ADSORPTION OF POLYSACCHARIDES ON PYRITE AND THEIR UTILISATION AS DEPRESSANTS

POLİSAKKARİTLERİN PİRİT YÜZEYİNE SOĞURUMU VE BASTIRICI OLARAK KULLANIMI

ÖZLEM BIÇAK

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Özlem Bıçak

ABSTRACT

In this thesis, adsorption mechanisms of two types of polysaccharides (namely CMC and Guar Gum) having different chemical and structural properties on pyrite are discussed in detail based on micro-flotation, zeta potential measurements and adsorption tests.

The effects of depressant type and dosage, pH, degree of oxidation, ultrasonic treatment and calcium ions on the flotation behaviour of pyrite were investigated. Micro-flotation experiments, zeta potential measurements and adsorption test were performed to clarify the adsorption mechanism and to determine the conditions for the uptake rates of these depressants on pyrite surfaces.

Guar was very effective depressant for pyrite at even very low dosages however CMCs were ineffective depressant for pyrite except at very high dosage. The results showed that strong depression of pyrite was achieved as the guar molecular weight was increased. Relatively high depression was achieved as the degree of substitution of CMC was decreased. Calcium ion addition increased the depressive performance of CMCs but there is no effect on guar adsorption on pyrite.

The adsorption isotherms follow Langmuirian behaviour for both guar gum and CMC. Guar adsorption was attributed to hydrogen bonding at pH 5 and Bronsted acid base interaction at alkaline pH values. However CMC adsorption was attributed to both electrostatic interaction and Bronsted acid base interaction.

Keywords: Flotation, depressants, polisaccharides, pyrite, adsorption.

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ÖZ

Bu çalışmada guar gum ve CMC türü farklı kimyasal ve yüzey özelliklerine sahip iki farklı polisakkaritin soğurum mekanizması, mikroflotasyon, zeta potansiyel ve soğurum testleri ile araştırılmıştır.

Bu deneylerde bastırıcı türü ve dozajı, pH, oksitlenme derecesi, ultrasonik banyo ve kalsiyum iyonlarının piritin flotasyon davranımına etkisi incelenmektedir. Yapılmış olan mikroflotasyon, zeta potansiyel ve soğurum çalışmaları ışığında polisakkarit soğurumunun maksimum olduğu koşullar ve polisakkaritlerin pirit yüzeyine soğurum mekanizması araştırılmıştır.

Sonuçlar guarın çok düşük dozajlarda bile pirit için çok etkili bir bastırıcı olmasına rağmen CMC'nin çok yüksek dozajlar hariç pirit için etkisiz olduğunu göstermiştir. Ayrıca guarın molekül ağırlığı arttıkça CMC'nin ise yer değiştirme derecesi azaldıkça, soğurumun arttığı gözlenmiştir. Kalsiyum iyonun eklenmesi CMC'nin bastırma performansını arttırıken guarın soğurumu üzerinde etkisi olmamıştır.

Çalışılan guar ve CMC ler için soğurum izotermleri her iki polisakkaritinde soğurumun fiziksel olduğunu gösteren Langmuir tipi soğurum izotermi olarak bulunmuştur. Guar soğurumunun pH 5'te hidrojen bağları ile bazik pH larda ise Bronsted asit baz etkileşimi olarak gerçekleştiği düşünülmektedir. Buna karşılık CMC soğurumunun hem elektrostatik etkileşim hem de Bronsted asit baz etkileşimi ile pirit yüzeyine soğurulduğu düşünülmektedir.

Anahtar Kelimeler: Flotasyon, bastırıcılar, polisakkaritler, pyrite, soğurum.
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1. INTRODUCTION

The concentration of minerals by froth flotation depends primarily upon the differences in the hydrophobicity (or wettability) of mineral particles. Mineral particles to be floated must selectively attach to air bubbles; the particle bubble aggregates then rise through the pulp phase up to the froth phase. A few minerals like talc, sulphur, graphite, stibnite, coal and molybdenite are naturally hydrophobic as a result of preferential cleavage along planes that have all chemical bonds satisfied (Woods, 2003); therefore, they can be floated without collectors.

Polymeric depressants are used to prevent flotation of talcaceous minerals especially in the South African platinum industry (Robertson, 2003). The two most commonly used classes of depressant are carboxymethyl cellulose (CMC) and guar gum. One of the major differences between these two polysaccharides is that CMCs are negatively charged in solution whereas guars are typically only slightly charged. As a result of this charged nature, CMC adsorption can induce particle dispersion in addition to having a depressant effect.

Polysaccharide type depressants are typically water soluble polymers that adsorb onto the mineral surface. They are typically substituted with various hydrophilic functional groups so their adsorption leads to a decrease in the hydrophobicity of the surface.

Pyrite (FeS_2) is the most widespread and abundant of naturally occurring metal (iron) sulfides. It is commonly present in base metal sulfides and frequently appears in coal as a major source of sulfur in coal and as the main sulphide gangue mineral in sulphide ores. Pyrite lowers the quality of base metal concentrates and increases the amount of sulfur compounds produced in the base metal extraction processes. Therefore, depression of pyrite is desirable in the concentration of base metal sulfides by depressants.

Selective flotation of sulphide minerals from a complex sulphide ore is generally difficult to achieve without loss in recovery since most of the sulphide minerals are readily floated with short chain collectors, or indeed without collectors under certain chemical conditions. Selective flotation against pyrite is best achieved at strongly alkaline pH values (pH>11) in the presence of inorganic depressants such as sulphur dioxide, sodium metabisulphite, sodium sulphite and sodium cyanide. However, most of these types of depressants are toxic and aggravate environmental problems. Therefore, in recent years research has focused on the use of organic depressants which are non-toxic and naturally degradable reagents in place of these inorganic depressants.

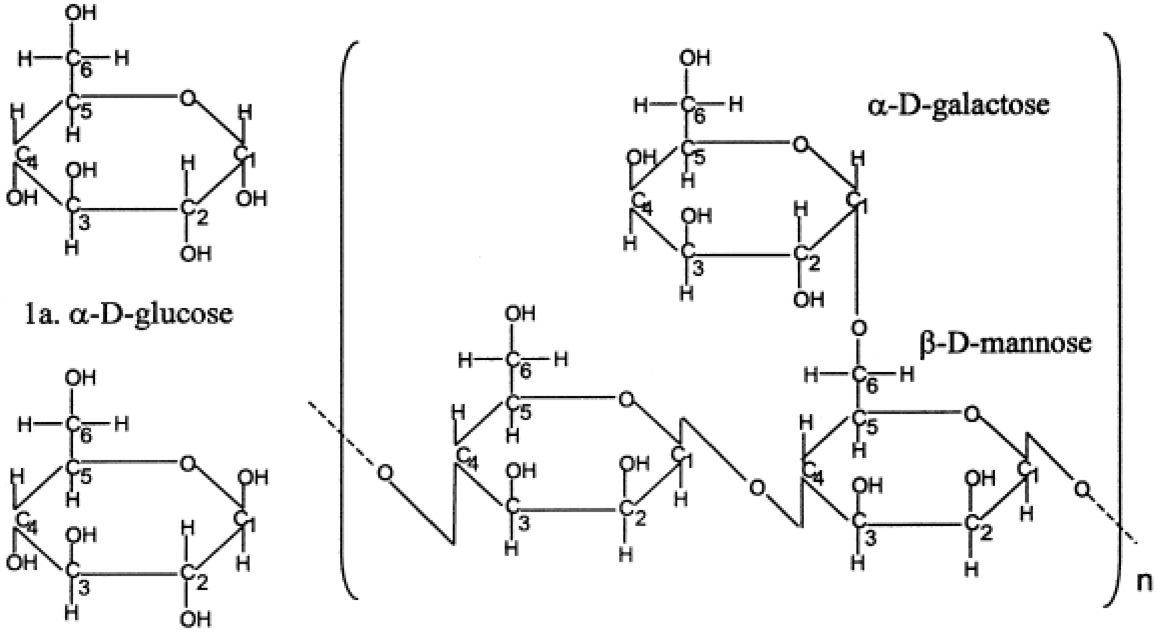
The main objectives of this thesis were to investigate the use of polysaccharides (using two different types as CMC and Guar Gum) as depressants for pyrite, to elucidate their adsorption mechanisms on pyrite and discuss the differences based on their chemical structure. Microflotation tests, zeta potential measurements and adsorption tests were performed to investigate effects of various operating parameters such as pH, sonification, dissolved oxygen concentration of the solution and, molecular weight and degree of substitution of the depressants.

1.1. Polysaccharides

The basic structural units of polysaccharides are sugar monomers. Various polysaccharides are built of many different types of such monomers joined together in different ways. Starch, dextrin, cellulose and guar gum are the polysaccharides that have been most extensively used in mineral processing and only these polysaccharides will be discussed. Cellulose and starch are the most abundant and most important natural polysaccharides. They are found in various plants. Both are made of D-glucose monomers. The D-glucose monomers have a cyclic structure that is made of five carbon atoms and one oxygen atom. The hydroxyl groups attached to the carbon atoms at position 1 C-1 can have either of two orientations, α and β Figure 1.1.a and b, which represent the axial and equatorial positions, respectively. Starch is made of the α-D-glucose and cellulose is made of the β-D-glucose. Cellulose is a linear polymer in which the β-D-glucose monomers are joined by the C-1–C-4 connections. Starch, on the other hand, consists of two fractions, a linear polymer Amylose, which contains the α-D-glucose monomer joined through C-1–C-4 connections, and a branched polymer Amylopectin, which contains the α-D-glucose monomers joined through both C-1–C-4 and C-1–C-6 connections. In D-glucose, the hydroxyl groups attached to C-2 and C-3, and the CH_2OH groups attached to C-5, are all in equatorial positions (Davidson, 1967).

Guar gum (Fig 1.2) is a branched polysaccharide belonging to the group of galactomannan. Structurally, it is made of a straight chain of β-D-mannose connected through C-1–C-4 linkage with attached α-D-galactose units through C-1–C-6 linkage every second β-D-mannose monomers Figure 1.1.c . The α-D-galactose is similar to α-D-glucose except that the –OH on C-4 is in axial position. The β-D-mannose is similar to β-D-glucose. However, the –OH group on C-2 is in axial position rather than equatorial. This makes the two –OH groups on C-2 and C-3 in a A *cis* B conformation, i.e., they are on the same side of the monomer ring. It is known that the two –OH groups on C-2 and C-3, when in the *cis axial-equatorial* conformation or in the *trans diequatorial* conformation, can participate in complexation reactions (Davidson, 1967).

Dextrin naturally degrades to carbon dioxide and water. Dextrin is derived from starch by partial thermal degradation under acidic conditions. The treatment causes the break down of starch macromolecules resulting in smaller molecules that are more branched (dextrin). The structure of dextrin is given in figure 1.3 and resembles amylopectin. All the three hydroxyl group (–OH) in the glucose monomeric unit may rotate in such a way that they face one side of the monomeric ring, making that side hydrophilic. The opposite side is consequently slightly hydrophobic due to the exposed –CH groups.



1a. α-D-glucose

1b. β-D-glucose

1c. Galactomannan

Figure 1.1. Structural units of polysaccharides commonly used in mineral flotation. a-D-glucose is the basic unit for starch and dextrin; b-D-glucose is the basic unit for cellulose, and c-galactomannan is the basic unit for guar gum (Liu et.al., 2000).

All the three hydroxyl groups –OH in the glucose monomeric units may rotate in such a way that they face one side of the monomer ring, making that side hydrophilic. The opposite side is consequently slightly hydrophobic due to the exposed –CH groups. In fact, in aqueous solutions, amylose forms a helix with six glucose monomers per turn. The interior of the helix is hydrophobic, whereas the outer shell is hydrophilic (Foster, 1965).

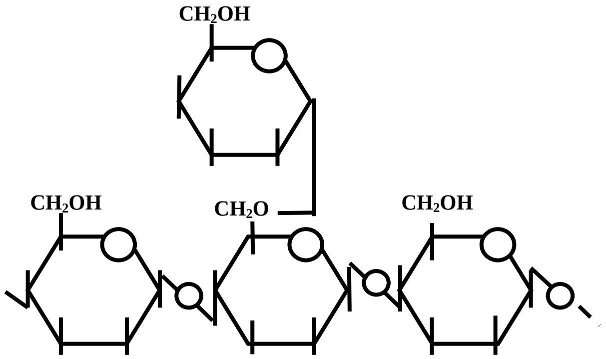


Figure 1.2. Schematic diagram of molecular structure of guar gum (Shortridge et.al., 2000)

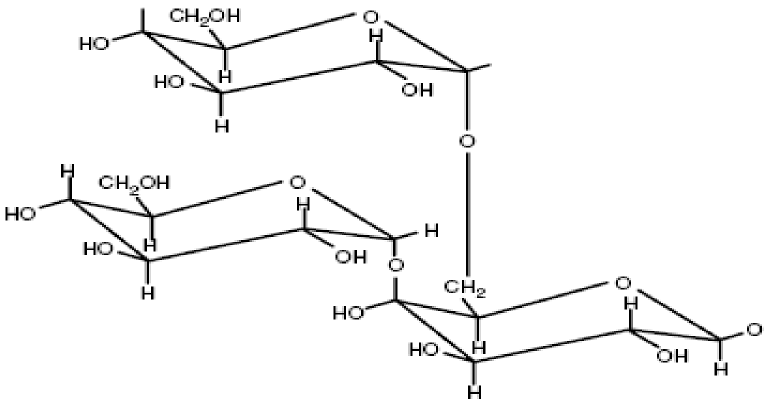


Figure 1.3. Schematic of the molecular structure of dextrin (Valdivieso et.al., 2004).

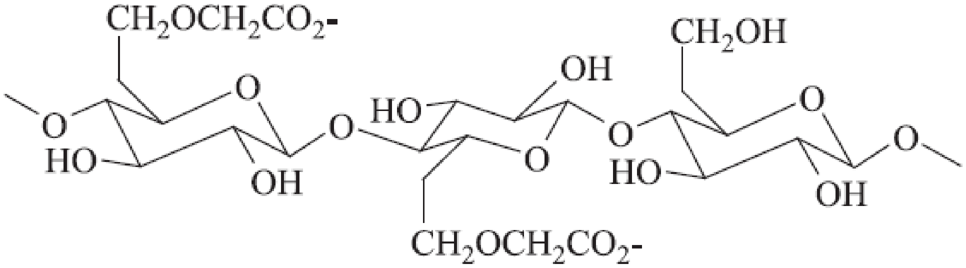


Figure 1.4. Schematic of the moleculer structure of CMC (Harris et.al., 2005).

Therefore, natural starch, dextrin, cellulose and guar gum potentially have the ability to form complexes with foreign guests. The above descriptions show the monomeric structures of starch, dextrin, cellulose and guar gum. In reality, these polysaccharides can be extracted from different sources and the chain length and configuration, molecular weights, and the contents of impurities may vary considerably.

A number of different functional groups can be introduced to the polysaccharides through etherification or esterification reactions with the hydroxyl groups. This results in the "modified" polysaccharides. Carboxymethyl cellulose (Figure 1.4) is a typical example of such modification in which the carboxymethyl groups have replaced the protons in some of the hydroxyl groups. The number of these substituted functional groups per monomer is called the "Degree of Substitution, DS". In the case of carboxymethyl cellulose, the maximum DS is 3, in which case all the three hydroxyl groups in one monomer are replaced by the carboxymethyl groups. Commercial carboxymethyl cellulose typically has a lower DS than this maximum value, which usually ranges in between 0.3 - 1.2.

In solution, guar is typically uncharged due to the absence of ionizing carboxyl functional groups. Natural guars have high molecular weights up to $4x10^6$. This is typically reduced by chemical modifications such as the addition of a preservative agent. Guars used as flotation depressants typically have molecular weights of $2\text{-}6 \times 10^5$. Since guar is a natural product, the fraction of active material can vary (Robertson, 2003).

CMC is produced via the reaction of alkaline cellulose with sodium chloroacetate (Oliviera and Gomes, 1995). The basic structure of a CMC monomer is shown in Figure 1.4. CMCs are generally classified according to three properties. One of these is the degree of carboxymethyl substitution. The degree of substitution determines the extent to which a CMC is charged in solution since the charge is brought about by the ionization of the carboxylmethyl group. CMCs used in flotation have a degree of substitution typically between 0.6 and 0.9 and so in comparison to guars are highly charged polymers.

The second property is the percentage of “active content” which indicates the percent CMC in a particular product. The inactive material brought about by the production of by-products in the synthesis process. Typically CMCs used in flotation are not pure and contain about 70% CMC by weight the remaining mass being glycolates and salt.

The third property is the molecular weight of the polymers. The moleculer weight of CMCs used in flotation is similar to that of guars and varies between $2 - 6 \times 10^5$. Generally, the viscosity of the polymer in solution is proportional to the molecular weight (Shortridge et al. 1999).

A major distinction between guar and CMC types of polymers arises from the difference in surface charge. CMC is typically anionic in solution and so upon adsorption onto a particle surface CMC typically renders that surface negatively charged. Guar, by contrast, is typically non-ionic in solution and so upon adsorption, surfaces are rendered uncharged. Therefore CMC addition leads to an increase in the magnitude of the negative zeta potential. Guar by contrast, leads to a decrease in the magnitude of the negative zeta potential, and hence decreases in surface charge.

One of the effects of an increase in the magnitude of the particle surface charge is that particles within the system remain dispersed. Particle dispersion is a measure of the degree to which particles remained independent i.e. resist coagulation. In the case of CMC, surfaces that are coated with negatively charged CMC molecules repel each other. CMCs can be characterized as ‘charged/dispersing’ depressants. In contrast, in the case of guar, there is no such electrostatic force of repulsion. In addition, molecules that are adsorbed onto either of the particle surfaces are equally capable of adsorbing onto other available surfaces, and this leads to further coagulation. Hence guars can be characterized as ‘uncharged/coagulating’ depressants.

However it is important to note that the effect of enhanced particle dispersion cannot be investigated by directly comparing CMC and guar. In the absence of information regarding their relative abilities as depressants, it would be impossible to determine whether differences observed are due to dispersion or due to other properties such as the change in surface hydrophobicity (Robertson C., 2003).

1.2. Use of Polysaccharides in Mineral Flotation

Polysaccharides have been used in mineral beneficiation for almost 70 years. Generally, starches have been used mainly as flocculants or flotation depressants for iron oxide minerals and phosphate minerals while the associated silica is floated. Dextrin has been mainly tested as depressants for inherently hydrophobic minerals such as talc, molybdenite and coal. Carboxymethyl cellulose and guar gum are widely used as depressants for hydrophobic talcaceous minerals in Cu–Ni bulk sulfide flotation.

Table 1.1 summarizes the application of polysaccharides in different mineral flotation systems. This table is not exhaustive and shows only selected examples. As can be seen, the polysaccharides have been used or tested as selective depressants in practically all types of mineral systems, ranging from oxides, sulfides, salt-type and inherently hydrophobic minerals.

In the flotation of Cu–Pb sulfide ores at Kidd Creek, dextrin is utilized in alkaline environment whenever the content of galena in copper concentrate is too high. Its use along with sulfur dioxide in Brunswick Mines has also been reported (Schnarr, 1978). It was discovered that dextrin could be used in the differential flotation of Cu–Ni concentrate; in this process pentlandite was depressed with dextrin while chalcopyrite was floated with xanthate under alkaline conditions (Laskowski and Liu 1999b). According to Laskowski and Nyamekye (1994) this scheme was used in the Kotalahti mine in Finland until 1987 when the mine closed down. In the laboratory, Liu and Laskowski (1989a) showed that in acidic solutions chalcopyrite can be depressed by dextrin while galena can be floated with ethyl xanthate; whereas in alkaline solutions chalcopyrite is floated while galena is depressed. They have used dextrin to selectively depress heazlewoodite (Ni_3S_2) in the flotation of chalcocite in the processing of INCO matte with amyl xanthate at a pH of 11.7.

Reports on the use of dextrin as a depressant for pyrite in sulphide flotation are limited. Kydros et.al. (1994) have shown that dextrin depressed pyrite effectively at pH 4 and higher in the presence of ethyl xanthate. At pH 4, copper-activated sphalerite was floated using ethyl xanthate as a collector, while pyrite was depressed with dextrin in the flotation of the pyrite–sphalerite mixture. Xu and Aplan (1994) have proposed to use polysaccharides in the presence of iron ions to depress pyrite in coal cleaning.

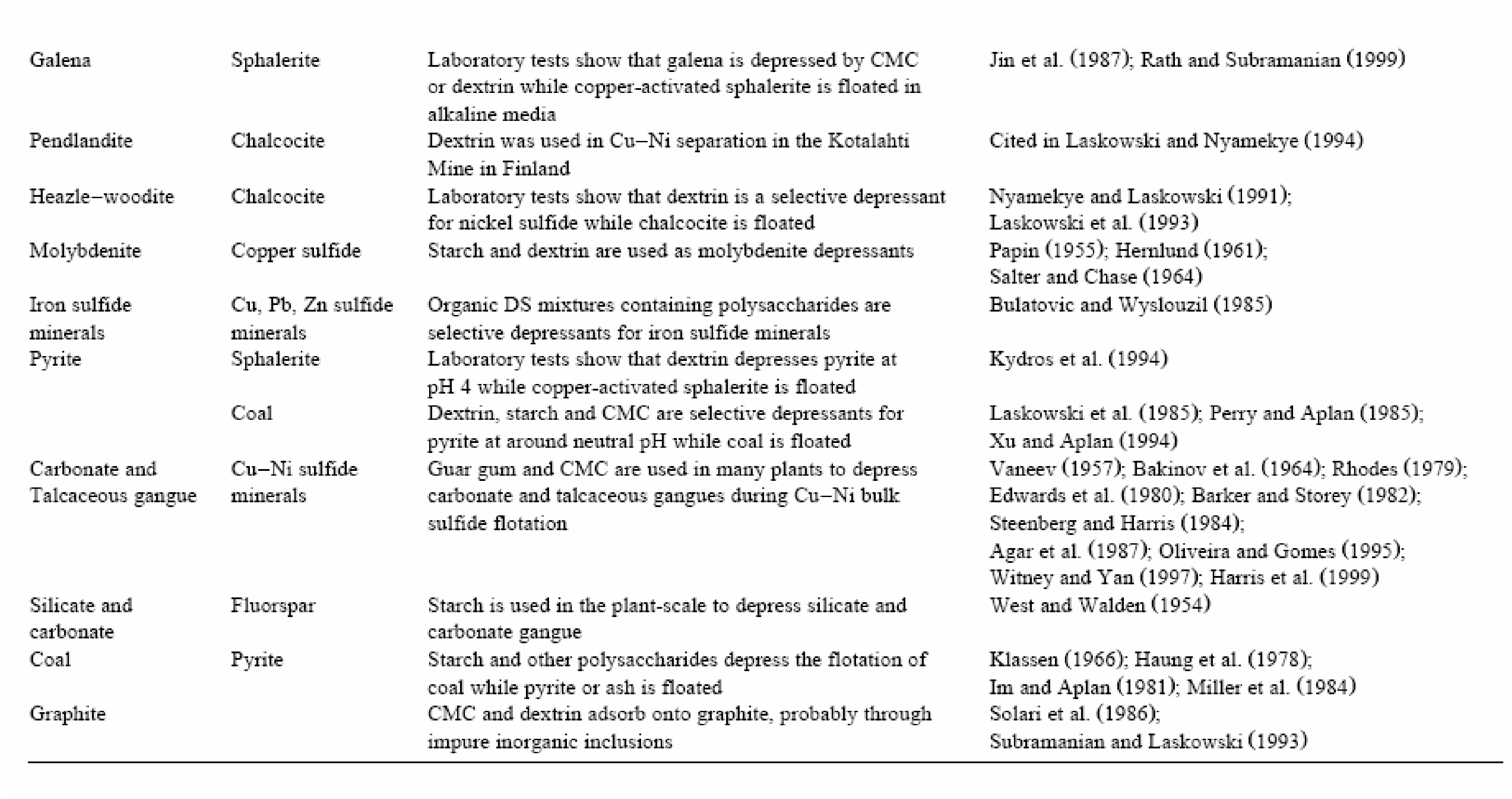
According to Boulton et al, (2001), in the flotation of complex sulfide ores, a high pH value is generally used to separate valuable sulfide minerals from pyrite or pyrrhotite with xanthate collectors. pH values higher than 11 are necessary to markedly depress pyrite flotation in the presence of xanthate collectors. The flotation of copper-activated sphalerite is more or less independent of pH, but pyrite recovery decreases from approximately 82% after 8 min of flotation at pH 8.5 to 15% at pH 12.0. Copper activation of pyrite is mainly responsible for the recovery of this mineral in alkaline pH conditions, while its depression is due to the higher proportion of surface oxidation products inhibiting collector adsorption, or/and a reduced stability of collector such as dixanthogen. A large quantity of lime has to be added to maintain this high pH value, increasing the plant operating cost. A similar explanation may be given for the improved separation of sphalerite from pyrite with oxygen gas conditioning. The preferential depression of pyrite observed as a result of the faster oxidation of pyrite than sphalerite. A recent study has shown that thionocarbamate and thiourea collectors are more selective than xanthates against pyrite and produced a better separation of chalcopyrite or copper-activated sphalerite from pyrite in alkaline and neutral pH conditions (Fairthorne et al., 1997). The high selectivity of ethoxycarbonyl thionocarbamate (ECTC) collector against pyrite is illustrated where pyrite recovery (8 min) is decreased from 51% with isobutyl xanthate (IBX) to 21% with IBECTC while sphalerite flotation is only slightly reduced. Other reagents such as cyanide (Ball and Rickard, 1976), thioglycolic acid (Chmielewski and Wheelock, 1991), diethylenetriamine (Kelebek et. al., 1995) have been used to depress iron sulfide minerals. Polymers are well-known depressants of both sulfide and non-sulfide minerals and have also been used to depress pyrite (Xu and Aplan, 1994; Kydros et al., 1994). In particular, a recent review by Nagaraj (1997) has indicated that polyacrylamide (PAM) polymers containing various functional groups can depress iron sulfide minerals.

The predominant perception regarding the use of polysaccharides in mineral flotation is that their adsorption is non-selective and their functions unpredictable. The applicability of the polysaccharides in such a wide range of mineral systems, however, seems to indicate that this general perception is probably oversimplified and uncorrected. In fact, the following sections will show that the adsorption mechanisms of the polysaccharides are more complicated than hydrogen bonding.

Table 1.1. Application of polysaccharides in mineral flotation (Laskowski and Liu, 1999b)

Mineral depressed	Mineral floated	Description	Reference
Hematite	Quartz	Starch depresses hematite at around neutral pH while quartz is floated by either cationic or anionic collectors	Cooke et al. (1952); Chang et al. (1953); Chang (1954); Iwasaki and Lai (1965); Iwasaki et al. (1969); Balajee and Iwasaki (1969a,b); Partridge and Smith (1971); Lin and Burdick (1988); Pinto et al. (1992); Uwadiale and Nwoke (1995)
Phosphate	Quartz	Starch depresses phosphate as quartz is floated by cationic collector	Lange (1931); Lin and Burdick (1988)
Apatite	Quartz	Starch depresses apatite as quartz is floated	De Araujo (1988); Pinto et al. (1992)
Calcite		Starch strongly adsorbs on calcite and depresses its flotation by oleate	Somasundaran (1969)
Calcite, barite	Fluorite	Laboratory tests show that starch selectively depresses calcite and barite while fluorite is floated	Hanna (1973); Wu and Gong (1989); Liu et al. (1993)
Chalcopyrite, sphalerite	Galena	Laboratory tests show that in neutral pH, starch depresses chalcopyrite and sphalerite while galena is floated	Dolivo-Dobrovosky and Rogachevskaia (1957)
Galena	Chalcopyrite	Dextrin with SO_2 to depress galena in Brunswick Mines in Canada	Schnarr (1978)
		Guar gum with SO_2 at pH 4 to depress galena in Matabi Mines	Allan and Bourke (1978)
		Laboratory tests show that CMC depresses galena when used together with pyrophosphate	Liu (1982)
		Corn starch or modified guar together with sulfurous acid to selectively depress galena	Lin and Burdick (1988)
		Laboratory tests show that in alkaline pH, dextrin depresses galena while chalcopyrite is floated	Liu and Laskowski (1989c)
		Bench and pilot tests show that dextrin and NaOH depress galena.	Bolin and Laskowski (1991)

Table 1.1 continued (Laskowski and Liu, 1999b):



Galena	Sphalerite	Laboratory tests show that galena is depressed by CMC or dextrin while copper-activated sphalerite is floated in alkaline media	Jin et al. (1987); Rath and Subramanian (1999)
Pendlandite	Chalcocite	Dextrin was used in Cu–Ni separation in the Kotalahti Mine in Finland	Cited in Laskowski and Nyamekye (1994)
Heazle–woodite	Chalcocite	Laboratory tests show that dextrin is a selective depressant for nickel sulfide while chalcocite is floated	Nyamekye and Laskowski (1991); Laskowski et al. (1993)
Molybdenite	Copper sulfide	Starch and dextrin are used as molybdenite depressants	Papin (1955); Hernlund (1961); Salter and Chase (1964)
Iron sulfide minerals	Cu, Pb, Zn sulfide minerals	Organic DS mixtures containing polysaccharides are selective depressants for iron sulfide minerals	Bulatovic and Wyslouzil (1985)
Pyrite	Sphalerite	Laboratory tests show that dextrin depresses pyrite at pH 4 while copper-activated sphalerite is floated	Kydros et al. (1994)
	Coal	Dextrin, starch and CMC are selective depressants for pyrite at around neutral pH while coal is floated	Laskowski et al. (1985); Perry and Aplan (1985); Xu and Aplan (1994)
Carbonate and Talcaceous gangue	Cu–Ni sulfide minerals	Guar gum and CMC are used in many plants to depress carbonate and talcaceous gangues during Cu–Ni bulk sulfide flotation	Vaneev (1957); Bakinov et al. (1964); Rhodes (1979); Edwards et al. (1980); Barker and Storey (1982); Steenberg and Harris (1984); Agar et al. (1987); Oliveira and Gomes (1995); Witney and Yan (1997); Harris et al. (1999)
Silicate and carbonate	Fluorspar	Starch is used in the plant-scale to depress silicate and carbonate gangue	West and Walden (1954)
Coal	Pyrite	Starch and other polysaccharides depress the flotation of coal while pyrite or ash is floated	Klassen (1966); Haung et al. (1978); Im and Aplan (1981); Miller et al. (1984)
Graphite		CMC and dextrin adsorb onto graphite, probably through impure inorganic inclusions	Solari et al. (1986); Subramanian and Laskowski (1993)

1.3. Adsorption Mechanisms of Polysaccharides

Selective depressants are indispensable ingredients in any flotation reagent scheme targeting selective separation of different minerals. Various inorganic depressants have been routinely used. Many of these depressants, especially the ones used in differential sulfide flotation, are extremely toxic and environmentally unacceptable. Examples of such depressants are sodium cyanide, sodium dichromate, sulfur dioxide, etc. Some of these inorganic depressants are reducing agents and thus are susceptible to oxidation in aerated flotation pulps. Therefore results in high reagent consumption.

On the other hand, polysaccharides are natural organic polymers that are non-toxic and biodegradable. They are also cheaper and more resistant to oxidation than the inorganic depressants. Not only do these properties make them ideal as flotation reagents, but they have also shown potential for use as selective depressants in many differential mineral flotation systems. Polysaccharides have been utilized in mineral industry for almost 70 years, mainly as depressants for iron oxides, inherently hydrophobic minerals and rock-forming gangue minerals. They are also reported as being selective in the differential flotation of sulfide minerals.

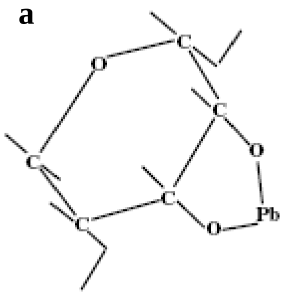
However, a general lack of understanding of the interaction mechanism between the polysaccharides and mineral surfaces has hindered the wider application of these polymers. In this paper, we study to summarize the current status in this important field and postulate the interaction mechanisms.

Polysaccharides are condensation polymers of high molecular weights based on simple monosaccharide sugar units. Many different types of polysaccharides exist in nature but only a small number of them have been used by mineral industry, especially in flotation. These include starch, dextrin, guar gum and carboxymethyl cellulose and they are mainly used as flotation depressants. In this part their adsorption behaviour were examined in 2 groups: natural polysaccharides and modified polysaccharides. Starch, dextrin and guar gum are the natural polysaccharides while CMC is the modified polysaccharide.

Application of dextrin as a flotation depressant, both in the laboratory and in commercial processes, has been reported. In the flotation of Cu–Pb sulfide ores at Kidd Creek dextrin is utilized in alkaline environment whenever the content of galena in copper concentrate is too high. Its use along with sulfur dioxide in Brunswick Mines has also been reported (Schnarr, 1978).

In the laboratory, Liu and Laskowski (1989a) showed that in acidic solutions chalcopyrite can be depressed by dextrin while galena can be floated with ethyl xanthate; whereas in alkaline solutions chalcopyrite is floated while galena is depressed. They have used dextrin to selectively depress heazlewoodite (Ni_3S_2) in the flotation of chalcocite in the processing of INCO matte with amyl xanthate at a pH of 11.7.

Adsorption of dextrin which renders metal sulfide surfaces hydrophilic has been proposed to be due to the interaction between the hydroxyl groups in the glucose unit and the metal hydroxides on the sulfide surface (Liu and Laskowski, 1989b). This mechanism is compatible with the findings by Angyal (1973), who showed, through Nuclear Magnetic Resonance studies, that the hydroxyl group of the C-2 and C-3 in D-Glucose interacts with multivalent metallic ions to form D-Glucose metal complex species. X-ray photoelectron spectroscopy and Auger electron spectroscopy studies performed by Liu et al. (1994) indicated chemical interaction of dextrin with metal hydroxide species on the surface of metal oxides. Through infrared studies, Khosla et al. (1984) have shown that amylopectin bonds chemically with Fe^{+3} ions, giving evidence of the existence of chemical bonding of amylopectin on hematite surface. The mechanism similar to the one postulated by Liu and Laskowski 1989a,b; Liu and Laskowski 1999a; Liu et al., 2000 (Fig 1.5.a) which involves formation of a complex between polysaccharide oxygen atoms at C-2 and C-3 and iron atoms in the flocculation of iron oxides with starch, was confirmed by Weissenborn (1993) (Fig 1.5.b).



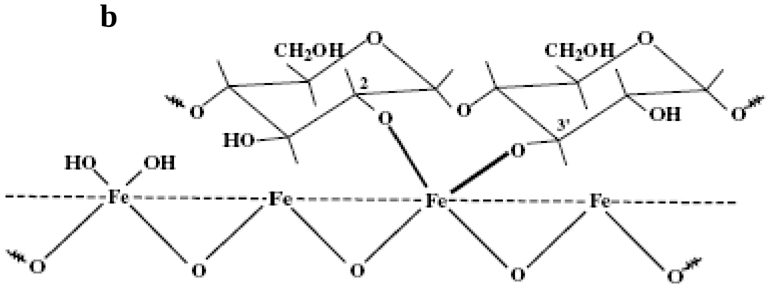


Figure 1.5.a. Complex probably involves OH groups on C-2 and C-3 carbons interaction with surface metal sites (Liu and Laskowski, 1989b) (Valdivieso et.al., 2004)

Figure 1.5.b. Complex for iron oxide interacting with starch (Weissenborn (1993)

Weissenborn (1993) showed the following complex (Fig 1.5.b) for iron oxide interacting with starch and Fig 1.5.a is a simplified version since a complete complex probably involves OH groups on C-2 and C-3 carbons interaction with surface metal sites as shown below (Liu and Laskowski, 1989b)

1.3.1. The role of metal-hydroxylated species in polysaccharide adsorption

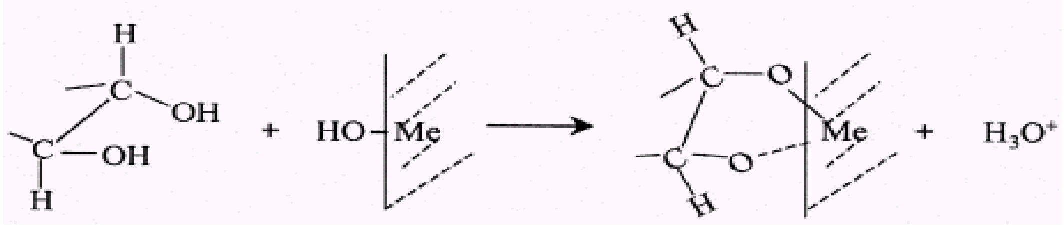
As can be seen from Figure 1.1, 1.2, 1.3 and 1.4, polysaccharides contain a large number of hydroxyl groups, which is why these polymers can be used as flotation depressants. For pure polysaccharides, the hydroxyl groups are the only polar groups available in the polymer chain. However, naturally occurring polysaccharides always contain impurities, resulting in the presence of varying amount of carboxylate, phosphate and amino acid groups. The concentrations of impurities depend on the type, source and manufacturing process of the polysaccharides, but are generally less than 1% (Gracza, 1965). The impurities in the polysaccharides used in many of the mineral flotation studies were usually not well characterized.

The observed depressant functions were broadly attributed to hydrogen bonding of the hydroxyl groups to mineral surfaces (Bakinov et al., 1964; Balajee and Iwasaki, 1969; Afenya, 1982; Steenberg, 1982; Rath and Subramanian, 1999) . Due to lack of the impurities content data, only the role of the hydroxyl groups in the polysaccharides will be discussed. This does not affect the validity of the conclusions since the impurity contents are usually very low and do not seem to contribute significantly to the adsorption. In fact, several authors (Khosla et al., 1984; Liu and Laskowski, 1989b; Weissenborn et al., 1995) took infrared spectra of different starches and dextrin used in their work and did not observe any absorption bands due to impurities.

Several hypotheses regarding polysaccharide adsorption mechanisms, principally hydrogen bonding (Bakinov et al., 1964; Balajee and Iwasaki, 1969a; Afenya, 1982; Steenberg, 1982 and hydrophobic interactions Wie and Fuerstenau, 1974; Haung et al., 1978; Miller et al., 1983 and 1984) were proposed in the early studies. Somasundaran (1969) and Khosla et al. 1984 also proposed chemical complexation of starch with calcite and hematite surfaces.

The current picture of the polysaccharide adsorption reflects the role of metal-hydroxylated species present on mineral surfaces. Through adsorption studies on intentionally modified adsorption substrates, Liu and Laskowski 1989a differentiated the effects of surface hydrophobicity and surface metallic sites on the adsorption of a Baker dextrin. A quartz sample was used and was modified to create different surface properties, i.e., unmodified, Pb-coated, methylated, and methylated following Pb-coating. They found that neither the unmodified hydrophilic quartz nor the methylated hydrophobic quartz adsorbed dextrin. However, when the Pb-coating was present on the quartz, the adsorption of dextrin increased significantly and became strongly pH-dependent. Maximum adsorption occurred around pH 10.5–11.0 (Liu and Laskowski, 1989a).

These observations led to a study of the interactions between the dextrin and several metal salts in aqueous solutions. It was found that the interactions of dextrin with the metal salts were pH-dependent. The optimum pH of interaction varied with the metal salts used, and coincided with the isoelectric point (iep) of the metal-hydroxide precipitates (Liu and Laskowski, 1989b). It was therefore concluded that the interaction was between dextrin and the metal-hydroxylated species. Further empirical evidence, including titration analysis, solution conductance measurements and infrared spectroscopic studies, led to the postulation that the interactions between metal-hydroxylated species and dextrin resulted in the formation of the five-member polysaccharide–metal ring complexes on mineral surfaces as shown in Reaction 1.1 (Liu and Laskowski, 1989b) .



(1.1)

It is noted that the reaction scheme shown in Reaction 1.1 is not a complete one since the charge is not balanced. However, the reason to propose the reaction as Reaction 1.1 was the observed pH drop as a result of the interaction between dextrin and metal-hydroxides (Laskowski and Liu, 1999b).

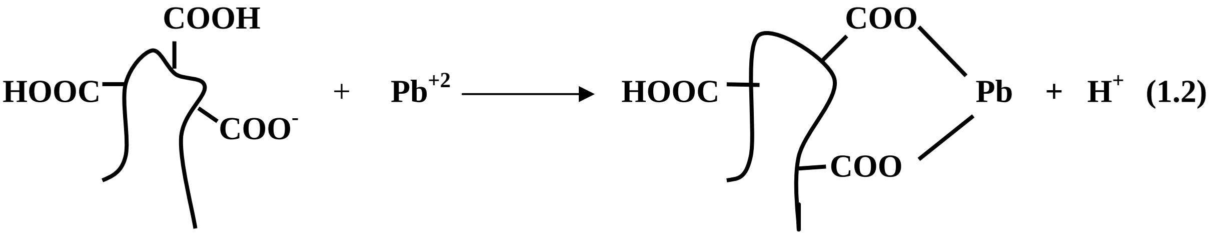
Obviously, other accompanying reactions must have been involved, which completed the reaction. Reaction 1.1 probably explained part of the interactions between dextrin and metal-hydroxides.

In fact, it had been observed in previously published researches that the addition of calcium or magnesium ions increased the adsorption or the depressive function of natural polysaccharides. These include the studies reported by Schulz and Cooke 1953, Iwasaki and Lai 1965 , Brien and Kar 1968 , Hanna 1973 and Parsonage et al. 1984, although the mechanisms of such enhancement had not been studied. A number of subsequent studies supported the observation that the unmodified natural polysaccharides, such as dextrin, starch or guar gum, adsorbed on mineral surfaces through interactions with mineral surface metal-hydroxylated species. These include the studies of Liu and Laskowski (1989c) on chalcopyrite–galena; Nyamekye and Laskowski (1991, 1993) on chalcocite–heazlewoodite; Subramanian and Laskowski (1993) on graphite; Weissenborn et al. (1995) on hematite; Bogusz et al. (1997) on pyrite; Raju et al. (1997) on galena, magnetite and several salt-type minerals; Rath et al. (1997) on talc; and Rath and Subramanian (1999) on sphalerite and galena. However, there were different opinions regarding the ways at which the polysaccharide hydroxyls interacted with the mineral surface metal-hydroxylated species.

Weissenborn et al., 1995 proposed that the interaction occurred between the two hydroxyl groups bonded to one Fe site on the iron oxide surface (Fig 1.5.b) and the -OH groups on the C-2 in one starch monomer and C-3 in the adjacent monomer, so that an eight-member ring was formed. Raju et al. 1998 studied the interactions between dextrin and $Ca(OH)_2$ or $Pb(OH)_2$ and proposed that the bonding involved all the three –OH groups in the 2 monomer, i.e., the –OH groups on C-2, C-3, and C-6 positions.

As it is clear from the published data, the unmodified polysaccharides, such as dextrin, adsorb on mineral surfaces through an interaction with surface metal hydroxy-species. The results obtained with CMC reveal some distinct differences in the adsorption behavior from that reported for the unmodified polysaccharides. CMC interacts with both metal hydroxy-species and metal cations. The observed differences are due to the introduction of carboxymethyl group.

Liu and Laskowski (1999a) show that, the titration tests provided results indicating that both carboxyl and the hydroxyl groups in CMC interacted with Pb ionic species. In these tests, an aliquot of the $Pb(NO_3)_2$ solution was adjusted to a certain pH, and was titrated with CMC solution of the same pH. At an initial pH of 4.3, the titration resulted in a decrease in the pH of the mixed solution (Figure 1.6, curve 3). The $Pb(NO_3)_2$ solution contained predominantly Pb^{+2} cations at pH 4.3. The pKa of the carboxymethyl groups in CMC is 4.4. Therefore, about half of the carboxyl groups in CMC are dissociated at pH 4.3. A decrease in solution pH points to the following Reaction 1.2.



Possible reaction that is taken place between CMC and metal species at pH 4.3

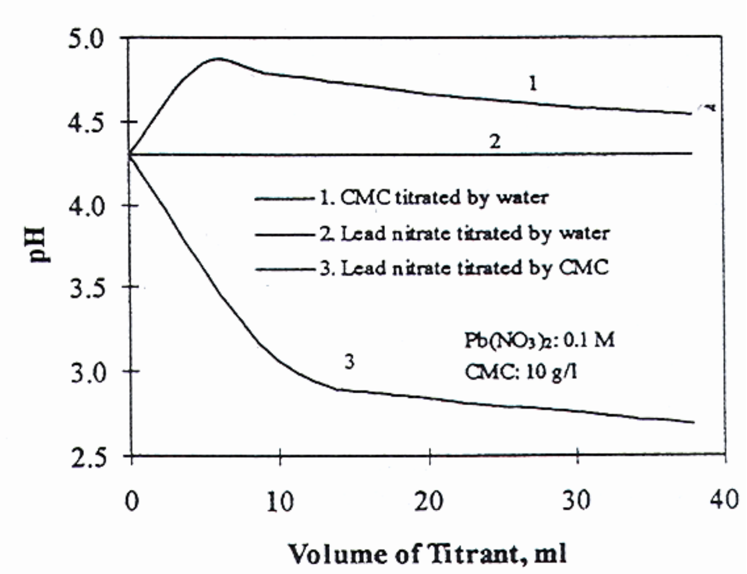
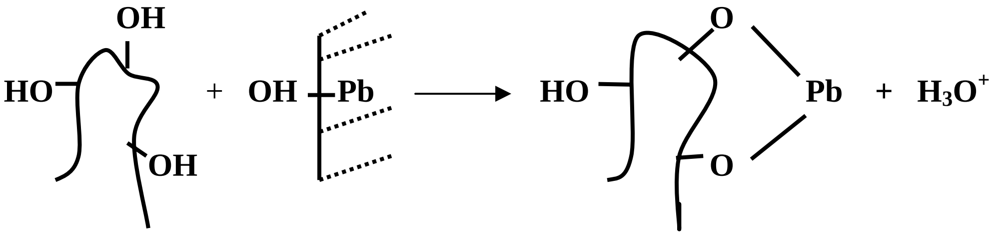


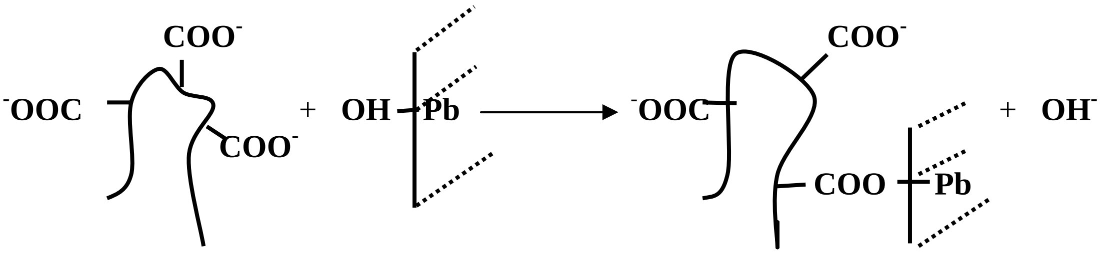
Figure1.6. Titration of $Pb(NO_3)_2$ solution by CMC at pH 4.3 (Laskowski and Liu, 1999a)

When the $Pb(NO_3)_2$ solution was titrated with CMC at pH 11.2, there was no change in the solution pH with increasing CMC addition, and this indicated that both carboxyl and hydroxyl groups in CMC participated in the reaction with Pb ionic species. In the tests with dextrin, the hydroxyl groups in dextrin interacted with Pb hydroxy-species and resulted in a decrease in solution pH at pH 11.2 (Liu and Laskowski, 1989a).

In fact, as shown in Figure 1.7, at pH 11.2, when $Pb(NO_3)_2$ solution was titrated by amylose, the a-form of the glucose linear polymer, solution pH decreased. On the other hand, when the $Pb(NO_3)_2$ solution was titrated by sodium laurate at the same pH, the solutions pH increased. CMC contained both functional groups (carboxyl groups and hydroxyl groups). It is likely that the following reactions have taken place. (Laskowski and Liu, 1999a)



(1.3)



(1.4)

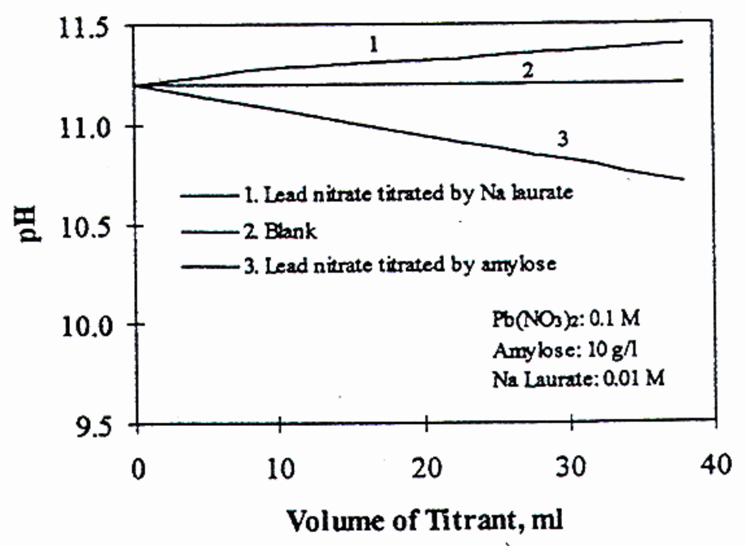


Figure 1.7. Titration of Pb(NO3)$_2$ by amylose and laurate at pH 11.2 (Laskowski and Liu, 1999a)

Although the above co-precipitation and titration tests do not provide a direct evidence of interaction with mineral surfaces, they reflect the chemical affinity of CMC towards Pb $^{+2}$ cations and Pb hydroxy-species.

In CMC, both the carboxymethyl groups and the hydroxyl groups interact with mineral surface metallic sites. The carboxymethyl groups of CMC react with both metal cations and metal hydroxy-species (Reaction 1.2 and 1.3) while the hydroxyl groups of CMC only interact with the metal hydroxy-species (Reaction 1.4).

Each D-glucose monomer in the cellulose molecule has three hydroxyl groups. The degree of substitution (DS) of the CMC used in the experiment is 0.7. This indicates that, on average, less than one hydroxyl group in each D-glucose monomer is substituted. The remaining two hydroxyl groups are thus available to interact with metal hydroxy-species on mineral surfaces. Since the DS of commercial CMC is less than 3, the interaction between the hydroxyl groups of CMC and mineral surfaces will always be present.

The solution pH is expected to have pronounced effect on CMC adsorption. This is because the solution pH affects the dissociation of the carboxyl groups, the hydroxylation of mineral surfaces, and the mineral surface charge. The presence of two types of adsorbing groups in CMC, coupled with the status of surface metal hydroxylation and surface charge, can result in very different adsorption and depression behavior of CMC in mineral flotation.

In fact, it is known that in aerated flotation pulp, the surfaces of sulfide minerals are covered by metal hydroxides due to superficial oxidation. Since Pb^{+2} ions form hydroxy-species at alkaline pH of 10-12, the interaction of CMC with galena surface is the strongest at this pH because both the carboxyl and the hydroxyl groups can interact with the surface metal hydroxy-species. In fact the hydroxyl groups of the polymer may have played a more important role at this pH, since dextrin, which does not have carboxylic groups, strongly depressed galena at alkaline pH. Pb^{+2} ions predominate when the solution pH is lowered. The hydroxyl groups of CMC cannot interact with the Pb^{+2} cations and only the carboxylic groups interact with Pb^{+2} at acidic pH. The affinity of CMC thus appears to be lower in the acidic medium.

1.3.2. Effect of pH on adsorption of polysaccharides

The direct consequence of the interaction of natural polysaccharides with metal-hydroxylated species is that the interaction, and thus the adsorption, is strongly dependent on pH. The pH dependence of polysaccharide adsorption was in fact first observed by Iwasaki and Lai 1965. They measured the adsorption of a corn starch on hematite and found that the adsorption was much higher at pH 6.8 than at pH 11.3. Khosla and Biswas (1984) observed a higher starch and amylopectin adsorption on Fe-O at pH 6 than at pH 8. Perry and Aplan 1985 studied the adsorption of a number of polysaccharides on pyrite and found that the maximum adsorption always occurred around pH 7. In fact, the iep of various iron oxides are around 5.2 to 8.6, as summarized by Parks (1965) (Figure 1.8).

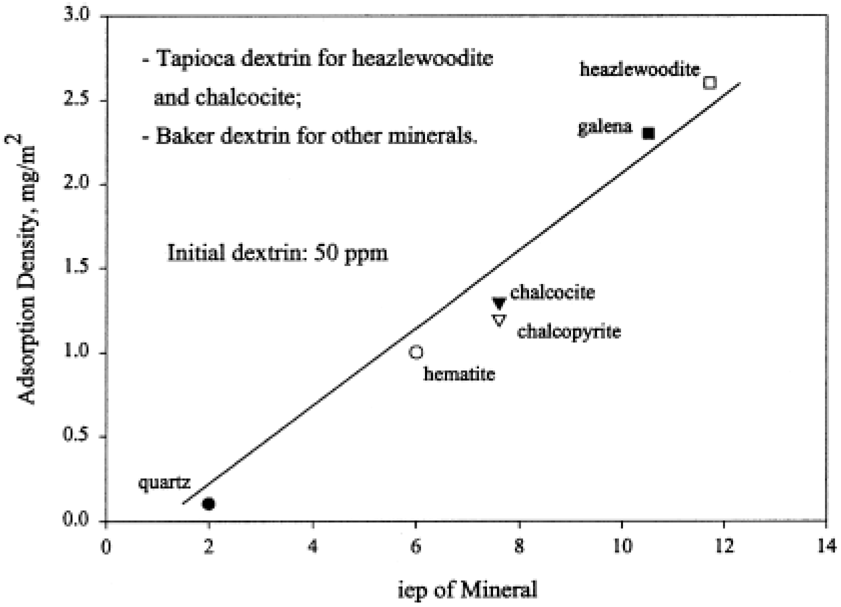


Figure 1.8. The maximum adsorption densities of dextrin on different minerals as a function of iep of the minerals. (Data points are extracted from Liu and Laskowski 1989 a,c and Nyamekye and Laskowski 1993).

It follows that around the iep, the iron oxide surfaces were fully hydroxylated. The observed adsorption maximum of natural polysaccharides around the iep of iron-bearing minerals is in line with the postulation that the polysaccharides interact with surface metal-hydroxylated species. However, iep of freshly fractured pyrite surface is about pH 2-3, not pH 7 as reported by Perry and Aplan (1985).

Isoelectric point of pyrite increases to pH 7 only after strong oxidation of the surface, which does not simulate the real conditions in a grinding mill where the major surface chemical interactions take place.

Liu and Laskowski 1989b studied the interaction of dextrin with several metal salts in aqueous solutions and observed the co-precipitation of the dextrin with metal-hydroxides. The maximum co-precipitation was found to be related to the iep of the metal-hydroxides. However, the foregoing discussion does not imply that the maximum adsorption of polysaccharides will always occur at the iep of minerals (Fig 1.8). This is because the iep does not always reflect the pH at which the surface metal sites are hydroxylated. One example is the Pb-coated quartz. Due to the incomplete Pb coverage of the quartz surface, the Pb-coated quartz had negative zeta potentials in the pH range 3 to 13 (Liu and Laskowski, 1989a) and probably had an iep around 2 by extrapolation. Maximum adsorption of dextrin was observed not around pH 2 but at 10.5. The maximum adsorption was obviously a result of the hydroxylation of the Pb sites on the quartz surfaces. Rath and Subramanian (1999) also observed that the iep for galena and sphalerite was around 3; however, the maximum adsorption of dextrin was observed at pH 11.5 and 7.5 on the galena and the sphalerite, respectively. These pHs of maximum dextrin adsorption coincided well with Pb and Zn hydroxylation. Raju et al. 1997 calculated the concentrations of surface species of galena, magnetite, fluorite, apatite and g-alumina immersed in aqueous solutions using a computer program. They observed a good correlation between the maximum dextrin adsorption and the pH at which maximum surface hydroxylated species appeared. The postulation is that the polysaccharides interact with mineral surface metal-hydroxylated species, and the fact that metal-hydroxylation is dependent on pH.

However, there are also several published results showed that the adsorption of polysaccharides is independent of pH. These include the adsorption of dextrin on chalcocite (Nyamekye and Laskowski, 1991) and graphite (Subramanian and Laskowski, 1993) and the adsorption of guar gum and dextrin on talc (Rath and Subramanian, 1997).

The forgoing summary shows that the natural polysaccharides interact only with metal-hydroxylated species at mineral surface. However, there are still many questions to be answered. Why do polysaccharides not interact with metal cations? Why do they interact more strongly with one metal hydroxyl than with other metal hydroxyls? Unfortunately, very little information is available with regard to these questions.

1.3.3. Acid-base interaction hypothesis

In mineral suspensions, the hydroxyl groups on mineral surfaces can either give away or accept a proton, thus behaving as a Brønsted acid or Brønsted base. The Brønsted acidity depends on the metal atom to which the hydroxyl group is attached. If the metal atom is relatively more electron attracting, e.g., a small metal atom with a high positive valence, the proton will be less strongly held to the oxygen and the acidity of the hydroxyl groups will be higher. The reaction mechanism proposed between the hydroxyl groups in polysaccharides and the mineral surface metal hydroxyls, i.e., Reaction 1.1, suggests that the mineral surfaces give away an –OH group, and each of the two hydroxyl groups in the polysaccharide give away a proton to form the five-member polysaccharide–metal ring complex. That is, the mineral surface metal- hydroxylated species would behave as a Brønsted base during the interactions with polysaccharides. The stronger the basicity, the stronger will be the interaction with the polysaccharides.

It is known that for solid oxide, the iep is an indication of the acidity-basicity of surface hydroxyl groups. A high iep indicates a basic surface. This can be visualized as follows: the solid surface will give away –OH groups and thus be positively charged unless the solution pH is high enough so that the hydroxyl groups are driven back to the surface, resulting in zero surface charge at this high pH. Similarly, a low iep indicates an acidic surface.

It is noted that the oxides of lead, nickel and magnesium have high ieps between 10 and 12 (Parks, 1965; Liu and Laskowski, 1989b; Nyamekye and Laskowski, 1993). These would indicate that the surface metal hydroxyl groups on galena, heazlewoodite and talc have a high basicity in the flotation pulp. It is not surprising that all the three minerals strongly adsorb polysaccharides, whether dextrin, starch, or guar gum, and are depressed in the corresponding flotation systems.

This acid-base interaction hypothesis also explains the use of starch in the separation of iron oxide minerals from quartz. Quartz has an iep around 2, indicating a strong surface acidity, which does not favor polysaccharide adsorption. In fact, all the literature data indicate that quartz does not strongly adsorb polysaccharides. Iron oxide minerals typically have ieps around 6–7. The surfaces of iron oxides are therefore less acidic than quartz. That is probably the reason why iron oxide adsorbs more starch than quartz and is depressed.

It follows that the hydroxyl groups in polysaccharides would behave as a Brønsted acid during the interaction with mineral surface hydroxyl groups. This is supported by the following observations.

1- Polysaccharides show very low adsorption on quartz surface which is known to be a strong Brønsted acid.
2- Polysaccharides do not interact with exposed surface metal ions, which are Lewis acids.

1.3.4. Hydrogen bonding chemical complexation

It is likely that the nature of the bonds between polysaccharides and mineral surfaces depends on the extent of the acid-base interactions. For weak acid-base interactions, only hydrogen bonds may be formed. For strong acid-base interactions, the interactions may gradually change to a chemical complexation.

1.3.5. Selectivity of polysaccharide adsorption

It is generally believed that the depressive behavior of polysaccharides in differential flotation is not specific, or not as specific as inorganic depressants. This certainly stems from the fact that the adsorption mechanism of the polysaccharides has not yet been fully understood. Bogusz et al. (1997) have recently pointed out that polysaccharides interacted with mineral surface metal-hydroxylated species, and hence selective adsorption of polysaccharides would not likely be achieved. This is because the flotation pulp contains various metal ions derived from dissolution of minerals, which inevitably mask the surfaces of minerals and make them all similar. In this context, the combined use of polysaccharides with other reagents, organic or inorganic, is one way to improve the selectivity, as reported in the literature (Schnarr, 1978). One of the reasons for its success seems to be the selective removal of those contaminating metal ions.

Substitution of foreign functional groups is also likely to increase the specificity of polysaccharide adsorption. For instance, Lin and Burdick (1988) reported that in the Cu–Pb separation process using a combination of various guar gums or starches and sulfurous acid, the sulfonated guar was the most effective, followed by a low molecular weight carboxymethyl guar, unsubstituted guar gum and finally, corn starch. It is apparent that the success of polysaccharide modification depends on the specificity of the substituted groups, as well as on the molecular weight of the polysaccharides. The polysaccharides should have the correct chain lengths so that the less-specific adsorption forces resulting from the unsubstituted hydroxyl groups will not mask the effects of the substituted groups.

In summary; natural polysaccharides, such as starch, dextrin and guar gum that are widely used in mineral flotation adsorb through the interaction with mineral surface metal-hydroxylated species. Based on the fact that the surface metal hydroxyl groups with a lower acidity exhibit stronger interaction with the natural polysaccharides, the nature of the interaction is likely an acid-base interaction (Reaction 1.1). The extent of the acid-base interaction probably determines whether the adsorption is hydrogen bonding or chemical complexation. Natural polysaccharides may be chosen as selective depressants to effect a separation based on the above adsorption mechanisms. The adsorption mechanisms may also guide further studies aimed at enhancing the selectivity of the natural polysaccharides.

However, for modified polysaccharides the situation is little different. Co-precipitation, titration, and infrared spectroscopic studies indicate that both the carboxyl groups and hydroxyl groups of CMC participate in the interaction with the surface metallic sites. Laskowski and Liu (1999a) shows that ; the hydroxyl groups of CMC interact only the metal hydroxy- speecies as natural polysaccharides (Reaction 1.3), whereas the carboxyl groups react with both metal cations and metal hydroxy-species (Reaction 1.2 and 1.4).

2. EXPERIMENTAL PROCEDURE

2.1. Overview of Test Work Program

The purpose of this research was to investigate adsorption mechanisms of two different types of polysaccharides (namely CMC and Guar Gum) on pyrite surface and effects of various operating parameters on their selective adsorption.

In the first stage, micro-flotation experiments were performed with pure pyrite obtained from Wards Scientific Establishment. In these experiments, the effects of depressant type and dosage, pH, degree of oxidation, ultrasonic treatment and calcium ions on the flotation behaviour of pyrite were investigated. Based on the results of these micro-flotation experiments, zeta potential measurements were performed to clarify the adsorption mechanism of the polysaccharides onto pyrite surface. Adsorption experiments measuring the uptake rates of these depressants on pyrite surfaces were carried out at laboratories of Mineral Processing Research Unit, University of Cape Town, South Africa.

The nature of the test work consists of:

- Micro-flotation experiments with pyrite at different pH values (pH 5, 9 and 11) in the presence and absence of 30 minutes aeration, with and without ultrasonic treatment at different dosages of depressants.
- Zeta-Potential measurements of pyrite under the same conditions.
- Adsorption tests to measure the uptake of the two selected polysaccharides under selected conditions.

2.2. Depressant Characteristics and Preparation Procedure

Table 2.1 shows the properties of the two classes of polysaccharides selected for the research program. Two different types of guar gum depressants were selected based on the difference in their molecular weight (MW), namely high (KU9 as HMW guar) and low (CZD 534 as LMW guar), while two forms of CMC depressants with different degrees of substitution (DS) that are high (Depramin 386 as HDS CMC) and low (Depramin 347 as LDS CMC), were examined.

All concentrations of depressants were determined by the means of their active content (A.C).

A.C (%) = Purity (%) – Insoluble (%)

Table 2.1. Properties of depressants

Guar's	**Supplier**	**Purity (%)**	**Insoluble (%)**	**M. W**	**Viscosity (1.5%)**	**A.C (%)**	
KU9	GM Associates	83	11	601051	88,00	72	
CZD 535	CYTEC	91.7	8.6	197000	11,30	83	
CMC's	**Supplier**	**Purity (%)**	**Insoluble (%)**	**M. W**	**Viscosity (1.5%)**	**A.C (%)**	**Degree of Substitution (D.S)**
Dep 386	Akzo Nobel Functional Chemicals	69	1	393800	14,42	68	0.86
Dep 347	Akzo Nobel Functional Chemicals	80	16	510600	49,46	64	0.47

The solid polymer samples were dried over night in an oven at a temperature of 106 °C, followed by cooling over night in vacuum desiccators. The polymer solutions were prepared by weighing out a portion of the dried solid to make a 0.5 % solution by weight. The solid was then added slowly to an agitated vessel containing distilled water and stirred for 30 minutes. The final solution was made up to the required volume by adding distilled water and left to equilibrate over night. It was then filtered and ready for use in test work. Fresh solutions were prepared every four days.

2.3 Micro-flotation Test Procedure

2.3.1. Mineral sample

Pyrite was obtained in the form of single mineral crystals (Ward Scientific Establishment Inc.) and prepared by grinding (ceramic ball mill) and sieving to obtain the desired size fraction (-106 µm + 75 µm) suitable for micro-flotation

Prior to use, the pyrite surface was cleaned by sonification for 5 min in an ultrasonic bath to remove oxidised species from the surface. The cleaned pyrite was then washed copiously with de-ionised water to remove any traces of the dissolved oxidised material.

2.3.2. Reagents

The reagents used for these tests were SIPX (sodium isopropyl xanthate), guars which have different molecular weights; KU9 (as high moleculer weight guar), CZD 534 (as low moleculer weight guar) and CMCs which have different degree of substitution; Dep 386 (as high degree of subsitution CMC) and Dep 347 (as low degree of substitution CMC). These were the same reagents that were used for zeta potential measurements and adsorption tests. The details of depressants were given in Table 2.1.

2.3.3. Procedure

For each test, a 2 g sample of pyrite was weighed and added to 50 ml of deionised water. The pulp was treated in the ultrasonic bath for 5 minutes and washed to remove oxidised material. The ore was then added together with 100 ml deionised water into the microflotation cell. A peristaltic pump set at 150 rpm was used to circulate the pulp. The pH of the solution was adjusted using NaOH. The reagents were added and the pulp was conditioned for five minutes. The cell was then carefully filled up with deionised water and the cone was then put in place. Air was introduced through a syringe at the base of the cell, at a set flowrate (8 ml/min).

Loaded bubbles rose through the cell and moved into the collection zone past the cone where the flotation product was deposited into the launder (Figure 2.1).

Figure 2.1. Picture of micro-flotation cell and its launder part.

After a series of set time intervals of 1,3,7 and 11 minutes, the syringe was removed and the flotation products washed through out of the launder to a beaker, then these samples filtered, dried in an oven at 106 ˚C for overnight and weighed.

2.3.3.1. The bubble size

Below a critical size, which depended on the size fraction of the pyrite, the bubbles became overloaded and were unable to rise until either collison with another bubble or until some of the mineral particles became detached. For the -106 +75 µm size fraction of pyrite the critical bubble size was 1.17 mm, for the -75 +53 µm size fraction of pyrite this was 0.82 mm and for the -53 +45 µm fraction of pyrite this was 0.62 mm (Bradshaw, 1997). This also affected the reproducibility and in order to obtain reproducible results the bubble size was kept above the critical bubble size for each size fraction.

The micro-flotation experiments were performed using a UCT flow – through micro-flotation cell (Bradshaw and O’Connor, 1996 - refer to Figure 2.2).

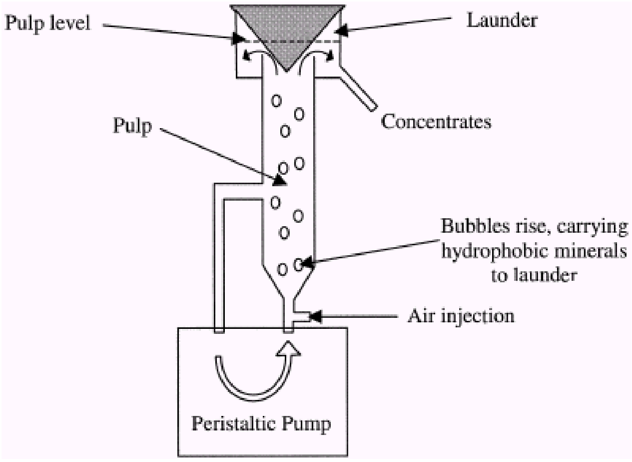


Figure 2.2. UCT flow through micro-flotation cell

The flotation details are summarized as follows:

- 2 grams of -150 µm / + 75 µm particle size fraction of pyrite sample
- 0.1% stock solution of SIPX (prepared daily)
- Depressants: CMC and Guar Gum
- Depressant dosages: 50, 100, 200, 500 ppm and 0.1, 5, 10, 20 ppm, respectively
- Molecular weights of guar depressants: 197 000 (LMW Guar), 601 000 (HMW Guar)
- Degree of Substitutions of CMC type depressants: 0.86 (Dep 386), 0.47 (Dep 347)
- 0,1 % stock solution of Guar Gum and 0.5 % stock solution of CMC were used in the experiments. (Fresh depressant solutions prepared every four days).
- Air Velocity: 7 ml/min
- Analytical grade NaOH was used as pH modifier.
- pH values for the experiments: 5, 9 and 11
- Concentrates were taken after 1, 3, 7 and 11. minutes
- The experiments were done in duplicates. The tests were chosen randomly for reproducibility. (Repeat tests are given in Table 3.1).

- In the experiments, the effects of molecular weight, degree of oxidation (aeration), pH and depressant dosage on the floatability of pyrite were investigated.
- 10^{-2} M $CaCl_2$ solution was used to study the effect of calcium ions on the depressive effect of the polysaccharides.

Order of addition of flotation reagents: All of the flotation experiments described above were performed with the polymer added to the reagent mixture before the collector. The order of reagent addition is often varied in flotation circuits to take advantage of possible site blocking (prevention of depressant adsorption due to the presence of a pre-adsorbed layer of collector). Order of addition is most likely to affect the valuable mineral phases. As xanthate type collectors strongly adsorbs onto the sulphide minerals studied, it is more sufficient to add depressant before collector for the interaction of mineral-depressant in the system (Beattie et al., 2006).

In the study of Beattie et al. (2006) effects of order of addition of depressant and xanthate on the sulphide phase have been investigated through the measurement of adsorption isotherms of the collector in the presence of excess polymer, and for the polymers in the presence of excess collector. Addition of polymer prior to the collector has been reported as the optimum condition.

- *Experiments with aeration:* In these micro-flotation experiments, the pyrite sample was aerated outside the flotation vessel for 30 minutes, followed by conditioning firstly with depressants for 5 minutes and then with SIPX for another 5 minutes before flotation.

- *Experiments without aeration:* Nitrogen gas was bubbled intensively through the solution for 5 minutes to remove the dissolved oxygen, then the solution with pyrite was transferred to the micro-flotation cell and conditioned with depressant first and then with SIPX for 5 minutes each before flotation.

2.4 Electrokinetic Measurements

The Zeta Potential, as measured by electrophoresis, is the potential developed at the plane of shear in the water associated with a particle as it moves. It is closely related to the surface charge at the mineral surface and can thus provide insight into physical adsorptions that may occur. More over, in the case of sulphide minerals, it is a reliable measure of the degree of surface oxidation (Fornasiero and Ralston, 1992).

2.4.1. Mineral preparation

The pyrite sample was dry ground in a ceramic mill with porcelain balls, screened to obtain the -106μm /+75 μm size fraction and then stored in a vacuum desiccators until required to minimize oxidation. Before each experiment, a sample was ground for 5 minutes using a ceramic mortar and pestle to reduce the particle size below approximately 20 μm. This procedure removed oxidation products and provided fresh surfaces for the measurements and consistent results.

2.4.2. Procedure

Zeta potential is measured by tracking the motion of charged particles in a DC voltage field. This is a direct measurement called electrophoretic mobility (EM). EM is expressed as microns/second per volts/centimetre. The first term (microns per second) is simply a velocity measurement, while the second (volts per centimetre) is an expression of the electric field strength. Electrophoretic mobility is, therefore, a relative measure of how fast a particle moves in an electric field. Zeta potential can be calculated from the measured electrophoretic mobility using a theoretical relation between the two that is also dependent on the dielectric constant and the viscosity of the suspending liquid. It is better to express the results in zeta potential units (mV), even though it is an approximation, because it is a more direct representation of colloidal stability and is easier to visualize.

Zeta potential measurements are made using a technique called micro electrophoresis. A high quality stereoscopic microscope is used to comfortably observe colloidal particles inside a chamber called an electrophoresis cell. Electrodes placed in each end of the chamber are connected to the Zeta Meter 3.0+ unit which creates an electric field across the chamber. Charged colloids move in the field and their velocity and direction are related to their zeta potential.

Sample solution transferred to the electrophoresis cell with the automatic sample transfer system then electrodes inserted to the plugs of the cell and connected to the Zeta-Meter 3.0+ unit. Specific conductance of the sample was determined to select the appropriate voltage to apply. Then electrodes were energized and colloids were watched as they moved across a grid in the microscope which can also be transferred to a video display. One was tracked by simply pressing a button and holding it down while the colloid moves across the grid. When the button was released, the colloid's zeta potential (or electrophoretic mobility) was instantly displayed.

The Zeta-Meter 3.0+ unit constantly maintains a record of the measurements, which you can review at any time. Status button allows to see how many colloids you have tracked, their average zeta potential, and the statistical standard deviation of the values.

All electrophoretic measurements were made using a Zeta Meter model 3.0+ (Figure 2.3) and were conducted in a 0.01 M NaCl indifferent electrolyte solution. The NaCl electrolyte is used to eliminate effects due to changes in ionic strength. A 0.05 g sample of freshly ground pyrite was placed in a 500 ml beaker and mixed for 5 minutes. In some experiments, a pre-aeration for 30 minutes was done. The coarse pyrite particles were then allowed to settle and the supernatant containing the fine particles were taken for Zeta Potential measurements. The results presented in this report are the average of three independent measurements with a typical variation of ±1.5 mV. Repeat tests showed that the conditioning procedure was capable of producing mineral surfaces that gave reproducible measurements suitable for studying the effect of various treatments (Table 3.2).

Zeta Potential= 12.85 * m.e.m (microelectrophoretic mobility)

(m.e.m) =(distance μm / time sec.) / (applied potential V./ lenght of cell 10 cm.)

Figure 2.3. Schematic representation of Zeta meter 3.0+

The solution was conditioned at a given pH for 5 minutes at 500 rpm. HCl and NaOH were used as pH modifiers. Calcium ions were added in the form of $CaCl_2$. The solution was prepared in a 500 ml specially designed beaker and transferred automatically to the Zeta-Meter cell for measurement. This system was closed to atmosphere to prevent diffusion of atmospheric oxygen into the solution. The measurements were carried out at room temperature (25 - 30 °C) and typically took approximately two minutes. SIPX was used as the collector and all the reagents used in the experiment conditioned for 5 minutes. The Zeta Potential measurements were corrected for temperature, since Zeta Potentials are referenced to 22.5 ^{o}C.

2.5. Adsorption Tests

2.5.1. Phenol and sulphuric acid method (Dubois Method)

Simple sugars, oligosaccharides, polysaccharides and their derivatives, including the methyl ethers with free or potentially free reducing groups, give an orange-yellow colour when treated with phenol and concentrated sulphuric acid.

The reaction is sensitive and the colour is stable. By use of this phenol-sulphuric acid reaction, a method has been developed to determine submicron amounts of sugars and related substances. The method is useful for the determination of the composition of polysaccharides and their methyl derivatives.

Phenol in the presence of sulphuric acid can be used for the quantitative colorimetric micro-determination of sugars and their methyl derivatives, oligosaccharides and polysaccharides. This method is simple, rapid, sensitive and gives reproducible results. The reagent is inexpensive and stable, and a given solution requires only one standard curve for each sugar. The colour produced is permanent and its unnecessary to pay special attention to the control of the conditions (Dubois et.al., 1956).

Sulphuric acid, reagent grade 95.5 %,. Phenol 5% by weight, prepared by adding 5 grams of distilled water to 5 grams of redistilled reagent grade phenol. This mixture forms a water-white liquid that is readily pipetted. Certain preparations have been known to remain water-white after a years’ storage, while others turn a pale yellow in 3 or 4 months. The pale yellow colour that sometimes develops does not interfere in the determination, in as much as a blank is included. In this method fast delivery of 5 ml of concentrated sulphuric acid in 10-20 seconds was essential (Dubois, 1956).

Series of test tubes which have an internal diameter of 16 mm were used. This diameter will allow good mixing without dissipating the heat too rapidly. A high maximum temperature is desired because it increases the sensitivity of the reagent.

One millilitres of sugar solution containing between 10-80 ppm of sugar is pipetted into a colorimetric tube and 1 ml phenol of 5% phenol in solution by weight is added, then 5 ml. of concentrated sulphuric acid is added rapidly, the stream of acid being directed against the liquid surface rather than the side of the test tube in order to obtain good mixing. The tubes are allowed to stand 10 minutes, then they were shaken and placed for 10 to 20 minutes in a water bath at 25 °C to 30 °C before readings may be made later if necessary. The absorbance of the characteristic yellow-orange colour is measured at 490 nm for hexoses. Blanks are prepared by substituting distilled water for the sugar solution. The amount of sugar may then be determined by reference to a standard curve previously constructed for the particular sugar under examination. All solutions are prepared in triplicate to minimize errors resulting from accidental contamination with cellulose lint.

2.5.2. Equilibrium adsorption

Pyrite was obtained in the form of single mineral crystals (Ward's Scientific Establishment Inc.) and prepared by grinding with ring pulverizer and sieving to recover the desired size fraction (-38 µm). Adsorption tests were carried out on the -38 µm size particles with the BET nitrogen specific area of the pyrite was determined as 1.054 m^2/g.

CMC and Guar type depressants whose specifications are given in Table 2.1. The depressants (Dep 347, Dep 386, KU9, CZD 534) used in this work were purified by UCT Depressant Research Unit before the experiments. The depressants were prepared as 5 % by weight stock solution and the solution also contained 0.01 M NaCl to maintain ionic strength. Depressants were stirred for 2 hours to obtain complete dissolution.

Analytical grade NaCl was used to adjust the ionic strength to 10^{-2} M. 10^{-2} M analytical grade of $CaCl_2$ was used to investigate the effect of calcium ions on the polysaccharide adsorption on pyrite. Analytical grade NaOH was used to adjust the pH to 9. All solutions were prepared using high purity water produced by reverse osmosis, two stages of mixed bed ion exchange, two stages of activated carbon treatment and a final filtering step through a 0.22 µm filter. The conductivity was less than 2 µs/cm.

A portion (1 g) of pyrite was added to 200 ml of polymer solution in a beaker and the pH adjusted to 9. The suspension was stirred at room temperature with an overhead stirrer. The timer was started at the time of addition of the pyrite and after 5 min a 20 ml aliquot was removed. The aliquots were filtered with 0.45 µm size Millipore in-line filters to remove pyrite particles and the solutions before and after adsorption were analysed for polysaccharide content. The solutions were analyzed for the concentration of the depressants remaining in solution with UV-VIS Double Beam model UV visible Spectrometer with the method suggested by Dubois et al. (1956). The absorbance readings obtained from UV spectrophotometer were converted to concentration from the calibration curve and the amount of polymer adsorbed per unit surface area of the pyrite was calculated. Each adsorption was done in duplicate and the results averaged.

In order to obtain adsorption isotherms of polysaccharides, the mass of adsorbate per unit mass of adsorbent (q_e) was plotted versus equilibrium concentration of drug (C). (q_e) values are calculated from the following equation (Equation 2.1).

$$\mathbf{q_e} = \left(\frac{(C_i - C)}{m} \right) x V_t \tag{2.1}$$

where q_e is in mg per gram dry adsorbent, C_i and C are the initial and equilibrium concentrations of adsorbate solution in mg/l , V_t is the volume of the solution treated in litres and m is the mass of dry adsorbent, mg.

3. REPRODUCIBILITY OF THE TESTS

3.1. Reproducibility of Micro-flotation Tests

A series of tests was conducted at pH 9 to explore a few experimental parameters as shown in Table 3.1, the standard deviation of some tests were found to be high. This may be due to a number of factors, including very fine size of particles, bubble size, deviations in pH in time in the cell and unintentional oxidation of the pyrite surfaces. Ultrasonic treatment removes the physically adsorbed species, precipitates and colloids such as iron oxide/hydroxide species from the surface of pyrite. Although care was taken during sample preparation and storage, reproducibility of the tests was diminished when the same sample was used for long periods due to oxidation of the sample.

Table 3.1. Statistics for the micro-flotation tests

	20 ppm SIPX	**20 ppm SIPX**	**Absence of depressant and SIPX**	**10 ppm LMW Guar + 20 ppm SIPX**	**5 ppm LMW Guar + 20 ppm SIPX**
pH	**9**	**9**	**9**	**9**	**9**
Aeration	**X**	√	√	√	√
Test Number	**Pyrite Rec. (%)**	**Pyrite Rec. (%)**	**Pyrite Rec. (%)**	**Pyrite Rec. (%)**	**Pyrite Rec. (%)**
1	90,92	92,50	21,36	47,88	36,60
2	82,44	90,64	16,83	44,94	30,14
3	94,06	87,25	18,39	60,27	27,96
4		87,47	19,10	53,81	
5		92,24		61,73	
6		83,26		56,05	
7		93,19		41,07	
8		82,85			
Average	**89,14**	**88,68**	**18,92**	**52,25**	**31,56**
Std Dev.	**6,01**	**4,11**	**1,88**	**7,84**	**4,49**

3.2. Reproducibility of Zeta Potential Measurements

As Table 3.2 shows, highly reproducible results are obtained as indicated by the standard deviation values in an acceptable range. This was probably due to the inherent nature of the measurement (compared to flotation where a number of variables can affect the accuracy of the measurement), the quality and accuracy of the electrophoretic measurement device, good sample preparation and the automatic sample transfer system.

Table 3.2. Statistics for Zeta Potential tests

	10^{-2} M Ca^{2+} 200 ppm HDS CMC +20 ppm SIPX	**20 ppm SIPX**	**20 ppm SIPX**	**500 ppm LDS CMC +20 ppm SIPX**	**10^{-2} M Ca+ 200 ppm LDS CMC+ 20 ppm SIPX**	**5 ppm LMW Guar + 20 ppm SIPX**
Aeration	√	√	**X**	√	**X**	**X**
pH	**9**	**9**	**9**	**9**	**9**	**9**
Test Number	**Zeta-Potential (mV)**	**Zeta-Potential (mV)**	**Zeta-Potential (mV)**	**Zeta-Potential (mV)**	**Zeta-Potential (mV)**	**Zeta-Potential (mV)**
1	-23,1	-10	-20,2	-33,4	-14,6	8,5
2	-21,6	-12,4	-21,4	-32,5	-15	7,75
3	-22,5	-12,2	-21,9	-32,6	-14,2	9,66
Average	**-22,4**	**-11,53**	**-21,17**	**-32,83**	**-14,6**	**8,64**
Std Dev.	**0,75**	**1,33**	**0,87**	**0,49**	**0,4**	**0,96**

3.3 Reproducibility of Adsorption Tests

As mentioned earlier, all solutions, which were prepared for UV readings, are prepared in triplicate to minimize errors resulting from accidental contamination. Each adsorption was done in duplicate and the results averaged. Under the proper conditions, the method was accurate within ±2%.

4. RESULTS

4.1. Micro-Flotation Experiments

4.1.1. Pyrite flotation with SIPX

The flotation of pyrite conditioned with 20 ppm (approximately10^{-4} M) SIPX was studied as a function of pH, aeration as well as the effect of ultrasonic treatment in the absence of depressant.

Ultrasonic treatment is essential to remove surface oxidation products such as iron oxy-hydroxy species and to provide a fresh pyrite surface for the experiments. Therefore the observed depression should only be attributed to the depressant not hydrophillic iron oxy/hydroxy species initially present on pyrite surface. Consequently this procedure was applied to freshly ground samples prior to either aeration and/or conditioning for the micro-flotation test work.

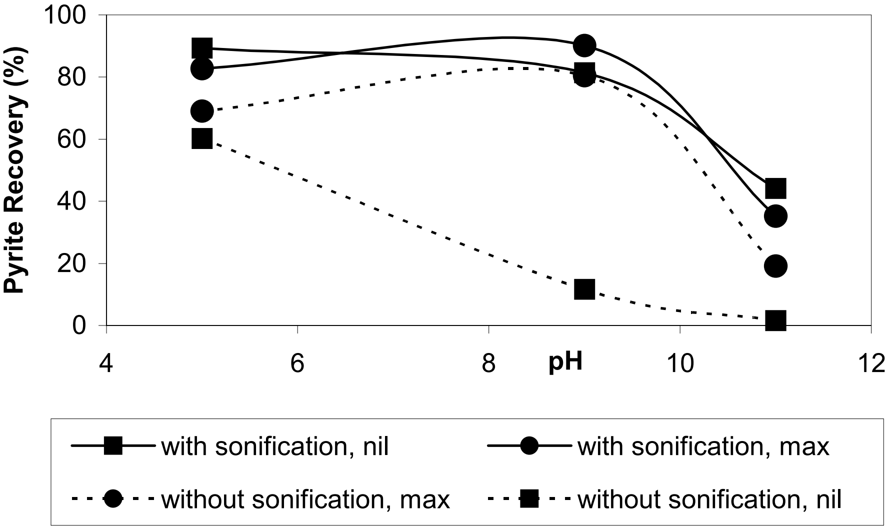


Figure 4.1. Flotation recovery of pyrite in the absence and presence of ultrasonic treatment at different pH values at 20 ppm SIPX in the absence of depressant. (Max: 30 minutes aeration, Nil: Non-aerated, flotation time: 11 min)

Figure 4.1 shows that pyrite recovery increased at low pH values. There was a huge difference between the flotation recoveries, especially at pH 9, in the presence and absence of aeration. The minumum flotation recovery was obtained for both aerated and non-aerated solutions at pH 11. The maximum flotation recoveries for conditions with and without aeration were obtained at pH 9 and pH 5, respectively. The final recoveries (after 11 minutes of flotation) without ultrasonic treatment which were given in Figure 4.1 can be summarized as follows;

In nil condition, $R_{pH\ 11}$ (≈5 %) < $R_{pH\ 9}$ (≈10%) < $R_{pH\ 5}$ (≈60 %)
After aeration, $R_{pH\ 11}$ (≈20 %) < $R_{pH\ 5}$ (≈70 %) < $R_{pH\ 9}$ (≈80 %)

As shown in Figure 4.1, after ultrasonic treatment, the recovery values increased at all pH values. The highest recovery was obtained at pH 5 without aeration. The lowest recovery was obtained at pH 11 with aeration. In the nil condition, the highest recovery was obtained at pH 5 (%90), the lowest recovery was obtained at pH 11(45%). In the aerated condition, the maximum recovery was obtained at pH 9 (90%) and the minimum recovery at pH 11 (35%) and there is a huge difference between pH 9 and pH 11. So in summary in the presence of ultrasonic treatment;

In nil condition, $R_{pH\ 11}$(≈ 45 %) < $R_{pH\ 9}$(≈ 80 %) < $R_{pH\ 5}$ (≈ 90 %)
After aeration, $R_{pH\ 11}$(≈ 35 %) < $R_{pH\ 5}$(≈ 80 %) < $R_{pH\ 9}$(≈90 %)

4.1.2. Effects of guar gum on flotation of pyrite

4.1.2.1. Effect of guar gum dosage

The effect of guar gum dosage on flotation of pyrite was investigated at pH 9 in the presence and absence of aeration.

Pyrite recovery decreased drastically after addition of as low as 0.1 ppm guar of both types in the nil condition. This effect was less pronounced after aeration. Depression with HMW guar was slightly higher particularly at high dosages.

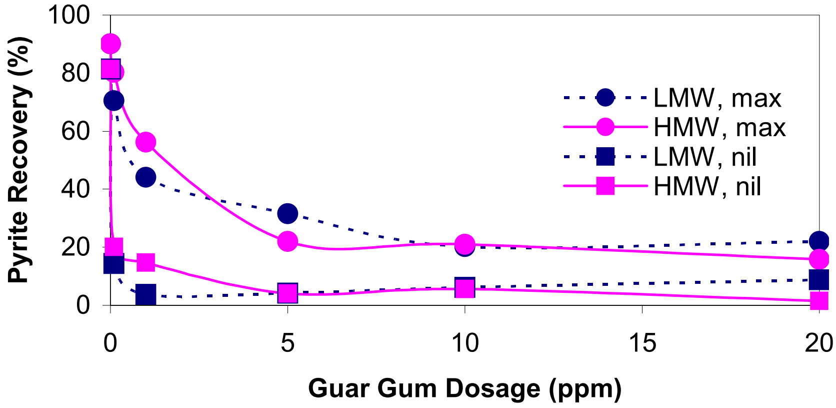


Figure 4.2. Effect of guar gum dosage on pyrite recovery with different moleculer weight guar gums in the presence of 20 ppm SIPX (pH: 9, max: 30 min aeration, nil: conditioning with nitrogen gas for 5 min, flotation time:11 min)

For both aerated and non-aerated conditions, pyrite flotation decreased as the dosage of guar gum was increased. Pyrite depression by guar gum was more effective in the absence of aeration. However, there was almost no difference between HMW and LWM guar depressants. The optimum guar gum dosage for the rest of the flotation experiments was taken as 10 ppm (Figure 4.2).

Considering the adsorption mechanism of guar gum explained on the basis of hydroxyl ion sites, higher rate of depression could be anticipated in the presence of aeration. However, opposite results were obtained in this work as shown in Figure 4.2, this contradiction is discussed in detail in Chapter 5. In addition to that presence of oxygen is in favour of dixanthogen formation which may be the reason for higher recoveries even at 20 ppm guar dosage. This was unexpected because, under non aerated conditions, less hydroxyl species form and hence there are less sites for the interaction with the hydroxyl groups of the guar gum. For convenience, 10 ppm was selected as the guar gum dosage for both high and low molecular weight guar gum (Figure 4.2).

4.1.2.2. Effect of ultrasonic treatment in the presence of guar gum

The effect of ultrasonic treatment onto pyrite recovery was investigated at pH 9 in the presence and absence of aeration.

Application of ultrasonic cleaning removes iron oxide precipitates or colloids from the surface. Therefore fresh surface is exposed for further reactions in the solution.

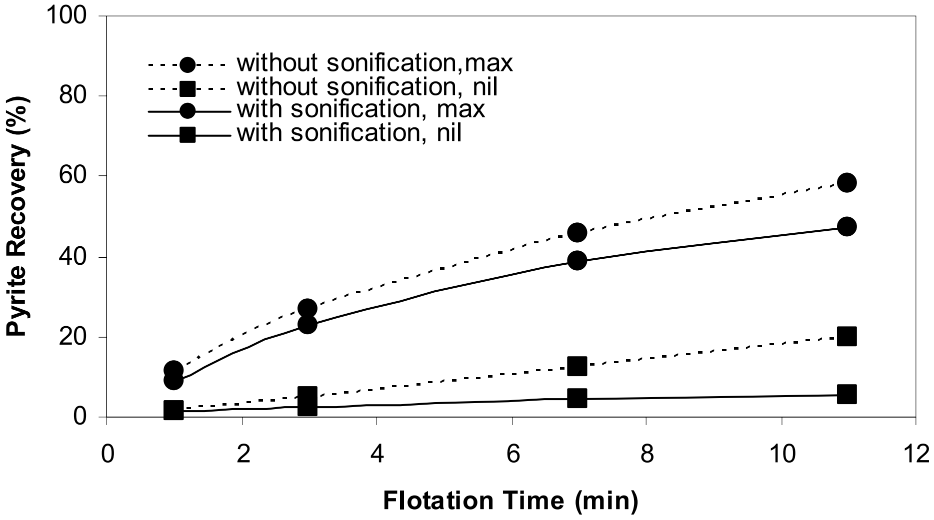


Figure 4.3. Effect of ultrasonic treatment on pyrite recovery with 10 ppm HMW guar gum under aerated (max) and non-aerated (nil) conditions at pH 9 with 20 ppm SIPX.

Figure 4.3 shows that pyrite was depressed more effectively after ultrasonic treatment both in aerated and non-aerated conditions. The ultrasonic treatment test work showed that guar gum was more effective onto fresh pyrite surface and pyrite was considerably depressed by guar gum in the nil condition. The experiments were conducted in the presence of ultrasonic treatment for the rest of the flotation experiments with guar gum.

4.1.2.3 Effect of pH in the presence of guar gum

The effect of pH on flotation recovery of pyrite was investigated in the presence and absence of aeration at a fixed guar gum dosage (10 ppm Guar Gum) and fixed SIPX dosage (20 ppm) (Figure 4.4). Both, HMW and LMW guars were tested.

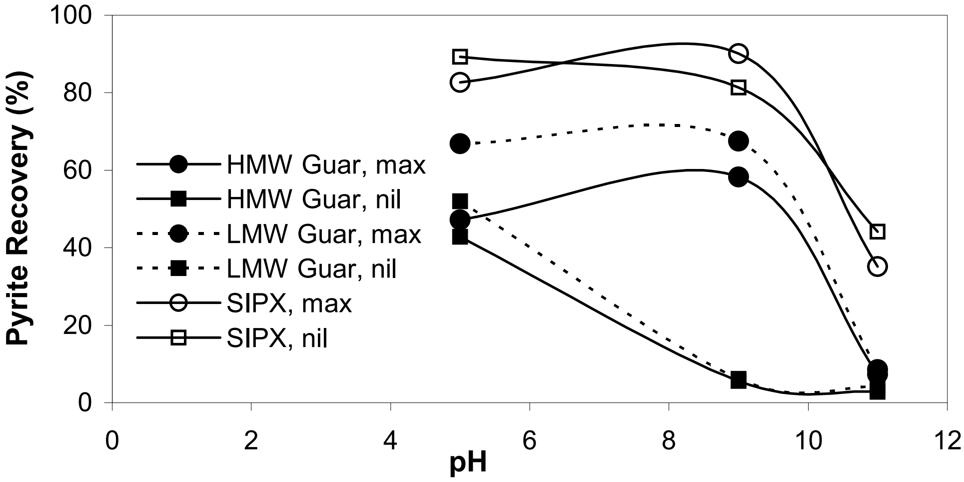


Figure 4.4. The effect of guar gum on the flotation of pyrite with SIPX at different pH values (Max: 30 minutes aeration, Nil: No aeration, 10 ppm Guar Gum, 20 ppm SIPX, flotation time: 11 min).

As shown in Figure 4.4 the difference in molecular weights affected slightly the depression. Pyrite depression was obtained under all conditions with both guar gums and reached maximum at pH 11. The maximum depressive effect for guar gums, irrespective of molecular weight, occurs at pH 9 under non-aerated conditions.

4.1.2.4. Effect of calcium ions in the presence of guar gum

In sulphide ore flotation, lime is usually used as pH regulator, which in turn resulted in high concentration of calcium ions in the pulp. Therefore, it is very important to investigate the effect of calcium ions on adsorption of guar gum (Figure 4.5).

Effect of calcium ions on flotation recovery of pyrite was investigated at pH 9 in the presence and absence of aeration at 10 ppm HMW guar gum and 20 ppm SIPX dosage.

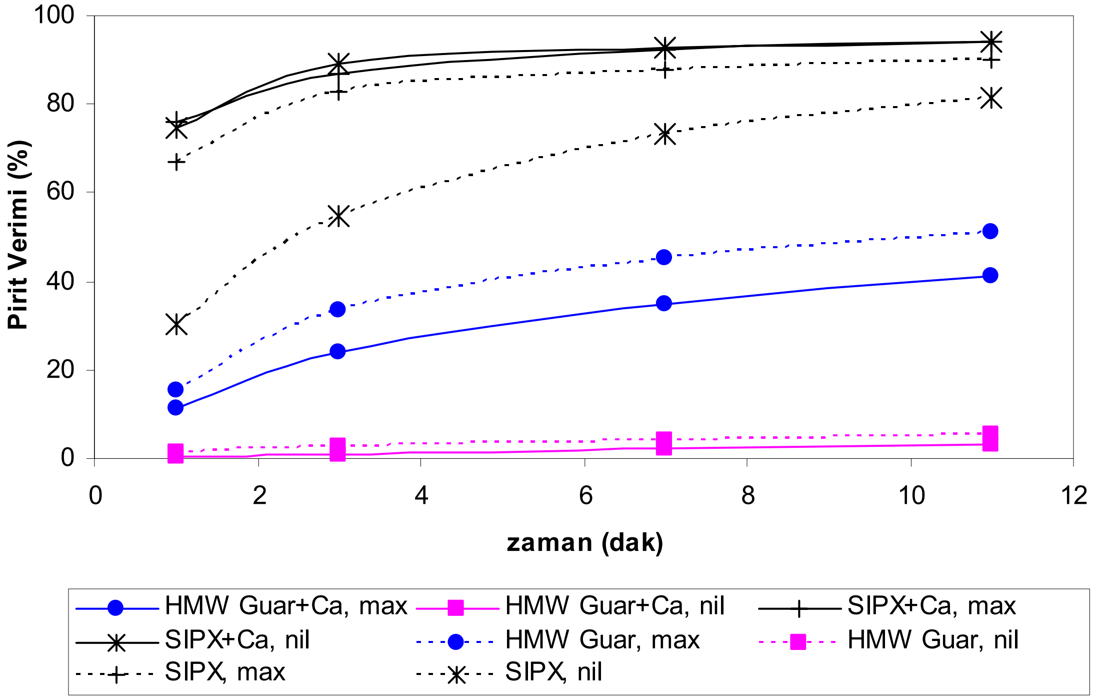


Figure 4.5. Effect of calcium ions on the performance of HMW guar gum (pH 9, Max: 30 minutes aeration, Nil: No aeration, 20 ppm SIPX).

The results given in Figure 4.5 showed that presence of calcium ion increased flotation recovery of pyrite in the absence of depressant. This was attributed to adsorption of $CaOH^+$ at the surface of pyrite which enhances electrostatic adsorption of the negatively charged xanthate ions. Addition of depressant decreased pyrite recovery considerably and presence of calcium ions further decreased pyrite recovery by 10 % particularly with aerated condition.

4.1.3. Effects of CMC (Carboxy Methyl Cellulose) on flotation of pyrite

4.1.3.1. Effect of CMC dosage

The effect of CMC dosage on flotation recovery of pyrite was investigated at pH 9 in the presence and absence of aeration.

Figure 4.6 shows that the effect of CMC is independent of dosage except very high dosages for LDS CMC. The explanation for the masking of the effect of dosage is not clear and it is expected to be revealed with zeta potential measurement and adsorption tests.

For the HDS CMC, there is no further depression with concentrations greater than 200 ppm (Figure 4.6). However for the LDS CMC, increasing the dose caused greater pyrite depression, particularly under nitrogen conditioning. Thus the highest depression was achieved in the absence of oxygen at the highest dosage. The optimum depressant dosage for further test work was chosen as 200 ppm since this is a more realistic addition rate in practice.

LDS CMC depressed pyrite only at very high dosage (Figure 4.6). This arises because some of the CMC is consumed in cleaning the surface and sufficient CMC remains to adsorb onto the freshly cleaned surfaces.

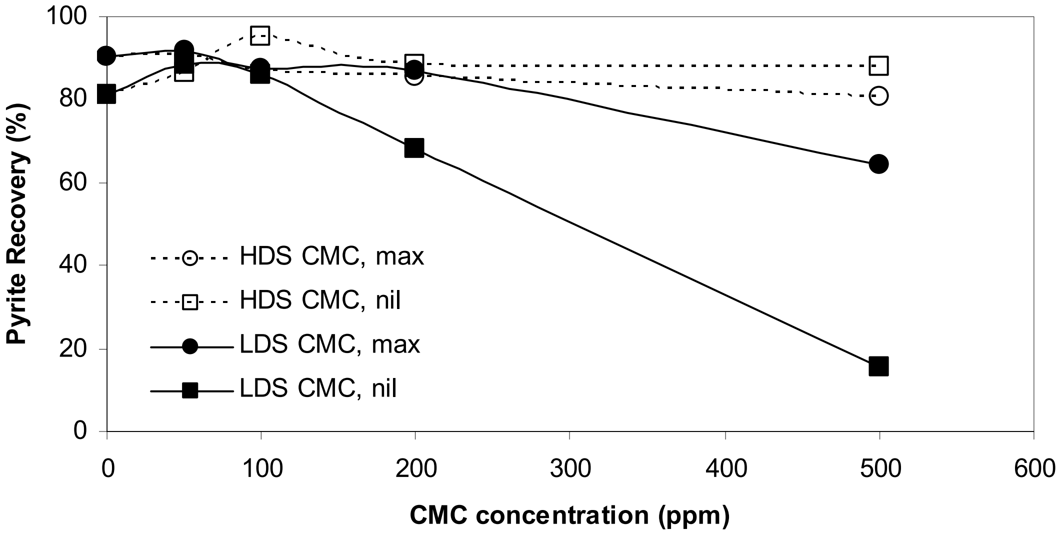


Figure 4.6. The effect of CMC dosage on pyrite flotation at pH 9 with ultrasonic treatment with 20 ppm SIPX under aerated (max) and non aerated (nil) solutions.

Thus at low dosages CMC can not be an effective depressant for pyrite, as shown in Figure 4.6. Without aeration, pyrite was more strongly depressed by CMC most likely due to the formation of $FeOH^+$ and subsequent interaction with SIPX under this condition.

4.1.3.2. Effect of pH and ultrasonic treatment in the presence of CMC

Effects of pH and ultrasonic treatment on flotation recovery of pyrite were investigated at pH 5,9 and 11 in the presence and absence of aeration and ultrasonic treatment at a fixed guar gum dosage (10 ppm Guar Gum) (Figure 4.7).

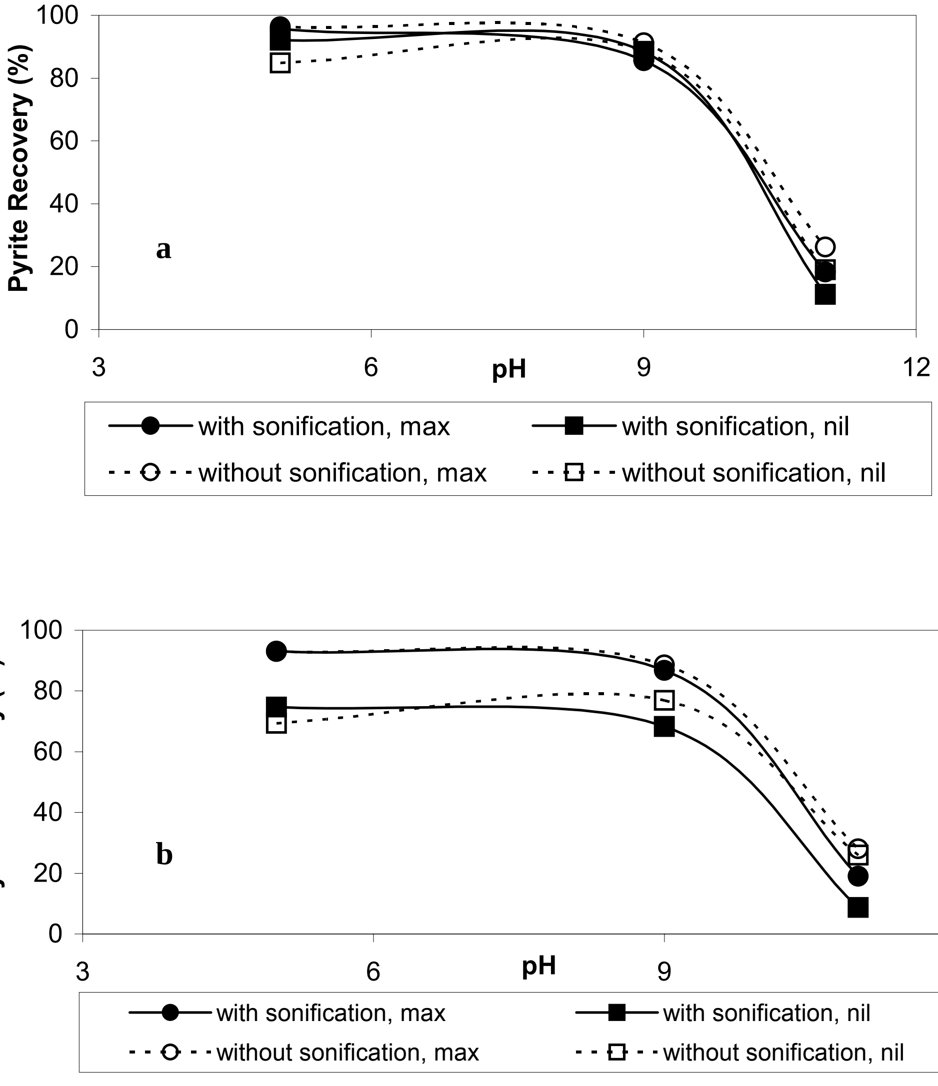


Figure 4.7. The effect of pH on the performance of CMC, a) HDS CMC b) LDS CMC (200 ppm Depramin 347, 20 ppm SIPX, Max: 30 minutes aeration, Nil: No aeration, Sonification: Ultrasonic Treatment)

There was little difference in the results at pH 5 and 9 for Depramin 386 under all conditions (Figure 4.7a). When pH was increased to 11, the flotation recovery dropped rapidly due to formation of stable $Fe(OH)_3$ as well as the instability of dixanthogen (Figure 4.7a, Figure 4.7b).

For LDS CMC, the effect of pH was similar to that of HDS CMC however there was differences due to nitrogen conditioning and ultrasonic treatment . Ultrasonic treatment increased depression, presumably by removing surface oxidation products and allowed more adsorption of CMC pyrite surface. However nitrogen had more significant effect, further lowering pyrite recovery by more than 15% at pH 5 as well as about 10% at pH 11 (Figure 4.7a, b). This was due to lack of dixantogen formation at this pH. Hence further experiments were done with ultrasonic treatment at pH 9.

4.1.3.3. Effect of calcium ions in the presence of CMC

The effect of calcium ions on flotation recovery of pyrite was investigated at pH 9 in the presence and absence of aeration at 10 ppm guar gum and 20 ppm SIPX dosage (Figure 4.8).

As shown in Figure 4.8a, under aerated conditions, the best pyrite depression was obtained in the presence of calcium ions for both CMCs, typically decreasing the pyrite recovery by another 20%. The LDS CMC (Depramin 347) consistently depressed more pyrite (about 10% less recovery) than HDS CMC (Depramin 386). This may be due to steric effects, since although less negative than Depramin 386, it has a smaller cross-sectional area and more CMC molecules can be adsorbed.

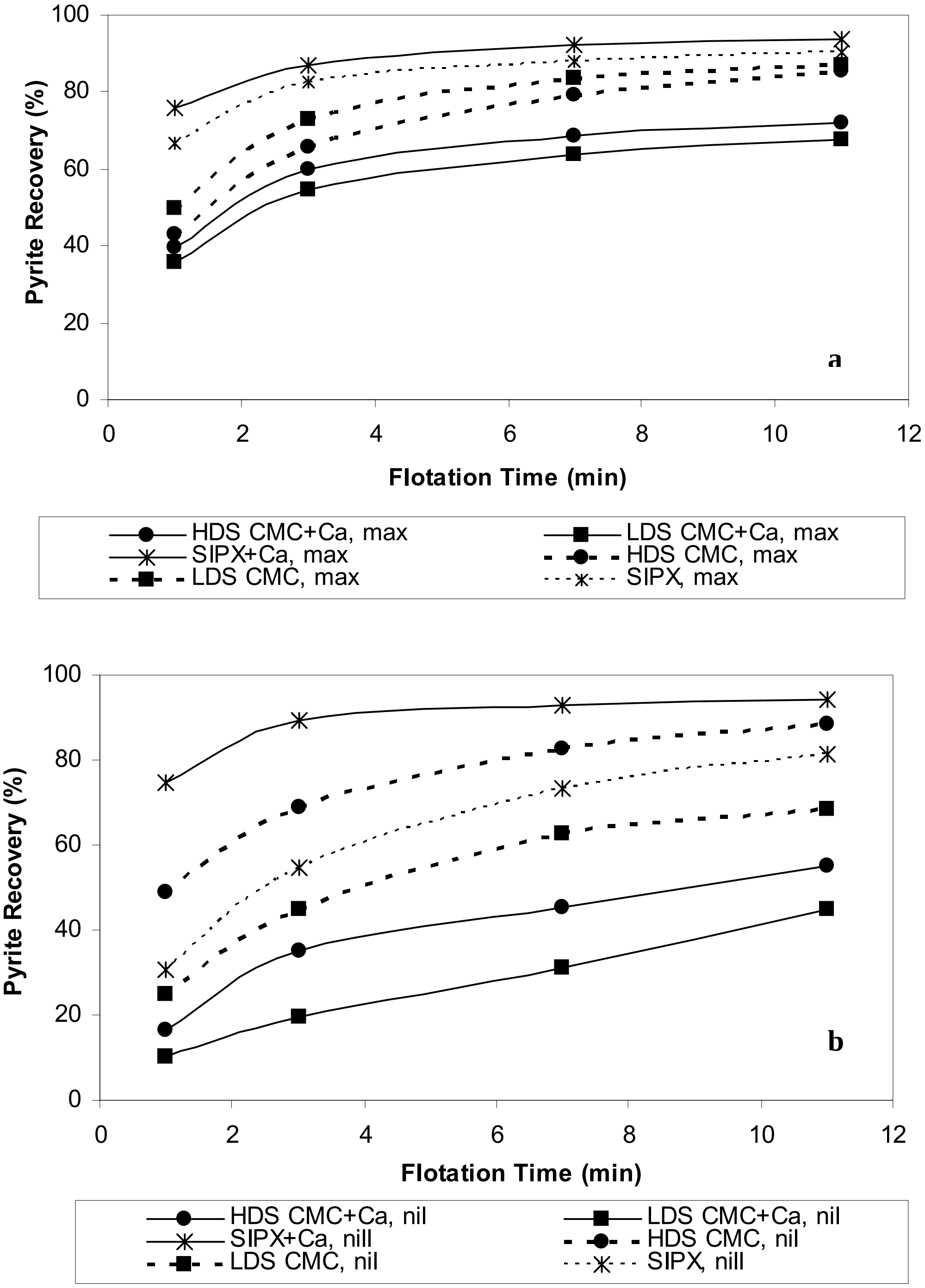


Figure 4.8. Effect of calcium ion on pyrite depression by CMC a)with aeration (max) b)without aeration (nil) at pH 9 with 200 ppm CMC and 10^{-2} M CaCl2.

Figure 4.8.b shows that in the absence of oxidation, depressant action of CMC was significantly improved. The presence of calcium ions greatly improved the depression of pyrite , might be due to improved electrostatic attraction between the

pyrite surface and the CMC. Flotation recovery of pyrite decreased further by 20-30 in the presence of 10^{-2} M Ca^{+2}. Also Ca ions seemed to activate pyrite flotation in the absence of depressant.

4.2. Zeta-Potential Experiments

4.2.1. Zeta potential of pyrite

Zeta-potential of pyrite was measured in the presence and absence of aeration as a function of pH (Figure 4.9).

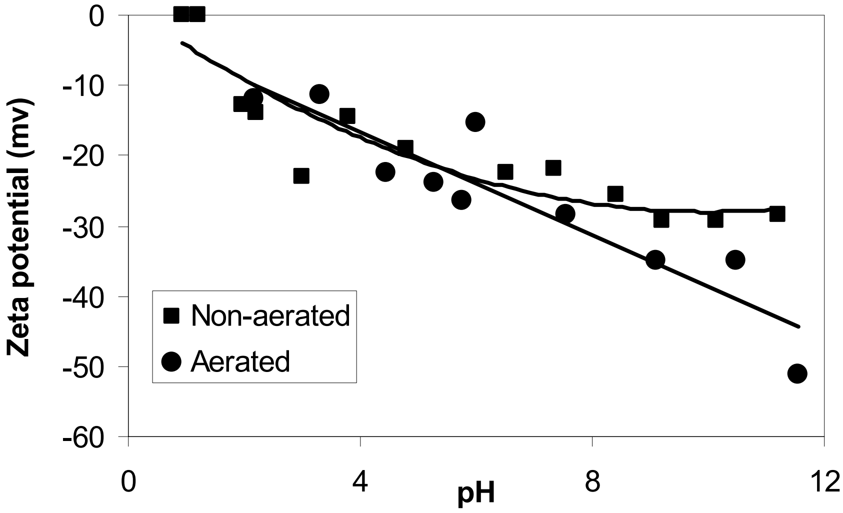


Figure 4.9. Zeta potential of pyrite in aerated (max) and non-aerated (nil) solutions without SIPX.

While the oxidation of pyrite can be done with hydrogen peroxide, oxygen gas or air, the latter method was selected since this approach can be readily applicable in the plant situation. However, as Figure 4.9 shows, there was no significant difference between the Zeta Potential curves of the aerated and non-aerated pyrite except at very alkaline pH values. The iep (isoelectric point) of pyrite was found around pH 2. The pyrite surface was negative at almost all pH values studied.

4.2.1.1. Effects of SIPX and calcium ion concentration on pyrite

The effects of SIPX and calcium ions on electrical charge of pyrite surface were investigated by means of electrokinetic measurements. 10^{-4} M (approximately 20 ppm) SIPX and 10^{-2} M $CaCl_2$ were chosen as reagent dosages for zeta potential measurements which were compatible with the dosages that were used in micro-flotation experiments (Figure 4.10 and 4.11).

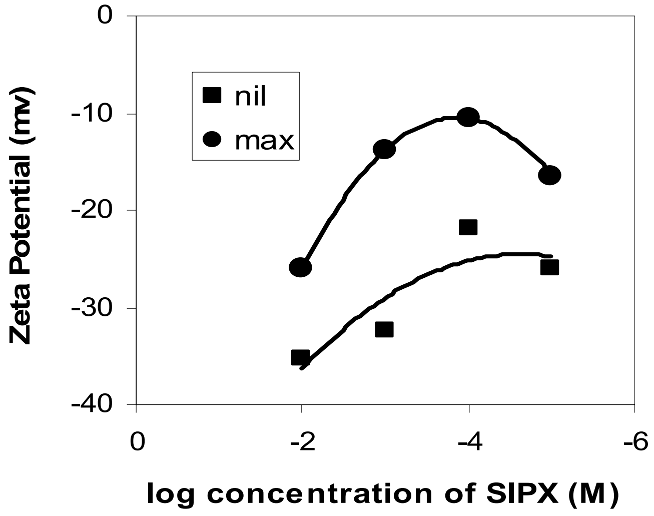


Figure 4.10. The effect SIPX dosages on zeta potential of pyrite in aerated (max) and non aerated (nil) solutions at pH 9.

Figure 4.10 shows the results measured in the presence of xanthate at pH 9. There was a slight decrease in the negative zeta-potential of pyrite at 10^{-4} M xanthate concentration. This was attributed to adsorption of neutral dimer formation of SIPX. This effect was more pronounced with aeration condition where maximum amount of dixanthogen formation was observed. As the xanthate concentration was increased, zeta potential of pyrite decreased irrespective of aeration condition, indicating possible micelle formation at excessive concentrations.

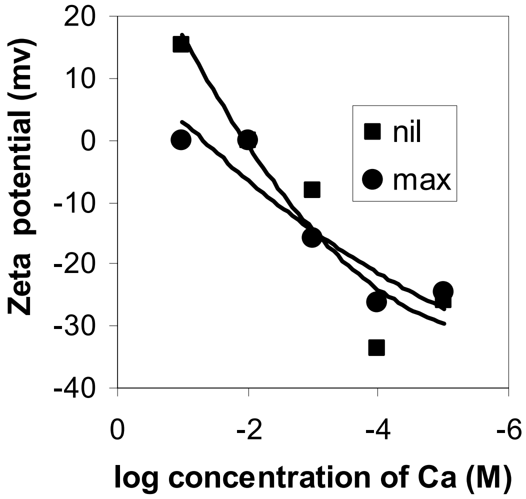


Figure 4.11. The effect of Ca^{+2} dosage on zeta potential of pyrite in aerated (max) and non aerated (nil) solutions at pH 9.

Similar experiments were performed with calcium ion addition at pH 9 (Figure 4.11). The results showed that zeta-potential of pyrite increased to positive values as calcium ion concentration was increased up to 10^{-1} M. There was no effect of aeration up to 10^{-2} M Ca ion concentration. However, zeta-potential of pyrite was more positive with aeration at very high Ca dosage.

4.2.2. Pyrite with Guar Gum

Zeta potential of pyrite in the presence and absence of SIPX was measured as a function of guar gum dosage. The measurements were performed using both LMW and HMW depressants. Figure 4.12a shows the variations in zeta-potential of pyrite in the presence of guar gum without SIPX addition. As the guar dosage was increased to 1 ppm, zeta potential of pyrite decreased to zero irrespective of guar type. This was attributed to adsorption of guar gum at pyrite. At lower concentrations, HMW was found to be more effective than LMW.

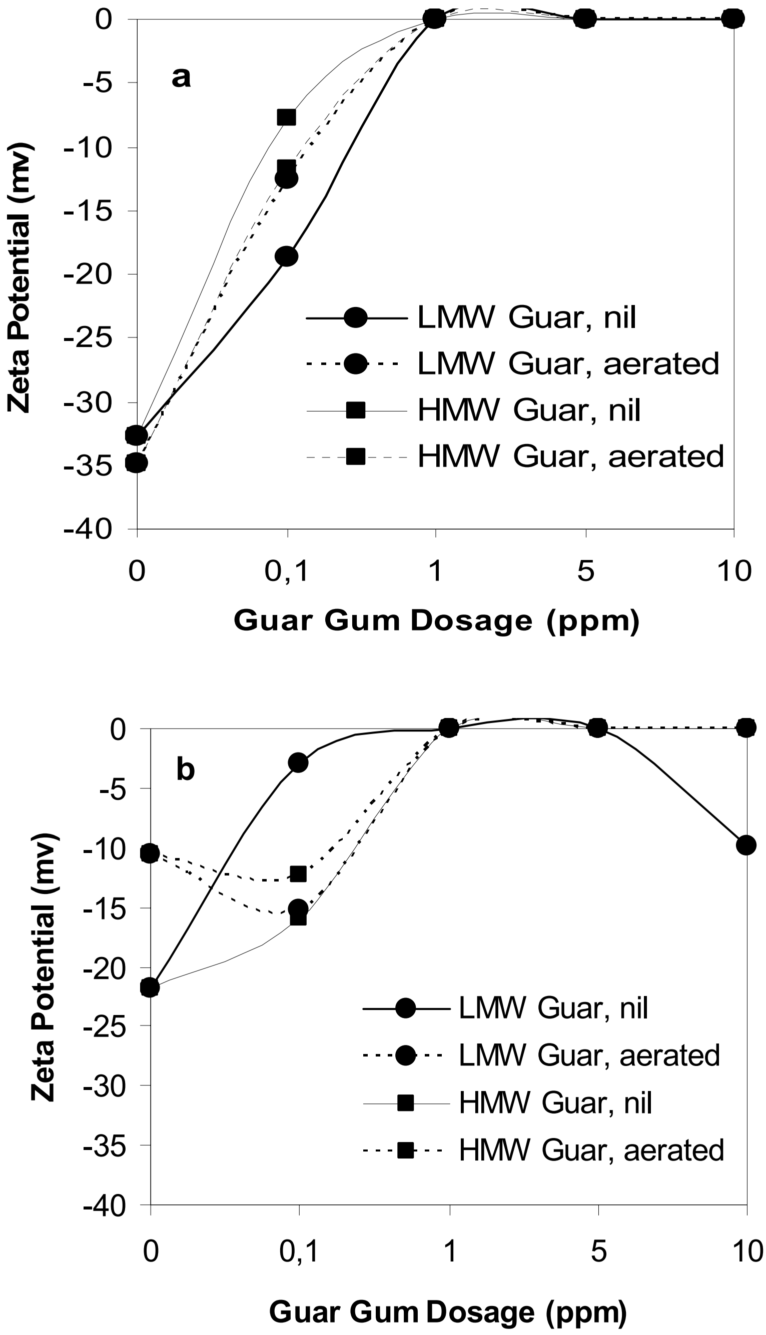


Figure 4.12. Zeta potential of pyrite as a function of guar gum a) in the absence of SIPX b) in the presence of SIPX at pH 9.

In both absence and presence of collector, guar gum makes the pyrite surface less negative with guar gum dosages greater than 1 ppm (Figure 4.12a and 12b). The results of experiments performed in the presence of SIPX (Figure 4.12b) showed that presence of SIPX after guar gum adsorption produces less negative surfaces at concentrations lower than 0.1 ppm of guar gum. However above this value similar behaviour was observed for both guar gums under aerated and non-aerated conditions. In the absence of dissolved oxygen, at high dosages of LMW guar gum the pyrite surface became negative.

However, aeration caused a reduction in zeta potential, particularly for the lower MW guar gum at a concentration of 1 ppm and at 10 ppm for the higher MW guar gum. This would suggest that less adsorption is occurring and that the oxidised surface of pyrite does not readily interact with guar gums.

Guar gum reduced the zeta potential at pH 9 which is compatible with the findings in literature (Wang et. al., 2005, Rath et. al., 1999 and 2000).Thus the primary effect of the large molecules appears to shift the slipping plane further away from the interface. Moreover, the addition of guar gum in the range of 0.1 to 10 ppm correspondingly reduces the negative zeta potential values in proportion to the polymer concentration. These findings suggest that some conformational rearrangements of the macromolecules is taking place with increasing extension of the looping chain as the polymer concentration is further increased. These observations are in agreement with the effect of the adsorption of large non-ionic molecules on the zeta potential as reported by other researchers (Rath et. al, 2000 and Nyamekye et.al., 1993). However these reported findings failed to find any shift in the i.e.p. values yet, in this research, a positive zeta potential value was measured at pH 9.2 and with SIPX at 10 ppm. The reason for this behavior is not clear and it is expected to be resolved through adsorption studies.

4.2.3 Pyrite with CMC

Figure 4.13 shows the effect of both LDS and HDS CMC dosage on zeta potential of pyrite in the presence of 20 ppm SIPX at pH 9.

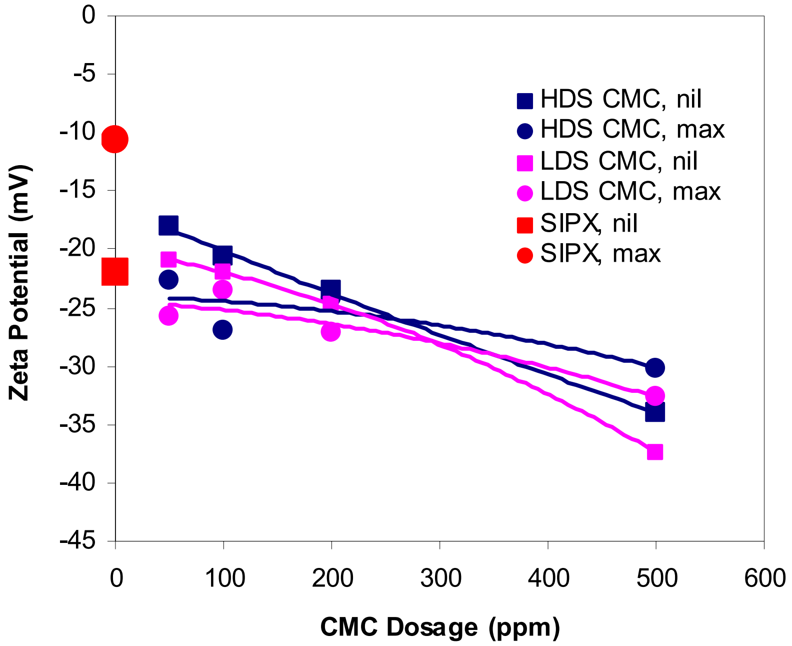


Figure 4.13. Effect of dosage on zeta potential in the presence 20 ppm SIPX at pH 9 under aerated (max) and non-aerated (nil) solutions.

In both aerated and non-aerated solutions with CMC the negativity of the surface charge of pyrite increased with increasing dosage (Figure 4.13). Therefore, there can be no electrostatic adsorption with pyrite surface, since CMC is negatively charged. But further increase in negative charge of pyrite as a function of LDS CMC dosage can be considered as an indication of adsorption of CMC on pyrite which is not compatible with micro-flotation results except very high dosage. This can be attributed the competitive adsorption between SIPX and CMC onto pyrite surface.

4.2.3.1. Effect of calcium ions

The effect of calcium ions on the surface charge of pyrite was investigated in the presence of 200 ppm HDS CMC and LDS CMC at 10 $^{-2}$M $CaCl_2$ and 20 ppm SIPX dosage at pH 9 (Figure 4.14).

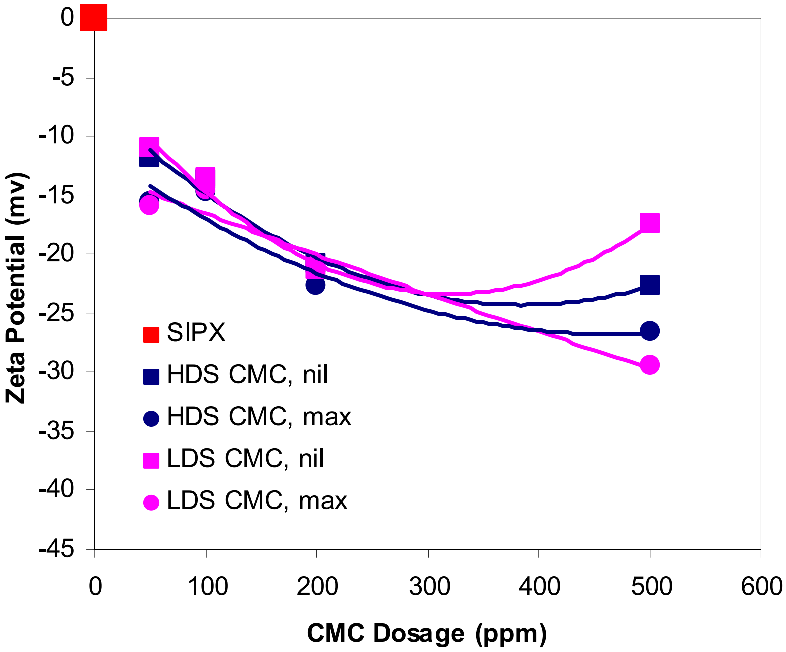


Figure 4.14. Effect of CMC dosage on zeta potential of pyrite in the presence of calcium ions and SIPX under aerated (max) and non aerated (nil) solutions (10^{-2}M CaCl2, 20 ppm SIPX, pH 9).

As shown in Figure 4.14, calcium ions tended to make the pyrite surface less negative, particularly at high dosages of CMC. This indicates that adsorption clearly chemical adsorption, since both the surface and the CMC molecule are negatively charged.

As it was shown previously in Figure 4.11, addition of 10^{-2} M Ca^{2+} neutralized the negatively charged pyrite at pH 9. However, addition of CMC, both LDS and HDS, changed the zeta potential to negative values, showing adsorption of CMC under this condition. The negativity of the surface increase almost linearly for all types of CMCs irrespective of aeration condition up to 200 ppm CMC dosage. However further increase in the dosage to 500 ppm resulted in abnormal results, probably due to limitations of the measurement technique at high reagent dosages.

4.3. Adsorption Experiments

Detailed adsorption experiments were carried out to study the effect of time, pH and polymer concentration on the adsorption densities of high moleculer weight guar gum (KU9), Carboxymethyl cellulose (CMC) with low degree of substitution (Dep 347) and high degree of substitution (Dep 386) on pyrite. Also the effect of Ca ions and aeration on depressant performance were studied.

4.3.1. Effect of time

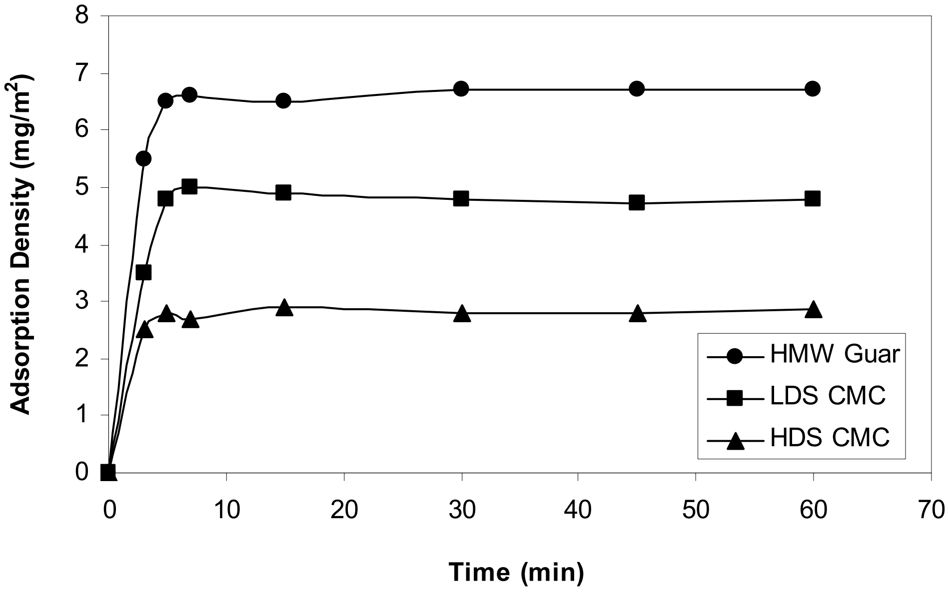


Figure 4.15. Adsorption density of guar and CMCs onto pyrite as a function of time (Depressant Dosage: 60 ppm, pH 9).

The adsorption densities of high moleculer weight guar, low degree of substitution CMC and high degree of substitution CMC are shown in Figure 4.15. The experiments were conducted at pH 9. As seen in Figure 4.15, adsorption reached its saturation value in about 5 minutes. It was also observed that the adsorption of guar gum was greater than CMCs. In the case of guar, this can be attributed to its high moleculer weight and in the case of CMC, this can be attributed to electrostatic repulsion between negatively charged CMC and negatively charged pyrite. In all further adsorption studies, the time of equilibration was fixed at 5 min for pyrite.

Therefore adsorption densities of these depressants onto pyrite can be arranged as; HDS CMC < LDS CMC < HMW Guar Gum.

4.3.2. Adsorption isotherms of polysaccharides

The adsorption isotherms of guar gum and CMCs onto pyrite at pH 9 are shown in Figure 4.16a. As seen in figure adsorption density of all depressants that were used in the experiments increased with increasing depressant concentration. Also Figure 4.16a can be converted to adsorption density versus concentration (ppm) graph (Figure 4.16b) to determine equilibrium dosage.

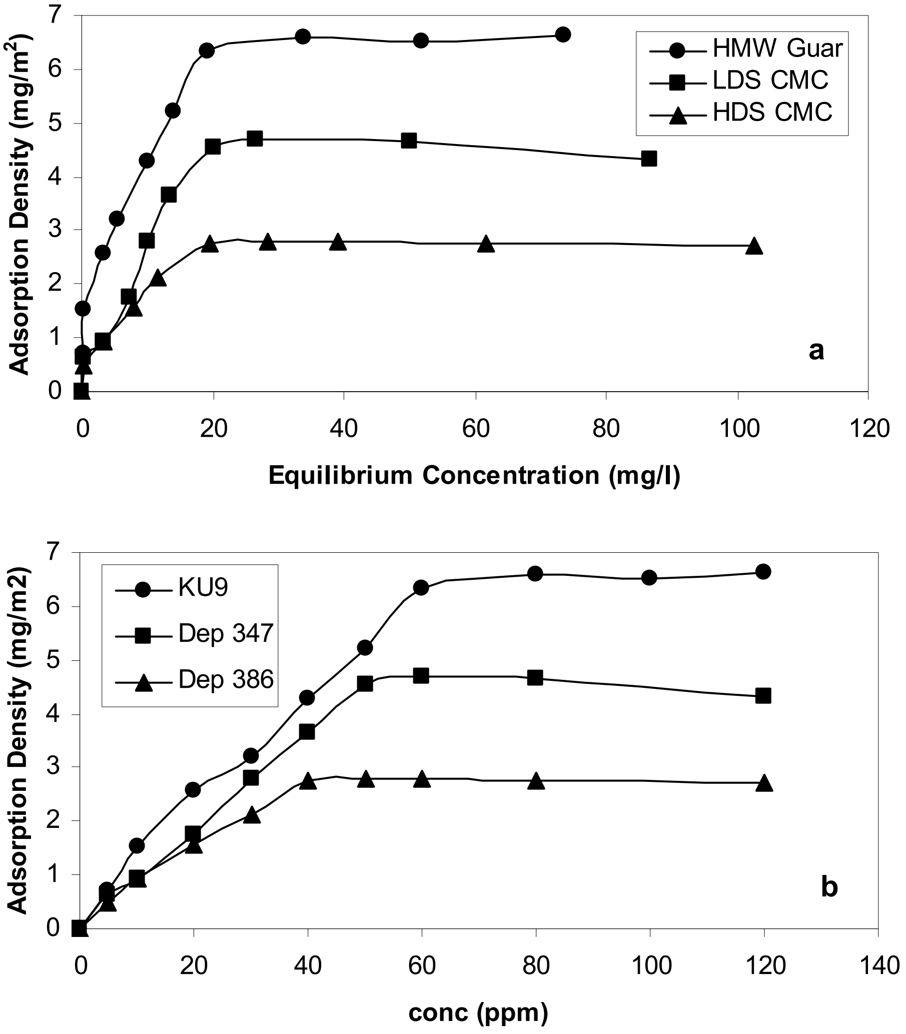


Figure 4.16a. Adsorption isotherms of polysaccharides at pH 9 (conditioning time: 5 min).

Figure 4.16b. Effect of dosage of polysaccharides at pH 9 (conditioning time: 5 min).

The isotherm at pH 9 exhibit a steep rise in the adsorption density especially at low concentrations and then reached their equilibrium concentrations at 60 ppm. In all further adsorption studies, the concentration of polymer was fixed at 60 ppm (Fig 4.16b). The isotherms follow Langmuirian behaviour and resemble the L1 type of the Giles classification (Giles et al., 1960). In keeping with the earlier trend, the adsorption densities of depressants may be arranged in the following sequence;

HDS CMC < LDS CMC < HMW Guar Gum.

Lower adsorption of CMC type depressants may be attributed to electrostatic repulsion between highly negative polymer and negatively charged pyrite at this pH value.

4.3.3. Effect of pH

The effect of pH on the adsorption densities of guar gum and CMC is shown in Figure 4.17.

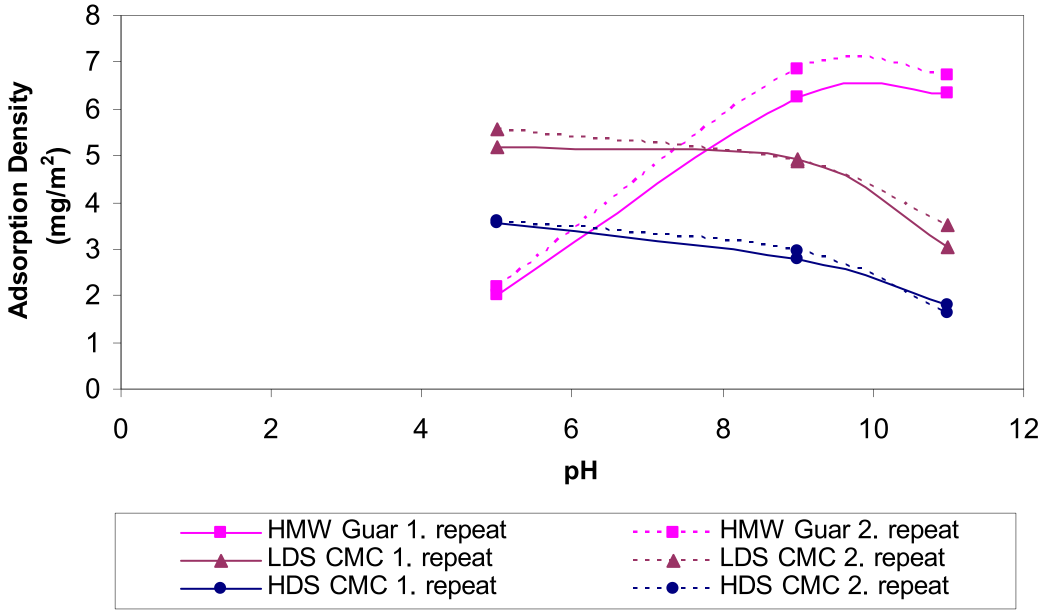


Figure 4.17. Effect of pH on adsorption (Depressant dosage: 60 ppm, conditioning time: 5 min)

It was observed that the adsorption density of KU9 steadily increases with increasing pH from 5 to about 9 and thereafter decreases slightly at pH 11. In the case of CMCs, the adsorption densities seemed to be independent of pH between pH 5 and 9, but thereafter there was a slight decrese from pH 9 to pH 11. It is compatible with the findings in the literature that a region of higher adsorption density in the alkaline pH range may be attributed to the role of hydroxylated and hydrous oxide species. Therefore, for all further adsorption studies the pH was selected as pH 9.

4.3.4. Effect of oxidation

Figure 4.18 shows the effect of aeration on adsorption density of the three depressants tested.

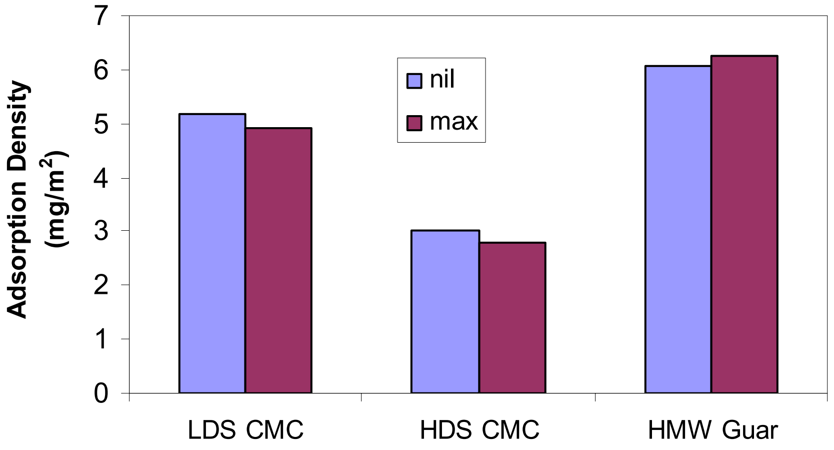


Figure 4.18. Effect of aeration on adsorption at pH 9 (Polysaccharide dosage: 60 ppm, conditioning time: 5 min)

The results clearly showed that aeration, in the term used here, did not effect adsorption of the depressants.

4.3.5. Effect of Ca ions

In Figure 4.19, the effect of Ca ions on adsorption densities of different polysaccharides on pyrite. As shown in figure, there was a big difference between adsorption densities of CMC type depressants in the presence of calcium ions. In spite of this, there was no difference with guar gum. The divalent cation was very effective in improving adsorption of CMCs. This was also in agreement with the results of microflotation tests and also with the findings reported by Shortridge et al., (1999) who showed that the flotation of talc was reduced more in a microflotation system by the addition of divalent calcium ions.

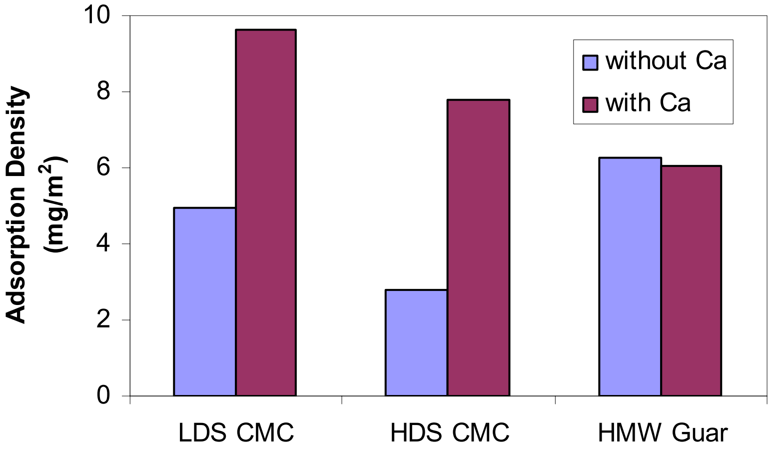


Figure 4.19. Effect of pH on adsorption at pH 9 (Depressant dosage: 60 ppm, pH 9, conditioning time: 5 min)

It is also possible that the calcium ions interact more strongly with the CMC molecules with regard to charge neutralisation along the chains or in forming linkage. On the other hand the guar studied (KU9) showed no difference by means of adsorption densities in the presence of calcium ions. This indicates that the guar performance was not affected by the ions in solution.

5. DISCUSSION

5.1. Pyrite with SIPX

Xanthate is the most widely used collector in sulfide mineral flotation. Its effective concentration in the flotation pulp plays a decisive role for the flotability of sulfide minerals. The effects of pH, concentration of solutions, as well as temperature and hydrocarbon chain length of xanthate on the degradation of xanthate have been reported (Zhongxi and Forsling, 1997). In this section adsorption of SIPX on pyrite is discussed based on the results of micro-flotation and zeta-potential experiments. The results of flotation tests with and without ultrasonic treatment show that flotation recovery of pyrite was very low at alkaline pH values in the absence of air. It is well known from the electrochemical studies that surface composition of pyrite changes as a function of pH and redox potential (Figure 5.1) (Trahar, 1984, Ekmekçi, 1995).

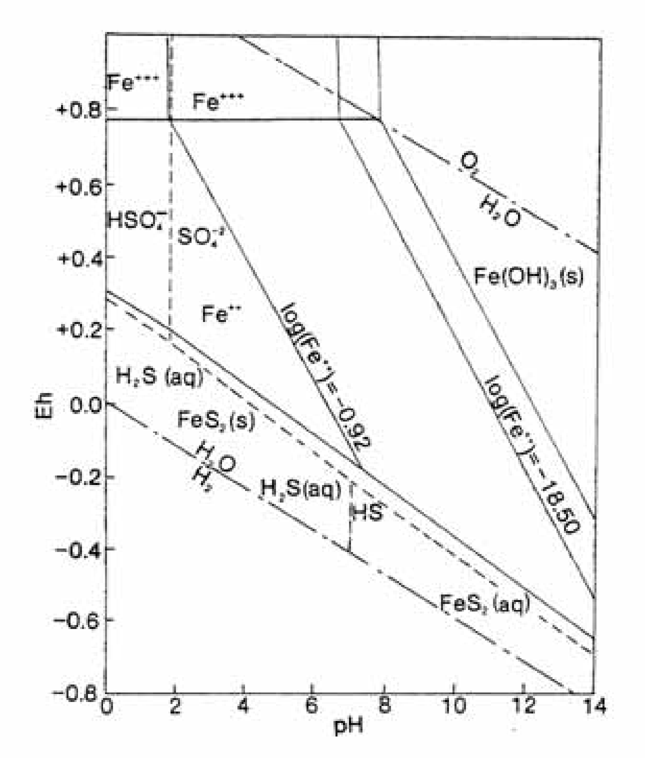


Figure 5.1 Stability relations of pyrite and ferric hydroxide at 25 C and 1 atm. (King, 1982)

In slightly acidic solutions, the surface is mostly covered by elemental sulphur (Reaction 5.1) or metal deficient sulphur layer (Reaction 5.2). These species give natural hydrophobicity to pyrite in slightly acidic solutions. As the pH was increased to alkaline values, the surface composition changes considerably according to reaction 5.3. Formation of $Fe(OH)_3$ and elemental sulphur takes place simultaneously, but as the pH is increased to strongly alkaline values hydrophilic $Fe(OH)_3$ becomes dominant at the surface. Variation in zeta-potential of pyrite as a function pH showed that pyrite is negatively charged at all pH values and had a pzc of about pH 2. The negative surface charge of “virgin” pyrite surface was attributed to formation of –FeS- and $Fe(OH)_3^-$ sites in acidic solutions (Fornasiero and Ralston, 1992). However, it is very well known that the pyrite surface bears positive and negative surface sites whose extent was determined mainly by pH and degree of oxidation of the mineral. Therefore, positively charged iron hydroxide compounds, such as $–Fe(OH)^{2+}$ and $Fe(OH)_2^+$, are likely to form at pyrite surface together with the negatively charged compounds. As the pH was increased to alkaline values, the negative charge of the surface increased due to formation of negatively charged iron hydroxy compound, such as $Fe(OH)_4^-$. These results are compatible with the findings of Fornasiero and Ralston, 1992.

$FeS_2 \rightarrow Fe^{2+} + 2S^0 + 2e$ in slightly acidic solutions (5.1)

or

$FeS_2 \rightarrow xFe^{2+} + Fe_{1-x}S_2$ (5.2)

$FeS_2 + 3H_2O \rightarrow Fe(OH)_3 + S^0 + 3H^+ + 3e$ in alkaline solutions (5.3)

In the presence of xanthate, adsorption certainly occurs and dixanthogen is formed. Dixantogen is certainly retained on the surface of pyrite, but also appears in solution, along with the charged decomposition products of xanthate (X), monothiocarbonate (MTC) and ethylperxanthate (EPX). The EPX are not detectable surface active and the kinetics of their formation can be predicted on the basis of a model where charged surface sites adsorb xanthate, which then desorbs along various pH dependent reaction pathways (Figure 5.2).

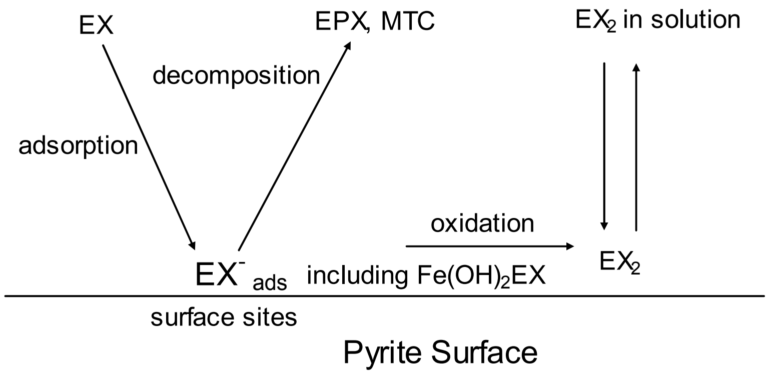


Figure 5.2. The possible reaction pathways between negative and positive sites on the pyrite surface and xanthate and degradation products of xanthate.

Dixanthogen is not the only surface product, however, and to explain the observed zeta potential-pH and flotation recovery-pH data, the formation of ferric and ferrous hydroxide-xanthate species on the pyrite surface must be presented (Figure 5.3).

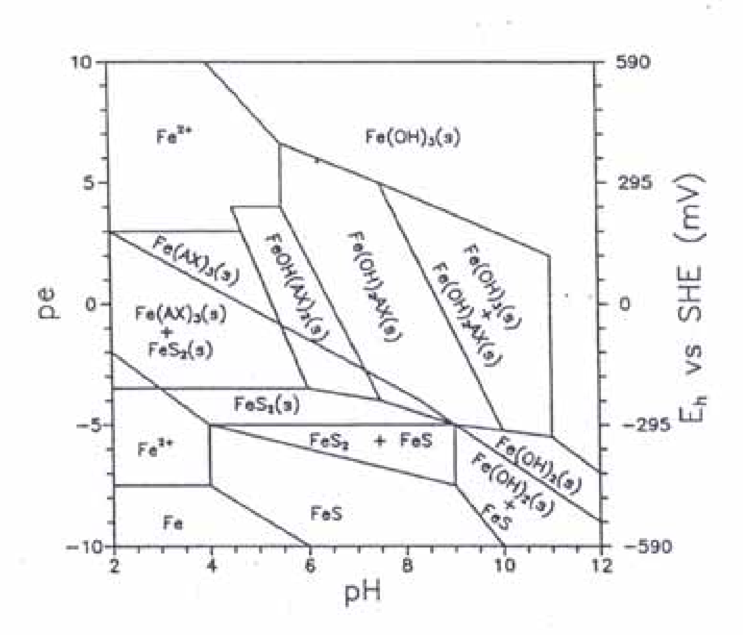


Figure 5.3. pe-pH stability diagram of Fe-species for the Fe-AX-S-H2O system. (Wang and Forsberg, 1991).

Since dixanthogen is not the only species present at the pyrite interface but in addition to that it is the active collector species for pyrite flotation with xanthate, especially in the presence of oxygen the reaction kinetic is higher (Reaction 5.4). (Allison et al., 1972, Poling and Finkelstein, 1977).

This is an anodic reaction and the coupled cathodic reaction, which is reduction of dissolved oxygen in the solution (Reaction 5.5) is essential. Otherwise, there will be no dixanthogen formation at the surface of pyrite.

$$2X^- \longrightarrow X_2 + 2e^- \qquad (5.4)$$

$$\tfrac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^- \qquad (5.5)$$

Therefore, low recoveries of pyrite in alkaline solutions in the absence of air was attributed to the presence of large amount of hydrophilic iron oxide/hydroxide species which gives hydrophilic property to the surface and very low amount of dixanthogen formation due to absence of dissolved oxygen in the solution. In spite of that the flotation recovery was very high at pH 5 even in the absence of air, but this was clearly due to formation of hydrophobic elemental sulphur and/or metal deficient sulphur layer, in other words natural floatability of pyrite at this pH (Ekmekçi and Demirel, 1997).

However, presence of oxygen after 30 minutes of aeration improves flotation of pyrite at all pH values, but particularly at pH 9. It is very well known that dixanthogen is the hydrophobic collector compound responsible for flotation of pyrite.

Ultrasonic treatment removes the physically adsorbed species, precipitates and colloids such as iron oxide/hydroxide species from the surface of pyrite. Although care was taken during sample preparation and storage, reproducibility of the tests was diminished when the same sample was used for long periods due to oxidation of the sample. Removal of hydrophilic iron oxide/hydroxide species from pyrite surface enhanced its flotation at all pH values irrespective aeration (Figure 4.1b). Both the rate and recovery of flotation increased significantly. The increase in the recovery in the absence of aeration was largely attributed to exposure of naturally hydrophobic elemental sulphur and metal deficient sulphur compounds after removal of iron oxide/hydroxide species. In addition to that xanthate adsorption was presumably enhanced due to removal of the electrochemically passive layer of iron oxide/hydroxide which may also inhibit the electron transfer between pyrite and xanthate.

As the pH was increased the pyrite recovery decreased due to the formation of iron oxy- hydroxy species on the pyrite surfaces, which lowered the amount of collector adsorbed. The lowest flotation recovery was obtained for both aerated and non-aerated solutions at pH 11 due to formation of stable hydrophilic $Fe(OH)_3$ species at this pH.

5.2. Adsorption of Guar Gum on Pyrite

The effect of molecular weight of guar gum on flotation recovery of pyrite was investigated at pH 5, 9 and 11 in the presence and absence of aeration. As it was shown in Figure 4.4, pyrite recovery was decreased by 20-40 %, particularly with HMW guar. The results of adsorption experiments (Figure 4.17) also showed guar adsorption of approximately 2 mg/m^2 at pH 5.

At pH 5, the surface of pyrite was naturally hydrophobic and as noted earlier, both positively and negatively charged iron hydroxy groups ($Fe(OH)_3^-$, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$) present on the surface at pH 5. Therefore, guar gum adsorption on pyrite may take place through hydroxyl groups on pyrite surface and guar molecule.

Rath et al. (2000) have also reported adsorption of guar gum on pyrite even at pH<4, and they have concluded that the hydroxyl groups on the polysaccharides interact with the iron hydroxy species formed on pyrite surface. Wang et al. (2005) have also studied adsorption of guar gum on talc, a naturally hydrophobic mineral, to examine the role of hydrophobic bonding on adsorption of guar gum. They have concluded that the main driving force for guar adsorption on talc is hydrogen bonding rather than electrostatic or hydrophobic force. Based on the experimental results obtained in this work, it was considered that both hydrogen bonding (Figure 5.4) and specific interaction with iron hydroxide species (Figure 5.5).

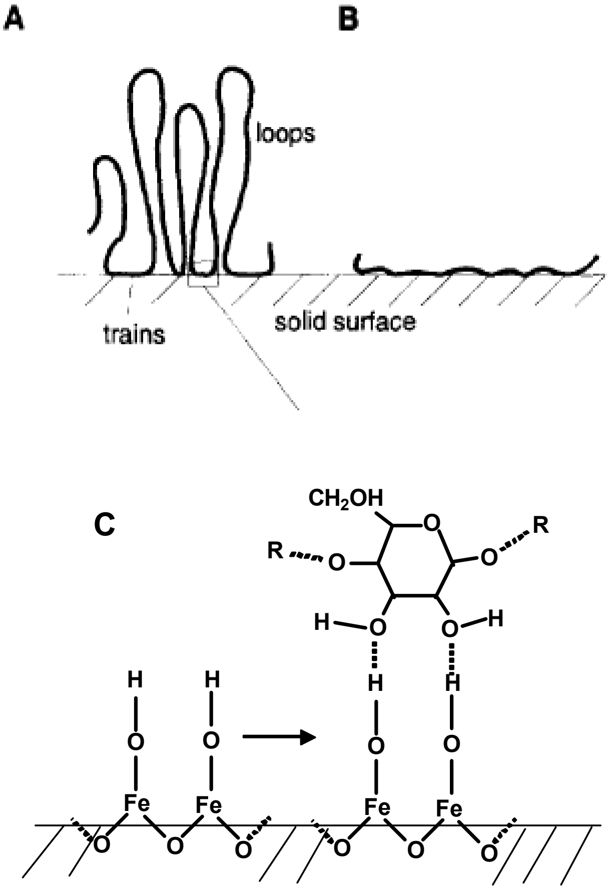


Figure 5.4. Schematic representation of polysaccharide adsorption on metal oxy/hydroxy surface. (A) and (B) show the integral polymer on a macro scale. (C) shows the interaction between polysaccharide (guar gum) monomers and the solid (Fe oxy/hydroxy) surface.

HMW guar depressed pyrite slightly more than LMW at alkaline pH values. However, the effect of molecular weight was more significant at acidic pH value. This may be attributed to the differences in the nature of surface species on pyrite surface at different pH values. The increased depression with moleculer weight exhibited by the guars could be due to the fact that, in general, a longer chain length leads to more adsorption and thicker adsorbed layer at the same polymer concentration due to the extension of the tails with increasing concentration.

In the alkaline conditions, the interaction mechanism postulated by Laskowski et al (1999b) appears applicable to the pyrite–guar gum system. Hydroxyl groups on the polysaccharides interact with the iron hydroxy species formed on the pyrite surface under alkaline pH values in a chemical complexing process. The mechanism is schematically represented below (Figure 5.5) (Subramanian et. al., 2000)

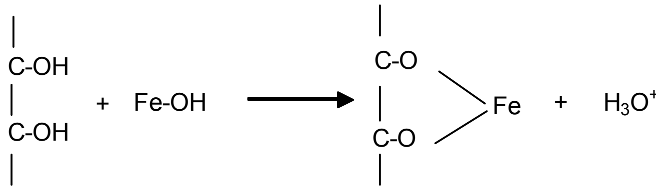


Figure 5.5. Mechanism between the hydroxyl groups of guar and Fe-OH

Electrophoretic experiments show that the negative zeta potential values reduced in proportion to the amount of the polymer adsorbed (Figure 4.12). Besides, with increasing pH, there were more hydroxyl species present and more reaction sites for the guar gum, which increased the adsorption density of guar gum as shown in Figure 4.17).

At pH 11 the flotation recovery was low (around 35-45%) (Figure 4.1) due to presence of the very stable $Fe(OH)_3$ species on the surface of the pyrite, which inhibited the adsorption of SIPX. With the addition of guar gum, the flotation recovery was further decreased to below 10%. This was a in correlation with the theory that guar gum interacts with surface iron oxy-hydroxy species on pyrite.

As it was discussed above, the flotation recovery naturally decreased due to the formation of the stable $Fe(OH)_3$ species in strongly alkaline pH values. This decrease in recovery was greater under non-aerated conditions, i.e. in the absence of dissolved oxygen, this may be attributed to less dixantogen formation or better guar gum adsorption. However, the results of adsorption tests showed clearly that there was no significant difference in adsorption densities of non aerated and aerated conditions (Figure 4.18). Therefore, the decrease in the recovery in nil condition was attributed to less dixanthogen formation rather than better guar adsorption.

The results showed that the depression was much more significant with HMW guar gum, particularly at high pH values (Figures 4.4). This was in agreement with the literature as guar gums with higher molecular weights adsorb more strongly than low molecular weights (Shortridge et.al., 2000). Addition of HMW guar gum tended to produce a less negative surface than the addition of LMW guar (Figure 4.12). Guar gum reduced the zeta potential at pH 9 which is compatible with the findings in literature (Rath et. al., 2000). Thus the primary effect of the large molecules appears to shift the slipping plane further away from the interface. Moreover the addition of guar gum in the range of 0.1 to 10 ppm correspondingly reduces the negative zeta potential values in proportion to the polymer concentration. These findings suggest that some conformational rearrangements of the macromolecules is taking place with increasing extension of the looping chain as the polymer concentration is further increased. These observations are in agreement with the effect of the adsorption of large non-ionic molecules on the zeta potential as reported by other researchers (Rath et. al, 2000; Nyamekye and Laskowski., 1993).

Zeta potential measurements for both HMW and LMW guar gums in the presence of calcium ions were found to be zero for all conditions. In fact, the surface charge became zero after addition of 10^{-2} M Ca^{2+} (Figure 4.11) and guar addition did not change it, as excepted. This indicates that calcium ions adsorb on pyrite surface and at pH 9, the most likely species are Ca^{+2} and $Ca(OH)^{+}$(Figure 5.6).

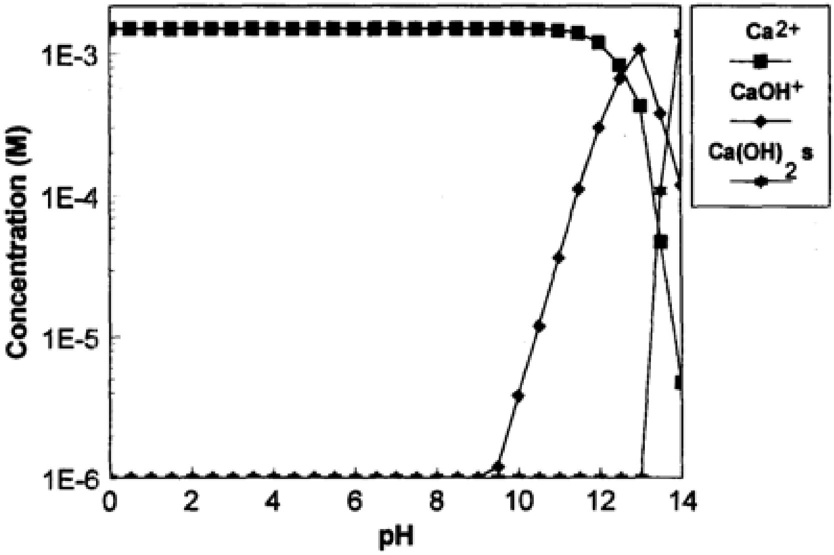


Figure 5.6. Solution species diagram for 60 ppm $CaCl_2$ (after Vergouw et.al, 1998)

It is also known that there is a special affinity of polysaccharides for calcium ions (Harris et. al., 2005). Thus the adsorbed calcium ions on the pyrite surface may act as a bridge for the guar gum, thus allowing indirect adsorption onto the pyrite surfaces.

Figure 4.5 shows that the calcium ions actually activate pyrite since the flotation recoveries increase with calcium ion additions. It appears that adsorbed cations (as confirmed by zeta-potential measurements) provided a high density of surface active sites which electrostatically attract negatively charged xanthate. As a result, the xanthate concentration in the surface region may be increased sufficiently to promote the redox reaction that forms dixanthogen in the boundary layer. It is also possible that the adsorbed metal ions reduce the electrochemical potential of xanthate oxidation (Zhang and Finch, 1997).

In spite of the findings in literature, the results of flotation (Figure 4.5), zeta-potential and adsorption experiments (Figure 4.19) in this study showed that adsorption of guar gum, both HMW and LMW, was slightly affected by addition of calcium ions. $Ca(OH)_2$ is considered to be a Bronsted base compound as charactarized by its high pzc. But as shown in figure 5.5 most of the calcium ions are found in the form of Ca^{+2}. Therefore Ca ions did not effect the adsorption of guars since they are neutral molecules there is no electrostatic repulsion between guars and pyrite. So we can also conclude that electrostatic interaction is not one of the adsorption mechanism between guar and pyrite. So as a result, the hydrogen bonding and Bronsted acid base interaction can be postulated as the dominant adsorption mechanisms between pyrite and guar gum.

5.3. Adsorption Mechanism of CMCs on Pyrite

In this work, adsorption mechanism of CMCs on pyrite was investigated by using two CMCs, as high degree of substitution (HDS) and low degree of substitution. The higher degree of substitution gives higher negative charge to the CMC molecule.

CMC type depressants are also classified as polysaccharides, like guar gum, but their structure is different. This difference brings them a negative electrical charge and capability to adsorbed both from –OH and -COO$^-$ groups in their structure. The mechanism is schematically represented below. (Figure 5.7a, b and c) (Laskowski and Liu, 1999b)

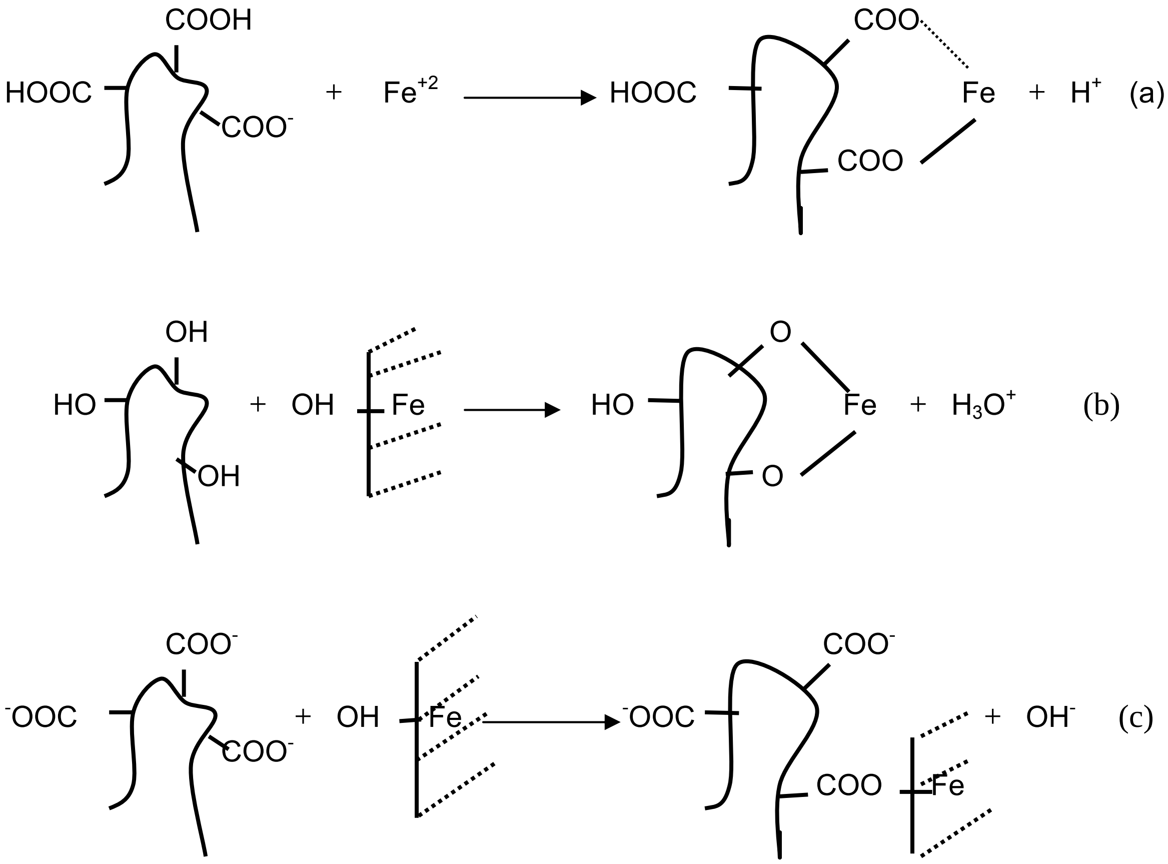


Figure 5.7 Possible interaction mechanisms on the adsorption of CMC
a) Possible reaction between carboxyl groups of CMC and ferrous ions
b) Possible reaction between hydroxyl groups of CMC and Fe-OH
c) Possible reaction between carboxyl groups of CMC and Fe-OH.

In CMC, both the carboxymethyl groups and hydroxyl groups interact with mineral surface metallic sites. The carboxymethyl groups and the hydroxyl groups interact with both metal cations and metal hydroxy-species (Figure 5.7a and c) while the hydroxyl groups can only interact with metal hydroxy species which is an Bronsted acid-base interaction. Therefore, the interaction depends on the pH. The strongest interaction can be expected at pH values where the surface metal ions are fully hydroxylated.

The solution pH is expected to have pronounced effect on CMC adsorption. This is because the solution pH affects the dissociation of the carboxyl groups, the hydroxylation of mineral surfaces, and the mineral surface charge. The presence of two types of adsorbing groups in CMC, coupled with the status of surface metal hydroxylation and surface charge, can result in very different adsorption and depression behaviour of CMC in mineral flotation.

The effects of solution pH on interaction of the carboxymethyl groups of CMC with mineral surfaces are more complicated. CMC macromolecules will become negatively charged when solution pH is raised above pH 4.4, and the charge density will depend on the degree of substitution. (Laskowski and Liu, 1999a) If mineral surfaces are also negatively charged at such pH, the adsorption of CMC will be affected due to electrostatic repulsion. This is why HDS CMC adsorb less on pyrite than LDS CMC.

The affinity of CMC was low at pH 11 because of stable ferric hydroxide species formed at this pH. So CMC can only interact with hydroxyl groups.

The flotation tests showed that there was no significant depression with HDS CMC, even at dosages as high as 500 ppm (Figure 4.6). However, LDS CMC was very effective at high dosage and in the absence of dissolved oxygen in the solution. The surface of pyrite and CMC are negatively charged at all pH values irrespective of aeration condition. Addition of CMC increased negative charge of pyrite linearly as a function of CMC dosage, indicating its adsorption on pyrite (Figure 4.13). Similar results were obtained with both CMCs. However, adsorption tests showed that adsorption density of HDS CMC is considerably lower than LDS CMC.

The results showed clearly that, unlike guar gums, both CMCs did not adsorb on pyrite effectively. This was mainly attributed to the electrostatic repulsion between the highly negatively charged substituted groups of the CMC and the negatively charged pyrite surface.

CMC with a low degree of substitution appeared to be readily adsorbed more than highly substituted CMC. Consequently, better depression of pyrite was obtained with less substituted CMCs. This may be due to the lower electrostatic repulsion associated with LDS CMC, allowing greater adsorption on pyrite surfaces.

CMCs require high dosages to depress pyrite since some of it appears to be consumed in surface cleaning. LDS CMC depressed pyrite more than HDS CMC at high dosages, possibly due to steric effects. This effect was more pronounced in the absence of oxygen in solution. In fact, HDS CMC had almost no depressing effect on pyrite.

Zeta potential of pyrite was slightly more negative at pH 9 with 30 minutes of aeration. This was attributed to formation of a higher amount of negatively charged Fe oxy/hydroxy species. Additionally, CMCs are known to have a negative charge which increases with higher degree of substitution of the reagent. Therefore, HDS CMC has higher negative charge than LDS CMC.

Since, the main adsorption mechanism of CMCs on pyrite is considered to occur through electrostatic attraction, there may be an electrostatic repulsion between negatively charged pyrite and CMCs, particularly with HDS CMC, at pH 9. The electrostatic repulsion was smaller between LDS CMC and pyrite in the absence of dissolved oxygen. Pyrite was best depressed at high LDS CMC dosages.

Addition of calcium changed zeta potential of pyrite from negative to positive depending on the concentration of calcium. The possible calcium species adsorbed on pyrite act pH 9 may be Ca^{+2} and $Ca(OH)^{+}$.

Flotation experiments performed in the presence of 10^{-2}M $CaCl_2$ and 200 ppm depressant dosage given in Figure 4.8 showed that addition of calcium promoted pyrite depression under all conditions. Although HDS CMC also depressed pyrite, LDS CMC was the more effective depressant particularly in the absence of dissolved oxygen. As it was observed with the experiments in the absence of calcium ions, 30 minutes of pre-aeration reduced the efficiency of the depressant. This could be attributed to the higher rate of dixanthogen formation in the presence of dissolved oxygen, which in turn competes with CMC molecules.

Zeta potential measurements showed that surface charge of pyrite changed from neutral to negative values with CMC addition, indicating adsorption of CMC on pyrite. There were no clear differences in zeta potential values between different CMCs and pre-conditioning, which could be correlated with flotation results. This interaction takes place between the carboxyl groups in CMC molecule and the positively charged metal hydroxy complexes.

The oxidation of pyrite leads the surface to be covered with oxidation products, and the degree of coverage reflecting the extent of the oxidation – which is readily detected through electrophoretic measurements (Fornasiero and Ralston, 1992 and Fullston et al, 1999). This indicates that there was not a full surface coverage of oxidation products on the aerated pyrite sample and moreover that the surface was not significantly oxidized at all.

Since dixanthogen is formed more readily in the aerated situation as noted in earlier, this may cause an increase in the zeta potential due to the formation of stable neutral dixantogen species. It may be expected that majority of the calcium is present as Ca^{+2} and small amount of $Ca(OH)^+$ at pH 9 (Figure 5.6). However, it must be noted that solubility diagrams are constructed using the thermodynamic data under equilibrium conditions and do not take into consideration the kinetics of the process. This appears reasonable for a 10^{-2} M $CaCl_2$, noting that the solubility of $Ca(OH)_2$ is about 1 g/l at room temperature. Therefore, positive zeta potential value (Figure 4.11) could be obtained at high dosages of $CaCl_2$ such as the amount used in this test work (King, 1992, Schindler and Stumm, 1987 and Stumm and Morgan, 1981).

The effect of Ca^{+2} ions on the adsorption of CMCs which have different degree of substitution also studied. The results indicate that for both CMCs with the presence of Ca^{+2} ions leading to the greatest adsorption density (Fig 4.19). This can be attributed to charge screening of the carboxyl groups on the polymer results in a lowering of the electrostatic repulsion between the pyrite surface and the CMC thus allowing for greater adsorption. Screening of charges along the chain lowers the intermolecular electrostatic repulsion. Therefore at the high ionic strength also has the effect of allowing the polymer to form a more tightly coiled conformation so allowing a higher adsorption density to be achieved (Morris et al., 2002).

Also the adsorption results indicate that higher adsorption densities are obtained as the degree of substitution of the polymer decreased which is compatible with the findings in the literature (Parolis et al, 2004). LDS CMC adsorb to a greater extent (Figure 4.15) than HDS CMC. It is possible that the ionic strength used is not high enough to ensure complete neutralization of the charge of the HDS CMC and so some charge repulsion is allowed to take place.

As mentioned earlier, with the presence of calcium ions the flotation recovery of pyrite decreased (Figure 4.14). This may be due to the formation of calcium polysaccharide bridge between the species Ca^{2+} or $Ca(OH)^{+}$ and CMC .

6. CONCLUSIONS

Guars achieved a strong depression even at low dosages. This indicates that maximum surface area coverage of the guar on the pyrite can be achieved at very low dosages. Their performance was affected by molecular weight and also aeration. Guars were more effective in non-aeration conditions due to lack dissolved oxygen content which is necessary for dixanthogen formation for pyrite flotation. They are not affected by the presence of calcium ions. Highest depressive effect was at pH 9. This supports the adsorption mechanism proposed by Laskowski at pH 9 but also suggests hydrogen bonding at pH 5. But the most effective depressant mechanism is considered to be Bronsted acid base interaction since hydrogen bond is very weak.

CMCs, on the other hand, showed poor depressing ability under the same solution conditions. The kinetics of CMC adsorption onto a negative surface is extremely slow as there is electrostatic repulsion between the surface and the polymer. CMC's are only effective if they have LDS which means less negatively charge and at high dosages their performance was affected by pH. Presence of calcium affected CMC adsorption substantially probably through steric effects but the mechanism is not clear yet.

In non oxidative condition, flotation of pyrite was inhibited presumably because of less dixanthogen formation and/or enhanced depressant adsorption under this condition. There was not a significant difference between oxidative and non-oxidative experiments in the adsorption tests. Therefore, 30 min aeration was not effective on depressive ability of these polysaccharides, directly.

The isotherms follow Langmuirian behaviour and resemble the L1 type of the Giles classification (Giles et al., 1960). The main adsorption mechanism for these types of depressants is generally accepted as Bronsted acid-base interaction. Guar has more hydroxyl groups which are responsible for adsorption while some of hydroxyl groups of CMC are substituted with carboxyl groups. Therefore, guar adsorption was stronger while CMC adsorption lower possibly because of electrostatic repulsion occurs between negatively charged carboxyl groups of CMC and negatively charged pyrite. Presence of calcium ions, however, changed completely adsorption behavior of CMCs. Calcium ions led to formation of positively charged spots on pyrite surface which interacted with CMCs through electrostatic attraction.

Also, it can be observed that the adsorption of guar gum was greater than CMC type of depressants onto pyrite. In the case of guar, this can be attributed to its high molecular weight and in the case of CMC, this can be attributed to electrostatic repulsion between highly negatively charged guar and negatively charged pyrite.

The adsorption mechanisms of polysaccharides are not fully understood, yet. There are a lot of mechanisms that can play role on adsorption, such as hydrogen bonding, hydrophobic bonding, electrostatic interaction and bronsted acid base interaction. These mechanisms mostly depend on species formed on the mineral surface according to pH and Eh.

Therefore for guar at pH 5 the most dominant mechanism can be postulated as hydrogen bonding. At alkaline pH values the mechanism can be postulated as Bronsted acid base interaction with the effect of Fe oxy/hydroxyl ions present at pH 9 and 11.

For CMC, the mechanisms can be hydrogen bonding as well as electrostatic interaction and Bronsted acid base interaction.

7. FURTHER STUDIES

In order to better understand the adsorption mechanisms of polysaccharides, polysaccharide - xanthate interaction should also be studied since xanthate adsorb chemically on pyrite surface so collector could passivate the effect of polysaccharides.

The tests in this work were performed with pyrite as the only mineral. However, the galvanic interaction between sulphide minerals has an important role on the surface reactions of the sulphide minerals. Therefore, adsorption of Guar gum and CMCs should also be investigated in the presence of a second sulphide mineral, e.g. chalcopyrite.

It is clear that guar is very strong depressant but it is reported as not very selective so all minerals can be depressed. However, it is possible to make them selective with the addition of functional groups to polysaccharides. The results of this work showed that CMC is not very effective depressant for pyrite, so carboxyl methyl groups are not suitable functional groups in the depression of pyrite. Therefore trial of other substitutional functional groups should also be tested for pyrite depression.

Guars and CMCs are natural polysaccharides, but there are also modified commercial polysaccharides like PAM (Polyacrylamide polymers) which have different substitutional groups and some commercial depressants including polysaccharides like S7261. Therefore, adsorption behaviour of these depressants should also be tested and compared with guar gum and CMCs.

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