels shown.

Figure 5.10 reveals a trend in the effect of pH on the adsorption density of dextrin on the two sulphide minerals. The adsorption density of dextrin on chalcocite remains fairly constant within the studied pH range of 7.0 - 13.0 at about 1.2 mg/m². For heazlewoodite, the adsorption density is highly pH dependent and increases from 0.3 mg/m² at pH 7.0 up to a maximum of 2.65 mg/m² at pH 11.7. The amount of dextrin adsorbed onto heazlewoodite above pH 10.9 is, as expected, (Figure 5.9) higher than on chalcocite. It is only below pH 9.0 that dextrin adsorption onto heazlewoodite is lower than that onto chalcocite. At the pH of maximum adsorption for heazlewoodite, the adsorption density is about twice that for chalcocite. Selective depression of heazlewoodite will therefore be more effective around this pH.

The adsorption isotherms for dextrin on heazlewoodite are shown in Figure 5.11 over the pH range 9.0 to 12.0. As can be seen, the variation of adsorption with pH corroborates the results shown in Figure 5.10 for heazlewoodite; adsorption is higher at pH 11.5 than pH 12.0 and again diminishes with a decrease in pH. An interesting aspect of these isotherms is that at lower pH levels, they assume the shape indicative of lower affinity, while at the optimum pH, the isotherm is of the high affinity type, which is usually associated with high interaction energies. The general shape of the isotherms conforms to the Langmuir curve.

A comparison of the adsorption isotherms for heazlewoodite at pH 11.7 and chalcocite at pH 8.5 is presented in Figure 5.12. As observed from previous plots, the curve for heazlewoodite shows a strong adsorption which pertains to a chemical interaction, while for chalcocite, the adsorption isotherm is of the low affinity type and is associated with weak interaction forces. Thus, for the two sulphide systems, although adsorption is carried out at the pH where metal hydroxide formation is expected on the mineral surface and dextrin interaction is supposed to be strong, two different bonding mechanisms becomes apparent.
Figure 5.8 - Adsorption densities of various dextrins on heazlewoodite.

Figure 5.9 - Rate of tapioca dextrin adsorption onto chalcocite and heazlewoodite.
3. Initial Dextrin Concentration - 50 mg/l

- **Figure 5.10** - Effect of pH on the adsorption of dextrin onto chalcocite and heazlewoodite

- **Figure 5.11** - Effect of pH on the adsorption isotherms of dextrin on heazlewoodite.

5.2 ADSORPTION STUDIES
By assuming a Langmuir behaviour and applying eqn. 5.2.2 to the data presented in Figure 5.12, a plot of $C/\Gamma$ against $C$ for both chalcocite and heazlewoodite should give straight lines with slopes $1/\Gamma_{\text{max}}$ and intercepts of $1/k\Gamma_{\text{max}}$. In Figure 5.13, straight lines were fitted to the data to by the method of least squares and the intercepts on the ordinate are 1.25 m$^2$/l and 30 m$^2$/l for heazlewoodite and chalcocite, respectively. The gradients of the lines were estimated to be 0.22 m$^2$/mg for Ni$_3$S$_2$ and 0.57 m$^2$/mg for Cu$_2$S.

For the heazlewoodite system, the amount of dextrin adsorbed at saturation, $\Gamma_{\text{max}}$, is calculated to be 4.62 mg/m$^2$, which translates into $28.6 \times 10^{-10}$ mol-monomer·cm$^2$ (molecular weight of a monomer, $C_6H_{10}O_5 = 162$). The equilibrium constant, $k$, is calculated to be 172.8 l/g, which is equivalent to $2.8 \times 10^4$ moles of monomer per litre. The free energy of adsorption, $\Delta G^\circ$, is related to the equilibrium constant, $k$, as:

$$k = \exp\left[-\frac{\Delta G^\circ}{RT}\right]$$  \hspace{1cm} (5.2.5)

and the value of $\Delta G^\circ$ is estimated as -6.1 kcal per mole of dextrin monomer.

The saturation level for dextrin adsorption onto chalcocite is estimated as 1.75 mg/m$^2$ or $10.8 \times 10^{-10}$ mol-monomer·cm$^2$. The equilibrium constant, expressed in moles of monomer per litre, is calculated to be $0.31 \times 10^4$ and the free energy of adsorption is estimated from eqn. 5.2.5 as -4.8 kcal per mole of dextrin monomer.

In the adsorption of corn dextrin on molybdenite, a naturally hydrophobic mineral, Wie and Fuerstenau (1974) calculated the $\Delta G^\circ$ value to be -5.4 kcal/mole monomer and attributed the adsorption process to hydrophobic bonding. A similar $\Delta G^\circ$ value of -5 kcal·mole$^{-1}$ of dextrose monomer, suggestive of hydrophobic interaction, was calculated for the adsorption of dextrin onto coal by Haung et al. (1978). For the chalcocite and heazlewoodite systems, dextrin adsorbs onto hydrophilic surfaces, which rules out the hydrophobic bonding mechanism.
Figure 5.12 - Adsorption isotherms of dextrin on chalcocite and heazlewoodite at pH 8.5 and 11.7, respectively.

Figure 5.13 - Langmuir plot for the adsorption of dextrin on chalcocite and heazlewoodite.
5.2.3 Co-adsorption of Dextrin and DPG onto Chalcocite and Heazlewoodite

Figure 5.14 illustrates the trends in the co-adsorption of dextrin and DPG onto heazlewoodite. It is observed that when the mineral is first conditioned with dextrin, the amount of DPG co-adsorbed is drastically reduced compared to DPG adsorption in the absence of dextrin. The low adsorption density under such conditions remains constant over the dextrin concentration range of 20 to 250 mg/l. When the order of conditioning is reversed, the adsorption trends stay virtually unchanged, though at lower dextrin concentrations, the uptake of DPG becomes slightly enhanced. Irrespective of the order of conditioning, dextrin always displaces DPG molecules from the surface of Ni$_3$S$_2$, confirming high adsorption energy of dextrin on heazlewoodite.

For the chalcocite system (Figure 5.15), it is shown that when conditioning with DPG precedes that of dextrin, DPG adsorption is not affected. However, when conditioning is first done with dextrin, the adsorption of DPG becomes progressively more inhibited with increasing dextrin concentration over the tested range from 20 to 250 mg/l of dextrin. Simultaneous conditioning of chalcocite with DPG and dextrin leads to lower adsorption densities for both reagents (Figure 5.16). These results confirm that dextrin interacts only weakly with Cu$_2$S and is not able to displace DPG molecules from the surface of Cu$_2$S when this mineral is contacted first with DPG prior to conditioning with dextrin.

It can be inferred that in a flotation system involving the presence of both dextrin and DPG, the order of reagent addition will play an important role in the selective depression of either chalcocite or heazlewoodite. The co-adsorption results for heazlewoodite, (Figure 5.14), show that at higher dextrin concentrations, the amount of DPG adsorbed is limited and does not depend on the order of DPG-dextrin addition. Dextrin adsorption is always high. In the co-adsorption of DPG and dextrin onto chalcocite, the reagent addition order affects the adsorption of both the collector and depressant. When DPG precedes dextrin in the order of conditioning, DPG adsorption is sustained throughout the dextrin concentration range.
Figure 5.14 - Co-adsorption of dextrin and DPG onto heazlewoodite at pH 11.7.
Although DPG has a high affinity towards chalcocite at pH 11.7, it is seen that when conditioning is first done with dextrin, there is a substantial reduction in DPG adsorption, particularly at higher dextrin concentrations.

5.2.4 Adsorption of Amyl Xanthate and Dextrin onto Chalcocite and Heazlewoodite

Adsorption isotherms for potassium amyl xanthate on chalcocite are given in Figure 5.17 for three different pH levels. The shape of the isotherms indicates that the affinity of xanthate towards chalcocite at pH 10.2 is higher than at pH 11.7 and 12.1. The effect of pH and initial xanthate concentration on the adsorption density of amyl xanthate on chalcocite is shown in Figure 5.18. At initial xanthate concentrations of 200 mg/l and 250 mg/l, adsorption is observed to be constant over the pH range 8.8 to 10.8, after which there is a gradual decrease in xanthate uptake with an increase in pH. However, when the initial xanthate concentration is raised to 320 mg/l or 350 mg/l, the process becomes pH dependent, the adsorption density increases with an increase in pH and a maximum adsorption appears around pH 11.6.

The adsorption isotherms of amyl xanthate on heazlewoodite are presented in Figure 5.19 for pHs 10.2, 11.7 and 12.1. The shape of these isotherms is an indication of weak interactions between amyl xanthate and the Ni$_3$S$_2$ surface. In this system, the adsorption density decreases with an increase in pH at all concentrations. The effect of pH on the adsorption of xanthate onto heazlewoodite at two different initial xanthate concentrations is shown in Figure 5.20. A comparison of the adsorption densities on chalcocite and heazlewoodite reveals that amyl xanthate adsorption onto chalcocite is about 10 times higher than onto heazlewoodite, at an initial xanthate concentration of 300 mg/l, in the pH range where maximum adsorption onto chalcocite occurs. Selective separation should be enhanced around pH 11.5 - 11.8.
2.5

0.5

100 mg/l DPG

pH 11.7

0.01 M NaCl

dextrin coadsorbed

DPG coadsorbed

Figure 5.15 - Co-adsorption of dextrin and DPG onto chalcocite at pH 11.7.

Figure 5.16 - Adsorption of dextrin and DPG onto chalcocite from a dextrin-DPG solution.
Figure 5.17 - Adsorption isotherms of potassium amyl xanthate on chalcocite.

Figure 5.18 - Effect of pH on the adsorption of amyl xanthate onto chalcocite.
Figure 5.19 - Adsorption isotherms of amyl xanthate on heazlewoodite.

Figure 5.20 - Effect of pH on the adsorption of amyl xanthate onto heazlewoodite.
Correlation between zeta potential and flotation recoveries for the Ni$_3$S$_2$-xanthate system has been established by Critchley and Straker (1981). The formation of dixanthogen on Ni$_3$S$_2$ was observed around pH 7.0 - 9.0 and it coincided with high floatability of Ni$_3$S$_2$. At higher pH levels, decomposition of NiX$_2$ occurred and could account for the low adsorption density for the Ni$_3$S$_2$-xanthate system in Figure 5.20. The equilibrium pH for the hydrolysis of NiX$_2$ under these conditions is represented by the reaction (Barsky's principle):

$$NiX_2 + 2OH^- \leftrightarrow Ni(OH)_2 + 2X^- \quad (5.2.8)$$

Thus, the formation of the hydroxide layer which is responsible for the enhanced dextrin adsorption on heazlewoodite is, in the case of xanthate, detrimental to the adsorption process.

The co-adsorption of dextrin and xanthate onto chalcocite, shown in Figure 5.21, indicates that when conditioning is first conducted with dextrin, and then is followed by amyl xanthate, there is initially an increase in the adsorption density of dextrin on chalcocite which becomes more pronounced at higher dextrin concentrations. Enhanced dextrin adsorption in the presence of amyl xanthate was also observed by Miller et al. (1983) for coal-pyrite. This was attributed to the presence of hydrophobic bonding. However, when amyl xanthate precedes dextrin in conditioning, xanthate adsorption is relatively strong. This in turn inhibits the adsorption of dextrin, which becomes more significant at higher xanthate concentrations.

Figure 5.22 shows the co-adsorption of dextrin and amyl xanthate onto heazlewoodite. In this system, the conditioning sequence does not seem to be critical and dextrin adsorption is always higher in the presence of amyl xanthate. The shape of the isotherms again confirms the predominance of chemical interaction.

The results from these co-adsorption studies indicate that if conditioning of the Inco matte is first carried out with xanthate before dextrin is introduced, amyl xanthate adsorption onto chalcocite will be augmented and dextrin adsorption will be curtailed. The adsorption density of dextrin on heazlewoodite will, under this condition, still be high since it is independent of the order of conditioning with the reagents. Comparison of Figs. 5.21 and 5.22 corroborates the results obtained with dextrin and DPG.

5.2 ADSORPTION STUDIES
Figure 5.21 - Adsorption isotherms of dextrin on chalcocite in the presence and absence of amyl xanthate.

Figure 5.22 - Adsorption isotherms of dextrin on heazlewoodite in the presence and absence of amyl xanthate.
These Figures confirm high affinity of dextrin towards Ni$_3$S$_2$ and low affinity towards Cu$_2$S. While dextrin is not able to displace amyl xanthate already adsorbed on the surface of Cu$_2$S, it adsorbs strongly onto Ni$_3$S$_2$ irrespective of the order of conditioning.

### 5.2.5 Adsorption-Desorption Studies

The effects of temperature on the adsorption of dextrin on Ni$_3$S$_2$ and Cu$_2$S at pH 11.7 and 8.5, respectively, are shown in Figures 5.23 and 5.24. These isotherms were obtained at a room temperature of 25° C and at an elevated temperature of 50° C. For heazlewoodite, the adsorption isotherms at these two temperature levels remain unchanged. By contrast, the two adsorption isotherms obtained for chalcocite at these two temperatures showed decreased adsorption density at the higher temperature of 50° C. Thus, while dextrin adsorption on Ni$_3$S$_2$ involves strong interactions which are not affected by increased temperature, the bonding between dextrin and chalcocite is weak and the adsorption falls off at an elevated temperature.

In general, adsorption processes are characterized by exothermic heat of adsorption and in accordance with Le Chatelier's principle, adsorption densities are expected to decrease with an increase in temperature. However, if adsorption is enhanced at higher temperatures, then entropic factors constitute the driving force of the process. In this way, chemisorption is favoured due to fast reaction kinetics. Increased adsorption density with rise in temperature has been observed by Khosla et al. (1984), and Subramanian and Natarajan (1988). They attributed such a behaviour to the possibility of a chemical interaction. The isotherms presented in Figures 5.25 and 5.26 reveal that the adsorption onto heazlewoodite is irreversible while almost total reversibility is observed for the adsorption on chalcocite. The desorption isotherms were obtained by diluting the suspension containing the mineral particles with adsorbed dextrin and shaking for a specified period. The adsorption onto chalcocite is obviously a physical process and the observed desorption of dextrin from chalcocite is an indication that the polymer molecules are held to the surface by weak forces. This agrees with results shown in Figure 5.24.
Figure 5.23 - Effect of increased temperature on the adsorption isotherm of dextrin on heazlewoodite at pH 11.7

Figure 5.24 - Effect of increased temperature on the adsorption isotherm of dextrin on chalcocite at pH 8.5.
5.2 ADSORPTION STUDIES

Figure 5.25 - Adsorption-desorption isotherms of dextrin on heazlewoodite. Desorption is achieved by the method of solution dilution.

Figure 5.26 - Adsorption-desorption isotherms of dextrin on chalcocite. Desorption is achieved by the method of solution dilution.
5.3 CO-PRECIPITATION STUDIES

For an aqueous solution of copper or nickel salts (nitrates were used in these tests), there is a change in turbidity as the pH is raised to the alkaline ranges. In a $1.7 \times 10^{-3}$ mol·dm$^{-3}$ (100 mg/l) Ni(NO$_3$)$_2$ solution, a green colloidal precipitate of nickel hydroxide begins to appear in solution around pH 9.0. As the pH is further increased, a complete precipitation of Ni$^{2+}$ ions from solution occurs at pH 11.5. The pH value for 100 percent Ni$^{2+}$ precipitation coincides with the i.e.p. of Ni(OH)$_2$. When 50 mg/l dextrin solution is added to the same nickel nitrate solution and the pH is varied, a similar nickel hydroxide and dextrin co-precipitate is obtained. Figure 5.27 shows that dextrin is completely removed from solution after centrifuging the precipitate in the pH range of maximum Ni(OH)$_2$ precipitation.

When the pH of a $1.7 \times 10^{-3}$ mol·dm$^{-3}$ (108 mg/l) copper nitrate solution is raised, a blue precipitate of copper hydroxide is observed under alkaline conditions and maximum precipitation is observed around pH 8.5 and above, which coincides with the pH$_{i.e.p.}$ of Cu(OH)$_2$. If the solutions of 108 ppm copper nitrate and 50 ppm dextrin are combined, the co-precipitation of dextrin occurs in the same pH range in which copper hydroxide precipitates. As seen in Figure 5.28, the maximum co-precipitation is apparent around the i.e.p. of copper hydroxide.

Comparison of Figures 5.27 and 5.28 reveals some differences in the affinity of dextrin for the precipitating copper and nickel hydroxides. In the nickel nitrate-dextrin solution, basically all the nickel ions are converted into hydroxide around the pH$_{i.e.p.}$ of nickel hydroxide and all dextrin is practically removed with the precipitated nickel hydroxide by centrifuging at this pH. In the case of copper nitrate and dextrin solutions, only about 50 percent of the Cu$^{2+}$ ions are removed from the solution and only about half the initial amount of dextrin is taken up together with the precipitate.
Figure 5.27 - Effect of pH on the Interaction of Dextrin with Nickel Ions in Aqueous Solution. Initial Concentration: Nickel Nitrate - 1.7 x 10^-3 M; Dextrin - 50 mg/l.
Figure 5.28 - Effect of pH on the Interaction of Dextrin with Copper Ions in Aqueous Solution. Initial Concentration: Copper Nitrate - 1.7 x 10⁻³ M; Dextrin - 50 mg/l.
This seems to indicate that while Ni\(^{2+}\) easily undergoes hydrolysis to form the hydroxide, the same reaction does not proceed easily in the case of Cu\(^{2+}\). It seems that the magnitude of dextrin abstraction can be attributed to the ease of formation of the hydroxide. (This subject will be discussed further in subsequent chapters).

The errors involved in the measurements of adsorption densities of reagents on heazlewoodite and chalcocite have been discussed in Appendix 5.

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5.3 CO-PRECIPITATION STUDIES
5.4 ELECTROKINETIC STUDIES

5.4.1 Electrokinetics of Sulphide-Water Interface

One of the tools utilized in this work to study the surface properties of sulphide minerals is electrokinetic measurements. This requires a very careful control of experimentally dependent parameters like conditioning time, percent solids and pH of pre-equilibration. Unlike oxide minerals, the ultimate surface properties (notably oxidation and precipitation reactions) of metal sulphides are highly dependent on the above conditions. In all the measurements, KNO$_3$ has been used as an indifferent electrolyte.

The variation of electrokinetic potential of chalcocite with pH under various experimental conditions is shown in Figure 5.29. At a pre-equilibration pH of 3.5, the potential-pH curve exhibits charge reversal at pH 5.5 and 10.2. However, when pre-equilibration is conducted at an alkaline pH of 10.8, charge reversal is observed at pH 4.5 and 8.0. It was suspected that pre-equilibration in acidic solutions could result in the leaching of chalcocite with the consequent release of Cu$^{2+}$ ions into the solution phase. These ions could then adsorb onto the mineral surface as the pH is increased (Scott and Poling, 1973). To verify this, $5 \times 10^{-4}$ M Cu$^{2+}$ ions were deliberately introduced into the suspension under nitrogen at pH 10.8. The resultant potential-pH curve indicates that the surface charge of the system was similar to the surface behaviour of the Cu$_2$S system pre-equilibrated at pH 3.5, with the same charge reversal at pH 5.5 and 10.2.

Thus, the trends in the potential-pH curve for the oxidation of Cu$_2$S are influenced by the presence of some form of Cu$^{2+}$ ions on the surface of the mineral. Attia (1975) observed traces of Cu$^{2+}$ ions in suspension when finely divided copper minerals were dispersed in water in equilibrium with atmospheric carbon dioxide.
Figure 5.29 - Zeta Potential-pH Curves for Chalcocite Pre-equilibrated Under Acidic or Alkaline Conditions in Air or Nitrogen.
Perrin (1969) indicated that in the aqueous phase, copper(II) ions are hydrolyzed to form polynuclear complexes of the type \( \text{Cu}_n(\text{OH})_{2n-2}^{2+} \) which are adsorbed onto the surface. Anionic species like \( \text{OH}^- \), \( \text{Cu}(\text{CO}_3)_2^{2-} \), \( \text{HCO}_3^- \), \( \text{Cu}((\text{OH})_3^- \) and \( \text{S}_x\text{O}_y^- \) have also been found to be potential-determining ions for chalcocite (Yoon and Salman, 1971; Oestreicher and McGlashan, 1972; Attia, 1975). Charge reversal can therefore be attributed to these two categories of ionic species, and the potential at any particular pH of which will depend on the abundance of the specific charged species.

The adsorption of polynuclear polyhydroxy species at the solid-water interface has been observed to be highly favoured as opposed to that of non-hydrolyzed metal ions (Prédali and Cases, 1973). Schindler and Stumm, (1987) explained that hydrolyzed species are larger and less hydrated. It could also be due to the presence of coordinated hydroxyl groups whose central atoms form covalent bonds with specific sites on the solid surface.

If the concentration of \( \text{Cu}^{2+} \) ion aqueous solution is not high enough, precipitation of \( \text{Cu(OH)}_2 \) cannot be achieved and one or more of the following hydrolysis reactions occur (Attia, 1975):  

\[
\begin{align*}
\text{Cu}^{2+} + H_2O &\rightleftharpoons \frac{1}{2} \text{Cu}_2(\text{OH})_2^{2+} + H^+ \quad (5.4.1) \\
\text{Cu}^{2+} + 3\text{OH}^- &\rightleftharpoons \text{Cu}(\text{OH})_3^- \quad (5.4.2) \\
\text{Cu}(\text{OH})_3^- + H_2O &\rightleftharpoons \text{Cu}(\text{OH})_4^{2-} + H^+ \quad (5.4.3) \\
\text{Cu}^{2+} + 2\text{OH}^- &\rightleftharpoons \text{Cu}(\text{OH})_2 \quad (5.4.4)
\end{align*}
\]

Since in these tests the suspensions were allowed to reach equilibrium with air after long conditioning times, the effect of the \( \text{CO}_2^-\text{H}_2\text{O} \) equilibrium had to be taken into account as well.  

\[
\begin{align*}
\text{CO}_2 + H_2O &\rightleftharpoons \text{CO}_3^{2-} + 2H^+ \quad (5.4.5) \\
\text{Cu}^{2+} + 2\text{CO}_3^{2-} &\rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-} \quad (5.4.6) \\
\text{Cu}^{2+} + \text{CO}_3^{2-} &\rightleftharpoons \text{CuCO}_3(aq) \quad (5.4.7)
\end{align*}
\]
For the oxidation of chalcocite in acidic medium, two different reactions have been proposed. Reaction [5.4.6] involves the production of Cu$^{2+}$ ions and S$^{0}$ as surface products (Walker et al., 1984), while reaction 5.4.7 produces a metal deficient sulphide matrix (Sato, 1960; Koch and McIntyre, 1976; Buckley and Walker, 1988; Smart, 1991;).

\[
\begin{align*}
Cu_2S &\rightarrow 2Cu^{2+} + S^{0} + 4e^- \quad (5.4.8) \\
Cu_2S &\rightarrow Cu^{2+} + CuS + 2e^- \quad (5.4.9)
\end{align*}
\]

pH$_{\text{iep}}$ for colloidal sulphur was reported by Moignard et al. (1977) to be closer to 2.0. From Figure 5.31, the most realistic reaction describing the oxidation of Cu$_2$S seems to be reaction 5.4.7, since there is no indication of a surface imitating that of an elemental sulphur curve. Under strong acidic conditions in the presence of nitrogen, evolution of hydrogen sulphide was observed, which is probably due to the reaction:

\[ Cu_2S + 2H^+ \rightarrow Cu^{2+} + H_2S(g) \quad (5.4.10) \]

For freshly exposed chalcocite, the surface charge is negative for the entire pH range. The same observation was made by Oestreicher and McGlashan (1972).

Figures 5.30 and 5.31 show clearly that different surface products exist on chalcocite when pre-equilibration occurs under acidic and alkaline conditions. The pH$_{\text{iep}}$ for tenorite (CuO) can be located at 9.6 - 9.7 and the pH$_{\text{iep}}$ of copper hydroxide is at 8.6 - 8.7. When chalcocite is pre-equilibrated at pH 3.5, the surface simulates that of tenorite in the alkaline range (Figure 5.30). At a pre-equilibration pH of 10.8 (Figure 5.31), the potential curve shifts in the direction of the copper hydroxide curve, indicating that the surface has been partially converted to some form of hydroxide. There is always a high tendency for the surface to be converted to the hydroxide when pre-equilibration takes place under alkaline conditions. For chalcocite, however, the copper hydroxide is metastable and it was observed by Müller (1923) and McDowell and Johnston (1936) to be converted to a hydrated oxide with time and therefore forms a metastable phase.

5.4 ELECTROKINETIC STUDIES
5.4 ELECTROKINETIC STUDIES

Figure 5.30 - Zeta potential-pH relation for tenorite, copper hydroxide and chalcocite pre-equilibrated at pH 3.5.

Figure 5.31 - Zeta potential-pH curves for copper hydroxide, tenorite and chalcocite pre-equilibrated at pH 10.8.
The \( \zeta \)-potential-pH curves for heazlewoodite in 10^{-2} \text{ M KNO}_3 are shown in Figure 5.32 under various pre-equilibration conditions. Generally, the curves for the Ni\(_3\)S\(_2\) system are quite different from those for Cu\(_2\)S under similar conditions. At a pre-equilibration pH of 3.0, the curve follows a pattern of negative to positive potential and then at higher pH, the potential tends to move to zero. Charge reversal in this case is similar to that of the chalcocite suspension and is characteristic of hydrolyzable metal ion adsorption (McKenzie and O'Brien, 1969). However, unlike the Cu\(_2\)S potential-pH curve, there is an indication that at lower pH the surface of heazlewoodite is covered with a sulphur-rich material since that portion of the curve coincides with the \( \zeta \)-potential of S\(^\circ\). Using X-ray photoelectron spectroscopy, Buckley and Woods (1991) observed that at pH 4.6, Ni\(_3\)S\(_2\) oxidizes to form a sulphur-rich heazlewoodite phase with an ultimate reconstruction to form a surface layer of NiS. Further oxidation of NiS was also indicated to be possible in accordance with the following reactions:

\[
\begin{align*}
\text{Ni}_3\text{S}_2 & \rightarrow \text{Ni}_{3-x}\text{S}_2 + x\text{Ni}^{2+} + 2xe \\
\text{Ni}_3\text{S}_2 & \rightarrow 2\text{NiS} + \text{Ni}^{2+} + 2e \\
\text{NiS} & \rightarrow \text{Ni}^{2+} + \text{S}^\circ + 2e
\end{align*}
\]

When pre-equilibration is conducted in an alkaline medium, i.e. pH 9.5 and 11.0, it is observed that this pattern of charge reversals is absent and the curves resemble that for Ni(OH)\(_2\) shown in Figure 5.34. In Figure 5.32, the i.e.p. for Ni\(_3\)S\(_2\) can be located at pH 11.5 and it coincides with that of the nickel hydroxide. In a cyclic voltammogram for Ni\(_3\)S\(_2\), Critchley and Hunter (1987) observed a suppressed anodic current at pH 11.5, which they attributed to the formation of a passivating surface film of Ni(OH)\(_2\). In the presence of nitrogen, the surface of heazlewoodite in the alkaline pH range behaves as that of Ni\(_3\)S\(_2\) pre-equilibrated at an acidic medium.

From the \( \zeta \)-potential results for the two studied mineral systems, it is clear that their oxidation under alkaline and acidic conditions results in different surface products. For Ni\(_3\)S\(_2\), oxidation at an acidic pH results in the formation of a sulphur-rich surface; such a product is absent in the Cu\(_2\)S system. The formation of a nickel hydroxide surface is observed by equilibrating Ni\(_3\)S\(_2\) suspension in aerated alkaline solutions.

5.4 ELECTROKINETIC STUDIES
Equilibrated at pH 3.0
Equilibrated at pH 11.0
Equilibrated at pH 9.5
Equilibrated at pH 9.5 in nitrogen saturated water

Figure 5.32 - Zeta potential-pH relation for heazlewoodite, pre-equilibrated under acidic or alkaline conditions in air or nitrogen.
5.4.2 Electrokinetics of Dextrin-Mineral Sulphide Systems

Figure 5.33 shows that the i.e.p. of freshly precipitated copper hydroxide is located at pH 8.5 and it coincides with the pH of minimum solubility of copper hydroxide (Attia, 1975). In an alkaline medium above the pH_{lep}, anionic complexes are formed on the surface through the adsorption of hydrolyzed products of Cu(II). In much the same way, the positive zeta potential below pH 8.5 is due to the presence of hydrolyzed cationic species of Cu(II).

Also shown is the zeta potential of copper hydroxide in the presence of various concentrations of tapioca dextrin. Above the pH_{lep}, the potential remains negative and its value is reduced in proportion to the dextrin concentration without any shift in the i.e.p. value, resembling the influence of indifferent electrolyte. Below the pH_{lep}, increasing concentrations of dextrin also tend to diminish the zeta potential in proportional magnitudes. This indicates the lack of specific adsorption of the polymer onto copper hydroxide. Copper hydroxide is known to be metastable and decomposes to the more thermodynamically stable CuO or the hydrated oxide and this may explain the differences between the surface layers on heazlewoodite and chalcocite when pre-equilibrated at alkaline pH.

The charge of colloidal tapioca dextrin has been determined to be negative above pH 9.0 (Figure 5.35). A feeble positive charge, displayed below pH 9.0, is an indication of the nonionic character of the dextrin within this pH range. The abstraction of dextrin by aqueous copper ions around pH 8.5 (Figure 5.28) is very moderate, and involves weak interactions. The presence of nonionic dextrin macromolecules on the surface of the solid merely shifts the shear plane further from the interface, resulting in the observed reduced zeta potential values (Figure 5.33).

Figure 5.34 shows the variation of zeta potential of nickel hydroxide with pH in the absence and presence of various concentrations of dextrin. The i.e.p. of the hydroxide is located at pH 11.5. From pH 10.0 through the i.e.p. and above, it is seen that in the presence of dextrin, the electrokinetic behaviour is unchanged and is independent of the polymer concentration.
Figure 5.33 - Zeta Potential-pH Curves for Copper Hydroxide in the Presence and Absence of Dextrin.

Figure 5.34 - Zeta Potential-pH Curves for Nickel Hydroxide in the Presence and Absence of Dextrin.
It could be expected that the interaction between two negatively charged surfaces within this pH range would not favour the abstraction of dextrin due to repulsive forces. However, the interaction of dextrin reaches a maximum at the pH where nickel ions exist in the form of the hydroxide (Figure 5.27). The high adsorption density within this pH range (for example on heazlewoodite, Figure 5.10) and the high affinity type adsorption isotherm (Figure 5.12) indicate strong interactions. In Figure 5.34, strong interactions likely result in a flat orientation of dextrin macromolecules at the nickel hydroxide-water interface.

A manifestation of the strong dextrin-nickel hydroxide interaction is clearly exhibited through the electrokinetic behaviour of the dextrin-Ni$_3$S$_2$ system (Figure 5.36). Following pre-equilibration at pH 10.8, the electrokinetic behaviour of Ni$_3$S$_2$ imitates that of nickel hydroxide, indicating the presence of a hydroxide layer on the Ni$_3$S$_2$ surface. In the presence of dextrin, the zeta potential of Ni$_3$S$_2$ is strongly affected. It is interesting to note that even under nitrogen atmosphere, the studied effects do not vary significantly.

The zeta potential-pH curves for the dextrin-chalcocite system, pre-equilibrated at pH 10.0 in the presence and absence of oxygen, are shown in Figure 5.37. Under alkaline conditions the electrokinetic curve for chalcocite moves closer to that of Cu(OH)$_2$. In the presence of dextrin, the potential-pH curve is not very different from that of the dextrin-Cu(OH)$_2$ system. This may further indicate the presence of a hydrated oxide layer on the surface of chalcocite as opposed to the hydroxide layer on the surface of heazlewoodite.

The effect of adsorption of large non-ionic macromolecules on the zeta potential has been studied by many researchers (Wie and Fuerstenau, 1973; Brooks, 1973; Brooks and Seaman, 1973; Garvey et al., 1976; Lyklema, 1976). The author's tests on the effect of dextrin on the zeta potential of copper hydroxide and copper sulphide (Cu$_2$S) confirm their conclusions. Such adsorption seems to drive the shear plane further away from the interface, thus reducing the zeta potential value.
Figure 5.35 - pH Dependence of the Zeta Potential of Tapioca Dextrin in 10^{-2} M Potassium Nitrate Solution at Dextrin Concentration of 1000 mg/l.

Figure 5.36 - Effect of pH and Dextrin on the Zeta Potential of Heazlewoodite. Suspension Pre-equilibrated at pH 10.8 in the Presence of Air or Nitrogen.
Figure 5.37 - Effect of pH and dextrin on the zeta potential of chalcocite. Suspension pre-equilibrated at pH 10.0 in the presence of air or nitrogen.
The same dextrin, however, was found to affect the zeta potential pH-curves for both copper hydroxide and copper sulphide (Cu₂S) in quite a different way. Since our adsorption tests revealed high adsorption affinity of dextrin towards heazlewoodite, and low adsorption affinity towards chalcocite, this should result in a quite different orientation of dextrin macromolecules at the surfaces of these two minerals. These postulated differences seem to explain quite well the strong ability of dextrin to depress flotation of heazlewoodite in alkaline solutions; differential flotation under such conditions permits chalcocite to float selectively while inhibiting the flotation of heazlewoodite (Nyamekye and Laskowski, 1991).

The reproducibility of the electrokinetic measurements has been provided in Appendix 6.

5.4 ELECTROKINETIC STUDIES
5.5 CONDUCTOMETRIC STUDIES

5.5.1 Dextrin-Aqueous Cu$^{2+}$ species

Conductometric studies have recently been used as an effective tool in studying the nature of interaction between reagents and mineral species in aqueous solutions (Kholsa et al., 1984; Kholsa and Biswa, 1984; Cross et al., 1985; Subramanian and Natarajan, 1988; de Araujo, 1988; Liu, 1988). In order to provide further proof of the mode of interaction between the dextrin and Cu$^{2+}$/Ni$^{2+}$ systems, conductivity measurements were carried out at varying concentrations of metal ions at fixed pH values. Details of the method and principles of this approach have been given in section 4.3.8.

Figure 5.38 shows the effect of copper ion concentration at pH 6.0 on conductivity. It can be observed that the conductance of the dextrin solution at pH 6.0 is almost nil. This is corroborated, in part, by the electrokinetic measurement for tapioca dextrin (Figure 5.35) where the charge within this pH range is very low. A look at the trend in the data presented for the measured and calculated conductivities shows that at all concentrations of copper ion species, positive and negative deviations from the additive values of the conductances are negligible. This is an indication of negligible interactions. Figure 5.39 shows similar data obtained for a similar system at pH 8.9, where copper hydroxy-species precipitate. Again, it can be observed that the conductance discrepancy from the additive values on mixing is very low, symptomatic of weak interactions. This is a confirmation of the results obtained from adsorption tests, electrokinetic measurements and co-precipitation studies for the dextrin-copper interactions. There is a marked increase in the conductance of dextrin at pH 11.7, (Figure 5.40), possibly due to the presence of various hydrolysis products. Once again, there is no indication of any strong interaction for the system at this pH.
Figure 5.38 - Effect of dextrin on the electrical conductivity of copper nitrate solution at pH 6.0.

Figure 5.39 - Effect of dextrin on the electrical conductivity of copper nitrate solution at pH 8.9.
Figure 5.40 - Effect of dextrin on the electrical conductivity of copper nitrate solution at pH 11.5.

Figure 5.41 - Effect of dextrin on the electrical conductivity of nickel nitrate solution at pH 6.0.
Figure 5.42 - Effect of dextrin on the electrical conductivity of nickel nitrate solution at pH 11.7.
5.5.2 Dextrin-Aqueous Ni$^{2+}$ species

When the measured conductivity of a dextrin-aqueous nickel ions solution is compared to that of the calculated conductivity, which is derived from the additive values of the conductances of the separate dextrin and nickel ions solutions, it is observed in Figure 5.41 that the discrepancies at various concentrations of the metal ions are negligible at pH 6.0. At pH 11.7, however, when the conductivity of the composite solution is compared to the sum of the individual conductivity contributions separately determined, there is a large positive discrepancy in conductance which increases with an increase in the nickel ions concentration (Figure 5.42). This signifies a substantial interaction which is absent in the dextrin-Cu$^{2+}$ composite solution. The high conductivity of dextrin at pH 11.7 is not surprising, since the hydroxyl groups of polysaccharides are known to undergo ionization under alkaline conditions (Davidson, 1967).

It is clear from the above discussion that while dextrin exhibits weak or no interaction with nickel ions at pH 6.0, there is a strong bonding of dextrin to nickel hydroxide at pH 11.7, which is in the neighbourhood of the pH$_{iep}$ for Ni(OH)$_2$. The bonding mechanism under this condition may lead to the formation of a new complex. It is to be noted, however, that in the case of copper ion-dextrin systems there is no indication of any strong bonding, even around the pH$_{iep}$ of Cu(OH)$_2$. 

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5.5 CONDUCTOMETRIC STUDIES
5.6  INTERNAL REFLECTION SPECTROSCOPY

5.6.1  Reference Spectra of Dextrin 12, Cu(OH)$_2$ and Ni(OH)$_2$

The infrared transmission spectrum of tapioca dextrin 12 is shown in Figure 5.43 and bears a close resemblance to that of starches (Baker et al., 1954; Samec, 1957; De Araujo, 1988). The strong diffuse band centered at 3416 cm$^{-1}$ can be attributed to the stretching vibration of the hydroxyl groups in the dextrin structure. This indicates that the O—H groups are strongly hydrogen bonded. The band at 2932 cm$^{-1}$ can be assigned to the asymmetric CH stretching vibration in —CH$_2$ groups. The intense band at 1651 cm$^{-1}$ indicates a ring stretching of the glucopyranose ring. The bands from 1456 to 1341 are the consequence of OH bending modes mixed with —CH$_2$ stretching. Absorption band at 1241 cm$^{-1}$ is associated with external deformation vibration bond angles and bonds of —CH$_2$ groups (Zhbankov, 1966). The intense bands at 1157 and 1080 cm$^{-1}$ are due to the stretching modes of C-O-C bond and primary alcohol, —CH$_2$OH, respectively. A strong peak at 1022 cm$^{-1}$ is a pointer to —CH$_2$ twisting vibrations, that at 764 cm$^{-1}$ is symmetric ring stretching vibration and 710 cm$^{-1}$ is assigned to rocking vibrations. Absorptions at 929 and 860 cm$^{-1}$ are the result of asymmetric ring stretching and ring deformation modes, respectively. Figure 5.44 depicts an in-situ ATR spectrum of aqueous tapioca dextrin 12, showing the 1750 - 600 cm$^{-1}$ region, which correlates very well with the transmission spectrum described above.

In the electronic structure of a basic hydroxide, an O—H group interacting with an electropositive atom (e.g. Ni or Cu) imparts a weak proton-donor ability to the OH$^-$ ion and is the principal cause of its very characteristic internal vibration which gives rise to a strong, sharp O—H stretching band in the region 3700 - 3500 cm$^{-1}$. This stretching vibrational mode in hydroxides is, however, partnered by a bending vibration since in an M—OH band, the oxygen atom is fixed relative to the cation, leaving the hydrogen free to vibrate about the oxygen in a bending mode. The O—H bending frequency in this case is distinguishable from that of absorbed water by occurring in the 1200 - 600 cm$^{-1}$ region.
Figure 5.43 - FTIR Transmission Spectrum of Tapioca Dextrin 12.

Figure 5.44 - FTIR Reflection Spectrum of Tapioca Dextrin.

5.6 INTERNAL REFLECTION SPECTROSCOPY
As shown in Figure 5.45, the peaks exhibited by nickel hydroxide in the 3750 - 600 \text{ cm}^{-1} infrared range are limited and the most noticeable one is the sharp O—H stretching frequency at 3636 and again at 1382 \text{ cm}^{-1} (Figlarz and Bihan, 1971). Unlike the Cu(OH)$_2$ spectrum, the metallic oxide (M=O) character of Ni(OH)$_2$ is nil, since there is no stretching band in the region 1050 - 800 \text{ cm}^{-1}. This again confirms the stability of a freshly precipitated Ni(OH)$_2$ as opposed to that of Cu(OH)$_2$.

Figure 5.46 shows the infrared spectrum of copper hydroxide. The doublets peaks at 3573 and 3559 \text{ cm}^{-1} are assigned to the O—H stretching frequencies of the amphoteric copper hydroxide. It should be noted that Cu(OH)$_2$ behaves as an isostructural hydroxide where H-bonds connect O—H groups belonging to two crystallographic sets and each O—H group is involved in two H-bonds of different lengths. One should therefore expect doubling of the O—H stretching maxima due to hydroxyls belonging to different sets. The sharp band at 682 \text{ cm}^{-1} can be assigned to O—H bending mode (Jaggi and Oswald, 1961) whereas the peak at 932 is an indication of a Cu=O stretching mode. The peaks at 3300 and 1601 \text{ cm}^{-1} are due to the O—H stretching and bending vibrations of water of hydration, respectively (Gadsden, 1975).

### 5.6.2 ATR Spectra of Dextrin Interacted with Ni(OH)$_2$ and Cu(OH)$_2$

The in-situ FTIR-ATR spectra of the interaction product of dextrin and freshly precipitated nickel hydroxide at pH 11.7 under various desorption conditions are given in Figure 5.47. Only the 1750 - 600 \text{ cm}^{-1} region is shown, where most of the important vibrations of the dextrin functional groups are observed. A comparison of these spectra to the dextrin reference spectrum in Figure 5.44 indicates that the typical asymmetric and symmetric stretching frequency of the glucose ring is at 929 and 764 \text{ cm}^{-1}, respectively, and the ring deformation mode frequency at 860 \text{ cm}^{-1} vanishes after the interaction. Attempts to desorb the dextrin from the surface of the nickel hydroxide, even after 5 washing cycles, did not yield any difference in the spectra.
Figure 5.45 - IR Reflection Spectrum of a Fresh Precipitate of Nickel Hydroxide.

Figure 5.46 - IR Reflection Spectrum of a Fresh Precipitate of Copper Hydroxide.

5.6 INTERNAL REFLECTION SPECTROSCOPY
These experiments reveal a significant change in the absorption band at 860 cm$^{-1}$ and suggest that the entire grouping at C$_1$ is involved in the bonding process rather than a substitution at either the —H or —OH positions (Davidson, 1967). The elimination of the 929 and 764 cm$^{-1}$ bands also gives an indication that the new bond that has been formed through the interaction transforms the glucose ring into a rigid and a more stable structure which is strong enough to resist any ring deformation and is responsible for the elimination of these frequencies.

By considering the geometry of the strainless 6-membered structure of the glucose ring, it is known (Davidson, 1967) that equatorial hydroxyl groups are more reactive than the axial —OH groups. The presence of a particularly bulky substituent group can also render adjacent hydroxyls relatively unreactive, even when they are in the equatorial conformation. This will then mean that the integration of a Ni atom in the glucose ring to form an organometallic complex will stabilize other —OH groups on the mineral surface.

Figure 5.48 depicts the ATR spectra of a co-precipitated product of dextrin and copper solution at pH 9.0 before and after undergoing desorption. A critical look at the co-precipitated product indicates that the spectrum is made up of bands which are a mixture of dextrin and copper precipitate. Combination tones that also appear in the spectrum are merely due to the difference of 2 or more fundamental bands (Davidson, 1967). This gives an indication that dextrin is physically bonded to the copper precipitate since there are no changes in its vibrational frequencies. This is supported by the spectra of the desorbed samples. As the desorption proceeds, the intensity of the dextrin bands decreases and finally, the resultant spectrum is basically that of the copper precipitate. The spectrum of the copper hydroxide precipitate seems to indicate that the surface consisted of a mixture of hydrated copper oxide and hydroxide. It is also known that copper hydroxide is unstable and can easily be converted to the oxide. Since it has been established that strong dextrin interaction is favoured by the presence of a stable hydroxide (Liu, 1988; Nyamekye and Laskowski, 1992), it is not surprising to observe the weak bonding interactions between dextrin and copper hydroxide.

5.6 INTERNAL REFLECTION SPECTROSCOPY
Figure 5.47 - FTIR Reflection Spectra of Co-precipitated Dextrin and Ni(OH)$_2$.
Figure 5.48 - FTIR Reflection Spectra of Co-precipitated Dextrin and Cu(OH)\(_2\).
In view of the more stable product formed between dextrin molecules and nickel hydroxide, a proposed mechanism of interaction involving the stability of a more favored 6-membered ring (the structure consisting of 3 carbons, 2 oxygens and one nickel atom) and a hydroxylated nickel surface is presented in Figure 5.49. Thus, the increase in conductivity of the aqueous system, when both dextrin and Ni(OH)$_2$ at pH 11.7, are mixed, can be accounted for by the release of the hydrogen ion as shown by the interaction mechanism below.

Figure 5.49 - Mechanism of interaction between dextrin and nickel hydroxide.

Figure 5.50 shows the in-situ ATR spectrum of tapioca dextrin adsorbed onto heazlewoodite at pH 11.7. This compares very well with the dextrin-Ni(OH)$_2$ precipitate spectrum, indicating that similar interaction mechanisms are involved in the two systems. The intensity of the frequency bands in the Ni$_3$S$_2$ system are, however, lower as should be expected, since the degree of hydroxide layer formation on the sulphide surface is much lower than in the nickel precipitate.

5.6 INTERNAL REFLECTION SPECTROSCOPY
Figure 5.50 - In-situ ATR Spectrum of Dextrin Adsorbed onto Heazlewoodite.

Figure 5.51 - In-situ ATR Spectrum of Dextrin Adsorbed onto Chalcocite.
In Figure 5.51, the spectrum of tapioca dextrin adsorbed onto chalcocite also approximates that of dextrin-copper precipitate, without any change in the absorption bands of dextrin on the surface. It again shows some sort of physical interaction between dextrin and chalcocite.

It is worth mentioning that ATR-FTIR technique was utilized in this work as a confirmatory test to support the presence of a chemical complex when dextrin interacts with heazlewoodite or nickel hydroxide around the pH_{iep} of Ni(OH)_2. Evidence for the formation of a chemical interaction between dextrin and heazlewoodite is strongly supported by previous tests as follows:

- Adsorption isotherm of dextrin on heazlewoodite is of the high affinity type and once dextrin is adsorbed, it becomes almost impossible to desorb it from the surface of the mineral. The reverse argument holds for the dextrin-chalcocite system.

- Co-precipitation test shows strong interaction between dextrin and Ni(OH)_2 precipitate, resulting in the complete removal of dextrin from solution around the pH_{iep} of Ni(OH)_2. The interaction of dextrin with the copper hydroxide precipitate, in this case, is not complete.

- Flat orientation of dextrin macromolecules at the nickel hydroxide-water interface as shown by electrokinetic studies can only occur from strong interactions between dextrin and nickel hydroxide. Interactions between weakly adsorbed, extended dextrin macromolecules and chalcocite or copper hydroxide result in an extension of electrical double layer which drives the shear plane further away from the surface.
5.7 SMALL SCALE FLOTATION STUDIES

5.7.1 Flotation of Cu$_2$S and Ni$_3$S$_2$ with Amyl Xanthate

The flotation response of chalcocite with $1 \times 10^{-4}$ mol·dm$^{-3}$ and $2 \times 10^{-4}$ mol·dm$^{-3}$ amyl xanthate, using nitrogen as the flotation gas, is shown in Figure 5.52. As can be noted, strong floatability is exhibited in the pH range 2.0 - 3.0 and again at 10.0 - 11.5. Complete flotation is effected with $2 \times 10^{-4}$ mol·dm$^{-3}$ amyl xanthate within the alkaline range. Flotation is slightly depressed in the pH range 3.0 - 9.0.

As explained in section 5.2.4, the floatability of chalcocite in the pH range 2 to 12 is due to the presence of two hydrophobic entities on the surface of chalcocite, xanthate chemisorbed at monolayer coverage and bulk-precipitated cuprous xanthate adsorbed at multilayer coverage. In the alkaline pH range where flotation is enhanced, xanthates are more stable than cuprous carbonate, sulphate or thiosulphate, which form on the surface of chalcocite through oxidation processes. Metathetic replacement of these surface products by cuprous amyl xanthate is then augmented. This observation correlates very well with the adsorption-pH behaviour of chalcocite in Figure 5.18.

The flotation response of heazlewoodite with amyl xanthate over the pH range from 2.0 to 12.0 is shown in Figure 5.53. Complete flotation is obtained only in the pH range 2 - 3.5 with $2 \times 10^{-4}$ mol·dm$^{-3}$ amyl xanthate. Beyond this pH range there is a sharp drop in recovery and two flotation regions can be observed, especially at the lower xanthate concentration ($1.0 \times 10^{-4}$ mol·dm$^{-3}$). The reduction in floatability in the pH range 6.0 - 10.0 signifies the hydrolytic decomposition of nickel xanthate into alcohol, carbon disulphide and OH$^-$ (Leja, 1982). Above pH 10.0 dixanthogen is unstable and surface hydrophobicity is further reduced. It is therefore not surprising to observe a low flotation recovery in this pH range (at around 35% Ni$_3$S$_2$). The correlation between the results shown in Figure 5.53 and the adsorption-pH curves for amyl xanthate on heazlewoodite (Figure 5.20) is quite good.
Figure 5.52 - Effect of pH on Hallimond Tube Flotation of Chalcocite Using Potassium Amyl Xanthate as Collector.

Figure 5.53 - Effect of pH on Hallimond Tube Flotation of Heazlewoodite Using Potassium Amyl Xanthate as Collector.
5.7.2 Floatability of Cu$_2$S and Ni$_3$S$_2$ in the Presence of Dextrin

The effect of dextrin concentration on the Hallimond tube flotation of heazlewoodite and chalcocite is presented in Figures 5.54 and 5.55, respectively. Flotation studies were conducted by testing the order of addition of both the collector (xanthate) and the depressant (dextrin) based on the observations made in the adsorption studies. These tests were carried out at pH 11.7, where dextrin adsorption on heazlewoodite is maximum and the depression effect is assumed to be strong.

With 2.0 x 10$^{-4}$ mol·dm$^{-3}$ amyl xanthate, it can be seen from Figure 5.54 that irrespective of the order of addition of dextrin, the recovery of heazlewoodite does not vary appreciably. In the absence of dextrin, the recovery of heazlewoodite is 33%, but as the concentration of dextrin is increased from 0 to 500 mg/l, floatability is drastically suppressed, especially up to 100 mg/l dextrin where the recovery is only 6% Ni$_3$S$_2$. There is a gradual decrease in recovery when dextrin concentration is increased from 100 mg/l to 300 mg/l to about 4% Ni$_3$S$_2$ and above 300 mg/l dextrin there is no observable change in the recovery.

The flotation of chalcocite is very sensitive to the order of dextrin addition and it follows the same trend as the adsorption curve. In Figure 5.55, chalcocite is highly depressed when the suspension is first conditioned with dextrin prior to the addition of amyl xanthate. The drop in recovery is approximately proportional to the concentration of dextrin. From 0 to 300 mg/l dextrin, the recovery of Cu$_2$S drops from 100% to 68%. As observed in the adsorption tests, dextrin adsorption is hindered when chalcocite is initially conditioned with amyl xanthate. Figure 5.55 shows that the depression of chalcocite is less significant under such conditions and the recovery of Cu$_2$S drops from 100% in the absence of dextrin to only 92% in the presence of 300 mg/l dextrin dosage.
Figure 5.54 - Effect of Dextrin Concentration on the Hallimond Tube Flotation of Heazlewoodite Using Amyl Xanthate as Collector at pH 11.7.

Figure 5.55 - Effect of Dextrin Concentration on the Hallimond Tube Flotation of Chalcocite Using Amyl Xanthate as Collector at pH 11.7.
Thus, the best condition for selective flotation of the mixture consisting of chalcocite and heazlewoodite particles is by the initial conditioning with amyl xanthate for a period of time to ensure its adsorption on chalcocite before dextrin is added to depress heazlewoodite. These results indicate that there is a good correlation between the adsorption and flotation processes.
5.8 BATCH FLOTATION STUDIES

All batch flotation experiments were conducted following the conclusions drawn from the adsorption and electrokinetic measurements, co-precipitation tests, and Hallimond tube flotation experiments. The conditions in these tests were used as a standard, whenever necessary, in setting parameters for batch flotation. Pulp pH was adjusted using lime in accordance with industrial practice and it was always added to the grinding media. The ultimate aim of these batch flotation studies is to identify the flotation conditions which give the highest copper concentrate grade with a resultant minimum nickel content, taking into account the level of copper recovery.

5.8.1 Flotation of Matte with DPG

The grade-recovery curves for the blank flotation of chalcocite using DPG and lime in the absence of a modifier at pH 12.4 are shown in Figure 5.56. For the 7-minute flotation time used in these tests, it was observed that flotation recovery was very high during the first 3 minutes while the percent copper recovered in the last 4 minutes of flotation was very slow and contains a high proportion of Ni.

At DPG dosages of 100 g/t, 200 g/t and 300 g/t in a single-stage rougher flotation, it is observed that the highest copper grade with the minimum nickel content is achieved with the lowest collector dosage. As expected, the level of recovery is quite low, 87.3% Cu compared to the 92.4% and 94% Cu for 200 g/t and 300 g/t DPG, respectively. Conversely, the higher recovery at 300 g/t DPG results in a poor copper selectivity. As a compromise, a 200 g/t DPG dosage which gives a copper concentrate grade of 57.9% with a 23% Ni content was adopted for all the subsequent tests.
Figure 5.56 - Grade-Recovery Curves for Rougher Flotation of Inco Matte with DPG at pH 12.4 (Without a Modifier).

Figure 5.57 - Grade-Recovery Curves for Cleaning of the Inco Matte Concentrate at pH 12.4 in the Absence of a Modifier.
### Table 5.3 - Metallurgical Balance for Rougher Flotation of Inco Matte at 200 g/t DPG

<table>
<thead>
<tr>
<th>Flotation Products</th>
<th>Yield (%)</th>
<th>Cum Yld (%)</th>
<th>Con Grade %Cu</th>
<th>%Ni</th>
<th>Recovery %Cu</th>
<th>%Ni</th>
<th>Cum Recovery %Cu</th>
<th>%Ni</th>
<th>Cum Grade %Cu</th>
<th>%Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc 1</td>
<td>16.6</td>
<td>16.6</td>
<td>67.0</td>
<td>17.0</td>
<td>50.3</td>
<td>5.5</td>
<td>50.3</td>
<td>5.5</td>
<td>67.0</td>
<td>17.0</td>
</tr>
<tr>
<td>Conc 2</td>
<td>8.1</td>
<td>25.0</td>
<td>57.5</td>
<td>24.0</td>
<td>21.8</td>
<td>3.9</td>
<td>72.1</td>
<td>9.4</td>
<td>63.7</td>
<td>19.6</td>
</tr>
<tr>
<td>Conc 3</td>
<td>7.3</td>
<td>32.3</td>
<td>48.0</td>
<td>28.0</td>
<td>15.8</td>
<td>3.9</td>
<td>87.9</td>
<td>13.3</td>
<td>60.1</td>
<td>21.4</td>
</tr>
<tr>
<td>Conc 4</td>
<td>3.0</td>
<td>35.3</td>
<td>33.0</td>
<td>40.0</td>
<td>4.5</td>
<td>2.3</td>
<td>92.4</td>
<td>15.6</td>
<td>57.9</td>
<td>23.0</td>
</tr>
<tr>
<td>Tailing</td>
<td>64.7</td>
<td>-</td>
<td>2.6</td>
<td>68.0</td>
<td>7.6</td>
<td>84.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Total</td>
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<td></td>
<td></td>
<td>100.0</td>
<td></td>
<td>100.0</td>
<td></td>
<td>22.1</td>
<td>52.1</td>
</tr>
</tbody>
</table>

**Flotation Feed Weight** - 1.184 kg

**Head Assay:** %Cu - 21.0; %Ni - 52.0

---

### Table 5.4 - Metallurgical Balance for Cleaning of Rougher Concentrate Using DPG.

<table>
<thead>
<tr>
<th>Flotation Products</th>
<th>Yield (%)</th>
<th>Cum Yld (%)</th>
<th>Con Grade %Cu</th>
<th>%Ni</th>
<th>Recovery %Cu</th>
<th>%Ni</th>
<th>Cum Recovery %Cu</th>
<th>%Ni</th>
<th>Cum Grade %Cu</th>
<th>%Ni</th>
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<tbody>
<tr>
<td>Conc 1</td>
<td>53.2</td>
<td>53.2</td>
<td>66.0</td>
<td>10.8</td>
<td>64.7</td>
<td>27.0</td>
<td>64.7</td>
<td>27.0</td>
<td>66.0</td>
<td>10.8</td>
</tr>
<tr>
<td>Conc 2</td>
<td>21.4</td>
<td>74.6</td>
<td>54.0</td>
<td>22.0</td>
<td>21.3</td>
<td>22.1</td>
<td>86.0</td>
<td>49.1</td>
<td>62.6</td>
<td>14.0</td>
</tr>
<tr>
<td>Conc 3</td>
<td>8.4</td>
<td>83.1</td>
<td>60.0</td>
<td>16.0</td>
<td>9.3</td>
<td>6.6</td>
<td>95.3</td>
<td>55.7</td>
<td>62.3</td>
<td>14.3</td>
</tr>
<tr>
<td>Conc 4</td>
<td>3.4</td>
<td>86.4</td>
<td>52.0</td>
<td>22.0</td>
<td>3.2</td>
<td>3.5</td>
<td>98.5</td>
<td>59.2</td>
<td>61.9</td>
<td>14.6</td>
</tr>
<tr>
<td>Tailing</td>
<td>13.6</td>
<td>-</td>
<td>6.0</td>
<td>64.0</td>
<td>1.5</td>
<td>40.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td></td>
<td></td>
<td></td>
<td>100.0</td>
<td></td>
<td>100.0</td>
<td></td>
<td>54.3</td>
<td>21.3</td>
</tr>
</tbody>
</table>

**Flotation Feed Weight** - 0.641 kg

**Head Assay:** %Cu - 54.0; %Ni - 22.0

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5.8 BATCH FLOTATION STUDIES
The metallurgical balance for the blank matte flotation with 200 g/t DPG at pH 12.4 is given in Table 5.3. The trend in the cleaning of the rougher copper concentrate in the absence of dextrin is shown in Figure 5.57. The flotation of chalcocite in this case is very fast with the recovery in this stage reaching as high as 98%. Selectivity of the flotation process, however, is poor and the cleaner concentrate grade suffers at the expense of the recovery. As shown in Table 5.4, a rougher concentrate grade of 54.3% Cu containing 21.3% Ni yielded a concentrate grade of 61.9% Cu with 14.6% Ni after one-stage cleaning. Cleaning was performed without any further addition of the collector to the rougher concentrate.

5.8.2 Differential Flotation of Chalcocite with DPG and Dextrin

The results of the batch flotation tests conducted at an optimum dosage of 200 g/t DPG in the presence of dextrin are shown in Figures 5.58 and 5.59. The effect of dextrin on the copper concentrate grade and recovery when used in rougher flotation of the matte can clearly be seen from Figure 5.58. At dextrin dosage of 300 g/t or 400 g/t, there is a significant drop of the Ni content in the copper concentrate which translates into the high copper grade of the concentrate. Although the final copper grade at 400 g/t dextrin is slightly higher than at 300 g/t the copper recovery is more attractive at the latter dosage. A comparison of the final copper concentrate grade of 68.5% Cu and 12.1% Ni at a recovery of 92.9% Cu at 300 g/t dextrin with that in the absence of dextrin (Table 5.3) proves the effectiveness of dextrin as a depressant for heazlewoodite. There is about a 50 percent reduction in the nickel level of the copper concentrate when 300 g/t dextrin is used in the rougher flotation of the matte without any noticeable reduction in the copper recovery.

In order to further reduce the nickel levels in the copper concentrate, rougher concentrate cleaning was carried out with dextrin. Tests involving the use of dextrin in both rougher and cleaner flotation and that which incorporates dextrin only in the cleaning process showed that the latter option was more practically feasible.
Figure 5.58 - Effect of Dextrin on Copper Concentrate Grade and Recovery in Rougher Flotation of the Inco Matte with DPG.

Figure 5.59 - Effect of Dextrin on the Copper Concentrate Grade and Recovery in the Cleaner Flotation of the Inco Matte with DPG.
Figure 5.59 shows the degree of selectivity when various dosages of dextrin are used in the cleaning flotation stage. The cleaner copper concentrate at 300 g/t dextrin shows a significant improvement in the grade, although the recovery is not as high as in the blank flotation test. Flotation rate was relatively slower but this resulted in a much improved selectivity. From the rougher concentrate grade (54.4% Cu and 21% Ni) the cleaner concentrate containing 70.5% Cu and 7.5% Ni at a Cu recovery of 81.7% Cu was obtained.

Table 5.5 - Metallurgical Balance for Cleaning of Rougher Chalcocite Concentrate at 350 g/t Dextrin and 200 g/t DPG.

<table>
<thead>
<tr>
<th>Flotation Products</th>
<th>Yield (%)</th>
<th>Cum Yld (%)</th>
<th>Con Grade</th>
<th>Recovery</th>
<th>Cum Recovery</th>
<th>Cum Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc 1</td>
<td>22.9</td>
<td>22.9</td>
<td>74.0</td>
<td>3.3</td>
<td>30.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Conc 2</td>
<td>16.6</td>
<td>39.6</td>
<td>73.0</td>
<td>3.8</td>
<td>21.9</td>
<td>3.3</td>
</tr>
<tr>
<td>Conc 3</td>
<td>13.8</td>
<td>53.4</td>
<td>72.0</td>
<td>5.0</td>
<td>17.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Conc 4</td>
<td>6.1</td>
<td>59.5</td>
<td>68.0</td>
<td>8.5</td>
<td>7.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Tailing</td>
<td>40.5</td>
<td>-</td>
<td>30.0</td>
<td>41.0</td>
<td>21.9</td>
<td>86.5</td>
</tr>
</tbody>
</table>

Total 100.0 100.0 55.4 19.2

Flotation Feed Weight - 0.656 kg
Head Assay: %Cu - 55.0; %Ni - 20.0

There is further improvement in the cleaner concentrate grade when the depressant dosage is increased up to 350 g/t dextrin. The best selectivity for chalcocite is achieved at this level, and as shown in Figure 5.59, suppression of the nickel level in the concentrate is persistent almost throughout the flotation. A concentrate grade of 72.6% Cu with 4.4% Ni is achieved at a recovery of 78% Cu. The metallurgical balance for this test is provided in Table 5.5 and can be compared to the blank cleaning results in Table 5.4. Cleaning without dextrin increases the Cu grade in the rougher concentrate by about 13%, while in the presence of dextrin the grade is improved by about 32%. In terms of the nickel contents associated with the cleaner concentrate, the blank cleaning gives a product containing 14.6% Ni while 350 g/t dextrin reduces it down to 4.4% Ni, at only
slightly lower copper recovery. Although a further increase in the depressant dosage to 450 g/t dextrin resulted in an improved concentrate grade, the level of copper recovery is prohibitively low.

5.8.3 Floatability of Chalcocite with Aerofloat 208, Ethyl and Amyl Xanthates

The use of xanthates and dithiophosphates in the selective flotation of chalcocite from the matte were tested in the presence of dextrin. These collectors are soluble in water and also very easy to handle compared to DPG. However, the DPG collector has been used by Inco in the matte flotation for a long time, since it provided better Cu recovery and better concentrate grades compared to those produced using thioCollectors.

The performance of aerofloat 208 in the differential flotation of chalcocite is presented in Figure 5.60, in the absence and presence of dextrin. The flotation results for this collector are not all that encouraging. Although a copper recovery of about 92% is achieved in the rougher flotation, at an optimum collector dosage of 200 g/t, the resultant concentrate grade is only around 46.0% Cu with a Ni content as high as 28.3%. Cleaning of the rougher concentrate with dextrin does not yield any better performance. At a dextrin dosage of as high as 400 g/t, the best copper grade obtained is 65.5% Cu and 13.1% Ni, with a significant drop in the Cu recovery (55% Cu).

Results for the batch flotation of the matte using sodium ethyl xanthate are presented in Figure 5.61. Various collector dosages were tested and it was at the 250 g/t level that the performance was on par with other tested collectors in terms of recovery. Chalcocite recovery in the rougher flotation was around 90.0% with a grade of 55% Cu and 19.2% Ni. At a depressant dosage of 400 g/t, the cleaning of the rougher concentrate resulted in a product of 72.5% Cu and 4.5% Ni at a copper recovery of 61.4% (Table 5.6). The effect of dextrin as a depressant for heazlewoodite can be observed in Figure 5.61, where blank cleaning yielded a concentrate with 13.5% Ni content (as compared to cleaning with dextrin which produces a concentrate assaying only 4.5% Ni).
Table 5.6 - Metallurgical Balance for Cleaning of Rougher Chalcocite Concentrate at 400 g/t Dextrin and 250 g/t Ethyl Xanthate.

<table>
<thead>
<tr>
<th>Flotation Products</th>
<th>Yield (%)</th>
<th>Cum Yld (%)</th>
<th>Con Grade</th>
<th>Recovery</th>
<th>Cum Recovery</th>
<th>Cum Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc 1</td>
<td>18.6</td>
<td>18.6</td>
<td>74.1</td>
<td>3.9</td>
<td>24.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Conc 2</td>
<td>12.7</td>
<td>31.3</td>
<td>72.8</td>
<td>4.3</td>
<td>16.7</td>
<td>2.8</td>
</tr>
<tr>
<td>Conc 3</td>
<td>15.6</td>
<td>46.9</td>
<td>61.4</td>
<td>5.5</td>
<td>19.8</td>
<td>4.5</td>
</tr>
<tr>
<td>Tailing</td>
<td>53.1</td>
<td>-</td>
<td>40.4</td>
<td>32.2</td>
<td>38.6</td>
<td>88.9</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>55.5</td>
<td>19.2</td>
<td></td>
</tr>
</tbody>
</table>

Flotation Feed Weight - 0.656 kg
Head Assay: %Cu - 55.0; %Ni - 20.0

Figure 5.62 shows the trend in the matte flotation with 175 g/t and 200 g/t potassium amyl xanthate. This is a more powerful, but less selective collector and as can be seen from the figure; at 200 g/t dosage, copper recovery is about 97% with very poor concentrate grade, the nickel content being around 28%. When the collector dosage is reduced to 175 g/t, a significant improvement is achieved in the concentrate grade, without sacrificing much of the recovery, indicating a possible overdose at the 200 g/t level. The rougher concentrate assay, in this case, yielded 52.4% Cu and 24% Ni at a Cu recovery of 93%.

The results for a single-stage cleaning of the rougher concentrate at 175 g/t amyl xanthate using 300 g/t and 400 g/t dextrin are shown in Figure 5.63. The curve for blank cleaning is also presented for comparison. A copper recovery of 88.6% is obtained at a grade of 64.7% Cu and 12.8% Ni when cleaning is done in the absence of dextrin. As can be seen, the best concentrate grade of 73.5% Cu and 4.6% Ni is achieved at a copper recovery of 78.5% Cu in the presence of 400 g/t dextrin. An analysis of the flotation results at this dextrin dosage is given in Table 5.7.

5.8 BATCH FLOTATION STUDIES
Figure 5.60 - Grade-Recovery Curves for the Inco Matte Flotation with Aerofloat 208 and Dextrin.

Figure 5.61 - Grade-Recovery Curves for the Inco Matte Flotation with Ethyl Xanthate and Dextrin.

5.8 BATCH FLOTATION STUDIES
Figure 5.62 - Grade-Recovery Curves for the Rougher Flotation of Inco Matte at Various Dosages of Potassium Amyl Xanthate.

Figure 5.63 - Grade-Recovery Curves for the Inco Matte Cleaner Concentrate with the Use of Amyl Xanthate and Dextrin.
Table 5.7 - Metallurgical Balance for Single-Stage Cleaning of Rougher Chalcocite Concentrate at 400 g/t Dextrin and 175 g/t Amyl Xanthate.

<table>
<thead>
<tr>
<th>Flotation Products</th>
<th>Yield (%)</th>
<th>Cum Yld (%)</th>
<th>Con Grade</th>
<th>Recovery</th>
<th>Cum Recovery</th>
<th>Cum Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc 1</td>
<td>20.7</td>
<td>20.7</td>
<td>75.5</td>
<td>3.5</td>
<td>30.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Conc 2</td>
<td>24.8</td>
<td>45.5</td>
<td>72.6</td>
<td>4.9</td>
<td>34.5</td>
<td>4.9</td>
</tr>
<tr>
<td>Conc 3</td>
<td>10.1</td>
<td>55.6</td>
<td>71.4</td>
<td>5.9</td>
<td>13.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Tailing</td>
<td>44.4</td>
<td>-</td>
<td>25.2</td>
<td>50.6</td>
<td>21.5</td>
<td>89.8</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>52.1</td>
<td>25.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Flotation Feed Weight - 0.653 kg
Head Assay: %Cu - 53.0; %Ni - 24.0

5.8.4 The Performance of the Tested Collectors in the Flotation of Matte with Dextrin

A look at the grade-recovery curves for the differential flotation of chalcocite with various collectors (Figure 5.64) indicates that, in the absence of dextrin, selectivity is better when DPG is used, as compared with the other tested collectors. At the various collector dosages, the order of selectivity is:

DPG > ethyl xanthate > amyl xanthate > aerofloat 208.

For the more powerful amyl xanthate collector, however, lower dosage (175 g/t) is needed to obtain copper recoveries equivalent to those obtained with DPG, while in the case of the more selective but less powerful ethyl xanthate collector, a higher dosage (250 g/t) is beneficial.

A comparison of the results for a single-stage cleaner flotation in Figure 5.65 reveals that while the cleaner concentrate grade using ethyl xanthate is high, the copper recovery is very low, even at the high collector dosages. The superiority of DPG is again shown by the higher grade of the cleaner concentrates at higher recoveries, as compared to ethyl and amyl xanthates.
Figure 5.66 reveals that the application of dextrin in the cleaner flotation process enhances the concentrate grade in all cases, making DPG and amyl xanthate equally effective in terms of the cleaner concentrate grade and recovery. Again, the recoveries for ethyl xanthate in the presence of dextrin are prohibitive, despite the high concentrate grade produced.

It has been shown that the selective flotation of chalcocite from heazlewoodite is highly enhanced in the presence of tapioca dextrin (Inco Patent, 1991). A simplified flowsheet for the production of high grade nickel and copper concentrates using either DPG or potassium amyl xanthate is given in Figure 5.67. Nickel concentrate is produced as the tails from the rougher flotation with as low as 2% Cu, content which is acceptable for the subsequent smelting.

Error analysis of the batch flotation tests can be found in Appendix 7.
Figure 5.64 - Performance of Various Tested Collectors at Their Optimum Dosages in Rougher Flotation of Inco Matte.

Figure 5.65 - Performance of Various Tested Collectors in the Cleaner Flotation of Inco Matte in the Absence of Dextrin.
Figure 5.66 - Performance of Various Collectors in the Cleaner Flotation of Inco Matte in the Presence of Optimum Dextrin Dosages.

5.8 BATCH FLOTATION STUDIES
Figure 5.67 - Simplified Flowsheet for Production of High Grade Copper Concentrate Using Dextrin as Depressant.
Chapter 6

CONCLUSIONS

1. Electrokinetic measurements revealed that the i.e.p. of nickel hydroxide is located around pH 11.7 while for copper hydroxide it was found to be 8.5. The electrokinetic technique also confirmed the presence of nickel hydroxide layer on the surface of heazlewoodite in alkaline solutions. The zeta potential-pH curves obtained for Cu$_2$S and for the precipitated copper hydroxy-species (according to thermodynamics, copper hydroxide is unstable), confirmed the presence of hydroxylated copper species on the surface of chalcocite.

2. The adsorption-pH curves for dextrin-heazlewoodite systems indicate a maximum around pH 11.7 which is at the i.e.p. of nickel hydroxide.

3. Tapioca dextrin has been shown to be the best depressant for heazlewoodite of all tested dextrins. Its molecular weight of 56,000, as determined by gel permeation chromatography, places it at the high end of the molecular weight scale for dextrins.

4. Adsorption studies carried out with tapioca dextrin and the DPG and potassium amyl xanthate collectors on chalcocite and heazlewoodite revealed the following:
   - Various dextrins have different adsorption affinities towards heazlewoodite; the adsorption is highly pH dependent with a maximum around pH 11.7. For chalcocite, dextrin adsorption densities are much lower and the process is independent of pH.
• While the adsorption isotherms of dextrin on heazlewoodite are of the high affinity type and reveal strong chemical interaction, the isotherms for chalcocite show only low affinity. These observations are confirmed by desorption tests which indicate that once dextrin adsorbs on heazlewoodite the process becomes irreversible. For chalcocite, it is very easy to desorb adsorbed dextrin from the surface through increased temperature or suspension dilution.

• The co-adsorption tests with dextrin and DPG and amyl xanthate, which are used as collectors for chalcocite, show that while dextrin displaces DPG and amyl xanthate from the surface of heazlewoodite around the pH 11.7, irrespective of the order of conditioning, it did not affect adsorption onto chalcocite when this mineral is first conditioned with the collectors.

5. Electrokinetic curves for heazlewoodite, chalcocite and nickel and copper hydroxides in the presence of dextrin exhibit quite different trends. The effect of dextrin on the zeta potential of copper hydroxide, which probably constitutes hydrated copper oxide, resembles the effect of indifferent electrolyte. It is postulated here that the decrease of the zeta potential values in such a case is caused by moving the slipping plane further away from the interface by fully extended, weakly adsorbed dextrin molecules. Strong interaction between dextrin molecules and nickel hydroxide makes these molecules adsorb flat onto the surface and, as a result, the effect of dextrin on the zeta potential for this system is quite different.

6. Co-precipitation tests conducted with dextrin and the aqueous solutions of copper or nickel nitrates, varying pH, confirm that the presence of a metal hydroxide is a prime factor for dextrin interaction. While dextrin interacts actively with freshly precipitated nickel hydroxide, which co-precipitates with the metal hydroxide and is entirely removed from the system, dextrin abstraction by precipitating copper hydroxylated species is not complete.

6.0 CONCLUSIONS
7. The large deviation in conductivity of the dextrin-nickel system at pH 11.7 is an indication of complex formation and occurs only around this pH where dextrin interacts strongly with the surface hydroxide. Such interaction effects in the dextrin-copper system are not so profound.

8. ATR-FTIR spectroscopy suggests that dextrin interacts with nickel hydroxide and heazlewoodite around pH 11.7 to form a chemical bond. The bonding mechanism for this system is based on the observation that a significant change in the ring deformation frequency at 860 cm\(^{-1}\) and the formation of a more rigid glucose ring due to the elimination of the 929 cm\(^{-1}\) and 764 cm\(^{-1}\) bands results in a more stable six-membered complex structure which links an Ni atom to C\(_1\) and C\(_3\) of a glucose monomer through oxygen atoms. For chalcocite, the adsorption does not depend on pH and the interaction of dextrin with a copper precipitate or chalcocite at pH 8.5 involves weak effects only.

9. Various experiments carried out using different techniques: adsorption, electrokinetic, co-precipitation, conductivity and FTIR, all confirmed strong interaction of dextrin with heazlewoodite and weak interaction with chalcocite. The interaction with Ni\(_3\)S\(_2\) is pH dependent with maximum around pH 11.7 which coincides with the i.e.p. of Ni(OH)\(_2\). Figure 5.49 shows the postulated adsorption mechanism.

10. While the presence of Ni(OH)\(_2\) on the surface of heazlewoodite was found to be favourable for the adsorption of dextrin, it inhibited the interaction with xanthate in accordance with Barsky's law. The same but reverse argument holds for the case of chalcocite. Since Cu(OH)\(_2\) is probably non-existent on the surface of chalcocite the effect of pH on the adsorption of dextrin onto chalcocite is also not observed.

11. The use of tapioca dextrin in the differential flotation of the Inco matte enhances selectivity when either DPG or potassium amyl xanthate is the collector and, high grade copper concentrates can be produced under the following conditions:

6.0 CONCLUSIONS
Copper concentrate grades of around 73.0% Cu with as low as 4.0% Ni content is achieved by using 175 g/t amyl xanthate and 400 g/t tapioca dextrin or 200 g/t DPG and 350 g/t tapioca dextrin in a single-stage cleaning flotation, with dextrin added only to the cleaning process.

Selective depression of heazlewoodite by dextrin is effective around pH 11.7, where nickel hydroxide forms on the surface and actively interacts with the dextrin. The adsorption of DPG and amyl xanthate onto chalcocite are also found to be strong around this pH.

Although amyl xanthate used without proper modifiers is not selective, its adsorption onto heazlewoodite is strongly inhibited by dextrin which thus drastically improves the selectivity of the chalcocite-heazlewoodite separation.

Adsorption of dextrin onto galena, from previous work (Qi Liu, 1988) and heazlewoodite in this work, indicates high adsorption densities in the pH range that coincides with the i.e.p.'s of the metal hydroxides of these minerals and involves a strong chemical interaction. In the case of copper sulphides, Cu₂S in this work, and CuFeS₂ (Qi Liu, 1988), only weak interactions with dextrin was found and the lack of pH-dependence. This is a pointer to the fact that the pH_{iep}'s of the metal hydroxides could be used as a yardstick to select the pH range of the most selective flotation of copper sulphides from galena and heazlewoodite.

6.0 CONCLUSIONS
Chapter 7

SUGGESTIONS FOR FUTURE WORK

1. Surface Phenomena Studies

It has been established in this work that the magnitude of the adsorption density of dextrin on a mineral surface depends on the ease of formation of some sort of hydroxylated surface product. It has also been determined that the adsorption of organic molecules from solution onto solid surfaces is controlled entirely by the acid-base interactions between solute and inorganic surface (Fowkes, 1981). In order to obtain information about the nature of the reactive surface and to explain the differences in adsorption of dextrin onto sulphide surfaces, tests may be conducted based on the hard and soft acids and bases (HSAB) principle (Pearson, 1963), and utilizing the Drago correlation (Drago and Wayland, 1965):

\[ \Delta H_{\text{int}} = C_A C_B + E_A E_B \]

where \( C_A \) and \( C_B \) are the susceptibility of the acid and base, respectively, to form a covalent bond; \( E_A \) and \( E_B \) are the susceptibility of the acid and base to undergo electrostatic interaction. A method has to be devised to determine the \( E_B \) and \( C_B \) values of dextrin, which is regarded as the base in this system. It was shown by Basilio (1989), that Pearson's HSAB principle could be successfully used in explaining the selective interaction of organic reagents with sulphide minerals in flotation processes.
2. **The Role of SO\(_2\) in the Separation of Sulphides - The Brunswick Experience**

The Brunswick No. 12 concentrator has changed over from the use of starch to dextrin in the differential flotation of Cu-Pb bulk concentrate (Shanon et al., 1992). In this operation, the pulp is conditioned with WC9524 dextrin at pH \(-9.6\), followed by the addition of SO\(_2\) and flotation of copper sulphides at pH 4.2 from the depressed galena. In accordance with Liu Qi's results and the results presented in this work, the adsorption of dextrin onto galena and heazlewoodite is irreversible once it is adsorbed under the alkaline environment. Since SO\(_2\) does not really depress galena (Misra et al., 1985), the separation at Brunswick is either due to the depression caused by the adsorbed dextrin onto galena (and SO\(_2\) is not needed) or is depressed by some sort of interaction between PbS-dextrin and SO\(_2\). Further clarification of this separation practice is therefore needed.

3. **Batch Flotation with Amyl Xanthate and Other Long Carbon-Chain Thio Collectors**

As a continuation of the flotation work in section 4.3.9, further experiments involving the differential flotation of copper sulphide minerals from galena, nickel sulphides and sphalerite, using tapioca dextrin as depressant, and long chain collectors like amyl xanthate, iso propyl xanthate, and a combination of xanthate and dithiophosphate, should be carried out. These tests can be performed effectively by using an experimental design, e.g., fractional two level factorial designs. Some of the advantages associated with such test procedures are:

- a minimum number of tests are performed to gain the information desired.
- the true value of the response is estimated with maximum accuracy.
- the cost of the experimental runs is minimized.

Two major responses to be considered are the grade and recovery of the cleaner concentrate. In the optimization of the process, the following factors are to be studied: concentration of tapioca dextrin, collector and lime, frothers, percent solids, conditioning time and possibly, feed size distribution.

7.0 SUGGESTIONS FOR FUTURE WORK
4. Testing of Guar Gums

A look at gums, which have so far received little attention, indicates that many of them are water-soluble, have a high proportion of hydroxyl groups and are highly branched with more structural flexibility. A typical example is guar gum (galactomannan), which has the two neighbouring OH groups in a cis-configuration, as opposed to starch or dextrin which have a trans-configuration. From the steric arrangements, it is expected that galactomannan will serve as a more effective depressant, especially at low dosages, since the cis-hydroxyl groups can easily form complexes with metallic adsorption centers. It is proposed that flotation tests be conducted with guar gums and other galactomannans with similar characteristics to investigate their effectiveness as an organic depressant.
REFERENCES


8.0 REFERENCES
189


8.0 REFERENCES


8.0 REFERENCES


8.0 REFERENCES
8.0 REFERENCES


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Klassen, V.I., 1963, Coal Flotation, Gosgortiekhizdat, Moscow.


References:


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8.0 REFERENCES


8.0 REFERENCES


Appendix 1. Calibration Curve for Tapioca Dextrin 12
Appendix 2. Calibration Curve for Amyl Xanthate

Wavelength, $\lambda = 301$ nm
Molar Absorptivity, $\varepsilon = 1.82 \times 10^4$ l.mol$^{-1}$.cm$^{-1}$

$10^{-2}$ M NaCl
Appendix 3. Calibration Curve for DPG
APPENDIX 4 - Basic Program for Computation of Surface Area Using the Quantasorb

10 REM THIS PROGRAM IS WRITTEN IN BASIC
20 "************************************************************************************************************" 
30 "**THIS IS A QUANTASORB PROGRAM FOR COMPUTING THE**" 
40 "** SPECIFIC SURFACE AREA OF POWDERS FOR A MULTI **" 
50 "** POINT AND SINGLE POINT B.E.T. DETERMINATION **" 
60 PRINT "************************************************************************************************************" 
70 PRINT : PRINT " ******** WRITTEN BY GEORGE A NYAMEKYE********" 
80 REM ADSORBATE IS NITROGEN AND CARRIER IS HELIUM 
90 REM ADSORBATE FLOW - Fad (ml/min) 
100 REM CARRIER FLOW - Fc (ml/min) 
110 REM TOTAL PRESSURE - Pt; SATURATED VAPOUR PRESSURE - Po; M.W.OF ADSORBATE-Ma 
120 REM CALIBRATION VOLUME - Vc; AMBIENT TEMPERATURE AND PRESSURE - T, Pa 
130 DATA 760, 763, 780, 294, 28.01 
140 READ PA, PT, PO, T, MA 
150 PRINT : PRINT : INPUT "ENTER NO. OF POINTS DETERMINED:"; N 
160 PRINT : PRINT 
170 IF N = 1 GOTO 880 
180 DIM(A(11,N) 
190 FOR I = 1 TO N 
200 PRINT I 
210 INPUT "ENTER ADSORBATE FLOW : "; A(1,I) 
220 IF I = N GOTO 240 
230 NEXT I 
240 PRINT : PRINT 
250 FOR I = 1 TO N 
260 PRINT I 
270 INPUT "ENTER CARRIER FLOW : "; A(2,I) 
280 IF I = N GOTO 300 
290 NEXT I 
300 PRINT : PRINT 
310 FOR J = 1 TO N 
320 A(3,J) = A(1,J) * PT/(A(1,J) + A(2,J)) 
330 A(4,J) = A(3,J)/PO
340 \( A(5,J) = 1/(A(4,J)) \)
350 \( A(6,J) = A(5,J) - 1 \)
360 NEXT J
370 FOR I = 1 TO N
380 PRINT I
390 INPUT "ENTER SIGNAL AREA :"; A(7,I)
400 IF I = N GOTO 420
410 NEXT I
420 PRINT : PRINT
430 FOR I = 1 TO N
440 PRINT I
450 INPUT "ENTER CALIBRATION AREA :"; A(8,I)
460 IF I = N GOTO 480
470 NEXT I
480 PRINT : PRINT
490 INPUT "ENTER CALIBRATION VOLUME :"; VC
500 \( XC = (PA \times MA \times VC)/62350! \times T \)
510 PRINT : PRINT
520 FOR J = 1 TO N
530 \( A(9,J) = (XC \times A(7,J))/A(8,J) \)
540 \( A(10,J) = A(9,J) \times A(6,J) \)
550 \( A(11,J) = 1/A(10,J) \)
560 NEXT J
570 REM SLOPE AND INTERCEPT OF 1/X[(POR)-1] VS P/PO
580 REM USING THE LEAST SQUARE FIT PROCEDURE
590 PRINT : PRINT
600 INPUT "ENTER WEIGHT OF POWDER SAMPLE :"; W
610 \( X1 = 0! \)
620 \( X2 = 0! \)
630 \( XY = 0! \)
640 \( X2 = 0! \)
650 FOR J = 1 TO N
660 \( X1 = X1 + A(4,J) \)
670 \( Y1 = Y1 + A(11,J) \)
680 \( XY = XY + A(4,J) \times A(11,J) \)
690 \( X2 = X2 + A(4,J) \times A(4,J) \)
700 NEXT J
710 I = N * X2 - X1*X1
720 SL = (N*XY - X1*Y1)/I
730 C = (Y1*X2 - X1*XY)/I
740 XM = 1/(SL + C)
750 ST = XM * 3483!
760 S = ST/W
770 PRINT :PRINT
780 PRINT "AF ","CF ","P/Po","1/X[(Po/P)-1]"
790 FOR I = 1 TO N
800 PRINT USING "##.##  ##.##  ###.##  ###.## ";A(1,I),A(2,I),A(7,I),A(8,I)
810 NEXT I
820 PRINT : PRINT
830 PRINT "THE SPECIFIC SURFACE AREA OF POWDER SAMPLE"
840 S = INT (1000! * S + .5)/1000!
850 PRINT "AS DETERMINED BY QUANTASORB = ", S
860 STOP
870 REM SINGLE POINT DETERMINATION
880 INPUT "ENTER ADSORBATE FLOWRATE (ml/min):"; FAD
890 INPUT "ENTER CARRIER FLOWRATE (ml/min):"; FCA
900 INPUT "ENTER SIGNAL AREA:"; ASIG
910 INPUT "ENTER CALIBRATION AREA:"; ACAL
920 INPUT "ENTER CALIBRATION VOLUME:"; VC
930 INPUT "ENTER WEIGHT OF POWDER SAMPLE:"; WS
940 P = FAD/(FAD + FCA) * PT
950 RPA = P/PO
960 TSA = (1 - RPA) * (ASIG/ACAL) * VC * 3.98
970 S = TSA/WS
980 GOTO 820
990 END
Appendix 5 - Reproducibility of Adsorption Tests

The level of reproducibility of the adsorption tests depended on whether heazlewoodite or chalcocite was being used. In general, it was observed that results were very reproducible for all heazlewoodite systems, which again reflects on the stability of its surface products in aqueous solutions. Data for repeated tests on the adsorption of dextrin onto chalcocite were, however, not easy to reproduce under the same experimental conditions. The level of error for the chalcocite adsorption system was even higher when tests were not performed immediately after grinding the sample. It can be seen from the data below that the adsorption densities at comparable pH values for the heazlewoodite mineral do not vary by more than 0.05 mg/m$^2$ while for chalcocite the adsorption density differ by as much as 0.2 mg/m$^2$. The set of data given below where obtained from tests performed under the same conditions.

a. Adsorption of tapioca dextrin onto heazlewoodite vs. pH, initial dextrin concentration was 50 mg/l.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Final pH</td>
<td>$\Gamma$, mg/m$^2$</td>
<td>Final pH</td>
</tr>
<tr>
<td>7.3</td>
<td>0.33</td>
<td>7.1</td>
</tr>
<tr>
<td>7.9</td>
<td>0.58</td>
<td>7.8</td>
</tr>
<tr>
<td>8.9</td>
<td>0.93</td>
<td>8.9</td>
</tr>
<tr>
<td>9.7</td>
<td>1.65</td>
<td>9.8</td>
</tr>
<tr>
<td>10.4</td>
<td>1.93</td>
<td>10.2</td>
</tr>
<tr>
<td>10.8</td>
<td>2.41</td>
<td>10.8</td>
</tr>
<tr>
<td>11.3</td>
<td>2.55</td>
<td>11.3</td>
</tr>
<tr>
<td>11.9</td>
<td>2.55</td>
<td>11.9</td>
</tr>
<tr>
<td>12.2</td>
<td>2.41</td>
<td>12.1</td>
</tr>
<tr>
<td>12.5</td>
<td>2.21</td>
<td>12.5</td>
</tr>
<tr>
<td>12.8</td>
<td>1.85</td>
<td>12.9</td>
</tr>
</tbody>
</table>

b. Adsorption of tapioca dextrin onto chalcocite versus pH, initial dextrin concentration was 50 mg/l.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Final pH</td>
<td>$\Gamma$, mg/m$^2$</td>
<td>Final pH</td>
</tr>
<tr>
<td>7.1</td>
<td>1.08</td>
<td>7.1</td>
</tr>
<tr>
<td>7.8</td>
<td>1.25</td>
<td>7.6</td>
</tr>
<tr>
<td>8.3</td>
<td>1.27</td>
<td>8.5</td>
</tr>
<tr>
<td>9.2</td>
<td>1.31</td>
<td>9.4</td>
</tr>
<tr>
<td>10.1</td>
<td>1.35</td>
<td>10.2</td>
</tr>
<tr>
<td>11.1</td>
<td>1.32</td>
<td>10.9</td>
</tr>
<tr>
<td>11.8</td>
<td>1.38</td>
<td>11.7</td>
</tr>
<tr>
<td>12.7</td>
<td>1.25</td>
<td>12.6</td>
</tr>
</tbody>
</table>
Appendix 6 - Reproducibility of Electrokinetic Measurements

Data for repeated electrokinetic tests followed the same trends as the adsorption measurements. Tracking of colloidal particles of heazlewoodite or nickel hydroxide was very easy and data for a given set of conditions could easily be reproduced. The zeta potential values under comparable pH conditions for this system did not differ by more than 1 mV. Error in measuring the zeta potential of chalcocite or colloidal copper hydroxide particles was comparatively higher and varied by as much as 2 - 3 mV under comparable pH values.

a. Zeta potential - pH data for heazlewoodite equilibrated for 1 hour at pH 3.0 in $10^{-2}$ M KNO$_3$ solution.

<table>
<thead>
<tr>
<th>April 1, 1991</th>
<th>April 12, 1991</th>
<th>April 17, 1991</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>$\zeta$, mV</td>
<td>pH</td>
</tr>
<tr>
<td>2.3</td>
<td>-8.5</td>
<td>2.3</td>
</tr>
<tr>
<td>3.6</td>
<td>-15.2</td>
<td>3.6</td>
</tr>
<tr>
<td>5.0</td>
<td>15.3</td>
<td>5.1</td>
</tr>
<tr>
<td>7.0</td>
<td>23.5</td>
<td>7.3</td>
</tr>
<tr>
<td>9.7</td>
<td>28.1</td>
<td>9.9</td>
</tr>
<tr>
<td>11.0</td>
<td>22.0</td>
<td>10.9</td>
</tr>
<tr>
<td>11.5</td>
<td>12.8</td>
<td>11.7</td>
</tr>
<tr>
<td>12.1</td>
<td>11.5</td>
<td>12.6</td>
</tr>
</tbody>
</table>

b. Zeta potential - pH data for chalcocite equilibrated for 1 hour at pH 10.8 in $10^{-2}$ M KNO$_3$ solution.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>$\zeta$, mV</td>
<td>pH</td>
</tr>
<tr>
<td>4.0</td>
<td>-9.0</td>
<td>4.1</td>
</tr>
<tr>
<td>5.0</td>
<td>10.1</td>
<td>5.2</td>
</tr>
<tr>
<td>6.7</td>
<td>15.2</td>
<td>6.5</td>
</tr>
<tr>
<td>7.0</td>
<td>14.7</td>
<td>7.2</td>
</tr>
<tr>
<td>7.4</td>
<td>8.1</td>
<td>7.6</td>
</tr>
<tr>
<td>8.4</td>
<td>-8.2</td>
<td>8.2</td>
</tr>
<tr>
<td>9.3</td>
<td>-17.5</td>
<td>9.5</td>
</tr>
<tr>
<td>10.7</td>
<td>-28.0</td>
<td>10.7</td>
</tr>
</tbody>
</table>
Appendix 7 - Reproducibility of Batch Flotation Tests

The reproducibility of the batch flotation experiments were checked by repeating some of the tests involving the cleaning of the rougher chalcocite concentrate in the presence of DPG and dextrin. Under similar conditions, data on the recovery of copper did not vary by more than 7% and the copper grade differed by a maximum of only 2%.

a. Flotation of rougher chalcocite concentrate with 350 g/t dextrin and 200 g/t DPG at pH 11.7.

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Rec.</td>
<td>% Grade</td>
<td>% Rec.</td>
</tr>
<tr>
<td>Conc 1</td>
<td>30.6</td>
<td>74.0</td>
<td>24.3</td>
</tr>
<tr>
<td>Conc 2</td>
<td>21.9</td>
<td>73.0</td>
<td>25.1</td>
</tr>
<tr>
<td>Conc 3</td>
<td>17.9</td>
<td>72.0</td>
<td>18.1</td>
</tr>
<tr>
<td>Conc 4</td>
<td>7.5</td>
<td>68.0</td>
<td>6.8</td>
</tr>
<tr>
<td>Tailing</td>
<td>21.9</td>
<td>30.0</td>
<td>25.7</td>
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</tbody>
</table>