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HYDROPHOBIC EFFECTS OF SULFUR AND XANTHATE ON METAL AND MINERAL SURFACES

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ABSTRACT

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The hydrophobic character of a variety of base-metal sulfides and gold has been examined in the presence of sodium hydrosulfide and potassium ethylxanthate. The degree of hydrophobicity induced by electrodeposition of sulfur and by electrochemical reaction between the minerals and ethylxanthate were determined by contact-angle measurements on polished surfaces and by flotation of mineral particles. During flotation, mineral—reagent interactions were followed by monitoring the solution composition spectrophotometrically. Results have shown that on gold and chalcopyrite, the oxidation of hydrosulfide to molecular sulfur and the oxidation of ethylxanthate to dixanthogen produced hydrophobic surfaces; on pyrite, sulfur deposition was more effective than dixanthogen in producing a hydrophobic surface. Chalcocite, in contrast to gold, chalcopyrite, and pyrite, was found to react directly with ethylxanthate and hydrosulfide, but only the metal xanthate product was hydrophobic.

INTRODUCTION

Considerable interest exists concerning the role of sulfur in the natural (collectorless or self-induced) flotation of sulfide minerals. Several authors have reported that chalcopyrite ($CuFeS_2$) is naturally hydrophobic (Finkelstein et al., 1975; Fuerstenau and Sabacky, 1981; Yoon, 1981). Yoon (1981) showed that chalcopyrite could be floated in the absence of collectors if it was first treated with sodium sulfide. He suggested that the reducing conditions brought about by the use of sodium sulfide removed superficial oxidation products from the mineral's surface, leaving a hydrophobic particle. Yoon was unable to detect elemental sulfur on the chalcopyrite recovered by collectorless flotation.

In contrast, it has been reported by Trahar (1983a) and Heyes and Trahar (1977) that chalcopyrite is not floatable under the reducing conditions caused by the addition of dithionite or sulfide, but under oxidizing conditions, such as in the presence of oxygen, significant flotation of chalcopyrite

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occurs. In a related study, Gardner and Woods (1979) found that in pH 11 solution the onset of collectorless flotation corresponded to the potential where anodic oxidation of chalcopyrite occurred. They proposed a reaction:

$$CuFeS_2 + 3H_2O = CuS + Fe(OH)_3 + S^0 + 3H^+ + 3e^- \qquad (1)$$

in which the production of sulfur was the primary factor producing collectorless flotation. Trahar concluded from the results of Gardner and Woods that it was not oxygen itself but the increase in pulp potential brought about by the presence of oxygen that produced a superficially oxidized surface leading to a floatable particle. He also suggested that, while Yoon's data showed flotation after treatment with reducing agents, the use of air to float chalcopyrite raised the pulp potential to a point where sulfur was formed on the surface and this, rather than natural hydrophobicity, produced flotation. Recently, Luttrell and Yoon (1984a,b) confirmed that freshly fractured or unoxidized chalcopyrite does not float under reducing conditions, and they showed that heavily oxidized chalcopyrite cannot be floated under oxidizing conditions until the surface has been cleaned under reducing conditions (i.e. Na_2S). They suggest that in light of the thermodynamic instability of elemental sulfur in alkaline solution, polysulfide (i.e. S_n^{2-}; $2 \leqslant n \leqslant 8$) rather than elemental sulfur (S^0) causes the collectorless flotation. They also suggest that the increased floatability at ~pH 6 is due to the greater stability of elemental sulfur at lower pH levels and the greater hydrophobicity of elemental sulfur compared to polysulfide.

The role of sulfur in producing hydrophobicity on chalcopyrite is not straightforward. Although Gardner and Woods (1979) have proposed sulfur as the key hydrophobic species, Heyes and Trahar (1977) were not able to detect sulfur on oxidized surfaces. Finkelstein et al. (1975) found that below a surface concentration equivalent to six sulfur layers, there is no correlation between the presence of sulfur and flotation. Luttrell and Yoon (1984a,b) observed instances in which substantial quantities of sulfur were found on chalcopyrite samples that did not float. Trahar (1983b) has also reported that a number of sulfides, in addition to chalcopyrite, exhibit flotation in the absence of collector. Included among those that float strongly are galena, pyrrhotite, and pentlandite.

The preceding discussion shows that natural flotation of sulfides is a topic of considerable interest and controversy. The process by which sulfides become hydrophobic in the absence of normal collecting reagents is poorly understood, but more and more evidence indicates that sulfur plays an influential role. In an attempt to better understand the role of sulfur in the flotation of base-metal sulfides, the effects of electrodeposited sulfur on contact angle and mineral flotation have been studied on a variety of sulfide minerals. The hydrophobic nature of electrodeposited sulfur has been compared to the hydrophobicity induced by ethylxanthate, a common collecting reagent, and by the hydrophobicity induced through electrochemical treatment of the mineral in the absence of a reducing reagent or a collector.

EXPERIMENTAL

Contact-angle measurements were performed in a three-compartment electrochemical cell utilizing parallel plate windows in the working electrode compartment to facilitate contact angle measurements (Fig. 1). The side compartments contained a saturated calomel reference electrode (SCE) and a platinized platinum counter electrode. Potential control was maintained on the working electrode with a potentiostat; all potentials reported here were measured against the saturated calomel electrode. The working electrodes were prepared by sealing the electrode material in a nonconducting epoxy, exposing a surface of the material, and then polishing that surface with 1-μm-size alumina. The polished electrode was then positioned in the center of the compartment with the exposed surface facing up. Contact angles were measured with a goniometer. Nitrogen bubbles were deposited on the surface with a capillary glass tube. If free-standing bubbles could not be obtained, the bubbles were contained on the electrode surface with the glass capillary. In the contained mode, the bubble was positioned so that it just made contact with the electrode surface. Forty-five degrees seemed to be the threshold value for forming a free-standing bubble. Contact angles ⩾50° always produced free-standing bubbles, but occasionally free-standing bubbles were observed with slightly smaller angles. Measurements of contact angles were made under potential sweep and potentiostatic

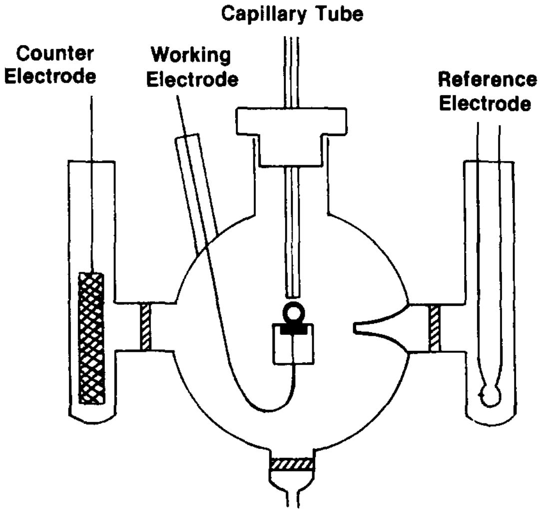

Fig. 1. Three-compartment contact-angle cell including the counter electrode, working electrode, capillary tube for generating and attaching bubbles, and reference electrode.

conditions. In some instances, one bubble was used throughout an experiment and contact angle was measured as a function potential, while in others, the bubbles were continually removed and new bubbles applied. Qualitatively, both techniques gave the same results.

For the flotation measurements, a microflotation-electrochemical cell was used. This system has been discussed in detail elsewhere (Walker et al., 1984a), but its basic characteristics are described below. Packed mineral beds were used as the working electrodes, and were connected to the potentiostat through a platinum current feeder. The mineral particle size range was usually 590—840 μm, but in some instances, smaller size particles were used. The counter electrode was housed in a fritted glass tube, which served to isolate the counter solution from the main compartment and to compact the bed, thus ensuring good contact between the mineral bed and the platinum current feeder during electrochemical treatment. During flotation measurements, the tube containing the counter electrode was raised up into the flotation head, and nitrogen gas was bubbled underneath the mineral bed. Recovery was determined by measuring the height of the mineral bed that remained unfloated. For 0 and 100% flotation, recoveries were exact, but between these limits accuracy was ~±10%. After completion of the flotation test, the floated particles were returned to the cell and the bed was recompacted. Typically, tests of mineral flotation involved a 5- to 10-min equilibration period at a given potential followed by a 2-min observation of flotation response. Changes in solution composition resulting from mineral reactions were monitored by circulating the electrolyte between the cell and a diode array UV-VIS spectrophotometer.

The supporting electrolyte was 0.05*M* sodium tetraborate, which produced a naturally buffered pH of 9.2. Reagent-grade potassium ethylxanthate (KEX) was recrystallized from acetone three times prior to use, and reagent-grade sodium sulfide was used as received. Solutions were made using 18-Mohm, deionized H_2O.

RESULTS

Gold

The hydrophobicity of gold was determined in pure borate solution and in borate solutions containing either hydrosulfide or ethylxanthate. Gold was chosen because of its large double-layer charging region, which permitted the observation of surface reactions, such as the deposition of sulfur or oxidation of xanthate, without interference from extraneous electrolysis reactions on the electrode. Voltammograms for clean gold in the absence and presence of hydrosulfide are shown in Fig. 2. In pure borate, gold oxides form above 0.5 V and hydrogen evolution occurs below −1.0 V; however, in the potential region of interest (−0.9 to 0.3 V), there is a complete absence of competing reactions (Hoare, 1984).

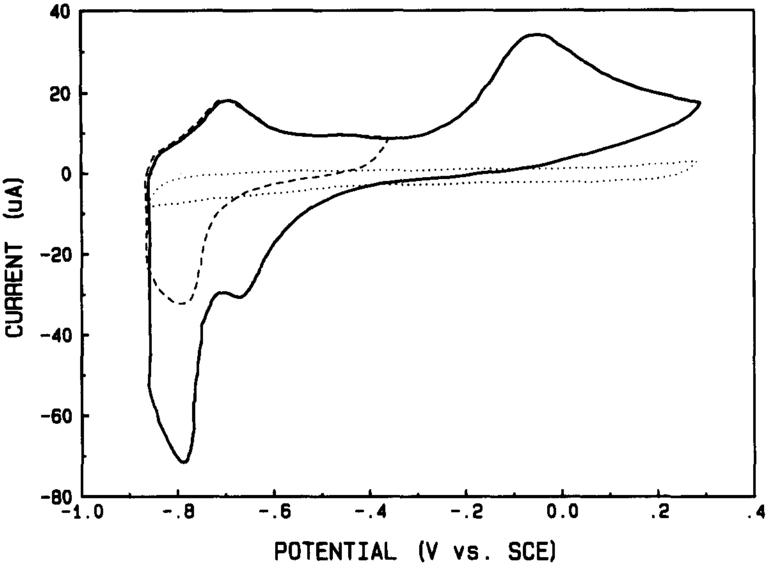

Fig. 2. Voltammograms of gold in 0.05*M* $Na_2B_4O_7$ solution (. . .) and in borate solution containing 1 X 10^{-4}*M* HS^- (——, - - -). Potential sweep rate of 50 mV/sec.

In the presence of 1 X 10^{-4}*M* hydrosulfide, the voltammogram is characterized by two oxidation processes with peaks near −0.7 and −0.1 V on the anodic potential sweep and two reduction peaks between −0.6 and −0.9 V on the cathodic sweep. Hamilton and Woods (1983) have made a detailed study of sulfur on gold, and according to their results, the anodic prewave with a peak at −0.7 V represents the underpotential deposition of sulfur which produces a coverage of ~90 μcoul/cm^2 or ~0.4 monolayer. They based these factors on a surface coverage of 0.72 X 10^{-5} atoms/cm^2 or 0.23 mcoul/cm^2 for sulfur on gold. Reduction of this species occurs in one step with a peak at −0.8 V, and the charge associated with reduction is equivalent to the anodic charge in both stirred and unstirred solution. When the anodic potential limit exceeds −0.3 V, coverages >1 monolayer can be achieved. Reduction of this bulk sulfur deposit occurs in two steps, and the anodic charge is always larger than the cathodic charge. Solution stirring increases the anodic charge and decreases the cathodic charge. Hamilton and Woods have attributed both of these variations in charge with agitation to the production of polysulfide intermediates which, because of their solubility, are not quantitatively converted to molecular sulfur above −0.3 V on the anodic sweep or back to hydrosulfide near −0.7 V during the cathodic sweep. The behavior of sulfur on gold in the present study (Fig. 2) is in excellent agreement with the results of Hamilton and Woods. However, it is not clear from these results or those of Hamilton and Woods whether polysulfide is a precursor to sulfur as suggested by Allen and Huckling (1957) or whether polysulfide is a product of the reaction between hydrosulfide and sulfur (Giggenbach, 1974). The fact that the underpotentially deposited sulfur must be formed prior to any evidence for the presence of polysulfide may favor the latter mechanism.

Figure 3 illustrates the dependence of contact angle on applied potential. In borate solution alone, the surface remained hydrophilic throughout the potential range −0.8 to 1.0 V, as was expected for clean gold (Wark and Cox, 1934). Apparent contact angles of ~10° were consistently observed on hydrophilic surfaces, which is in line with the findings of Wark and Cox that contact angles <10° are very difficult to measure. Therefore, the criterion, as described by Wark and Cox, that a bubble will not break the water film of a hydrophilic surface has been coupled with contact angle in determining the hydrophobic or hydrophilic nature of a surface. When a bubble fails to exhibit 'stickiness' during removal from a surface, the surface is defined as hydrophilic and assigned a contact angle of zero. During slow potential sweeps (<2 mV/s) in the presence of 0.01*M* HS^-, the surface remained hydrophilic until the potential exceeded ~−0.3 V. Above this potential, the surface became highly hydrophobic, supporting free-standing bubbles with contact angles of ⩾50°. The surface remained hydrophobic until the potential decreased below −0.8 V. Comparing Figs. 2 and 3, it is clear that the onset of hydrophobicity corresponds to the potential region where bulk sulfur deposition takes place, and loss of hydrophobicity corresponds to potentials where sulfur reduction occurs. A hydrophobic surface was not produced at potentials corresponding to the underpotential deposition of sulfur, which according to integration of the current in Fig. 2 and according to Hamilton and Woods (1983) amounted to ~0.4 equivalent monolayers (eml) of deposited sulfur.

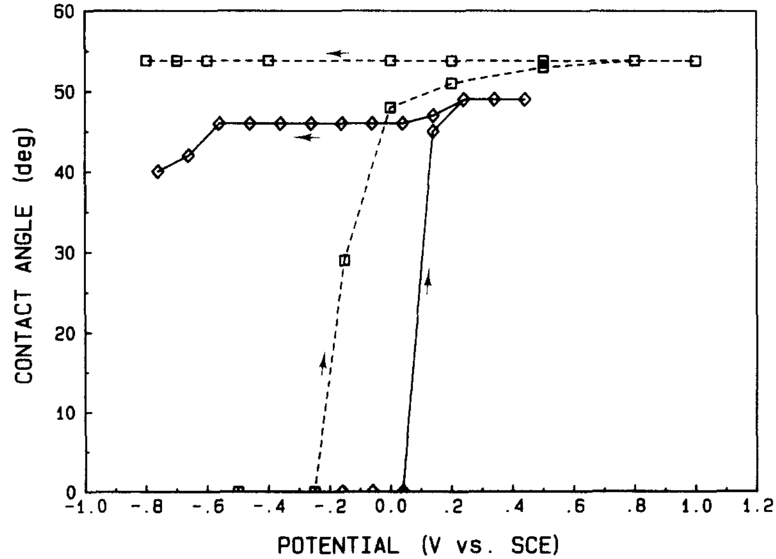

Fig. 3. Contact-angle measurements on gold in 0.05*M* $Na_2B_4O_7$ solutions containing 0.01*M* HS^- (- - -) and 2 × 10^{-5}*M* xanthate (——).

There has been considerable discussion in the literature concerning how much sulfur can be deposited on a surface and what degree of coverage constitutes a hydrophobic surface (Clifford, 1971; Wierse et al., 1978; Fuerstenau and Sabacky, 1981; Hamilton and Woods, 1983). The relationship between contact angle and sulfur coverage based on several methods of determining coverage is shown in Fig. 4. Using a deposition potential of 0.1 V and 0.23 mcoul/cm^2 (Hamilton and Woods, 1983) as the charge for a monolayer of sulfur, the coverages required to produce a free-standing bubble on gold were determined from the anodic charge used to form the deposit and the total cathodic charge needed to remove the deposit. Based on anodic charge, the coverage ranged from 6 eml in unstirred solution to 30 eml (not shown) in stirred solution. The cathodic charge gave ~3 eml in unstirred solution and <1.5 eml in stirred solution. The coverage determined by reduction in unstirred solution (~3 eml) appears to be the most reliable value since the anodic charge always overestimates the coverage because of the coproduction of polysulfides. Conversely, measurement of reduction charges in stirred solution underestimates the coverage because a portion of the soluble polysulfide produced during the reduction of molecular sulfur (Fig. 2) is removed from the vicinity of the electrode before it can be reduced to hydrosulfide. The results of Fig. 4 suggest that multiple layers of sulfur (i.e. ~3 eml) are required to produce a highly, hydrophobic gold surface with a contact angle of ~50°. The requirement of coverages of ~3 eml also explains why the underpotential deposited

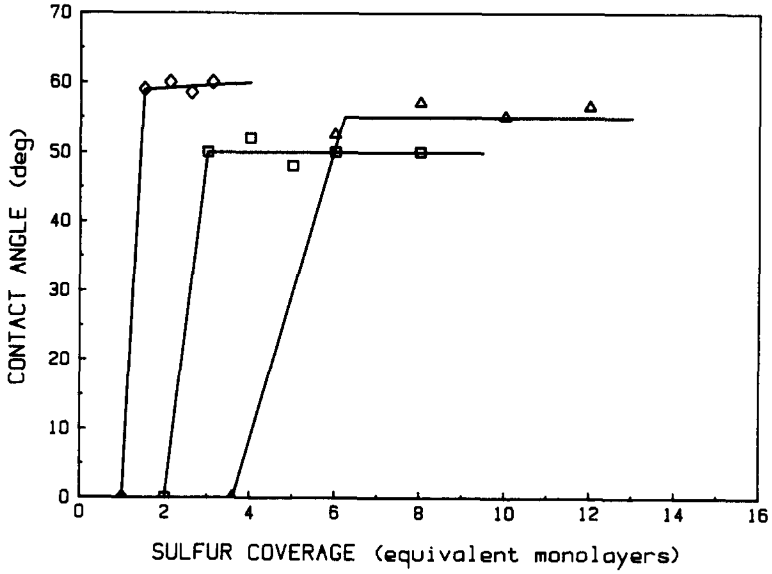

Fig. 4. Contact angle versus sulfur coverage on gold as determined by cathodic desorption charge in stirred solution (◇), cathodic desorption charge in unstirred solution (□), and anodic reaction charge (△).

sulfur, with a calculated coverage of ~0.4 eml, is not effective in producing a hydrophobic surface.

The composition of the hydrophobic species on gold is also still in question. The term 'elemental sulfur' is commonly used; however, a truly atomic species of sulfur on a substrate is unlikely (Meyer, 1976). Hamilton and Woods (1983) have identified it as 'polymeric sulfur' (S_n), but this term could refer to either a long-chained molecule or to a cyclic molecule. The latter is considered the more stable form of sulfur (Meyer, 1976) and is commonly referred to as molecular sulfur while the former is referred to as polymeric sulfur. Luttrell and Yoon (1984b) have suggested that metal polysulfides rather than elemental sulfur are the actual species conferring hydrophobicity at alkaline pH. On mineral surfaces, Buckley and Woods (1984) have observed both elemental sulfur and a metal-deficient sulfide which results when a loss of metal ions from the surface produces a sulfur-rich lattice. The choice of sulfur would appear to be between molecular sulfur and polysulfide on gold and between these two plus the metal-deficient sulfide on minerals. Unfortunately, there does not appear to be sufficient evidence to decide which species actually controls hydrophobicity. Therefore, the hydrophobic species will be referred to simply as sulfur for the remainder of this paper.

In the presence of ethylxanthate, a hydrophilic surface was observed below 0 V (Fig. 3); above 0 V, the surface became hydrophobic and remained hydrophobic until the potential was reduced to values <-0.55 V. The onset of hydrophobicity coincides with the oxidation of ethylxanthate to ethyldixanthogen that occurs at ~−0.02 V in $2 \times 10^{-5} M$ xanthate solution. In the earlier stages of this study, it was reported that the onset of hydrophobicity occurred between −0.2 and 0 V (Walker et al., 1984b). This would indicate underpotential deposition of xanthate, but there is no electrochemical evidence to support underpotential deposition of xanthate on gold. The onset of hydrophobicity at potentials >0 V is more in line with the findings of Gardner and Woods (1973), who found that flotation of gold occurred at or above the reversible potential of the xanthate/dixanthogen couple, even though there was evidence for the adsorption of xanthate in the double layer below the reversible potential. According to Gardner and Woods (1974), formation of a contact angle $\geqslant 50°$ corresponds to monolayer coverage of xanthate on gold. Since ~3 monolayers of sulfur are required to make a hydrophobic surface, xanthate would appear to be a more efficient collector. However, sulfur produces a hydrophobic surface at lower potentials than does xanthate.

Pyrite

The inertness of pyrite at moderate overvoltages (Peters, 1977) makes it an ideal mineral for studying the hydrophobic effect of sulfur on mineral surfaces. Figure 5 shows cyclic voltammograms for pyrite in the absence and presence of hydrosulfide with borate as the supporting electrolyte. In pure borate solution, pyrite showed little or no electrochemical activity between −1.0 and 0.2 V, and there was no tendency for the bubble to break the surface water film at any potential within this range. These findings are in agreement with the findings of Heyes and Trahar (1984) that pyrite is only floatable in the particle size range below 20 μm and that this is due to entrainment. Fuerstenau and Sabacky (1981) have observed natural flotation of pyrite but their work was carried out at pH 6. In a recent paper by Richardson and Walker (1985), it was shown that aged pyrite floats more readily at pH 7 than at pH 9, presumably because the oxides are more stable or more hydrophilic at the higher pH. This same pH effect could be controlling the natural flotation of pyrite observed by Fuerstenau and Sabacky (1981).

In the presence of hydrosulfide, an oxidation current begins at −0.5 V on the anodic potential scan, and a reduction current begins at −0.6 V on the cathodic scan. The onset of hydrosulfide oxidation is in excellent agreement with the thermodynamic calculation of −0.52 V for HS^-/S^0 in a pH 9.2 solution of $1 \times 10^{-2} M$ hydrosulfide (Valensi et al., 1974). The current-potential behavior of hydrosulfide on pyrite is somewhat different from that on a gold electrode in that underpotential deposition of sulfur is not observed on pyrite. Figure 6 is a comparison of pyrite voltammetry with contact-angle and flotation measurements obtained on pyrite in hydrosulfide solution. The contact angle rises sharply at potentials above −0.6 V and reaches a maximum at 0 V. The initial increase coincides with the

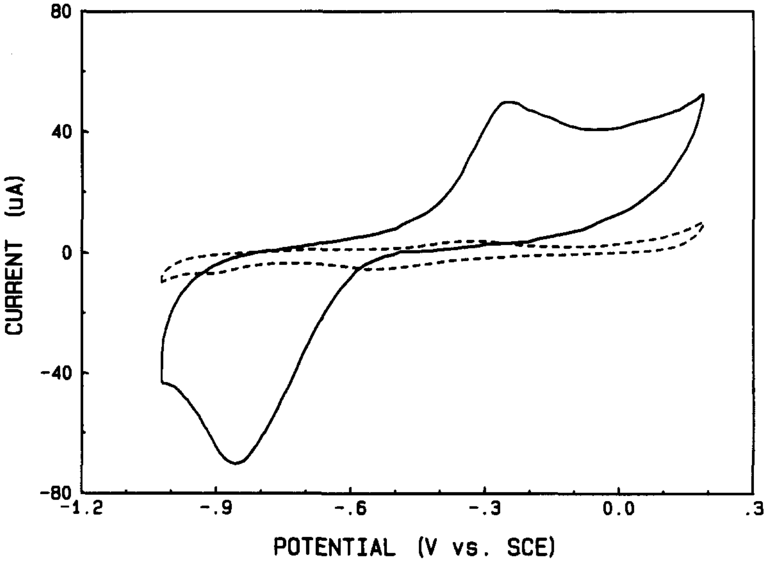

Fig. 5. Cyclic voltammogram of pyrite in $0.05M$ $Na_2B_4O_7$ (- - -) and in $0.01M$ HS^- dissolved in $0.05M$ $Na_2B_4O_7$ (——). Potential sweep rate = 1.5 mV/sec.

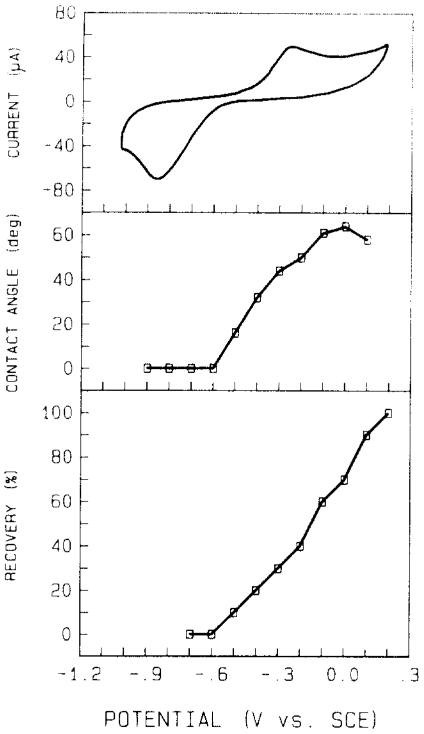

Fig. 6. Correlations of potentials for sulfur deposition, initiation of hydrophobic contact angle, and flotation of pyrite in 0.01*M* HS⁻ dissolved in 0.05*M* $Na_2B_4O_7$.

anodic current peak representing the formation of sulfur. Once formed on pyrite, a free-standing bubble is stable for hours at potentials >−0.7 V but quickly separates itself from the surface when the potential is reduced below −0.7 V. Loss of the hydrophobic surface corresponds to potentials where the sulfur is reduced to hydrosulfide. The results for both gold and pyrite support the observations of others (Peters, 1977; Richardson and Maust, 1976) that even though sulfur is thermodynamically unstable in alkaline solution, its conversion to sulfate is kinetically slow. Figure 6 illustrates the excellent correlations between the potentials where sulfur is formed and where hydrophobicity and flotation occur.

The hydrophobicity of pyrite in the presence of ethylxanthate is very different from that in hydrosulfide solution. With ethylxanthate, a free-standing bubble could not be achieved on a polished pyrite sample, and a contained bubble was not able to break the water film on the surface. The absence of a hydrophobic surface persisted even in the potential region where dixanthogen was formed (⩾0 V). The lack of hydrophobicity on polished samples agrees with the flotation behavior of slightly oxidized pyrite (Gardner and Woods, 1974). In a $2 \times 10^{-5}M$ ethylxanthate solution, freshly ground pyrite was found to float readily at potentials ⩾0 V, which is consistent with a dixanthogen mechanism (Richardson and Walker, 1984). However, if flotation tests were performed more than 24 h after grinding, pyrite recovery was negligible (<5%). The absence of flotation with these aged samples is thought to result from the cumulative buildup of oxides formed after grinding and during electrochemical treatment. The hydrophilic nature of the oxides, therefore, offsets the normally strong hydrophobic character of the dixanthogen, which is formed electrochemically at the pyrite surface at potentials $\geqslant 0$ V. The fact that aged samples can be floated in the presence of hydrosulfide is thought to occur because the hydrosulfide first acts to displace the oxides, thus restoring the pyrite surface, and then its oxidation to sulfur forms a hydrophobic layer on the surface preventing the formation of additional oxides.

The interaction between hydrosulfide and pyrite could be both beneficial and detrimental. On the one hand, hydrosulfide offers a new method for controlling pyrite flotation at potentials significantly cathodic of its normal flotation potential with xanthate (−0.5 V vis-a-vis 0 V). On the other hand, pyrite flotation could be promoted under conditions where it would ordinarily be depressed. An example would be the flotation of pyrite in a molybdenum circuit where hydrosulfide is normally used to depress the non-molybdenum sulfides. Both Yoon (1981) and Trahar (1983b) have reported that high concentrations of sulfide promote the flotation of pyrite.

Chalcopyrite

Table 1 compares chalcopyrite recovery versus potential in the absence of collector with its recovery in the presence of either hydrosulfide or ethylxanthate. Prior to determining flotation response at the various potentials, flotation was completely depressed by potentiostating the mineral at −0.55 V. Complete recovery of chalcopyrite in the 200 to 300 μm-size particle range was observed at −0.1 V in borate solution alone. Flotation

TABLE 1

Chalcopyrite flotation as a function of potential

Potential (V vs SCE)	Flotation (%)		
	Borate	HS^-	X^-
−0.55	0	0	0
−0.35	15	100	0
−0.1	100	100	20
0.1	—	—	100
Open circuit*	0	5	—

*OCV = −0.2 V in borate and −0.38 V in $4.6 \times 10^{-4} M$ HS^-.

at a potential approximately 100 mV above the open-circuit potential of chalcopyrite, would appear to be in complete agreement with the findings of Trahar (1983a,b) and Luttrell and Yoon (1984a), who observed collectorless flotation under oxidizing conditions sufficient to produce reaction 1. However, contact-angle measurements on polished samples showed no evidence of hydrophobicity in the potential range where collectorless flotation occurred. Based on the results with gold and pyrite, if the sulfur produced by reaction (1) is the species responsible for collectorless flotation, then a hydrophobic contact angle should have been observed on chalcopyrite above −0.1 V. This same contradiction was observed by Gardner and Woods (1979) and they were unable to give a good explanation for its cause. Buckley et al. (1985) suggested solubility or abrasion of the oxide in the flotation cell as a possible explanation for flotation when hydrophilic oxides would normally be expected to depress flotation. A more plausible explanation in this case may be that the nature and degree of surface oxidation on an abraded surface is more severe than on a fractured surface. Some indication of differences in reactivity of abraded and fractured pyrite surfaces has been reported by Buckley and Woods (1982). Elucidation of the mechanism of collectorless flotation of chalcopyrite is further complicated by the difficulties encountered in deriving a clear relationship between the presence or absence of sulfur and the flotation of chalcopyrite (Heyes and Trahar, 1977; Luttrell and Yoon, 1984b).

In an attempt to answer these questions, the electrosorption of sulfur on chalcopyrite was studied in a potential region free of the oxides produced during superficial oxidation of the mineral. Voltammograms of chalcopyrite in the presence and absence of hydrosulfide are shown in Fig. 7. The oxidation of hydrosulfide to sulfur above −0.4 V and the reduction of sulfur back to hydrosulfide below −0.6 V can clearly be seen. Since the open-circuit potential of chalcopyrite is generally between −0.2 and −0.1 V, the sulfur formed above −0.4 V is assumed to exist on a relatively oxide-free surface. Contact-angle measurements confirmed the onset of a hydrophobic surface above −0.4 V. A coverage of 25—30 eml of sulfur was required to form a free-standing bubble with a contact angle >45° when the electrode was potentiostated at −0.1 V in $0.01M$ hydrosulfide solution. This large coverage is again thought to result from the overestimation incurred when coverage is calculated from the anodic charge in a stirred solution.

Flotation results (Table 1) in the presence of $4.6 \times 10^{-4}M$ hydrosulfide show that under open-circuit conditions the potential is ~−0.38 V and recovery is ~5%, while at a controlled potential of −0.35 V, recovery is 100%. The negligible flotation under open circuit is again in excellent agreement with Trahar (1983a) and Luttrell and Yoon (1984a,b), who observed that chalcopyrite did not float under the reducing conditions imposed by hydrosulfide. However, the strong flotation at −0.35 V shows that chalcopyrite can be floated in the presence of hydrosulfide when a

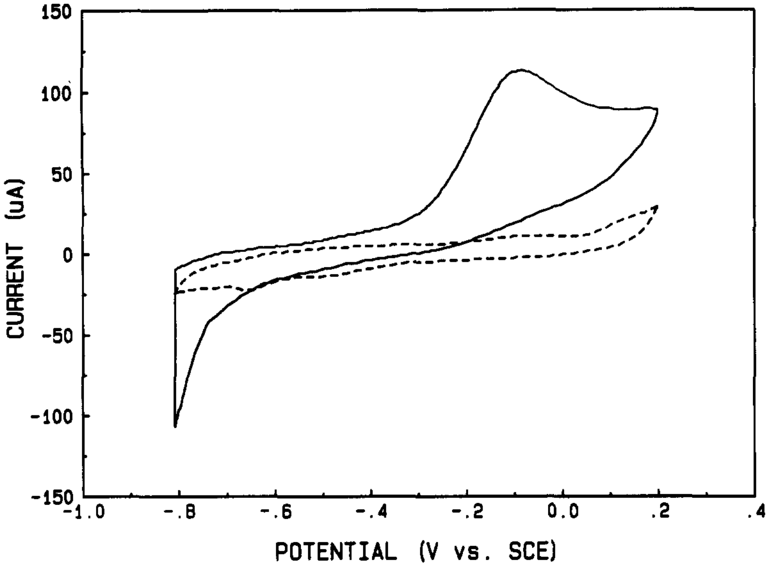

Fig. 7. Cyclic voltammograms of chalcopyrite in 0.05*M* $Na_2B_4O_7$ (- - -) and 0.01*M* HS^- dissolved in 0.05*M* $Na_2B_4O_7$ (——). Potential sweep rate = 1.5 mV/sec.

small anodic polarization (~30 mV) is imposed. This is not contradictory to Trahar's results but illustrates that under conditions where precise potential control is possible, hydrosulfide or more accurately molecular sulfur may induce chalcopyrite flotation.

These findings are important for two reasons. They show that in the absence of an oxidized surface, sulfur produces a hydrophobic surface that can be corroborated by both flotation and contact-angle measurements. This strongly suggests that the sulfur formed by superficial oxidation produces a hydrophobic surface. Unfortunately, these results cannot resolve whether abrasion or increased affinity for oxidation best explains the contradictory results obtained on superficially oxidized samples.

The second point concerns the possibility raised by Luttrell and Yoon that sulfide might impart some degree of hydrophobicity in addition to its normal role in 'sulfidization' (Castro et al., 1974; Luttrell and Yoon, 1984a). Based on the results at −0.35 V in Table 1, it is conceivable that with proper reagent control of the mineral potential, sulfur could be formed from the oxidation of sulfide rather than from the oxidation of the surface and that this would lead to flotation.

In comparison, flotation recoveries with $2 \times 10^{-5}M$ xanthate were 0% at −0.35 V, ~20% at −0.1 V, and 100% at potential $\geq$0.1 V. Chalcopyrite appears to float by a combination of mechanisms involving xanthate. Weak flotation is observed below the xanthate-dixanthogen potential ($<$0 V), which suggests that flotation is initiated by the formation of metal xanthates, while strong flotation above −0.1 V suggests that dixanthogen is enhancing recovery. Just as in the case with pyrite, hydrosulfide is capable of floating chalcopyrite at lower potentials than xanthate.

Chalcocite

The current-potential behavior of chalcocite in borate solution alone and in borate solutions containing 5 × $10^{-3}M$ hydrosulfide and 2 × $10^{-5}M$ ethylxanthate is shown in Fig. 8. In borate alone, chalcocite is characterized by the production of copper ions during anodic dissolution at potentials $\geqslant -0.05$ V and production of hydrosulfide ions during cathodic dissolution below −0.55 V (Walker et al., 1984a). Within the potential limits of −0.55 and −0.1 V, chalcocite is relatively inactive. Contact-angle measurements in borate alone showed that the surface film of water on chalcocite could not be broken with a nitrogen bubble either at the open-circuit potential (~−0.05 V) or during potential scan experiments in which the potential was varied from −0.6 to 0.2 V. These results contradict an earlier study in which natural flotation of chalcocite was observed (Walker et al., 1984a). Since differences in surface energies between polished and fractured surfaces of chalcocite could account for the disagreement between the flotation and contact-angle results, chalcocite samples were prepared by shaving

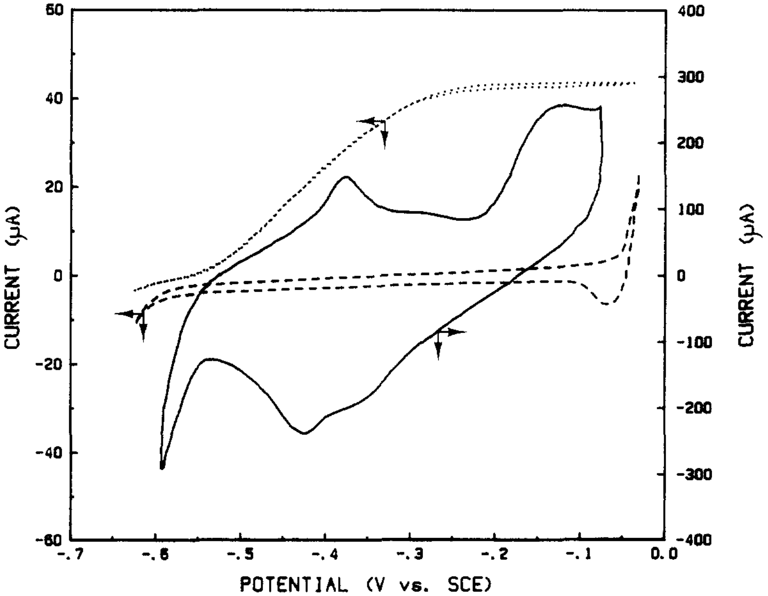

Fig. 8. Cyclic voltammogram of chalcocite in 0.05M $Na_2B_4O_7$ (- - -) and in 0.05M $Na_2B_4O_7$ solutions containing 5 × $10^{-3}M$ HS^- (. . .) and 2 × $10^{-5}M$ X^- (——) at a potential scan rate of 5 mV/s. The current scale for the borate-HS^- curve (. . .) is 40× that shown for the left side y-axis. The chalcocite-xanthate voltammogram (——) was produced using a particulate bed chalcocite electrode with particles in the 590—840 µm size range (O'Dell et al., 1984).

the surface nearly smooth with a razor blade. This procedure should approximate a fractured surface, but finite contact angles could not be obtained on these surfaces either. When flotation measurements were conducted in rigorously cleaned systems, natural flotation of chalcocite could not be achieved (Walker et al., 1984b). These flotation and contact-angle results agree with Trahar's observations (1983b) that chalcocite is not floatable in the absence of collectors and suggest that the earlier observations of natural hydrophobicity in chalcocite were induced by impurities.

Since the adsorption of sulfur produced hydrophobic surfaces on gold, pyrite, and chalcopyrite, the effects of sulfur on chalcocite were also investigated. Again, contact-angle measurements showed that the chalcocite surface remained completely hydrophilic throughout the potential region of −0.7 to 0 V. Voltammograms of chalcocite in the presence of $5 \times 10^{-3} M$ hydrosulfide (Fig. 8) revealed a large anodic current between −0.6 and −0.1 V that was accompanied by the formation of a blackish deposit on the surface. The reaction between chalcocite and hydrosulfide exhibits

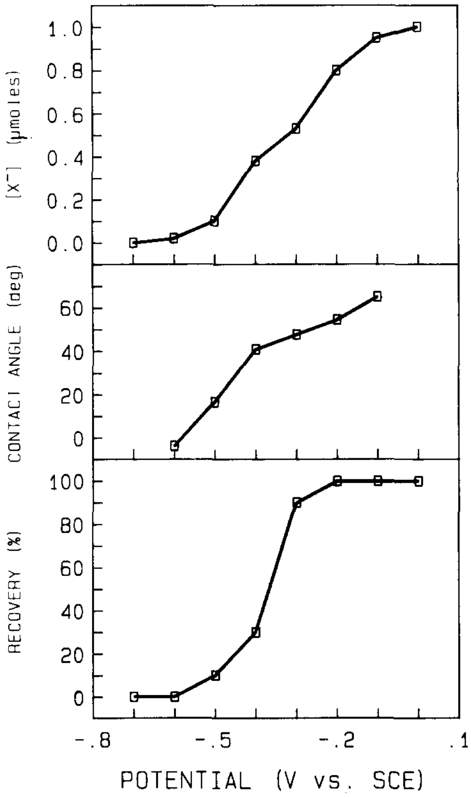

Fig. 9. Correlation between potentials for ethylxanthate adsorption, increasing contact angle, and flotation of chalcocite in $2 \times 10^{-5} M$ ethylxanthate dissolved in $0.05 M$ $Na_2B_4O_7$ solution.

a limiting current above −0.3 V, and its magnitude varies linearly with the square root of electrode rotation speed. The currents associated with this reaction were so large that the current scale for the hydrosulfide curve is actually 40× greater than the background current scale shown in the figure. Although the composition of the deposit is unknown, the reaction exhibits the classical behavior of a diffusion controlled process (Bard and Faulkner, 1980). A possible mechanism is that of chalcocite and hydrosulfide forming a copper sulfide with a higher sulfur-to-copper ratio ($Cu_{2-x}S$). In order for this reaction to be plausible, it must be assumed that the product film is very porous and the diffusion of copper within the chalcocite lattice must be rapid.

The electrochemical nature of the interaction between chalcocite and ethylxanthate is shown in Fig. 8. On the anodic scan the curve is characterized by a chemisorption process between −0.5 and −0.25 V, and the formation of a bulk metal xanthate above −0.25 V. On the cathodic scan, metal xanthate is reduced below −0.2 V (O'Dell et al., 1984). The anodic reaction coincides with the spectrophotometric evidence for the adsorption of xanthate on chalcocite in Fig. 9. Comparison of Figs. 8 and 9 illustrates the excellent correlation between the adsorption of xanthate, the formation of a hydrophobic surface as measured by contact angle, and the flotation of chalcocite.

CONCLUSIONS

The hydrophobicities induced by hydrosulfide and ethylxanthate have been studied on gold, pyrite, chalcopyrite, and chalcocite. A sulfur film can be electrodeposited on all samples except chalcocite. Contact angle measurements have confirmed that sulfur deposition leads to formation of hydrophobic surfaces, and, in most instances the onset of hydrophobicity corresponds to the potential where particle flotation occurs. With the exception of aged or oxidized pyrite at pH 9.2, all the minerals can be made hydrophobic with ethylxanthate by formation of a metal-xanthate species or oxidation of ethylxanthate to dixanthogen.

Chalcocite appears to be unique among the samples tested because it reacts directly with both hydrosulfide and ethylxanthate; the other minerals function more as catalysts for the oxidation of hydrosulfide or ethylxanthate. In the presence of hydrosulfide, a dark hydrophilic film is formed on chalcocite. Covellite or one of the nonstoichiometric intermediates ($Cu_{2-x}S$), with a higher sulfur-to-copper ratio than chalcocite, is a possible reaction product of the hydrosulfide—chalcocite interaction. Xanthate reacts to form a hydrophobic copper xanthate species.

In the case of freshly ground pyrite, oxidation of hydrosulfide to molecular sulfur causes flotation at potentials >-0.5 V; the oxidation of xanthate to dixanthogen causes flotation at potentials $\geqslant 0$ V. Aged or oxidized samples of pyrite can also be floated with hydrosulfide, but dixanthogen is ineffective in producing a flotation response. A possible explanation for hydrosulfide being the more effective flotation reagent is that it produces a restoration of the pyrite surface (sulfidization) prior to formation of a molecular sulfur deposit. In contrast, the hydrophobic character of dixanthogen is offset by the hydrophilic oxides that remain on the surface.

Finally, it has been shown that electrodeposition of sulfur, at potentials well below the potential where chalcopyrite oxidation occurs, results in a strongly hydrophobic surface. Therefore, formation of a sulfur film, in the course of sodium sulfide treatment to remove surface oxides from weathered samples of chalcopyrite, could produce a floatable particle.

The remaining uncertainty involves the composition of the hydrophobic species. Without question a stable sulfur species produces the hydrophobic effect but whether the species is molecular sulfur, a metal-polysulfide complex, a metal-deficient sulfide, or a combination of these is not known. Considerable work remains to be done before this question can be answered.

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