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Electrochemical Conditioning of a Mineral Particle Bed Electrode for Flotation

By J. E. Gebhardt, N. F. Dewsnap, and P. E. Richardson





Report of Investigations 8951

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CONTENTS

	Page		Page
Abstract	1	EX adsorption-flotation of mixed-mineral	_
Introduction	1	(chalcocite-pyrite) beds	. 6
Experimental materials and methods	2	Single mineral flotation in the presence of	
Results and discussion	2	dissolved ions	. 7
Potential distribution in the bed electrode	2	Chalcocite flotation-pyrite dissolution products	7
EX adsorption-flotation of single-mineral		Pyrite flotation-chalcocite dissolution products.	. 7
particle beds	4	Summary	9
Chalcocite-EX	4	References	
Pyrite-EX	4		

ILLUSTRATIONS

	Schematic of the electrochemical-flotation cell	- 3
2.	Particle and solution potential distribution within a chalcocite bed electrode at -0.5 V (SCE) at various	
	dissolved oxygen concentrations	4
3.	Flotation recovery and EX adsorption as a function of potential for single-component chalcocite and pyrite	
	beds at pH 9.2	5
	Spectra of EX solution at pH 9.2 in contact with a pyrite bed at -0.6 to 0.2 V (SCE)	5
5.	Flotation recovery of chalcocite and pyrite at pH 9.2 as a function of potential for single- and	
	mixed-mineral beds	6
6.	Flotation recovery of chalcocite and pyrite at pH 9.2 as a function of potential for single-mineral beds alone	
	and in the presence of dissolution products	8
	Spectra of the dissolution products from a chalcocite bed	8
8.	Spectra of EX solution at pH 9.2 in contact with a pyrite bed in the presence of chalcocite dissolution	
	products	9

TABLE

1. Decrease in EX concentration in contact with pyrite beds in the absence and presence of chalcocite	
dissolution products	9

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

 $\begin{array}{c} cm\\ cm^2\\ cm^2/g\\ cm^3/s\\ g\\ L/(mol \cdot cm)\\ \mu m\\ min \end{array}$

centimeter square centimeter square centimeter per gram cubic centimeter per second gram liter per mol per centimeter micrometer minute ${
m mol/L} \ \mu {
m mol/m^2} \ {
m mV} \ {
m nm} \ {
m nm^2} \ {
m ppm} \ {
m pct} \ {
m V}$

mol per liter micromol per square meter millivolt nanometer square nanometer parts per million percent volt

ELECTROCHEMICAL CONDITIONING OF A MINERAL PARTICLE BED ELECTRODE FOR FLOTATION

By J. E. Gebhardt,¹ N. F. Dewsnap,² and P. E. Richardson³

ABSTRACT

External control of the electrochemical potential of a bed of mineral particles has been investigated by the Bureau of Mines as a method for controlling particle interaction with organic collectors and thus, flotation response. A cylindrically shaped, 200to 300-g bed of sulfide mineral particles was used as the working electrode to examine the potential distribution in the bed. The dissolved oxygen concentration of the electrolyte had a significant effect on the potential profile across the mineral bed. Low oxygen levels were necessary to achieve uniform electrochemical potential distributions.

Flotation separation of a chalcocite-pyrite mineral mixture by controlled potential was achieved using ethylxanthate, but the flotation behavior of chalcocite and pyrite from the mixture does not follow the flotation behavior of the individual minerals. That is, the presence of another sulfide mineral alters the flotation behavior with ethylxanthate. Galvanic interaction due to mineral-to-mineral contact between chalcocite and pyrite contributes to differences in the recovery. Chalcocite dissolution products had a deleterious effect on pyrite flotation by activating flotation below -0.1 V (saturated calomel electrode) and depressing flotation above -0.1 V. Pyrite dissolution products had no effect on chalcocite flotation.

INTRODUCTION

The electrochemical nature of the interaction of xanthates with sulfide minerals has been established by numerous workers and is reviewed in reference 1. Part of the Bureau of Mines flotation research program has been an investigation into the fundamental nature of electrochemical reactions in sulfide mineral-reagent systems and the control of these reactions for selective flotation of sulfides. This report details the results of an investigation designed to use mineral particle beds as electrodes for electrochemical preconditioning in a cell capable of handling mineral samples several hundred grams in size.

Specific objectives of this work were to (1) determine whether mineral beds of this size capacity exhibit adsorption-flotation behavior similar to that observed with smaller beds, (2) investigate the potential distribution across the mineral bed and the factors that control the potential distribution, and (3) determine the feasibility of using electrochemical potential to achieve separation of mixtures of sulfide minerals by flotation.

The mineral system selected for this investigation was chalcocite-pyrite. The electrochemical potential dependence of xanthate interaction with chalcocite has been observed in flotation rate experiments (2)⁴ and in adsorption-flotation experiments (3). Working with a small (1.4 g) packed bed of the mineral as an electrode, the flotation of chalcocite was shown to parallel closely the adsorption of ethylxanthate (EX) on the bed. The reactions over the electrochemical potential range of flotation were suggested to be an exchange reaction and a charge transfer oxidation reaction. Electrochemical investigations (4) have indicated adsorption of EX occurs via a chemisorbed layer and by copper-EX formation at higher potentials. Chalcocite can be expected to adsorb EX by a charge transfer reaction and by ion exchange with oxidized surface species. An EXinjection method at controlled potentials (5) indicated the existence of a rapid nonelectrochemical reaction component in the absence of oxygen.

The accepted mechanism by which EX induces pyrite flotation is the formation of dixanthogen. This conclusion has been reached via electrochemical investigations (6-8),

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⁴Italic numbers in the parentheses refer to items in the list of references at the end of this report.

kinetic and thermochemistry experiments (9), and a combination of flotation, infrared spectroscopic, and electrokinetic data (10). The difference in the flotation response of chalcocite and pyrite as a function of potential is ideal for examining flotation separation of a mixed bed using electrochemical potential as a control. The interaction of xanthates with chalcocite and pyrite occurs by different mechanisms, resulting in the production of hydrophobic surfaces at different potential values.

EXPERIMENTAL MATERIALS AND METHODS

Samples of chalcocite from Transvaal, Republic of South Africa, and pyrite from Rico, CO, were obtained through Wards National Science Establishment, Inc.,⁵ Rochester, NY. Chalcocite was ground using ceramic plates in a Bico pulverizer (Bico Inc., Burbank, CA). Steel plates were used for grinding pyrite. The quantity of mineral for each bed ranged from 230 to 260 g. The particle size fraction, 300 to 425 μ m, was obtained by dry sieving.

The electrolyte was 0.05-mol/L reagent grade sodium tetraborate, which provided a buffered solution of pH 9.2. The EX used as a collector was twice purified by dissolution in acetone and recrystallization with petroleum ether.

A schematic of the plexiglass electrochemical flotation cell is shown in figure 1. A Masterflex centrifugal pump $(H)^{6}$ was used to circulate electrolyte continuously through the cell at a flow rate of 0.015 cm³/s. A separate pump was used to circulate the solution through a 1-cm flowthrough cell of a Hewlett-Packard 8451A diode array spectrophotometer and a Rexnord dissolved-oxygen meter.

Immediately prior to addition to the flotation cell, the minerals were washed several times, first with deionized water, followed by 0.05-mol/L sodium tetraborate. Equal weights of each mineral were used for the two-component beds, and each mineral was ground and washed separately and then either mixed immediately before addition or added in alternate layers.

A P.A.R. model 371 potentiostat, together with an EG&G model 17 universal programer, was used to control the potential of the particle bed by means of a threeelectrode system. An outer cylinder of platinum screen encircling the bed was used as the current feeder (F), while a platinized⁷ platinum screen, within a fine porosity fritted tube (B), acted as the counter electrode (A). The reference was a movable Ag:AgCl microelectrode (G) inserted through a hole in the cell wall. Solution potential measurements were made with another movable Ag:AgCl microelectrode (K). A chalcocite electrode (not shown) was constructed by attaching a conducting wire to a single particle of chalcocite with conductive epoxy resin. The wire was sealed into a fine glass tube with Torr Seal epoxy, so that only the particle and the Torr Seal epoxy were exposed to the solution. All electrodes could be moved to various positions in the bed between the current feeder and counter electrode, though the chalcocite particle electrode positions were limited by their size.

All solution and particle potential measurements were referenced to the current feeder and thus represent the potential drop between their location and the outer circumference of the working electrode bed. Measurements were made with a Keithley 616 digital electrometer. All electrochemical potentials are reported with respect to the saturated calomel electrode (SCE). Dissolved oxygen (DO) concentrations were controlled by varying flow rates of N₂ and N₂-10 pct O₂ gas purges.

The flotation of mineral particle beds with EX concentrations of approximately 5×10^{-5} mol/L was examined under electrochemical potential control at the low DO concentration (N₂ purge). The collector was added at -0.6 V (SCE). The mineral bed was conditioned for 10 min followed by a 10-min flotation test. The floated mineral was returned to the original bed position, and the electrochemical potential was adjusted, generally in 0.1-V intervals, for the next conditioning stage.

Continuous spectroscopic monitoring of the solution during the conditioning period allowed the concentration of EX in the solution phase to be correlated with flotation results. Flotation tests were performed in the same cell by introducing nitrogen gas bubbles through glass tubes with fritted disks (I) located in the distributor plate (J). Rising bubbles were deflected (L) toward the outer wall near the top of the cell. A particle weir (D) trapped floated particles at the top of the cell and could be raised (C) to return the particles to the electrode bed. When a single mineral was being tested, the flotation recovery was measured by the height of the bed of unfloated mineral remaining in the bottom of the cell, whereas with mixed beds, the floated particles of each test were removed from the upper portion of the cell by suction through two ports in the cell top. The supernatant solution removed with the particles was returned to the cell. Products were assayed either by hand separation of individual particles followed by weighing or by chemical analysis.

RESULTS AND DISCUSSION

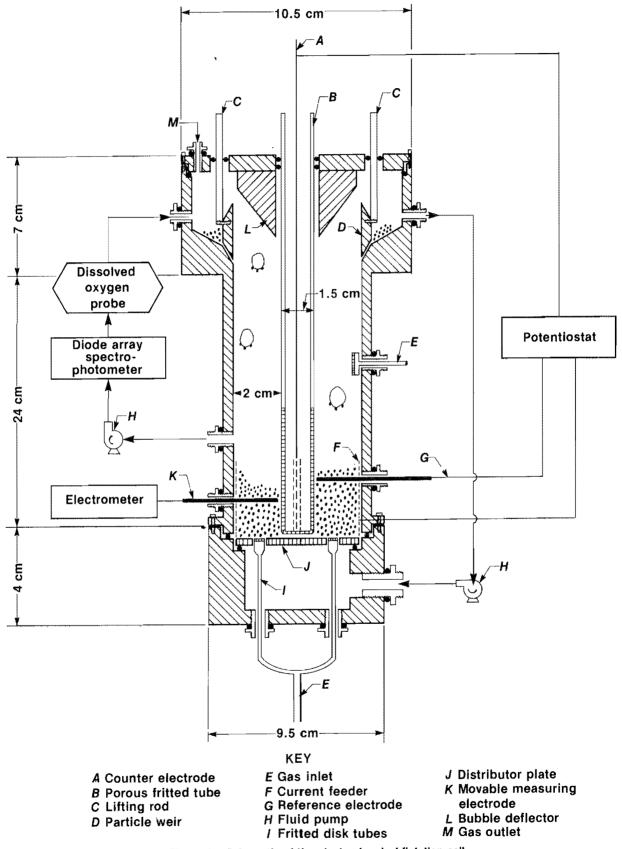
POTENTIAL DISTRIBUTION IN THE BED ELECTRODE

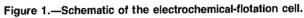
Models describing the electric potential in the continuous and dispersed phases of bed electrodes have been developed for porous, packed-bed electrodes (11) and for fluidized-bed electrodes (12-13). These models were developed with the objective of giving an understanding of the reaction processes within bed electrodes. The reaction processes can be influenced by the physical shape of the bed electrode and by the conductivity of the continuous and dispersed phases and are observed in the characteristic polarization curve for the reaction. The potential distribution within a cylindrical mineral bed electrode under external electrochemical potential control is examined in the present work.

 $^{^{6}\!\}mathrm{Reference}$ to specific products does not imply endorsement by the Bureau of Mines.

[&]quot;Italic letters refer to components identified in figure 1.

⁹A platinized electrode is one on which platinum has been electrodeposited from a solution of chloroplatinic acid to increase the total surface area.





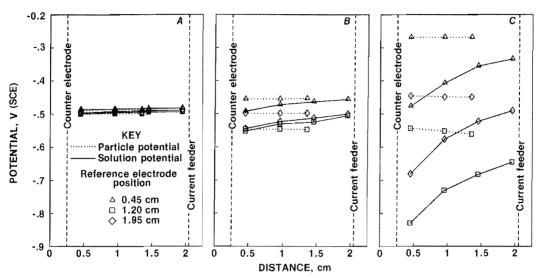


Figure 2.—Particle and solution potential distribution within a chalcocite bed electrode at -0.5 V (SCE) at dissolved oxygen concentrations (A) 0.12 to 0.19 ppm, (B) 0.9 to 1.05 ppm, and (C) 1.6 to 2.0 ppm. The dashed lines indicate the positions of the counter electrode and current feeder in the electrochemical-flotation cell.

The techniques used to measure the potential within the dispersed (particle) and continuous (solution) phases employed two measuring electrodes that could be moved to various positions in the bed, in addition to the reference electrode that was set at one of three fixed positions. The potential profiles for the dispersed and continuous phases, shown in figure 2, were measured with a single particle electrode and a Ag:AgCl microelectrode, respectively. Three oxygen concentrations were used at the reference potential of -0.5 V (SCE).

At the lowest oxygen level of 0.12 to 0.19 ppm (fig.2A), both particle and solution phase potentials were independent of position and exhibited very small deviations, 1 to 2 mV, from the reference potential. At oxygen concentrations, of 0.9 to 1.05 ppm (fig. 2B), deviations from the reference potential value were 35 to 45 mV for the solution potential. In general, the value of the particle electrode potential was independent of position and assumed a value similar to the solution potential at the current feeder. High oxygen concentration, 1.6 to 2.0 ppm (fig. 2C), resulted in a potential and a 1- to 18-mV change in the particle potential.

As would be expected, the value of the solution potential was nearly identical to that of the reference potential setpoint when both electrodes were at the same radial location. With changes in the reference electrode position, the shape of the potential profiles remained the same, but the curves were displaced. For example, when the reference electrode was at the current feeder position, the solution potential was close to the reference potential, with values of the solution potential at other positions being more negative.

In the present study, the potential drop across the cell occurs primarily in the solution or continuous phase; whereas the potential of the dispersed phase is nearly constant and is fixed by the oxygen level. The difference in the potential of the dispersed and continuous phases partially determines the electrochemical reaction rate, which has been expressed in terms of the concentrations of the components and the local potential difference between the particle and solution phases (11,13). The experimentally determined potential profiles indicate the importance of the effect of oxygen concentration. When using potential control as a preconditioning step for flotation, it is desirable to control the potential in a uniform manner. The presence of oxygen does not allow uniform external control of the electrochemical potential within the bed but rather gives rise to finite potential profiles in the dispersed and continuous phases.

EX ADSORPTION-FLOTATION OF SINGLE-MINERAL PARTICLE BEDS

Chalcocite-EX

EX shows two absorption peaks in the ultraviolet (UV) wavelength region. Maximum absorbance occurs at 301 nm with a molar absorptivity value of 17,750 L/(mol•cm) (14), and a smaller peak is observed at 227 nm. The 301-nm absorbance value was used to calculate the EX adsorption density at each electrode potential. The flotation behavior of chalcocite is shown in figure 3 along with the amount of EX adsorbed at each potential value. Based on surface area measurements of various size fractions of chalcocite particles, a specific surface area of $110 \text{ cm}^2/\text{g}$ was used as an estimate of the total available surface area. The dashed line in figure 3 indicates the amount of EX estimated to be required for monolayer coverage of the minerals. The average area occupied by one EX ion was taken as 0.25 nm². Flotation occurs at potentials >-0.5 V and reaches 100 pct at -0.3 V. A good correlation is observed between EX adsorption on Cu₂S and the flotation recovery of Cu₂S. Previous Bureau research (3) gave similar results for a 1.4-g chalcocite mineral bed floated by EX at controlled electrochemical potential.

Pyrite-EX

Spectra of an EX solution contacted with a pyrite bed under electrochemical potential control between -0.6 to 0.2V are shown in figure 4. The correlation between EX ad-

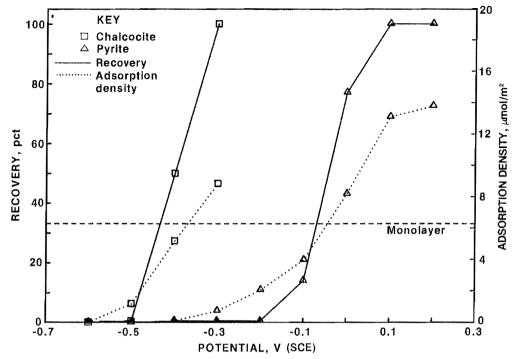


Figure 3.—Flotation recovery and EX adsorption as a function of potential for single-component chalcocite and pyrite beds at pH 9.2.

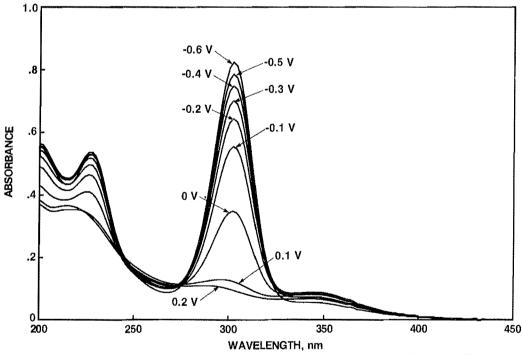


Figure 4.--Spectra of EX solution at pH 9.2 in contact with a pyrite bed at -0.6 to 0.2 V (SCE).

sorption and flotation recovery as a function of electrochemical potential is shown for pyrite in figure 3. As in the Cu₂S-EX system, there is a good correlation between EX adsorption and flotation recovery. Pyrite begins to float at potentials of approximately -0.1 V. Formation of perxanthate between -0.6 and -0.1 V is responsible for part of the EX concentration decrease. Using a value of

1

5,660 L/(mol·cm) (14) for the molar absorptivity of perxanthate at 348 nm, the amount of EX consumed by the formation of perxanthate at each 0.1-V interval has been deducted to determine the adsorption density for EX on FeS₂, shown in figure 3. The formation of dixanthogen on pyrite has been interpreted (8, 10) to be the mechanism leading to a hydrophobic surface. Xanthate oxidizes to form

or,

dixanthogen above the reversible potential of approximately -0.11 V (15). The flotation results are in good agreement with the potential for dixanthogen formation.

EX ADSORPTION-FLOTATION OF MIXED MINERAL (CHALCOCITE-PYRITE) BEDS

Electrochemical potential as a control to achieve separation of sulfide minerals was investigated using mixed beds of equal weights of chalcocite and pyrite. Three methods were used to introduce the mixed-mineral bed to the cell: (1) the two minerals were mixed together immediately prior to addition to the cell and held at the open circuit potential (-0.04 V) for 10 min before stepping the potential to -0.6V, (2) the potential of the cell was set to -0.6 V and the minerals were added separately in alternating layers of equal weight, and (3) the potential of the cell was set to -0.5V, and the minerals were added separately in alternating layers of equal weight. In cases 1 and 2, EX was added at -0.6 V and flotation was performed after a 10-min conditioning period. Subsequent flotation experiments were done at 0.1-V intervals after 10-min conditioning at each potential. In case 3, EX was added at -0.5 V, and the potential was stepped to -0.3 V for the first flotation test with collection of the fractions floated at -0.3 V and at subsequent 0.1-V intervals after conditioning at each potential. The flotation recoveries of the mineral components from the mixture are shown in figure 5 for the three cases. Flotation recoveries for the single-component mineral beds are also shown.

An important feature of figure 5 lies in the observation that the flotation behavior of Cu₂S and FeS₂ from the mixture does not follow the flotation behavior of the individual mineral beds. That is, the presence of another sulfide mineral alters the flotation behavior with EX. This effect is more pronounced for FeS_2 than for Cu_2S . The flotation of FeS₂ is activated at potentials between -0.4 to -0.1 V, where no flotation in the single-component bed was observed, and depressed above -0.1 V, where flotation recovery reached 100 pct in the single-component bed. The flotation of Cu₂S from the mineral mixture occurred in a similar potential range but was depressed to various degrees as compared to Cu₂S flotation in a single-component bed.

The apparent activation of pyrite and depression of chalcocite in a mixture can be partially explained by consideration of the electrochemical reactions that occur prior to addition of the collector. Voltammograms for massive Cu_sS electrodes and small bed electrodes have been reported to be nearly identical (16). Only small currents were observed between the limits of -0.5 and -0.1 V. However, an oxidation wave appeared at potentials greater than -0.1V that can be described by the reaction

$$Cu_2S=2Cu^{+2}+S^0+4e^-,$$
 (1)

or by consecutive reactions,

$$Cu_2S = Cu^{+2} + CuS + 2e^{-},$$
 (2)

and

$$CuS = Cu^{+2} + S^{0} + 2e^{-}.$$
 (3)

Below -0.55 V, there is a cathodic current and the reduction reaction is believed to be

$$Cu_2S+H_2O+2e^-=2Cu^0+HS^-+OH^-,$$
 (4)

or the following, if the surface contains CuS:

$$CuS+H_2O+2e^-=Cu^0+HS^-+OH^-,$$
 (5)

and

$$2CuS+H_2O+2e^-=Cu_2S+HS^-+OH^-.$$
 (6)

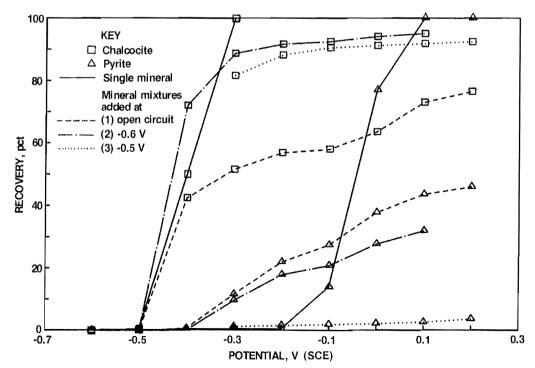


Figure 5.-Flotation recovery of chalcocite and pyrite at pH 9.2 as a function of potential for single- and mixed-mineral beds.

A soluble species with an absorbance band at 229 nm was observed in the reduction region below -0.55 V, supporting the reactions producing HS⁻.

Pyrite flotation from the mixed bed was activated at potentials between -0.4 to -0.1 V, but the overall pyrite recovery was lower than the pyrite recovery in the single component flotation. Chalcocite undergoes anodic oxidation with the production of soluble copper ions at open circuit (reactions 1-3). Copper ion has been shown to activate pyrite (17) and is believed to be responsible for the pyrite flotation at low potentials observed here, that is, <-0.1 V. The depression of pyrite in the mixture at potentials >-0.1 V suggests that the pyrite particles have become hydrophilic through a surface reaction involving galvanic coupling with chalcocite. If the presence of pyrite increases the oxidation rate of chalcocite, it is possible that the copper species hydrolyze and are responsible for the observed hydrophilic surface on pyrite particles. The depression of chalcocite by pyrite in case 1 may also be due to oxidized surface species that result from the increased oxidation rate of chalcocite in contact with pyrite.

When the mineral bed is kept at reducing potentials (cases 2 and 3), chalcocite flotation is similar to the singlemineral chalcocite flotation. Pyrite was activated for flotation in case 2 when the bed was held at -0.6 V and was totally depressed in case 3 over the investigated potential range of -0.3 to 0.2 V. By not permitting the two mineral components the opportunity for galvanic coupling at the open circuit potential, the opportunity for excessive surface oxidation of chalcocite is reduced and consequently, the flotation of chalcocite from the mixture resembles singlemineral flotation behavior.

The production of HS⁻ by reactions 4 through 6 at the preset potential -0.6 V (case 2) is believed to be responsible for the observed flotation of pyrite at potentials < -0.1V, where pyrite by itself would not be expected to float with EX. Bubble contact angles on a pyrite electrode and flotation recovery of a pyrite particle bed have been observed to increase with HS⁻ addition in a similar potential range (18). The hydrophobic species is believed to be sulfur produced by the oxidation of HS⁻. When the preset potential is -0.5 V (case 3) where the cathodic reduction of chalcocite does not release HS⁻, pyrite did not float from the mixture. In both case 2 and 3, pyrite flotation from the mixture is depressed at potentials >-0.1 V where pyrite exhibited good flotation in the single-mineral bed. This depression of pyrite can be attributed to the presence of surface hydroxy species. In case 3, pyrite depression is very pronounced, and the nonflotation behavior is very similar to an aged (strongly oxidized) pyrite bed.

EX is removed from solution either through adsorption or oxidation of EX to dixanthogen without resulting in flotation. One proposed explanation (19) for this behavior is that a xanthate collector can react with an oxidized mineral and produce irregular multilayer patches. These patches may detach from the particle when the strength of the xanthatemetal ion bond exceeds that of the surface bonds.

SINGLE MINERAL FLOTATION IN THE PRESENCE OF DISSOLVED IONS

The EX flotation results for mixed-mineral beds indicated that contact between chalcocite and pyrite had interrelated effects on the flotation. To investigate the role of dissolved ions from one mineral on the flotation behavior of the other mineral, flotation of single-component beds was performed in the presence of dissolution products of the other component.

Chalcocite Flotation-Pyrite Dissolution Products

The electrolyte solution of the electrochemical-flotation cell was contacted with an external pyrite bed that underwent dissolution at open circuit for 120 min. A special cell compartment housing the pyrite bed was used so that the bed could be excluded from the circuit after the dissolution period. Supernatant samples were periodically removed and immediately acidified. The soluble copper and iron concentrations were determined analytically by atomic absorption (AA) spectroscopy. The maximum soluble iron measured was 0.4 ppm; no copper was detected. At pH 9.2, surface oxide layers of $Fe(OH)_3$ form on pyrite electrodes under oxidizing conditions (20). The detected soluble iron probably occurs from surface hydroxides released to solution.

A chalcocite mineral bed was introduced into the cell and held at its open circuit potential for 10 min before the potential was stepped to -0.6 V. Upon addition of the chalcocite bed and adjustment of the potential to -0.6 V, the iron concentration decreased to 0.1 ppm. The adsorption behavior of EX on the chalcocite bed was not noticeably affected by the presence of the pyrite dissolution products. Flotation results for the single mineral also did not seem to be affected, although the percent recovered at -0.4 V (fig.6) was lower for the chalcocite bed in the presence of pyrite dissolution products. Complete flotation of the chalcocite bed was achieved at -0.3 V in the absence and in the presence of the pyrite dissolution products.

Pyrite Flotation-Chalcocite Dissolution Products

Electrolyte containing chalcocite dissolution products was obtained from a chalcocite bed after open circuit dissolution for 75 min, after which the chalcocite mineral was excluded from the circuit. A freshly ground pyrite bed was introduced into the cell and held at its open circuit potential for 10 min before the potential was stepped to -0.6 V. The dissolution products were monitored spectroscopically and sampled periodically for analytical determination of the soluble copper and iron concentrations by AA spectroscopy. Chalcocite at open circuit potential in borate solution releases Cu(II) ions to solution (16). The UV spectra indicating the copper absorption bands at 216 and 294 nm are shown in figure 7. The soluble iron concentration, 0.1 to 0.3 ppm, did not affect the flotation behavior.

The initial copper concentration of 7.2 ppm decreased to 4.5 ppm when the pyrite bed was added to the solution. The copper concentration decreased further to 1.2 ppm when the potential was stepped to -0.6 V. This decrease in solution copper suggests that copper was removed by adsorption or reduction (or a combination) on the pyrite particle bed, although the form of the surface species is not known.

The spectra of EX in contact with the pyrite bed in the presence of Cu_2S dissolution products are shown in figure 8. A comparison of figures 4 and 8 indicated that the presence of the Cu_2S dissolution products affected the EX adsorption on pyrite as the potential was stepped in 0.1-V intervals. The percent decrease in EX solution concentration, using the 301-nm absorbance value, at the end of 10-min conditioning periods at potentials ranging from -0.6

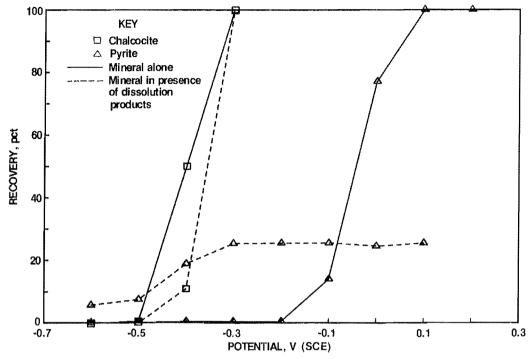


Figure 6.—Flotation recovery of chalcocite and pyrite at pH 9.2 as a function of potential for singlemineral beds alone and in the presence of dissolution products.

to 0.2 V for pyrite beds in the absence and in the presence of Cu_2S dissolution products is shown in table 1.

In the presence of Cu_2S dissolution products, a large decrease, 47 pct, in solution EX was observed in the 10-min conditioning period at -0.6 V, and subsequent potential steps between -0.5 and 0.1 V resulted in a constant

decrease in EX. When pyrite in the absence of chalcocite dissolution products was contacted with EX, a small decrease, approximately 25 pct, in solution EX occurred from -0.6 to -0.2 V. Above -0.1 V, the rate of EX decrease from solution increased dramatically.

As shown in figure 6, flotation recovery of pyrite by EX

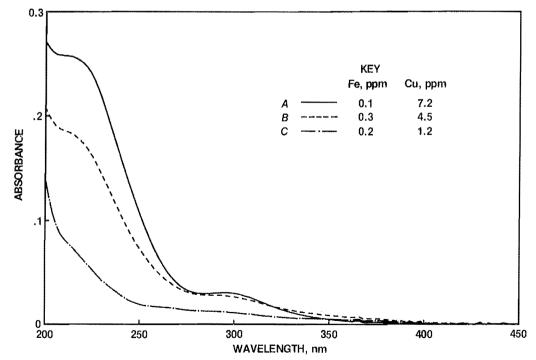


Figure 7.—Spectra of the dissolution products from a chalcocite bed after (A) a 75-min conditioning period at the open circuit potential of -0.04 V, (B) addition of a pyrite bed at open circuit, and (C) the potential of the pyrite bed was stepped to -0.6 V.

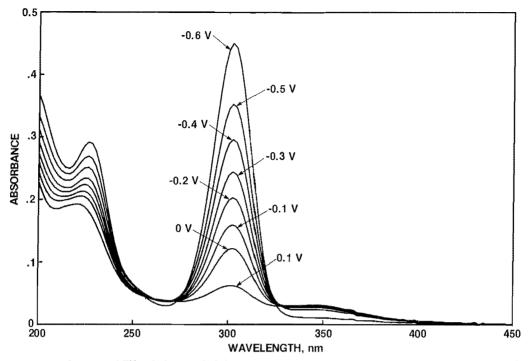


Figure 8.—Spectra of EX solution at pH 9.2 in contact with a pyrite bed in the presence of chalcocite dissolution products.

in the presence of Cu_2S dissolution products was quite different from that of the pyrite mineral alone. The flotation behavior in the presence of soluble copper products was similar to the pyrite recovery from the mixed bed experiments for case 1, bed added at open circuit, and case 2, bed added at -0.6 V. Pyrite flotation in the presence of the dissolution products was activated at potentials -0.6 to -0.2 V, where pyrite in the absence of Cu_2S dissolution products showed no flotation response. Above -0.1 V, the overall flotation recovery of pyrite was less than that expected for the mineral without exposure to Cu_2S dissolution products. The depressed flotation suggests the presence of a hydrophilic species, such as a surface oxide or hydroxide.

Table 1.—Decrease¹ in EX concentration in contact with pyrite beds in the absence and presence of chalcocite dissolution products, percent

Potential, V	Absence	Presence
-0.6	2.0	47
-0.5	6.6	58
-0.4	11	65
-0.3	19	71
-0.2	24	76
-0.1	34	81
0 ,	59	86
0.1	85	93
0.2	88	ND

ND Not determined.

¹After 10-min conditioning period.

SUMMARY

Mineral particle beds of cylindrical geometry were used as working electrodes in a cell designed for electrochemical conditioning and flotation. The potential distribution across a 200- to 300-g mineral particle bed electrode was found to be determined largely by the amount of dissolved oxygen (DO) in the system. Oxygen is reduced at the mineral bed electrode. Low DO levels resulted in low current and uniform values of particle and solution potentials. Increasing DO concentration resulted in increased current flow and larger potential drops across the cell. Low DO levels were necessary to achieve a uniform electrochemical potential for subsequent control of flotation.

Simultaneous spectrophotometric monitoring of the solution phase was used to correlate adsorption of ethylx-

anthate with the electrochemical potential and flotation. Flotation of single-mineral particle beds of chalcocite and pyrite was strongly dependent on the electrochemical potential. The potential-recovery curves for the single minerals were similar to those observed with small scale (1.4 g) mineral beds (3).

Flotation separation of a chalcocite-pyrite mixture by electrochemical potential control was achieved. The potential-flotation recovery behavior for minerals from mixed-mineral beds was different from that observed for single-component beds. The differences were attributed to galvanic interactions because of mineral-to-mineral contact. Cu(II) produced by anodic dissolution of Cu_zS in mineral mixtures activates pyrite so that it floats below the reversible xanthate-dixanthogen potential. HS^- produced by cathodic dissolution of Cu_2S in a mixture can be subsequently oxidized to sulfur on pyrite, inducing flotation of pyrite at reducing potentials. Chalcocite dissolution products were found to have a deleterious effect on single-component pyrite flotation. In the

presence of chalcocite dissolution products, pyrite flotation was activated at potentials between -0.4 to -0.1 V and depressed at potentials above -0.1 V as compared to flotation in the absence of dissolution products. Pyrite dissolution products appeared to have no effect on chalcocite flotation.

REFERENCES

1. Woods, R. Electrochemistry of Sulphide Flotation. Paper in Principles of Mineral Flotation—Wark Symposium, Adelaide, July 1983. Australian Inst. Min. Metall., in press.

2. Heyes, G.W., and W.J. Trahar. Oxidation-Reduction Effects in the Flotation of Chalcocite and Cuprite. Int. J. Miner. Process., v. 6, 1979, 229-252.

3. Richardson, P.E., J.V. Stout III, C.L. Proctor, and G.W. Walker. Electrochemical Flotation of Sulfides: Chalcocite-Ethylxanthate Interactions. Int. J. Miner. Process., v. 12, 1984, pp. 73-93.

4. Kowal, A., and A. Pomianowski. Cyclic Voltammetry of Ethyl Xanthate on a Natural Copper Sulfide Electrode. J. Electroanal. Chem., v. 46, 1973, pp. 411-420.

5. O'Dell, C.S., R.K. Dooley, G.W. Walker, and P.E. Richardson. Chemical and Electrochemical Reactions in the Chalcocite-Xanthate System. Paper in Proceedings of the International Symposium on Electrochemistry in Mineral and Metal Processing, ed. by P.E. Richardson, S. Srinivasan, and R. Woods (165th meeting sponsored by Electrochem. Soc., Cincinnati, OH, May 6-11, 1984). Electrochem. Soc., Inc., Pennington, NJ, v. 84-10, 1984, pp. 81-95.

6. Woods, R. Electrochemistry of Sulfide Flotation. Ch. in Flotation: A.M. Gaudin Memorial Volume, ed. by M.C. Fuerstenau. AIME, 1976, pp. 298-333.

7. Usul, A.H., and R. Tolun. Electrochemical Study of the Pyrite-Oxygen-Xanthate System. Int. J. Miner. Process., v. 1, 1974, pp. 135-140.

8. Majima, H., and M. Takeda. Electrochemical Studies of the Xanthate-Dixanthogen System on Pyrite. Trans. Soc. Min. Eng. AIME, v. 241, 1968, pp. 431-436.

9. Huang, H.H., and J.D. Miller. Kinetics and Thermochemistry of Amyl Xanthate Adsorption by Pyrite and Marcasite. Int. J. Miner. Process., v. 5, 1978, pp. 241-266.

 Fuerstenau, M.C., M.C. Kuhn, and D.A. Eligillani. The Role of Dixanthogen in Xanthate Flotation of Pyrite. Trans. Soc. Min. Eng. AIME, v. 241, 1968, pp. 148-156.
 Newman, J.S., and C.W. Tobias. Theoretical Analysis of Cur-

11. Newman, J.S., and C.W. Tobias. Theoretical Analysis of Current Distribution in Porous Electrodes. J. Electrochem. Soc., v. 109, 1962, pp. 1183-1191. 12. Goodridge, F., D.I. Holden, H.D. Murray, and R.F. Plimley. Fluidized Bed Electrodes. Part I. A Mathematical Model of the Fluidized Bed Electrode. Trans. Inst. Chem. Eng., v. 49, 1971, pp. 128-136.

13. Sabacky, B.J., and J.W. Evans. Electrodeposition of Metals in Fluidized Bed Electrodes. Part I. Mathematical Model. J. Electrochem. Soc., v. 126, No. 7, 1979, pp. 1176-1180.

14. Pomianowski, A., and J. Leja. Spectrophotometric Study of Xanthate and Dixanthogen Solutions. Can. J. Chem., v. 41, 1963, pp. 2219-2230.

15. Allison, S.A., L.A. Goold, M.J. Nichol, and A.A. Granville. Determination of the Products of Reaction Between Various Sulfide Minerals and Aqueous Xanthate Solution, and a Correlation of the Products With Electrode Rest Potentials. Metall. Trans., v. 3, 1972, pp. 2613-2618.

16. Walker, G.W., J.V. Stout III, and P.E. Richardson. Electrochemical Flotation of Sulfides: Reactions of Chalcocite in Aqueous Solution. Int. J. Miner. Process., v. 12, 1984, pp. 55-72.

17. Nichol, M.J. An Electrochemical Study of the Interaction of Copper (II) Ions With Sulfide Minerals. Paper in Proceedings of the International Symposium on Electrochemistry in Mineral and Metal Processing, ed. by P.E. Richardson, S. Srinivasan, and R. Woods (165th meeting sponsored by Electrochem. Soc., Cincinnati, OH, May 6-11, 1984). Electrochem. Soc., Inc., Pennington, NJ, v. 84-10, 1984, pp. 152-168.

18. Walker, G.W., C.P. Walters, and P.E. Richardson. Correlation of the Electrosorption of Sulfur and Thiol Collectors With Contact Angle and Flotation. Paper in Proceedings of the International Symposium on Electrochemistry in Mineral and Metal Processing, ed. by P.E. Richardson, S. Srinivasan, and R. Woods (165th meeting sponsored by Electrochem. Soc., Cincinnati, OH, May 6-11, 1984). Electrochem. Soc., Inc., Pennington, NJ, v. 84-10, 1984, pp. 202-218.

19. Leja, J. Surface Chemistry of Froth Flotation. Plenum, 1982, pp. 514-517.

20. Janetski, N.D., S.I. Woodburn, and R. Woods. An Electrochemical Investigation of Pyrite Flotation and Depression. Int. J. Miner. Process., v. 4, 1977, pp. 227-239.