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THE MECHANISM OF THE DEPRESSANT ACTION OF DEXTRIN ON PYRITE

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April 1995

A Thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfillment of the
requirements of the degree of
Masters of Engineering in Metallurgical Engineering

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ABSTRACT

The separation of minerals by flotation depends on the effectiveness of the reagents used. The performance of depressants is paramount in rejecting the undesirable minerals while maintaining acceptable recoveries of the desired mineral. Iron-bearing minerals are the main contaminants in many ores: their removal is critical. Several different types of depressants have been used for this purpose, many of which are toxic. A shift has been made towards more environmentally friendly reagents including starch and dextrin.

The purpose of this thesis was to determine the depression mechanism of dextrin on pyrite. A number of techniques were applied to give insight into the mechanism, including adsorption studies, microflotation tests, and solution and surface analyses. It was revealed that dextrin only adsorbed on mineral surfaces that contained some metal ionic sites. The degree of adsorption depended on the nature of the metal species, with lead being more reactive than iron. Dextrin was able to depress pyrite, regardless of whether dextrin adsorbed or not; however, adsorbed dextrin was more effective. It appeared as if dextrin inhibited the formation of dixanthogen on the surface, which could lead to reduced floatability of pyrite. Finally, it was observed that over time, adsorbed dextrin underwent a conformational change on the surface of the mineral. This change permitted a greater amount of xanthate to adsorb on the mineral.

RESUME

La séparation des minéraux par flotation dépend sur l'efficacité des réactifs utilisés. La performance des dépresseurs est d'une suprême importance pour rejeter les minéraux indésirables et pour maintenir des récupérations acceptables de minéraux désirables. Les minéraux ferrique sont les contaminants principaux dans la plupart des minerais: leur enlèvement est critique. Plusieurs sortes de dépresseurs sont utilisé pour ce but, et un grand nombre de ces dépresseurs sont toxiques. Un changement a été fait vers des réactifs, comprenant de l'amidon et de la dextrine, qui sont plus bienveillant pour l'environnement.

L'objective de cette thèse était de déterminer le mécanisme dépressif de la dextrine sur le pyrite. Plusieurs techniques sont appliqué pour donner la perspicacité sur le mécanisme, tel que des études d'adsorption, des tests de microflotation, et des analyses de solution et surface. Il a été découvert que la dextrine s'adsorbe seulement sur les surfaces minérals contenant des sites metals ioniques. Le degré d'adsorption dépend sur la nature de l'espèce metallique, avec le plomb étant plus réactif que le fer. La dextrine a été capable de déprimer le pyrite, indépendamment de l'adsorption de la dextrine; cependant la dextrine adsorbé a été plus efficace. Il apparait que la dextrine a empêché la formation de dixanthogen sur la surface, ce qui peut mener à reduire la flottabilité du pyrite. Enfin, il était observer que au cours de temps, la dextrine adsorbé a subi un changement de conformation sur la surface du minéral. Ce changement a permis l'adsorption d'un plus grand montant de xanthate sur le minéral.

ACKNOWLEDGEMENTS

I would like to thank the Natural Science and Engineering Research Council of Canada (NSERC) for their financial support throughout the project. Thanks also goes to Hart Chemical Limited for their interest in the project and both their financial support and supply of dextrin samples.

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CHAPTER 1

INTRODUCTION

One of the difficulties in concentrating valuable minerals from complex ores is the presence of iron sulphides: pyrite, marcasite and pyrrhotite. Their depression is often critical to the selective flotation of the desired minerals. The development of environmentally acceptable methods for the rejection of iron sulphides are continually being sought. These methods aim at replacing the use of, among other toxic reagents, sulphur dioxide and cyanide while maintaining or improving the selective flotation of the desired minerals.

More recently, there has been an interest in replacing toxic pyrite depressants with dextrins. These organic reagents offer the benefit of being less hazardous to the environment [1]. The major technical advantage organic depressants offer over inorganic ones is their greater flexibility to prepare a tailor made reagent for a specific application [1].

Dextrin depressants have been tested for a number of years. However, the mechanism of its action is not understood. With a better understanding of the mechanism, predictions concerning possible effects could be made and the optimum conditions selected.

The purpose of this testwork was to detemine the mechanism of the depressant action of dextrin on pyrite. This was achieved by studying the dextrin-xanthate-pyrite system, using a number of physico-chemical techniques. The techniques included adsorption studies, microflotation tests, and pulp potential measurements. Solution chemistry analysis was done using ultraviolet spectrophotometry and atomic absorption spectroscopy. Surface analysis was carried out by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The results of these tests gave insight into the interactions between dextrin and pyrite and the effect of dextrin on xanthate adsorption on pyrite.

The thesis is organized into chapters. In Chapter 2, a theoretical background into the chemistry of starches and dextrins is given along with some examples of uses for these reagents in the mineral processing industry. The adsorption of polymers is also discussed to provide a general understanding of the behaviour of macromolecules and their interactions. Finally, previous studies on the adsorption mechanism of starches and dextrins on various minerals is reviewed.

In Chapter 3, a brief description of the testwork is given in addition to the analytical equipment used.

In Chapter 4, the results are presented in the following order: adsorption studies, microflotation, solution tests, and surface analysis. These results are discussed in Chapter 5. Finally, in Chapter 6, conclusions are drawn. The list of references is at the end of the thesis.

CHAPTER 2

THEORY

2.1. Starches and Their Derivatives

2.1.1. Starch

Starch is one of the most widely distributed natural polymers. It is comprised of D-glucose units (or dextrose) with the chemical formula $C_6H_{12}O_6$. Each D-glucose unit is made up of a six member ring with 5 carbons and one oxygen [2]. Attached to the ring are five hydroxyl groups (Figure 2.1). Through α-glucosidic linkages between C-1 and C-4, dextrose units are formed into straight chain, water insoluble structures called amylose. Branching of the structure occurs when C-1 and C-6 form links [3]. The branched component of starch which is water soluble is called amylopectin. Starch is comprised of both amylose and amylopectin. The branches are themselves chains of amylose. A characteristic feature of starches is their very long straight chain structure with many long branches and extremely large molecular weights (in the millions of grams per mole) [4].

2.1.2. Dextrin

Dextrins are produced from starches by thermal degradation in acidic environment [5]. The procedure breaks up the many branches of the starch structure, producing a dextrin molecule with a highly branched yet smaller molecular weight. Depending on the source of the starch, the size of the polysaccharide will vary along with the degree of branching.

There are numerous ways to convert starches into dextrins [2]. The following is a list of possible methods: (1) acid hydrolysis in aqueous solutions, (2) degradation by the action of enzymes called amylases (α and ß), (3) specific action of *Bacillus macerans* enzymes producing cyclic Schardinger dextrins, and (4) breakdown by the action of heat and acid (pyrodextrination). The last method not only breaks down the starch molecules into smaller units but also is effective in forming carbon 1-6 linkages, producing a highly branched structure. The dextrins produced have various characteristics, depending on the time, temperature, and acidity of the starch treatment. Solubility of dextrins increases after heat treatment has been performed for approximately 2 hours. Meanwhile, the viscosity is reduced under the same conditions. Pyrodextrination produces many types of dextrins as shown in Table 2.1.

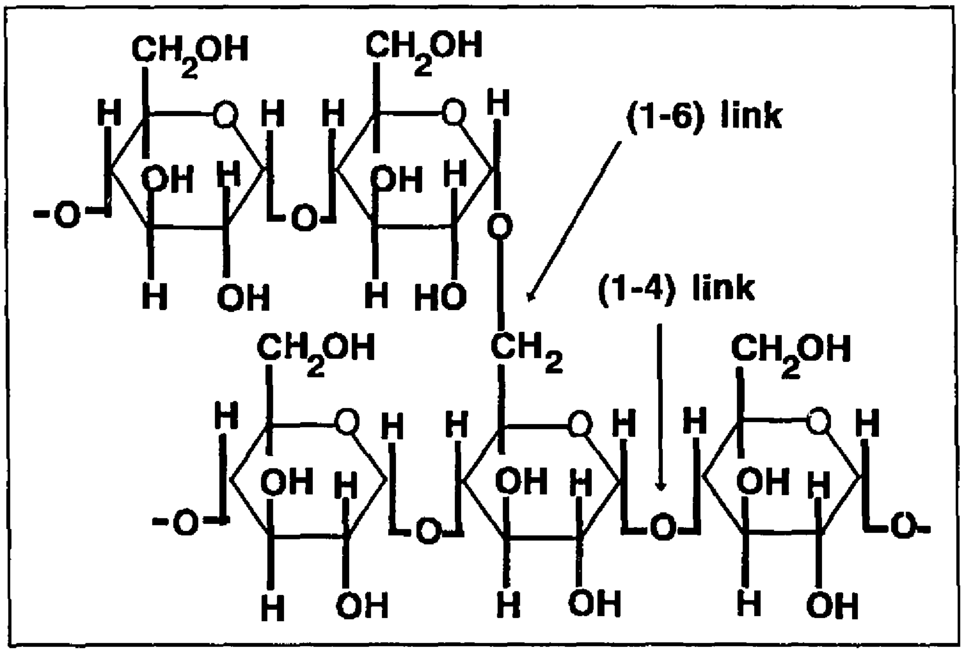


Figure 2.1: Structure of starch and dextrin

Table 2.1: Starch degradation products [2]

Starch	Temperature	Acidity	Viscosity	Branching
Thin Boiling Starches	Low	Low	High	Low
White Dextrins	Low	High	Low	Low
British Gums	High	Low	High	High
Yellow Dextrins	High	Medium	Low	High

2.1.3. Properties of starch and dextrin

A feature of polymers in solution is their high degree of conformational freedom. Rotations can occur about each bond in the main chain of the polymer, even if those rotations are coupled and hindered [6].

It has been reported that organic depressants including starches and dextrins do not ionize in aqueous solutions, but instead form colloids [7]. Even apparently clear solutions of starches and dextrins may contain colloidal aggregates or coiled molecules, detected by light scattering [2]. These colloidal particles will then reduce the flotation of minerals by depositing on the surface, similar to a slime coating. When excessive amounts of starch and dextrin are added, all minerals will be depressed. In this way, they are less selective than depressants which interact electrostatically or electrochemically.

Another report, however, states that polymeric reagents can be weakly anionic [1]. In solution, the numerous hydroxyl groups thoughout the structure take part in extensive hydrogen bonding within their own molecule and with water. This produces many possible structural conformations. Amylose forms a random coil or helix in aqueous solutions. The helix consists of 6 glucose units per turn, with the interior being hydrophobic and the exterior, hydrophilic [8].

The numerous hydroxyl groups distributed throughout the dextrin molecule can also undergo chemical reactions similar to alcohols, such as chemical complex formation with the hydroxyl groups [4].

Many organic macromolecules have been studied as possible depressants in mineral flotation. Regardless of their differences in structure and functional groups, all appear to exhibit some depressant action for certain minerals. In general, all these macromolecular depressants possess similar features [1]:

(1) A hydrocarbon component which is available to interact with the surface through hydrophobic interaction. Also, these hydrocarbon segments will be able to interact with each other within the adsorbed layer. This may cause enhanced adsorption on the mineral surface, although this effect is unselective with regard to the underlying substrate.

(2) The presence of many hydroxy groups throughout the polymeric depressant which enhance ionization and hydrogen bonding to the mineral surface.

(3) Other strongly hydrated groups may occur within the molecule, which can contribute to the specific interactions between the polymer and the mineral surface. Carboxyl, hydroxy, and phosphoryl groups are found to be actively involved in adsorption. These groups play a role in determining the specificity of the interaction between polymer and mineral.

2.1.4. Depressant action of starch and dextrin

The role of the depressant is to selectively inhibit the flotation of a particular mineral. This can be achieved either by hindering collector adsorption or by making the mineral surface hydrophilic. This can be accomplished by the depressant through at least the following means:

(1) removal of activating species such as metal ions;
(2) adsorption on sites otherwise occupied by collector;
(3) adsorption on sites making them hydrophilic; and
(4) adsorption which overwhelms any collector already adsorbed.

In flocculation studies, macromolecules were found to have outstanding adsorptive characteristics [9]. Because of this, it is expected that starch and dextrin would be effective depressants. Three possible mechanisms listed above require that the depressant adsorb for depression to occur. However, adsorption of the depressant is not always necessary to hinder the adsorption of collector. By removing the activating species from the mineral surface, the collector would be unable to adsorb, thereby reducing floatability.

2.2. Industrial Flotation Applications of Starch and Dextrin

Starches have been used extensively in iron ore flotation for many years, both as depressants and flocculants. Their use as depressants is reviewed in this section.

The importance of starches and their derivatives in iron ore flotation is evident from the amount of literature on the subject [10-20]. Many chemically substituted starches, both anionic and cationic, have been tested for their depressing efficiency. In anionic silica flotation, iron oxides are depressed using starches, in particular, anionically modified starches [10]. For oxidized iron ores, the most efficient depressants found were British gums and dextrins. None of the starches or derivatives were effective on magnetite-taconite concentrates [10].

The Sept-Iles plant used a wheat dextrine to depress the earthy hematite minerals [12]. The plant was operated at pH 10 to 10.5 using a diamine collector. At that pH, both hematite and quartz are negatively charged and a cationic collector, such as an amine, can adsorb on both minerals. Amines, in particular, are not selective for silica flotation from iron oxides at pH 10.

At the Tilden concentrator, the operating pH range is between 10 and 11 for cationic silica flotation. The high pH is a result of a carry over of caustic soda from the selective desliming step. Instead of controlling the pulp pH between the points of zero charge (PZC) of hematite and quartz, it is favourable to use a starch depressant at a moderately alkaline pH. This also avoids the problem of heterocoagulation [12].

Starches, along with other polymers, have been used as depressants in semisoluble salt flotation [3]. It has been reported in some systems that coadsorption of the collector with the starch or starch derivative occurs. For example, the calcite-oleate-starch system shows increased oleate adsorption in the presence of starch. However, the calcite surface becomes hydrophilic. It appears as if the organic macromolecule can blind the hydrocarbon chain of the collector and extend its polar hydroxyl groups into solution [3].

At Mount Isa Mines, in Australia, a carbon depressant was sought to improve selectivity in the chalcopyrite circuit [21]. The objective was to achieve a 25% copper concentrate grade without reducing copper recovery. Carbonaceaus pyrite and silica present in the ore were inherently floatable, which resulted in a lowering of the final copper concentrate grade. A mixture of 60:40 nigrosine and dextrin was used to control the flotation rates of the carbonaceous material in the copper circuit.

Flotation tests were performed to determine if the addition of a prefloat stage, prior to the rougher stage, would reduce the amount of carbonaceous material in the circuit. The tests revealed that the prefloat stage was highly selective towards chalcopyrite, indicating that the depressant action of the nigrosine-dextrin mixture was specific to the carbonaceous pyrite and silica. However, further flotation tests revealed that when tested separately, nigrosine was the more effective depressant and that perhaps dextrin was unnecessary for Mount Isa's current plant operation [21].

Since that time, the plant has operated using a 60/40 mixture of dextrin/naphthol sulphonated reagent to depress the naturally hydrophobic iron sulphides [22]. The depressant mixture was added to the copper cleaner feed.

The addition of the depressant mixture resulted in selectivity of chalcopyrite against pyrite for additions up to 100 g/t. Above that addition, chalcopyrite was severely depressed. Up to 100 g/t depressant, the inherently floatable iron sulphides were depressed. The size by size analysis revealed that the -10 micron fraction was depressed significantly during the initial stages of flotation. However, the floatability of chalcopyrite was also somewhat hindered under the same conditions. Only limited additions of this depressant could be added to the cleaner feed or copper rougher feed as excessive depressant resulted in large losses of chalcopyrite. Mount Isa decided to focus on a preflotaion stage to remove the iron sulphides because they found that the dextrin depressant mixture had limited potential [22].

Dextrin has also been used to improve pentlandite flotation [23]. It was believed that pentlandite was depressed by the presence of a tenacious slime coating of serpentine minerals, chrysotile and lizardite, due to heterocoagulation. At the pH of interest for flotation (pH 9), unoxidized pentlandite has a strong negative surface charge, while chrysotile exhibits a strong positive charge and lizardite, a weaker positive charge.

Various modifying agents, including dextrin, were used to change the surface charge of the slime minerals from positive to negative. The following was observed:

(1) The surface charge of the serpentine minerals became increasingly negative

with increasing addition of modifying agent, until a plateau was reached.

(2) Pentlandite recovery increased as the surface charge of the serpentine minerals became more and more negative, regardless of the modifying agent used.

For the aforementioned tests, the results were the same, no matter which modifier was used. The only difference was in the amount required to effect a change in surface charge for the serpentine minerals. In this case, dextrin was used as an activator rather than a depressant, by changing the surface charge of the minerals forming the slime coating on the valuable mineral, pentlandite.

Starch is sometimes used as a lead depressant in the separation from complex ores [7]. Common galena depressants include sodium dichromate, sulphur dioxide, and starch, or some combination of these. Dichromate can cause environmental problems, even with only small additions. Sulphite adsorption is the most widely used method of depressing galena, either by adding sulphur dioxide (liquid or gas) or less frequently, sodium sulphite or metabisulphite. Causticised starch is often added in lesser amounts as a supplementary depressant. Table 2.2 lists different concentrators that use (or have used) starch in separating copper-lead ores [7]. In all cases, galena is depressed while chalcopyrite is floated.

Table 2.2: Starch used in copper-lead separations [7]

Mine	Approx Ratio Pb/Cu	Method
St. Joe Minerals Corp. Missouri, U.S.A.	45:1	SO_2-Starch-Dichromate
Brunswick Mining, Canada	20:1	SO_2-Starch-Heat
Mattabi Mines, Canada*	1:1	SO_2-Starch-Heat

*closed 1991.

At Brunswick Mining, galena is depressed by conditioning the bulk copper-lead concentrate for 20 minutes with 0.03 kg/t of a wheat dextrine-tannin extract mixture [7]. Activated carbon is added to eliminate excess reagents and contaminants. The pH is lowered to pH 4.8 by adding liquid SO_2. After further conditioning for 20 minutes, 0.005 kg/t of thionocarbamate is added and chalcopyrite is recovered.

At Woodlawn in Australia, the feed (1.3% Cu, 5.5% Pb, and 13% Zn) is conditioned with SO_2, starch, sodium metabisulphite, and a dithiophosphate collector. A copper concentrate is collected and cleaned twice. The copper tailings are conditioned with lime, NaCN, starch, and sodium secondary butyl xanthate. A lead concentrate is produced, containing the less floatable copper minerals [7].

2.3. Adsorption of Polymers: General

Polymer adsorption is unlike adsorption of small molecules or ions. The unique feature of polymer adsorption is the presence of chains. Particular problems associated with polymers at interfaces include [6]:

(1) "(ir)reversibility" -- a problem that arises from the time-dependent phenomenon of a multipoint attachment to the surface which calls into question the validity of applying equilibrium thermodynamics to derive adsorption isotherms.

(2) problem of adsorption-desorption kinetics -- steady state levels of adsorption may take some time to be reached because of two features: (i) low diffusion coefficients of polymer molecules in solution, and (ii) the rearrangement time (i.e., the time necessary for the polymer to adopt its steady state adsorbed conformation, especially when there is high coverage.) The second problem is especially a concern for polydisperse polymers whereby the small rapidly diffusing molecules become replaced by the larger preferentially adsorbed molecules. Unless all the polymer molecules are the same size, there will be competitive adsorption. Also special is the case of copolymers where different elements of the chain may be preferentially adsorbed.

(3) problem of assigning a value to the specific surface area in the case of a nonplanar (e.g., porous) solid surface. This difficulty is amplified in the case of polydisperse polymers where smaller molecules may be able to penetrate pore openings whereas larger molecules may not.

Some detailed studies on the kinetics of polymer adsorption have been carried out, especially as it relates to flocculation. The results of these investigations follow.

2.3.1. Kinetics of polymer adsorption

Studies of the kinetics of polymer adsorption are usually related to flocculation [24]. In this case, the particles involved are quite fine (in the order of 1 micron in diameter), much smaller than would normally be considered for flotation. An attempt will be made to extend the results to include flotation.

In a system of dispersed particles at relatively low dextrin concentration, it seems reasonable to assume that polymer adsorption is transport-limited (i.e, the rate depends on the arrival of the polymer to the surface) [24]. For optimum flocculation, less than complete coverage is necessary, so this assumption of transport-limited kinetics remains valid.

Adsorption time is inversely proportional to the particle number concentration [24]. Therefore, for solutions with low percent solids, adsorption will be quite slow. The rate of adsorption increases for higher concentrations of particles and lower molecular weight polymers, indicating diffusion control.

In modelling polymer adsorption, two processes for having polymers and particles meet have to be considered: diffusion and fluid motion (i.e., the equivalent of perikinetic and orthokinetic). It is assumed that the polymer molecules are smaller than the particles in the derivation of the model. In the perikinetic (diffusion only) case, the adsorption rate would be faster with lower molecular weight polymers. In the orthokinetic (with added shear) case, the opposite would be true: with larger polymers, the adsorption rate would increase. This implies that there is a limit for the molecular weight of the polymer (for a given particle size) in which diffusion gives the highest adsorption rate and over that limit, adding some fluid motion will improve the kinetics of adsorption. In terms of particle sizes considered during flotation, the limiting size of polymer for perikinetic control versus orthokinetic control will decrease as the particle size increases (or as shear is increased). It should be noted that this argument is quite qualitative and does not take into consideration all the factors affecting polymer adsorption. In fact, with increasing shear, a decrease in polymer adsorption has been observed, especially for high molecular weight polymers [24].

Little information on the rate of reconformation of the polymer on the surface exists. The point to consider is whether the polymer will attain equilibrium conformation quickly or slowly relative to the rate in which particles collide (for flocculation). If reconformation is slower than the particle collision rate, then the polymers adsorbed onto the surface will be extended out into solution. This, in theory, will improve the flocculation rate by enhancing the bridging effect of the polymers. In practice, flocculants are unlikely to achieve equilibrium configuration [24].

Applying the same principles to flotation, if polymer reconformation takes long to occur, then the polymer will also be extended out into solution. The hydrophilic chains and branches of starches and dextrins could expand, thus overwhelming any collectors adsorbed on the mineral surfaces. This would in fact depress the mineral.

2.3.2. Interactions during polymer adsorption

It is believed that starch and its derivatives adsorb through dipole interactions or electrostatic interactions because of their multiple polar groups [2]. Multiple bonding occurs, leaving a highly hydrophilic surface with extended or coiled polymers.

Many adsorption mechanisms for starch have been proposed [25]:

(1) hydrogen bonding (quartz and hematite system),

(2) electrostatic interactions (demonstrated by the increased adsorption of cationic starch on the surface of quartz which is more negative than hematite),

(3) chemical adsorption between lattice ions, in particular, of calcium bearing minerals, and the polar groups of starch,

(4) salt formation established by the bridging effect of metallic cations added to the system (e.g., calcium), and

(5) hydrophobic bonding (e.g., dextrin adsorption on hydrophobic minerals).

The adsorption of polymers is due to either chemical short-range interactions (e.g., covalent bonding, coordination bonding and hydrogen bonding) or physical longer-distance forces (e.g., electrostatic bonding, dipole attraction, London-van der Waals attraction and hydrophobic association) [9]. Usually several types of bonding take place, depending on the chemical nature of the mineral surface, the presence of solutes and the functional groups of the polymer. Hydrogen bonding is significant in the adsorption of nonionic polymers while both hydrogen bonding and electrostatic interactions are important for ionic polymers.

A review of macromolecular organic depressants has been presented where the author listed the possible interactions that may influence the adsorption of a depressant on a mineral surface [1]. They included:

(1) coulombic interaction between ionic groups on the surface and in the depressant,

(2) replacement of water contacts with hydrophobic surface sites by depressant contacts,

(3) hydrogen bonding or other specific interactions between the depressant and the surface (in competition with similar contacts with water),

(4) the possibility to form energetically favourable structures of the adsorbed layer (e.g. hydrophobic interaction between hydrophobic segments of the depressant), and

(5) the solubility of the depressant in the aqueous medium surrounding the particles.

As mentioned previously, macromolecules have excellent adsorptive properties [9]. When considering polymer adsorption, only a few segments of the polymer are attached to the surface, while the remainder extend out toward the continuous phase. The competition for surface sites between solvent molecules and polymer molecules does not involve the entire polymer molecule, but only a few chain segments [9].

Pugh [1] also reported that for the organic depressants studied, performance was strongly dependent on the dosage used. It was shown that when the dosage was changed 50% greater than or less than the optimum, a significant loss in efficiency was experienced.

For starches, in particular, not all give satisfactory depressant action, and selectivity is dependent on many factors including the type of starch used, the extent of branching, mode of preparation, solution pH and electrolytes present [1].

Numerous theories on the particular interactions involved in the adsorption of starches and dextrins on mineral surfaces have been proposed. La Mer and Smellie (1956, as reported in [1]) suggested that the adsorption of potato starch to mineral slimes is by the interaction of the phosphate groups from the starch with polyvalent cations in the pulp. Kitchener (1972, as reported in [1]) believed that hydrophobic bonding could also participate or predominate.

Comparative adsorption tests on coal samples between dextrin (highly branched polymer) and amylose (long chain component of starches) have been performed (Haung et al., 1978, as reported in [1]). At low concentrations, amylose had a higher adsorption density, indicating that the long chain uncoils to cover a larger surface area, while the relatively rigid dextrin structure retains its configuration. These tests suggest that the mechanism of adsorption is physical, possibly associated with hydrophobic bonding.

Further tests confirmed the importance of hydrophobic bonding. While dextrin selectively adsorbed on hydrophobic minerals such as molybdenite, talc, and coal, it had little affinity for hydrophilic minerals such as quartz or pyrite. It was believed that adsorption involved the hydrophobic interaction between the dextrose monomeric units or nonpolar groups of dextrin and the mineral surface.

Studies on kaolinite and silica were conducted to observe the effect of the adsorption of nonionic/anionic surfactant mixtures and nonionic surfactants on mineral dispersion and wettability [26]. These studies did not test starch or dextrin but are mentioned here because the surfactants are similarly characterized with long chains of hydrocarbons which could interfere with the adsorption of other surfactants and hence affect surface properties.

The coadsorption of anionic sodium dodecyl sulphate (SDS) with nonionic octaethylene glycol mono-n-dodecyl ether ($C_{12}EO_8$) revealed that multilayer formation occurred which restored hydrophilicity to the kaolinite surface.

The authors [26] proposed an adsorption mechanism which took into account the synergistic effect of the coadsorption of SDS and $C_{12}EO_8$ (Figure 2.2): (a) At low concentrations, hydrophobic chain-chain interactions between SDS and $C_{12}EO_8$ resulted in increased adsorption; (b) Further adsorption of SDS was reduced because of blocking of positive surface sites on kaolinite by the long ethylene oxide chains of adsorbed $C_{12}EO_8$ (i.e., electrostatic attraction was reduced); (c) Reverse adsorption of $C_{12}EO_8$ occurred in regions where the hydrophobic interactions between the chains of the adsorbed SDS and $C_{12}EO_8$ incorporated the additional hydrocarbon chains of $C_{12}EO_8$, leaving the hydrophilic ethylene oxide chains pointing into solution. The dangling ethylene oxide chains caused steric stabilization of the kaolinite particles. Evidence of reverse adsorption was demonstrated by the fact that as $C_{12}EO_8$ concentration was increased, the floatability and settling rate of kaolinite were reduced [26].

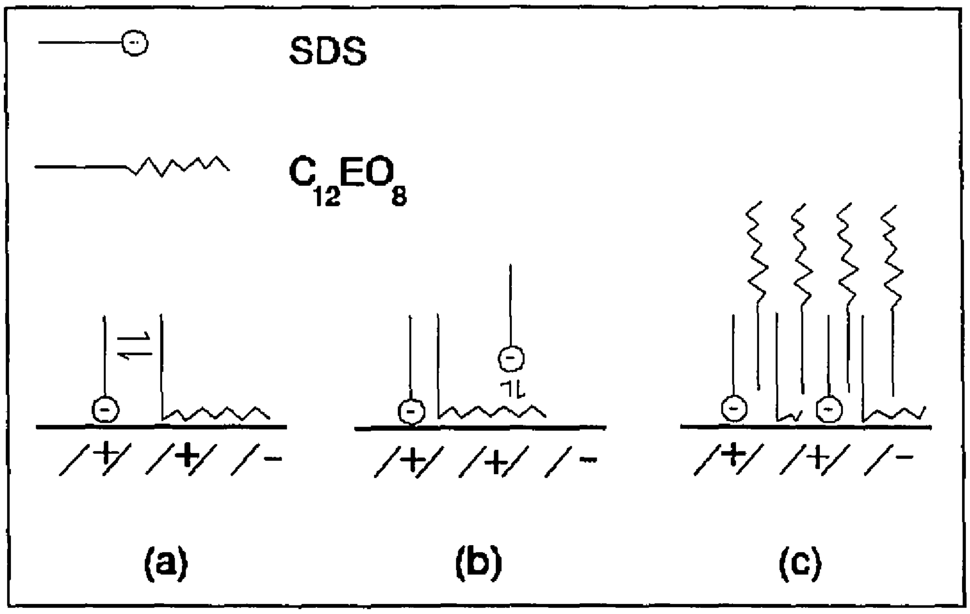


Figure 2.2: Schematic representation of the coadsorption of a mixture of SDS and $C_{12}EO_8$ on kaolinite [26]:
(a) In the low concentration region, chain-chain interactions between SDS and $C_{12}EO_8$;
(b) Masking of positive surface sites by the adsorbed ethylene oxide chains effectively reduces electrostatic attraction for further SDS adsorption;
(c) Reversed $C_{12}EO_8$ adsorption causing steric stabilization and hydrophilicity of kaolinite.

The adsorption of nonionic alkylphenoxy polyethoxyethanols ($C_8\phi EO_{10}$ and $C_8\phi EO_{40}$) on silica showed differences in the floatability depending on the concentration added. Adsorption of nonionic ethoxylated alcohols caused changes in the hydrophobicity of silica particles due possibly to the changes in orientation of the adsorbed surfactant molecules at the interface.

The longer chained $C_8\phi EO_{40}$ adsorbed on silica more than the shorter chained $C_8\phi EO_{10}$ at lower concentrations because of increased hydrogen bonding available from the silica surface. However at higher concentrations of surfactant, $C_8\phi EO_{10}$ adsorbed more than $C_8\phi EO_{40}$ because of the smaller area required on the surface for the ethylene oxide chains [26].

Complete hydrophobicity was achieved and maintained for $C_8\phi EO_{10}$. In contrast, while at low additions of $C_8\phi EO_{40}$, the hydrophobicity of silica was 100%, as the concentration was increased, the hydrophobicity decreased until complete hydrophilicity of silica had been restored. The authors dismissed the possibility of bilayer formation to explain the change in hydrophobicity of silica, unlike in the case of kaolinite. The possibility of bilayer formation would be greater in the case of $C_8\phi EO_{10}$ rather than $C_8\phi EO_{40}$ because the higher degree of aggregation for $C_8\phi EO_{10}$ would form hydrophobic regions increasing the chance of bilayer formation. Steric repulsion caused by the long chains of $C_8\phi EO_{40}$ would prohibit aggregation and eliminate bilayer adsorption. Therefore, if bilayer formation was used to explain the change in silica hydrophobicity, silica would be more hydrophilic after $C_8\phi EO_{10}$ addition, rather than $C_8\phi EO_{40}$ [26].

The authors instead suggested that the effects were due to changes in the conformation of the hydrocarbon chains of the adsorbed surfactant molecules at the silica/liquid interface. At low concentration, the hydrocarbon chains would likely lie flat on the surface. This would give maximum coverage and render the surface hydrophobic. As the concentration increased, the additional adsorbing ethylene oxide chains would push the chains already present into a more vertical orientation, thereby effectively reducing the surface coverage of a single chain. In the case of $C_8\phi EO_{40}$, this would result in a decrease in the hydrophobicity of the silica particles. For the shorter chained $C_8\phi EO_{10}$, the higher adsorption density and the higher degree of aggregation would offset the effect of conformational changes of the hydrocarbon chains, resulting in an increase in surface hydrophobicity until a maximum was reached [26].

2.3.3. Depressant mechanism of macromolecules

It has been reported that the adsorption of certain macromolecules onto naturally hydrophobic minerals causes depression by increasing the stability of the thin (disjoining) film which forms between the bubble and particle in the final stages of the collision process [27].

Bubble attachment is dependent on the stability of the disjoining film. A low energy barrier, and hence an unstable film, is produced when the net disjoining pressure between the particle and bubble is negative. This can result from strong van der Waals attraction, electrostatic attractive forces and hydrophobic interactions [27]. A stable film can be produced by an adsorbed hydrophilic depressant. An effective depressant will prevent the rupture of the film between the air bubble and particle, thus eliminating bubble-particle attachment.

Double layer interactions have been used to explain the depressant effect of macromolecules. When the polymer-coated mineral particle encounters a bubble, their double layers overlap. It has been previously stated that macromolecules are slightly negatively charged. Since the surface of air bubbles has also been found to possess a negative charge, the like charged double layers will be electrostatically repelled from each other.

The surface charge studies were carried out on very small bubbles ($<10\ \mu m$). In flotation, however, bubbles are typically much larger (0.5 - 3 mm) and therefore the surface charge on the bubble may become unevenly distributed as the surface is swept rearwards as the bubble moves through the liquid. This could result in a dipolar surface that would influence the types of interactions occurring between the bubble and the particle.

The adsorption of hydrophilic macromolecules on the surface of a particle can greatly reduce the hydrophobic interactions that help in the process of bubble attachment. In addition, the presence of the polymer on the mineral surface may change the double layer interactions because of the many groups in the polymer molecule capable of dissociating (e.g., hydroxy groups). The macromolecules may also be able to alter the double layer itself by shifting the shear plane further from the surface.

When considering the attachment of a bubble to a particle that is coated with a polymeric reagent, other repulsive forces need to be regarded. The other repulsive forces include:

(1) Steric repulsive forces which result when polymeric chains interpenetrate, and

(2) Structural hydration forces that are caused by the presence of an organized molecular structure near the surface.

Steric interactions are the result of long chain bulky macromolecules adsorbed onto the surface of particles. When polymer-coated particles meet, repulsive forces can occur due to: (1) osmotic effects produced by the high concentration of chains where the double layers overlap, and (2) effects due to volume restriction in the region between particles, reducing the configurations possible for the adsorbed chains [27].

It has been shown that the conformation of the polymer plays an important role in these types of interactions. However, steric interactions are not likely to take part in depression because the air bubbles are not coated with the long macromolecules. Steric interactions are only considered for two approaching particles that are similarly coated. The bubble is more likely to deform - since it is not rigid - when approached by the adsorbed polymer layer on the mineral surface rather than actively repel the particle.

In addition, it has been shown that a fairly thick polymer layer needs to be present for steric interactions to take place. Optimum depression, however, occurs at relatively low concentrations of polymer.

The second type of repulsive force associated with the adsorption of polymers on a mineral surface is structural hydration forces. This is caused by the interaction of water with the mineral surface and hence any reagent adsorbed on the surface. When molecules are strongly hydrated or water is bound to the mineral surface through hydrophilic groups including hydroxy groups, repulsive hydration forces result. The magnitude of this force is dependent on the energy required to dehydrate the end groups of the depressant, hence removing the ordered structure of the water near the surface.

Depressant films formed by starches and other macromolecules contain numerous hydrophilic groups that may produce a strong ion-dipole effect on the water nearby. The resulting ordered structural zone could possibly lead to repulsive hydration forces strong enough to prevent bubble-particle attachment [27].

Because of the common practice of recirculating plant water, a build-up of ions such as Ca^{2+}, Mg^{2+}, Fe^{2+}, SO_4^{2-}, etc., in the water can take place. This produces a fairly high ionic strength, thus reducing the effect of electrostatic interactions. Since both the depressant and the bubble are weakly anionic, there would be a weak repulsive interaction. However, it is difficult to explain the depressant action based only in terms of the electrostatic interactions, hence non-electrostatic contributions must also be considered [27]. More work needs to be done to determine the importance of hydration forces in the depressant mechanism of macromolecules [27].

2.4. Adsorption Studies in Iron Ore Flotation

Flotation in the iron ore industry has been used in two ways [11]: (1) for direct production of an iron oxide concentrate, and (2) to remove the final fraction of silica remaining in iron concentrates (i.e., reverse flotation). Selectivity - as always - is essential. Starch plays a major role as a selective depressant.

One study on the adsorption mechanism (and hence depressant action) of starches and their derivatives in the iron ore industry has shown that the adsorption of various starch products on quartz and hematite was dependent on both electrostatic interactions and the extent of hydrogen bonding [16]. The depressant action of starches and dextrins in the cationic flotation of quartz from hematite has been found to increase with increasing molecular weight, branching, and amount of hydroxyl groups. In addition, the selectivity of the separation was affected by a change in the configuration of the starch molecules [17].

Cationic and anionic substituted starches were also tested for their depressing efficiency [16]. Chemically modifiied starches have substituent groups, either anionic or cationic, introduced in varying amounts in the structure. Depending on the substituent, the starch can be made cationic or anionic in aqueous solutions [11].

The adsorption of cationic starch onto quartz increased with increasing pH [16]. Meanwhile, adsorption of the same starch onto hematite was much less. This indicated the importance of electrostatic interactions in the adsorption of starches. The magnitude of the negative surface charge for quartz between pH 7 and 11 was much greater than for hematite since the isoelectric points for the two minerals are pH 2 and 6.7, respectively. Therefore, the positive functional groups of the substituted starch interacted with the highly negative surface of quartz more than hematite [16].

Similarly, corn starch, British gum, and anionic starch are negatively charged in aqueous solutions. Their adsorption on hematite was greater than on quartz for the same pH range. Also, adsorption decreased with increasing pH (i.e, the reverse for cationic starches). This again showed the importance of electrostatic interactions in starch adsorption [16].

The amount of anionic starch adsorbed onto either mineral was less than the amount of cationic starch adsorbed. The adsorption of anionic starch was hindered by electrostatic repulsion. Following this, it was evident that the adsorption mechanism did not depend only on electrostatic forces, but also involved nonionic interactions [16]. It was postulated that hydrogen bonding between hydrogen from the starch and oxygen on the oxide mineral was responsible for the remainder of the adsorption [16]. In a more recent report [11], hydrogen bonding was said to be the main mechanism for starch adsorption, with coulombic interactions between the mineral surface and the charged functional groups of the starch also affecting adsorption.

Starches are effective depressants because their relatively large size, as compared to collector ions, may overshadow the hydrophobic effect produced by the collector [16]. In anionic silica flotation, a critical amount of corn starch must be added, below which the iron oxides will not be effectively depressed [11]. Because the iron ore was extremely fine grained, the starch requirement was quite high. Methods to reduce the starch addition were sought.

Homogenization is the process whereby the average molecular weight of the starch is reduced. Homogenizing the starch solution lowered the dosage requirements substantially [11]. This implied that an optimum molecular size existed for maximum effectiveness. In fact, excessive homogenization resulted in a decrease in iron recovery. Finally, anionic modification of starch also lowered the level of addition since saturation coverage was reached sooner [11].

The adsorption of polyacrylic acid (PAA) and polyacrylamide (PAM) onto hematite and silica was studied for selective flocculation purposes [9]. The adsorption of PAM onto silica followed the same trend with pH as for hematite (i.e., increased PAM adsorption with decreasing pH). The difference in adsorption of the same polymer onto the two oxide minerals suggested that the surface characteristics of the oxide were important.

To get polymer adsorption, the polymer molecule must have preferential affinity for the surface versus the water molecules. The nature of the polymer-water and solid surface-water interactions determine the affinity of polymers for the surface. PAM contains amide groups which can be both hydrogen donating and hydrogen accepting by the presence of hydrogen atoms and an oxygen atom, respectively. The molecular structure of PAM is not expected to change with pH, so the hydrogen accepting properties of PAM will remain constant while the hydrogen donating properties of the surface will be altered with pH. Oxide surfaces can contain charged species in any proportion depending on the pH of the aqueous solution: MOH_2^+, MOH, and MO^-. Both MOH_2^+ and MOH are hydrogen donating groups. The observations showed that PAM adsorbed more on hematite than on silica at pH 5 (for example). At pH 5, the majority of surface groups on hematite would be in the form MOH_2^+ and on silica, MO^-. The increase in hydrogen donating power followed the same order. This supported the hypothesis that nonionic PAM adsorbed via hydrogen bonding. The proof that electrostatic forces do not take part in nonionic polymer adsorption was that the carboxyl groups in the PAM structure would be fully ionized between pH 6 and 10, and would be undissociated below pH 4. No change in the slope of the PAM adsorption versus pH curve was observed, supporting the theory that electrostatic forces were negligible in nonionic polymer adsorption.

The adsorption of PAA onto hematite was different than for PAM. No adsorption occurred above pH 8.8 which correlated well with the i.e.p. (iso-electric point) of hematite (pH 8.1). It was postulated that both hydrogen bonding and electrostatic interactions were involved in the adsorption process. The observation that adsorption decreased with increasing pH correlated well also with the reduction of hydrogen donor groups (OH_2^+) under the same conditions. The carboxyl groups of the polymer acted as the hydrogen acceptor while the OH_2^+ on the surface donated the hydrogen to form a hydrogen bond. Electrostatic interactions between OH_2^+ on the solid surface and partially dissociated, negatively charged carboxyl groups of the polymer chain could enhance adsorption. Above the i.e.p., there would not be sufficient hydrogen donor groups to allow hydrogen bonding to occur. The presence of a hydrogen accepting group such as O^- on the surface would not promote adsorption since the dissociated carboxylic groups did not contain hydrogen to form hydrogen bonds. In addition, there would be strong electrostatic repulsion between the O^- on the surface and the COO^- functional groups of PAA.

2.4.1. Other tests on oxygen-containing minerals

The depressant action of starch, amylose and amylopectin on various oxygen-containing minerals was measured by microflotation tests [25]. The single mineral samples studied were calcite, apatite, quartz and hematite. Sodium oleate was the collector tested on apatite and calcite, and dodecylamine hydrochloride was used on quartz and hematite. The depressants tested were amylose and amylopectin separated from potato starch and a tapioca starch sample (approximately 17% amylose and 83% amylopectin).

The results of the flotation tests revealed that for calcite and apatite, the depressant action of the polysaccharides decreased in the following order: starch, amylopectin, and amylose. For hematite, the polysaccharides in order of decreasing depression action were amylopectin, starch, and amylose and for quartz, the order was starch, amylose, and amylopectin. The depressant action of starch was stronger for hematite and calcite, and less effective for quartz and apatite [25].

The authors concluded that the reason for starch more effectively depressing hematite than quatrz was because of electrostatic interactions. Calcite was depressed by starch more than apatite because of complexation occurring between starch and the calcium cation [25]. It should be noted that no further testwork was done on these mineral systems to confirm the above statements.

Selectivity between quartz and hematite, and calcite and apatite could be achieved by exploiting differences in the ratio of collector to depressant concentration necessary for depression to occur. The mineral the most amenable to depression by starch was calcite, demonstrated by the collector/depressant ratio of 3 to 1. Quartz was least affected by starch as indicated by the collector/depressant ratio of 1 to 11 [25]. However, no flotation tests were performed to separate quartz from hematite and apatite from calcite to confirm the selectivity of starch.

2.5. Adsorption Mechanism on Sulphide Minerals

The following gives an outline of the work done on the use of starch and dextrin in the sulphide mineral industry. Section 2.5.1. (Galena and pyrite) gives some of the earliest work performed on the adsorption of dextrin on two mineral samples and their flotation behaviour after conditioning with dextrin. More recent reports on other mineral systems are then presented. Some of the claims made in the first part are later contested by other reports. However, both views will be presented.

2.5.1. Galena and pyrite

A study on the effect of various polymeric depressants was conducted by Steenberg and Harris on samples of pure galena and pyrite [28]. The investigation included zeta potential measurements, adsorption studies, and single mineral flotation tests. The polymers tested were carboxymethylcellulose, a modified guar gum and a modified potato starch and the collectors were sodium ethyl xanthate and mercaptobenzothiazole (MBT). Only the results for starch will be reviewed here.

The zeta potential measurements showed there was a significant amount of polymer adsorbed on both minerals. For the pH values studied (4 and 7.5), the zeta potential of galena was increased from a negative value to the isoelectric point at low concentrations of starch. This was more evident at pH 7.5. For pyrite, the zeta potential became less negative, but never did reach the isoelectric point for the concentrations of starch added.

The adsorption of starch can cause a reduction in the negative zeta potential of a mineral either by the inclusion of counterions in the polymer layer or by a significant extension of the double layer caused by the dangling chains in solution [28]. The zeta potential measurements for galena with starch gave evidence of the inclusion of counterions in the polymer layer. A reduction of the negative zeta potential due to the extension of the double layer only occurs at much higher starch concentrations. At the pH values tested, Pb^{2+} and $PbOH^{+}$ were present in solution [28]. Both these ions interacted with the polymer layer; $PbOH^{+}$ more easily than Pb^{2+}. This was demonstrated by the fact that the isoelectric point for galena was reached at lower concentrations of polymer at pH 7.5 than at pH 4.

The reason that the isoelectric point for pyrite was never reached when starch was added may be that neutral $Fe(OH)_3$ was forming. Even though these ions may be included in the double layer, they would not take part in the overall charge balance [28].

The results for the coadsorption tests showed some interesting observations:

(1) PbS + xanthate added prior to starch: Subsequent xanthate adsorption after starch addition was unaffected. Starch adsorption on xanthated galena was strongly inhibited.

(2) PbS + starch added prior to xanthate: Xanthate adsorption was not affected by the presence of starch on the mineral surface. Xanthate caused some desorption of starch from the galena surface.

(3) FeS_2 + xanthate added prior to starch: Subsequent adsorption of xanthate was not changed after the addition of starch (like PbS). Starch adsorption was inhibited by the presence of xanthate on the pyrite surface.

(4) FeS_2 + starch added prior to xanthate: Xanthate adsorption was unaffected by the presence of starch on the mineral surface. No desorption of starch was observed after adding xanthate (unlike the same conditions for PbS).

The variations in the adsorption behaviour of xanthate and starch listed above were dependent on the order of addition. However, the flotation response of both galena and pyrite were not influenced by the order of reagent addition. Therefore, only the results from the flotation tests where starch was added before xanthate are presented.

Starch successfully depressed galena at low concentrations of xanthate, but as xanthate concentration was increased, the depressing action was reduced. Similar results were observed for pyrite with xanthate and MBT.

It was postulated that the adsorption of polymers onto negatively charged surfaces occurred through hydrogen bonding. Electrostatic forces only became significant if the surface was oppositely charged to the polymer or if both polymer and surface were like charged with high charge densities [28]. In the first instance, an enhancement of adsorption occurred, while in the latter case, adsorption was decreased.

The bond between collector and surface is expected to be much stronger than the bond between polymer and surface. This is due to the mechanism of thiol collector adsorption onto sulphide minerals; through either chemisorption or catalytic oxidation of the collector to dithiolate. The observation that polymers and collectors can coadsorb on mineral surfaces is, therefore, interesting.

When galena and pyrite were treated with collector, the addition of polymer did not affect the subsequent adsorption of collector. However, the amount of polymer adsorbed depended on whether the mineral had been pretreated with collector and what type of collector and polymer it was and what mineral was tested. In the case of the adsorption of starch versus guar gum onto a pretreated surface, starch adsorption was inhibited but this was not the case for guar gum [28]. The difference in molecular size of the two molecules could have accounted for this (starch is nearly two orders of magnitude larger than guar gum [28]).

The adsorption of xanthate onto polymer treated galena caused the polymer to desorb to some extent. This did not occur for pyrite samples treated in the same way. This was explained by the different adsorption mechanisms of xanthate on galena and pyrite. When xanthate adsorbs onto galena, the zeta potential becomes very negative. The polymer molecules, which are not so strongly bonded to the mineral surface, could be electrostatically repulsed. For pyrite, however, xanthate adsorption occurs through the formation of dixanthogen, which does not change the zeta potential of the mineral. Therefore, the polymers would not be desorbed from the surface [28].

The adsorption results indicated that the adsorption of a collector was not uniform over the mineral surface [28]. Previous results have shown that hydrophilic polymers cannot be adsorbed onto charged hydrophobic surfaces, like those produced when a collector adsorbs onto a mineral surface (reference listed in [28]). Therefore, since polymers did adsorb onto sulphides pretreated with collector, adsorption must be occurring on sites free of collector [28].

2.5.2. Dextrin-metal hydroxide interactions in aqueous solutions

Recently, a detailed investigation of dextrin-mineral interactions was carried out by Laskowski and co-workers [4, 5]. From a review of the literature they found evidence that minerals interacted with these polysaccharides through nonselective hydrogen bonding and a hydrophobic bonding mechanism. In both cases, chemical complexation had been ruled out.

They challenged the hydrogen bonding theory for starch adsorption because the energy requirements for such a process did not seem to be compatible with the system energy available. In order for a starch-mineral hydrogen bond to form, the breakage of two existing mineral-water hydrogen bonds needs to occur.

Dextrin has been used successfully as a depressant for many different hydrophobic minerals (e.g., molybdenite, coal, talc). This is why the hydrophobic bonding theory was first postulated.

A number of tests were conducted on samples of dextrin and metal nitrate or metal chloride aqueous solutions [4]. The results of the coprecipitation tests revealed that dextrin only coprecipitated in the pH range where metal hydroxides existed. Outside of that pH range, no dextrin abstraction from solution was observed.

During the coprecipitation tests, a decrease in the solution pH was recorded when dextrin interacted with the metal hydroxides. This demonstrated that chemical complexation was occurring, since hydrogen bonding would not result in a change in pH. Lead hydroxide-dextrin interactions, for example, occurred optimally at pH 11, which corresponds well with the i.e.p. of lead hydroxide. In addition, the conductance of the dextrin-lead mixture decreased with increasing dextrin concentration which also supported the hypothesis of complex formation between dextrin and metal hydroxides.

The infrared spectrum for the dextrin-lead hydroxide precipitates [4] showed that the absorption bands representing glucose ring deformation were eliminated. The authors postulated that this may be due to the bonding of lead ions with the hydroxyl groups at C-2 and C-3 positions in the dextrin molecule [4].

Based on this work, the authors concluded that dextrin formed a chemical complex with lead through interactions with lead hydroxide [4]. These results were confirmed with other metal-dextrin mixtures including ferric-dextrin and cupric-dextrin systems.

Non-hydrated metal cations did not appear to take part in the complex formation between dextrin and metal. In the pH ranges where metal cations predominate, no coprecipitation was observed. In addition, the pH and optical rotation of the metal-dextrin solutions were unchanged when metal cations were prevalent. A change in the optical rotation of the solution would be expected if a metal-dextrin complex had formed [4].

2.5.3. Modified quartz samples

There have been reports which cite that starch can form chemical complexes with metal ions. In the iron ore industry, for example, it was discovered that the addition of metal ions can enhance the adsorption of starch (References listed in [5]).

It appeared that dextrin adsorption depends on the hydrophobicity of the mineral surface. But all the minerals studied are known to have hydrophilic sites along with metal ionic sites which could have influenced dextrin adsorption.

Tests were conducted on quartz and modified quartz samples to observe, on an individual basis, the effects of metal ionic sites and surface hydrophobicity on dextrin adsorption [5, 29]. The results were as follows.

The adsorption of dextrin on unmodified quartz was negligible. Methylated quartz, which was hydrophobic, also did not experience dextrin adsorption, resulting in no effect on floatability.

Quartz samples that were first lead-coated followed by methylation showed significantly higher dextrin adsorption. As a result, dextrin successfully depressed this type of modified quartz sample.

The presence of only lead ionic sites on the quartz surface also enhanced dextrin adsorption compared with lead-free quartz. Lead-coated quartz was depressed by dextrin, in particular when dextrin was added prior to collector (sodium oleate, in this case). This could imply that there was competition between dextrin and sodium oleate for surface lead ionic sites.

The pH at which dextrin adsorption was the highest corresponded well with the i.e.p. of the metal hydroxide being studied. This was also shown in an earlier report by the same authors [4].

Once again, the authors concluded that dextrin adsorption occurred by interaction of dextrin with surface metal hydroxide species [5, 29]. The hydrophobicity of the mineral surface, in addition to the presence of metal hydroxide species, further enhanced dextrin adsorption to some degree.

The authors tested this theory with litharge (PbO) and hematite [5]. Predicting that maximum dextrin adsorption would occur at the i.e.p. of the metal hydroxides, it was expected that for hematite and litharge, optimum adsorption would be observed around pH 7 and 11, respectively. Experimental evidence supported this theory. Other studies have demonstrated that maximum adsorption of polysaccharides on iron-bearing minerals occurs around neutral pH [14, others listed in 5].

The chemical properties of the metal ions influence the ease with which complexation can occur. Lead ions are larger and can be polarized more readily compared to ferric ions. Therefore, lead would be expected to form chemical complexes more easily than iron. It was demonstrated that, in fact, dextrin adsorption on litharge was greater than on hematite [5].

Additional evidence to support the theory of chemical complex formation was that at pH 10, where maximum dextrin adsorption on lead-coated quartz was observed, both dextrin and the mineral surface were negative. If only electrostatic interactions were important, little adsorption would be observed.

It was observed that there was more dextrin adsorption on methylated lead-coated quartz (as described above) than on simply lead-coated quartz [5, 29]. This indicated that the surface hydrophobicity can enhance dextrin adsorption. However, it was also noted that when the samples were treated with sodium oleate (collector) prior to dextrin, the amount of dextrin adsorbed was lower. This could imply that the nature of the hydrophobic sites plays a role in dextrin adsorption. Short hydrocarbon chains or the natural hydrophobicity of some mineral surfaces can enhance dextrin adsorption by becoming wrapped inside the loop of an adsorbing dextrin molecule because of increased hydrophobic bonding. Long chain polymers, however, are more likely to stretch out into solution, thus having no influence on dextrin adsorption (Figure 2.3).

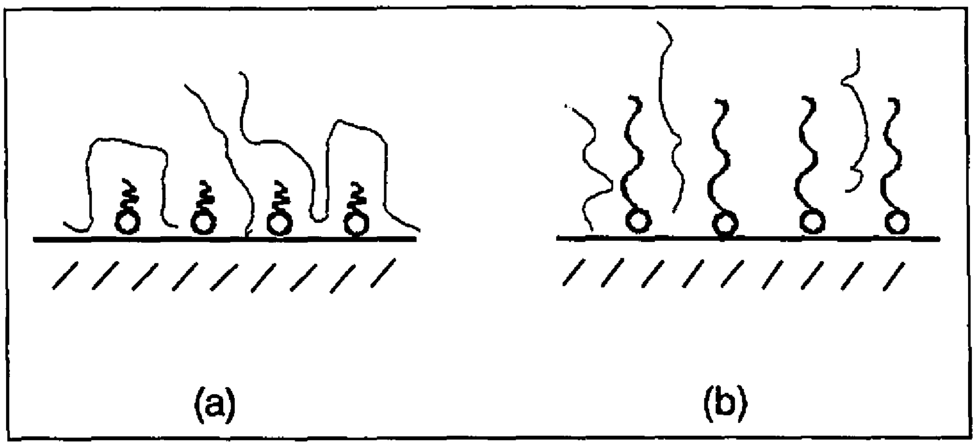


Figure 2.3: Dextrin coadsorption with (a) short- and (b) long-chained collectors

2.5.4. Galena and chalcopyrite

Further tests were conducted to examine the adsorption theory proposed in the previous work (i.e., that metal hydroxides are instrumental in the adsorption of dextrin on the mineral surface) [5, 29]. The authors attempted to separate galena from chalcopyrite using dextrin and by applying the pH dependency of dextrin adsorption for each specific mineral [30]. They were successful at separating the two minerals in two different pH regions.

It had been noted earlier that starch-type polysaccharides have been used in industrial applications of Cu-Pb separation (See Section 2.2.). But in these cases, sulphur dioxide was used to assist in the separation.

Optimum dextrin adsorption on galena was found to be around pH 11, while dextrin adsorption on chalcopyrite was fairly constant below pH 8 with a small maximum observed around pH 9 [30]. It has already been noted that lead hydroxides predominate on the surface of galena around pH 11. But the surface of chalcopyrite may contain hydroxides of both copper (cupric and cuprous) and iron (ferric and ferrous). The wide range of pH where dextrin adsorbed on chalcopyrite could be due to the formation of these numerous metal hydroxide species. In general, the amount of dextrin adsorbed on galena was greater than that on chalcopyrite. The higher chemical reactivity of lead versus copper could explain this higher adsorption of dextrin on galena compared to chalcopyrite.

Flotation tests were conducted on 1:1 mixtures of pure galena and pure chalcopyrite. Effective separation was achieved in two pH regions: (1) around pH 6, chalcopyrite was depressed by adding dextrin prior to xanthate while galena was recovered, or (2) around pH 12, galena was depressed and chalcopyrite was floated when dextrin was added after xanthate.

From these results, the authors concluded that the mechanism of dextrin adsorption, postulated from the modified quartz tests, was valid when applied to mineral systems [30].

Having established evidence to support the theory that the adsorption of dextrin on mineral surfaces involved the formation of chemical complexes, the development of a flotation procedure to separate copper/lead bulk concentrate using dextrin was undertaken [31].

In this case, galena was to be depressed while chalcopyrite was floated. It is common to use dichromate as the lead depressant either alone or in combination with lime, sulphur dioxide, starch or by heating the pulp prior to flotation [7]. The new method proposed would utilize dextrin with very strict pH control. Advantages to be gained by replacing dichromate would be the possible economic benefits, and the use of more environmentally acceptable reagents.

The new process replaced lime with sodium hydroxide and dichromate with dextrin. The experiments included a reference float with dichromate to compare the results obtained when using dextrin. Bench scale tests, pilot plant tests and finally, full scale plant tests were conducted to evaluate the efficiency of the copper-lead separation under the new conditions.

The results of the batch flotation tests indicated that a low dosage of dextrin at pH 12 gave better results than the reference. Higher pH and a further increase in dextrin dosage also depressed chalcopyrite. It should be noted that the initial goal of these tests was to achieve a less than 1% Cu grade in the lead concentrate. The bench-scale results indicated that chalcopyrite was over depressed since the target grade was never obtained when dextrin was added [31].

In pilot plant tests, the process showed great sensitivity to excessive additions of dextrin. The chalcopyrite was severely depressed, which in turn increased Cu content in the lead concentrate. In real systems, lead contamination on the surface of chalcopyrite does occur and could explain the higher chalcopyrite depression.

In full scale plant tests, maintaining a constant addition rate of dextrin in grams per tonne was difficult because of variations in the circuit feed. Hence, the problem associated with overdosing of dextrin was experienced in these tests as well (i.e., high copper content in the lead concentrate).

The results of these tests revealed that dextrin addition must be carefully controlled so as not to over depress chalcopyrite. The effect of overdosing could not be counteracted by increased collector addition [31].

2.5.5. Heazlewoodite and chalcocite

Based on the theory of chemical interaction between dextrin and mineral surfaces, studies on the differential flotation of INCO matte were conducted [32]. The matte, consisting of heazlewoodite (Ni_3S_2) and chalcocite (Cu_2S), was mixed with a tapioca dextrin and either collector diphenyl guanidine (DPG) or amyl xanthate (KAX).

The need to improve the flotation of INCO matte stemmed from the fact that while DPG is exceptionally selective towards chalcocite, it is insoluble in water and therefore difficult to handle. On the other hand, xanthates are easier to handle, but on their own do not give the selectivity of DPG.

Adsorption studies of three different dextrins on heazlewoodite were performed. The adsorption of tapioca dextrin on Ni_3S_2 was twice that of either wheat or yellow corn dextrins. Maximum adsorption for all three dextrins occurred between pH 11.5 and 11.8. It has been reported that the i.e.p. for heazlewoodite is around pH 11.5 (reference listed in [32]). This observation, therefore, was consistent with the previous findings [5, 29, 30].

The amount of dextrin adsorbed onto Ni_3S_2 was greater than on Cu_2S above a pH of 10.9, while below pH 9, this was reversed. Dextrin adsorption onto Ni_3S_2 was pH dependent while not so for Cu_2S ($pH > 8$), similar to earlier work with chalcopyrite [30].

DPG adsorption on Cu_2S was about 3 times greater at the maximum compared to Ni_3S_2. Also amyl xanthate adsorption on Cu_2S was about 10 times greater than on Ni_3S_2. Both collectors adsorbed well on Cu_2S at high pH. This was the pH region where the strongest depressant action of dextrin on Ni_3S_2 was experienced, so separation seemed possible between pH 11.5 and 11.9.

Preliminary coadsorption studies were performed to study the effect of dextrin addition on collector adsorption. The order in which the reagents were added to the individual minerals was switched to observe any differences in adsorption behaviour. The coadsorption results were as follows [32]:

(1) Ni_3S_2-DPG-dextrin: When dextrin was added first, very low DPG adsorption occurred, which remained constant over the dextrin concentration range studied. When DPG was added first, the trend did not change much, but at lower concentrations of dextrin, there was a slight increase in DPG adsorption.

(2) Cu_2S-DPG-dextrin: With DPG added first, the uptake of DPG was enhanced. With dextrin added first, the adsorption of DPG was greatly reduced, but the adsorption of dextrin was also lowered.

(3) Cu_2S-KAX-dextrin: With dextrin added first, there was an increase in dextrin adsorption. This was especially pronounced at higher dextrin concentrations. At higher KAX concentrations, dextrin adsorption decreased.

(4) Ni_3S_2-KAX-dextrin: Irrespective of the order of addition, dextrin adsorption was always higher in the presence of KAX. But, when conditioning was first done with a high concentration of KAX, dextrin adsorption was inhibited to some extent.

The adsorption of DPG on chalcocite was significantly reduced by the presence of dextrin. In addition, the sequence of reagent addition also played a role. When conditioning was first done with dextrin, DPG adsorption decreased considerably, especially at high dextrin concentrations. Two possible explanations given were first, that DPG adsorbed on specific surface sites while dextrin adsorbed on all sites, thus DPG adsorption was inhibited when added second. The second explanation was that dextrin adsorbed on specific sites on the mineral surface, but as surface coverage increased, intermolecular interactions between adsorbed dextrin molecules effectively limited DPG adsorption by blocking surface sites still available [32].

It was shown for the Ni_3S_2-KAX-dextrin system that dextrin adsorption always increased in the presence of xanthate, regardless of the order of reagent addition. The only exception to this was for high concentrations of KAX, when dextrin adsorption did decrease to some extent. This effect had been previously reported, i.e. where an increase in the mineral hydrophobicity promoted the adsorption of dextrin [5, 29]. It was stated by Liu and Laskowski [5] that for short hydrocarbon chains, dextrin adsorption could be enhanced by additional hydrophobic bonding in conjunction with chemical complex formation.

The benefit of using dextrin in the differential flotation of INCO matte was demonstrated by the improvement in copper grade after one stage of cleaning. Without dextrin, single-stage cleaning of the rougher concentrate usually increased the copper grade by 13%. Adding dextrin resulted in an upgrading of copper by 32%. The effect on the nickel grade in the copper concentrate was also affected by the addition of dextrin. In the absence of dextrin, the cleaner concentrate contained 14.5% nickel. With 350 g/t dextrin added, the nickel content was reduced to 4.4% nickel, with only a slight reduction in copper recovery [32].

Further testing on INCO matte was carried out to better understand the interactions that take place between heazlewoodite and chalcocite and dextrin [33].

Dextrin was added to solutions of cupric chloride and nickel nitrate to record the abstraction of metal ions and dextrin from solution. As in other cases, dextrin removal from both the copper and nickel solutions occurred around the pH where the respective metal hydroxide formed. More dextrin was removed from the solutions containing nickel than copper. The ease with which the metal hydroxide can form was believed to be responsible for the differences in dextrin abstraction. Nickel can easily undergo hydrolysis while for copper, this reaction does not proceed as readily. As previously reported, the amount of dextrin adsorbed on heazlewoodite was greater than that on chalcocite [32].

Zeta potential measurements of the metal hydroxide species in the presence of dextrin were conducted [33, 34]. Dextrin acted as an indifferent electrolyte in the presence of copper hydroxide. The decrease in zeta potential was attributed to the adsorbed dextrin molecules pushing the shear plane further from the interface. The strong interactions between nickel hydroxide and dextrin could result in the adsorbed dextrin layer being flat on the surface, thereby not affecting the zeta potential in the same way as for copper hydroxide. It was shown that the zeta potential of nickel hydroxide was independent of the concentration of dextrin added.

Further zeta potential measurements were done on heazlewoodite and chalcocite to determine the orientation of the dextrin molecules on the mineral surface [34]. Around the i.e.p. of heazlewoodite, the electrokinetic curves of heazlewoodite matched those curves produced by nickel hydroxides, indicating the presence of hydroxide species on the mineral surface. Heazlewoodite that had been treated with dextrin showed flat oriented dextrin molecules on the surface because of the strong interaction between the two. The orientation of dextrin molecules on chalcocite appeared to be extended chains because of the weaker association of dextrin with chalcocite [34].

2.5.6. Galena

Using a high frequency dielectrical method, studies on the adsorption of xanthate and dextrin on galena were performed [35]. The objective of these tests was to examine the effect of the presence of dextrin on xanthate adsorption. Dielectrical analysis was used to detect differences in the dielectric constant produced by the adsorption of the collector and the depressant.

There have been numerous studies on the mechanism of xanthate adsorption on sulphide minerals, including galena (references listed in [35]). It is accepted that a strong chemical bond is formed between xanthate and the lead atom of the galena surface. Xanthate adsorption on galena caused a significant decrease in the dielectric constant of the pulp. Even at xanthate concentrations where only 20% flotation was achieved, the dielectric constant was lowered. Even after washing, the collector was still present, as indicated by the low dielectric constant.

It was mentioned previously that dextrin has been suggested as a depressant for galena in the flotation of complex ores containing chalcopyrite [8, 30, 31]. According to earlier reports, it was believed that dextrin adsorbed on galena through the formation of a chemical bond between the macromolecule and lead hydroxide on the mineral surface [4, 5, 8, 29]. Experimental evidence illustrated that these chemical bonds were most likely different from the bonds formed between xanthate and the mineral.

The presence of dextrin increased the dielectric constant of the pulp at a dextrin concentration of 5 ppm, lower than necessary to completely depress PbS (20 ppm). The increase in the dielectric constant of the pulp was interpreted as an increase in the polarity of the system due to the adsorption of the polar hydrophilic dextrin at the solid/solution interface. After washing, there was a slight decrease in the dielectric constant. However, dextrin remained on the mineral surface.

The different effects on the dielectric constant caused by the adsorption of xanthate and dextrin demonstrated that the bonding between these two surfactants and the galena surface were not the same. Another important finding was that the adsorption of dextrin did not inhibit xanthate adsorption nor did it remove xanthate already present on the mineral surface.

According to flotation results, if dextrin was added first, only 20 ppm was necessary to completely depress galena, whereas if xanthate was added first, even with 50 ppm dextrin, depression was difficult. The dielectrical results showed that the value of the dielectric constant was strongly influenced by which reagent was added first. When dextrin was added first, the dielectric constant was high and remained so even after xanthate adsorption. Conversely, when dextrin was added after xanthate, the dielectric constant increased slightly, but remained low. In this case, dextrin did not completely depress galena because lead hydroxide was partially excluded from the surface by the adsorption of xanthate [35].

The oxidation state of the pulp played an important role in the depressant action of dextrin on galena. When conditions were oxidizing, the minimum amount of collector needed for complete recovery by flotation was higher. The amount of dextrin necessary to completely depress galena, however was much lower, regardless of addition order. Xanthate adsorption was inhibited due to the presence of oxidation products on the surface. Dextrin adsorption improved with increasing oxidation because lead hydroxide was predominant on the galena surface [35].

An interesting observation made was the reversibility of the adsorption of dextrin on oxidized galena. At pH 10.8, galena was completely depressed with 5×10^{-4} M xanthate and 10 ppm dextrin. When the pH was changed to 4.5 by adding a drop of acid, galena was able to float (i.e., dextrin had no depressing effect). When the pH of the same pulp was returned to 10.8 by adding a few drops of base, galena was once again completely depressed by dextrin [35].

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. Reagents and Instruments

3.1.1. Reagents

Table 3.1 a) lists the dextrins supplied by Hart Chemical Limited. The dextrins were selected on the basis of their properites, including degree of branching and molecular weight. Variations in the properties of the dextrins were required to test the effect of those differences. All other reagents are listed in Table 3.1 b) along with their use(s) in this work.

Table 3.1 a): Dextrins used and nomenclature

Dextrin	Molecular weight (g/mol)	d. of Branching (%)
SD 501	52,000	75
SD 502	120,000	75
SD 503	24,000	75
SD 512	20,400	85
SD 513	20,800	100

3.1.2. Analytical instruments

The following is a list of analytical instruments used in the experimentation:

- UV Spectrophotometer: Milton Roy Spectronic (R) 1201 Spectrophotometer
- AA Spectrophotometer: Instrumentation Laboratory AA/AE Spectrophotometer
- pH and pulp potential meter: Hanna Instruments HI 8424 pH meter
- DRIFTS: Bruker IFS 66 MCT (Mg-Cd-Te) detector - Spectratech Baseline KBr background - Ratio to single beam spectra versus clean pyrite DRIFTS accessory - 2000 scans/spectra, Resolution set at 4.

Table 3.1 b): Chemicals used during experimentation

Chemical	Grade	Supplier	Usage
HCl	A.C.S. reagent	Stanchem	pH regulator and acid washing of pyrite
NaOH	Analytical reagent	Mallinckrodt Inc.	pH regulator
H_2SO_4	A.C.S. reagent	Stanchem	Determination of dextrin concentration
Phenol	A.C.S. reagent	American Chemicals Ltd.	same as above
EDTA	Reagent grade	Fisher Scientific Co.	Determination of iron concentration
Acetone	A.C.S. reagent	BDH Chemicals	Dry mineral storage
$Pb(NO_3)_2$	Pure	Merck & Co. Ltd.	Lead pretreatment
$FeSO_4 \cdot 7H_2O$	99+% pure	Sigma Chemical Co.	Iron pretreatment
H_2O_2	A.C.S. reagent	American Chemicals Ltd.	Pyrite oxidation
NaCl	Reagent grade	Fisher Scientific Co.	Maintain ionic strength
KEX	Purified	American Cyanamid Co.	Collector
Petroleum spirit (ether)	Analytical reagent	BDH Chemicals	Purification and storage of KEX
MIBC	Reagent grade	Aldrich Chemical Co.	Frother

3.2. Mineral Preparation

Pyrite samples were purchased from Ward's Scientific Establishment, Inc. The pyrite was high grade single mineral chunks up to 4 cm across. The following was the procedure for preparing the mineral sample, unless otherwise stated.

The mineral chunks were first crushed in a cone crusher to obtain minus 1 cm pieces. The sample was then ground in a puck-and-ring pulveriser for 15 seconds. It was screened on a 270 mesh (53 μm) screen for 30 minutes. The -270 mesh fraction was further wet screened on a 400 mesh (38 μm) screen. The three size fractions were collected and stored individually in sealed jars filled with acetone, to reduce oxidation of the mineral. To prepare the mineral for use, a portion of the -270 +400 mesh (-53 μm+38 μm) was removed from acetone storage and filtered. The mineral was washed with 0.1 N HCl for 3 minutes to dissolve any oxide products that may have formed. The acid solution was then decanted. Distilled water was added to rinse away any remaining acid and decanted. Finally, the mineral was rinsed in acetone, filtered, and allowed to air-dry.

3.3. Pyrite Pretreatment

A way was sought to controllably produce oxidation products, iron oxyhydroxides, on the surface of pyrite. The oxidation of pyrite can be induced or accelerated by additions of oxidizing agents. As such, hydrogen peroxide was used. In the second approach, ferrous sulphate solution was added to pyrite to create a layer of iron ions by adsorption on the mineral surface to simulate the products of oxidation. In a similar pretreatment, pyrite was exposed to lead nitrate to test the effect of the type of metal ion on the mineral surface to simulate the contamination by foreign metal ions which is known to occur in practice.

3.3.1. Hydrogen peroxide pretreatment

After the standard mineral preparation procedure described above, a given amount of hydrogen peroxide was added to 1 g of pyrite and allowed to condition for a predetermined length of time. In certain cases, the strength of the hydrogen peroxide was changed by diluting with distilled water. At the end of the conditioning period, the hydrogen peroxide was decanted from the mineral sample.

In the initial tests, after decanting the hydrogen peroxide solution, the pH was not altered prior to adding the dextrin solution. However, there was a concern that because hydrogen peroxide is acidic, any residual peroxide left after decantation could affect the dextrin. Therefore, during the second series of tests, the pH was adjusted prior to dextrin addition.

3.3.2 Ferrous sulphate pretreatment

Ferrous sulphate pretreatment of pyrite was used to place iron ions on the surface of the mineral. To 1 g of pyrite, 50 mL of ferrous sulphate solution at a given concentration was added. The pH was adjusted to the desired value using NaOH or HCl. The mixture was shaken for 5 minutes unless otherwise stated. The solution was decanted from the mineral (except during the preliminary tests where the procedure was still being determined). The mineral samples were then rinsed with distilled water to complete the removal of metal solution and precipitates. The samples that were not rinsed are indicated. The mineral samples were then treated with dextrin and/or xanthate, depending on the test.

3.3.3. Lead nitrate pretreatment

Pyrite pretreatment with lead was performed to determine the role of contaminant metal ions on the mineral surface on the interaction with dextrin and xanthate. Lead was chosen since it has been found on the surface of minerals in flotation systems whenever galena is present. The procedure for pretreating the pyrite samples with lead was adapted from the method used by Liu to lead-coat quartz samples [29]. The method was as follows:

After mineral preparation, 25 mL 0.0025 M $Pb(NO_3)_2$ was added to 1 g pyrite. The mixture was shaken for 20 minutes at 300 rpm at pH 10.5. After mixing, the lead nitrate solution was decanted. The sample was then rinsed with distilled water to remove any excess lead ions left in solution. The mineral was then ready to be treated with xanthate and/or dextrin.

3.4. Purification of KEX

Potassium ethyl xanthate (KEX) was purchased from American Cyanimid Co. The following procedure was used to purify the reagent: The maximum amount possible of KEX was dissolved in 5 mL acetone. The KEX-saturated solution was filtered into 50 mL of petroleum ether (spirit) to recrystallize the KEX. The purified KEX was then collected and stored in petroleum ether until needed. The KEX was filtered and air-dried before being measured to make the desired concentration solution.

3.5. Dextrin Stock Solution Preparation

The preparation of 1000 ppm dextrin stock solution was done daily due to its rapid deterioration [36]. From the stock solution, other solutions of various dextrin concentrations were made. The procedure used to make the stock solution was as follows:

A few mL of distilled water was added to 1.000 g of dextrin to produce a thick paste. The paste was added to approximately 100 mL of boiling distilled water and mixed thoroughly. The solution was then added to a 1 L volumetric flask and brought to the mark. The ionic strength was maintained at 0.01 M NaCl by adding 0.5844 g NaCl to the flask. The solution was then cooled to room temperature prior to making the dilute solutions.

3.6. UV Analysis

3.6.1. Dextrin concentration determination

The method described by Dubois and coworkers [37] was used to analyze solutions containing dextrin. The modification employed by Liu [29] was adopted whereby the optimum amount of phenol was determined to get the maximum peak for dextrin. It was determined that 0.75 mL of phenol was optimum. This corresponded to the amount that Liu used during his experiments. A summary of the procedure is given below.

Into glass vials were added, in order: 2 mL dextrin solution, 0.75 mL 80% (w/w) phenol solution, and 5 mL concentrated sulphuric acid (rapidly). The vials were left standing for 10 minutes. The vials were then covered and shaken. Before analyzing by UV spectrophotometry, the solutions were cooled in air to room temperature.

The absorbance value at a wavelength of 487.7 nm was obtained using Spec-Scan, a software package used with the UV spectrophotometer. The values were plotted versus concentration in ppm to obtain a standard curve. Each concentration was tested in triplicate.

3.6.2. Dextrin-xanthate interference

Tests were performed to determine whether the presence of dextrin in solution interfered with the UV spectrum of xanthate and vice versa. The experimental procedure was as follows:

Dextrin and xanthate solutions (5 mL of each) were added to a beaker. The mixture was stirred for 3 minutes. The final pH was measured and recorded. The UV spectra of the mixture was obtained for both dextrin and xanthate in triplicate. Comparisons were made to determine whether any differences were observed between the spectra for the individual solutions and those of the mixture.

3.7. Adsorption Studies

Adsorption tests included rate tests, kinetic studies, and adsorption and coadsorption tests. Tests were performed with and without pyrite pretreatment. (The pretreatment stage followed mineral preparation and preceeded dextrin and/or xanthate addition.) All studies were performed at room temperature. UV analysis was performed in triplicate and the readings did not differ by more than 0.05 mg/g.

3.7.1. Rate tests and kinetic studies

Rate tests were performed to determine the time necessary for dextrin solution and pyrite to reach equilibrium. The procedure for the rate tests is described below. Similar tests were conducted for xanthate.

Following the mineral preparation procedure (and pyrite pretreatment, if applicable), 25 mL 0.01 M NaCl solution was added to 1.000 g of pyrite to thoroughly wet the mineral sample. Then, 25 mL of dextrin solution was added to the flask and the pH was adjusted to the desired value and recorded. The flask was covered and shaken at 300 rpm for the desired amount of time. At the end of the period, the pH was measured and recorded. Three 2 mL samples were extracted and poured into vials. The flasks were recovered and replaced in the shaker for the desired time. This procedure was repeated until 2 hours had elapsed. The supernatant solutions were analyzed by UV spectrophotometry, applying the phenol-sulphuric acid method.

Kinetic studies for both dextrin and xanthate were conducted similar to the rate tests. However, the method of pretreatment was altered to determine its effect on adsorption. For example, the concentration of ferrous sulphate solution for pyrite pretreatment was changed, and its effect on dextrin adsorption kinetics was studied.

3.7.2. Adsorption and coadsorption tests

Coadsorption tests were conducted to determine the effect on the adsorption of xanthate and dextrin on pyrite when the two reagents are added together. Three different conditioning sequences were studied (Table 3.2). The adsorption and coadsorption tests were conducted both with and without pyrite pretreatment. The experimental procedure is given below.

After mineral preparation and pyrite pretreatment (if applicable), the required solutions were added to 1.000 g pyrite. The concentration of the dextrin and xanthate solutions varied, depending on the test, and also the type of dextrin used. The pH was measured and adjusted if necessary to the desired value using solutions of NaOH and HCl. For cases D/X and X/D, the pH was measured and recorded after the first 30 minutes of shaking. After addition of the second solution, the pH was recorded again. Finally, the pH was adjusted to the desired value prior to the last 30 minutes of shaking. The final pH of solution was measured and recorded. Samples of the solutions were extracted and centrifuged to analyze for dextrin and xanthate concentration by UV spectrophotometry.

3.8. Microflotation Tests

The pyrite samples were prepared just as they were for the adsorption studies except 1 drop MIBC was added to the flask just prior to being poured into the microflotation apparatus. Flotation tests were carried out at room temperature for 3 minutes with air. The concentrate and tails were collected, filtered, allowed to air-dry, and weighed to calculate pyrite recovery. Tests were performed in triplicate and pyrite recovery was reproducible to within 10% in the moderate flotation range and less than 5% difference in the high and low flotation regions.

Table 3.2: Conditioning sequences for coadsorption tests

Abbreviation	Description
X+D	Add 25 mL each of dextrin and xanthate, shake for 1 hour.
D/X	Add 25 mL dextrin, shake for 30 minutes. Add 25 mL xanthate, shake for 30 minutes.
X/D	Add 25 mL xanthate, shake for 30 minutes. Add 25 mL dextrin, shake for 30 minutes.

3.9. Solution Tests

3.9.1. Fe removal from pyrite surface by dextrin

Samples of pyrite were prepared just as in the adsorption studies. However, instead of taking a sample of the solution for dextrin or xanthate analysis by UV, the solution was analyzed for iron content using AA spectroscopy. Triplicate readings were taken and the difference between readings did not exceed 0.05 mg/g.

3.9.2. EDTA tests

The EDTA used was Disodium Ethylene Diamine Tetraacetate with a formal weight of 372.24 g. A solution of 0.3 M EDTA was used in all the tests.

The pyrite samples were prepared just as they were for the adsorption tests. After shaking, the solution was decanted and 25 mL of 0.3 M EDTA was added. The mineral and EDTA was allowed to sit for 2 hours in a stoppered flask. The solutions were filtered and analyzed by AA spectroscopy to determine iron content. Similar reproducibility as in Section 3.9.1. was achieved.

3.9.3. Pulp potential measurements

The mineral samples were prepared in the same manner as in the adsorption studies. At the end of shaking, a standard Ag/AgCl electrode was inserted into the slurry to obtain a reading in mV. The mixture was constantly stirred using a magnetic stirrer.

3.10. DRIFTS Analysis

Infrared spectroscopy (IR) is used to study the structure of molecules [38]. It can detect when a bond is formed between the surface of the mineral and the reagent. One such procedure is known as DRIFTS - diffuse reflectance Fourier transform infrared spectroscopy. DRIFTS is a method of IR analysis, modified to be sensitive to surface species. A diagram of the optics is given in Figure 3.1. The arrangement enables the diffusely reflected IR from the surfaces of the randomly oriented particles to be collected giving high sensitivity to surface species. DRIFTS has the advantage of using particles but is an ex-situ procedure, which is a disadvantage.

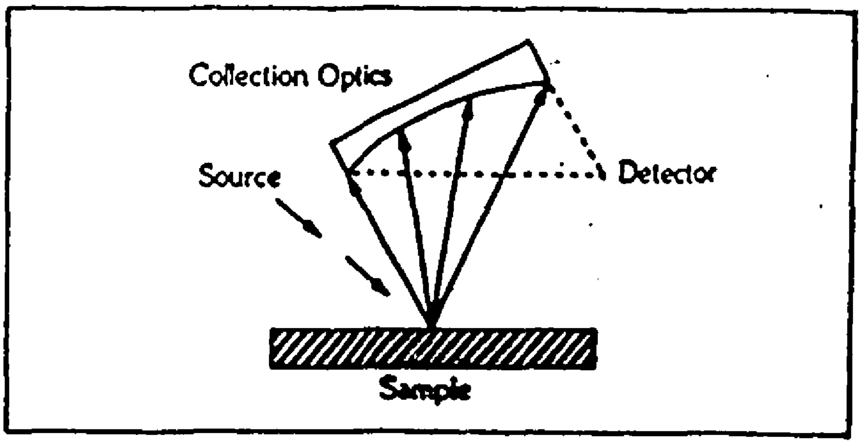


Figure 3.1: Schematic of optics arrangement for DRIFTS

The pyrite samples were prepared just as in the adsorption studies. After shaking, the mineral samples were filtered and rinsed with distilled water and air-dried. The sampling cup was filled and the sample was scanned 2000 times to obtain the spectrum.

CHAPTER 4

RESULTS

4.1. Adsorption Studies

4.1.1. No pyrite pretreatment

4.1.1.1. Dextrin adsorption rate tests

Rate tests were performed to determine the time necessary to reach equilibrium between the dextrin solution and the mineral. This time was used in subsequent tests as the conditioning (shaking) time. Rate tests were conducted at pH 6 and 8 and initial dextrin concentrations of 50 and 100 ppm. The dextrin studied was SD 501 which was used for the remainder of the tests. Dextrin adsorption was studied over a period of 2 hours.

The results showed that even for shaking times of up to 2 hours, no dextrin adsorbed onto the pyrite surface. This was observed by the steady concentration of dextrin in the supernatant solution during the entire experiment (Figure 4.1). Figure 4.2 shows the change in pH during the period of shaking for initial dextrin concentrations of 0, 50, and 100 ppm at pH 6 and 8, set by adding NaOH or HCl. The pH was observed to decrease during the period of shaking. The blank test (0 ppm dextrin) displayed the same observed decrease in pH for the test at pH 8. However, at pH 6, the decrease in pH was slightly less in the absence of dextrin. Therefore, the pH drop at pH 6 may be attributed to the presence of dextrin in solution even when no adsorption was observed.

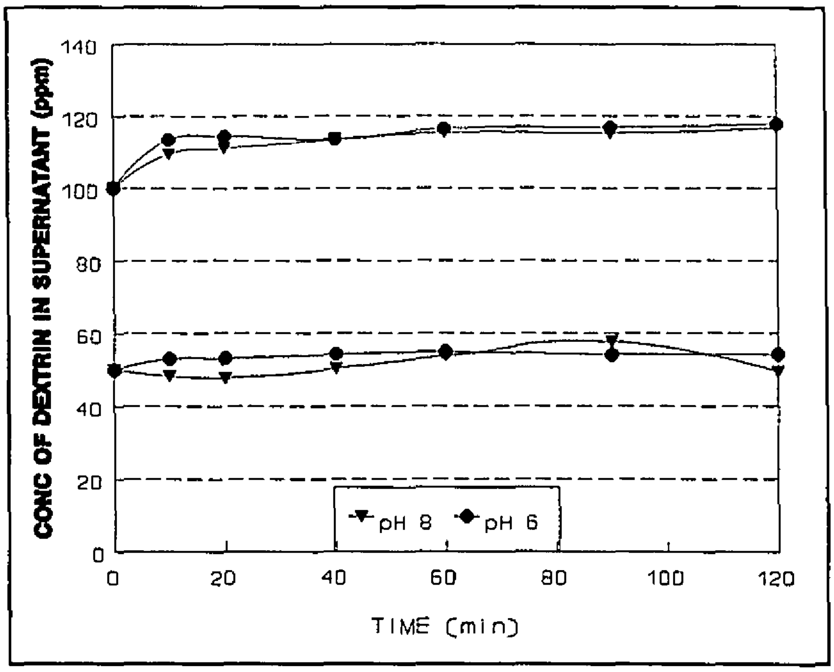


Figure 4.1: Concentration of dextrin in supernatant versus time

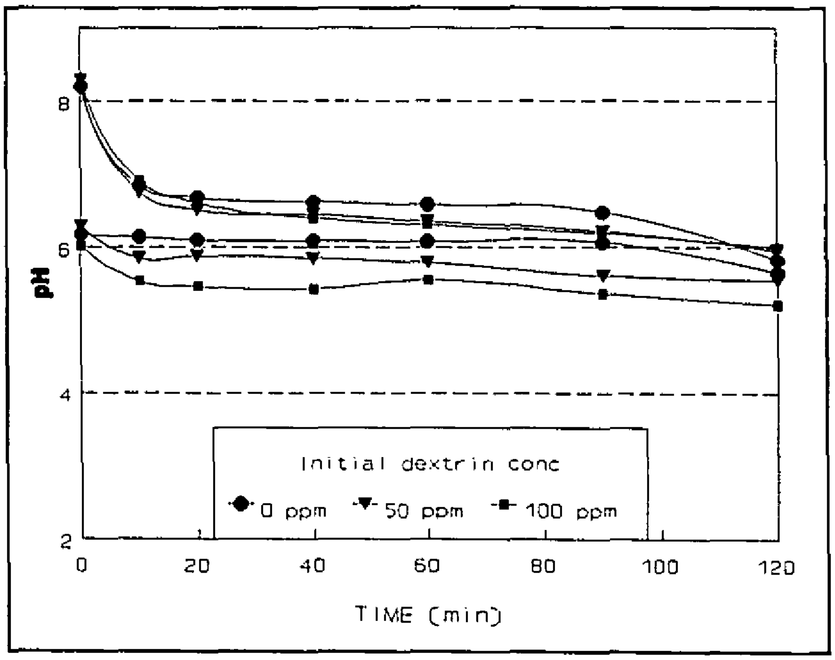


Figure 4.2: Change in pH over time for dextrin adsorption rate tests

4.1.1.2. Solution tests - dextrin and xanthate

Tests were conducted to determine whether the presence of potassium ethyl xanthate in solution interfered with the spectrum of dextrin, and vice versa. A number of solutions were mixed with varying amounts of dextrin and xanthate with no mineral added. The ionic strength of the solutions was maintained by using 0.01 M NaCl solution. The tests were performed at pH 6 and 8. Different concentration ratios of dextrin and xanthate solutions were studied.

The solution tests revealed that the presence of dextrin in solution had little to no effect on the UV spectrum of xanthate (Figure 4.3). When analyzing for dextrin, any xanthate in solution was destroyed by the addition of sulphuric acid. Hence, no effect on the resulting UV spectrum of dextrin occurred. Therefore, the UV analysis in the testwork following did not require any special precautions when analyzing for both dextrin and xanthate concentrations in a single solution.

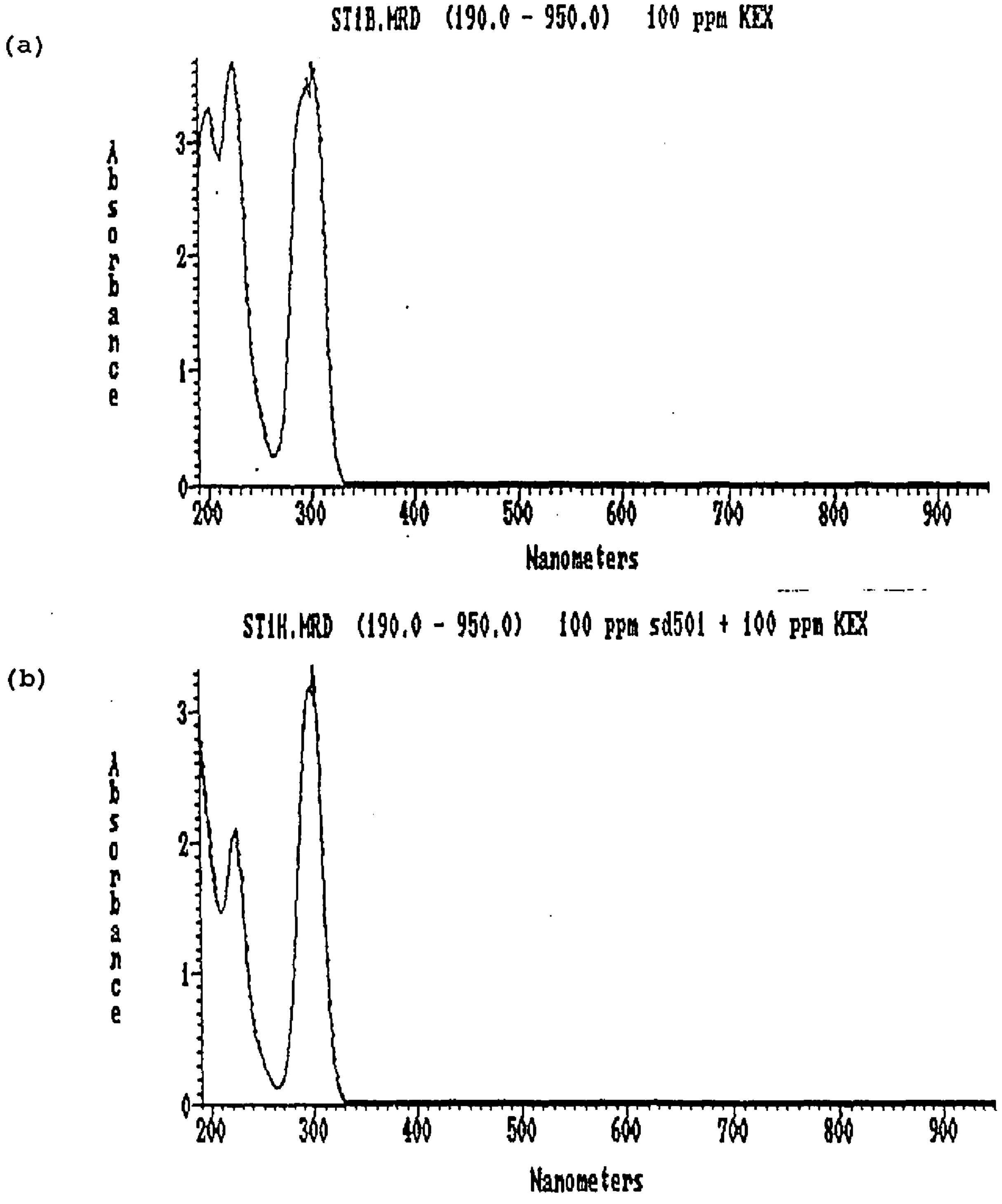


Figure 4.3: (a) UV spectrum of 100 ppm xanthate (b) Overlay display of mixtures of 100 ppm xanthate with 50, 100, and 200 ppm dextrin solutions (all curves overlap)

4.1.1.3. Adsorption and coadsorption tests

These tests were done to determine the effect of adding dextrin and xanthate solutions together with pyrite. The effect of the order of reagent addition was studied to determine whether a competition for surface sites existed between dextrin and xanthate. The pH was varied between 6 and 10. Once again, the ionic strength of the solution was kept constant by using 0.01 M NaCl solution. The concentration of both the dextrin and xanthate solutions was 100 ppm.

The adsorption tests showed an effect of the order of addition of reagents. The rate tests had revealed that dextrin did not adsorb onto the mineral surface. In the presence of xanthate, the same was true. However, there was an effect on xanthate adsorption when dextrin was present in solution. Some qualitative results follow.

The xanthate absorbance peak (at 301 nm) changed in magnitude depending on the order of reagent addition (Figure 4.4). The peak was the largest when no pyrite was added, as expected. The smallest xanthate peak appeared when xanthate was added before dextrin. This implied that the xanthate adsorbed onto the mineral surface. The second smallest peak occurred when dextrin and xanthate were added simultaneously. This indicated that less xanthate adsorbed in the presence of dextrin. Finally, the second largest peak occurred when dextrin was added first. The dextrin appeared to interfere with xanthate adsorption even though dextrin itself did not adsorb onto the mineral. Similar trends were followed over the pH range 6 to 10.

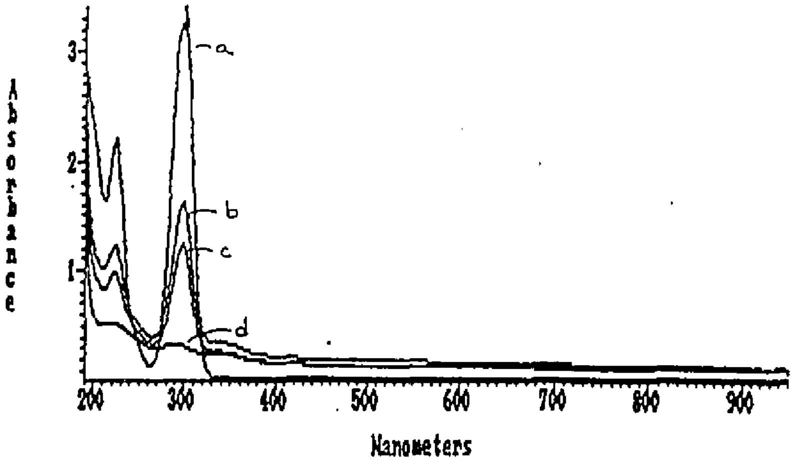


Figure 4.4: Xanthate spectra for adsorption test at pH 6.
(a) dextrin and xanthate (no pyrite),
(b) dextrin added first,
(c) dextrin and xanthate added simultaneously,
(d) xanthate added first.

Combined with the results in Figure 4.3, there was an indication that dextrin did not interact with xanthate directly but did block it from adsorbing onto the mineral surface. However, this "blocking" action was not the result of competition for adsorption sites on the mineral surface since dextrin did not adsorb.

The pH at which these tests were conducted may have also been an important factor in determining the degree to which dextrin blocked xanthate adsorption. The combined effects of the different operating pH and the presence of dextrin are difficult to separate since the behaviour of xanthate changes with pH (Figure 4.5). At pH 10, the adsorption of xanthate was the lowest, compared to the adsorption for the conditions at lower pH. For all the pH values tested (6, 8, and 10), the amount of xanthate adsorbed decreased in the order: xanthate added only (X), xanthate added first (X/D), xanthate and dextrin added simultaneously (X+D), and dextrin added first (D/X). At pH 10, the amount of xanthate adsorbed was always lower than at pH 6 and 8 for every order of xanthate/dextrin addition. The amount of xanthate adsorbed was approximately equal for pH 6 and 8 for each test.

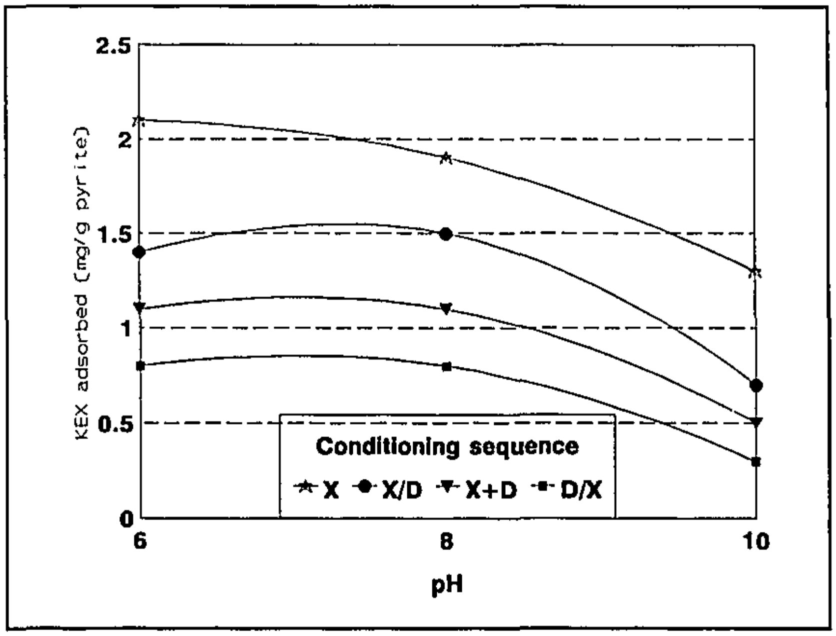


Figure 4.5: KEX adsorption versus pH and conditioning sequence
(initial KEX and dextrin = 2.5 mg/g pyrite)

4.1.1.4. KEX desorption studies

Studies on the desorption of xanthate from the surface of pyrite were carried out. The aim of the tests was to determine whether dextrin caused xanthate to desorb from the mineral surface (a possible depressant mechanism that requires no dextrin adsorption).

The results of the xanthate desorption tests indicated that no desorption of xanthate was observed in the presence of dextrin. Xanthate continued to adsorb after the addition of dextrin. A kinetics study was undertaken (see Section 4.1.2.4.) to determine if the rate at which xanthate adsorbs was lower when dextrin was present.

4.1.1.5. Effect of the type of dextrin on KEX adsorption

The following experiments were conducted to determine the effect of the molecular weight of dextrin used and the initial concentration on xanthate adsorption.

The results of these tests are given below.

When the initial concentration of dextrin SD 501 was increased tenfold (from 50 ppm to 500 ppm), the amount of xanthate adsorbed decreased for each order of reagent addition. The decrease in xanthate adsorption was modest, ranging from approximately 0.2 to 0.3 mg/g of pyrite compared to the amount of xanthate adsorbed at an initial concentration of dextrin equal to 50 ppm which ranged from 0.75 to 1.5 mg/g of pyrite (i.e., approximately 20% decrease).

When using dextrin SD 502 (i.e., molecular weight 2.3 times greater than dextrin SD 501) at the same initial concentration (50 ppm), the change (decrease) in xanthate adsorption compared to that with dextrin SD 501 was slight, ranging from approximately 0.01 to 0.06 mg/g pyrite.

The results of both sets of tests indicated that the molecular weight and amount of dextrin present in solution have little effect on xanthate adsorption. While dextrin did not adsorb on the untreated pyrite surface, it did hinder xanthate adsorption. However under the conditions tested, differences in molecular weight did not enhance or diminish this effect, while concentration had a modest effect.

4.1.2. Pyrite pretreatment

4.1.2.1. The role of iron ions

Preliminary tests to determine whether surface iron species were necessary to obtain dextrin adsorption were performed under different conditions. The first set was performed using hydrogen peroxide to oxidize pyrite and produce iron ions on the surface. The second method was to simulate oxidation by placing iron ions on the surface by mixing the mineral with ferrous sulphate solution.

4.1.2.1.1. Hydrogen peroxide treatment

A test was conducted to determine whether aeration could be used to sufficiently oxidize the pyrite samples. The results showed that after 30 minutes of aeration, the amount of dextrin adsorbed was the same as with no aeration. Therefore, simple aeration was not the method of choice to produce surface sites for adsorption. The idea behind treating pyrite with hydrogen peroxide was to oxidize the surface quickly and efficiently. Table 4.1 shows that 15 minutes was more than enough time to oxidize the surface and produce iron ions, or more importantly, surface sites for adsorption. Clearly, the full strength (30% v/v) was the most effective at enhancing the amount of dextrin adsorbed.

Table 4.2 shows the dextrin adsorption results when the amount of H_2O_2 (30% v/v) was varied. Because H_2O_2 is very acidic, any residual amount remaining after decanting may affect the dextrin. For this reason, the pH was adjusted prior to dextrin addition. These results are shown in Table 4.2.

Table 4.1: Dextrin adsorption (mg/g pyrite) versus H_2O_2 conditioning time and strength (Note: no pH adjustment prior to adding dextrin.)

H_2O_2 soln strength	15 minutes	30 minutes	60 minutes
6%	0.55	0.4	0.3
12%	0.6	0.3	0.4
30%	1.3	1.0	1.1

When adjusting the pH, at first the solution was clear (pH < 4), then as the pH increased (pH --> 6) orange precipitates started to appear. It was clear from this that there was some residual iron not attached to the surface after the hydrogen peroxide solution was decanted, and also confirmed the production of iron species as a result of the H_2O_2 treatment.

Table 4.2: Dextrin adsorption (mg/g pyrite) versus volume of H_2O_2 with and without pH adjustment prior to dextrin

mL H_2O_2 (30%)	no pH adjustment	with pH adjustment
5	1.7	1.3
10	1.1	0.9
25	1.3	0.6

Table 4.3 shows the amount of iron generated during the H_2O_2 treatment experiments in Table 4.2. It shows that more iron was produced on the mineral surface (as measured by EDTA extraction) using the lower volumes. However more total iron (i.e., including Fe in solution) was produced with the highest volume of hydrogen peroxide added. This correlated well with the results in Table 4.2 where the the amount of dextrin adsorbed increased with a decrease in H_2O_2 added (for the pH adjusted case). Moreover, the two tables show a correlation between the amount of dextrin adsorbed with the amount of Fe at the mineral surface.

Table 4.3: Iron generated after treating pyrite with different volumes of H_2O_2

mL H_2O_2 (30%)	EDTA extract (mg Fe/g pyrite)	Total Fe generated (mg/g pyrite)
5	1.434	11
10	1.412	14.5
25	0.903	18

The treatment of pyrite with H_2O_2 gave quite a violent reaction, with a great deal of heat and gas being evolved. This procedure was hard to control and for this reason was not used further in the testwork.

4.1.2.1.2. Ferrous sulphate solution treatment

Table 4.4 shows the amount of dextrin adsorbed after 2 hours shaking under different conditioning environments using ferrous sulphate solutions. Note that the gas was injected into the system only during the 5 minute conditioning time, not after the dextrin was added. The results show that dextrin adsorption was very high (initial dextrin added was 2.5 mg).

The iron remaining in solution when adding dextrin may have also played a role as any iron precipitates present also reacted with dextrin (see Section 4.1.2.2.), as discovered by Liu and Laskowski [4].

Table 4.4: Dextrin adsorbed versus type of pyrite conditioning

Type of mineral conditioning	mg dextrin adsorbed/g pyrite
1.0 g/L $FeSO_4 \cdot 7H_20$ + N_2*	1.8 (72% of total)
1.0 g/L $FeSO_4 \cdot 7H_20$ + air*	2.0 (80% of total)
1.0 g/L $FeSO_4 \cdot 7H_20$*	2.2 (88% of total)

*25 mL of this solution was left in the flask when the dextrin was added.

Table 4.5 shows the amount of dextrin adsorbed when using different concentrations of ferrous sulphate solutions, with and without decanting. With no decanting, there was considerable dextrin adsorption, except at the lowest concentration of $FeSO_4 \cdot 7H_2O$. In general, more dextrin adsorbed as Fe concentration increased. When the supernatant was decanted prior to dextrin addition, there was a reduction in the observed amount adsorbed. The iron in solution was responsible for the apparent high adsorption. The repeat tests, indicated by (**) did not show good correspondence, except for the general trend. This could reflect how well the solution was decanted. To try to alleviate this problem, a rinsing stage was added to remove iron not present on the mineral surface.

Table 4.5: Dextrin adsorption (mg/g pyrite) versus $FeSO_4 \cdot 7H_2O$ solution concentration with and without decanting

$FeSO_4 \cdot 7H_2O$ conc	no decanting*	with decanting	
0.1 g/L	0.4	0.38	0.11**
0.5 g/L	2.0	0.7	0.25**
1.0 g/L	2.2		0.4**

*25 mL of this solution was left in the flask when the dextrin was added.
**repeat tests

An iron balance was performed for the pyrite samples after ferrous sulphate pretreatment. The balance was calculated by measuring the initial amount of iron added during the pyrite pretreatment stage ("mg Fe, init" in Table 4.6). This was determined by the volume and concentration of ferrous sulphate solution added during pretreatment. The final mg Fe was determined by adding the amount of iron in solution after pretreatment with the iron extracted from the pyrite surface using EDTA ("EDTA extract" in Table 4.6) and subtracting the amount of iron generated during the blank test (also shown in Table 4.6). The last component was subtracted from the total because that was the iron produced on the pyrite surface simply by the mixing action of pyrite in water.

The difference between the initial amount of Fe introduced to the system and the final Fe both on the mineral surface and in solution was determined. Applying the rinsing procedure, 84 to 99% of the iron in the system was accounted for in the iron balance (Table 4.6). In addition, good duplicate tests were obtained. In Section 4.1.2.3., the results for the dextrin adsorption kinetics are presented, which show that the rinsing stage also gave good repeatability for dextrin adsorption. The discrepancy in the iron balance ranged from 1 to 16%, which was judged acceptable, considering the procedure used. As expected, when conditioning with higher concentrations of ferrous sulphate solutions, the amount of iron on the surface of the mineral was generally greater (as determined by EDTA).

Table 4.6: Iron balance after treating pyrite with different concentrations of $FeSO_4 \cdot 7H_2O$, decanting and rinsing

$FeSO_4 \cdot 7H_2O$ conc (g/L)	EDTA extract (mg Fe)	mg Fe		% difference (Fe_f - Fe_i)/avg
		init	final	
0.1	0.178*	0.9	1.0	+ 11
0.5	0.282*	4.7	5.0	+ 6
1.0	0.354*	9.4	9.5	+ 1
DUPLICATE TESTS				
0.1	0.141**	1.0	0.9	- 11
0.5	0.328**	5.0	5.3	+ 6
1.0	0.300**	10.5	8.9	- 16

*Blank test: pyrite plus water generated 0.043 mg Fe in solution and 0.132 mg on the surface (EDTA extract) for a total of 0.175 mg Fe.
**Blank test: pyrite plus water generated 0.07 mg Fe in solution and 0.09 mg on the surface (EDTA extract) for a total of 0.16 mg Fe.

4.1.2.2. Ferrous versus ferric

It was demonstrated that when iron was present on the surface, dextrin interacted with pyrite. However, if this iron was present in solution as precipitates, and not on the surface of pyrite, the dextrin also reacted with these precipitates, giving a false high adsorption reading [4]. Table 4.7 shows the results of mixing dextrin solution with ferrous sulphate solution in the absence of mineral. A significant amount of dextrin was removed from solution, even though no mineral was present. This explains why just decanting the iron solution after conditioning was not sufficient to get neither accurate nor reproducible results. Certainly leaving any amount of ferrous sulphate solution in the flask prior to dextrin addition could lead to misinterpretation of the results.

Table 4.7: Dextrin plus 1.0 g/L $FeSO_4 \cdot 7H_2O$ solutions (no mineral)

gas injected	pH	color of ppt	mg dextrin removed from solution
none	5-6	orange	0.86
N_2	11	orange	2

Table 4.7 shows the removal of dextrin from ferrous sulphate solutions under nitrogen. The nitrogen was added in an attempt to keep the ferrous from oxidizing to ferric (identified by formation of orange precipitates). However, even under nitrogen, the green precipitates of ferrous hydroxides were not present. Dextrin abstraction was higher than the previous test with no gas injection. The difference could have been due to the higher pH yielding a greater mass of precipitates.

The ferrous solutions (no mineral) under nitrogen always gave orange precipitates (i.e. it was impossible to keep a sufficiently reducing environment to prevent ferrous from oxidizing to ferric). It was suggested that, since the analysis of dextrin with phenol involved a redox reaction, perhaps the presence of dextrin also caused a redox reaction between ferrous and ferric, making it difficult to maintain Fe^{2+}.

Finally, in the presence of pyrite, maintaining a reducing environment was possible (indicated by the presence of green precipitates) when nitrogen was injected for the entire time of mixing. Table 4.8 shows that less dextrin was adsorbed under those conditions. This could imply that dextrin was more reactive with ferric than ferrous ions. However, there was also the difference in operating pH to consider.

Table 4.8: Pyrite treated with 1.0 g/L $FeSO_4 \cdot 7H_2O$ (25 mL of iron solution left in flask when adding dextrin)

gas injected during dextrin	pH	color of ppt	dextrin ads (mg/g pyrite)
none*	6	orange	1.8
N_2	11	green	1.2

*N_2 injected only during ferrous sulphate conditioning

4.1.2.3. Dextrin adsorption kinetics

Figure 4.6 shows the dextrin adsorption kinetics after treating pyrite with ferrous sulphate solution (different concentrations: 1.0, 0.5, 0.1 g/L), decanting all of the Fe solution but no rinsing. All the tests were done in duplicate, as observed in the figure. There was a general trend: the more iron used during conditioning, the more dextrin was adsorbed (partly because decanting left iron precipitates to react with the dextrin, as shown previously). It was clear that a substantial amount of dextrin remained in solution and did not interact with the mineral surface.

Another observation made in each case was that, with time, a decrease in the amount of dextrin adsorbed occurred, meaning that some of the adsorbed dextrin had come off the mineral surface. This could indicate that interaction between dextrin and the mineral surface was weak and would eventually break. Mackenzie [39] has reported a "scrub-off" phenomenon experienced with organic depressants. As the mineral treated with organic polymers became overconditioned, the depressants tended to scrub-off the mineral surface, becoming less effective.

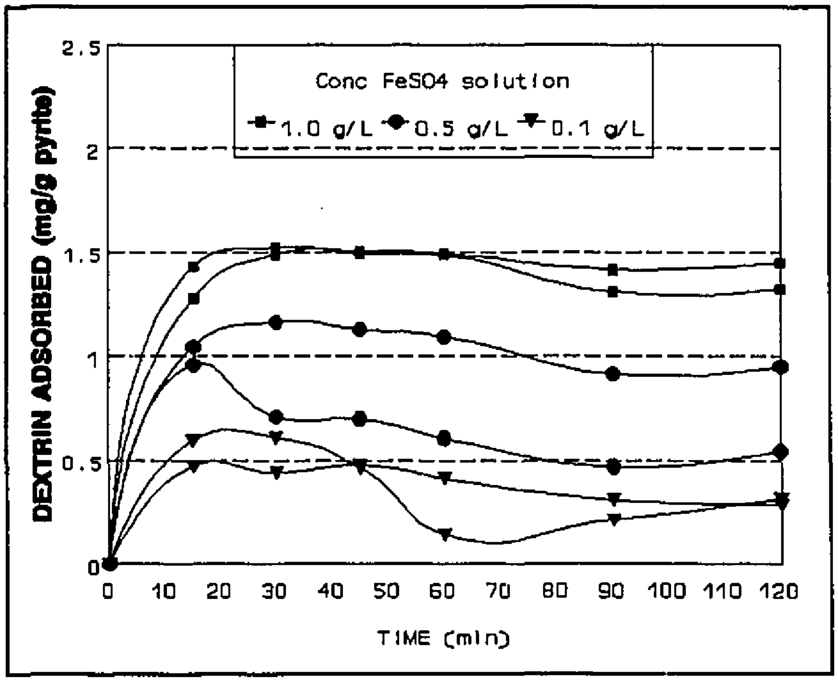


Figure 4.6: Dextrin adsorption kinetics after ferrous sulphate pretreatment (decant, no rinse) (initial dextrin, 2.5 mg/g pyrite)

Similar tests to those above with an additional rinsing stage were performed. The results, shown in Figure 4.7, revealed a significant reduction in the amount of dextrin adsorbed after rinsing, although it still remained much greater than that in the absence of any iron treatment. There was again a slight amount of dextrin desorption observed after an extended period of mixing.

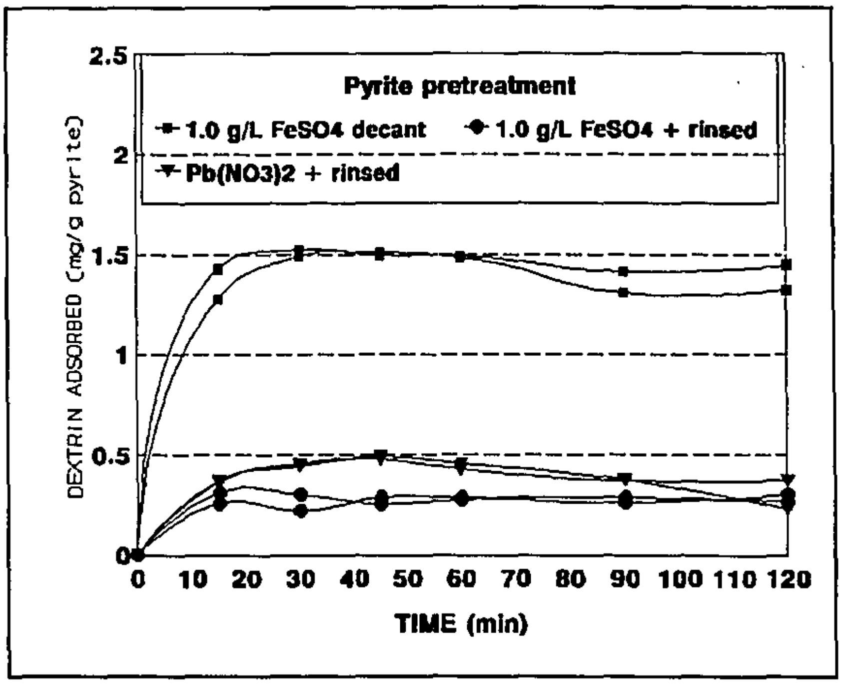


Figure 4.7: Dextrin adsorption kinetics after various pyrite pretreatments

4.1.2.3.1. Pretreatment with lead nitrate

The adsorption kinetics of dextrin after pyrite treatment with lead nitrate solution is also shown in Figure 4.7. The adsorption kinetics indicated that more dextrin adsorbed onto the lead treated surface than on the iron treated one. This could be due to the chemical reactivity of the metal ion present on the mineral surface as described in an earlier section (Section 2.5.3.).

4.1.2.4. Xanthate adsorption kinetics

Following the results of the dextrin adsorption studies, xanthate adsorption studies were carried out on pyrite samples that were pretreated with 1.0 g/L ferrous sulphate solution, decanted and rinsed, unless otherwise stated.

Figure 4.8 shows the xanthate adsorption kinetics. Also shown in the figure is a repeat of the above test but treating pyrite with dextrin for (a) 30 minutes and (b) 2 hours prior to adding xanthate.

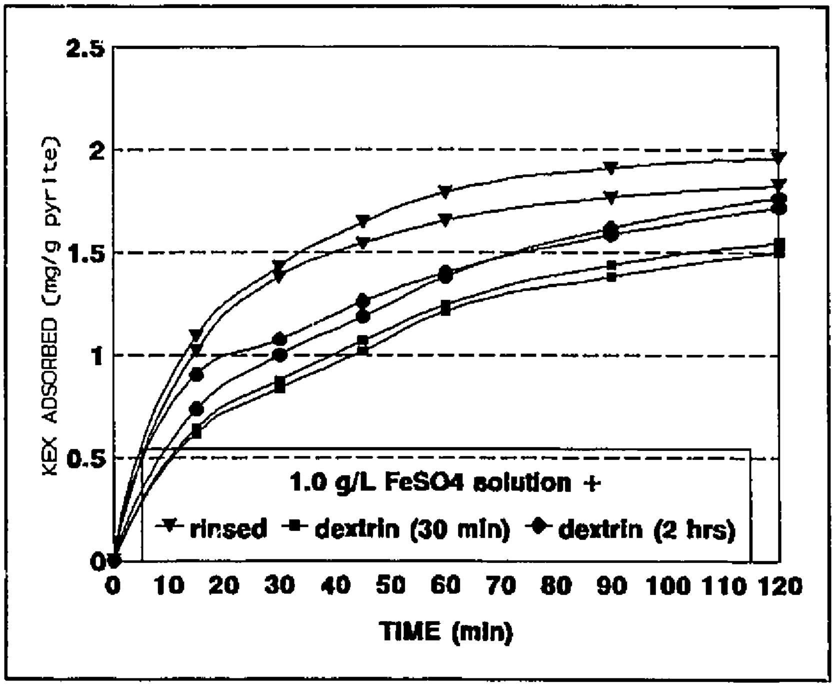


Figure 4.8: Xanthate adsorption kinetics after various pretreatment methods.

An important finding was that significantly less xanthate adsorbed onto the surface after being treated with dextrin for either 30 minutes or 2 hours of conditioning. Xanthate adsorption after conditioning pyrite with dextrin for 2 hours was higher than after only treating for 30 minutes. This corresponded well with the observed desorption of dextrin after extended mixing. Once again, desorption of dextrin from the mineral surface was observed during the kinetics studies. The shape of the kinetics curves under all conditions was similar, indicating that the mechanism of xanthate adsortion did not change in the presence of dextrin, but only the amount of xanthate adsorbed was less.

4.1.2.5. KEX-dextrin coadsorption tests

Six different cases with three conditioning sequences were tested: dextrin added prior to xanthate (D/X), xanthate added prior to dextrin (X/D), and xanthate and dextrin added simultaneously (X+D). The different dextrins studied were listed in Table 3.1 a). The conditions for the six tests are listed in Table 4.9.

The results of these tests (Figure 4.9) showed that xanthate adsorbed, no matter in which order it was added. However, for the first five tests (50 ppm KEX) there was a slight decrease in the amount adsorbed when it was added simultaneously with dextrin, and even less was adsorbed when added after dextrin (as seen in the kinetic study, Section 4.1.2.4.). In addition, the molecular weight and degree of branching of the dextrin added did not have an effect on xanthate adsorption. For the sixth test (5 ppm KEX) however, KEX adsorption followed the opposite trend with respect to the conditioning sequence. The differences in xanthate adsorption due to conditioning sequence may not have an effect on flotation because in all cases, there was still some xanthate present on the surface. The results of the microflotation tests in the following section will reveal which species will be dominant in determining floatability.

Table 4.9: Conditions tested in coadsorption studies (See Figure 4.9)

Test No.	Dextrin	conc. dextrin (ppm)	conc. KEX (ppm)
1	SD 501	50	50
2	SD 502	50	50
3	SD 503	50	50
4	SD 512	50	50
5	SD 513	50	50
6	SD 501	50	5

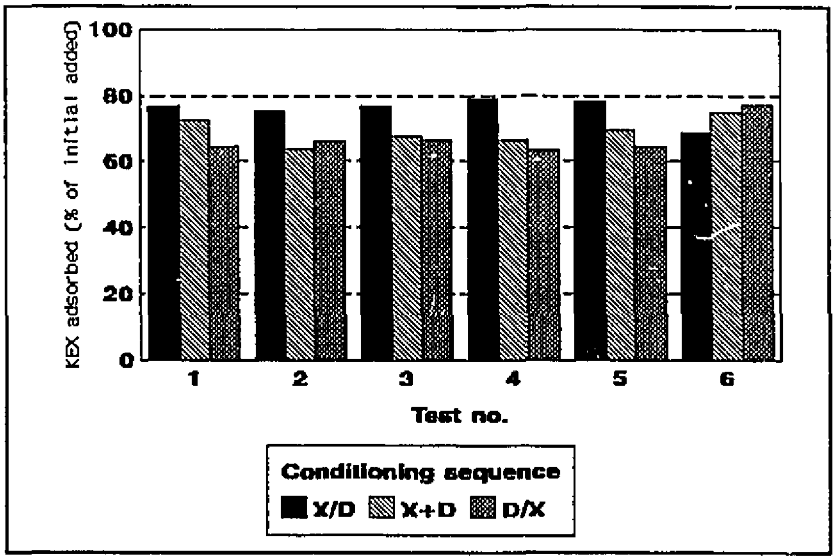


Figure 4.9: KEX adsorbed (% of initial added) vs conditioning sequence for six test conditions listed in Table 4.9.

4.2. Microflotation Results

4.2.1. No pyrite pretreatment

4.2.1.1. Initial tests

Microflotation tests on pyrite treated with xanthate and dextrin were conducted. The results of these tests were compared with the results of the previous adsorption studies.

Table 4.10 shows the results of the adsorption and flotation studies. A correlation between the amount of xanthate adsorbed and the flotation recovery of pyrite was observed for the pH range tested (pH 6 to 10). The order of reagent addition had an effect on xanthate adsorption, which had a corresponding effect on the floatability of pyrite. That is, when more xanthate was adsorbed, more pyrite floated.

Table 4.10: Amount of KEX adsorbed and pyrite recovery versus conditioning sequence (initial KEX = 2.5 mg/g pyrite)

Conditioning Sequence*	pH 6		pH 8		pH 10	
	KEX ads mg/g	Pyrite rec (%)	KEX ads mg/g	Pyrite rec (%)	KEX ads mg/g	Pyrite rec (%)
X	2.1 ±0.02	84 ± 1	1.9 ±0.01	85 ± 3	1.3 ±0.02	87 ± 1
X/D	1.4 ±0.03	78 ± 4	1.5 ±0.01	81 ± 1	0.7 ±0.01	62 ± 4
X+D	1.1 ±0.01	60 ± 9	1.1 ±0.01	54 ± 5	0.5 ±0.05	38 ± 4
D/X	0.8 ±0.02	62 ± 7	0.8 ±0.04	54 ± 7	0.3 ±0.02	32 ± 8
W	0	5 ± 1	0	9 ± 2	0	13 ± 4

* The conditioning sequences are abbreviated as follows: X = xanthate only added, X/D = xanthate added first, X+D = xanthate and dextrin added simultaneously, D/X = dextrin added first, and W = water only (i.e., no dextrin or xanthate added).
Initial KEX and dextrin = 50 ppm.

4.2.1.2. Effect of dextrin properties

Microflotation tests of the pyrite-dextrin-xanthate system at pH 6 were conducted to study the effects of:

(i) initial concentration of dextrin,
(ii) molecular weight of dextrin, and
(iii) degree of branching of dextrin.

The xanthate concentration in all of the above tests was 50 ppm.

Figure 4.10 shows the results of the microflotation tests with varying amounts of initial dextrin concentration and different conditioning sequences. The abbreviations shown in the figure (X, etc.) are the same used in Table 4.10 in Section 4.2.1.1. These tests were carried out using dextrin SD 501. In general, there was a trend of decreasing pyrite recovery with increasing dextrin concentration. The order of reagent addition also appeared to have an effect, corresponding to that observed during xanthate adsorption in the presence of dextrin.

Figure 4.11 shows the results of the microflotation tests using dextrins with different molecular weights. The initial dextrin concentration was 50 ppm. It appeared as if an intermediate size dextrin molecule gave the best pyrite depression.

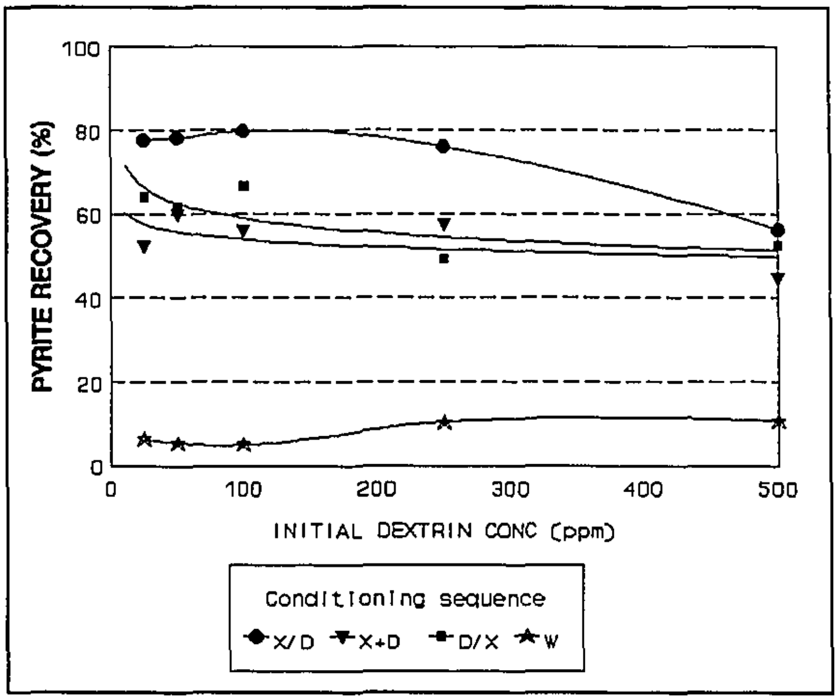


Figure 4.10: Recovery of pyrite versus initial dextrin concentration

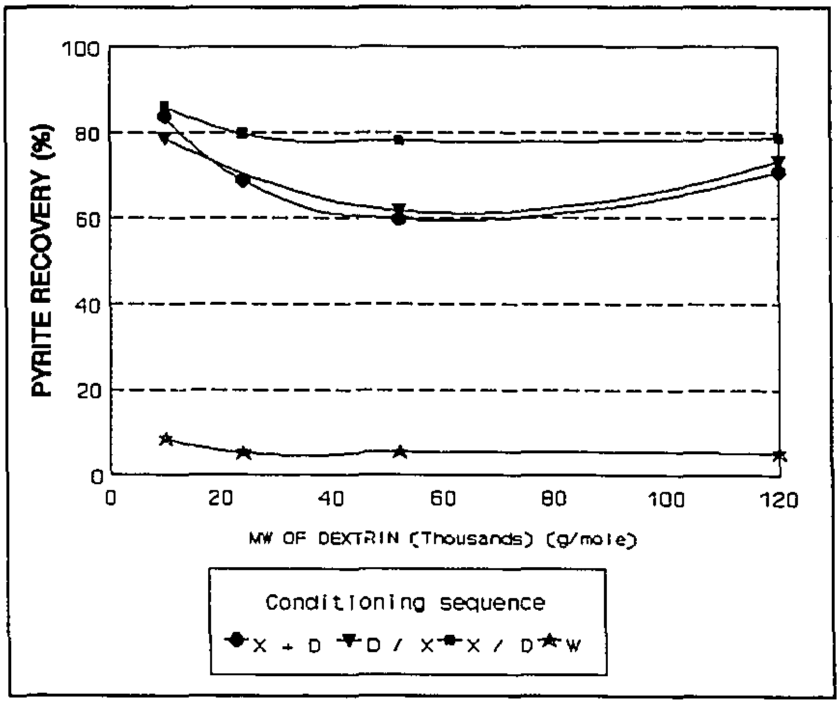


Figure 4.11: Pyrite recovery versus molecular weight of dextrin added

Figure 4.12 shows the results of the pyrite recovery versus the degree of branching of dextrin. Once again, the initial dextrin concentration added was 50 ppm. To cancel any effect that the molecular weight of dextrin may have had on the flotation response of pyrite, the dextrins chosen were all of similar weights. The molecular weights of the dextrins tested ranged from 20,400 to 24,000 g/mol. The type of dextrin used determined the degree of branching. Corn based dextrin is comprised of 25% amylose and 75% amylopectin. Therefore, these dextrins are referred to as having 75% degree of branching. Amioca and tapioca based dextrins contain 100% and 85% amylopectin, respectively. The results showed that pyrite was least depressed by the tapioca based dextrin and most depressed by the corn based dextrin when added simultaneously with xanthate. For the selected conditions, the absolute extent of dextrin depression was always small.

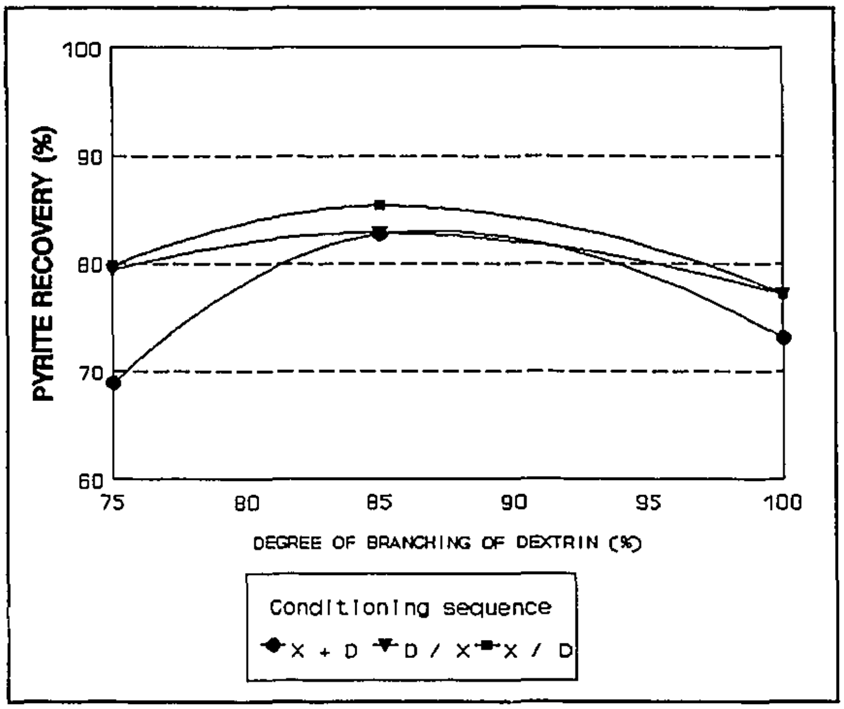


Figure 4.12: Pyrite recovery versus the degree of branching of dextrin added.

Above and beyond the amount of dextrin added or the molecular weight or degree of branching of dextrin used, the importance of the conditioning sequence on the degree of depression experienced by pyrite cannot be overlooked. The depressant action of dextrin was the strongest when dextrin was added before xanthate or in conjunction with it. Therefore, for the remainder of the testwork microflotation tests were performed after conditioning pyrite with xanthate and dextrin added simultaneously to observe the greatest amount of depression possible.

4.2.1.3. Pyrite recovery versus dextrin and xanthate concentration

The effect of the initial concentration of dextrin and xanthate on the flotation recovery of pyrite. The results (Figure 4.13) showed that the depressant action of dextrin increased as the concentration of KEX decreased. With 5 ppm KEX, only 5 ppm dextrin was needed to reduce pyrite recovery from ~50% to ~10%. When the xanthate concentration was increased to 50 ppm, 5 ppm dextrin only reduced pyrite recovery from ~70% to ~55%. The higher concentrations of xanthate almost eliminated the effect of dextrin.

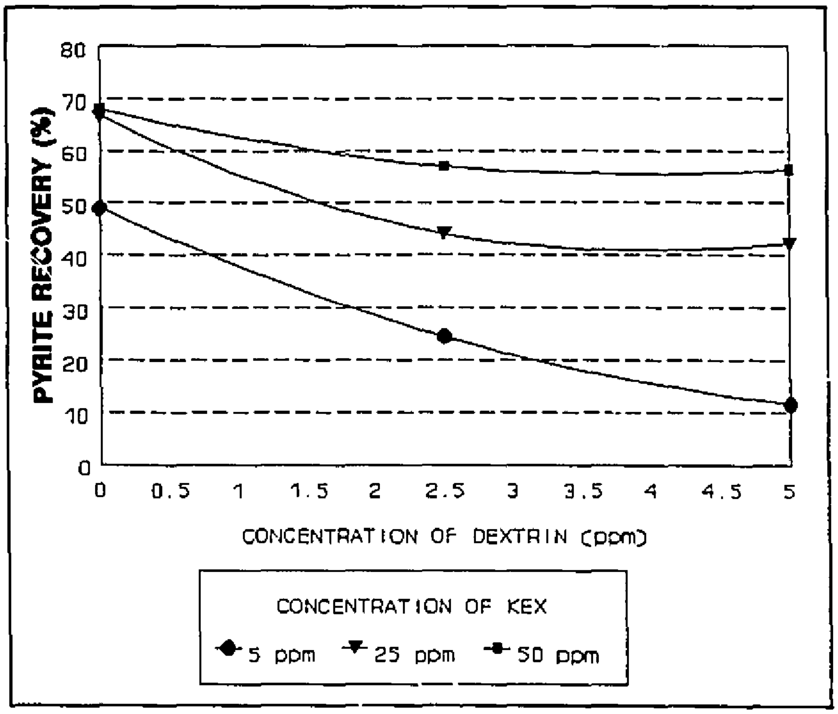


Figure 4.13: Pyrite recovery versus dextrin and xanthate concentration at pH 6.

4.2.1.4 Effect of dextrin type

The following tests were similar to the above tests in Section 4.1.1.2., except the concentration of xanthate was lowered to 5 ppm from 50 ppm, so that any effect dextrin may have had on pyrite would not be overridden by the effect of xanthate concentration. Once again the tests were conducted by adding dextrin and xanthate simultaneously. The tests were performed at pH 6. The effects of the molecular weight and degree of branching of dextrin on pyrite flotation are shown in Figures 4.14 and 4.15, respectively.

As the molecular weight of dextrin was increased, the recovery of pyrite was decreased. This could imply that the larger molecule was more successful at inhibiting xanthate from adsorbing on the mineral surface than the smaller dextrin molecule. This depressant mechanism would have to occur in the solution phase since no dextrin adsorption was observed during these tests. Noticeable changes in the flotation recovery were observed with as little as 1 ppm of dextrin.

Testing dextrins of similar molecular weights with different degrees of branching resulted in the lowest pyrite recovery (i.e., best depression) when dextrin was 100% branched. The flotation response of pyrite treated with 75% and 85% branched dextrins gave similar pyrite recoveries. Once again, at these low dextrin and xanthate concentrations with no dextrin adsorption occurring, the completely branched structure of dextrin appeared more effective at depressing pyrite, possibly by sterically interfering with xanthate adsorption.

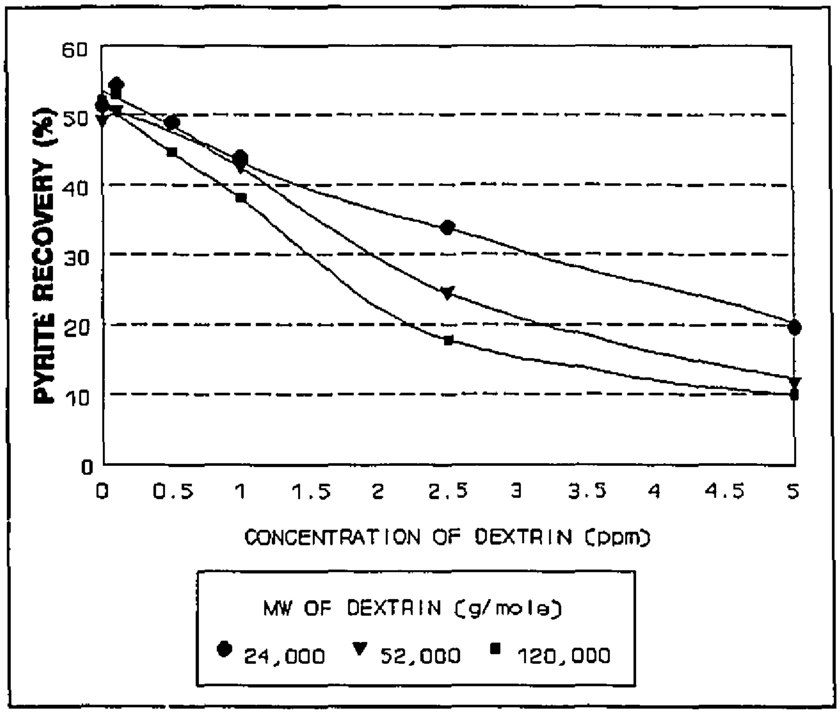


Figure 4.14: Pyrite recovery versus molecular weight of dextrin (5 ppm KEX conc)

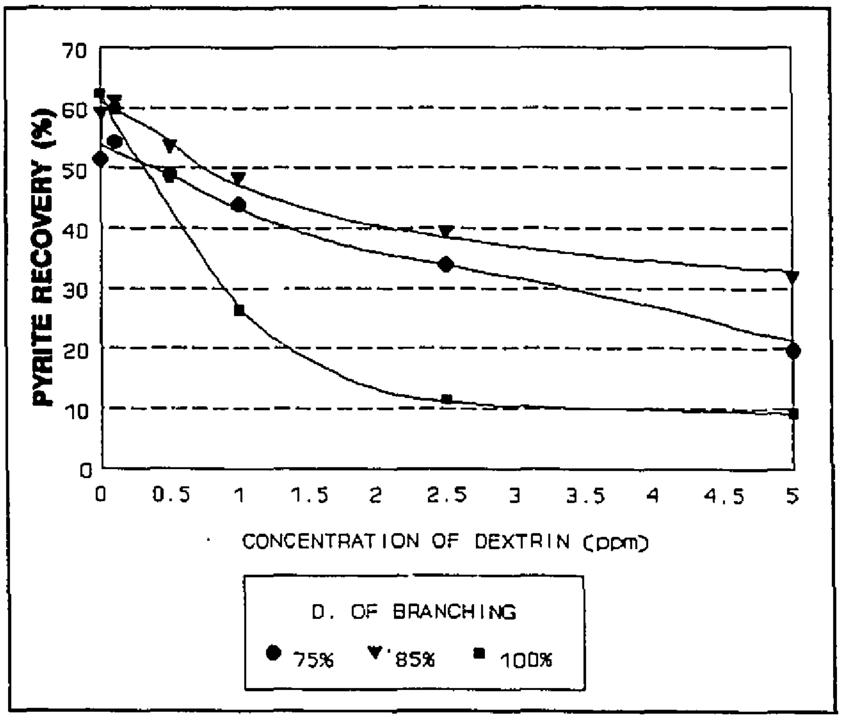


Figure 4.15: Pyrite recovery versus degree of branching of dextrin (5 ppm KEX conc)

4.2.2. Pyrite pretreatment

The results of the microflotation tests for pyrite, pretreated with ferrous sulphate solution prior to xanthate and dextrin conditioning, are shown in Figure 4.16. At low xanthate concentration, pyrite was easily depressed by low concentrations of dextrin. At higher xanthate concentration, the depressant action of dextrin was reduced. With 5 ppm KEX, pyrite was completely depressed with 5 ppm dextrin, as shown in the figure. With 50 ppm xanthate, complete depression of pyrite was never achieved, even at extremely high concentrations of dextrin (500 ppm). This may imply that at high xanthate concentrations, its effect on the mineral surface will always be felt over that of dextrin. This has important implications in plant operation, as overdosing of xanthate cannot be overcome just by adding more dextrin to the system.

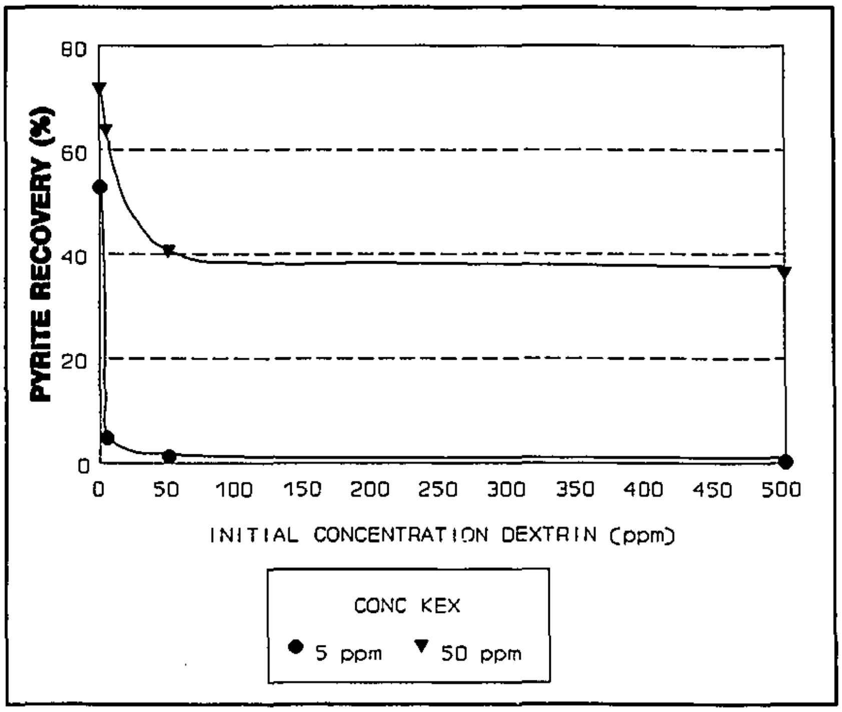


Figure 4.16: Pyrite recovery versus dextrin and xanthate concentration (with pyrite pretreatment)

Comparing the results in Figure 4.16 with those in Figure 4.13, depression was facilitated by pretreatment (i.e., when dextrin adsorption occurred). With 5 ppm KEX and dextrin, less than 5% pyrite was recovered when dextrin adsorbed while over 10% of pyrite floated when no adsorption occurred. This could imply that the depressant action of dextrin is a combination of mechanisms. For example, the mechanism could be based partly on inhibiting xanthate adsorption by dextrin in solution and partly by blocking xanthate adsorption sites by adsorbed dextrin molecules. The first component would require no dextrin adsorption while for the second component, adsorption would be necessary. Since in "real" systems metal ion contamination of surfaces will likely be present, the adsorption of dextrin would seem to be active.

4.3. Solution Tests

4.3.1. No pyrite pretreatment

4.3.1.1. Dextrin removing Fe ions from pyrite surface

A study to determine whether the presence of dextrin removed Fe ions from the surface of pyrite was carried out. The removal of iron ions from the mineral surface could cause a reduction in xanthate adsorption (a possible depressant mechanism).

The presence of dextrin did not appear to remove much Fe from the surface of the pyrite as compared to the removal ability of either EDTA or KEX (Table 4.11). Therefore, the reduction in xanthate adsorption observed in the previous studies was not caused by the lack of available Fe surface sites brought about by their removal by dextrin.

Table 4.11: Solution analysis for Fe after various conditioning sequences

Conditioning sequence	mg Fe/g pyrite
Water	0.05
D	0.05
X	0.26
X+D	0.12
D/X	0.14
X/D	0.26
EDTA	0.22

4.3.2. Pyrite pretreatment

4.3.2.1. Dextrin removing Fe ions from pyrite surface

Identical tests to those above in Section 4.3.1.1. were performed to determine whether the addition of dextrin to the pulp removed iron ions from the surface of pyrite after pretreatment. If dextrin was capable of removing iron ions from the surface of pyrite, it was more likely to occur in this set of tests since iron was more abundant compared with the mineral surface when no Fe pretreatment was applied.

The results (Table 4.12) were the same as when no pretreatment stage was used: dextrin did not remove iron ions from the surface. Therefore, the possibilty of the depressant mechanism of dextrin on pyrite being the removal of iron ions from the mineral surface, thereby reducing xanthate adsorption, has been rejected.

Table 4.12: Solution analysis

Pretreated?	Reagent	Mixing time	mg Fe/g pyrite
No	Water	30 min	0.05
Yes	Water	30 min	0.07
Yes	50 ppm dextrin	30 min	0.10
Yes	5 ppm dextrin	30 min	0.07
No	Water	2 hrs	0.13
Yes	Water	2 hrs	0.12
Yes	50 ppm dextrin	2 hrs	0.15
Yes	5 ppm dextrin	2 hrs	0.15

4.3.2.2. Pulp potential measurements

It is accepted that the adsorption of xanthate on pyrite occurs via the formation of dixanthogen [40]. The anodic reaction is:

$$2X^{-} \dashrightarrow X_2 + 2e \qquad E^{\circ} = 0.09\ V$$

The open circuit potential of pyrite in water is about 0.28 V (S.H.E.) [41]. Pyrite flotation generally occurs at potentials greater than 0.3 V (S.H.E.), which corresponds well with the oxidation of xanthate to dixanthogen.

The pulp potential (Ep) was recorded to determine whether the addition of dextrin lowered the oxidation state of the pulp, thereby lowering xanthate adsorption. The results are shown in Table 4.13. In this series of tests, no difference in pulp potential was observed between samples of pyrite that had been pretreated and not, or those that had been conditioned with dextrin except for possibly after pretreatment.

The results in Table 4.13 indicated that the pulp potential was reduced strongly in the presence of xanthate. Even when pyrite was conditioned with dextrin alone for 30 minutes to 2 hours, the subsequent addition of xanthate dictated the oxidation state of the pulp. The pulp potential behaved as if dextrin was not present.

The comparison of the pulp potential for pyrite samples that had been pretreated against those that had no pretreatment showed that the potential was slightly higher for the untreated pyrite samples.

The concentration of xanthate used in the tests was considerably higher than that normally used during flotation. The excess addition of xanthate was applied because the surface of these pyrite samples were later studied using DRIFTS, which required a relatively high dosage of xanthate in order to be able to detect it on the mineral surface.

Table 4.13: Pulp potential measurements of pyrite suspensions

Pretreated?	Conditioning Sequence	SD 501 (ppm)	KEX (M)	Ep (mV)**
No	Water only			284
Yes	Water only			279
No	Dextrin only	100 (30 min)***		262
No	Dextrin only	100 (2 hrs)		274
Yes	Dextrin only	100 (30 min)		213
Yes	Dextrin only	100 (2 hrs)		215
Yes	Xanthate only		0.0025*	-42
No	X+D	100	0.0025	-44
Yes	X+D	100	0.0025	-40
Yes	D/X	100 (30 min)	0.0025	-49
Yes	D/X	100 (2 hrs)	0.0025	-38

*0.0025M = 400 ppm KEX
**Pt sensing electrode, mV vs. Ag/AgCl
***time in ( ) indicate dextrin conditioning time prior to xanthate addition (if applicable)

Further pulp potential measurements were taken over concentration of xanthate in the range normally encountered during flotation. The results are shown in Table 4.14.

Table 4.14: Pulp potential measurements of pyrite pretreated samples

dextrin (ppm)	KEX (ppm)	Ep (mV)*
		279
5		239
50		234
500		259
	50	210
5	50	134
50	50	169
500	50	175
	25	212
5	25	146
50	25	168
500	25	203
50	5	235
500	5	199

*Pt sensing electrode, mV vs. Ag/AgCl

The addition of dextrin alone tended to lower the pulp potential, by 20 to 40 mV (as in Table 4.13). With the addition of xanthate alone, the pulp potential decreased by ~70 mV. With the addition of dextrin together with xanthate, the pulp potential was even lower, up to a decrease of 130 mV with a slight tendency for Ep to rise again as dextrin concentration increased. This could imply the existence of a synergistic effect of the dextrin and xanthate on reducing potentials, possibly contributing to depression of pyrite.

4.4. Surface Analysis

4.4.1. Initial investigations

To determine the effect of dextrin and iron pretreatment on pyrite, samples of pyrite were analyzed by DRIFTS. This method is surface specific and should be able to determine the nature of the species present on the surface of the mineral. The spectra were ratioed against that of clean pyrite and therefore represent the differences obtained due to treatment conditions.

The effect of iron pretreatment on the DRIFTS spectra was studied [Figure 4.17 (c)]. The spectrum comparing clean pyrite (i.e., no pretreatment) and pretreated pyrite samples showed peaks at 1129 and 1021 cm^{-1} indicating various oxide products on the mineral surface. These peaks were absent from the clean pyrite surface because of the storage procedure and the preparation of the mineral sample, specifically designed to eliminate oxidation products from the surface.

Spectra were obtained for pyrite samples, pretreated with ferrous sulphate, and conditioned with 5000 ppm dextrin for 15 minutes [Figure 4.17 (b)]. Peaks were observed between 1200 and 1000 cm^{-1}, similar to those present on the spectra of pure dextrin [Figure 4.17 (a)]. The presence of these bands suggested that dextrin was present at the surface of pyrite. However at this level of dextrin, it was possible that the dextrin was present as a thick layer on the mineral.

To determine the effect of xanthate in the absence of dextrin for pretreated pyrite, spectra were obtained from pyrite treated with 0.1 M ethyl xanthate [Figure 4.17 (d)]. Xanthate was present in the form of dixanthogen, by the observation of the two peaks at 1250 and 1020 cm^{-1} [42].

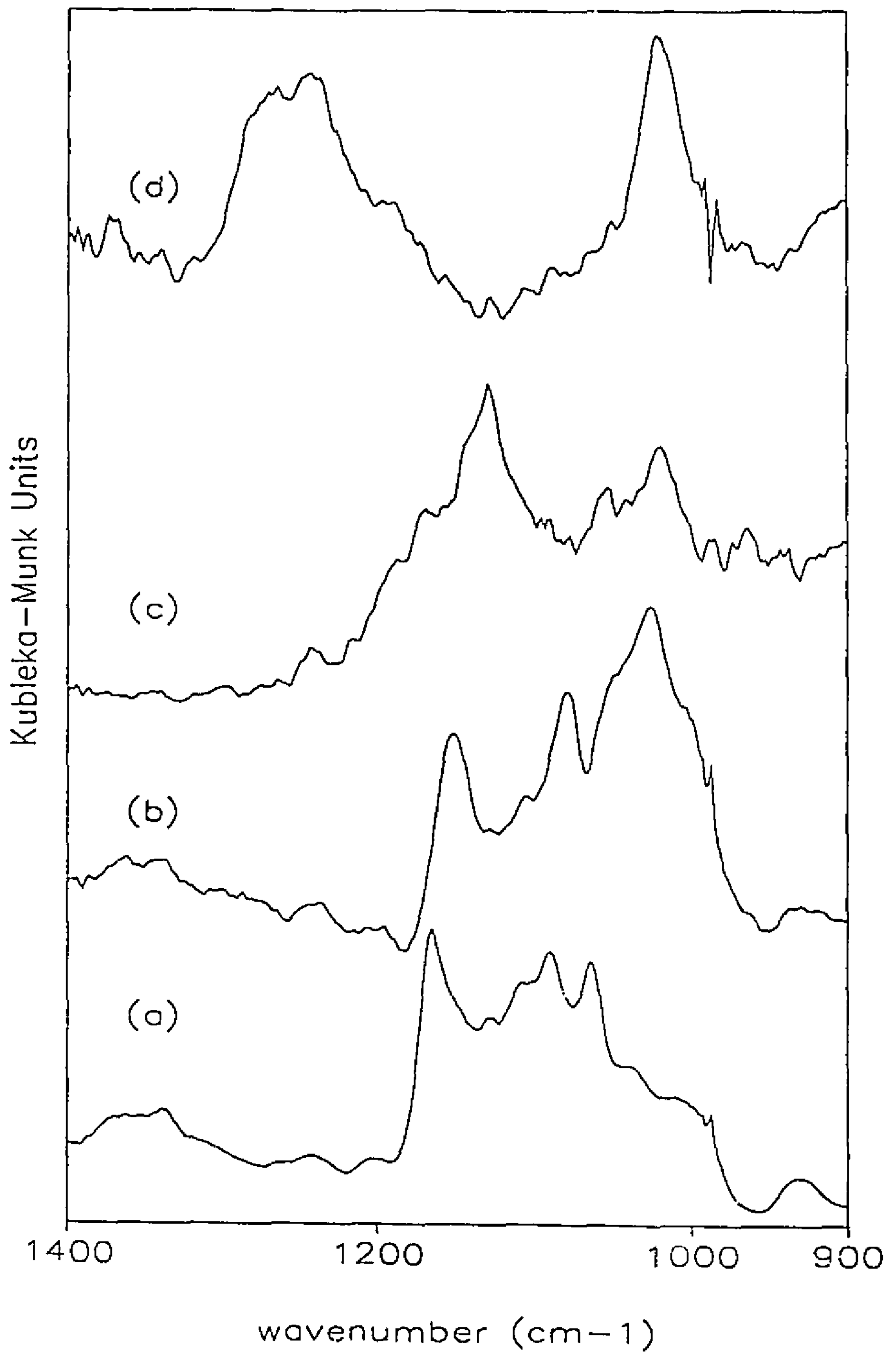


Figure 4.17: DRIFTS spectra, (a) dextrin, neat; (b) pretreated pyrite + 5000 ppm dextrin; (c) pretreated pyrite; (d) pretreated pyrite + 0.1 M KEX

4.4.2. Pyrite and dextrin

Samples of pretreated pyrite were conditioned with various concentrations of dextrin and the DRIFTS spectra were obtained. These experiments were conducted to determine the lower limit of detection for dextrin on the surface of pyrite. This concentration of dextrin would then be used for the next series of tests where pyrite would be conditioned with both dextrin and xanthate. The spectra of pyrite that had been treated with dextrin at 1000 and 100 ppm are presented in Figure 4.18 (b) and (c), respectively. The spectrum of bulk dextrin is shown again for comparison [Figure 4.18 (a)]. Spectral bands between 1200 and 1000 cm^{-1} were observed for dextrin concentrations as low as 100 ppm.

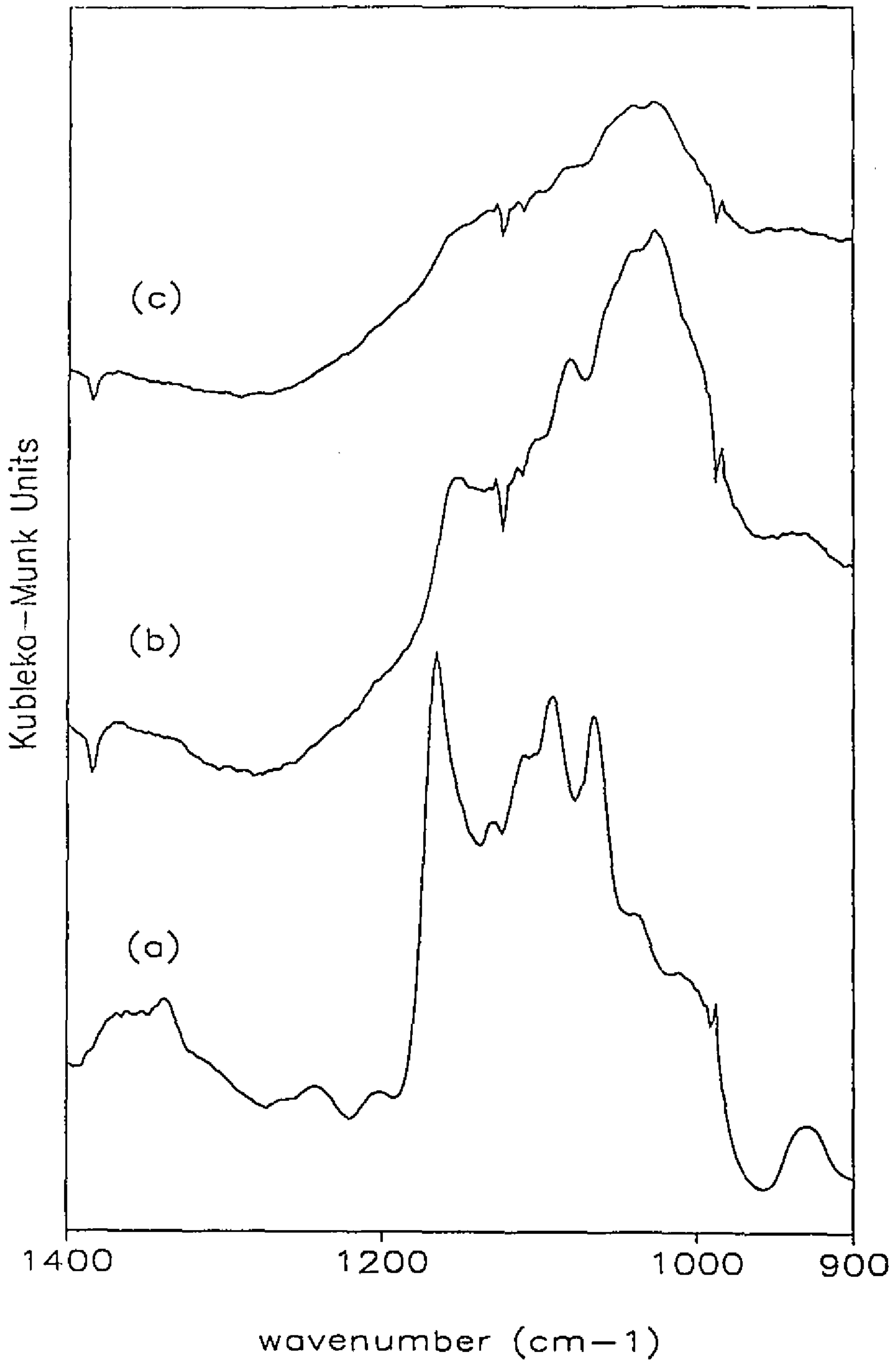


Figure 4.18: DRIFTS spectra, (a) dextrin, neat; (b) pretreated pyrite + 1000 ppm dextrin; (c) pretreated pyrite + 100 ppm dextrin

4.4.3. Pyrite and KEX

In a similar manner to that presented above, the lower detection limit for DRIFTS was determined for xanthate. Cases and coworkers [42] reported that DRIFTS could not detect the presence of diamyl dixanthogen on pyrite because it was insensitive to less than monolayer coverage. The concentrations of xanthate tested ranged from 0.01 M to 10^{-5} M. The spectra show that the dixanthogen doublet peaks can be observed only down to about 0.001 M KEX [Figure 4.19 (c)]. For the following series of tests, 0.0025 M KEX was used to condition the pyrite samples.

An interesting observation was made on the spectra of pyrite conditioned with 0.01 M xanthate (Figure 4.20). A doublet of peaks was present around 2070 and 2050 cm^{-1} and another around 1540 and 1520 cm^{-1} were observed. These bands represent the rotation-vibration bands of COS and CS_2 peaks respectively [42], indicating that at this level of xanthate, the surface layer had started to decompose.

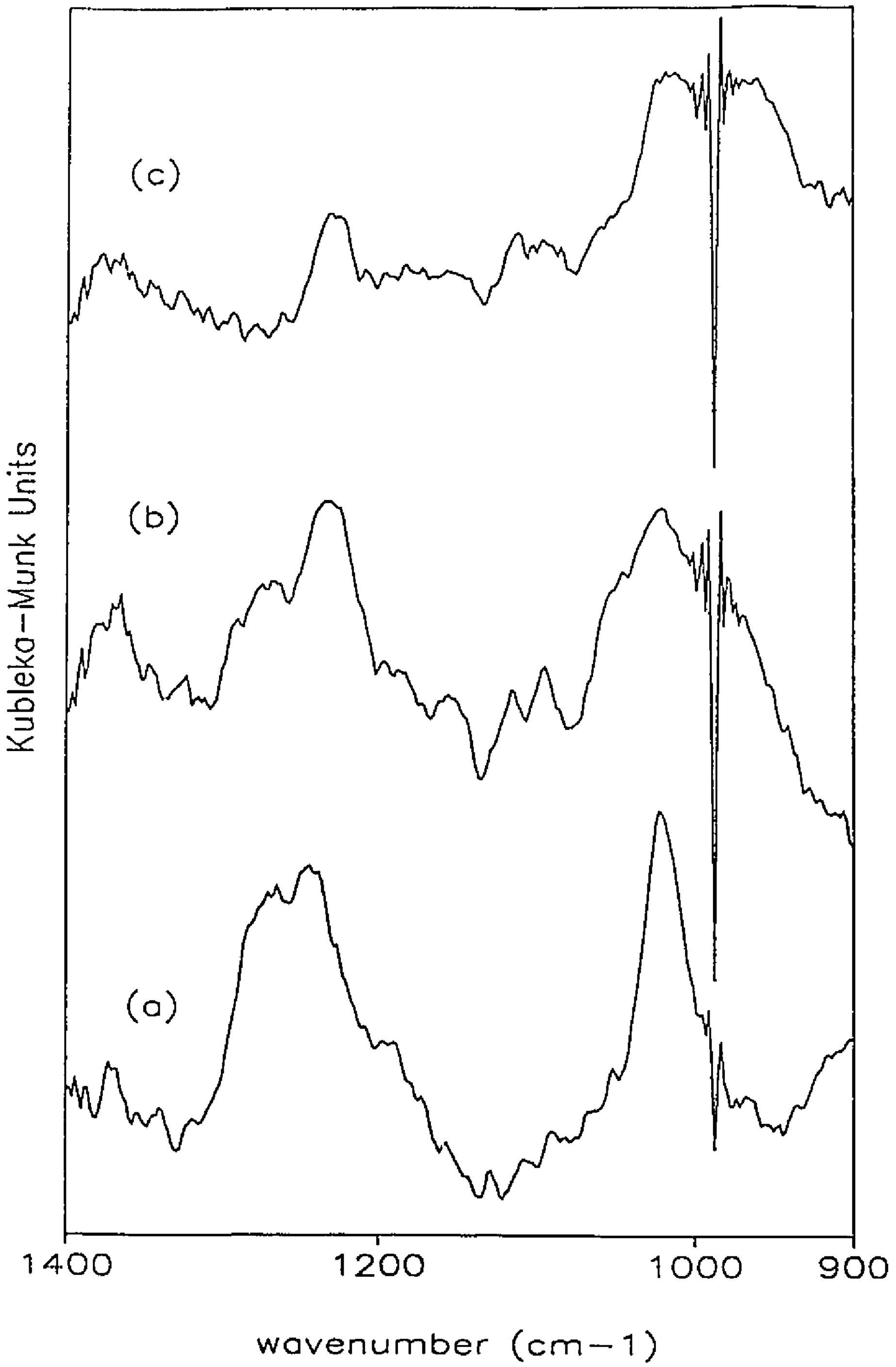


Figure 4.19: DRIFTS spectra, pretreated pyrite + (a) 0.1 M KEX; (b) 0.01 M KEX; (c) 0.001 M KEX

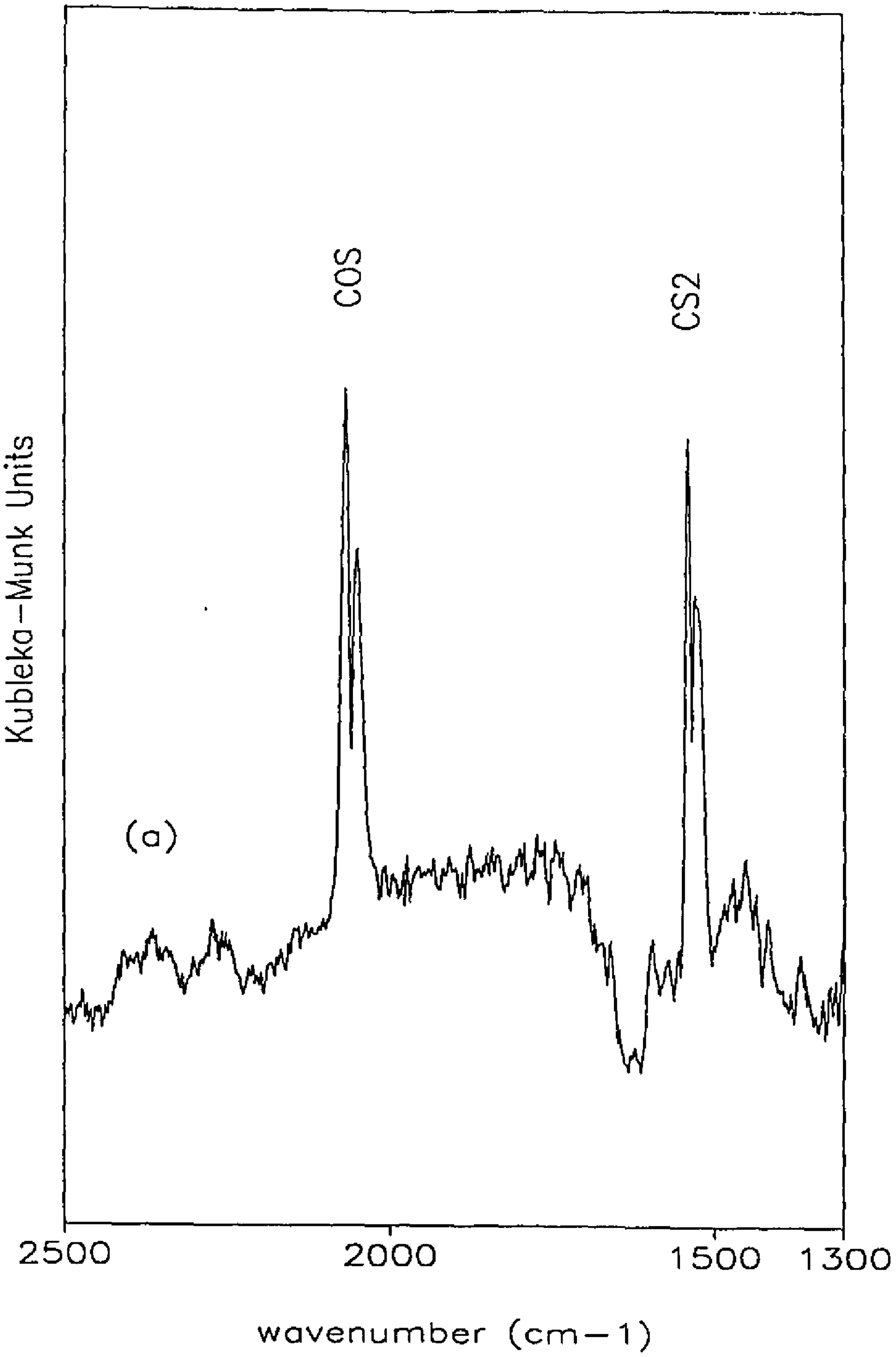


Figure 4.20: DRIFTS spectra, xanthate decomposition products on pretreated pyrite + 0.01 M KEX

4.4.4. Pyrite, dextrin and KEX

Figures 4.21, 4.22 and 4.23 show spectra for samples of pyrite under various conditions. Each figure shows three spectra. The top spectra (c) in each figure is for pyrite treated with both dextrin and xanthate for a given time. The bottom spectra (a) in each figure is pyrite conditioned with dextrin. The middle spectra (b) is pyrite conditioned with xanthate. The three spectra in each figure are presented to compare the peaks so that surface speciation can be attempted. Figure 4.21 shows the effect of dextrin and xanthate on untreated pyrite while Figures 4.22 and 4.23 show the effect of contact time of dextrin with pretreated pyrite (2 hours and 30 minutes, respectively).

Figure 4.21 (a) displays the spectra of clean pyrite conditioned with dextrin for 30 minutes. The peaks representing dextrin on the clean pyrite [Figure 4.21 (a)] were much less well defined compared with the corresponding spectra in Figures 4.22 (a) and 4.23 (a) (i.e., after pyrite pretreatment). There did not appear to be any differences dependant on dextrin treatment time in the spectra 4.22 (a) and 4.23 (a): three peaks were clearly visible in the range 1150 to 1020 cm^{-1}. These peaks were more distinct than in Figure 4.21 (a), suggesting that more dextrin was present at the pretreated pyrite surface than on the clean pyrite. The relatively sharper peaks present in Figures 4.22 (a) and 4.23 (a) with respect to the bulk dextrin [Figure 4.17 (a)] may indicate that the structure of the dextrin was more ordered on the surface than in the bulk. This may indicate that adsorption occurred at specific sites causing a certain orientation of the dextrin.

The spectra of pyrite treated with both xanthate and dextrin are presented in Figures 4.21 (c), 4.22 (c) and 4.23 (c). The presence of both xanthate and dextrin on the pyrite surface was evident in Figure 4.21 (c) for untreated pyrite. This indicated that the pyrite under these conditions had a surface containing both hydrophobic and hydrophilic sites. The dextrin peaks were somewhat distorted because of the intensity of bands associated with dixanthogen. The spectrum for treated pyrite [Figures 4.22 (c) and 4.23 (c)] showed some significant changes in the appearance of the peaks compared to the untreated pyrite [Figure 4.21 (c)]. On the clean pyrite sample, the dextrin peaks were extremely distorted, with almost elimination of two of the three peaks.

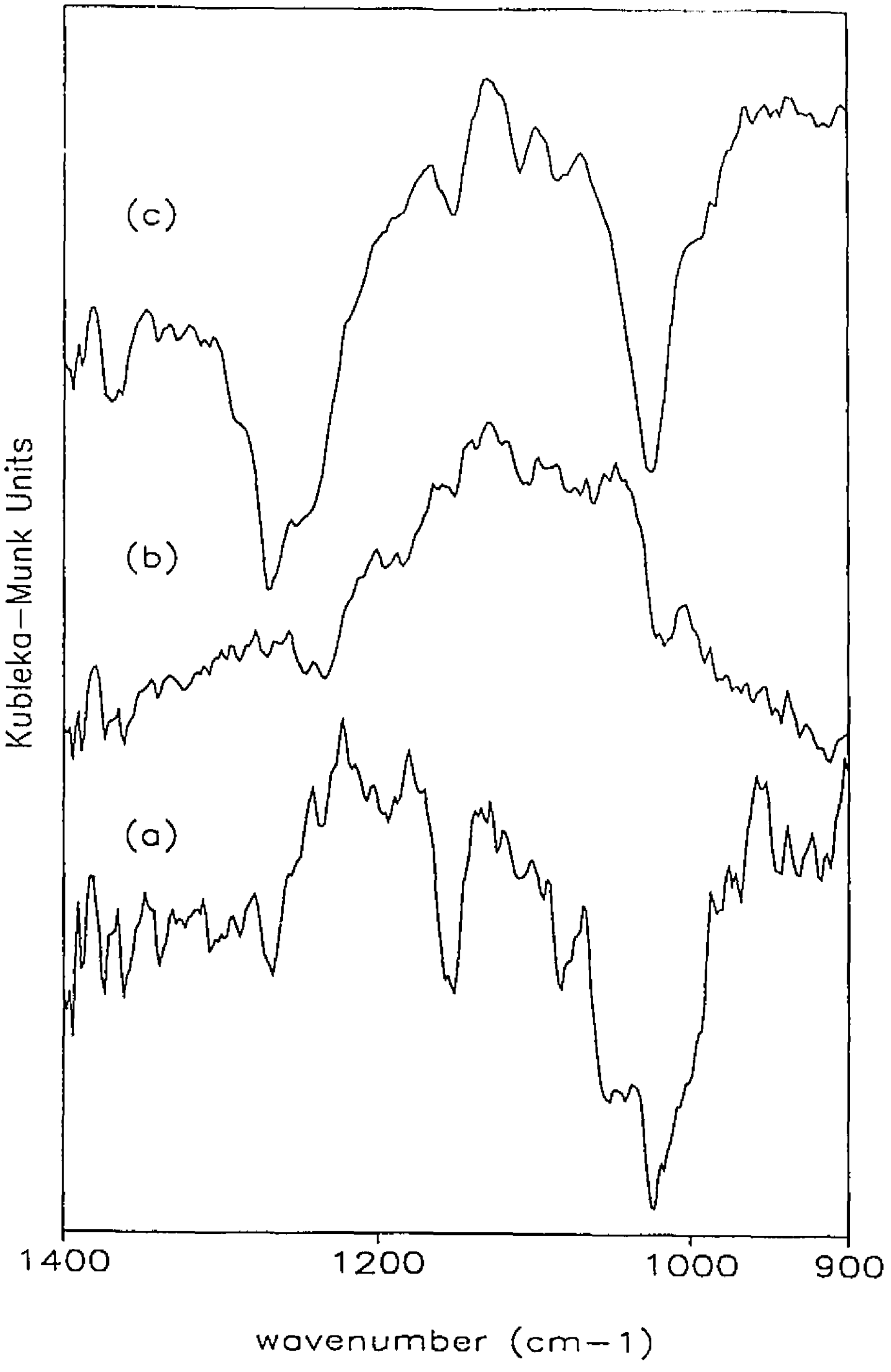


Figure 4.21: DRIFTS spectra, (a) untreated pyrite + dextrin; (b) untreated pyrite + 0.005 M KEX; (c) untreated pyrite + xanthate + dextrin

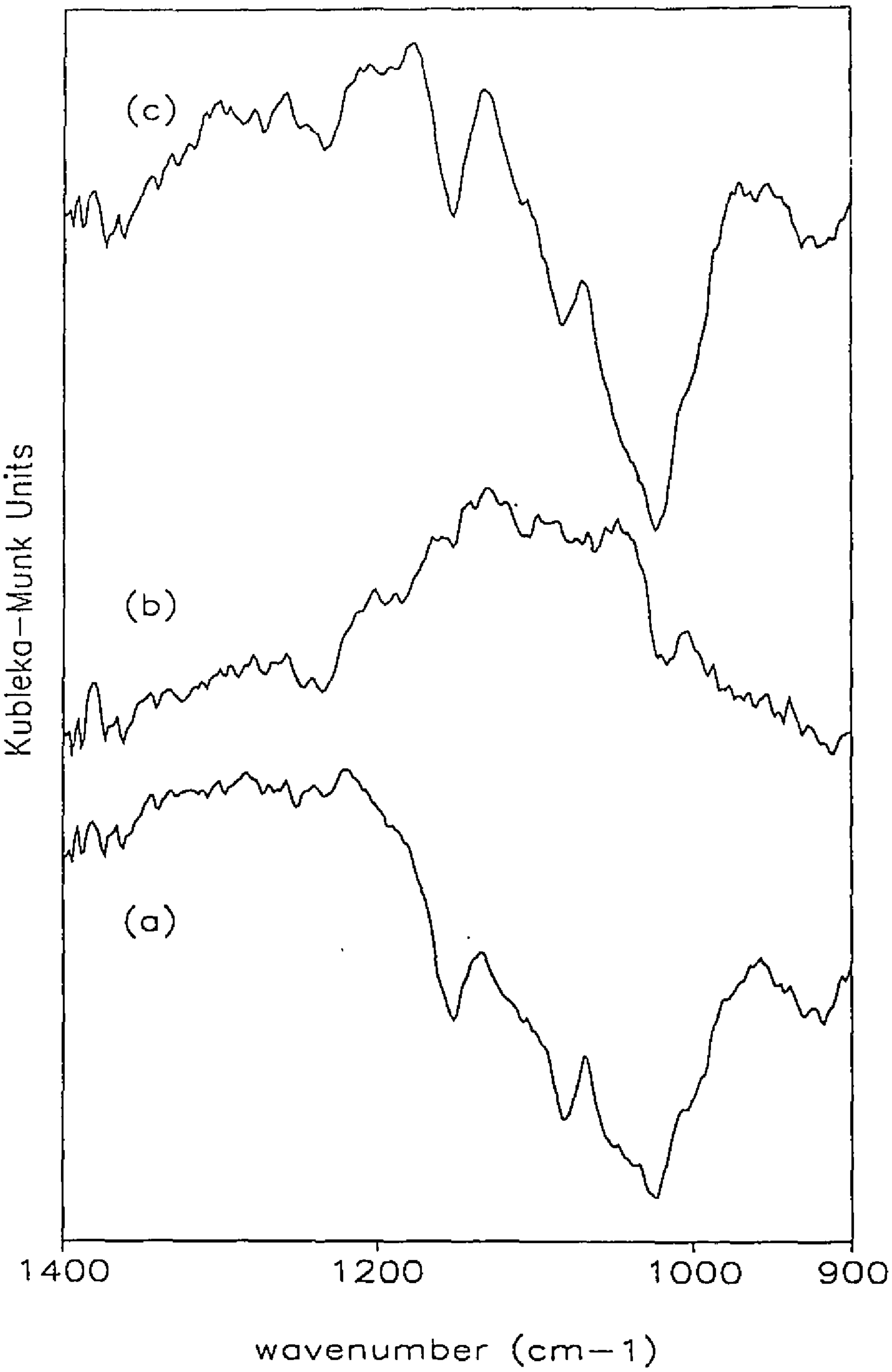


Figure 4.22: DRIFTS spectra, pretreated pyrite + (a) dextrin, 2 hours; (b) 0.005 M KEX; (c) dextrin, 2 hours and KEX

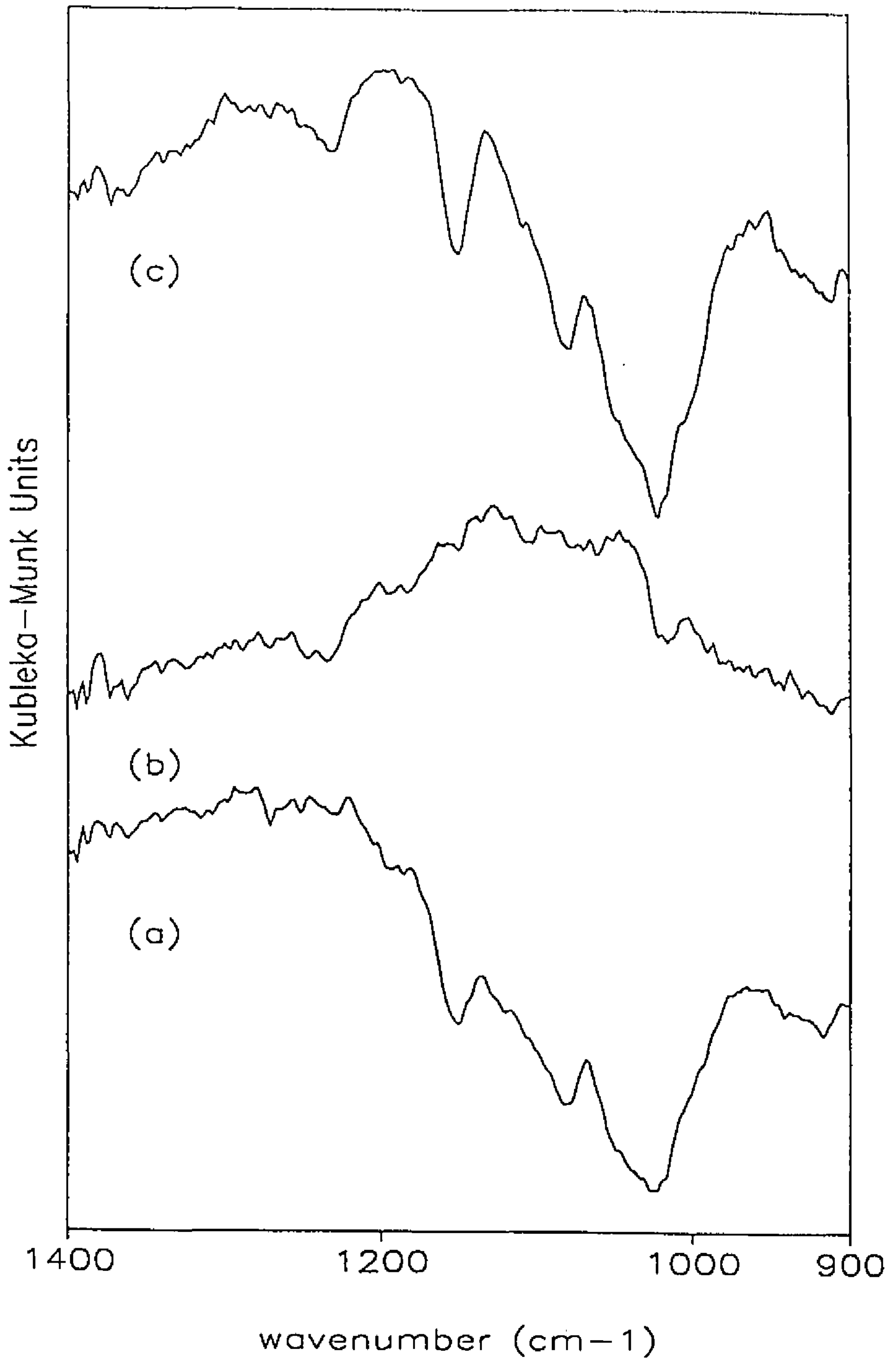


Figure 4.23: DRIFTS spectra, pretreated pyrite + (a) dextrin, 30 minutes; (b) 0.005 M KEX; (c) dextrin, 30 minutes and KEX

Dixanthogen peaks, visible in the 1270 to 1240 cm^{-1} range in Figure 4.21 (c) were absent in the spectra of the pretreated pyrite. This indicated that this hydrophobic species was absent from the surface. This last result suggested the reason for the depressant action of dextrin on pyrite. The presence of dextrin at the surface of the mineral inhibits the formation of dixanthogen. Pyrite under these conditions will not float.

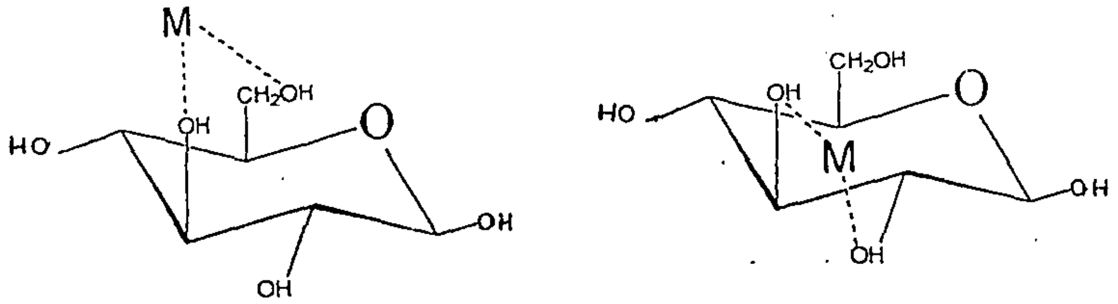
CHAPTER 5

DISCUSSION

The results of the adsorption studies showed the importance of the presence of metal ion species on the surface of pyrite for dextrin adsorption to occur. Dextrin adsorption was not observed on the pyrite samples that had received no pretreatment. Some adsorption was measured for the samples that were pretreated with ferrous sulphate solutions. Even greater dextrin adsorption occurred on the pyrite samples pretreated with lead nitrate. This suggested that not only the presence of metal ion species was important for adsorption, but the particular metal species also played a role. As mentioned in Section 2.5.3., Pb has been found to be more reactive than iron [5], and hence would be expected to interact more readily with dextrin (i.e., lead to increased adsorption). The results of the adsorption studies confirmed this.

Two possible mechanisms for the adsorption of dextrin are illustrated in Figure 5.1. In Figure 5.1(a), the metal ion M on the surface of the mineral bonds with the hydroxyl groups on the same side of the glucose ring. In Figure 5.1(b), the metal ion interacts with hydroxyl groups on opposite sides of the ring. Both conformations are possible, but from the IR spectrum, it is impossible to determine which structure would be more likely to occur. Liu and Laskowski [41] proposed that the structure in Figure 5.1 (b) would form, however they did not examine the exact structure. Any metal ionic site on the mineral surface could provide an anchor for the dextrin molecule. The presence of many metal ions on the mineral surface and the flexibility of the dextrin molecule would facilitate the adsorption of dextrin. The branched portion of the dextrin molecule would still be free to extend into the solution. Interactions with other surface sites (and even xanthate) would still be possible.

The adsorption and microflotation tests revealed that even when no dextrin adsorbed, pyrite/xanthate interaction was depressed. The pyrite samples with dextrin on the surface were depressed to a greater extent than those without, suggesting that dextrin on the surface acted more effectively as a depressant. This suggested there were two depressant mechanisms occurring, separately or in combination: (1) by hindering the adsorption of collector and/or (2) by rendering the mineral surface hydrophilic.



(a) (b)

Figure 5.1: Possible adsorption mechanisms for dextrin.

When both were present, the interactions between xanthate and dextrin determined the hydrophobicity of the mineral surface [43]. These interactions can change the extent of adsorption of both species and the orientation of the molecules, which could alter the surface characteristics of the mineral. The conformation of adsorbed dextrin could either permit or prevent the adsorption of xanthate. Because dextrin molecules are so much larger than xanthate molecules, it would be expected that the hydrophobicity of pyrite with both xanthate and dextrin on its surface would be governed by the properties of dextrin. However, if xanthate interacts with adsorbed dextrin molecules, this could modify the result.

The results of the KEX adsorption studies after dextrin treatment showed that more KEX adsorbed on the sample treated with dextrin for 2 hours than after only 30 minutes of treatment. This suggested that dextrin desorbed or that the orientation of the dextrin molecules changed in such a way that KEX can adsorb more readily. However, more KEX adsorbed when no dextrin treatment was applied, implying that dextrin did block KEX adsorption in some way, most likely by blocking surface sites.

Another example of the interactions affecting KEX adsorption was when pyrite was treated with a low concentration of KEX (5 ppm). With this low concentration, the amount of KEX adsorbed was less when added prior to dextrin than after. The interactions between the KEX and dextrin molecules could have caused KEX to become entangled in the long stretched out branches of adsorbed dextrin molecules, thus giving the appearance of being adsorbed.

Dextrin was observed to depress pyrite with no apparent adsorption on the samples receiving no pretreatment. A study was performed to determine whether dextrin stripped the pyrite surface of iron ions. Orthgiess and Dobias [44] found that the addition of complexing agents in salt-type mineral flotation resulted in decreased collector adsorption, but did not necessarily depress the mineral. They found no correlation between the decrease in collector adsorption and the degree of depression. The complexing agents tested did not adsorb onto the mineral, even when the mineral was depressed. It was postulated that dextrin was acting as a complexing agent in the same manner as the agent studied in [44].

Complexing agents such as DETA have been tested for pyrrhotite depression [45]. No adsorption of DETA was observed, although pyrrhotite depression was achieved. Through solution analysis, it was discovered that DETA was stripping the mineral surface of metal ions through complexation. This cleaning mechanism effectively inhibited the adsorption of collector onto the mineral surface, resulting in depression.

The results of this testwork showed no evidence of an increase of iron ions in solution after pyrite treatment with dextrin versus treatment with KEX. Therefore, this mechanism was dismissed as an explanation for the depressant action of dextrin on pyrite. Indeed, Nagaraj has noted that even though polysaccharides such as dextrin contain many hydroxyl groups, they do not possess strong complexing characteristics because the alcohols are quite weak donors [46]. Therefore, dextrin would not be expected to act as a complexing agent.

The mechanism of xanthate adsorption has been discussed on many occasions [e.g., 40, 47]. In an aqueous solution, each mineral has a specific rest potential. For pyrite, the rest potential is usually greater than the potential for xanthate oxidation, thus xanthate oxidizes to dixanthogen on the mineral surface, releasing hydroxyls into solution [40]. This mechanism of adsorption could cause an increase in pH. This could explain why in the adsorption studies with dextrin and xanthate on pyrite, no decrease in pH was observed, unlike during the studies of Liu and Laskowski [4]. If xanthate adsorption on the minerals tested did not involve OH^- release, any acid generated during dextrin adsorption would affect pH. For pyrite, the hydroxyls released during xanthate adsorption would neutralize any acid released during dextrin adsorption, and the pH could remain relatively constant.

Hornsby and Leja [47] emphasized the importance of potential in achieving collector adsorption. The potential must be sufficiently anodic (oxidizing) to develop a chemical bond between thio collector and sulfide mineral. The testwork here revealed that there was a synergistic effect on the pulp potential when pretreated pyrite was conditioned with both xanthate and dextrin. At high concentrations of KEX, any additions of dextrin had no effect on the pulp potential. However at KEX levels closer to those used for flotation, the presence of dextrin had an effect. Different amounts of KEX and dextrin added alone to pyrite had little effect on pulp potential. When added together, the pulp potential was lowered significantly. Once again, the interactions of the two molecules became a factor in determining the behaviour of the mineral in a pulp.

Hornsby and Leja [47] further stated that to obtain hydrophobicity, not only bonding is necessary, but sufficient density of the collector species. In some cases, electrostatic adsorption with reinforcing lateral bonds may produce a hydrophobic surface. They stressed the importance of collector adsorption relative to the bonding of water molecules, to determine the overall hydrophobicity of a mineral surface. In addition, the strength of the collector bonds, whether chemisorbed or physisorbed in nature, versus kinetic and hydrodynamic forces also determined the floatability of the mineral. For the adsorption of dextrin, the strength of the bonding appeared to be quite weak, as evidenced by the desorption observed after prolonged periods of shaking. This could have had an effect on its ability to depress pyrite, by being relatively unstable on the mineral surface.

The DRIFTS analysis revealed that on the untreated pyrite samples, the dextrin peaks were much less well-defined than on the pretreated pyrite. On pretreated pyrite the dextrin had a more ordered structure than on the untreated sample [48]. In fact, the dextrin peaks on the untreated pyrite could actually be dextrin lying on the surface, and not physically attached or bonded to the surface (regardless of the extensive rinsing applied). The more ordered structure could also imply that dextrin underwent a conformational change as it adsorbed on the surface of pyrite. Dextrin and starch molecules form helical structures in aqueous solutions under the proper conditions, as mentioned in Section 2.1.3. The change in conformation of the dextrin molecules observed in the DRIFTS spectra could indicate that specific segments of the dextrin molecule chemically reacted with the metallic sites on the mineral surface, while the hydrophobic portion of the helical structure interacted with hydrophobic sites on the mineral surface [49].

On untreated pyrite samples conditioned with KEX and dextrin, peaks for both reagents were visible. This implied that the surface of the mineral contained hydrophobic and hydrophilic sites. The overall floatability of pyrite in this case depended on the concentrations of each reagent, as shown in the flotation results.

On pretreated pyrite conditioned with KEX and dextrin, the resulting spectra showed significant differences compared to untreated pyrite under the same conditions. The peaks representing dixanthogen were missing from the spectra. It appeared as if xanthate was inhibited from forming dixanthogen on pretreated pyrite by the presence of dextrin.

This could lead to some insight into the mechanism of the depressant action of dextrin on pyrite. The synergistic effect of the combined presence of dextrin and KEX will reduce the formation of dixanthogen, thereby reducing mineral floatability.

However, these samples may still float. DRIFTS is unable to detect below monolayer coverage [42], while flotation normally occurs with less than monolayer coverage of collector. It has been shown that at low concentrations of KEX (5 ppm), pyrite can be completely depressed with equal additions of dextrin. But at higher concentrations (50 ppm), additions of dextrin 10 times greater than KEX cannot completely depress the mineral.

CHAPTER 6

CONCLUSIONS

The purpose of this thesis was to determine the mechanism of the depressant action of dextrin on pyrite. Through a series of tests, the following conclusions can be drawn:

1. Pyrite was depressed without apparent adsorption of dextrin. The adsorption tests revealed that on samples conditioned with dextrin prior to xanthate addition, less xanthate adsorbed, even though no dextrin adsorption occurred. The order of addition of xanthate and dextrin had an effect on the amount of KEX adsorbed. When xanthate was added prior to dextrin more KEX adsorbed than when added after dextrin conditioning. There was a correlation between the reduction in xanthate adsorption and the reduction in pyrite recovery. The "cleaning" mechanism whereby dextrin strips the mineral surface of metallic species was dismissed since no increase in metal ions in solution was detected after dextrin conditioning. Some degree of depression was achieved solely from interactions between dextrin and xanthate in solution, possibly by their effect on reducing the pulp potential.

2. The adsorption of dextrin was enhanced in the presence of metal ionic sites on the surface of the mineral. The nature of the metal species also played a role in determining the degree of dextrin adsorption. It was observed that the presence of lead ions on the pyrite surface resulted in greater dextrin adsorption than on the pyrite samples with iron ions on the surface. It has been postulated that the chemical reactivity of the specific metal was responsible for these differences. These observations are in general agreement with Laskowski et al. [5, 30, 31].

   In addition, the presence of precipitates in solution resulted in the removal of dextrin from solution. Reaction between the precipitates and dextrin effectively eliminated dextrin from solution. (In fact, no mineral was necessary to observe the removal of dextrin.) This emphasized the importance of the metallic sites on the mineral surface in order to achieve adsorption.

3. The formation of dixanthogen was inhibited on pyrite samples pretreated with ferrous sulphate solution in the presence of dextrin. DRIFTS analysis illustrated this by the reduction or elimination of the dixanthogen peaks from the spectra. The same reduction was not observed for untreated pyrite samples treated under the same conditions. The adsorbed dextrin on the pretreated samples inhibited dixanthogen formation. When no dextrin adsorption was observed, dixanthogen was able to form. Dextrin present in solution was not capable of preventing dixanthogen formation, even though it did act to block xanthate from the surface of the mineral. The combined presence of dextrin and xanthate on the pyrite surface resulted in a synergistic effect whereby dixanthogen formation was reduced thus reducing pyrite floatabilty.

4. Dextrin underwent a conformational change on the surface of pyrite as it adsorbed. The changes were observed by the differences between the DRIFTS spectrum of untreated pyrite samples and pretreated pyrite samples. With no metallic sites available on untreated pyrite, the only possible bonding would be hydrophobic bonding. The more well-defined spectrum of pretreated pyrite samples conditioned with dextrin implied a specific interaction between dextrin and the mineral surface (i.e., with the metal ionic sites).

The conformational change also revealed itself during the xanthate adsorption studies after conditioning pretreated pyrite with dextrin. More xanthate adsorbed on the sample that was conditioned with dextrin for 2 hours than after only 30 minutes of conditioning. It is possible that the dextrin molecules on the mineral surface were able to rearrange themselves during the 2 hours of conditioning in such a way that would promote xanthate adsorption. However, pyrite was still depressed to some extent so that the effect of xanthate adsorption did not completely override the effect of dextrin on the surface.

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