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ELECTROCHEMICAL FLOTATION OF SULFIDES: CHALCOCITE-ETHYLXANTHATE INTERACTIONS

P.E. RICHARDSON, J.V. STOUT III, C.L. PROCTOR and G.W. WALKER

U.S. Department of the Interior, Bureau of Mines, Avondale Research Center, Avondale, MD 20782 (U.S.A.)

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ABSTRACT

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This paper discusses part of a U.S. Bureau of Mines research effort to use electrochemical techniques to control sulfide flotation with the aim of developing new methods to process low-grade, complex domestic ores. The interactions between chalcocite and ethylxanthate (EtX^-) have been studied in an electrochemical-microflotation cell containing a packed bed of the mineral as a working electrode. Spectrophotometric and electrochemical techniques have shown that in the potential range −0.7 to 0 V (SCE) at a pH of 9.2 there are at least four distinct reactions: (1) a reaction of EtX^- to form ethylperxanthate at reducing potentials near −0.5 V; (2) a reaction of EtX^- with soluble Cu(II) at the open circuit potential (−0.028 V); (3) an exchange reaction whereby EtX^- displaces an oxidation product; and (4) a charge transfer oxidation reaction. The exchange and charge transfer oxidation reactions occur over the same potential range (−0.5 to −0.1 V) and are both believed to produce cuprous xanthate and possibly cupric xanthate as an adsorbed hydrophobic species. Xanthate adsorbed at −0.1 V can be desorbed as the ethylxanthate ion at more negative potentials. The flotation response of chalcocite is also shown to parallel closely the adsorption of EtX^- by reactions 3 and 4 and the reduction of the adsorbed product during cathodic decreases in potential.

INTRODUCTION

Previous research (Walker et al., 1984), showed that a bed of chalcocite particles in a microflotation-electrochemical cell can be used as a working electrode with current-voltage characteristics nearly identical to those of single-particle electrodes during slow potentiodynamic scans or during potentiostatic control. A soluble Cu(II) species was spectrophotometrically identified as an anodic dissolution product, and HS^- was identified as a cathodic dissolution product. The strong dependence of these dissolution products on potential established that the composition of the solution and the surface of the mineral bed can be altered electrochemically and studied

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quantitatively using spectrophotometric techniques. The research reported in this paper was carried out to (1) determine if the interactions between ethylxanthate and chalcocite and the resulting flotation response can be controlled electrochemically, and (2) to determine how the reactions between chalcocite and ethylxanthate depend on compositional changes of the mineral surface and in solution brought about by electrochemical pretreatments.

Particulate beds of conducting particles have been previously used by Gardner and Woods (1973) in a study of the ethylxanthate flotation of gold, lead, and galena and by Chander and Fuerstenau (1975) in a study of the dithiophosphate flotation of chalcocite. Both studies established that the flotation of particulate beds could be controlled electrochemically. However this approach has not been pursued in detail, apparently because once a bed is rendered floatable, particle-to-particle contact is lost and no further electrochemical studies are possible. The use of a packed bed eliminates this problem so that both the production of a hydrophobic bed (usually at anodic potentials) and the return of the bed to a hydrophillic state (usually at cathodic potentials) can be studied. Moreover, the relatively large surface area of bed electrodes coupled with the strong characteristic ultraviolet absorption bands of thiol collectors permits the solution phase to be monitored to detect relatively small changes in collector concentration due to adsorption and/or desorption processes.

EXPERIMENTAL MATERIALS AND TECHNIQUES

The microflotation-electrochemical cell, flow system, and equipment have been described previously (Walker et al., 1984). For electrochemical studies and during electrochemical preconditioning, the chalcocite (Cu_2S) particle beds were compacted to improve particle-to-particle contact. The electrolyte was also continuously circulated between the cell and a UV spectrophotometer so the solution phase could be continuously monitored. The bed potential was controlled with a potentiostat and measured versus a calomel reference electrode connected to a Luggin capillary inserted near the center of the bed. The cell design permits flotation to be carried out without a frother.

Hand-selected samples of chalcocite from Messina, Transvaal, were ground dry with an agate mortar and pestle, sized to 590—840 μm, rinsed to remove fines, dried, and stored under nitrogen. Reagent-grade potassium ethylxanthate was recrystallized three times from acetone and also stored under nitrogen. Stock solutions of 10^{-3} mol/l xanthate were prepared daily to ensure minimum decomposition. Nitrogen for purging and as a carrier gas for flotation was water-pumped, ultra high purity, and was passed over hot copper filings to remove trace oxygen.

All experiments were conducted in 0.05 mol/l sodium tetraborate to obtain a buffered pH of 9.2. The usual procedure was to fill the cell with 0.05 mol/l borate ($\simeq$35 ml), purge the cell for approximately 30 min with

nitrogen, load the cell with 1.4 g of mineral on open circuit, and electrochemically precondition the bed for 10 min at the potential at which the collector was to be added. The 10-min conditioning period is believed to be sufficient for the surface to reach a steady-state condition with respect to both stoichiometry and coverage with hydroxides or oxides. The existence of a steady state condition was evident from observations of current and solution absorbance during potential step changes in the region of −0.7 to −0.1 V. Large transients in both current and absorbance occurred at the beginning of a potential step but the current decayed rapidly (≃1 min) and reached a steady-state value due primarily to the reduction of dissolved oxygen in solution and the absorbance exhibited no further changes.

RESULTS

Electrochemical and spectrophotometric characterization

Initial experiments were carried out by preconditioning the bed at −0.7 V for 10 min before adding the collector. This potential was selected on the basis of previous studies which established that beds conditioned at −0.7 V exhibit no natural flotation and that the concentration of Cu(II) in solution was negligible (Walker et al., 1984).

Figure 1 shows a plot of the ethylxanthate 301-nm absorption band as a function of time after adding sufficient potassium ethylxanthate to give a concentration of 2×10^{-5} mol/l to a bed potentiostated at −0.7 V. The spectrometer responded to ethylxanthate within ≃2 s after addition, and the absorbance stabilized within ≃15 s. Based on a molar absorptivity (ϵ_{301}) value of 17,750 l/mol-cm (Pomianowski and Leja, 1963), the concentration

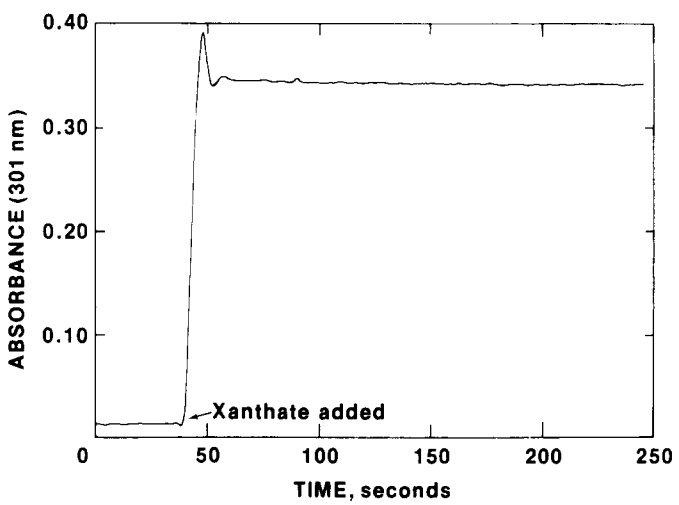

Fig. 1. Absorbance at 301 nm as a function of time after adding potassium ethylxanthate (2×10^{-5} mol/l) to a Cu_2S bed potentiostated at −0.7 V (SCE).

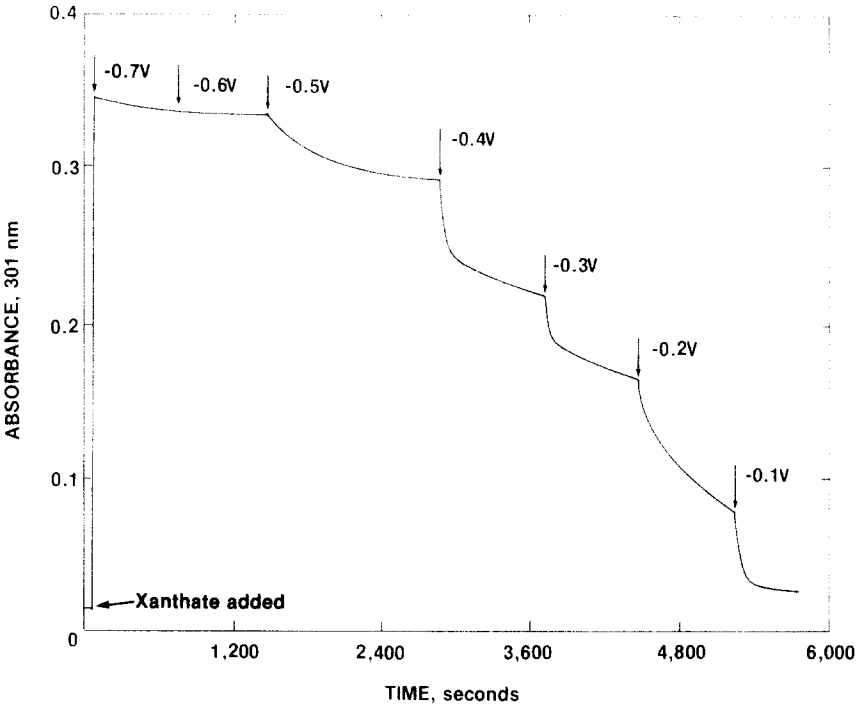

Fig. 2. Effect of anodic step potential increases on the ethylxanthate 301 nm absorption maximum.

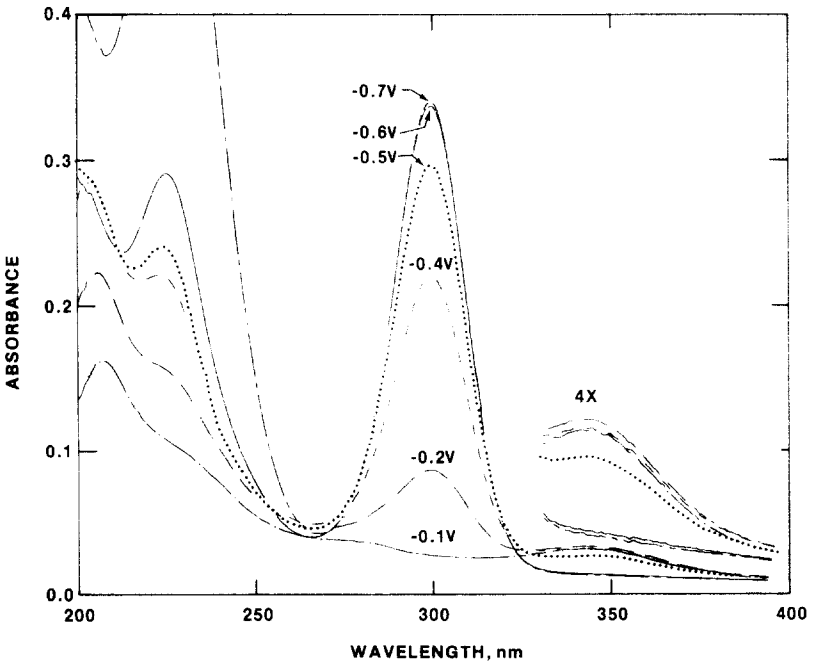

Fig. 3. Spectra of the solution phase of the Cu_2S-ethylxanthate system following anodic potential steps between −0.7 and −0.1 V (SCE). The region between 330 and 390 nm is also shown with 4-fold magnification.

of ethylxanthate 15 s after addition is in agreement with the total amount added. From 15 s to 10 min after addition, the change in absorbance at 301 nm corresponds to a decrease in [EtX^-] of less than 5% per hour. Simultaneous measurement of the electrolysis charge shows that there is no charge transfer between the Cu_2S and ethylxanthate at –0.7 V.

When the bed potential is subsequently stepped from –0.7 to –0.1 V in 0.1-V increments (Fig. 2), each change in potential above –0.6 V produces an instantaneous decrease in [EtX^-] followed by a slower decay. Studies carried out using longer reaction times show that over the range –0.5 to –0.1 V, the slow decay in [EtX^-] at fixed potential continues at least for several hours, indicating that the system reaches equilibrium slowly if at all (Harris and Finkelstein, 1977). The continuous decrease in [EtX^-] cannot be accounted for by natural decomposition (Rao, 1971).

Figure 3 shows spectral scans obtained immediately prior to each stepwise change in potential. Ethylxanthate has a second absorption maximum at 227 nm, which, at –0.7 V, is obscured by the 229-nm HS^- band produced by the cathodic dissolution of Cu_2S (Walker et al., 1984). The most interesting feature of the spectra is the appearance of a new absorption maximum at 348 nm. A compound with the same UV absorption maximum has been reported by Garbacik et al. (1972) and Jones and Woodcock (1978) when xanthates were oxidized with hydrogen peroxide. The latter authors also obtained a similar maximum in an analysis of Mount Isa copper flotation plant solutions. Both groups concluded the most probable reaction was:

$$R-O-C\begin{matrix}=S\\ \diagdown S^-\end{matrix} + H_2O_2 = R-O-C\begin{matrix}=S\\ \diagdown S\text{-}O^-\end{matrix} + H_2O \qquad (1)$$

and Jones and Woodcock (1978) termed the product perxanthate ("0"-alkyl dithiomonoperoxycarbonate) and suggested that in flotation pulps the peroxide is formed as an intermediate in oxygen reduction. The sodium salt of sec-butylperxanthate has been synthesized in this laboratory by reaction of sec-butylxanthate with hydrogen peroxide, and a spectrum in agreement with that of Garbacik et al. (1972) and Jones and Woodcock (1978) is shown in Fig. 4. The shoulder at 301 nm shows sec-butylxanthate as an impurity, and the shoulder near 280 nm suggests that dixanthogen may also be present (Pomianowski and Leja, 1963). Beer's law plots for the two maxima of sec-butylperxanthate yield ϵ_{348} = 5660 l/mol-cm and ϵ_{215} = 6410 l/mol-cm. From Fig. 3, ethylperxanthate accounts for approximately 60 percent of the decrease in [EtX^-] between –0.7 and –0.5 V, but for only less than 5% of the decrease between –0.7 and –0.1 V. The fact that the 348-nm maximum is detected at –0.5 V and not at –0.7 and –0.6 V is believed to reflect the kinetics of oxygen reduction, which may proceed completely to water at large overvoltages (presumably –0.7 and –0.6 V) but may permit the diffusion of intermediate peroxide away from the surface at smaller overvoltages (Beigler et al., 1975). The above experiments were carried out with continuous nitrogen purging of the electrolyte but

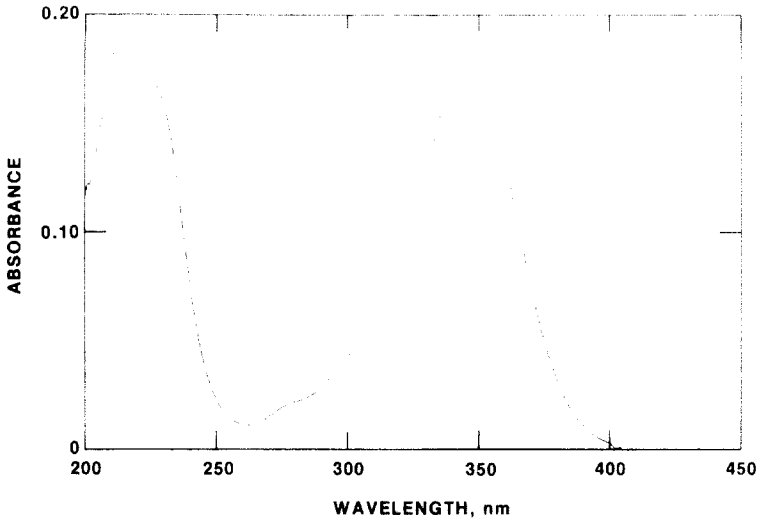

Fig. 4. Spectrum of sodium sec-butylperxanthate.

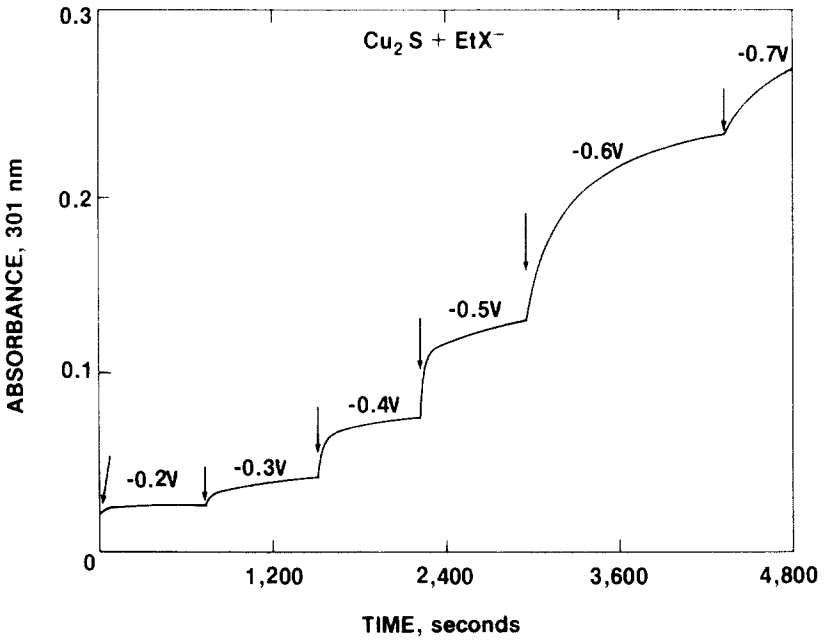

Fig. 5. Effect of cathodic step potential decreases on the ethylxanthate 301-nm absorption maximum.

with the cell top open, permitting some oxygen to diffuse into the solution. When the cell top was sealed and the experiments repeated, the decrease in ethylxanthate was similar to that shown in Fig. 3 but no ethylperxanthate was detected between −0.7 and −0.1 V.

To determine if the progressive decrease in [EtX^-] with increasing poten-

tial can be reversed, the bed potential was decreased from −0.1 to −0.7 V in 0.1 V increments. Figure 5 shows the change in the 301-nm absorbance maximum as a function of time, and Fig. 6 shows the spectra obtained at each potential. The xanthate ion concentration increases with decreasing potential with a maximum change between −0.5 and −0.6 V. It can also be seen in Fig. 6 that the 348-nm band does not change during reduction when account is taken of the apparent increase in absorbance at all wavelengths for the −0.6 and −0.7 V spectrum, and thus the perxanthate concentrate remains constant during reduction; at −0.7 V, the 229-nm HS^- absorption band arising from Cu_2S reduction (Walker et al., 1984) obscures the 227-nm xanthate band. The origin or species responsible for the overall increase in absorbance from 200 to 400 nm for the −0.6- and −0.7-V spectra is not known, but if it is a soluble species it must have very broad absorbance bands. It may also reflect a turbidity increase due to an insoluble species. At present, no attempts have been made to identify this species.

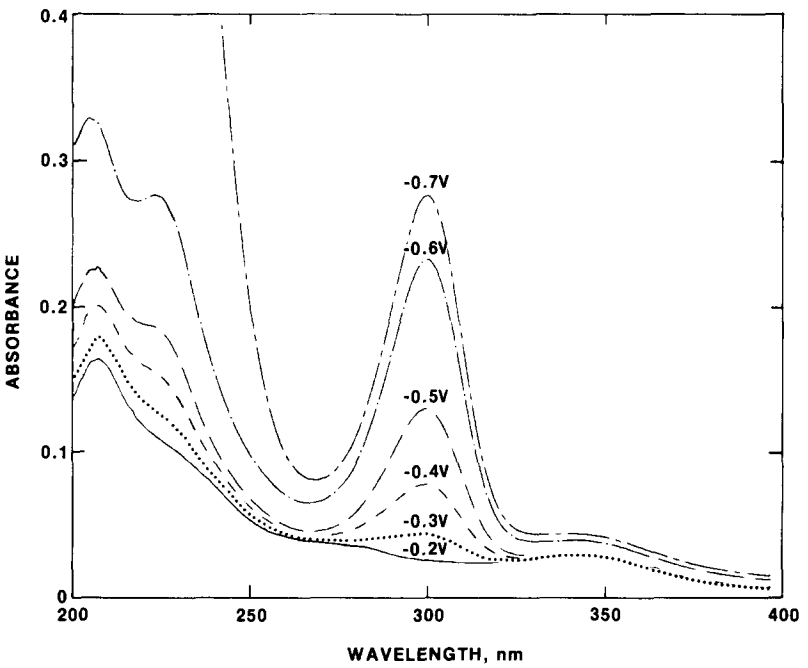

Fig. 6. Spectra of the solution phase of the Cu_2S-ethylxanthate system following cathodic potential steps between −0.2 and −0.7 V (SCE).

Confirmation of an adsorption and desorption reaction

In a separate experiment, xanthate was reacted with Cu_2S at −0.1 V, and the cell was thoroughly flushed with fresh 0.05 mol/l borate to remove any soluble xanthate derivatives. Upon subsequent reduction at −0.7 V, the xanthate ion concentration increased similar to that shown in Fig. 6, estab-

lishing that the product of the anodic reaction is adsorbed on Cu_2S and can be reduced back to the free xanthate ion.

Effect of repeated step potential changes

In the above experiment in which ethylxanthate is added at −0.7 V, adsorbed at −0.1 V, and then desorbed at −0.7 V, 70% of the xanthate ion initially added to the system reappears in solution at −0.7 V, that is, 30% is lost (compare Figs. 3 and 6 at −0.7 V). In experiments that were otherwise identical, except the potential was repeatedly stepped from −0.7 to −0.1 V to −0.7 in −0.1 V increments, approximately 30% of the xanthate ion present at −0.7 V is lost each time the bed potential is stepped to −0.1 V and then stepped back to −0.7 V. Ultimately the free xanthate ion in solution approaches zero and no potential despendent adsorption or desorption occurs.

Effects of preconditioning potential

The above results may seem to imply that with increasing potentials in the range of −0.5 to −0.1 V, the reaction of EtX^- with chalcocite occurs primarily by a charge transfer adsorption process and that the adsorbed product is reducible. However, confirmation of the charge transfer mech-

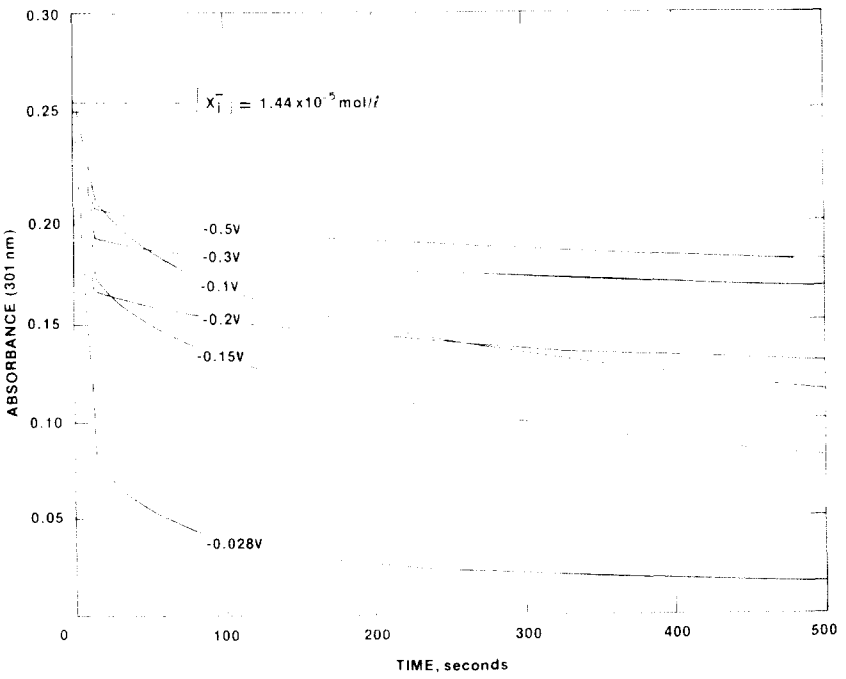

Fig. 7. Absorbance at 301 nm as a function of time after adding ethylxanthate (1.44×10^{-5} mol/l) to Cu_2S beds potentiostated between −0.5 and −0.028 V (SCE).

anism requires measurement of the electrolysis charge associated with the reaction. In the previous experiments, the charge could not be accurately determined because of the coexistence of potential dependent faradic currents associated with oxygen reduction and the oxidation of chalcocite itself.

An alternative method for studying the xanthate reactions was to precondition different chalcocite beds for 10 min at different potentials prior to adding EtX^- in order to maintain a nearly constant contribution from oxygen reduction and to permit the electrode to approach equilibrium with respect to coverage with oxides or hydroxides. Figure 7 shows the resulting change in the ethylxanthate 301-nm absorption maximum, and Fig. 8 shows the electrolysis current associated with adding ethylxanthate to beds conditioned at different potentials. The procedure was the same as described above except the cell top was sealed to minimize oxygen entering the system. Ethylperxanthate was not detected in spectra obtained after the 10-min reaction times, consistent with a lower oxygen level. Spectra taken immediately prior to adding ethylxanthate established that the absorbance between 200 and 400 nm was <0.005 absorbance unit for beds conditioned between -0.5 and -0.1 V. This would correspond to Cu(II) or (HS^-) concen-

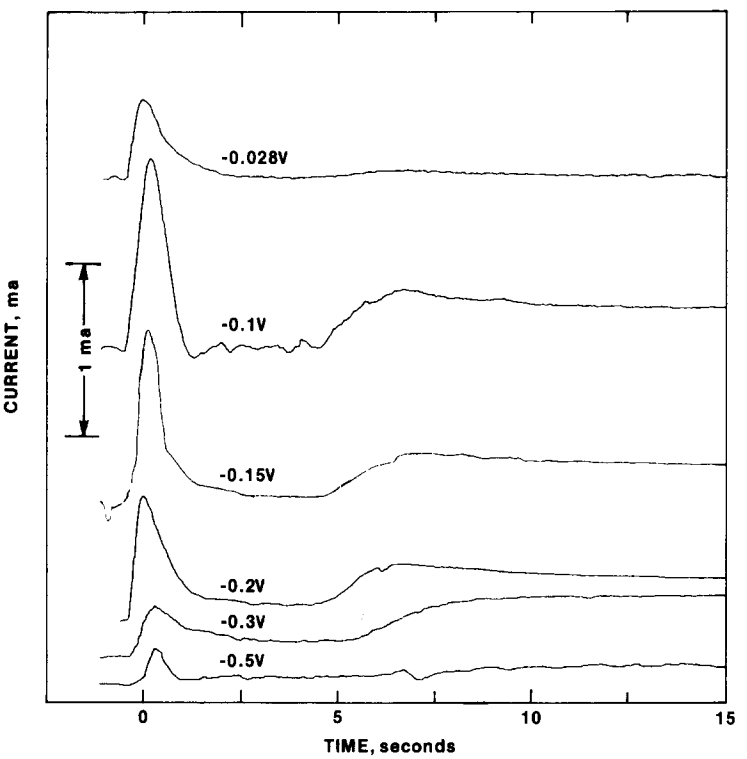

Fig. 8. Faradaic current associated with adding ethylxanthate (1.44×10^{-5} mol/l) to Cu_2S beds potentiostated between -0.5 and -0.028 V.

trations $\leqslant 10^{-6}$ mol/l (Walker et al., 1984), which is much less than the concentration of xanthate. For the bed conditioned at the open circuit potential (−0.028 V) the absorbance at 216 nm (not shown) indicated a Cu(II) concentration of 4×10^{-5} mol/l (Walker et al., 1984). Since xanthate is known to react with Cu(II), the curves in Figs. 7 and 8 at −0.028 V are expected to have a significant homogeneous reaction component and will be discussed separately below.

Based on the above arguments, the reactions between −0.5 and −0.1 V must involve primarily heterogeneous adsorption processes. However, the dependence of the curves on potential is not consistent with purely a charge transfer mechanism. For example, if we consider the relative decrease, ΔX, in EtX^- over the time intervals t = 0 to 600 s, t = 0 to 15 s, and t = 15 to 600 s as tabulated in Table I, it can be seen that the potential dependence of the reactions is complicated, with $\Delta X(t = 0 - 600\ s)$ exhibiting a maximum at −0.15 V, $\Delta X(t = 0 - 15\ s)$ a maximum at −0.2 V, and $\Delta X(t = 15 - 600\ s)$ a minimum at −0.3 V. Potential ranges where ΔX increases with increasing potential are consistent with an electrochemical oxidation reaction, while ranges where it decreases are inconsistent. The general dependence of the reactions on potential as illustrated in Fig. 7 and Table I has been reproduced several times at each potential to establish that the results are not due to differences in surface area or to differences in the concentration of soluble dissolution products from one experiment to the next. Rather, the evidence is that the complex potential dependence of the overall reactions arises from compositional changes in the electrode surface region which have been induced by the preconditioning potential.

Whereas Fig. 7 represents a direct measure of all reactions that affect the concentration of the ethylxanthate ion, the curves of Fig. 8 measure only the electrochemical component of the reaction. The first current peak of each curve corresponds to an anodic oxidation reaction as a locally concentrated slug of ethylxanthate is carried past the bed by the flowing

TABLE I

Relative decrease in $[EtX^-]$ as a function of time interval and potential

Potential, V (SCE)	ΔX(0—600s)		ΔX(0—15s)		ΔX(15—600s)		ΔXq(0—15s)[2]	
	μmol/l	%[X_i][1]	μmol/l	%[X_i]	μmol/l	%[X_i]	μmol/l	%ΔX(0—15s)
−0.028	14.0	97	9.5	66	4.5	31	0.2	2
−0.100	8.2	57	2.4	17	5.8	40	1.2	50
−0.150	10.0	69	4.5	31	5.5	38	1.0	22
−0.200	7.6	53	5.4	38	2.3	16	1.2	22
−0.300	5.3	37	3.9	27	1.4	10	1.2	31
−0.500	4.6	32	2.6	18	2.0	14	0.4	15

[1] Calculated as a percentage of the initial xanthate concentration, $[X_i] = 1.44 \times 10^{-5}$ mol/l.
[2] Calculated assuming a 1-e^- oxidation reaction.

electrolyte; the oxidation wave at ≈5 s corresponds to the same reaction as the somewhat diluted xanthate solution makes a second pass through the bed. Assuming a 1 e^- oxidation process, integration of the current-time curves of Fig. 8 from t=0 to 15 s gives the equivalent changes in xanthate concentration, ΔX_q(t=0—15 s), listed in Table I. In carrying out the integration, the baseline was chosen at the value of the bed current immediately prior to xanthate addition. This steady state current was cathodic and believed to arise from reduction of residual oxygen in the electrolyte. Since xanthate adsorption reportedly inhibits oxygen reduction on sulfides (Nicol, 1972), this choice of baseline may overestimate the charge associated with xanthate oxidation and may be partly responsible for the potential dependence of the ΔY_q values listed in Table I. Although it is not possible to determine accurately the error introduced by the baseline choice, it has been estimated to be less than 25% when the integration is truncated at 15 s; that is, at the time when the first measurement of EtX^- can be obtained spectrophotometrically. The error increases significantly with longer integration times and prevents a comparison of the electrochemical and total reaction components for $t > 15$ s. Assuming xanthate reduction inhibits oxygen reduction, the error is such that the ΔX_q values in Table I may be larger than the true electrochemical component. It can be seen in Table I that during the first 15 s of the reactions, the charge [ΔX_q(0—15 s)] accounts for at most 15% of the total reaction at −0.5 V and 50% at −0.1 V. It can be concluded that in addition to the charge transfer oxidation mechanism, ethylxanthate must also react with chalcocite by an exchange reaction without charge transfer, or as discussed later, an exchange reaction coupled with a reduction reaction.

Preconditioning at the open-circuit potential, −0.028 V

To study the effects of soluble Cu(II), a Cu_2S bed was allowed to undergo dissolution until $\simeq 3\times10^{-5}$ mol/l of Cu(II) was produced in solution as determined by its absorption at 216 nm (Walker et al., 1984). The Cu(II) containing electrolyte was removed from the cell and titrated with ethylxanthate. Figure 9 shows a plot of the ethylxanthate 301-nm absorption maximum as a function of titrant addition. The apparent equivalence point at $\approx 7\times10^{-5}$ mol/l is in reasonable agreement with the initial Cu(II), assuming the reaction:

$$2Cu(II) + 4X^- = 2CuX_2 = 2CuX + X_2 \qquad (2)$$

where cupric xanthate is unstable and disproportionates to cuprous xanthate and dixanthogen (Sparrow et al., 1977).

Spectral scans established that the increase in absorbance prior to the apparent equivalence point is not due to the free xanthate ion but is caused by an increase in absorbance over the range of 200 to 400 nm, suggestive of an increase in turbidity. The increase in turbidity probably arises from

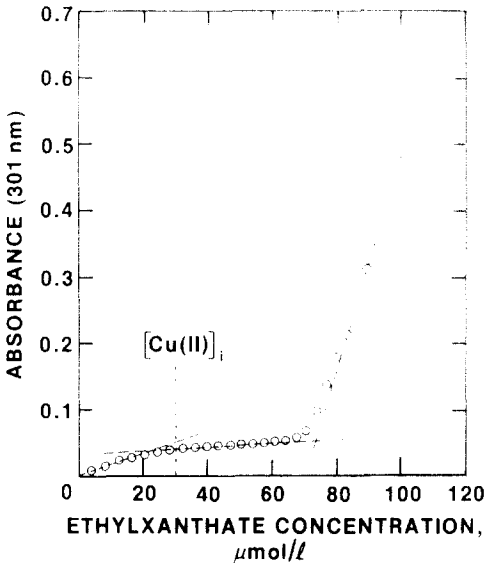

Fig. 9. Absorbance at 301 nm as a function of the concentration of ethylxanthate added to a Cu(II)-containing solution produced by the open-circuit dissolution of Cu_2S.

colloidal cuprous xanthate and dixanthogen, consistent with the low solubilities of the products of reaction (2) in aqueous solutions (Kakovsky, 1957). For EtX^- concentrations up to the equivalence point, two additional absorbance bands with maxima near 256 and 283 nm were observed to increase with increasing xanthate additions. Maxima at 256 and 283 nm for the Cu(II)-EtX^- system have been seen by Yamasaki and Nanjo (1969) and Sparrow et al. (1977) and attributed to the cupric monoxanthate ion CuX^+. Above the equivalence point, the absorbance at 301 nm is linear, but the slope yields an apparent molar absorptivity of 15,500 l/mol-cm compared with the expected value of 17,750 l/mol-cm. Spectral scans taken just beyond the apparent equivalence point show isosbestic points at 241, 276, and 323 nm (Fig. 10), indicating that EtX^- continues to undergo a reaction. The presence of other reactions could account for the low slope. Difference spectra (not shown) obtained by subtracting scaled spectra of pure ethylxanthate from the spectra of Fig. 10 show the 256- and 283-nm maxima decrease above the equivalence point, suggesting a reaction between the cupric monoxanthate complex and the xanthate ion.

The existence of a homogeneous solution reaction between ethylxanthate and Cu(II) at −0.028 V qualitatively accounts for the fast decrease in EtX^- (Fig. 7) and for the smaller current (Fig. 8) compared to the behavior at the more negative potentials. Cuprous xanthate and dixanthogen could precipitate or physically adsorb on Cu_2S as hydrophobic entities. It can be argued that this reaction would not be as efficient as chemisorption since xanthate would be consumed on a 2:1 basis by Cu(II) and precipitation or physical adsorption may not necessarily occur preferentially on Cu_2S but also on other minerals, possibly leading to poor selectivity.

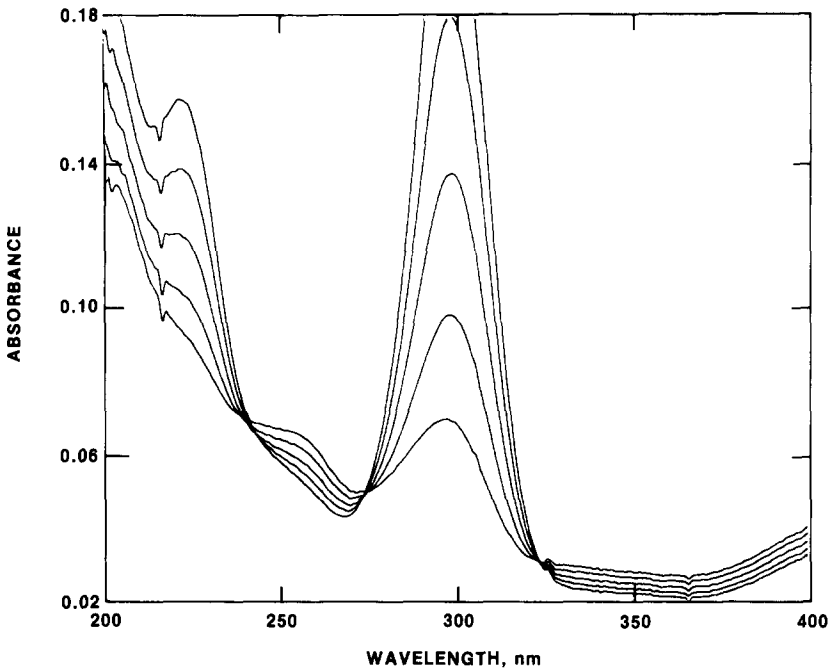

Fig. 10. Spectra of the Cu(II)-ethylxanthate system for ethylxanthate concentrations between 7.08×10^{-5} and 8.38×10^{-5} mol/l.

Flotation

Flotation tests were carried out in a separate set of experiments using, as nearly as possible, the same procedures used in the spectrophotometric and electrochemical studies. The major reason for conducting these tests separately was that the electrolyte could not be circulated at the same time that the carrier gas was introduced for flotation without trapping gas in the UV cuvette. Recovery was visually estimated from the height of the mineral bed after 2-min flotation periods. This procedure gave exact recoveries at zero and 100%, but between these units the accuracy was $\cong \pm 10\%$.

Figure 11 shows a plot of recovery versus potential when Cu_2S was preconditioned at −0.6 V, xanthate added, and the potential subsequently stepped anodically from −0.6 to −0.1 V and then cathodically back to −0.6 V. At each potential the bed was conditioned for 10 min prior to the 2-min flotation tests, and the floated fraction then returned to the cell for conditioning at the next potential. The flotation response is markedly dependent on potential, and a comparison of Fig. 11 with Figs. 2 and 5 shows that the flotation response correlates reasonably well with the adsorption of EtX^- during the anodic cycle and with its desorption during the cathodic cycle. The hysteresis appears to parallel a similar hysteresis in EtX^- adsorption during anodic steps (Fig. 2) and desorption during cathodic steps (Fig. 5). In experiments where the beds were repeatedly cycled be-

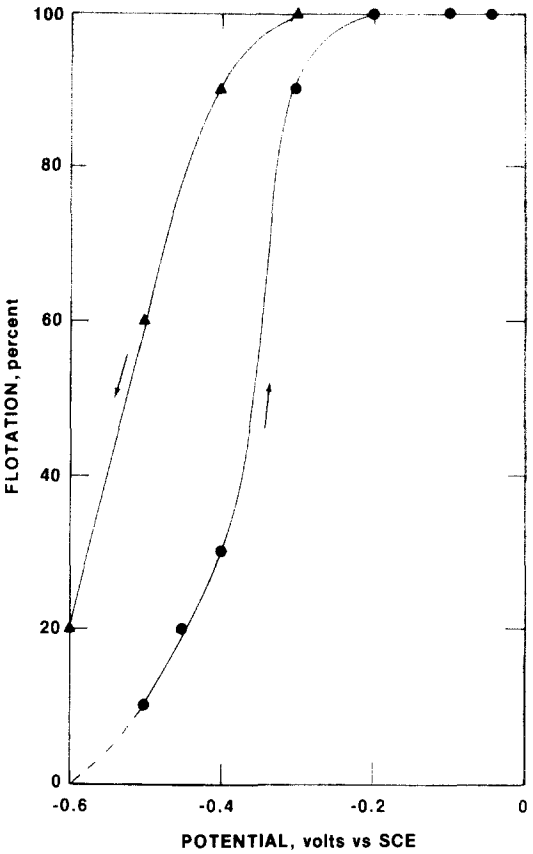

Fig. 11. Recovery of Cu_2S as a function of potential using ethylxanthate (1.44×10^{-5} mol/l) as the collector.

tween −0.7 and −0.1 V until no desorbable or reducible xanthate could be detected, the recovery leveled off at ≃20%, becoming independent of potential. Flotation curves obtained after preconditioning at −0.7 V and those obtained by conditioning at flotation potentials between −0.5 and −0.1 V were essentially the same as the anodic curve of Fig. 11, i.e., within the ≃10% uncertainty inherent in visually estimating the recovery.

As established previously, conditioning near the open-circuit potential gives rise to a finite soluble Cu(II) concentration, and it was anticipated that competition between the homogeneous Cu(II)/EtX^- reaction and the heterogeneous surface reactions may give rise to an increase in the quantity of EtX^- required to initiate flotation as suggested by Taggart and Hassialis (1946). Chander and Fuerstenau (1975) also report that under conditions where Cu^{2+} is an oxidation product of chalcocite and diffuses away from the surface, a bulk precipitate of cuprous diethyldithiophosphate is observed at low dithiophosphate concentrations, and that when a precipitate is capable of forming, the flotation recovery is low and at the same time large

reagent losses can occur. Attempts to correlate the threshold concentrations of EtX^- required for flotation with the Cu(II) concentration were inconclusive owing to experimental difficulties in accurately determining when flotation was induced. However, it was found that when small quantities of EtX^- were added to the cell, that is, for $[EtX^-] \ll [Cu(II)]$, the collector reacted completely within ≃15 s while the concentration of Cu(II) continued to increase. Once sufficient EtX^- was added to induce flotation, no further buildup of Cu(II) was observed. It appears that the collector coverage required to induce flotation is sufficient to inhibit the open-circuit corrosion reaction, perhaps reflecting a decrease in the catalytic ability of collector covered Cu_2S to reduce oxygen.

The laboratory-synthesized sodium salt sec-butylperxanthate was used to determine if perxanthates have collecting properties. Spectrophotometric studies established that sec-butylperxanthate does not react with copper salts or with Cu_2S in aqueous solutions between −0.7 and 0 V. Some flotation was induced at potentials near −0.3 V; however, the perxanthate contained xanthate and possibly dixanthogen as impurities (see Fig. 4), and the flotation is probably associated with the xanthate impurity. Subsequent studies confirmed that the quantity of xanthate impurity in the perxanthate was sufficient to float Cu_2S.

DISCUSSION

Reaction mechanisms

Heyes and Trahar (1979) have recently used oxidizing and reducing reagents to control the electrochemical potential of chalcocite flotation pulps and obtained recovery curves that were qualitatively similar to those in Fig. 11, with the onset of flotation occurring at ≃−0.43 V (SCE) at both pH 8 and 11. They also obtained some spectrophotometric evidence that EtX^- is reversibly abstracted by chalcocite, as confirmed in this paper. Gaudin and Schuhmann (1936) and Harris and Finkelstein (1977) have shown that the most likely adsorbed species inducing hydrophobicity is cuprous xanthate, which led Heyes and Trahar (1979) to consider the reactions:

$$Cu_2S + X^- = CuS + CuX + e^-, \quad E_h^0 = -0.234 \text{ V} \tag{3}$$

$$Cu_2S + 2X^- = 2\,CuX + S + 2e^-, \quad E_h^0 = -0.171 \text{ V} \tag{4}$$

$$Cu_2S + 2X^- + 4H_2O = 2CuX + SO_4^{2-} + 8H^+ + 8e^-, \quad E_h^0 = 0.225 \text{ V} \tag{5}$$

However, the potentials for these reactions do not agree with either the results of Heyes and Trahar (1979) or the results of this study for the onset of a chalcocite-xanthate reaction.

It is known (Gaudin and Schumann, 1936; Mellgren, 1966) that xan-

thate can also react with sulfides by exchange or metathesis. Such reactions would seem to be particularly relevant to experiments in which Cu_2S is preconditioned at various potentials prior to adding the collector. For example, the major effect of preconditioning in the range −0.5 to −0.1 V appears to be an alteration in the surface of Cu_2S, probably by reactions of the form[a]:

$$Cu_2S + 2\delta H_2O = \delta Cu(OH)_2 + Cu_{2-\delta}S + 2\delta H^+ + 2\delta e^- \quad (6)$$

Subsequent thermodynamically favored exchange reactions with ethylxanthate can then be written as:

$$Cu(OH)_2 + X^- + e^- = CuX + 2OH^-, \qquad E_h^0 = 0.181 \text{ V} \quad (7)$$

or

$$Cu(OH)_2 + 2X^- = CuX_2 + 2OH^- \quad (8)$$

Reaction 7 involves exchange with an associated reduction[b], and reaction 8 involves exchange without charge transfer. Both reactions may involve the cupric monoxanthate ion CuX^+ as an intermediate, with reaction 7 proceeding by:

$$CuX^+ + e^- = CuX$$

and reaction 8 by:

$$CuX^+ + X^- = CuX_2$$

where cupric monoxanthate has been suggested as a $Cu(II)/EtX^-$ reaction product by Yamasaki and Nanjo (1969) and Sparrow et al. (1977). It should be noted that xanthate produced by reaction 8 is expected to decompose by reaction 2 to cuprous xanthate and dixanthogen. At potentials less than that of the reversible xanthate-dixanthogen couple, the dixanthogen would be simultaneously reduced to xanthate. Therefore, reaction 8 followed by decomposition (reaction 2) and reduction of dixanthogen is equivalent to reaction 7.

With reference to reaction 6, the simplest anodic reaction involving ethylxanthate may be assumed to occur at a bare (nonhydrolyzed) cation site:

$$Cu_{2-\delta}S + \lambda X^- = Cu_{2-\delta-\lambda}S + \lambda CuX + \lambda e^- \quad (9)$$

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[a] With reference to reaction 6, other adsorbed oxide or hydroxide species that may be present in alkaline solution include $CuOH^+$, CuO, Cu_2O, and $HCuO_2^-$. $Cu(OH)_2$ has been chosen as a representative product on the basis of the free energy change for the various reactions.

[b] It is noteworthy that exchange reactions in which ethylxanthate displaces other likely oxidation products (CuO, $CuOH^+$, Cu_2O, and $HCuO_2^-$) also involve a net reduction whenever the products are cuprous xanthate and hydroxyl ions.

Reactions 6 and 9 have been written in incremental form to stress that the ratio of copper to sulfur in copper sulfides may have a wide range of values and that oxidation reactions such as 6 or 9 may induce other stable or metastable copper sulfide phases. For example, Goble (1981) has shown that anilite ($Cu_{1.75}S$) in ferric sulfate solutions undergoes a major structural change to geerite ($Cu_{1.6}S$) after several hours of leaching. With further removal of copper, the material remains metastable in the geerite structure to compositions approaching covellite (CuS). In the case of thin films, Koch and McIntyre (1976) have shown the oxidation in acids proceeds through the following sequence of distinct phases:

$$Cu_2S \rightarrow Cu_{1.93}S \rightarrow Cu_{1.83}S \rightarrow Cu_{1.66}S \rightarrow Cu_{1.38}S \rightarrow CuS \qquad (10)$$

Without a knowledge of the exact copper sulfide phase and composition (Sato, 1966), the thermodynamic potential for reaction 9 cannot be calculated. However, a range of maximum potentials can be estimated by starting at a hypothetical potential where the electrode surface is assumed to be characteristic of stoichiometric Cu_2S and then successively advancing reaction 9 to form CuX and the coexisting neighboring sulfide phases in sequence 10. Assuming a xanthate concentration of 1.44×10^{-5} mol/l and using thermodynamic data for the xanthate species taken from Hepel and Pomianowski (1977) and for the Cu-S system from Koch and McIntyre (1976), the calculated potentials for reaction 9 for $(2\text{-}\delta, \lambda)$ values of (2,0.07), (1.93,0.1), (1.83,0.17), (1.66,0.28), and (1.38, 0.38) are −0.299, −0.236, −0.221, −0.190 and 0.018 V (SCE), respectively. For comparison, reaction 3, which is usually used to represent the Cu_2S-EtX^- reaction, has a potential of −0.193 V (SCE). By recognizing that at low coverages, the activity of surface CuX may be less than unity (Heyes and Trahar, 1979) and that the reactions do not necessarily induce a second Cu-S phase, the potentials may reasonably be expected to be shifted to $\simeq$−0.5 V (SCE); i.e., to the potential where an anodic reaction is first observed (Figs. 2 and 8).

The present experiments do not permit a definitive choice of either reaction 7 or reaction 8 as the favored exchange reaction. However, since the net current (Fig. 8) corresponds to an oxidation process, it can be concluded that if the exchange reaction is followed by the reduction of CuX^+ or dixanthogen, then electrochemical oxidation (reaction 9) is the dominant reaction over the first 15 s. If the exchange reaction does not involve a reduction step, as suggested by reaction 8, the electrochemical oxidation reaction accounts for, at most, the percentages listed in Table I.

Recent research in sulfide flotation has focused extensively on the role of oxygen in the overall reactions between xanthate collectors and sulfides, and the two most widely accepted theories are that it either acts as an oxidant to form products that react with xanthate by exchange or else raises and maintains the potential to a thermodynamically favored region such that the metal xanthate or dixanthogen can form by an anodic reaction. The results presented in this paper suggest that, during the first 15 s, both the exchange and charge transfer reaction occur simultaneously on

chalcocite over the same potential region. Reactions 7—9 suggest that, in the absence of an external circuit, oxygen is a prerequisite for a xanthate reaction to occur to any significant extent. With respect to reactions 7 and 8, the surface must be either superficially oxidized by prior atmospheric exposure to oxygen or, as indicated in reaction 6, it may be oxidized in aqueous environments. The presumption in the latter case is that dissolved oxygen provides a charge-compensating reduction process so that reaction 6 can proceed from left to right. With respect to reaction 9, oxygen reduction also provides the necessary cathodic process to compensate for the oxidation reaction. It should also be noted that once the surface is oxidized, reduction reaction 7 can partially compensate the oxidation process represented by reaction 9 without the need of dissolved oxygen.

General

The most significant result obtained in this work is the clear demonstration that: (1) chalcocite flotation is related to electrochemical potential; and (2) the potential dependence follows whether one considers an electrochemical oxidation reaction or an exchange reaction, or as shown in this paper, both types of reactions occur simultaneously over the same potential region. Heyes and Trahar (1979) have discussed some of the practical consequences of potential dependent flotation reactions and suggested several areas where the redox conditions may be important. They also correctly state that "in normal practice, E_h cannot be used as a control variable because it is set by the oxygen in the air supply and nothing short of flotation in nitrogen would permit the type of control which can be exercised in laboratory tests." In this context, it should be noted that Southern Peru Copper's Cuajone plant (Podobnik and Shirley, 1981) and the Gibraltar Mines Limited plant, Vancouver Island (M.A. Redfearn, pers. commun., 1982) use nitrogen as the carrier gas in the molybdenum recovery circuits. The copper ores are depressed with reducing reagents, and the use of nitrogen rather than air cuts the depressant consumption by >50%. Based on the results presented in this paper, the most plausible mechanism by which reducing agents depress the copper ores is through electrodesorption (reduction) of hydrophobic collector coatings produced during the rougher bulk float, with the naturally hydrophobic molybdenite retaining its floatability. Obviously, the efficiency of the reducing reagents is increased by using nitrogen rather than air as the carrier gas, since the competing oxygen reduction reaction is minimized with nitrogen, permitting more reducing potentials to be maintained and also inhibiting the oxygen decomposition of HS^-.

Results of similar studies on the galena-xanthate system (Gardner and Woods, 1973) and on the chalcocite-dithiophosphate system (Chander and Fuerstenau, 1975) show that flotation and collector-mineral interactions in these systems are also strongly dependent on potential. Therefore, the

results on chalcocite can probably be generalized to a number of other sulfides as suggested by Heyes and Trahar (1979). Similar studies (unpublished) show the recovery-potential curves for chalcocite, galena, and pyrite are distinctly different (shifted along the potential axis), suggesting that potential may be used to effect or optimize differential separations.

SUMMARY

It has been shown that there are at least four and probably five distinct reactions in the Cu_2S, O_2, H_2O, EtX^- system:

(1) Ethylxanthate is oxidized to ethylperxanthate, probably by a reaction of hydrogen peroxide formed as a coproduct in oxygen reduction. Perxanthate is produced at reducing potentials ($\simeq$–0.5 V), in the presence of dissolved molecular oxygen. Perxanthate does not react with Cu_2S and does not appear to induce hydrophobicity. The ethylxanthate-peroxide reaction is thus detrimental to flotation because it consumes collector nonproductively, albeit in small amounts for the low-oxygen concentrations of the present experiments.

(2) Ethylxanthate reacts with Cu(II) produced from the anodic dissolution of Cu_2S. At pH 9.18, this reaction becomes significant at potentials $\geqslant$–0.040 V, that is, at potentials near or more positive than the open-circuit potential. The ethylxanthate-Cu(II) reaction most likely produces cupric xanthate, which disproportionates to cuprous xanthate and dixanthogen, and smaller quantities of ionized cupric monoxanthate. This reaction is not believed to be efficient from the standpoint of flotation and may lead to poor selectivity.

(3) There is an "inferred" reaction which converts EtX^- to a nonreducible xanthate derivative. This reaction is "inferred" from the fact that repeated cycling between –0.7 and –0.1 V eventually leads to a situation where no desorbable or reducible xanthate derivative is observable at –0.7 V. The nonreducible product is apparently detrimental to flotation since it leads to a potential independent recovery of $\simeq$20%.

(4) Ethylxanthate reacts by an electrochemical reaction believed to be of the form:

$$Cu_xS + \lambda X^- = Cu_{x-\lambda}S + \lambda CuX + \lambda e^-$$

with discharge occurring at a bare (nonhydrolyzed) cation site and the value of x determined by the prior weathering and electrochemical history of the chalcocite. The onset of this reaction occurs near –0.5 V, and the magnitude increases with increasing potential between –0.5 and –0.1 V.

(5) Ethylxanthate reacts by an exchange reaction with the product also adsorbed on Cu_2S. This reaction also appears to begin near –0.5 V, and between –0.5 and –0.1 V it exhibits a complex dependence on the preconditioning potential of the Cu_2S. This reaction may lead to cuprous

xanthate by the reaction:

$$Cu(OH)_2 + X^- + e^- = CuX + 2OH^-$$

or to cupric xanthate by the reaction:

$$Cu(OH)_2 + 2X^- = CuX_2 + 2OH^-$$

where at longer times it is assumed that cupric xanthate decomposes to cuprous xanthate and dixanthogen. The reactions discussed in 4 and 5 are both believed to produce a product that can be subsequently reduced at more negative potentials, with the release of xanthate to the solution phase. In general, there is a good correlation between flotation and the adsorption reactions and between the decrease in flotation and the reduction of the adsorbed xanthate product.

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