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SULFIDIZATION AND FLOTATION OF CHRYSOCOLLA AND BROCHANTITE

THE UNIVERISTY OF ARIZONA

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SULFIDIZATION AND FLOTATION OF
CHRYSOCOLLA AND BROCHANTITE

by

Ling Lee

A Thesis Submitted to the Faculty of the
DEPARTMENT OF METALLURGICAL ENGINEERING
In Partial Fulfillment of the Requirements
for the Degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

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ACKNOWLEDGMENTS

I would like to express my deep appreciation to my advisor, Dr. S. Raghavan, for his guidance and support to make this work possible.

The financial support for this project from Phelps Dodge, Morenci, Arizona is deeply appreciated. I extend my gratitude to all those who helped me, in one way or another, to complete this work.

Finally, special thanks are extended to my parents and wife for their encouragement during my academic years.

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ABSTRACT

An investigation of the physical chemistry of interaction of oxide copper minerals, chrysocolla and brochantite, with aqueous ammonium sulfide solutions has been carried out. The experimental variables are solution pH, degree of agitation, conditioning time, and sulfide ion concentration. Attempts have been made to assess the change in the surface characteristics of the minerals using gas adsorption (surface area), X-ray diffraction, and microelectrophoresis techniques. The results obtained indicate that sulfide ions interact more intensely and rapidly with oxide copper mineral at acidic pH values than at basic pH values. Sulfidization affects the surface charge characteristics of brochantite more than it does chrysocolla. The porous nature of chrysocolla is hardly reduced by sulfidization. Sulfidization followed by flotation is an effective way to recover brochantite, irrespective of either sulfidization or flotation pH. Chrysocolla responds poorly to flotation even after sulfidization. Conditioning at acidic pH values makes chrysocolla more amenable to flotation.

I. INTRODUCTION

Copper sulfide minerals,¹ chalcopyrite (CuFeS_2) and chalcocite (Cu_2S), serve as the main source of raw materials for the production of copper in the world. These sulfides frequently occur along with oxide copper minerals in many ore bodies. It is not unusual to find 10-20 wt% of the total copper in many ores as oxides. While the sulfide minerals are easily concentrated by froth flotation, the oxide minerals respond rather poorly to flotation.

The major copper oxide minerals are azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), brochantite ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$), chrysocolla ($\text{CuOSiO}_2 \cdot 2\text{H}_2\text{O}$), and malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$).¹ Industrially, leaching is the most commonly used method for treating copper oxide minerals, but in some areas of the world they are first concentrated by flotation before being leached.² Today two methods have been commercially successful for floating copper oxide ores. In one, carboxylic acids are used as collectors; and in the other, a preliminary sulfidizing treatment of the copper oxide minerals is necessary before floating with sulphydryl collectors such as amyl xanthate. The main trouble with the carboxylic acid process is its lack of selectivity. It can be used only when the gangue is non-calcarous. The sulfidization process is now the most currently used method to float copper oxide ores. It offers the advantage of ensuring a more selective flotation; and its use ought not to be limited to non-calcarous ores. However, the copper oxide ores flotation has been intentionally limited to the case of malachite ores, for which two flotation processes are

already currently used on an industrial scale, with some success. In Arizona, the Phelps Dodge Mine at Morenci uses $(\text{NH}_4)_2\text{S}$ at acid pH values (5.5~6) to effect sulfidization.

The available literature on sulfidization indicates that malachite responds much better than chrysocolla to the sulfidization treatment. Basic knowledge of what the sulfidization treatment really does is very limited. It was the primary objective of this research to investigate the physical chemistry of the interaction of sulfide/hydrosulfide ions with chrysocolla and brochantite was also investigated with a view to assess the beneficial effects of sulfidization prior to flotation.

II. BACKGROUND AND LITERATURE REVIEW

Brochantite is a basic copper sulfate and has the chemical formula $\text{Cu}_4\text{SO}_4(\text{OH})_6$. It is green in color and has a density of 3.9.¹ Pure chrysocolla is turquoise blue in color and has the chemical formula $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$. Until the late 1960s, chrysocolla was considered to be a mixture of a crystalline copper silicate phase dispersed in an amorphous silica hydrogel, with a composition that can be expressed in terms of CuO , SiO_2 and H_2O .³ Van Oosterwyck-Gastuche⁴ revealed that chrysocolla is a definite mineral having an orthorhombic unit cell and a characteristic fibrous structure.

The literature contains a few reported investigations on the interaction of sulfide ions with copper oxide minerals. Wright and Prosser⁵ conducted investigations to compare chrysocolla and malachite in terms of their affinity for NaHS and found malachite to react much more rapidly than chrysocolla. In both cases almost half of the total adsorption (or interaction) was complete within ten minutes.

Castro et al.⁶ obtained experimental evidence to show that the interaction between soluble sulfide and oxidized copper minerals is not a simple adsorption process. In their opinion two main reactions take place: the formation of copper sulfide and the oxidation of sulfide ions to thiosulfate ions.

The kinetics of hydrosulfide ion uptake has been studied in some detail by Castro et al.⁷ By using a colorimetric technique, they found the uptake of hydrosulfide ions to reach completion in a matter of

minutes; on the contrary, an iodometric technique indicated the uptake to continue beyond 60 minutes. They have attributed the discrepancy between the results obtained by the two techniques to the difference in selectivity of the two techniques to sulfide ions. Queirolo and Castro⁸ are of the opinion that the reluctance of some chrysocolla samples from Chile to become activated in the presence of sodium sulfide is due to the low density of copper sites at the surface of the mineral. They contend that thermal activation (heating) should increase the surface copper site density, thereby increasing the response of chrysocolla to activation. Raghavan and Fuerstenau³ found that heat treatment of chrysocolla considerably reduced its microporous nature. Reduction in the microporous nature of chrysocolla may considerably decrease the formation of metal-reagent precipitates inside the pores, thereby increasing the effectiveness of the sulfidization process.

Jones and Woodcock⁹ used a sulfide ion selective electrode to control and optimize sulfidization of oxidized copper ores in the pH range 10-11. The optimum potential for sulfidization was found to be about -500 mV versus saturated calomel electrode (SCE). Simultaneous sulfidization and flotation were efficient when conducted at a (sulfide ion electrode) potential of -450 mV versus SCE.

The flotation of copper oxide minerals after sulfidization has been investigated by several researchers. Castro et al.⁶ found that chrysocolla floated well when excess sulfide ions used in sulfidization were removed after sulfidization. Gonzalez et al.¹⁰ found that without sulfidization fresh chrysocolla floated better than the aged chrysocolla.

Sota¹¹ found that calcium ions are detrimental to the flotation of sulfidized chrysocolla.

In flotation, the point of zero charge (PZC) plays an important role. There are conflicting results in the literature as to the PZC of chrysocolla. Reported PZCs for chrysocolla are pH 6.5 by titration,¹² pH 2.2 by electrokinetics,¹³ plus two different studies,^{14,15} in which chrysocolla particles were observed to be negatively charged in the pH range of 3-11, with no apparent evidence for a PZC. The PZC of brochantite is not available in the literature.

III. EXPERIMENTAL MATERIALS AND METHODS

Experimental Materials

Samples of chrysocolla and brochantite were handpicked from the Morenci area in Arizona. The samples were crushed, ground and sieved into different (Tyler) size fractions. These size fractions were assayed for Cu and SiO₂ content at the University of Arizona Analytical Center and the results are shown in Table 1.

The ammonium sulfide solutions were obtained from Kerley Chemical Corporation, Sahuarita, Arizona. Reagent grade HCl and NH₄OH were used for pH adjustments. In flotation, amyl and ethyl xanthate were used as the collectors and MIBC was used as the frother.

Experimental Methods

The interaction experiments were carried out in a three-neck, round-bottom flask. For all the experimental investigations, 2 gm of solid and 500 cc of sulfide solution were used. During the experiment purified nitrogen was bubbled through the solution to prevent oxidation of ammonium sulfide. The solid was kept suspended in the solution by using a glass stirrer attached to a stirrer motor and controller. For a majority of the experiments, a speed of 1450 rpm was used.

The sulfide ion concentration in solution was measured with an Orion Model 94-16 Sulfide ion electrode using the method suggested in the Orion manual. This involved raising the pH to convert any HS⁻ and H₂S(aq) to the S⁼ form before measurement. A saturated calomel electrode was used as the reference electrode. The redox potential of the system

TABLE 1

Chemical Analysis of Chrysocolla and Brochantite Samples

<u>Sample</u>	<u>Mesh Size</u>	<u>% SiO₂</u>	<u>% Cu</u>
Brochantite	35 x 48	7.9	54
"	48 x 65	6.6	47
"	100 x 150	9.6	49
"	150 x 200	12.0	42
"	-200	6.9	43
	Theoretical	0	56.2
Chrysocolla	35 x 48	28.0	29
"	48 x 65	28.0	32
"	-200	24.0	31
	Theoretical	34.2	36.2

was measured by using an Orion Model 96-78 platinum combination redox electrode. The redox electrode was calibrated using solutions containing potassium ferrocyanide and potassium ferricyanide. Some attempts were made to measure the dissolved oxygen in solution using a YSI Model 54ARC oxygen meter; however, the technique was rather unsuccessful.

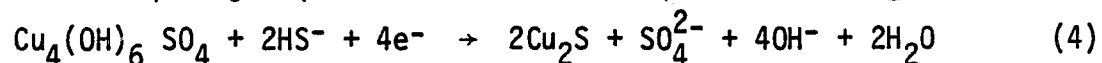
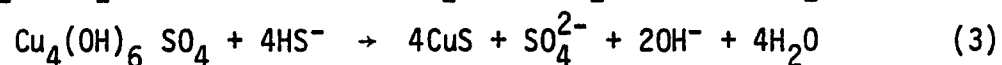
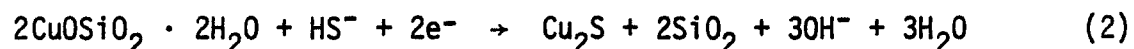
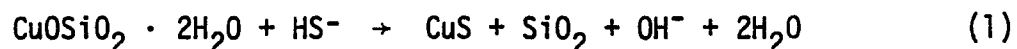
The surface area measurements were carried out using Micromeretics' Model 2100D Orr Surface-Area Pore-Volume Analyzer. Nitrogen gas was used as the adsorbate.

The flotation experiments were carried out in a 50-gm Denver cell at a pulp density of five percent. A conditioning time of 15 minutes was used for sulfidization. Conditioning with xanthate was effected for 10 minutes. Flotation was carried out for 2 minutes.

IV. RESULTS AND DISCUSSION

Eh-pH Diagrams for Sulfidization

In an attempt to understand the sulfidization of chrysocolla and brochantite, several Eh-pH diagrams were constructed. The thermodynamic data used in the construction of Eh-pH diagrams is tabulated in Table 2. The possible chemical reactions between copper oxide minerals and hydrosulfide ions are:



The Eh-pH diagrams for chrysocolla are presented in Figs. 1 and 2. Fig. 1 has been drawn for a silicic acid activity of 10^{-4} and a hydrosulfide activity of 10^{-22} . It is very clear from this figure that even at a very low hydrosulfide activity chrysocolla can be sulfidized to Cu_2S in the pH range 3.5 to 8. Increasing the hydrosulfide activity to 10^{-11} vastly expands the pH region over which chrysocolla can be sulfidized as is shown in Fig. 2. In fact, Fig. 2 shows that chrysocolla can be sulfidized to CuS as well as Cu_2S under proper conditions. Increasing the hydrosulfide activity above a value of 10^{-11} would cause the chrysocolla phase to disappear and only copper sulfide phases would be present in the entire Eh-pH range. Hence, with the sulfide concentrations used for sulfidization (10^{-4} - 10^{-2}M) one would expect to achieve complete sulfidization.

TABLE 2
Thermodynamic Data for Eh-pH Diagrams

Species	ΔG_f^0 , 298, kcal/mole
$\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$	-345.1*
CuS	- 11.7**
Cu_2S	- 20.6**
$\text{Cu}_4(\text{OH})_6\text{SO}_4$	-434.62**
$\text{H}_4\text{SiO}_4(\text{aq})$	-300.3**
$\text{HS}^-(\text{aq})$	- 6.5**
H_2O	- 56.7**

* Newberg, D.W., Econ. Geol., p. 950 (1967)

** Garrels, R.M., and Christ, C.L., Appendix 2, Solutions, Minerals and Equilibria, Freeman, Cooper and Company, San Francisco, (1965)

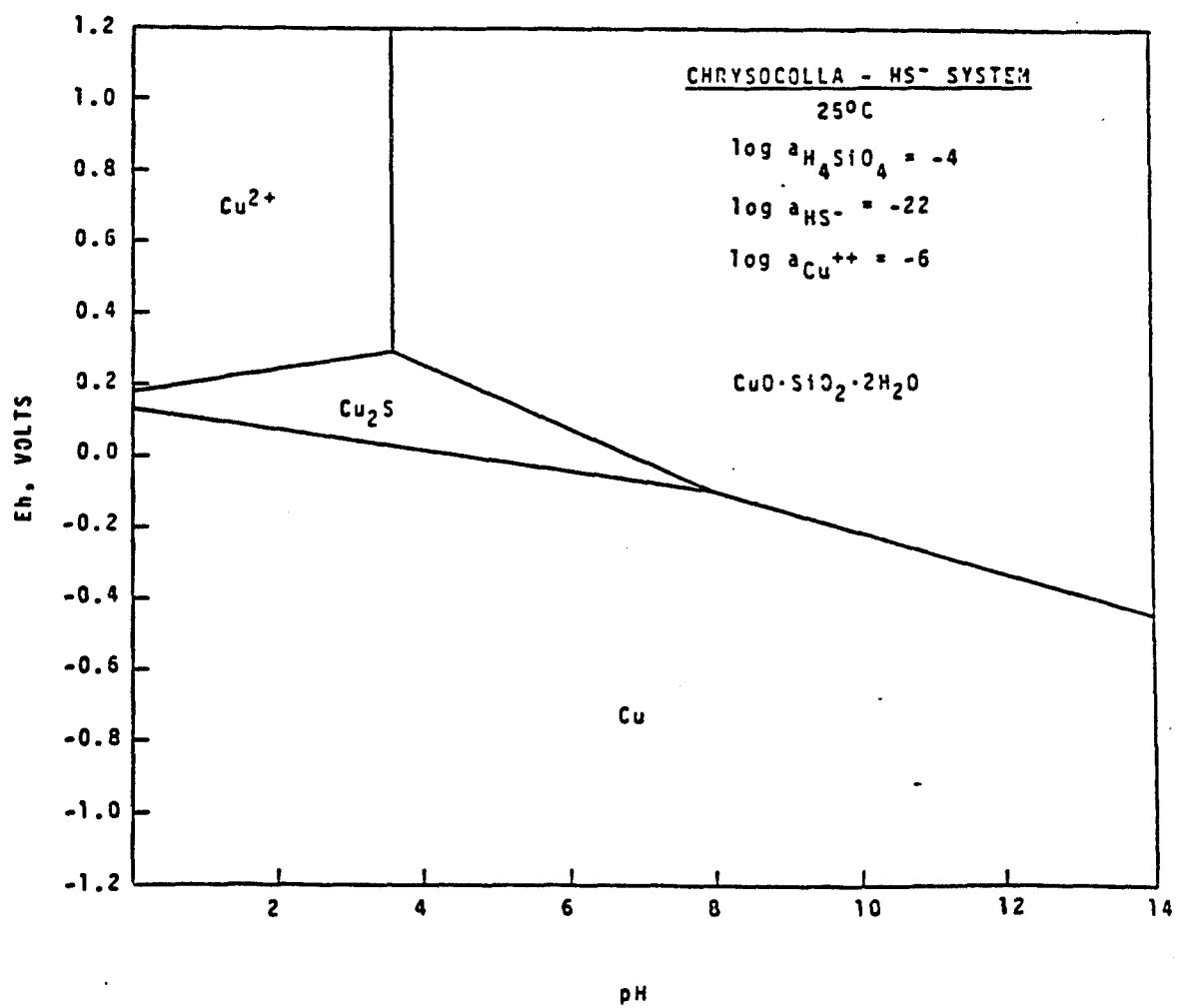


Figure 1. Eh-pH diagram for the chrysocolla -HS⁻ system at 25°C for a hydrosulfide activity of 10⁻²².

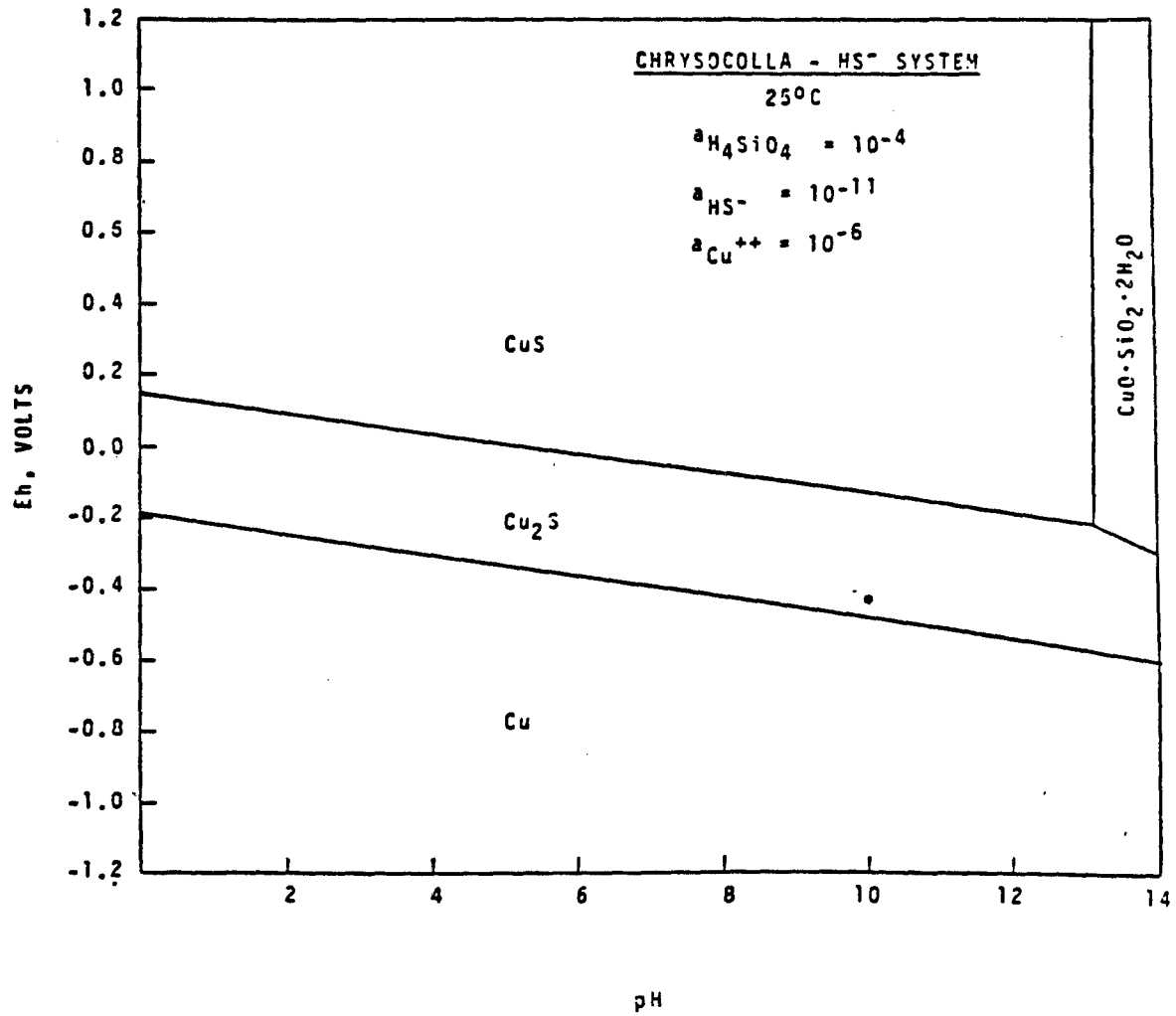


Figure 2. Eh-pH diagram for the chrysocolla -HS⁻ system for a hydrosulfide activity of 10^{-11} .

The Eh-pH diagrams depicting the feasibility of the sulfidization of brochantite are given in Figs. 3 and 4. Fig. 3 shows the stability of the various phases at three different hydrosulfide activities, namely 10^{-16} , 10^{-20} , and 10^{-26} . At a hydrosulfide activity of 10^{-26} brochantite can be sulfidized to only Cu_2S in the pH range 4 to 7. At higher sulfide ion activities it is possible to sulfidize brochantite not only to Cu_2S but also to CuS . In fact at a hydrosulfide activity of 10^{-16} brochantite can be sulfidized to CuS below pH 7. The sulfidization characteristics of brochantite at a hydrosulfide activity of 10^{-6} and 10^{-2} are displayed in Fig. 4. The results of this figure show that CuS and Cu_2S are the products of sulfidization and their predominance will depend on the Eh value of the system.

Interaction of Sulfide Ions with Brochantite

Effect of Agitation Speed. As a first step towards investigating the interaction of ammonium sulfide with brochantite, the effect of stirring speed on the kinetics of interaction was examined. Fig. 5 presents the results of investigations conducted with 35 x 48 mesh brochantite and 5×10^{-3} M ammonium sulfide at a pH of 9.4 at three different speeds of agitation (90, 1450, and 2800 rpm). There is only a very slight difference in the rate at which sulfide ions disappear from solution at the three different speeds investigated. This indicates that mass transfer of sulfide ions through a boundary layer around the particles plays an insignificant role in the kinetics of the interaction process. It should be mentioned that the majority of the experiments were conducted at a stirring speed of 1450 rpm. Even though the lowest

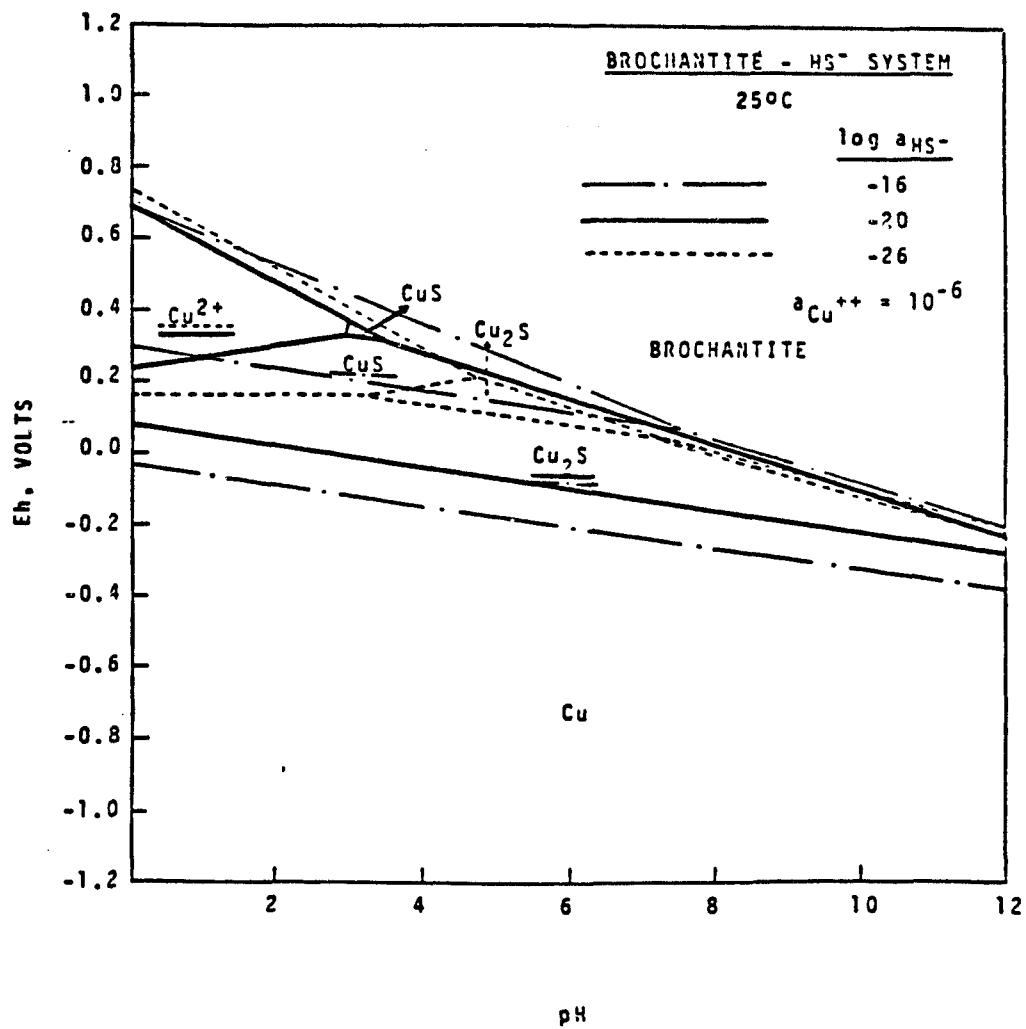


Figure 3. Eh-pH diagram for the brochantite -HS⁻ system at hydrosulfide activities of 10⁻²⁶, 10⁻²⁰, and 10⁻¹⁶.

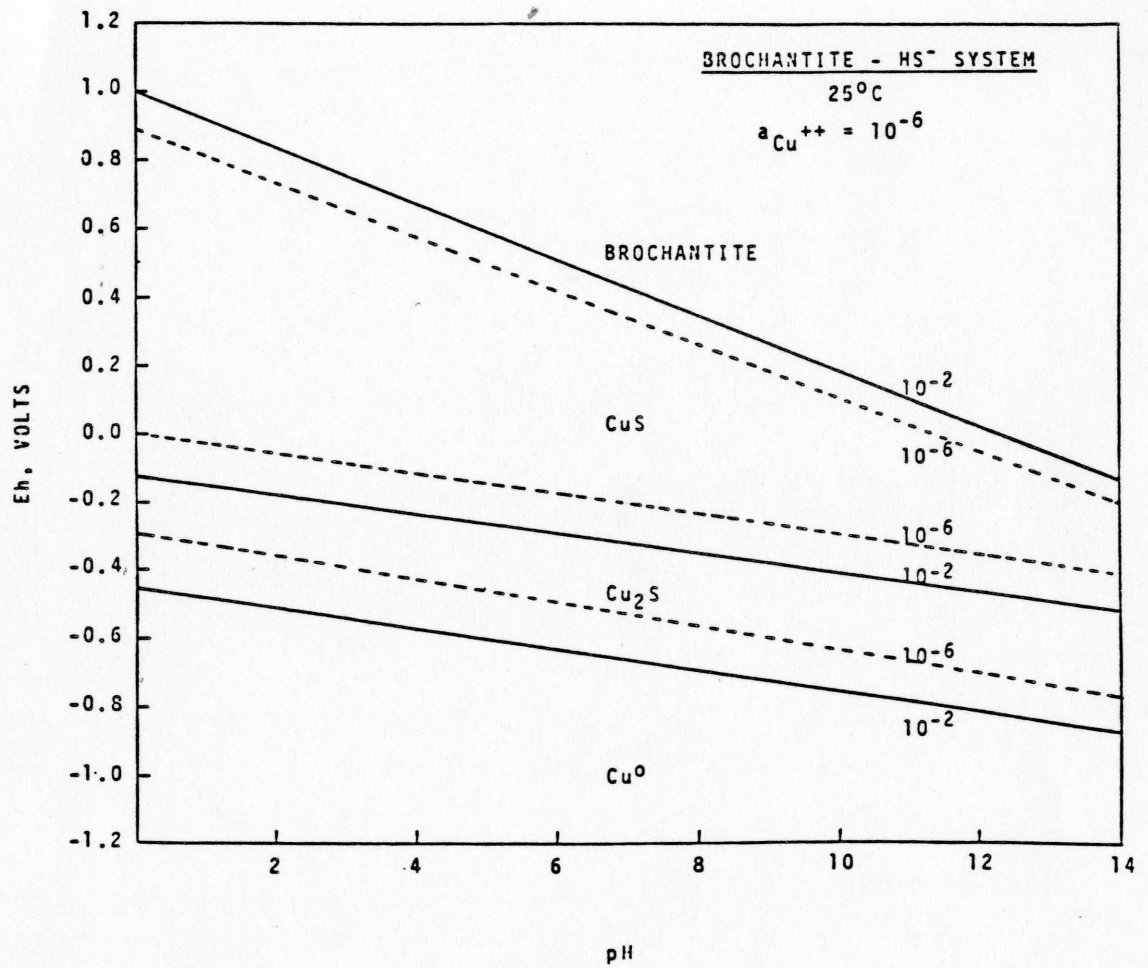


Figure 4. Eh-pH diagram for the brochantite -HS⁻ system at hydrosulfide activities of 10⁻⁶ and 10⁻².

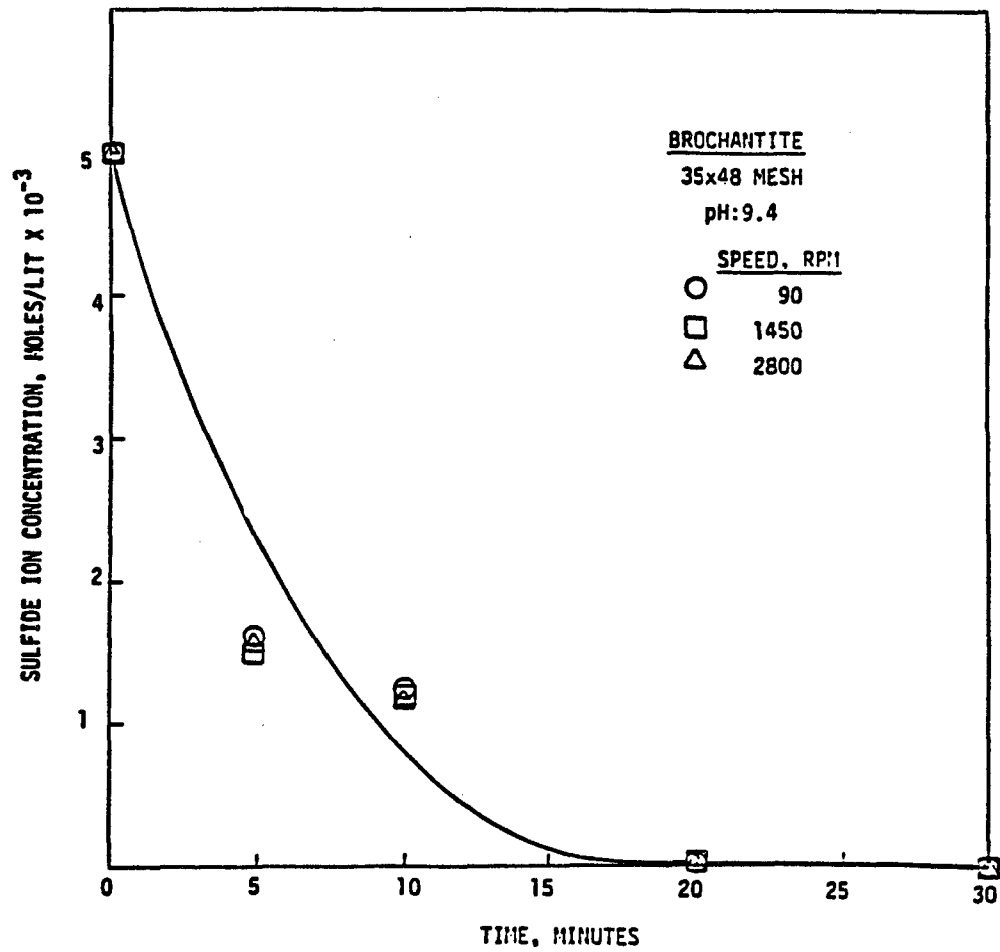


Figure 5. Interaction of sulfide ions with brochantite at different agitation speeds.

speed investigated, namely 90 rpm, did not affect the kinetics very much, the particles could not be suspended well in the medium.

Effect of Particle Size

To investigate the effect of particle size, five different size fractions were chosen. These were 35 x 48, 48 x 65, 100 x 150, 150 x 200, and -200 mesh. A 10^{-3} M ammonium sulfide solution at a pH of 9.3 was used in all the investigations. The change in sulfide ion concentration and the redox potential in solution at different stages during the interaction process are given in Figs. 6 and 7. Two conclusions can be drawn from the data presented in these two figures: 1) the redox potential becomes more positive as the sulfide ion is abstracted from solution; 2) the abstraction of sulfide ions from solution is a rather fast process and is dependent on the particle size. For particle sizes below 100 mesh almost all the sulfide ions in solution are consumed within five minutes. Particles larger than 100 mesh interact less rapidly with the sulfide ions in solution with the rapidity decreasing with increasing particle size.

Effect of Solution pH

The dependence of the interaction of sulfide ions with brochantite on the pH of the aqueous solution was investigated with 35 x 48 mesh brochantite. The experiments were conducted with 5×10^{-3} M ammonium sulfide solutions adjusted to pH values of 5.1,¹ 7.4, 9.3, and 10.5. The results of the experiments are displayed in Figs. 8 and 9. It is apparent from the data of these figures that the kinetics of sulfide ion abstraction from solution is quite sensitive to pH above a value of 7.4. Below a pH

1. pK_1 of $H_2S(aq)$ is 7. Hence at pH 5.1, $H_2S(aq)$ is the predominant sulfur species in solution.

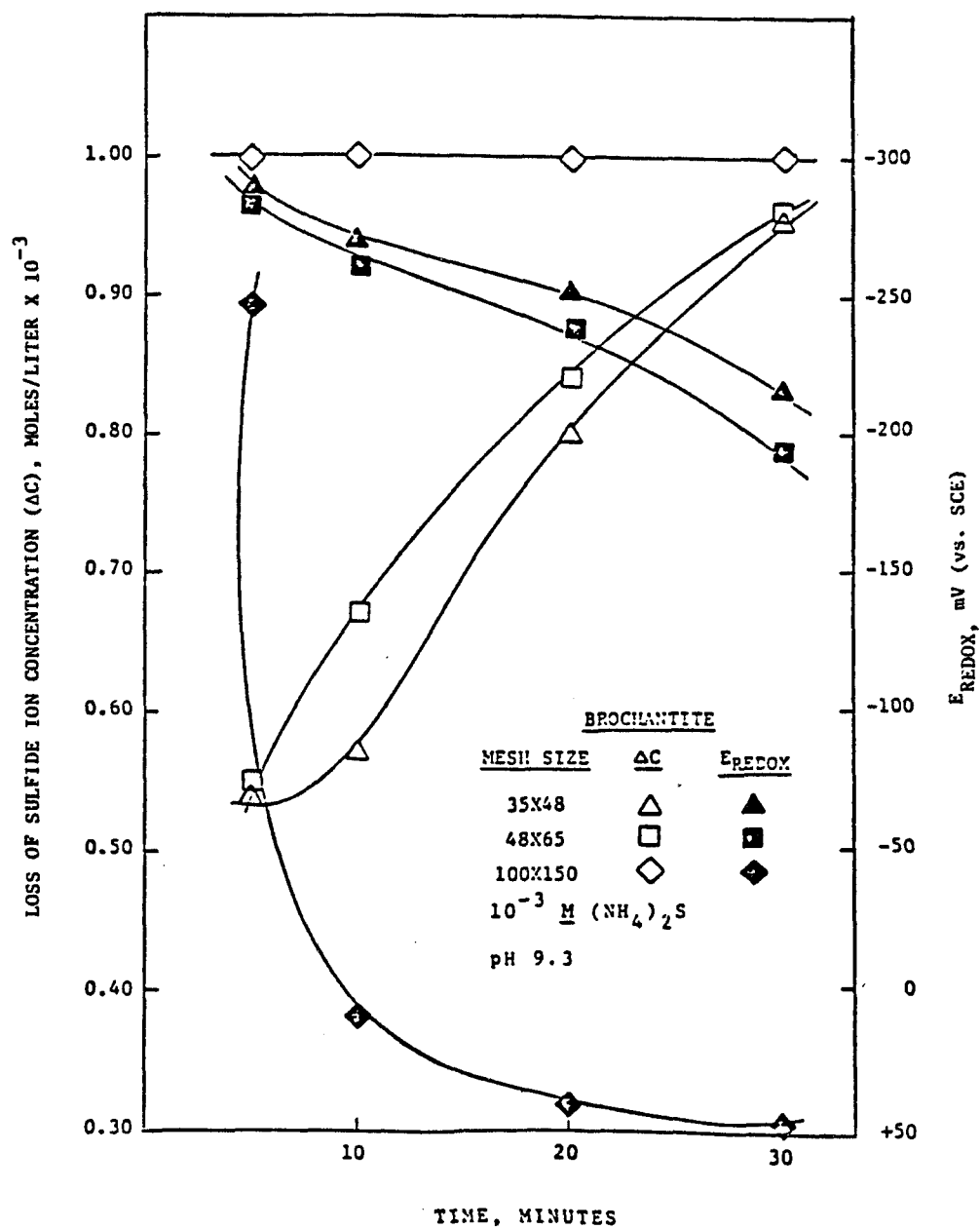


Figure 6. Effect of particle size on the kinetics of interaction of sulfide ions with brochantite (larger than 150 mesh).

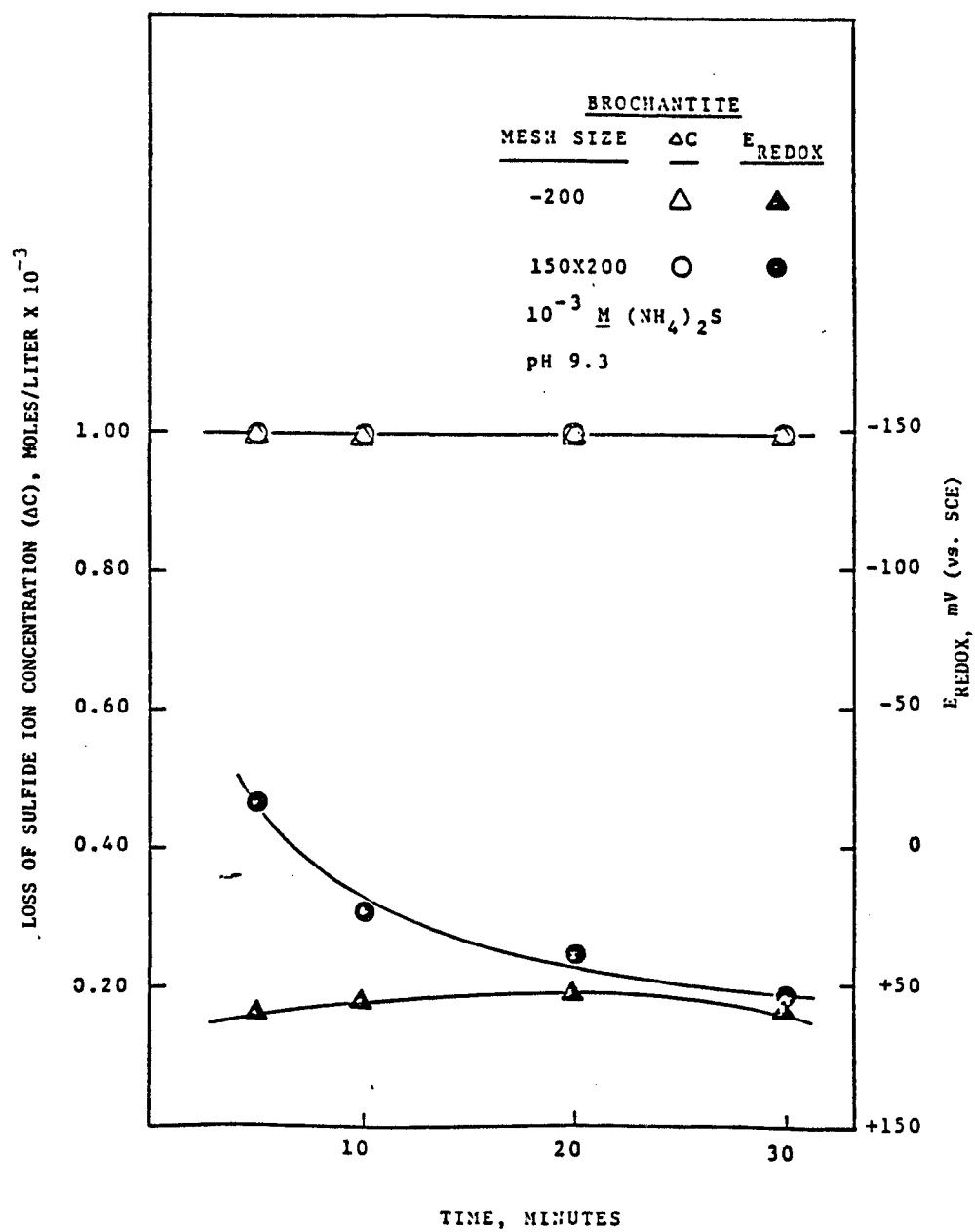


Figure 7. Effect of particle size on the kinetics of interaction of sulfide ions with brochantite (smaller than 150 mesh).

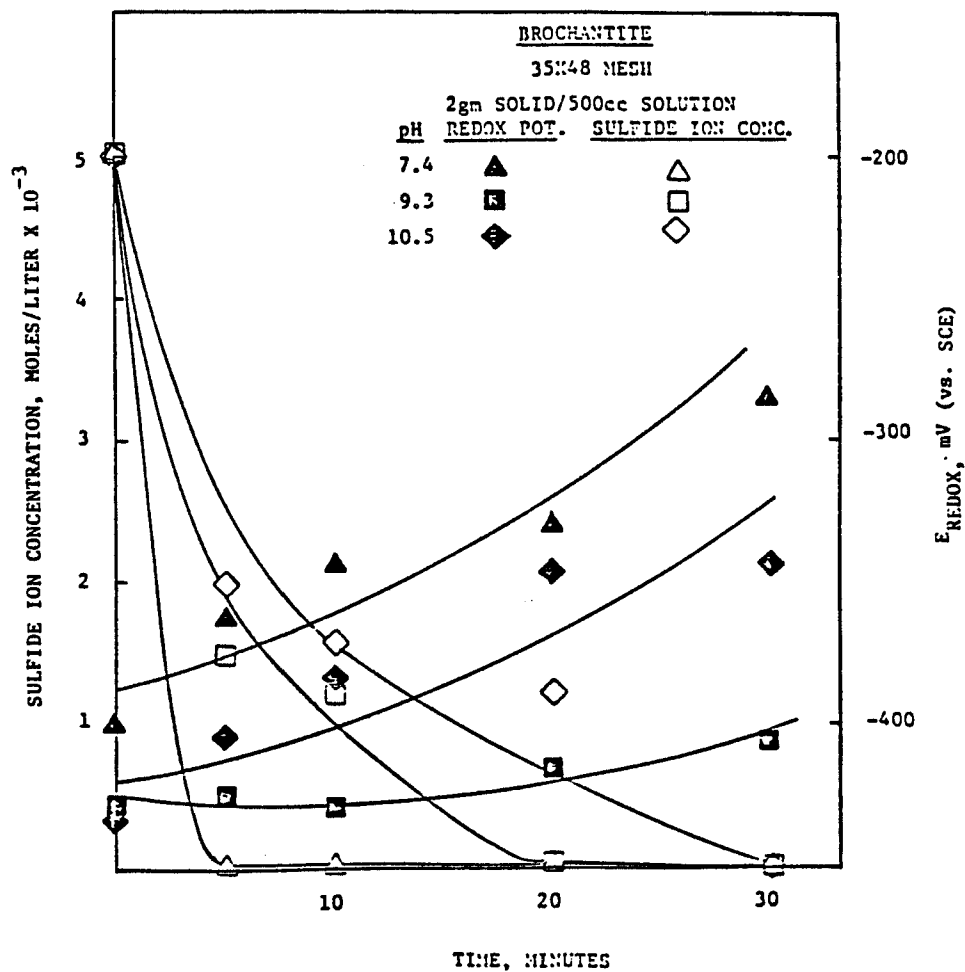


Figure 8. Effect of pH (larger than 7.4) on the interaction of 35 x 48 mesh brochantite with 5×10^{-3} M ammonium sulfide solution.

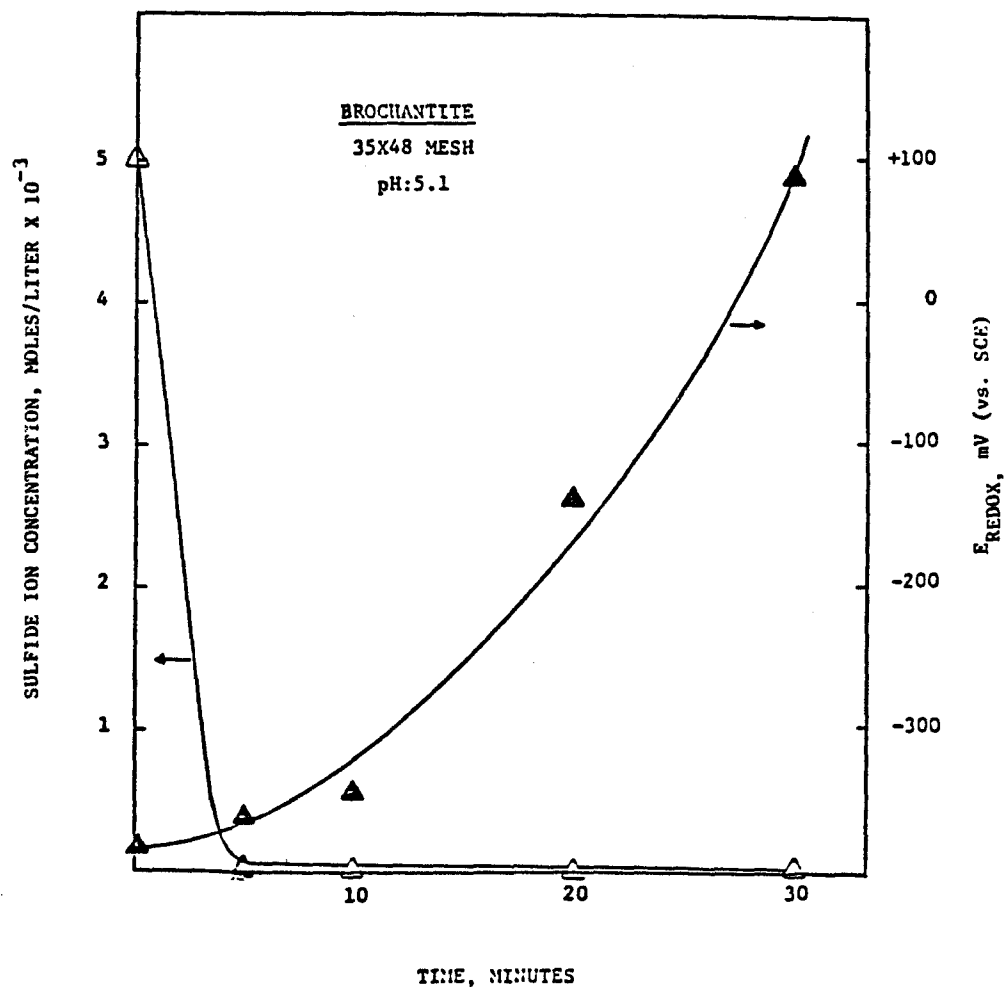


Figure 9. The interaction of 35 x 48 mesh brochantite with a 5×10^{-3} M ammonium sulfide solution at pH 5.1.

value of 7.4 the consumption of sulfide ions by the solid is almost complete in a matter of five minutes (Fig. 9). The data in Figs. 8 and 9 are replotted in Fig. 10 as disappearance of sulfide ion (mole/gm) vs. time. This figure accentuates the role of pH in the kinetics of the interaction process.

One interesting observation that can be made in Figs. 8 and 9 is that the redox potential in solution at the end of conditioning (30 minutes) differs at different solution pH values even though almost complete sulfide ion abstraction has occurred at all pH values. In fact at pH 5.1 the redox potential becomes positive towards the end of the conditioning period. This perhaps indicates that two different mechanisms can account for sulfide ion disappearance from solution. These are: 1) adsorption/surface reaction process and 2) oxidation catalyzed by the sulfidized surface.

Interaction of Sulfide Ions with Chrysocolla

Effect of Particle Size

The interaction of chrysocolla with sulfide ions was investigated with 10^{-2} M ammonium sulfide and 10^{-3} M ammonium sulfide at different particle sizes. Fig. 11 displays the results obtained with 10^{-3} M ammonium sulfide solution contacted with 35 x 48, 48 x 65, 65 x 100, and -200 mesh chrysocolla particles. As was observed for brochantite the larger particles interact less rapidly than the smaller particles. In fact the -200 mesh particles consume almost all the sulfide ions from solution in a matter of five minutes. Fig. 12, which gives the results of tests carried out with 10^{-2} M ammonium sulfide, also confirms the general trend,

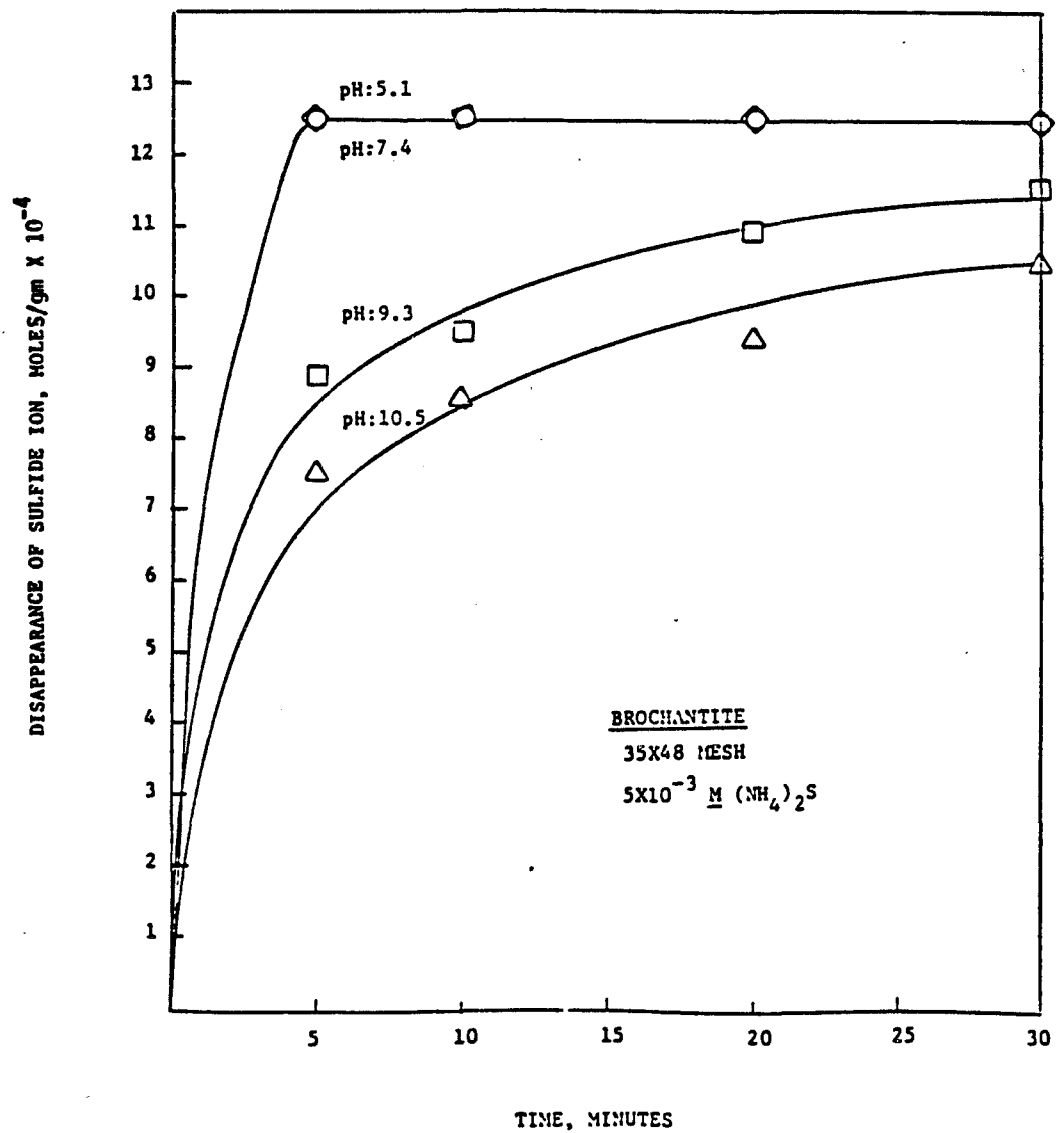


Figure 10. Effect of pH on the disappearance of sulfide ions from $5 \times 10^{-3} \text{ M}$ ammonium sulfide solution when contacted with 35 x 48 mesh brochantite.

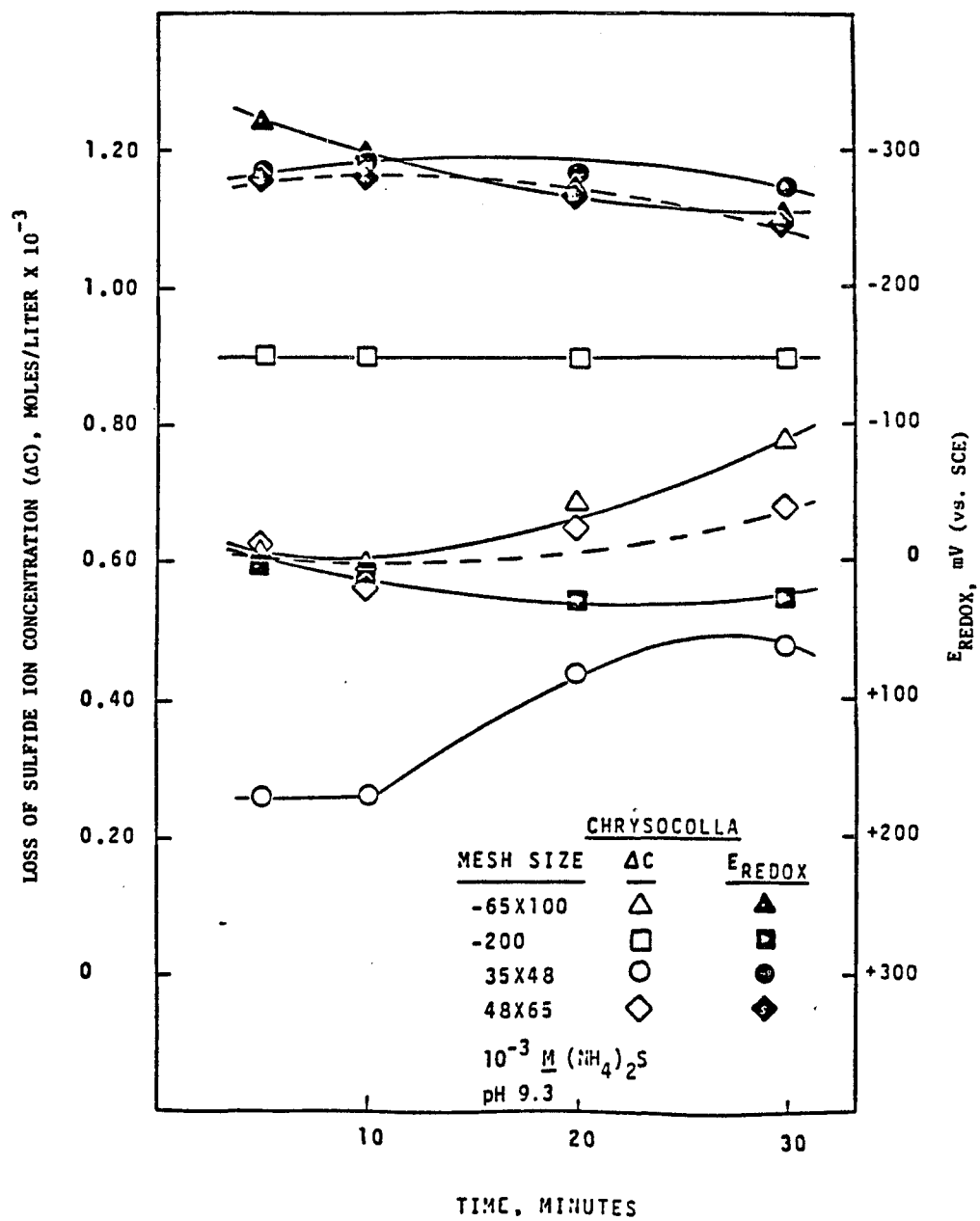


Figure 11. Effect of particle size on the interaction of $10^{-3} \text{ M } (\text{NH}_4)_2\text{S}$ solution with chrysocolla.

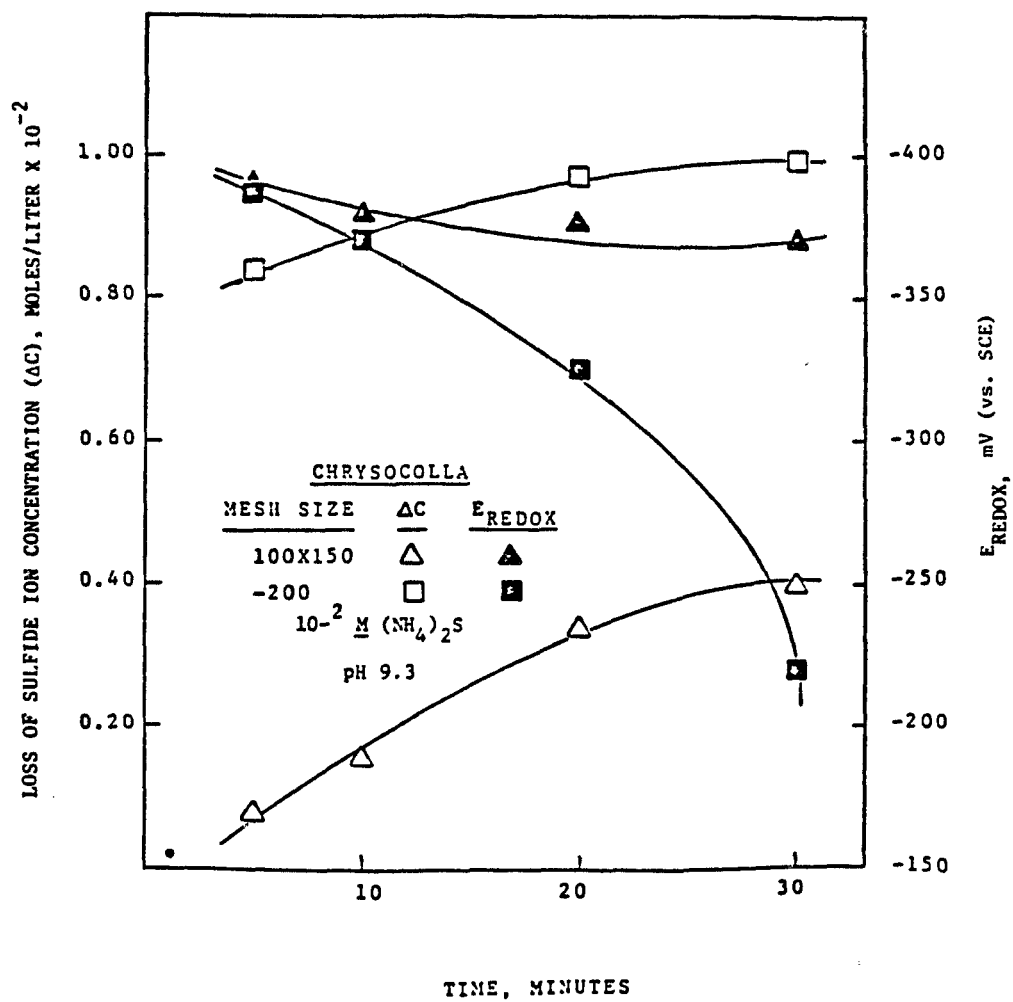


Figure 12. Effect of particle size on the interaction of 10^{-2} M $(\text{NH}_4)_2\text{S}$ solution with chrysocolla.

namely that finer particles can be sulfidized much more rapidly.

Effect of pH

The effect of the pH of 5×10^{-3} M ammonium sulfide solution on the kinetics of sulfide ion uptake from solution is presented in Fig. 13. It can be easily seen from this figure that a pH value of 7 or below yields the most rapid interaction; at pH values of 9 or above, the interaction is rather slow. It is not very clear why the pH value of 10.8 is better than 9.1. As was observed with brochantite, the redox potential in solution increases sharply during the interaction process at low pH values.

The data in Fig. 13 are replotted in the form of disappearance of sulfide ions vs. time in Fig. 14. It is very clear from this figure that low pH values facilitate the interaction kinetics.

X-ray Diffraction Analysis of Sulfidized and Untreated Chrysocolla and Brochantite Samples

The peaks observed in the X-ray diffraction patterns of -200 mesh chrysocolla and -200 mesh chrysocolla treated with 10^{-2} M $(\text{NH}_4)_2\text{S}$ solution are tabulated in Table 3. The data in this table reveal very minute differences in the patterns for untreated and sulfidized chrysocolla. Two peaks, one at a '2 θ ' value of 36.6° and the other at 48.0° , seem to appear on sulfidization. On checking the published X-ray patterns for different copper sulfide minerals, these peaks seem to indicate the formation of Cu_2S .

A comparison of the X-ray patterns of natural and sulfidized brochantite, Table 4, indicates little change on sulfidization. Both

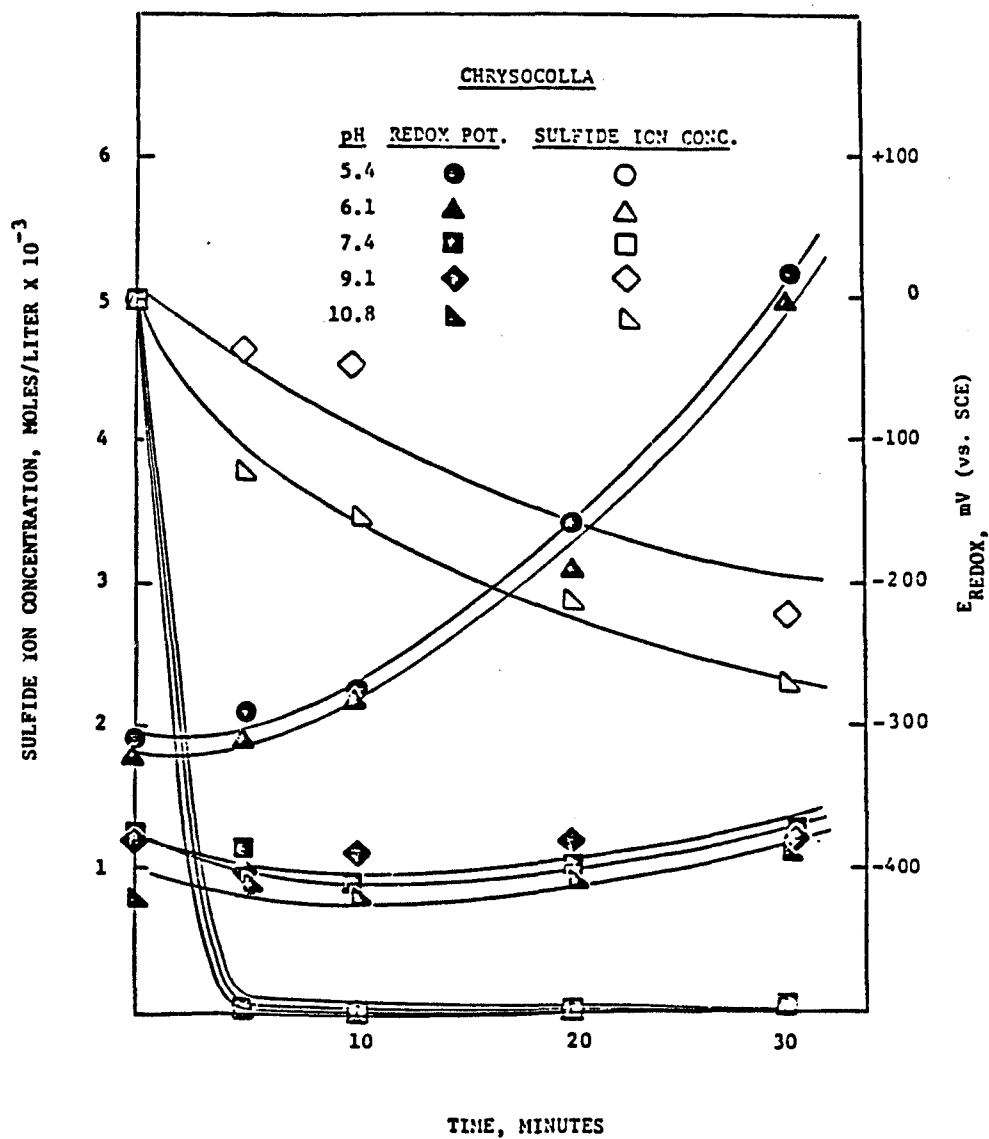


Figure 13. Kinetics of sulfide ion disappearance from solution as a function of pH for the chrysocolla/ammonium sulfide system.

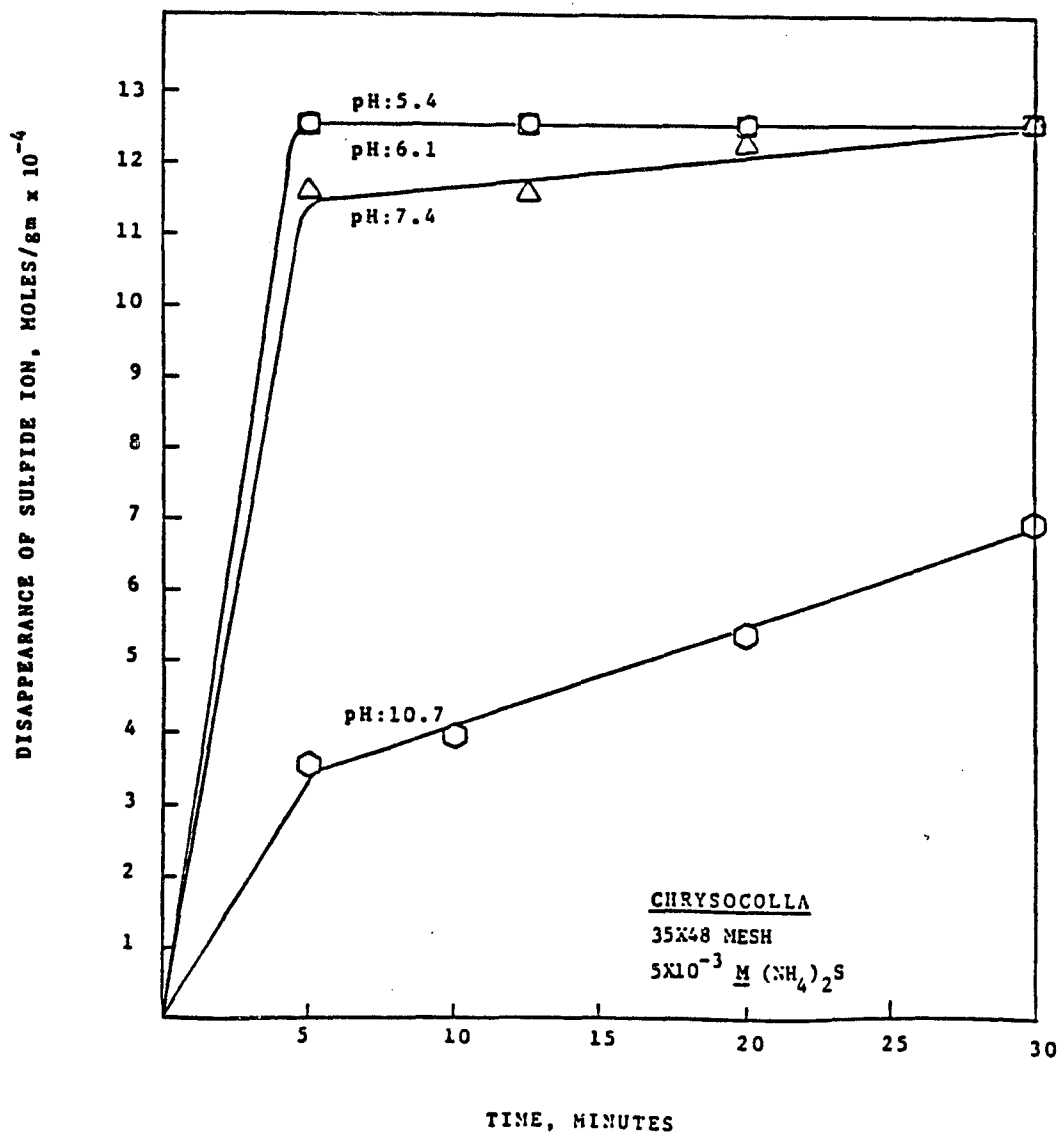


Figure 14. Disappearance of sulfide ions as a function of time when 35 x 48 mesh chrysocolla is contacted with 5 x 10⁻³ M sulfide solution at different pH values.

TABLE 3

X-RAY DATA FOR UNTREATED AND SULFIDIZED CHRYSOCOLLA

Untreated			Sulfidized		
2 θ , deg	d, Å	I/I ₀	2 θ , deg	d, Å	I/I ₀
15.00	5.901	56.45	14.85	5.945	31.15
17.64	5.023	62.90	17.60	5.034	33.60
20.98	4.246	20.97	20.90	4.246	18.85
24.20	3.674	75	24.18	3.677	36
26.78	3.326	100	26.70	3.335	100
30.00	2.966	30.65	31.48	2.839	43.11
31.40	2.846	97	32.17	2.779	28.36
32.3	2.769	26.60	35.58	2.521	26.56
35.7	2.512	49.68	<u>36.60</u>	2.453	21.31
39.0	2.307	31.29	<u>48.00</u>	1.893	27.87
42.6	2.120	37.10	50.25	1.815	18.69
50.24	1.814	20.97			
57.0	1.614	21.77			
63.14	1.471	24.19			

TABLE 4
X-RAY DATA FOR UNTREATED AND SULFIDIZED BROCHANTITE

Untreated			Sulfidized		
2 θ , deg	d, Å	I/I ₀	2 θ , deg	d, Å	I/I ₀
15.1	5.8623	32.65	14.9	5.9405	14.06
16.7	5.3040	16.38	16.6	5.3358	23.77
18.5	4.7918	100	18.6	4.7663	100
25.0	3.5587	43.39	25.0	3.5587	58.14
26.9	3.3115	18.37	27.0	3.2995	19.14
30.0	2.9760	13.33	30.0	2.9760	30.25
33.6	2.6649	28.28	33.6	2.6649	27.56
35.2	2.5474	86.22	35.2	2.5474	52.56
42.7	2.1157	58.05	42.6	2.1204	56.25
			59.8	1.5452	14.06
			61.6	1.5043	10.56

chrysocolla and brochantite turn black on contact with $(\text{NH}_4)_2\text{S}$ solution, and, based on this observation, one would expect to see peaks corresponding to one or more copper sulfide minerals in the pattern for sulfidized chrysocolla and brochantite. The absence of any intense peaks for copper sulfide minerals in the sulfidized samples may indicate that the thickness of the sulfide layer is below the detection limit of X-ray diffraction.

Surface Area Analysis of Untreated and Sulfidized Brochantite and Chrysocolla

It has been surmised by many researchers that sulfidization renders chrysocolla more amenable to flotation by reducing its porous nature through the formation of a non-porous sulfide coating. To test the postulate, the surface area of two different size fractions of chrysocolla prior to and after sulfidization with $10^{-2} \text{ M } (\text{NH}_4)_2\text{S}$ were measured and the results are tabulated in Table 5. It can be easily discerned from Table 5 that the surface areas of chrysocolla samples do not significantly change with sulfidization. If the porous nature of chrysocolla is responsible for its poor floatability, sulfidization will provide very little improvement.

The results of the surface area measurements conducted on untreated and treated (with $10^{-2} \text{ M } (\text{NH}_4)_2\text{S}$) -200 mesh brochantite are also tabulated in Table 5. Unlike the case for chrysocolla, the surface area of brochantite decreases significantly on sulfidization.

Chrysocolla is a microporous material and hence the surface area is not a significant function of particle size (Table 5). In spite of this the kinetics of interaction of sulfide ions depend on particle size.

TABLE 5
SURFACE AREAS OF CHRYSOCOLLA AND BROCHANTITE

<u>Material</u>	<u>Treatment</u>	<u>Surface area, m²/gm</u>
Brochantite -200 mesh	Untreated	1.884
" "	Treated with 10^{-2} M (NH ₄) ₂ S for 30 min. (pH = 9.3)	0.87
Chrysocolla 35 x 48 mesh	Untreated	126.00
" "	Treated with 10^{-2} M (NH ₄) ₂ S for 30 min. (pH = 9.3)	123.20
Chrysocolla -200 mesh	Untreated	114.3
" "	Treated with 10^{-2} M (NH ₄) ₂ S for 30 min. (pH = 9.3)	94.6 100.2

A plausible explanation for this is the fact that the finer-size fractions expose more copper sites per gram than the coarser-size fractions. The specific surface area of brochantite was measured to be slightly dependent on particle size ($1.5 \text{ m}^2/\text{gm}$ for the 65 x 100 mesh compared to $1.9 \text{ m}^2/\text{gm}$ for the minus 200 mesh). However, this difference cannot totally account for the tremendous change in the sulfide ion disappearance kinetics.

Electrokinetic Characteristics of Sulfidized and Unsulfidized Brochantite and Chrysocolla

In order to gain experimental support to the possibilities indicated by the Eh-pH diagrams, the electrokinetic characteristics of brochantite and chrysocolla were measured prior to and after sulfidization in an ammonium sulfide solution at a pH of 9.3. The electrokinetic characteristics of unsulfidized brochantite are given in Fig. 15. The point of zero charge (PZC) of brochantite occurs in the vicinity of pH 9.5. Conditioning with a $10^{-4} \text{ M } (\text{NH}_4)_2\text{S}$ solution at a pH of 9.4 seems to decrease the point of zeta potential reversal of brochantite to a pH value of 8.5. Increasing the concentration of the sulfidizing solution to 10^{-2} M drastically alters the electrokinetic characteristics of brochantite particles. These particles are negatively charged in the entire pH range investigated and exhibit a trend similar to that reported for copper sulfide particles. It should be reasonable to conclude that a sulfidizing treatment results in the formation of a surface sulfide coating.

In contrast to brochantite, the electrokinetic characteristics of chrysocolla do not seem to be affected very much by sulfidization, as

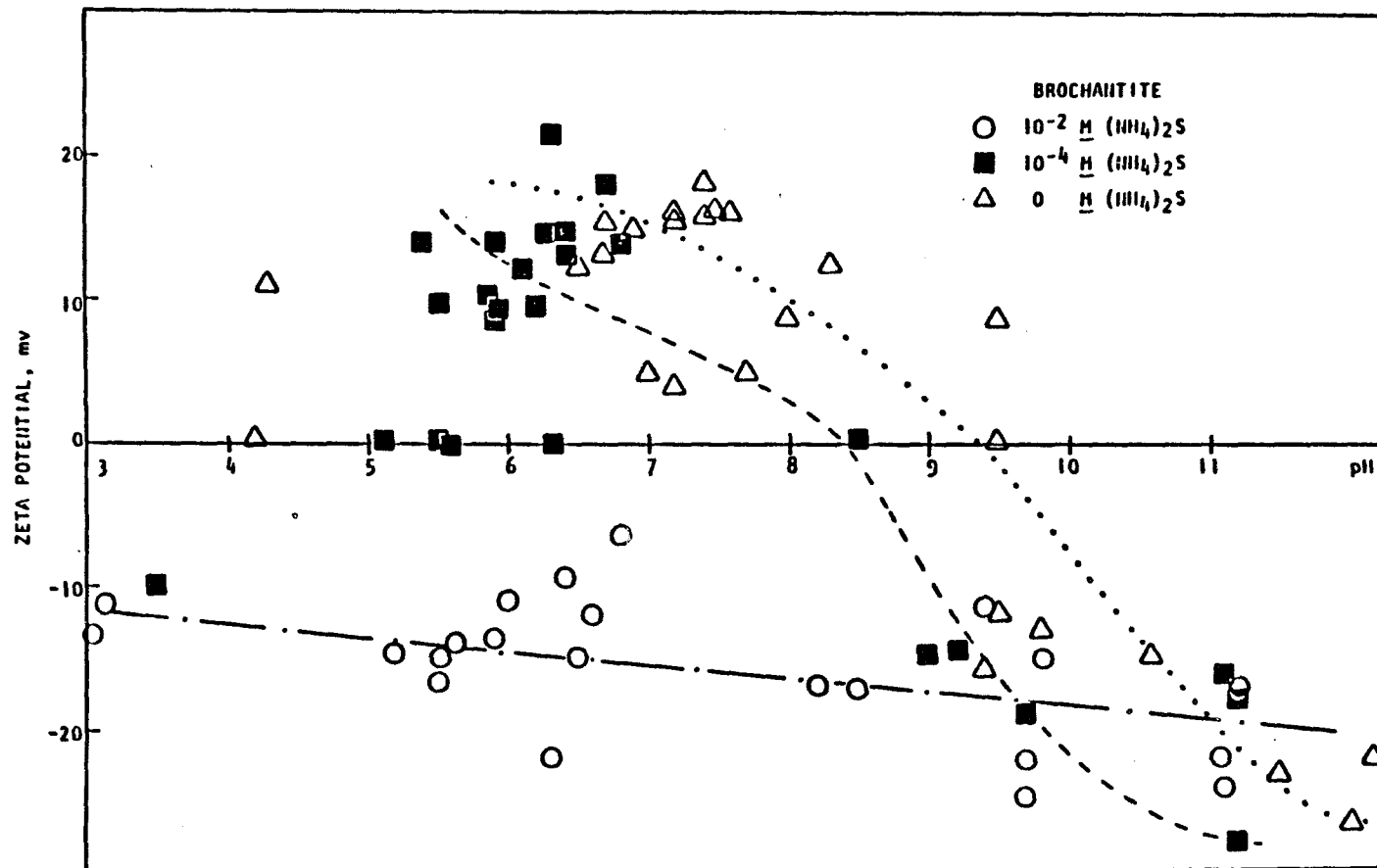


Figure 15. Electrokinetic characteristics of natural and sulfidized brochantite.

will be clear from Fig. 16. The point of zero charge of the chrysocolla sample used in the investigations occurs around a pH value of 2.5. It is worth mentioning at this stage that the electrokinetic characteristics of chrysocolla are known to be very dependent on their origin, and PZC values between 2.2 and 6.5 have been reported in literature.³ Even though the electrokinetic trends for the three different experimental conditions (0 M , 10^{-4} M , and 10^{-2} M $(\text{NH}_4)_2\text{S}$) have been represented with three different lines, the data points are so close that there is no significant discernible difference between them. It is difficult to conclude from the data in Fig. 16 whether sulfidization results in a copper sulfide coating on the particles.

A comment deserves to be made regarding the mechanisms of hydrosulfide interaction with the oxide copper minerals. The consumption of sulfide ions can take place via adsorption, precipitation, and/or oxidation reactions. Assuming that the radius of a hydrosulfide ion is 2\AA , it can be shown that it will require 1.33×10^{-9} moles of hydrosulfide ion to cover 1 cm^2 of the mineral surface. If hydrosulfide ions are specific to the copper sites, then based on the fibrous structure proposed for chrysocolla,⁴ the monolayer capacity can be calculated to be 0.9×10^{-9} moles/ cm^2 (i.e., two-thirds of 1.33×10^{-9} moles/ cm^2). In the case of chrysocolla, experiments performed with $5 \times 10^{-3} \text{ M}$ ammonium sulfide solutions reveal that 1×10^{-9} moles of hydrosulfide per cm^2 of mineral surface disappear from solution. This perhaps points to the chemisorption of hydrosulfide ions to be the predominant mechanism. However, results obtained with brochantite show that the disappearance of sulfide ion is approximately 6×10^{-8} moles/ cm^2 of the mineral surface.

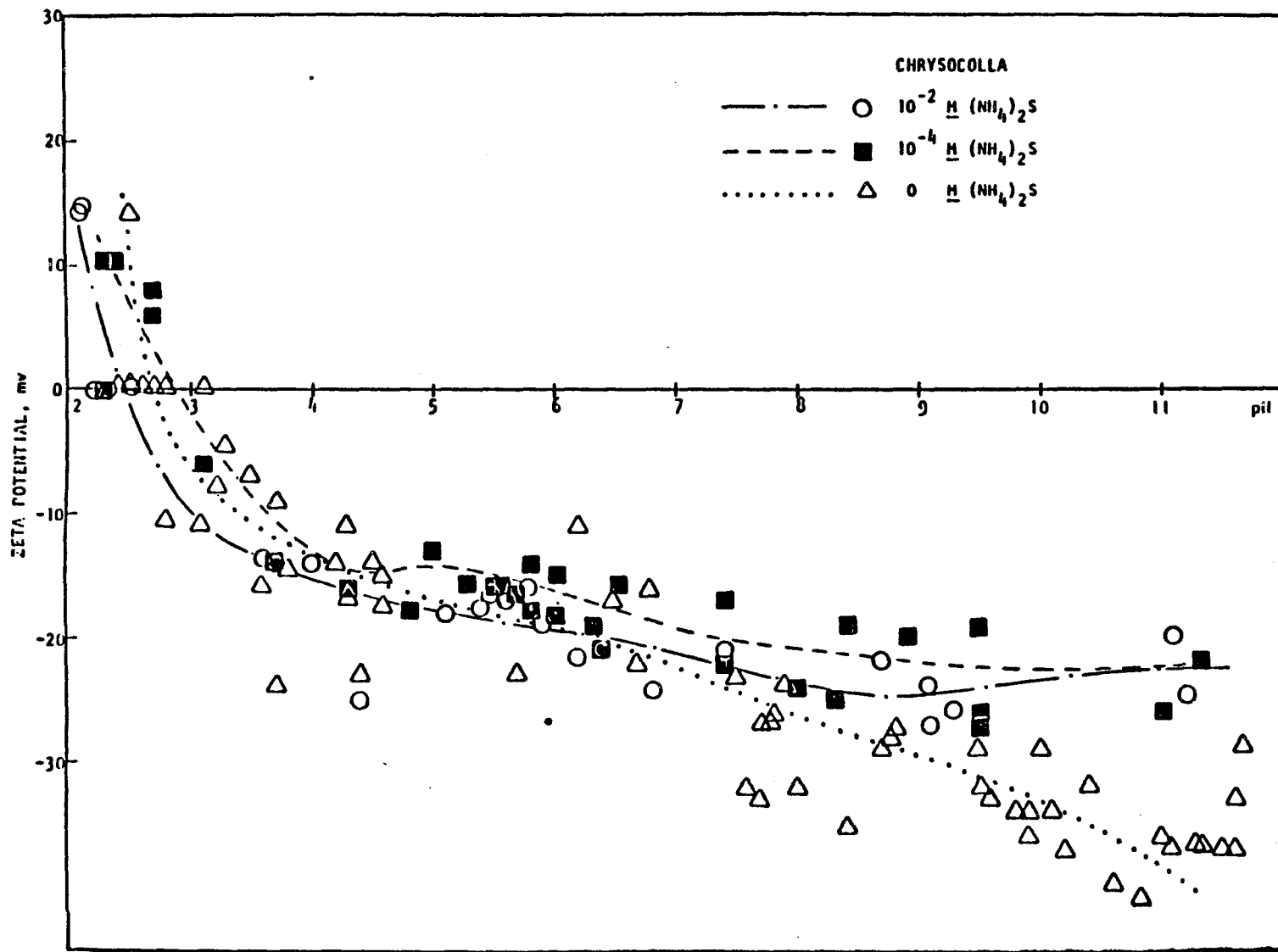


Figure 16. Electrokinetic characteristics of natural and sulfidized chrysocolla.

This depletion of sulfide ions is approximately 40 times the amount needed for monolayer coverage. This suggests that adsorption as well as reaction (surface as well as bulk) plays a role in the interaction of brochantite with hydrosulfide ions.

Flotation of Sulfidized Chrysocolla and Brochantite with Xanthate

The results of the flotation experiments are shown in Fig. 17. As is evident from the data in this figure, chrysocolla responds very poorly to flotation. The flotation of brochantite under similar conditions is shown in Fig. 18. The flotation of brochantite is also very poor but somewhat better than chrysocolla. A maximum in the flotation of brochantite was observed in the pH range of 7 to 8.

A second set of flotation experiments was performed in which the sulfide solution used for sulfidizing was decanted prior to the addition of xanthate solution. This set of experiments was conducted with 10^{-3} M ethyl and amyl xanthates. A 10^{-2} M ammonium sulfide solution was used for sulfidization. The results of the tests conducted with chrysocolla are presented in Fig. 19. Decanting the sulfide solution prior to the xanthate addition seems to improve the floatability of chrysocolla. The flotation response of chrysocolla is much better if the pH during sulfidization is in the acidic range. However, the best recovery under the conditions investigated was only about 25%. This is in contrast to the results of Castro et al.⁶, who were able to recover above 90% of chrysocolla using a xanthate collector. One experiment was carried out in which the chrysocolla was sulfidized at a pH of 5.8 but floated at a pH of 10.5. A recovery of 18% was obtained in this

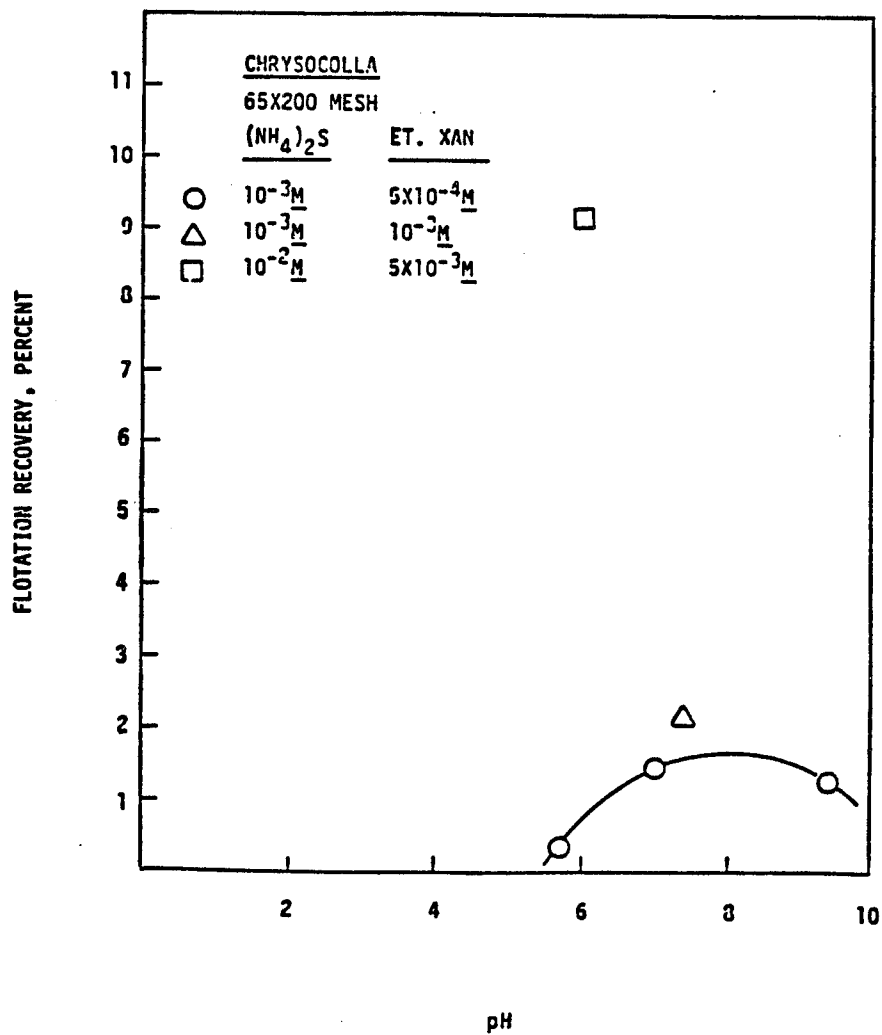


Figure 17. Flotation of sulfidized 65 x 200 mesh chrysocolla as a function of sulfidization pH [no decantation of sulfidizing solution prior to collector addition].

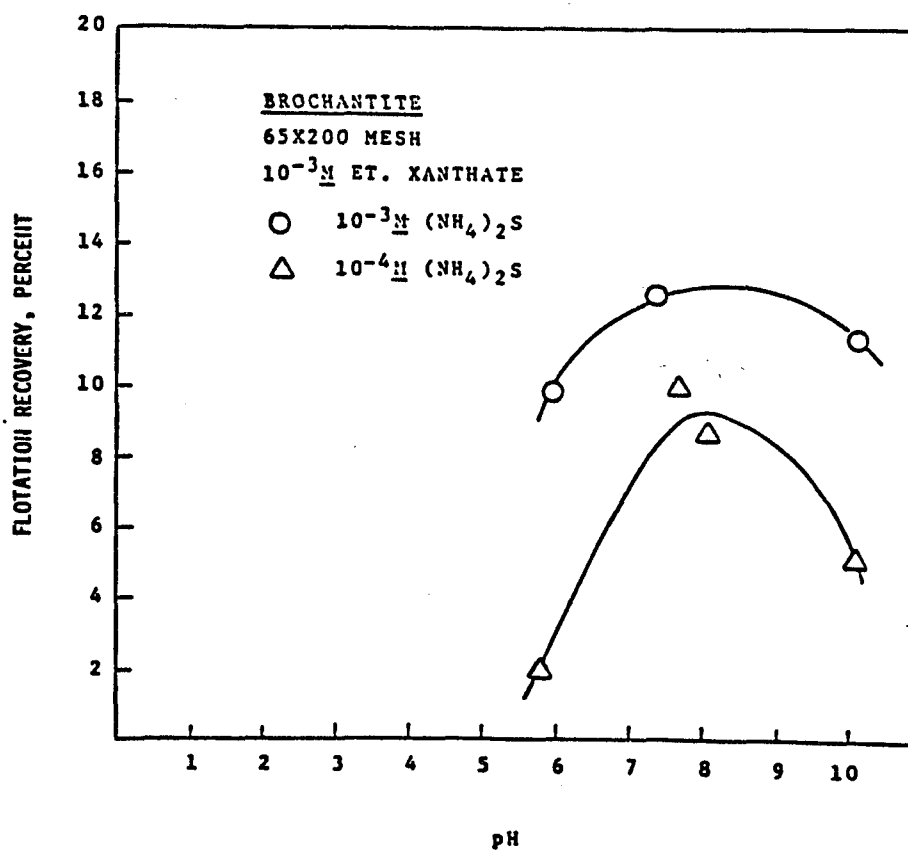


Figure 18. Flotation of sulfidized 65 x 200 mesh brochantite as a function of sulfidization pH [no decantation of sulfidization solution prior to collector addition].

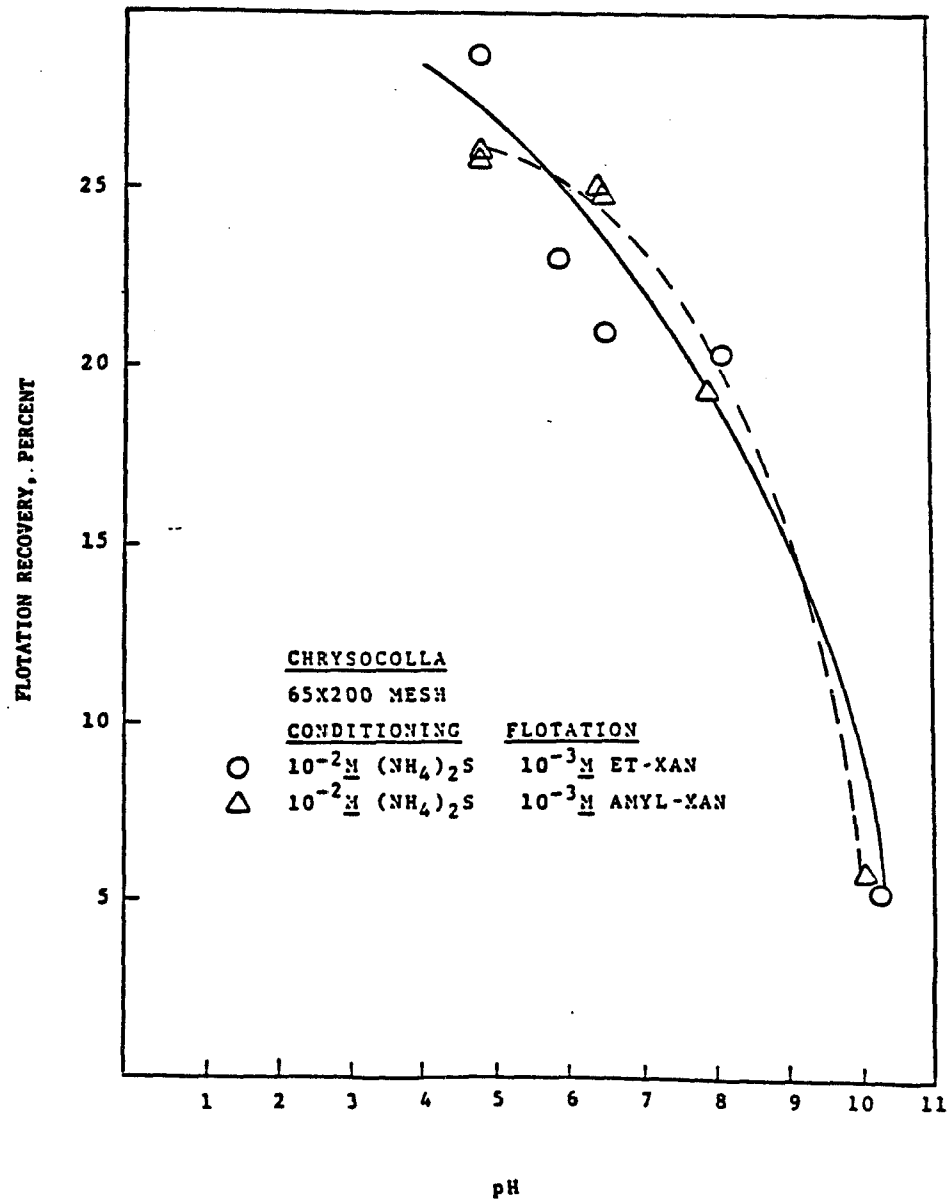


Figure 19. Flotation of 65 x 200 mesh chrysocolla sulfidized with $10^{-2} \text{ M } (\text{NH}_4)_2\text{S}$. [The sulfidizing solution was decanted prior to collector addition].

experiment which stresses the beneficial effect of conditioning at low pH values. There is very little difference in the flotation response of chrysocolla with ethyl and amyl xanthates.

The flotability of brochantite conditioned with 10^{-2} M $(\text{NH}_4)_2\text{S}$ with ethyl xanthate is shown in Fig. 20. It should be remembered that in this series of experiments the sulfide solution was decanted prior to xanthate addition. Excellent recovery (90%) of brochantite was obtained in the pH range 5-10.

The improvement in flotation when the sulfidizing solution is decanted can perhaps be explained as due to two reasons: 1) the unreacted sulfide ions in the sulfidizing solution may act as a depressant for the sulfide coating on the oxide mineral surface (it is well known that copper sulfides can be depressed by aqueous sulfide solutions); and 2) the sulfidizing solution is most likely to contain thiosulfate ions which are formed by the oxidation of sulfide ions. These thiosulfate ions may inhibit the oxidation of xanthate ions to dixanthogen. It has been proven by many researchers that the flotation of copper sulfide minerals, Cu_2S and CuS , with xanthate is made possible by the formation of dixanthogen on the mineral surface. Hence the thiosulfate ions will prove detrimental to the flotation of sulfidized chrysocolla and brochantite.

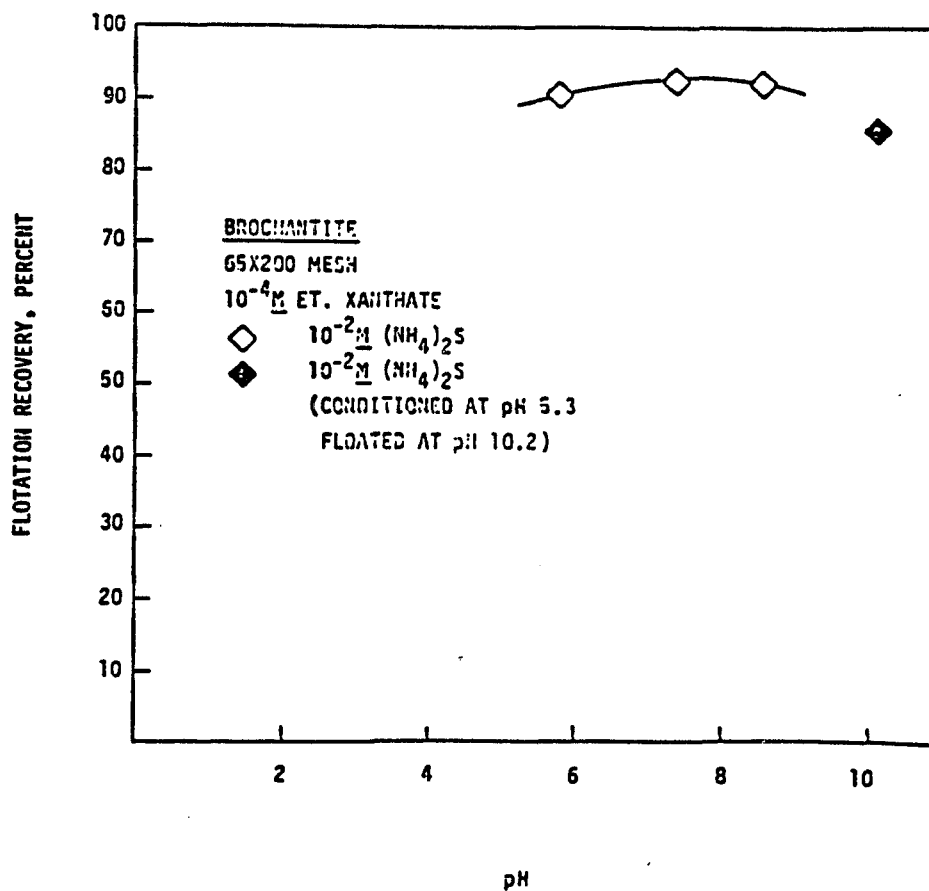


Figure 20. Flotation of 65 x 200 mesh brochantite sulfidized with 10^{-2} M $(\text{NH}_4)_2\text{S}$. [The sulfidizing solution was decanted prior to collector addition].

V. CONCLUSION

The study of the flotation of copper oxide minerals by sulfidization was investigated. From the data of interaction, X-ray, surface area, electrokinetic characteristics and flotation recovery, the following conclusions can be drawn:

1. The kinetics of interaction of hydrosulfide ions with copper minerals does not depend on the intensity of agitation during the conditioning step.
2. Sulfide solutions interact much more rapidly and intensely with oxide copper minerals at acidic pH values. This perhaps indicates that $H_2S(aq)$ species, which predominates at pH values below 7, is a much better sulfidizing agent.
3. Particle size plays an important role in the interaction process. The finer the particles the faster is the rate of interaction.
4. The redox potential in solution becomes more positive during the interaction process.
5. Eh-pH diagrams drawn for chrysocolla- HS^- and brochantite- HS^- systems show that both chrysocolla and brochantite can be sulfidized at very low hydrosulfide activities. However, X-ray diffraction analysis of sulfidized chrysocolla and brochantite samples do not yield any strong peaks characteristic of copper sulfide minerals.
6. Sulfidization seems to hardly affect the porous nature and surface area of chrysocolla. On the contrary, the specific surface area of brochantite is considerably reduced upon a sulfidizing treatment.

7. Sulfidization shifts the PZC of brochantite to a lower pH value. Unlike brochantite, the PZC of chrysocolla does not change after sulfidization.
8. Sulfidization followed by xanthate flotation is a very effective method to recover brochantite provided the sulfidizing solution is decanted before collector addition. The sulfidizing pH does not affect the flotation recovery very much.
9. Chrysocolla responds rather poorly to flotation even after sulfidization. Unlike the case of brochantite, sulfidization pH is quite important for chrysocolla flotation. Acidic conditioning pH values make chrysocolla much more amenable to flotation.

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