

Surface Chemical Studies on Pyrite in the Presence of Polysaccharide-Based Flotation Depressants

R. K. Rath,* S. Subramanian,*¹ and T. Pradeep†

*Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India; and †Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai 600036, India

Received October 20, 1999; accepted May 30, 2000

The interaction of dextrin and guar gum with pyrite has been investigated through adsorption, flotation, and electrokinetic measurements. The adsorption densities of the polysaccharides onto pyrite reveal a region of higher adsorption density in the pH range 7.5–11, with a maximum around pH 10 for both polymers. The isotherms exhibit Langmuirian behavior. The adsorption density of guar gum onto pyrite is higher than that of dextrin. Electrokinetic measurements indicate a decrease in the electrophoretic mobility values in proportion to the concentration of the polymer added. Co-precipitation tests confirm polymer–ferric species interaction in the bulk solution, especially in the pH range 5.5–8.5. The pH range for higher adsorption, significant co-precipitation, and appreciable depression of pyrite encompass each other. XPS and FTIR spectroscopic studies provide evidence in support of chemical interaction between hydroxylated pyrite and the hydroxyl groups of the polymeric depressants. © 2000 Academic Press

Key Words: polysaccharide; pyrite; flotation; adsorption; co-precipitation; FTIR; XPS.

INTRODUCTION

Pyrite is commonly associated as a gangue mineral with several base metal sulfides such as copper, lead, and zinc. It occurs as an impurity in the Indian copper deposits found at Chitradurga, Karnataka; Malankhand, Madhya Pradesh; Khetri, Rajasthan, and Rakha; and other deposits of Bihar. The Pb–Zn ores of Rajasthan also contain pyrite as a constituent sulfide (1). It thus becomes important to selectively separate pyrite from the base metal sulfides. Cyanide, sulfide, and hydroxides are the commonly used flotation depressants for pyrite (2). Some of these inorganic depressants, though effective, are found to be toxic and pose environmental hazards during handling. Consequently, attempts are being made to develop alternate reagent schemes, which are environmentally benign. Polysaccharide-based reagents have been utilized in the mineral industry for over seven decades, principally as a depressant for a variety of

minerals. These organic polymers are not only nontoxic but are also biodegradable and relatively inexpensive.

Pioneering contributions have been made by Laskowski and co-workers with respect to the interaction of dextrin with several sulfides and oxides (3–9). These studies have highlighted the importance of surface metallic species for adsorption to take place. Further, a good correlation was observed between the pH of maximum co-precipitation and the isoelectric points of the corresponding metal hydroxides. Based on these systematic and detailed studies, it was concluded that the interaction between the metal-hydroxy species and dextrin takes place through a complexation mechanism (3). The interaction of dextrin with metal hydroxides was studied by FTIR and UV-vis spectroscopic studies by Bhaskar Raju *et al.*, and a condensation mechanism was proposed (10). Bogusz and co-workers (11) have shown that dextrin adsorption on pyrite is enhanced in the presence of metal ions. Xu and Aplan (12) have developed a novel system using metal ion hydroxy complexes and organic polymers for pyrite depression in coal flotation. The role of dextrin in the xanthate flotation of pyrite and sphalerite has been examined by Kydros *et al.* (13).

As a part of an ongoing program, the application of polysaccharide-based depressants, such as dextrin and guar gum, in the flotation of sulfides and hydrophobic minerals has been assessed by us (14–18). In the present investigation, the surface property of pyrite in the presence of the above polymers has been studied through adsorption, electrokinetic, and flotation tests. The bulk solution interaction of the polymers with pyrite has been examined by co-precipitation studies. FTIR and XPS studies have been conducted to elucidate possible mechanisms of interaction between the polysaccharide-based reagents and pyrite.

EXPERIMENTAL

Materials

A pure mineral sample of pyrite was obtained from Alminrock Indscer Fabriks, Bangalore, India. Mineralogical and X-ray powder diffraction data confirmed that the pyrite sample was of high purity with only a trace amount of quartz. The sample was dry ground using a porcelain ball mill at a speed of 60 rpm.

¹ To whom correspondence should be addressed. Fax: 91-80-3600472/3600683. E-mail: ssmani@metallrg.iisc.ernet.in.

The ground sample was then dry screened through 150-, 75-, and 37- μm BSS sieves and stored in plastic containers. The $-37\text{-}\mu\text{m}$ size fraction was used for the electrokinetic and adsorption studies, while the $(-150 + 75)\text{ }\mu\text{m}$ fraction was used for the flotation tests. The BET nitrogen specific surface area of $-37\text{ }\mu\text{m}$ pyrite was found to be $2.98\text{ m}^2/\text{g}$.

The sample of guar gum used in the study was obtained from s.d.Fine-Chem Ltd., Bombay, India, whereas the white dextrin sample was a J. T. Baker product. The molecular weights of guar gum and white dextrin were determined by HPLC to be 4.22×10^6 and 3980, respectively. The polysaccharide solutions were prepared by dispersing a known weight in cold distilled water and then dissolving it with boiling distilled water. The polymer solutions were prepared fresh each day.

Potassium nitrate was used to maintain the ionic strength and nitric acid and potassium hydroxide were used as pH modifiers. All the reagents used in this study were of analytical grade. Deionized double-distilled water with a final conductivity of $<1.5\text{ }\mu\text{mho}$ was used for all tests.

Methods

Adsorption studies. In a typical adsorption test, 0.5 g of pyrite powder was taken and made up to 50 ml after addition of desired amounts of 10^{-2} M KNO_3 , polymer solution of known concentration and pH in 250-ml Erlenmeyer flasks. The suspensions were then agitated for 2 h using a Remi Orbital Shaking Incubator at 250 rpm at 25°C . After equilibration, the solution pH was again recorded. The solution was then centrifuged for 10 min at 5000 rpm using a Remi Laboratory Centrifuge R8C. The supernatant liquid was then clarified using Whatman 42 filter paper and analyzed for equilibrium concentration of polymer using a Shimadzu UV-260 Spectrophotometer as per the method suggested by Dubois *et al.* (19).

Electrokinetic measurements. Electrophoretic mobility measurements on pyrite, with and without polymers, were carried out using a Zeta meter 3.0 instrument (Zeta Meter Inc., USA) with bright molybdenum anode and platinum cathode electrodes. Potassium nitrate was used to maintain the ionic strength at 10^{-3} M . A suspension of pyrite at 0.2 g/l was conditioned at a particular pH and equilibrated for one hour at room temperature (27°C). Measurements were made on pyrite both in the absence and presence of different concentrations of guar gum or dextrin.

Flotation tests. Flotation tests were carried out using a modified Hallimond tube (20). Potassium ethyl xanthate (PEX, 10^{-3} M) was used as collector for the pyrite flotation. For the flotation tests, 1 g of $(-150 + 75)\text{ }\mu\text{m}$ pyrite sample was conditioned with 200 ml of double-distilled water at a particular pH for 10 min using a magnetic stirrer. The sample was then transferred to the Hallimond tube, and nitrogen gas was passed at the rate of 100 ml per min. After flotation for 3 min, the concentrate and the tailing fractions were separately filtered, dried, and weighed. The recoveries are expressed on a percentage weight

basis. In experiments where the polymers were used as depressants, the sample was further conditioned for 10 min at a given pH with the polymer prior to flotation.

Co-precipitation tests. Co-precipitation tests were carried out between dextrin/guar gum and ferric ions in aqueous solution to elucidate the interaction mechanism in the bulk solution. A known amount of ferric nitrate solution was mixed with polymer solution in such a way that the final concentration of ferric ions was 55 ppm and that of dextrin/guar gum solution 100 ppm in 100 ml solution. The desired pH was adjusted by adding either nitric acid or potassium hydroxide solution. After 30 min, the solution was centrifuged at 5000 rpm for 10 min in a Remi Laboratory Centrifuge R8C. The supernatant was then analyzed for total iron by using a Thermo Jarrell Ash atomic absorption spectrophotometer. Polymer concentration was determined using the method of Dubois *et al.* (19). Similar tests were also carried out in 100-ml solutions of Fe^{3+} ions or polymer as control experiments.

FTIR studies. The infrared spectra of pyrite, dextrin, guar gum, and the products of interaction between the mineral and the polymers were recorded using a Nicolet Model 400D Fourier Transform Infrared Spectrometer operating in the range $4000\text{--}400\text{ cm}^{-1}$. The KBr pellet technique was adopted for recording the spectra. Approximately 2 mg of the desired powder sample was thoroughly mixed with 200 mg of spectroscopic grade KBr and pressed into pellets for recording the spectra.

XPS studies. The X-ray photoelectron spectra of the samples were recorded using the ESCALAB MK-II instrument of V.G. Scientific Ltd., UK. A vacuum of 10^{-8} Mbar was maintained during the data collection. $\text{Mg K}\alpha$ was the target used in this study.

RESULTS AND DISCUSSION

Adsorption Studies

Detailed adsorption experiments have been carried out to study the effect of time, pH, and polymer concentration on the adsorption densities of dextrin and guar gum onto pyrite.

Kinetics. The adsorption densities of dextrin and guar gum onto pyrite as a function of time are shown in Fig. 1. The experiments were carried out at a natural pH of 2.7. It is evident that the adsorption density reaches its saturation value in about 1 h for both dextrin and guar gum. In all further adsorption studies, the time of equilibration was fixed at 2 h for both polymers. It is apparent from the figure that the adsorption density of guar gum onto pyrite is higher than that of dextrin.

Effect of pH. The effect of pH on the adsorption densities of dextrin and guar gum onto pyrite is shown in Fig. 2. It can be observed that the adsorption density of dextrin steadily increases with increase in pH from 2.6 to about 10 and thereafter decreases slightly with increase in pH. In the case of guar gum, there is a steep increase in the adsorption density from pH 2 to 4 followed

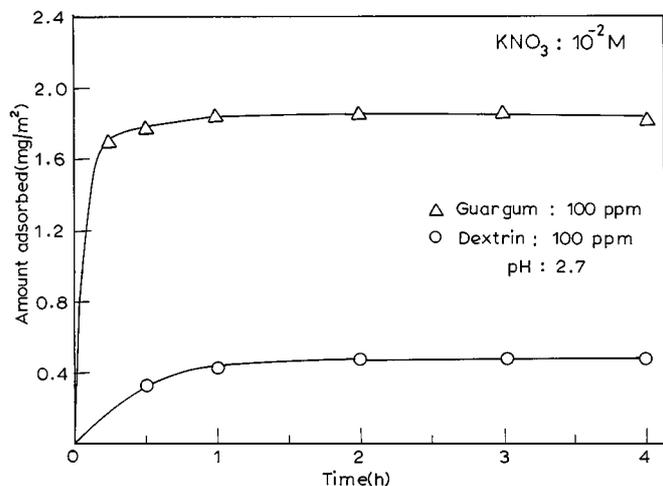


FIG. 1. Adsorption of dextrin and guar gum onto pyrite as a function of time.

by a marginal increase up to pH 10, and beyond that pH, the adsorption density again decreases. It is interesting to note that a region of higher adsorption density is observed in the pH range 7.5–11. The higher adsorption density in the alkaline pH range may be attributed to the role of hydroxylated and hydrous oxide species. At low pH (<4), there is little hydrous oxide precipitated, and above pH 11, complete precipitation of the hydrous oxide occurs leading to a decrease in the adsorption density. Beyond pH 11, the decrease in adsorption density could also be due to increased electrostatic repulsion between the negatively

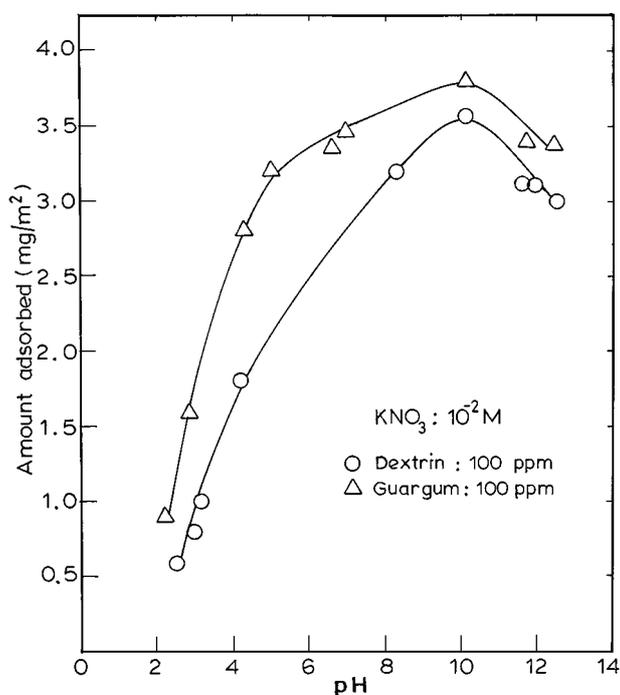


FIG. 2. Effect of pH on the adsorption density of dextrin and guar gum onto pyrite.

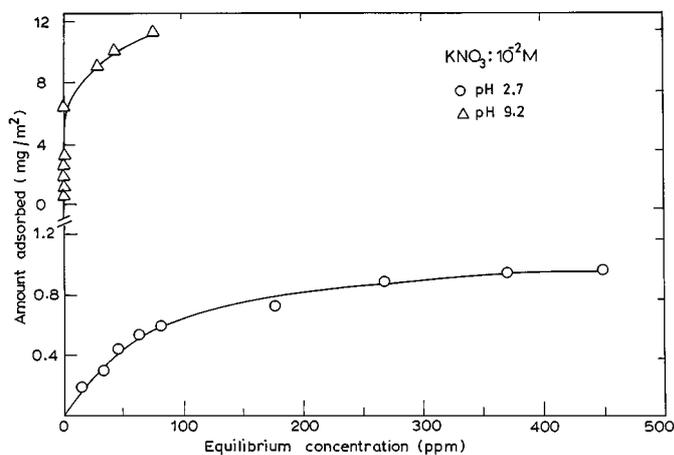


FIG. 3. Adsorption isotherms of dextrin onto pyrite.

charged pyrite and the anionic polymeric chain. Here again, the higher adsorbability of guar gum compared to that of dextrin is clearly reflected.

It is well known that the hydroxyl groups in guar gum are in *cis* conformation while those in dextrin have a *trans* configuration (21). The higher adsorption of guar gum than that of dextrin onto pyrite may be attributed to the more favorable *cis* conformation of its hydroxyl groups apart from its higher molecular weight.

Adsorption isotherms. The adsorption isotherms of dextrin onto pyrite at two different pH values are depicted in Fig. 3. The adsorption density of dextrin onto pyrite at pH 2.7 shows an increase with an increase in equilibrium concentration upto about 250 ppm and thereafter attains saturation. The isotherm at pH 9.2 exhibits a steep rise in the adsorption density especially at lower concentrations and then gradually tends to a plateau region at high concentrations. The adsorption isotherm at pH 2.7 follows the L1 type of the Giles classification (22). On the other hand, the isotherm at pH 9.2 indicates that it is of the high affinity H1 type of the Giles classification (22).

Figure 4 portrays the adsorption isotherms of guar gum onto pyrite at three different pH values namely 2.9, 9.1, and 12.3. An increase in the adsorption density with an increase in concentration is observed. It is noteworthy that the isotherm at pH 9.1 shows the highest adsorption density followed by the isotherms at pH 12.3 and 2.9 in that order. These trends complement the results reported in Fig. 2. The isotherms at pH 9.1 and 12.3 may be classified as high-affinity H1 type, whereas that at pH 2.9 may be categorized as L1 type as per the Giles category (22).

The plot of the reciprocal of the amount adsorbed as a function of the reciprocal of the equilibrium concentration at all pH values studied shows a linear relationship for both dextrin and guar gum (Fig. 5) conforming to the Langmuir equation (23).

Electrokinetic Studies

The electrophoretic mobilities of pyrite as a function of pH in the absence and presence of different concentrations of dextrin

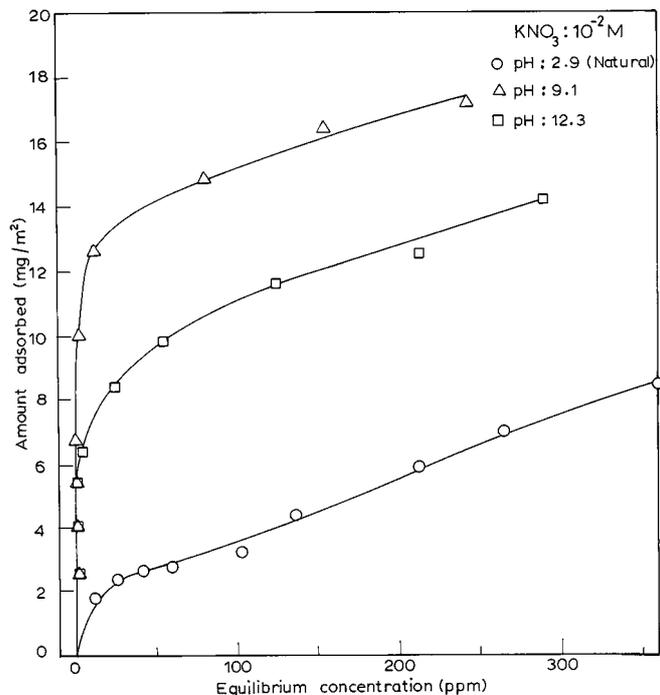


FIG. 4. Adsorption isotherms of guar gum onto pyrite.

and guar gum are shown in Figs. 6a and 6b, respectively. The measurements have been conducted using 10^{-3} M KNO_3 as an indifferent electrolyte. It is apparent from the figures that the isoelectric point (iep) of pyrite is located around pH 6.8. At acidic pH values, pyrite shows positive electrophoretic mobility, whereas in the alkaline pH range, it is negatively charged. It has been reported that the positive charge originates from the formation of a partially hydrolyzed cationic species, and it is eliminated in the pH range of complete hydrolysis (24). Similar iep values around pH 6–7 have been reported by other workers (13, 25) for pyrite. The addition of different concentrations of dextrin (Fig. 6a) or guar gum (Fig. 6b) in the range of 1 to 10 ppm

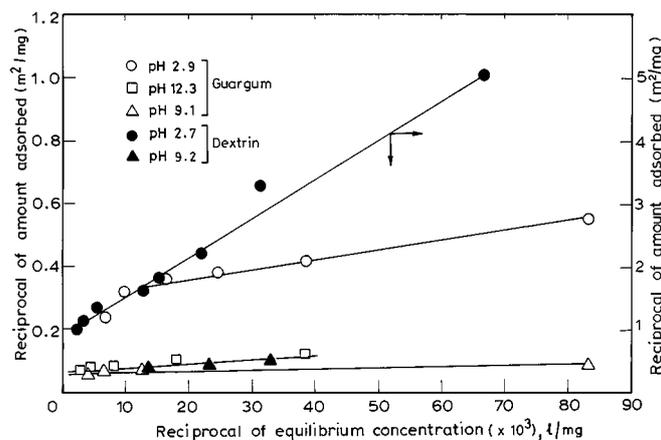


FIG. 5. Plot of reciprocal of adsorption density versus reciprocal of equilibrium concentration of dextrin and guar gum.

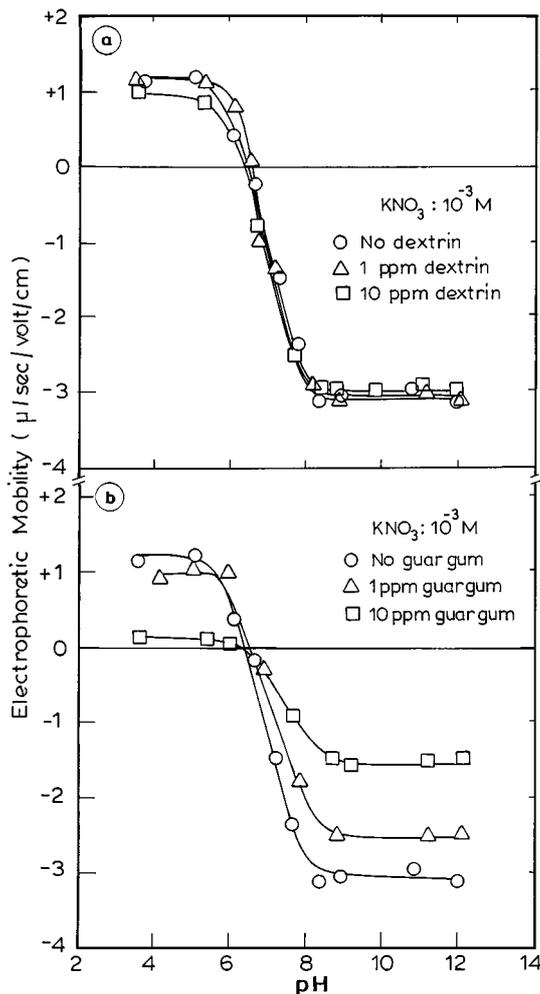


FIG. 6. Electrophoretic mobility of pyrite as a function of pH in the absence and presence of different concentrations of (a) dextrin and (b) guar gum.

correspondingly reduces the negative electrophoretic mobility values in proportion to the polymer concentration, presumably without any shift in the iep value, resembling the influence of an indifferent electrolyte. A similar depression of the surface charge of pyrite in the presence of dextrin was also observed by Kydros *et al.* (13).

Since the polymers appear merely to reduce the electrophoretic mobility in absolute magnitude under all the pH conditions studied, the primary effect of the large macromolecules seems to be to shift the slipping plane further away from the interface. These results suggest that some conformational rearrangements of the macromolecules take place with increasing extension of the looping chain, when the polymer concentration is further increased. These observations are in consonance with the results of the effect of the adsorption of large nonionic molecules on the zeta potentials reported by many researchers (9, 26–29).

The adsorption of the polymeric depressants, namely dextrin and gum, at the pyrite surface brings about a reduction of

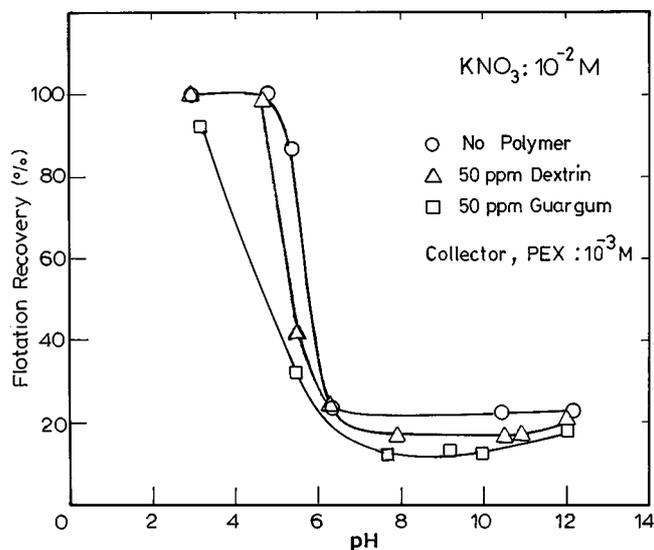


FIG. 7. Effect of pH on the flotation recovery of pyrite in the absence and presence of dextrin and guar gum.

the electrophoretic mobility values, rendering the pyrite surface hydrophilic.

Flotation Studies

The flotation recovery of pyrite as a function of pH, in the absence and presence of dextrin/guar gum, is depicted in Fig. 7. Potassium ethyl xanthate (PEX, 10^{-3} M) was used as the collector for pyrite. It is apparent that complete floatability of pyrite is observed up to pH 5.5. Beyond pH 5.5, the recovery decreases drastically to around 20% at pH \sim 6.5 and remains at that value up to pH 12. The depression of pyrite at alkaline pH is due to the preferential adsorption of hydroxyl ions in comparison to the collector ions. Similar results have been obtained by other workers (11, 13).

In the presence of dextrin, there is not much of a change in the flotation recovery up to pH 5, but it steeply drops to about 40% at pH 5.6, and in the pH range 7–12 the flotation recovery is further reduced (\approx 18%). With respect to guar gum, the flotation recovery of pyrite decreases steeply from about 90% at pH 3 to about 30% at pH 5.5. It is further lowered to about 15% at pH 8 and remains close to that value upto pH 12. It can be observed from the figure that the depression action with guar gum is marginally better than that with dextrin, complementing the adsorption data.

The effect of dextrin/guar gum concentration on the flotation recovery of pyrite at three different pH values is portrayed in Fig. 8. It can be observed that the flotation of pyrite is hardly affected at pH 3.5 up to 10 ppm dextrin/guar gum concentration. A marginal depression is observed in the concentration range 10–100 ppm of dextrin/guar gum at pH 3.5. The flotation recovery of pyrite at pH \sim 5.5 drops appreciably to about 40 and 30% by the addition of 50 ppm of dextrin and guar gum, respectively. It may be recalled that in the absence of the depressants, the

recovery of pyrite is close to 85% at this pH (Fig. 7). It can be observed that pyrite is significantly depressed at pH 10.5 in the presence of 1–100 ppm dextrin/guar gum concentration, though similar results were obtained even in the absence of the polymeric depressants. Here again, guar gum is found to be a slightly better depressant than dextrin. The flotation recoveries are considerably reduced in the pH range 6–12, both in the absence and in the presence of the polysaccharides. In other words, the pH range of efficient depressant action of the polysaccharides overlaps with that of pyrite depression in presence of hydroxyl ions of the added alkali. However, the depressant action of the tested polysaccharides is also clearly discernible in the pH range 5 to 5.5, wherein the flotation recoveries are reduced to about 30–40%, when compared to \sim 85% floatability of pyrite in the absence of the polymers at this pH value.

Co-precipitation Studies

The results of the co-precipitation tests conducted by interacting dextrin or guar gum with ferric ions are given in Fig. 9. It is apparent from the figure that the total concentration of iron species decreases significantly from about 50 to below 5 ppm in the pH range 6 to 8.5 and thereafter increases once again to about 45 ppm at pH 12. It has been reported (30) that ferric ion hydrolyzes much more readily than ferrous iron commencing at pH 1. At acidic pH, di- $[\text{Fe}_2(\text{OH})_2^{4+}]$ and mononuclear $[\text{FeOH}^{2+}]$ and $[\text{Fe}(\text{OH})_2^+]$ species are formed while $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_4^-$ appear in neutral and basic media. The enhancement in the residual concentration of iron above pH 8.5 may be attributed to the formation of such soluble species. From Fig. 9 it can be observed that there is not much of a change in the residual concentration of ferric species in the pH range investigated in the presence of dextrin/guar gum. However, there is a significant decrease in the concentration of dextrin or guar gum in the presence of ferric species, particularly in the pH range 5.5 to 8.5, attesting to their interaction in the bulk solution. The pH values for maximum co-precipitation are close to

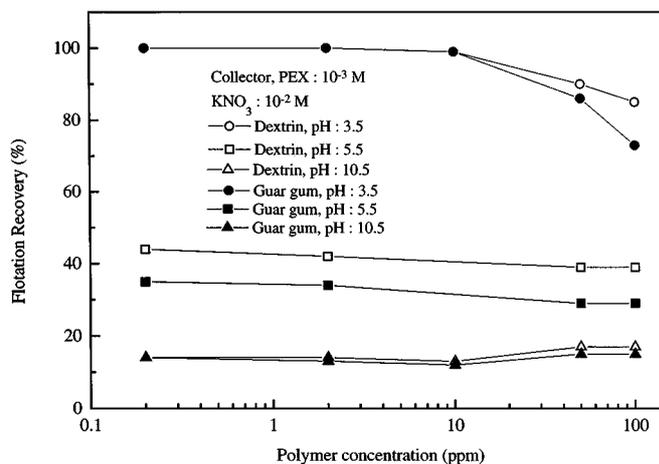


FIG. 8. Effect of dextrin and guar gum concentration on the flotation recovery of pyrite.

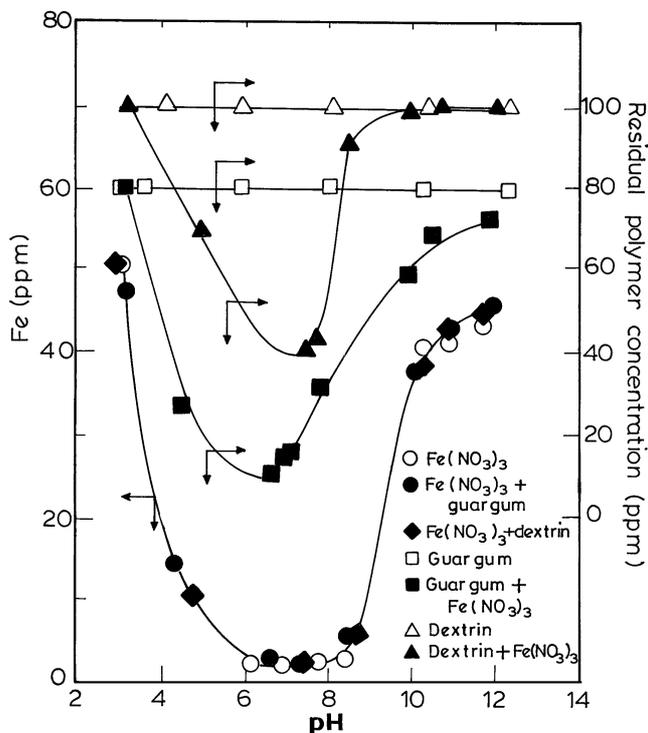


FIG. 9. Effect of pH on the residual concentration of dextrin or guar gum and iron.

7.5 and 7 for dextrin and guar gum, respectively. In the absence of ferric ion, the dextrin or guar gum concentration is unaltered as a function of pH. These studies further testify to the ferric hydroxy species-polymer complex formation in the bulk solution and are in close agreement with the results of interaction of various metal ions with polysaccharides (3, 31-34). In this context, it is pertinent to recall that Liu and Laskowski (3) found a good correlation between the pH of optimum co-precipitation of dextrin/metal ion and the isoelectric point of the corresponding metal hydroxide. In the case of the ferric-dextrin system, the pH of maximum co-precipitation was found to be about 7.5, which is in good agreement with the results of this study. The iep values of ferric hydroxide and other hydroxo-complexes of iron are reported to be in the range of pH 7.4 to 8.4 (35), which falls in the pH range of maximum co-precipitation found in this investigation. Although the adsorption densities of dextrin and guar gum onto pyrite were found to maximum at pH 10, a region of higher adsorption density was clearly observed in the pH range 7.5 to 11, which encompasses the pH range of maximum co-precipitation found in this study, as well as the reported values of the isoelectric point of ferric hydroxy species.

Infrared Spectroscopic Results

The FTIR spectrum of pyrite is portrayed in Fig. 10a. There is a broad band centered around 3255 cm^{-1} that may be attributed

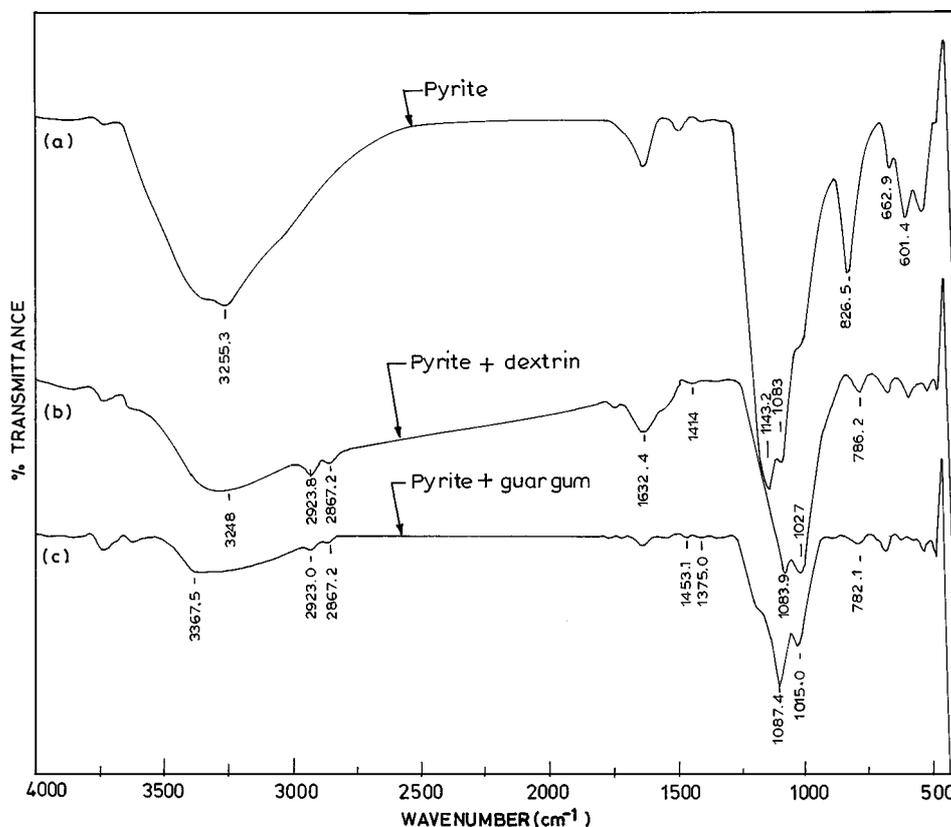


FIG. 10. FTIR spectra of (a) pyrite, (b) pyrite interacted with dextrin, and (c) pyrite interacted with guar gum.

TABLE 1
Characteristic IR Frequencies of the Polymers

| Wave number for dextrin (cm^{-1}) | Wave number for guar gum (cm^{-1}) | Characteristic group |
|----------------------------------------------|-----------------------------------------------|-------------------------------------------------------------------------------------------------|
| 3384 | 3384 | O–H stretching vibration |
| 2924 | 2924 | C–H stretching of CH_2 group |
| 1641 | 1657 | Ring stretching of glucopyranose or galactose/mannose |
| 1440, 1419, 1372 | 1450, 1414, 1350 | Symmetrical deformations of CH_2 group and numerous C–OH deformations |
| 1155, 1083 | 1155, 1078 | C–OH and primary alcoholic – CH_2OH stretching mode |
| 1021 | 1021 | – CH_2 twisting vibration |
| 860, 767 | 871 | Glucopyranose or galactose/mannose |
| 933, 767 | 930, 770 | Ring stretching and ring deformation modes of the α -D-(1–4), α -D-(1–6) linkages |

to hydrogen-bonded hydroxyl groups. The absorption bands in the range $1200\text{--}1000\text{ cm}^{-1}$ may be assigned to pyrite (36). In this region, there is an intense band at 1143 cm^{-1} and a shoulder at 1083 cm^{-1} . Similar bands have been reported by other workers (37). The bands in the region $600\text{--}800\text{ cm}^{-1}$ arise due to the surface oxidation of pyrite. The characteristic IR frequencies of dextrin and guar gum are summarized in Table 1.

The FTIR spectra of pyrite after interaction with dextrin and guar gum are depicted, respectively, in Figs. 10b and 10c. The band at 2924 cm^{-1} in the case of free polymer due to C–H stretching of the – CH_2 groups is split into a doublet and appears at ~ 2923 and 2867 cm^{-1} , both in the case of dextrin- and guar gum-adsorbed pyrite samples. The bands at 1641 and 1657 cm^{-1} due to ring stretching of glucopyranose in the case of dextrin and that due to galactose and mannose for guar gum appear at slightly lower wave numbers, namely 1632 and 1627 cm^{-1} , for pyrite containing adsorbed dextrin and guar gum, respectively. The weak bands in the region $1350\text{--}1450\text{ cm}^{-1}$ due to symmetrical deformations of CH_2 and COH groups appears at almost the same wavenumbers after adsorption, though with reduced intensities. The bands at 1083 and 1021 cm^{-1} due to primary alcoholic – CH_2OH stretching mode and CH_2 twisting vibrations, respectively, for dextrin appear slightly altered after adsorption at 1084 and 1027 cm^{-1} , respectively (Fig. 10b), due to interaction of the –CO groups of the polymers with pyrite. On the other hand, in the case of the guar gum-adsorbed pyrite, the same bands appear at 1087 and 1015 cm^{-1} as those at 1078 and 1021 cm^{-1} for free guar gum. It is noteworthy that the band at $\sim 930\text{ cm}^{-1}$ in the free polysaccharides is absent after adsorption onto pyrite, due to chemical interaction. The weak bands at $\sim 770\text{ cm}^{-1}$ due to ring stretching and ring deformation of α -D-(1–4) and α -D-(1–6) linkages are reduced in the intensity and appear at 786 and 782 cm^{-1} after adsorption of dextrin and guar gum, respectively.

Based on IR studies with respect to the interaction of lead hydroxide with dextrin, Liu and Laskowski (3) have reported that

the intensities of the bands at 930 and 760 cm^{-1} are strongly influenced by substitution on the hydroxyl groups. An interesting observation made by them was that these peaks of dextrin disappeared, when lead hydroxide was in excess, due to complex formation with dextrin involving C-2 and C-3 hydroxyl groups. In a subsequent FTIR study, Bhaskar Raju and co-workers have proposed that the complexation between dextrin and calcium hydroxide proceeded through a condensation mechanism involving the hydroxyl groups at the C-2, C-3, and C-6 positions of dextrin. Further, the intensity of the band at $\sim 930\text{ cm}^{-1}$ was also found to be strongly reduced (10). The IR spectral results of the present study also revealed the absence of the 930 cm^{-1} band, while the band at 770 cm^{-1} was reduced in intensity due to chemical interaction. Moreover, in the IR spectra of ferric hydroxide interacted with dextrin or guar gum, the characteristic peaks at 770 and 930 cm^{-1} originating from the polysaccharides were conspicuously absent (Fig. 11). The spectral results thus corroborate the chemical complexation mechanism, originally proposed by Liu and Laskowski (3).

XPS Results

Fe $2p_{3/2}$ in FeS_2 is expected about 707 eV B. E. The as-received sample shows no intensity in this region (Fig. 12(i)a). The peak maximum of $2p_{3/2}$ appears at 711.2 eV B.E., which is attributable to a trivalent ion (Fe^{3+}), while the $2p_{1/2}$ peak appears at 725.5 eV B.E. After interaction with the polymers, the intensities of both the $2p_{3/2}$ and $2p_{1/2}$ peaks of pyrite are reduced and the binding energy values are slightly lowered, attesting to its chemical interaction with the polymers (Fig. 12(i)a–c).

An examination of the as-received mineral shows (Fig. 12(ii)a) a rather sharp S $2p$ feature at 168.1 eV B. E. The spectrum also portrays a weak peak at 161.3 eV B. E. The former could be attributed to sulfate, whereas the latter is due to sulfide (FeS_2) (38). Upon adsorption of guar gum (Fig. 12(ii)c), the low binding energy feature gains in intensity at the expense of the high binding energy structure. In the dextrin-treated sample, the enhancement of the 161-eV feature is comparatively lower (Fig. 12(ii)b).

O $1s$ in all these samples (Figs. 12(iii)a–c), appears as a single peak around 530 eV B. E. This could be attributed to a surface oxide or sulfate. O $1s$ in the case of pyrite appears at 530.8 eV B.E., while it is slightly shifted to lower B.E. after interaction with dextrin and guar gum. The C $1s$ region of the polymer-exposed samples (Fig. 12(iv)c) is shifted to lower binding energy values ($\sim 283\text{ eV}$ B.E.), confirming the adsorption of the polymers (Figs. 12(iv)b and 12(iv)c). The C $1s$ in the case of the pyrite sample at 285 eV B.E. is due to the presence of impurity carbon.

An evaluation of all the regions suggests the presence of a thick oxide and sulfate layer at the surface of the free mineral. Bulk sulfide is evident from S $2p$ spectrum, whereas it is not apparent from the Fe $2p$ spectrum. This is because of the larger attenuation length of S $2p$ electrons. This suggests an upper limit of the thickness of the contaminant layer, on the order

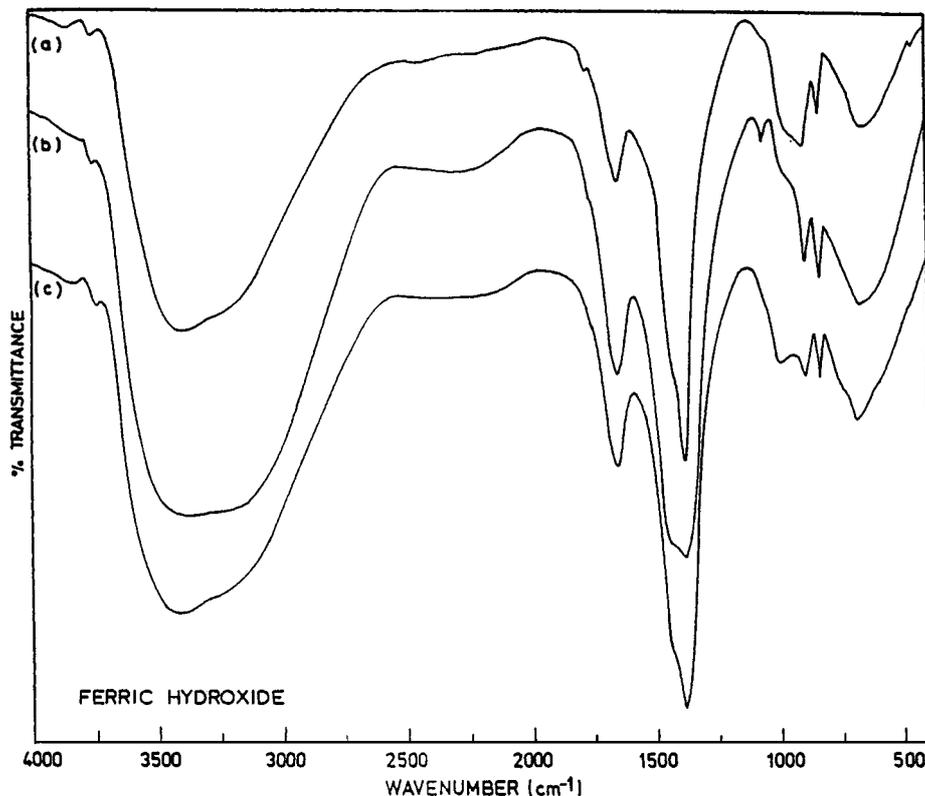


FIG. 11. FTIR spectra of (a) ferric hydroxide, (b) ferric hydroxide interacted with dextrin, and (c) ferric hydroxide interacted with guar gum.

of 50 Å, for the attenuation length of S 2*p* electrons. The fact that the sulfate peak decreases in intensity upon exposure to the polymer shows that it acts as an inhibitor layer preventing reaction with atmospheric oxygen. While the intensity of S 2*p* features due to sulfide is large, corresponding enhancement is not seen for Fe 2*p* features. This is again attributed to the lower mean-free path of the Fe 2*p* electrons. In the dextrin-treated sample, the intensity of S 2*p* due to sulfide is low compared to the guar gum-interacted sample; correspondingly, the intensity of the 711-eV B. E. structure in the Fe 2*p* spectrum is also weak. This could be due to a relatively weaker interaction of dextrin with the mineral. The lower S 2*p* intensity of the sulfide peak in this sample cannot be attributed to a larger overlayer thickness, since the molecular weight of dextrin is substantially smaller. This suggests that the interaction strength of dextrin to the mineral is weaker than that of guar gum. This also leads to poorer surface passivation. The XPS data reinforce the results of the FTIR spectroscopic studies in support of the chemical interaction mechanism for the pyrite-polymer systems.

Adsorption Mechanisms

Based on the studies carried out at the pyrite-solution interface and in the bulk solution, the following facts emerge:

(1) A region of higher adsorption density of dextrin/guar gum onto pyrite is observed in the pH range 7.5–11, with the adsorption maximum being around pH 10.

(2) The co-precipitation tests show strong interaction between the polysaccharides and the ferric species in the pH range 5.5–8.5, with the maximum co-precipitation taking place around pH 7–7.5 for the two polymers. These results are in good agreement with those reported earlier for the ferric hydroxide-dextrin system (3).

(3) Significant depression of pyrite is seen in the pH range 6–12, both in the absence and in the presence of the polysaccharide samples. Thus, there is an overlapping of the pH region of effective depressant action of the polysaccharides and that due to the hydroxyl ions of the alkali alone. However, the depressant action of the polymers is unambiguously discernible at pH 5–5.5, wherein the recoveries drop to about 30–40%, compared to about 85% in the absence of the polysaccharides.

(4) Electrokinetic studies indicate that the isoelectric point of the pyrite sample is located around pH 6.8, suggestive of surface oxidation, which is confirmed by the X-ray photoelectron and FTIR spectroscopic studies. The isoelectric points of the ferric hydroxo complexes are reported (35) in the range of pH 7.4–8.4, which falls in the pH range of maximum co-precipitation of ferric hydroxy species-polysaccharide systems studied in this investigation.

(5) FTIR data indicate the disappearance of the 930-cm⁻¹ band and a decrease in the intensities of the 770-cm⁻¹ peak in the case of both dextrin- and guar gum-interacted and hydroxylated pyrite samples. These facts may be attributed to the chemical complexation between the ferric hydroxy species on pyrite and

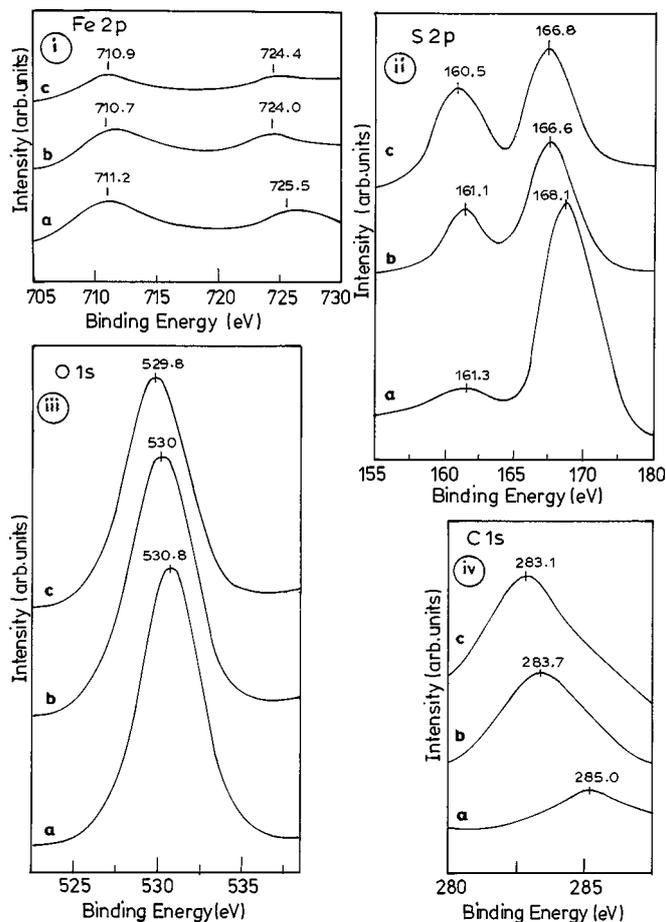


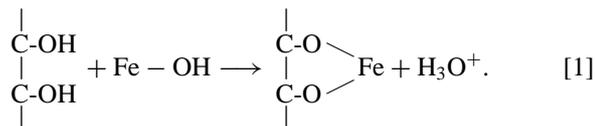
FIG. 12. X-ray photoelectron spectra of pyrite in the absence and presence of dextrin and guar gum for (i) Fe 2p, (ii) S 2p, (iii) O 1s, and (iv) C 1s regions.

the hydroxyl groups of the polysaccharides, in keeping with the mechanism postulated by Liu and Laskowski (3).

(6) The results of the XPS studies are also indicative of chemical interaction between ferric species and the polysaccharides.

From the foregoing discussion, it is evident that there is an overlap in the pH ranges of higher adsorption, significant co-precipitation, and pronounced depression. Additionally, the reported values of the isoelectric points of ferric hydroxide encompass the pH range of maximum co-precipitation observed in this study. Thus, in the pH range of strong hydroxylation of pyrite surface, higher adsorption of the polysaccharides takes place, leading to appreciable depression of pyrite. At this juncture, it is pertinent to recapitulate that a good correlation was observed between the pH values of optimum co-precipitation, maximum adsorption density, significant depression, and the isoelectric points of the relevant hydroxides in the case of the interaction of dextrin with galena and heazlewoodite (3, 39). Since iron exists in variable valency states, several hydroxy species are formed in solution, and consequently, the region of higher adsorption, optimum co-precipitation, and the isoelectric points of the hydroxy species of iron are spread over a pH range. The findings of this in-

vestigation are in good agreement with the results of Laskowski and co-workers for various minerals (39). The interaction mechanism postulated by them is applicable to the pyrite-dextrin/guar gum system, namely that the hydroxyl groups on the polysaccharides interact with the iron hydroxy species formed on the pyrite surface in a certain pH range, through a chemical complexation process. This is schematically represented below:



CONCLUSIONS

From the results of this investigation, the following conclusions can be drawn:

1. Adsorption measurements indicate that a higher amount of dextrin and guar gum are adsorbed onto pyrite in the pH range 7.5–11 and exhibit a maximum around pH 10. The adsorption isotherms follow Langmuirian behavior for both dextrin and guar gum. Additionally, guar gum adsorption onto pyrite is higher than that of dextrin.
2. Electrokinetic experiments show that the electrophoretic mobility values are reduced in proportion to the amount of the polymer adsorbed.
3. Co-precipitation tests show significant interaction between the polysaccharides and ferric hydroxy species in the pH range 5.5–8.5.
4. The pH range of higher adsorption density, significant co-precipitation, and appreciable depression of pyrite encompass each other.
5. XPS and FTIR spectroscopic studies provide evidence in support of chemical interaction between hydroxylated pyrite and the hydroxyl groups of the polymers.

ACKNOWLEDGMENTS

The authors are grateful to the Head, Regional Sophisticated Instrumentation Centre, Chennai for extending the XPS facilities to carry out this investigation. One of the authors (R. K. Rath) gratefully acknowledges the Indian Institute of Science, Bangalore for the grant of a research associateship. The authors express their gratitude to the anonymous reviewer for his valuable comments to enhance the quality of the paper.

REFERENCES

1. Deshpande, S. B., and Raju, K. S., *J. Mines Metals Fuels* **37**, 458 (1989).
2. Ball, B., and Rickard, R. S., in "A. M. Gaudin Memorial Volume" (M. C. Fuerstenau, Ed.), p. 458. American Institute of Mining Metallurgical and Petroleum Engineers, New York, 1976.
3. Liu, Q., and Laskowski, J. S., *J. Colloid Interface Sci.* **130**, 101 (1989).
4. Liu, Q., and Laskowski, J. S., *Int. J. Miner. Process.* **26**, 297 (1989).
5. Liu, Q., and Laskowski, J. S., *Int. J. Miner. Process.* **27**, 147 (1989).
6. Laskowski, J. S., Liu, Q., and Bolin, N. J., *Int. J. Miner. Process.* **33**, 223 (1991).

7. Liu, Q., Laskowski, J. S., Li, Y., and Wang, D., *Int. J. Miner. Process.* **42**, 251 (1994).
8. Laskowski, J. S., Subramanian, S., and Nyamekye, G. A., in "Proceedings of XVIII International Mineral Processing Congress," p. 593. Sydney, The AusIMM Publ., 1993.
9. Nyamekye, G. A., and Laskowski, J. S., *J. Colloid Interface Sci.* **157**, 160 (1993).
10. Bhaskar Raju, G., Holmgren, A., and Forsling, W., *J. Colloid Interface Sci.* **200**, 1 (1998).
11. Bogusz, E., Brienne, S. R., Butler, I., Rao, S. R., and Finch, J. A., *Miner. Engg.* **10**, 441 (1997).
12. Xu, D. D., and Aplan, F. F., *Miner. Metal. Process.* **11**, 223 (1994).
13. Kydros, K. A., Gallios, G. P., and Matis, K. A., *Separation Sci. and Technol.* **29**, 2263 (1994).
14. Rath, R. K., Subramanian, S., and Laskowski, J. S., *Langmuir* **13**, 6260 (1997).
15. Rath, R. K., and Subramanian, S., *Miner. Engg.* **10**, 1405 (1997).
16. Rath, R. K., and Subramanian, S., *Langmuir* **14**, 4005 (1998).
17. Rath, R. K., and Subramanian, S., *Trans. IMM-Miner. Process. Extract. Metal. Sect. C* **108**, C1 (1999).
18. Rath, R. K., and Subramanian, S., *Int. J. Miner. Process.* **57**, 265 (1999).
19. Dubois, M., Giles, K. A., Hamilton, J. K., Rebers, P. A., and Smith, F., *Anal. Chem.* **28**, 350 (1956).
20. Fuerstenau, D. W., Metzger, P. H., and Seele, G. D., *Engg. Mining J.* **158**, 93 (1957).
21. Lin, K. F., and Burdick, C. L., in "Reagents in Mineral Processing" (P. Somasundaran and B. M. Moudgil, Eds.), p. 471. Dekker, New York, 1988.
22. Giles, C. H., MacEwan, T. H., Nakhwa, S. N., and Smith, D., *J. Chem. Soc. Part IV*, 3973 (1960).
23. Langmuir, I., *J. Am. Chem. Soc.* **40**, 1361 (1918).
24. Kydros, K. A., Matis, K. A., and Stalidis, G. A., *J. Colloid Interface Sci.* **155**, 409 (1993).
25. Healy, T. W., and Moignard, M. S., "Flotation. A. M. Gaudin Memorial Volume" (M. C. Fuerstenau, Ed.), p. 298. American Institute of Mining Metallurgical and Petroleum Engineers, New York, 1976.
26. Subramanian, S., and Laskowski, J. S., *Langmuir* **9**, 1330 (1993).
27. Brooks, D. E., *J. Colloid Interface Sci.* **43**, 687 (1973).
28. Lyklema, J. A., *Pure Appl. Chem.* **46**, 149 (1976).
29. Garvey, M. J., Tadros, Th. F., and Vincent, B., *J. Colloid Interface Sci.* **55**, 440 (1976).
30. Baes, C. F., and Mesmer, R. E., Jr., "The Hydrolysis of Cations," p. 95. Krieger Malabar, FL, 1986.
31. BeMiller, J. N., in "Starch Chemistry and Technology" (R. L. Whistler and E. F. Paschall, Eds.). Academic Press, New York, 1965.
32. Zaidi, S. A. H., and Mahdihassan, S., *Pakistan J. Sci. Ind. Res.* **6**, 103 (1963).
33. Williams, R. M., and Atalla, R. H., in "Solution Properties of Polysaccharides" (D. A. Brant, Ed.), ACS Symposium Series, Vol. 150, Am. Chem. Soc., Washington, DC, 1981.
34. Subramanian, S., and Natarajan, K. A., *Miner. Engg.* **1**, 241 (1988).
35. Parks, G. A., *Chem. Review* **65**, 177 (1965).
36. Gadsden, J. A., "Infrared Spectra of Minerals and Related Inorganic Compounds." Butterworths, London, 1975.
37. Cases, J. M., Donato, P. D., Kongolo, K. M., and Michot, L., *Colloids Surf.* **36**, 323 (1989).
38. Briggs, D., and Seah, M. P., "Practical Surface Analysis." Wiley, New York, 1990.
39. Liu, Q., and Laskowski, J. S., in "Polymers in Mineral Processing" (J. S. Laskowski Ed.), p. 71. Canadian Institute of Mining, Metallurgy and Petroleum, Canada, 1999.