Canadian Metallurgical Quarterly, Vol 40, No 1 pp 01-12, 2001

Published by Canadian Institute of Mining, Metallurgy and Petroleum
Printed in Canada.

STUDIES ON THE INTERACTION OF GUAR GUM WITH CHALCOPYRITE

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(Received October 1999; in revised form August 2000)

Abstract — Adsorption, electrokinetic and flotation studies have been carried out to investigate the interaction of guar gum with chalcopyrite. The adsorption density of guar gum onto chalcopyrite shows a weak adsorption maximum at pH 9.5. The adsorption isotherms exhibit Langmuirian behaviour. The electrophoretic mobilities of chalcopyrite are decreased in proportion to the added concentration of guar gum. Flotation tests reveal that guar gum depresses chalcopyrite in agreement with the adsorption data. Dissolution experiments indicate release of lattice metal ions from chalcopyrite, while co-precipitation and conductivity tests confirm guar gum-metal ion interaction in the bulk solution. The pH of maximum co-precipitation between guar gum and copper species is observed in the range 9-9.5. The adsorption process is governed primarily by chemical interaction between the hydroxyl groups of guar gum and hydroxylated chalcopyrite apart from hydrogen bonding. Fourier Transform Infrared Spectrometer (FTIR) and X-ray Photoelectron Spectroscopic Studies (XPS) provide evidence in support of the interaction mechanisms proposed.

Résumé —On a exécuté des études d'adsorption, d'électrocinétique et de flottation afin d'examiner –l'interaction de la gomme de guar avec la chalcopyrite. La densité d'adsorption de la gomme de guar sur la chalcopyrite montre un maximum d'adsorption faible à un pH de 9.5. Les isothermes d'adsorption exhibent un comportement langmuirien. Les mobilités électrophorétiques de la chalcopyrite diminuent en proportion de la concentration de gomme de guar. Les tests de flottation révélent que la gomme de guar déprime la chalcopyrit, en accord avec les données d'adsorption. Les expériences de dissolution indiquent un reléchement des ions métalliques du réseau de la chalcopyrite, alors que des tests de co-précipitation et de conductivité confirment l'interaction gomme de guar – ion métallique dans la solution en vrac. Le pH de co-précipitation maximum entre la gomme de guar et les espéces de cuivre se trouve entre 9 et 9.5. Le procédé d'adsorption est gouverné principalement par l'interaction chimique entre les groupes hydroxyles de la gomme de guar et la chalcopyrite hydroxylée, à l'écart des liens hydrogénes. Les études par FTIR et XPS fournissent l'évidence supportant les mécanismes d'interaction propoés.

INTRODUCTION

Inorganic modifiers such as sodium cyanide, sodium sulphide or hydrosulphide, ferro-cyanides and Nokes reagent are conventionally used for the depression of copper minerals [1]. These reagents are found to be quite effective, but their use has raised concern on environmental grounds in recent times. In order to circumvent this problem, polysaccharide-based depressants have been assessed as potential substitutes. With respect to sulphide minerals, the use of starch, dextrin and carboxy methyl cellulose has been reported [2-8]. The interaction of dextrin with several sulphides and oxide minerals has been extensively studied by Laskowski and co-workers and a chemical adsorption mechanism has been proposed [9-14].

In an ongoing research programme, the interaction mechanisms of guar gum with several hydrophobic and sulphide minerals have been investigated. The findings with respect to talc, mica, sphalerite and galena have been reported recently [15-17]. In the present communication, the surface chemical studies carried out on chalcopyrite using guar gum are highlighted. Co-precipitation and conductivity tests have been conducted to ascertain guar gum-metal ion interaction in the bulk solution. Fourier transform infra red (FTIR) and X-ray photoelectron spectroscopic

(XPS) studies have been carried out to characterise the adsorbed species.

EXPERIMENTAL

Materials

Chalcopyrite was obtained from Ward's Natural Science Establishment Inc., U.S.A. for this study. Mineralogical and X-ray powder diffraction data indicated that the sample was of high purity. The samples were dry ground using a porcelain ball mill and then dry screened through 150, 75, 53 and 37 µm British Standard Sieves (BSS) and stored in sealed polythene containers. The –53 and –37 µm size fractions were used for the adsorption and electrokinetic studies, while the (–150+75) µm fraction was used for the flotation tests. The BET nitrogen specific surface areas of the –53 and 37 µm size fractions of chalcopyrite were found to be 0.79 and 1.41 m^2/g.

The sample of guar gum used in the study was obtained from s.d.Fine-Chem Ltd., Bombay, India. The molecular weight of guar gum was determined by High Performance Liquid Chromatography to be $4.22x10^6$. The guar gum solution was prepared fresh each day by dispersing a known weight in cold distilled water and then dissolving it in boiling distilled water. A schematic diagram of the typical structure of guar gum is shown in Figure 1.

Potassium nitrate was used to maintain the ionic strength and nitric acid or potassium hydroxide was used as a pH modifier. All the reagents used in this study were of analytical reagent grade. Deionised, double distilled water with a final conductivity of <1.5μohm^{-1} was used for all tests.

METHODS

Adsorption Studies

For the adsorption tests, 0.5 g of mineral powder was taken and pulped to 50 ml after the addition of desired amounts of $10^{-2}M$ KNO_3 and guar gum solution of known concentration and pH in 250 ml Erlenmeyer flasks. The suspension was agitated for a given period of time using a Remi Orbital Shaking Incubator at 250 rpm and 25 °C. After equilibration, the slurry pH was again recorded. The suspension was then centrifuged at 5000 rpm for 10 minutes using a Remi Laboratory Centrifuge R8C. The supernatant solution was further filtered through a Whatman 42 filter paper and the clear solution was then analysed to determine the equilibrium concentration of guar gum using a Shimadzu UV-260 Spectrophotometer as per the method suggested by Dubois *et al.* [18].

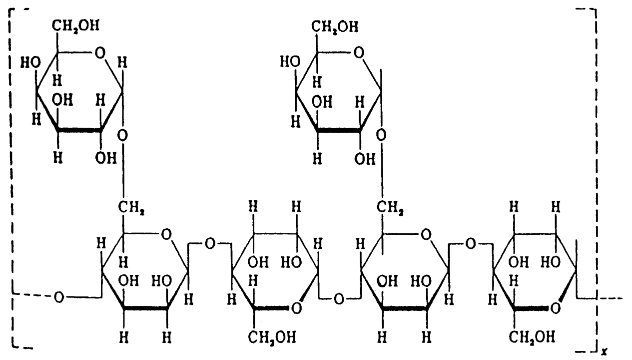

Fig. 1. Schematic diagram of the structure of guar gum.

Electrokinetic Measurements

Electrophoretic mobility measurements were carried out on chalcopyrite using a model 3.0 Zeta meter (Zetameter Inc., U.S.A.) with bright molybdenum anode and platinum cathode electrodes. Potassium nitrate was used to maintain the ionic strength at $10^{-3}M$. 0.2 g/l mineral suspension was conditioned at a particular pH for one hour at room temperature (27 °C), both in the absence and presence of guar gum, before making the measurements.

Dissolution Tests

Dissolution of chalcopyrite was studied as a function of pH, both in the absence and presence of guar gum, by taking 1g of –37 micron fraction of the mineral in 100 ml aqueous solution. After agitation for a given period of time and at a desired pH, the suspensions were centrifuged, filtered and analysed for metal ions such as Cu and Fe using a Video 11E model Thermo Jarrell Ash atomic absorption spectrophotometer.

Co-precipitation Tests

Co-precipitation tests were carried out between guar gum and cupric nitrate solution as a function of pH. A known amount of cupric nitrate solution was mixed with the guar gum solution in such a way that the final concentration of cupric nitrate was $10^{-3}M$ and that of guar gum 80 ppm in 100 ml solution. The desired pH was adjusted by adding either nitric acid or potassium hydroxide solution. After agitation for 30 minutes in an orbital shaker, the solution was centrifuged at 5000 rpm for 10 minutes in a Remi Laboratory Centrifuge R8C. The supernatant was then analysed for copper and iron contents using a Thermo Jarrell Ash atomic absorption spectrophotometer. The guar gum concentration was also determined. In the control experiments, 100 ml solutions containing Cu or Fe ions or guar gum of chosen initial concentration were agitated for 30 minutes as a function of pH and the residual concentrations analysed.

Conductivity Tests

The specific conductance of 400 ppm guar gum solution was measured as a function of pH in the absence and presence of ferric and cupric ions using a Systronics direct reading digital conductivity meter type 304. All the solutions were prepared using deionised, double distilled water with a specific conductivity < 1.5 μohm^{-1}.

Microflotation Tests

Microflotation tests were performed using a modified Hallimond tube [19]. Potassium ethyl xanthate of 10^{-3}M concentration was used as a collector for chalcopyrite. For these tests, 1 g of (-150+75) µm mineral sample was pulped to 200 ml with double distilled water and conditioned with the reagents at a desired pH for 10 minutes 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 minute. After flotation for 3 minutes, the concentrate and the tailing fractions were separately filtered, dried and weighed. The recoveries are expressed on a weight basis. In experiments where guar gum was used as a depressant, the suspension was conditioned with it for a further period of 10 minutes at a given pH prior to flotation.

SPECTROSCOPIC STUDIES

Procedure for Sample Preparation for FTIR and XPS Studies

Exactly 0.5 g of mineral sample was treated with 50 ml of guar gum solution at a desired pH and agitated in an orbital shaker for 2 hours. After the agitation, the mineral was separated from the polymer solution by filtration and the solids were rinsed twice to remove the excess guar gum on the surface. The solid was vacuum dried in a desiccator for about 8 hours.

FTIR Spectroscopic Studies

Fourier Transform Infrared spectra of chalcopyrite and the product of interaction between the mineral and guar gum at a particular pH (8.5-9) were recorded using a Nicolet Model 400D Fourier Transform Infrared Spectrometer operating in the 4000-400 cm^{-1} range. 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 spectrum. The FTIR spectrum of copper hydroxide-guar gum was also recorded adopting the same procedure.

X-ray Photoelectron Spectroscopic Studies (XPS)

The X-ray photoelectron spectra of chalcopyrite as well as the sample containing adsorbed guar gum were recorded using ESCALAB MK-II of M/s V.G. Scientific Ltd. U.K. A vacuum of 10^{-8} Mbar was maintained during the data collection. 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, guar gum concentration and sample weight on the adsorption density of guar gum onto chalcopyrite.

Kinetics

The adsorption density of guar gum onto chalcopyrite as a function of time is shown in Figure 2. These experiments were carried out at the natural pH of 5.5. It is evident from the figure that the adsorption density reaches its saturation value in about 1 hour. In all further adsorption studies, the time of equilibration was fixed at 2 hours.

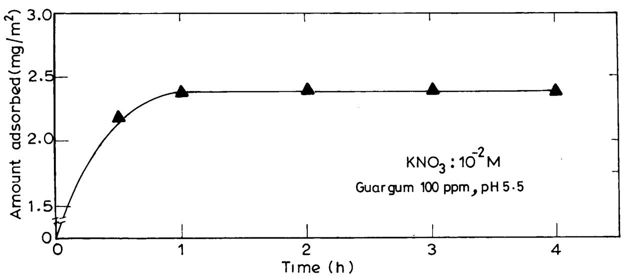

Fig. 2. Adsorption density of guar gum onto chalcopyrite as a function of time.

Effect of pH

The effect of pH on the adsorption density of guar gum onto chalcopyrite is portrayed in Figure 3. The adsorption density marginally increases with an increase of pH up to about 9.5 and thereafter slightly decreases with an increase in pH. A weak adsorption maximum is observed at around pH 9.5. Since chalcopyrite is comprised of both copper and iron sulphide and hydroxylation of both can take place, the adsorption maximum with respect to pH is not as pronounced as that observed with other sulphides [17]. Additionally, it has been reported that copper hydroxide which is expected to form at alkaline pH is metastable and decomposes to the oxide [20], unlike those of the other metal hydroxides. These results are in good agreement with the findings of earlier workers [10].

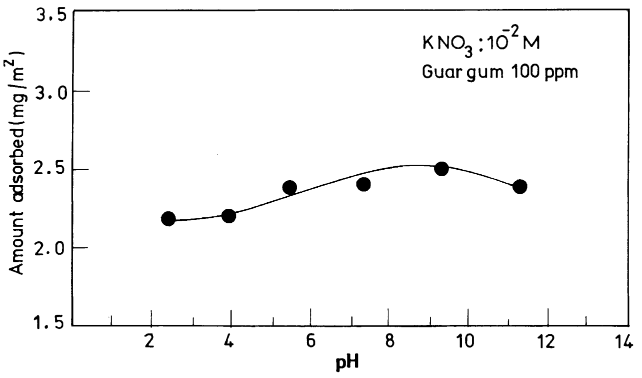

Fig. 3. Effect of pH on the adsorption density of guar gum onto chalcopyrite.

Adsorption Isotherms

Figure 4 depicts the adsorption isotherms of guar gum onto chalcopyrite. The adsorption density of guar gum increases with an increase in guar gum concentration at both the pH values studied. The adsorption density at pH 8.5 is slightly higher than that at pH 4.8. Both the isotherms for guar gum can be categorised as type L1 of the Giles classification [21]. The isotherms were found to conform to the Langmuir equation. Letting K equal the equilibrium constant for the adsorption reaction, the following relationship can be written

$$K= \exp(-\Delta G^o / RT) = [m/(m_o - m)(D)] \qquad (1)$$

where ΔG^o is the free energy of adsorption, R is the gas constant, T is the absolute temperature, m is the equilibrium quantity of guar gum adsorbed, m_o is the amount adsorbed at saturation and D is equilibrium concentration of guar gum in solution. Using the linear form of Equation 1, a plot of (D)/ m as a function of (D) yielded a straight line from which m_o and K were evaluated from the slope and intercept, respectively. Considering the monomer molecular weight of guar gum as 162 (for $C_6H_{10}O_5$), the free energy of adsorption was calculated to be about –28 to 30 kJ per mole of monomer of guar gum [22] which is suggestive of interaction forces stronger than hydrogen bonding. A value of – 32 kJ/mole has been reported for the free energy of adsorption of octylhydroxamate on hematite [23].

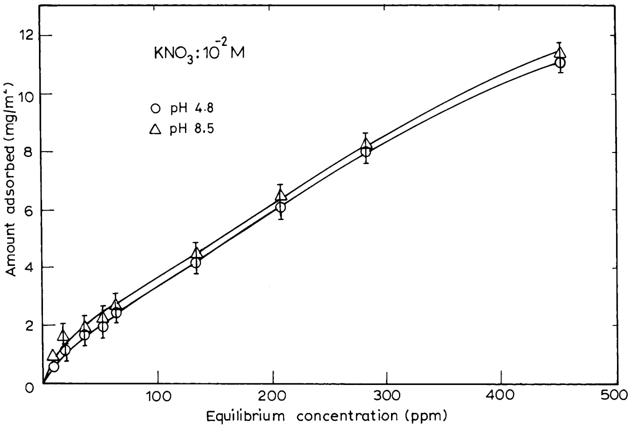

Fig. 4. Adsorption isotherms of guar gum onto chalcopyrite.

Effect of Sample Weight

The adsorption densities of guar gum onto chalcopyrite as a function of pH for different sample weights ranging from 0.25 to 1 g are shown in Figure 5. It is apparent that the adsorption densities of guar gum onto chalcopyrite increase with a decrease in the weight of the sample. Understandably, as the solid-to-liquid ratio increases, the adsorption density decreases. This may be attributed to greater particle-particle interactions due to crowding at high pulp densities with a consequent decrease in guar gum-mineral interaction. A similar behaviour has been observed by other workers [24]. It is noteworthy that the trend observed earlier with respect to pH and the magnitude of the adsorption density is unaltered. It is also interesting to note that the weak adsorption maximum around pH 9-9.5 is preserved.

Electrokinetic Tests

Figure 6 portrays the electrophoretic mobilities of chalcopyrite as a function of pH in the absence and presence of different concentrations of guar gum. In these measure-

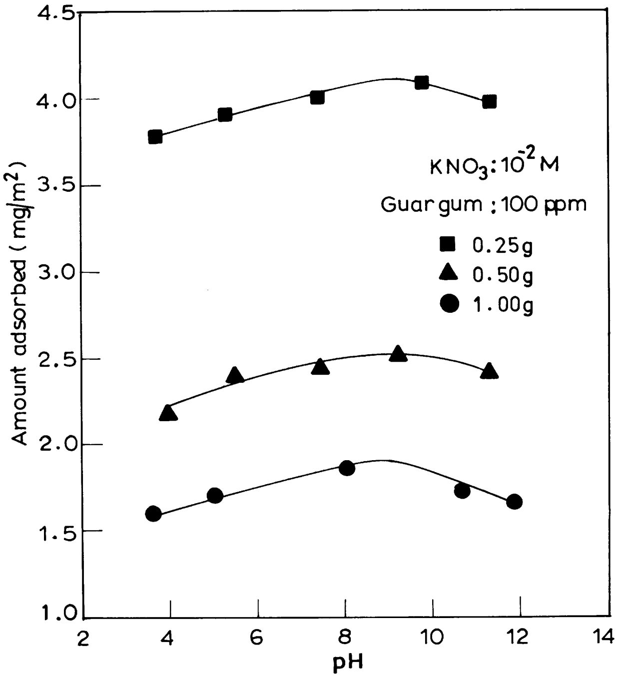

Fig. 5. Effect of pH on the adsorption of guar gum for different amounts of chalcopyrite.

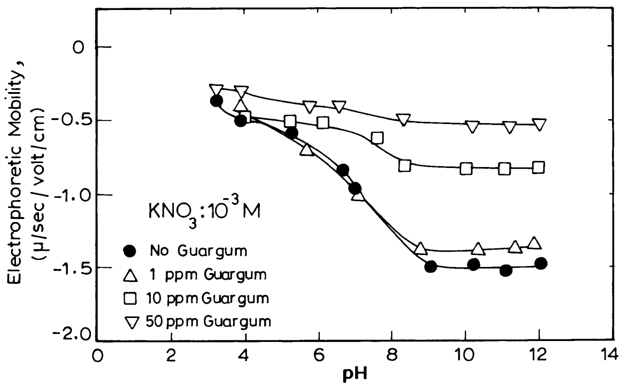

Fig. 6. Electrophoretic mobility of chalcopyrite as a function of pH in the absence and presence of different concentrations of guar gum.

ments 10^{-3} M KNO_3 has been used as an indifferent electrolyte. It is evident from the figure that the electrophoretic mobility of chalcopyrite in the absence of guar gum becomes more negative from -0.3 to -1.5 (μm sec^{-1}/volt cm^{-1}) with an increase in pH from 3 to 9 and thereafter remains more or less constant in the high alkaline pH range. The isoelectric point (iep) of chalcopyrite is plausibly located below pH 3. Other researchers have also observed similar iep values for chalcopyrite [25-27]. The addition of different concentrations of guar gum in the range of 1 to 50 ppm correspondingly reduces the negative electrophoretic mobility values in proportion to its concentration (Figure 6) presumably without any shift in the iep value. Since guar gum appears merely to reduce the electrophoretic mobility in absolute magnitude under all the pH conditions studied, the primary effect of the large macromolecule seems to be to shift the slipping plane farther away from the interface. These results suggest that some conformational rearrangements of the macromolecule take place with increasing extension of the looping chain when its 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 [14, 28-31].

Polymeric depressants such as guar gum show a great capacity for hydrogen bonding with hydrated minerals in a colloidal system suggesting orientation of the non-polar part of the guar gum at the mineral surface. This will cause a reduction of the negative potentials thereby rendering the surface hydrophilic and resulting in depression [32]. This is confirmed by the flotation tests reported subsequently.

Flotation Tests

The effect of pH on the floatability of chalcopyrite in the absence and presence of guar gum is shown in Figure 7. Potassium ethyl xanthate (PEX, 10^{-3}M) was used as the collector. It is evident from the figure that the floatability of chalcopyrite remains independent of pH using xanthate collector in the absence of guar gum.

In the presence of 50 ppm guar gum, the flotation recovery of chalcopyrite at pH 4.5 reduces to about 65 per cent and drops steeply to below 20 per cent in the pH range of 7-12.

The effect of guar gum concentration on the flotation recovery of chalcopyrite is portrayed in Figure 8. The flotation tests were carried out at pH 8.5. With the addition of guar gum, the flotation recovery decreases from 90 per cent at 0.2 ppm to 18 per cent at 10 ppm concentration. Further addition of guar gum up to 100 ppm does not alter the flotation recovery.

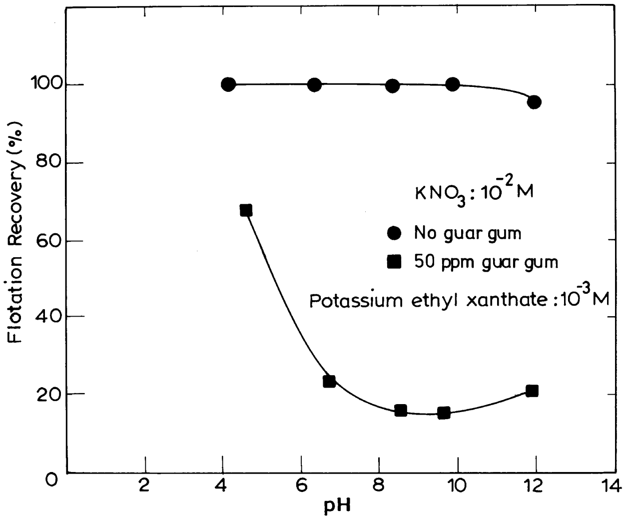

Fig. 7. Effect of pH on the flotation recovery of chalcopyrite in the absence and presence of guar gum.

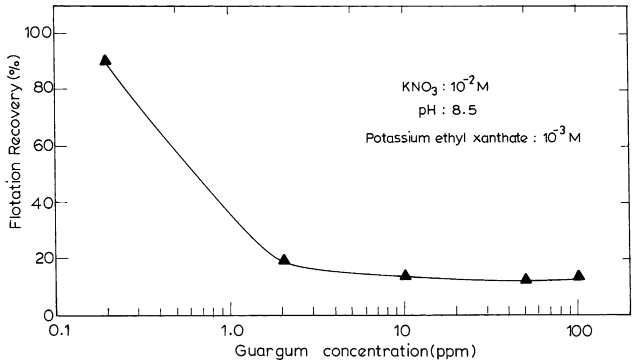

Fig. 8. Effect of guar gum concentration on the flotation recovery of chalcopyrite.

Depression Mechanisms

It has been well described by Pugh [33] that the interaction forces involved in depressant action include electrostatic, dispersion and structural hydration forces associated with the adsorbed hydrophilic surface coating on the mineral surface. In the case of macromolecular depressant films where the molecules are associated with several hydrophilic groups, it has been suggested that the strong ion-dipole effects may impose a structure on the neighbouring water sufficient to repel an approaching air bubble or particle and prevent contact [33].

In order to examine the flotation depression mechanism, the nature of the interaction between guar gum and potassium ethyl xanthate collector was assessed by conducting co-adsorption experiments as a function of guar gum and xanthate concentrations in solution. The effect of the addition of xanthate on the adsorption of guar gum is depicted in Figure 9. It is evident that with an increase in the xanthate concentration the adsorption density of guar gum onto chalcopyrite is increased. The results obtained for xanthate adsorption on chalcopyrite as a function of guar gum concentration are portrayed in Figure 10. It is noteworthy that an increase of guar gum concentration enhances the adsorption of xanthate. This mutual enhancement of adsorption by guar gum and xanthate is suggestive of an association between them. Evidence for similar association between surfactants and starch has been reported and a non-polar type of bonding has been suggested with the surfactant molecules occupying a position inside the starch helix with their long axes parallel to the helix axis [34-37]. Such a mechanism with the xanthate held inside the guar gum can also explain the observed enhanced adsorption of xanthate at the chalcopyrite-solution interface in the presence of guar gum without rendering the chalcopyrite surface hydrophobic. Thus, the wrapping of xanthate by guar gum can explain the loss of hydrophobicity of the chalcopyrite surface leading to its depression.

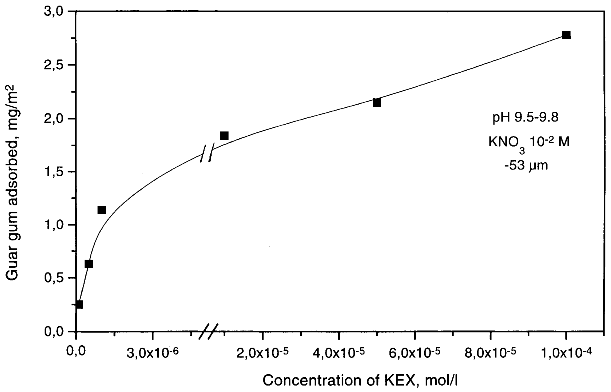

Fig. 9. Adsorption density of guar gum onto chalcopyrite as a function of xanthate concentration.

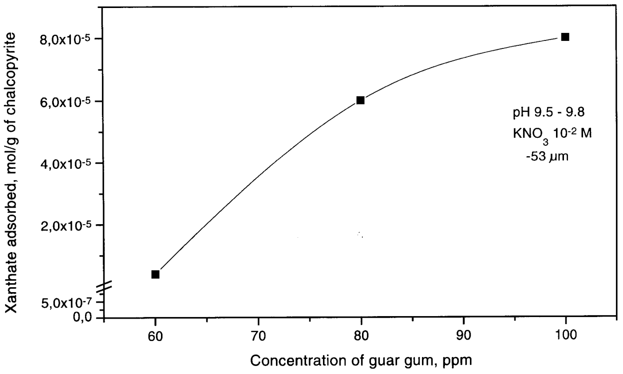

Fig. 10. Adsorption density of xanthate onto chalcopyrite as a function of guar gum concentration.

Dissolution and Co-precipitation Tests

The results of the dissolution tests carried out on chalcopyrite in the absence and presence of guar gum as a function of pH are depicted in Figure 11. It is apparent that the dissolution of Fe from chalcopyrite decreases steeply from about 3 ppm at pH 4.5 to 0.5 ppm at pH 5 and thereafter remains more or less constant in the pH range investigated both in the absence and presence of guar gum. The dissolution characteristics in the presence of guar gum are thus very similar to that in its absence.

With respect to the dissolution of Cu, it decreases sharply from pH 3.5 to 5 and thereafter increases with increase in pH in the absence of guar gum. A decrease in the Cu concentration is observed especially in the alkaline pH range in the presence of 100 ppm guar gum compared

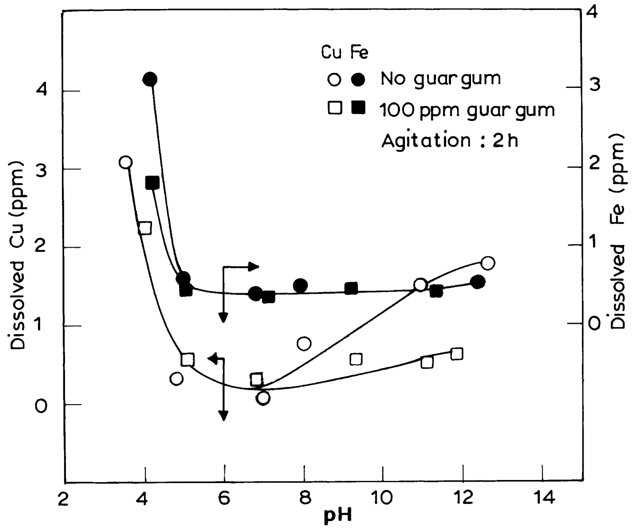

Fig. 11. Dissolution of copper and iron from chalcopyrite as a function of pH both in the absence and presence of guar gum.

to that observed in its absence. This decrease in Cu ion concentration attests to the chemical interaction of Cu species with guar gum in the bulk solution in the alkaline pH range.

Figure 12 depicts the results of the co-precipitation tests carried out with $Cu(NO_3)_2$ and guar gum as a function of pH. It can be observed that, both in the absence and presence of guar gum, there is a slight decrease in the copper content in the pH range 3 to 5 followed by a steep decrease to about 5 ppm copper at pH 7 and thereafter it marginally decreases in the alkaline pH range. There is a significant decrease in the guar gum concentration from pH 5 to 9.5 wherein the decrease is maximum. The pH of maximum adsorption observed earlier at pH 9.5 coincides with the pH of maximum co-precipitation. The guar gum concentration remains unaffected in the absence of copper ions as a function pH.

The results of the co-precipitation tests carried out for Fe^{3+}-guar gum system have been reported elsewhere [15]. Here also the chemical interaction of ferric hydroxy species with guar gum was confirmed. These findings are in good agreement with those observed for the interaction of these metal ions with dextrin [11].

Solution Conductivity Tests

The results of the solution conductivity measurements carried out on guar gum containing varying concentrations of cupric/ferric at different pH values are illustrated in Table I. It is evident from the results given in the table that in all cases negative deviations from the additive values of the conductances are observed. These results are indicative of complexation between cupric or ferric ions and guar gum. These findings reinforce the results of the co-precipitation tests.

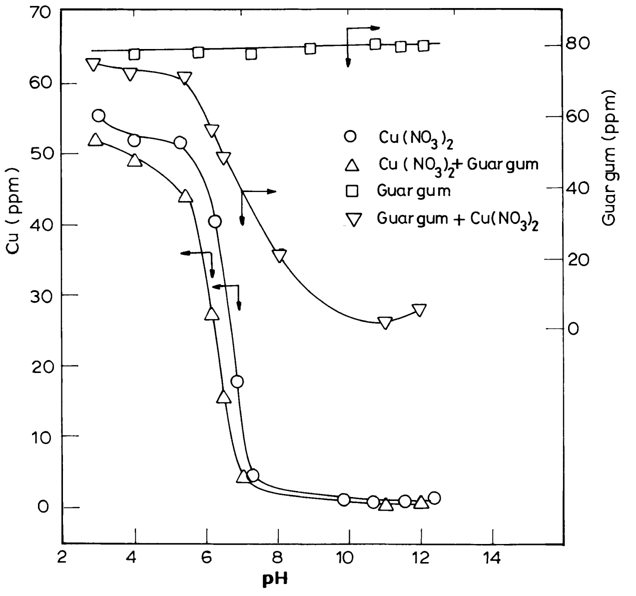

Fig. 12. Effect of pH on the residual concentration of guar gum and copper.

Table I – Discrepancies from the Additive Values of Conductivity for Cu^{2+}/ Fe^{3+}- Guar Gum System.

Metal ion Cu^{2+}/ Fe^{3+}-	Metal ion concentration (M)	pH	Discrepancy from the additive values (%)
Cu^{2+}	10^{-2}	4.1	-2.48
		4.8	-1.52
		5.7	-1.57
	10^{-3}	4.2	-15.73
		5.0	-0.96
		6.2	-34.89
Fe^{3+}	10^{-2}	2.6	-11.39
		2.8	-27.30
		3.0	-19.38
	10^{-3}	2.7	-1.94
		3.5	-56.04
		4.3	-48.74

FTIR Study of Chalcopyrite-Guar Gum System

The FTIR spectrum of guar gum depicted in Figure13 displays the following characteristic wave numbers and their assignments are summarised in Table II.

The FTIR spectrum of chalcopyrite is shown in Figure 14. The broad band at 3356 cm^{-1} may be attributed to hydrogen bonded hydroxyl groups. The bands between 1094-1200 cm^{-1}

Table II – Characteristic IR Frequencies of Guar Gum

Wavenumber (cm^{-1})	Characteristic group
3384	O–H stretching vibration
2924	C–H stretching of CH_2 group
1657	ring stretching
1350, 1414, 1450	symmetrical deformations of CH_2 group
1155, 1078	C–OH and primary alcoholic $-CH_2OH$ stretching mode
1021	$-CH_2$ twisting vibration
871	galactose and mannose
930, 770	(1–4), (1–6) linkage of galactose and mannose respectively

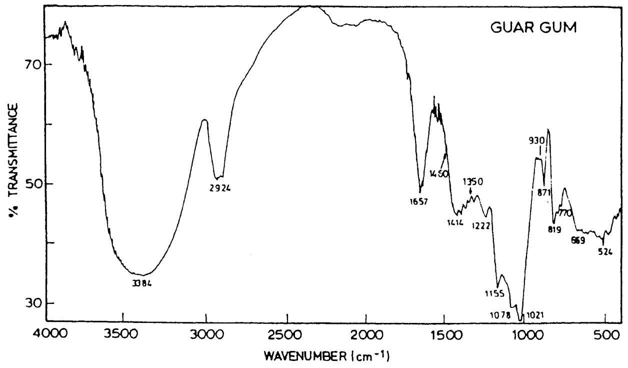

Fig. 13. FTIR spectrum of guar gum.

are characteristic of chalcopyrite [38]. The peaks between 500-700 cm^{-1} may be assigned to sulphate ions.

The FTIR spectrum of chalcopyrite containing adsorbed guar gum is also portrayed in Figure 14. The band centered at 3356 cm^{-1} due to hydroxyl stretching vibrations is broadened after interaction with guar gum. The characteristic peaks at 1094.5 and 1009.2 cm^{-1} are slightly enhanced in intensity and appear at 1091 and 1013 cm^{-1} after adsorption. Additionally, the weak bands in the region 1150 and 1200 cm^{-1} in the case of chalcopyrite are merged into a sharp peak after adsorption which is observed at 1204 cm^{-1}. A distinct shoulder is observed at ~930 cm^{-1} attributed to ring stretching and it has diminished in intensity consequent to chemical interaction. Similarly, the band at 770 cm^{-1} due to ring deformation is also significantly reduced after interaction. It has been reported that the intensities of these bands are strongly influenced by substitution on the hydroxyl groups [11].

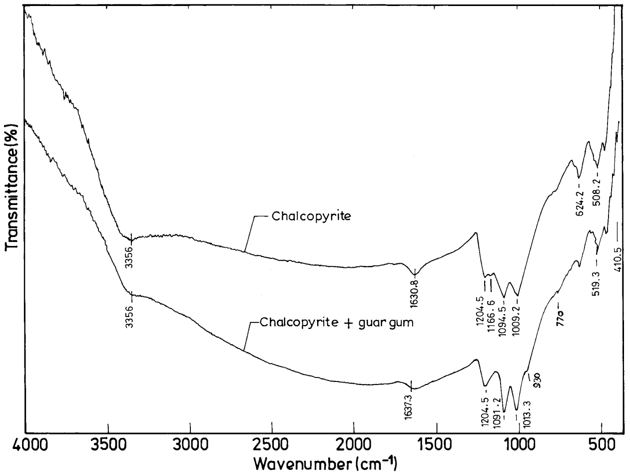

Fig. 14. FTIR spectra of chalcopyrite both in the absence and presence of guar gum.

Figure 15 depicts the FTIR spectrum of Cu(OH)$_2$ precipitate. A broad band centered around 3320 cm^{-1} is observed which may be attributed to hydrogen bonded hydroxyl groups. An intense band is observed around 1382 cm^{-1} which may be assigned to Cu–OH bond [38]. The spectrum obtained after interaction with guar gum is also shown in Figure 15. A comparison of this spectrum with that obtained for Cu(OH)$_2$ reveals that the band centered at 3320 cm^{-1} is significantly reduced in intensity and is further broadened suggestive of interaction with guar gum. The typical hydroxide peak at 1382 cm^{-1} is also observed in the case of the guar gum interacted sample but with a sharper intensity. It is noteworthy that the characteristic peaks of guar gum are absent due to complexation.

The spectral changes manifested after adsorption of guar gum onto chalcopyrite and copper hydroxide reveal that hydrogen bonding and chemical forces are involved in the adsorption process.

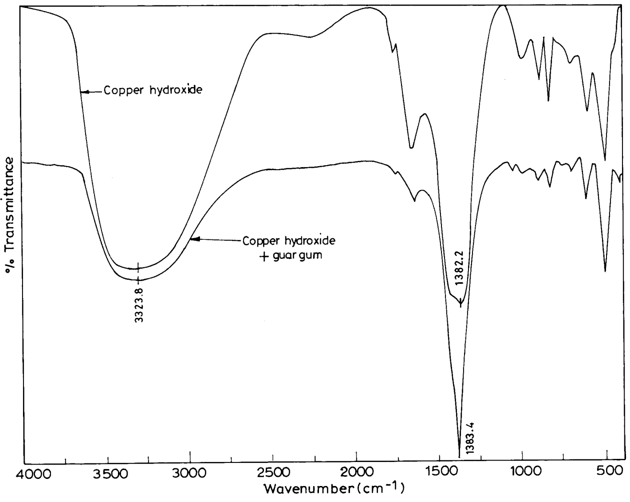

Fig. 15. FTIR spectra of copper hydroxide both in the absence and presence of guar gum.

XPS Studies

The Cu 2p region in the chalcopyrite sample is shown in Figure 16(a). Cu 2p binding energy (B.E.) occurs at 932 and 953.1 eV corresponding to 2p$_{3/2}$ and 2p$_{1/2}$, respectively. The position and peak separation are characteristic of a divalent Cu [39]. Upon interaction with guar gum (Figure 16a), the intensities of Cu 2p are reduced significantly and a slight shift in the B.E. to higher values for both 2p$_{3/2}$ and 2p$_{1/2}$ is observed. This clearly reveals that Cu(II) is involved in the interaction with guar gum.

The Fe 2p region in this sample is shown in Figure 16(b). The Fe 2p$_{3/2}$ and 2p$_{1/2}$ occur at 710.5 and 725.3 eV B.E., respectively. Upon interaction, there is a slight change in the Fe 2p B.E. values, though the intensities are more or

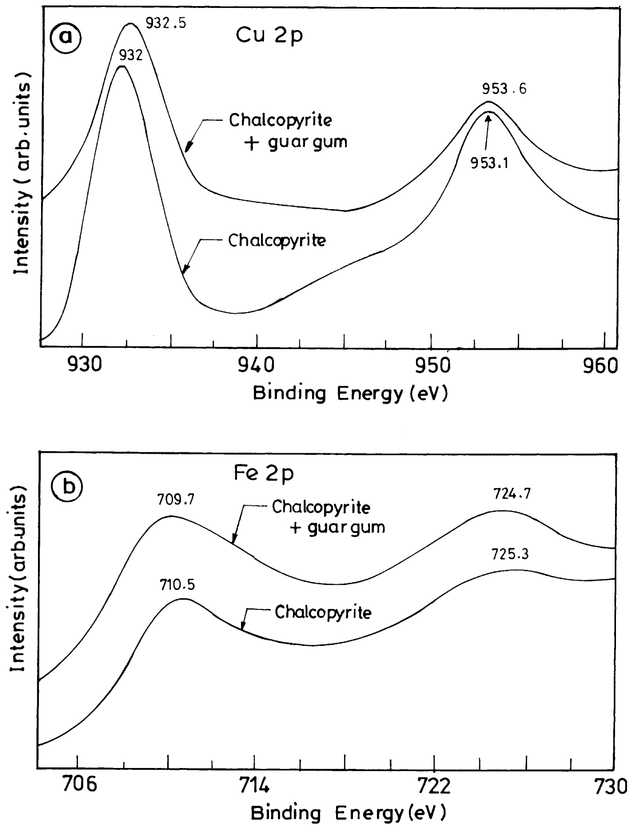

Fig. 16. Cu 2p and Fe 2p X ray photoelectron spectra of chalcopyrite in the absence and presence of guar gum.

less unaltered. This shows that the interaction of guar gum with Fe is not pronounced.

The XPS spectra of the S 2p region of chalcopyrite and that obtained after treatment with guar gum are depicted in Figure 17(a). The peak at 164.2 eV B.E. is attributed to bulk S^{-}, whereas the peak at 171 eV B.E. arises due to sulphate as a result of partial oxidation of chalcopyrite. In the presence of guar gum, the sulphide intensity is appreciably reduced and there is a small shift in the B.E. values indicative of chemical interaction.

The O 1s region in the free chalcopyrite sample (Figure 17(b)) occurs at 530 eV B.E. due to partial surface oxidation. Consequent to interaction with guar gum, a feeble shift in the binding energy value is observed. The C 1s region in the chalcopyrite sample may be traced to carbon impurity due to charging (Figure 17(c)). However, after adsorption there is a significant shift in the B.E. value arising from the 'C' of guar gum. The C 1s region in guar gum is found to occur at 283.3 eV B.E.

The changes observed in the intensities of Cu (2p), S (2p) and C (1s) regions as well as the B.E. values provide

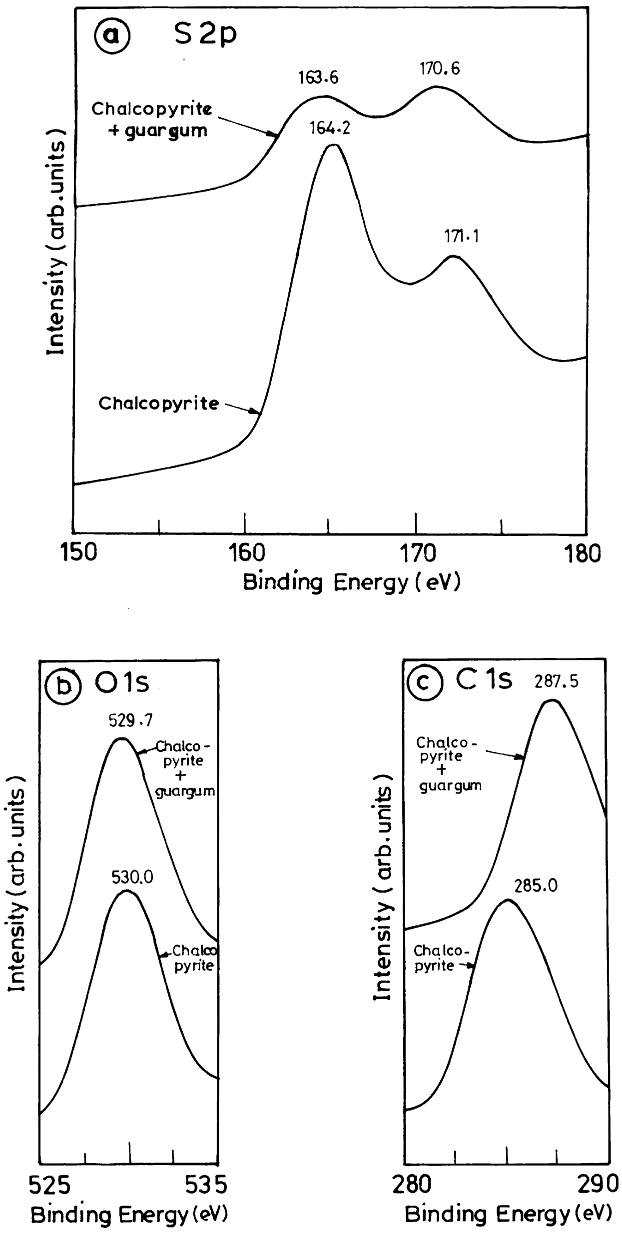

Fig. 17. S 2p , O 1s and C 1s X ray photoelectron spectra of chalcopyrite in the absence and presence of guar gum.

evidence in support of chemical interaction between chalcopyrite and guar gum.

Adsorption Mechanisms

On the basis of the results of the various investigations carried out both at the solid-solution interface and in the bulk solution, the following facts emerge:

1. Adsorption density measurements reveal that a weak adsorption maximum is observed around pH 9.5.

2. Co-precipitation tests also indicate that the pH of maximum interaction between guar gum and copper species is around pH 9-9.5.

3. Microflotation experiments show good depression in the pH range 8-10 corroborating the adsorption data.

These findings are in good agreement with those published by Laskowski and co-workers [9-14] for the interaction of dextrin with several systems. The isoelectric point of copper hydroxy species has been reported in the range of pH 9-9.5 [40]. Thus, a good correlation is observed between the maximum adsorption density, optimum co-precipitation and the isoelectric point of the corresponding hydroxide in line with that reported earlier for dextrin adsoption [11]. The primary adsorption mechanism involves the chemical interaction between the hydroxyl groups of guar gum with the hydroxylated chalcopyrite surface as originally postulated [11]. Thus, the interaction mechanisms of guar gum with chalcopyrite can be summarised as follows:

The dissolution of the mineral releases metal ions which could form neutral or charged complexes depending upon the pH of the medium. The hydroxo complexes could react with guar gum both at the hydroxylated mineral surface as well as in the bulk solution, chiefly by chemical interaction, apart from hydrogen bonding.

CONCLUSIONS

The major conclusions of this study are enumerated below:

1. Studies on adsorption kinetics using guar gum indicate that equilibration is attained within an hour for chalcopyrite. A feeble adsorption maximum is observed at pH 9.5.

2. The adsorption isotherms of guar gum exhibit Langmuirian behaviour for both pH values studied and the isotherms correspond to L1 type of the Giles classification.

3. Electrokinetic experiments show a decrease in the electrophoretic mobilities in proportion to the added guar gum concentration.

4. Flotation results indicate that guar gum depresses chalcopyrite in keeping with the adsorption data.

5. Dissolution tests indicate release of copper and iron ions from the mineral surface.

6. Conductivity and co-precipitation tests confirm metal ion-guar gum complex formation in the bulk solution.

7. FTIR and XPS studies provide evidence in support of the interaction mechanisms proposed.

ACKNOWLEDGEMENTS

The authors are thankful to the Head of the Regional Sophisticated Instrumentation Centre, Chennai for extending the XPS facilities for this investigation. Dr. R. K. Rath expresses his gratitude to the Indian Institute of Science, Bangalore for the grant of a research associateship.

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