A Study of Surface Properties of Chrysocolla
As Related to Sulfidization and Flotation

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering

by

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June 1969
The thesis of Thomas Michael Plouf is approved:

The author wishes to express his deepest appreciation to Dr. Frank W. Bowdish for suggesting the original problem and for his counsel and guidance.

The author wishes to acknowledge the financial assistance of the United States Bureau of Mines, in both purchasing of equipment and supplies, which enabled this thesis to be possible.

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Although the concentrations of the sulfide and thiosulfate ions increase with increasing pH values, the adsorption of sulfur on the chrysocolla surface decreases. This indicates that surface conditions depend upon pH. Under surface conditions determined by factors other than pH, the adsorption of sulfur may also play a significant role. The precipitation of copper as a result of high pH levels.
The surface properties of chrysocolla are related to its amenability to sulfidization and flotation. Micro flotation techniques are applied to define more clearly the parameters effecting collectable and non-collectable surfaces and to further the understanding of chrysocolla flotation by sulfidization.

Two of the parameters that effect the recovery of sulfidized chrysocolla are the attainment of a stable surface, produced by aging, and the pH at which the chrysocolla is sulfidized. Aging of sulfidized chrysocolla accompanied by a rejection of sulfur, believed to be as $\text{H}_2\text{S}$, resulted in flotation recovery increasing from 3.54 percent to 81 percent. The recovery of aged sulfidized chrysocolla increased from 36 percent on material sulfidized at pH 5.40 to 89 percent when sulfidized at pH 4.00. The concentration of the sulfidizing solution, above a required minimum, is not an important parameter effecting flotation recovery.

Although the concentrations of the sulfide and bisulfide ions increase with increasing pH value, the adsorption of sulfur on the chrysocolla surface decreases. This indicates surface conditions dependent upon pH. These surface conditions are measured as a function of pH by electrokinetic measurements, and indicate a region of increasing incipient leaching of copper as a result of decreasing pH.
The volume of sulfidizing solution and the minimum concentration of sodium sulfide for sulfidization of chrysocolla are also important parameters. Activities of both the sulfide and bisulfide ions below 200 mg/l of 63 percent Na₂S appear to be too low to effect sulfidization and a minimum weight ratio of sulfidizing solution to mineral sulfidized of 100 to 1 is sufficient to maintain a constant sulfide ion concentration throughout sulfidization.
INTRODUCTION

Research on the recovery of copper from oxide ores by methods other than leaching is of considerable interest to the copper industry. One of the principal copper oxide minerals is chrysocolla, a hydrated copper silicate.

Chrysocolla ores occur in many areas of the United States and have widely varying properties depending on the origin of the sample. Chrysocolla is usually found in areas associated with the other copper bearing minerals malachite, azurite and cuprite. These minerals are recoverable by present day flotation practice; however, chrysocolla is usually lost in the tailings. Acid leaching is used on ore to recover the copper in chrysocolla; however, acid consuming gangue can make this process economically prohibitive.\(^{1,2}\)

Copper segregation processes or froth flotation processes\(^{(3,4,5,6,7,8,9,10)}\) are the only amenable methods of processing chrysocolla other than by conventional hydrometallurgical methods. Of the two processes, froth flotation is of more interest because of the possibility of concentrating the mineral in fewer steps. Presently, chrysocolla is not considered suitable for flotation because no commercially acceptable process is available. Small scale flotation of chrysocolla has been reported in the literature. The U. S. Bureau of Mines studied its froth flotation using fatty acid soap and high xanthate collector\(^{(7)}\); they also studied its flotation using hydrogen sulfide and xanthate.\(^{(6)}\) Ludt and DeWitt suggested the use of butyl, hexyl or octyl substituted malachite green as a collector in chrysocolla froth flotation. Jeckel combined aerofloat 31, pine oil, reagents 404 and 425 with sodium sulfide and zinc hydrosulfide as conditioning
agents, and recovered 98% of the copper from a chrysocolla ore. Petersen and others floated it with the chelating agent potassium octyl hydroxamate and obtained complete recovery at pH 6.0. Parks and Kovacs improved chrysocolla flotation by thermal activation of the ore at 500 to 600°C followed by xanthate flotation. Wright and Prosser have floated chrysocolla with potassium ethyl xanthate and obtained good recovery. Bowdish and Chen suggested sulfidization followed by xanthate flotation. None of these studies have yielded a commercially acceptable process for chrysocolla flotation.

It is believed a further understanding of the sulfidization mechanism may prove of value in the froth flotation of chrysocolla by this method. For this reason a study was made using micro-flotation techniques in an effort to define more clearly the boundary between areas of collectable and non-collectable surfaces as outlined by Bowdish and Chen and to determine other surface properties of chrysocolla.
MINERAL AND SURFACE PROPERTIES

MINERAL

Chrysocolla is found in the oxidation zones of copper ore deposits. It occurs in small openings and cracks and is commonly associated with quartz, malachite and limonite. Being a member of the hydrated copper silicate group, it varies in composition. To a certain extent this composition change can be detected by color changes in the mineral. Chrysocolla color changes include blue, blue-green, pale blue and pale green.

There are many known copper silicates and although they are all similar to chrysocolla in chemical composition, their differences can be detected by x-ray diffraction, differential thermal analysis, thermo gravimetric analysis, and infrared adsorption. Whether chrysocolla is cryptocrystalline or a montmorillonite is in controversy. Chukhrov and Anosov suggest its classification among the montmorillonite minerals having a chemical formula of Cu$_3$(OH)$_2$Si$_4$O$_{10} \cdot n$H$_2$O or Cu$_3.5$(OH)$_2$(AlSi$_3$O$_9$)O$_{10} \cdot n$H$_2$O. Sun, in a detailed description of chrysocolla from the Inspiration Mine in Arizona, suggests that it is a hydrogel with a cryptocrystalline phase of undetermined composition or chemical formula. This controversy has not yet been resolved because chrysocolla samples from different parts of the world have different chemical compositions. However, almost all investigators consider chrysocolla to be a solid solution of CuO, SiO$_2$ and H$_2$O with a general formula of CuOSi$_2$O$_2 \cdot n$H$_2$O.

For this experimental investigation a hand-picked sample of chrysocolla from Inspiration Mine, Gila County, Arizona was used. This
sample was obtained by hand-picking solid blue particles at -3+8 mesh, grinding to 10 mesh and repicking the +28 mesh sizes, cleaning by magnetic separation, and finally grinding and separating into fractions for final magnetic separation. Details of this sample purification may be found in the purification flowsheet, Appendix 1, Figure 7. All subsequent testing was done on a -100+150 mesh fraction called ultra-pure. The chemical analysis of the ultra-pure sample is shown in Table I.

**TABLE I**

CHEMICAL ANALYSIS OF ULTRA-PURE CHRYSOCOLLA
(-100+150 Mesh Fraction)

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>PERCENT BY WEIGHT</th>
<th>MOLE FRACTION</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>CuO</td>
<td>44.09</td>
<td>0.284</td>
</tr>
<tr>
<td>SiO₂</td>
<td>42.58</td>
<td>0.357</td>
</tr>
<tr>
<td>H₂O</td>
<td>12.65</td>
<td>0.357</td>
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</table>

Formula: (CuO)₀.₇₉₅ SiO₂·H₂O

Further analysis of the sample was made by x-ray diffraction. The d spacings observed are shown in Table II along with those observed for chrysocolla by others.
The $d$ spacings as recorded for the ultra-pure sample indicate it to be true chrysocolla as confirmed by the predominant $d$ spacings of 4.29, 1.60, 1.48 and 1.32 in all the chrysocolla patterns.

The ultra-pure sample was examined under the binocular microscope using reflected light and particles of varying blue intensity were found. A smaller mesh fraction, -200+270, was also examined. A definite decrease in the blue intensity was noted in this mesh fraction. It was concluded that the varying intensity of the ultra-pure sample was the result of plate-like particles as opposed to cube-like particles rather than particles of varying copper composition. All the $d$ spacings reported for chrysocolla are assumed to be for the pure mineral.

In conducting the study of the diffraction pattern of chrysocolla, problems were encountered in obtaining clear and distinct peaks. It was
believed that other minerals found in the same ore deposit could help assure the identity of the chrysocolla peaks. A study was then undertaken to analyse the three main non-chrysocolla minerals found in this ore. The three minerals were hand-picked and x-ray patterns were taken. The d spacings observed are shown in Table III. Also shown are the ASTM standards for alpha quartz and malachite.

**TABLE III**

**d SPACINGS OF NON-CHRYSOCOLLA MINERALS**

<table>
<thead>
<tr>
<th>SAMPLE No 1</th>
<th>MALACHITE</th>
<th>SAMPLE No 2</th>
<th>ALPHA QUARTZ</th>
<th>SAMPLE No 3</th>
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<tr>
<td>(Malachite)</td>
<td>ASTM 10-399</td>
<td>(Quartz)</td>
<td>ASTM 5-490</td>
<td>(Unidentified)</td>
</tr>
<tr>
<td>7.38</td>
<td>7.41</td>
<td>4.25</td>
<td>4.26</td>
<td>4.31</td>
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<tr>
<td>5.99</td>
<td>5.99</td>
<td>3.33</td>
<td>3.34</td>
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<td>5.04</td>
<td>5.05</td>
<td>2.46</td>
<td>2.46</td>
<td>3.36</td>
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<tr>
<td>4.70</td>
<td>4.70</td>
<td>2.28</td>
<td>2.28</td>
<td>2.72</td>
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<td>3.68</td>
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<td>3.03</td>
<td>3.03</td>
<td>2.13</td>
<td>2.13</td>
<td>1.85</td>
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<td>2.99</td>
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<td>1.98</td>
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<td>1.70</td>
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<tr>
<td>2.86</td>
<td>2.86</td>
<td>1.82</td>
<td>1.82</td>
<td></td>
</tr>
</tbody>
</table>

These two standards confirmed that alpha quartz and malachite are the main contaminations, along with an unidentified mineral, in the specimens from Inspiration. Spectrographic analysis of the unidentified mineral indicated Fe, Al, Cu, Ba, Mo and Si. The mineral is brick red in color of varying intensity, forms a brown streak, and shows predominant quartz peaks in its x-ray pattern.
SURFACE PROPERTIES

Silica surfaces in water solutions have been depicted as being hydrated. The nature of chrysocolla surfaces should not be appreciably different in water solutions because CuO also exhibits a hydrated surface in water. If chrysocolla is assumed to be CuOSiO$_2$·nH$_2$O, and if in applying the theory of Parks the water of hydration and space charge effects can be neglected in calculating the zero point of charge (ZPC), chrysocolla would have a ZPC of 5.85. To help understand the sulfidizing mechanism, electrophoretic measurements were made to determine the ZPC of chrysocolla. In Figure 1 are presented the results of electrophoretic mobility measurements on ultra-pure chrysocolla.

The difference between this curve and those reported for some other minerals is that at no pH is the charge on chrysocolla reduced to zero. However when all the hydrocomplexes of copper become soluble, at pH 4.0 or below, the effect of CuO is lost and the ZPC of quartz is attainable. If the experimental curve for chrysocolla as it trends downward from about pH 8 to about pH 6.2 is extrapolated to zero point of charge, as indicated by the dashed line, a ZPC value of 5.5 results. This value is within the experimental error of the value calculated.

\[ ZPC_{AB} = f(\text{space charge}) + \left( \frac{1}{1+x} \right) ZPC_A + \left( \frac{x}{1+x} \right) ZPC_B \]

If A = SiO$_2$ and B = CuO

\[ ZPC_A = 2.2 \quad ZPC_B = 9.5 \quad ZPC_{AB} = 5.85 \]

Healy and Jellett have reported similar curves for ZnO in water as a function of pH and they conclude that the ions from dissolutions are hydrolyzed and readorsbbed as polynuclears to generate an equilibrium interface at each pH.
FIGURE 1

ELECTROPHORETIC MOBILITY OF CHRYSOCOLLA

ELECTROPHORETIC MOBILITY (microns/sec per volt/cm)

pH

3 4 5 6 7 8 9 10 11

0 1 2
EXPERIMENTAL

REAGENTS

The sodium sulfide used for all sulfidizing experiments in the present study was in the form of fused chips. The manufacturer, W. H. Curtin Company, stated that the fused chips were "60/62 % Na$_2$S". The sample of chips used was kept in a closed glass container and was analyzed to contain 63% Na$_2$S with the remaining 37% being soluble inert material. All the concentrations referred to in this thesis are in milligrams of 63% fused Na$_2$S chips per liter of distilled water.

The calcium metal used in the adsorbed sulfur analysis work was chemically pure material obtained from J. T. Baker Chemical Company. The calcium was kept in a tightly closed glass container to prevent its reaction with water in the atmosphere.

Potassium n-amyl xanthate was used as the collector in all flotation tests. The manufacturer, American Cyanamid Company, stated that the reagent was pure and is available under the trade name Aero Xanthate 350.

X-RAY DIFFRACTION

The x-ray diffraction patterns were obtained with a North American Philips Company Diffractometer. All the samples of chrysocolla and non-chrysocolla minerals were ground into powders and put into powder sample holders for diffraction studies. The scanning speed used was 1 degree per minute. The slits were 1° divergence and scatter, and the receiving slit was 0.006 inch. All patterns were obtained with a copper x-ray tube operating at 35 kilovolts and 15 milliamps. A nickel filter was used to eliminate copper K$_\beta$ radiation.
ELECTROPHORETIC MOBILITY

The surface charges on chrysocolla at various pH values were measured with a Zeta-meter. This is a commercially available apparatus manufactured by Zeta-meter, Inc., New York, N.Y.. A sample of ultra-pure chrysocolla was ground into powder and stored, in low conductivity water, in a closed container for one week to establish a double layer on the particles. In making the measurements low conductivity water was adjusted to a desired pH using dilute solutions of NaOH or HCl. A very dilute suspension of the conditioned chrysocolla was then added and stirred. This suspension was placed in the Riddick Cell and measurements were made at 100 volts and after each measurement the final pH of the suspension was measured. Detailed operating instructions for this instrument are given in the literature.

SULFIDE ION ACTIVITY AND pH

The sulfide ion activity of each of the sulfidizing solutions was measured with the sulfide ion activity electrode model 94-16 manufactured by Orion Research Incorporated, Cambridge, Mass.. Before any sulfide ion activities were measured this electrode was calibrated in the manner prescribed by its manufacturer in reference 23.

The pH values of the sulfidizing solutions and solutions prepared for electrophoretic measurements were measured using Orion's digital pH meter indicating 0.001 pH units.

 ADSORBED SULFUR

A quantitative method for the determination of adsorbed sulfur on a sulfidized sample has been described by Bowdish and Stahmann. This method was used with a modification in the reaction flask to eliminate the contact with rubber stoppers of the released H₂ and H₂S gases.
Before any adsorbed sulfur analysis work was done, the system was calibrated using a standard solution of sodium thiosulfate to standardize the lead acetate coated sand prepared as indicated in reference 24. A known amount of 0.001537 N sodium thiosulfate, ranging from 2 ml to 8 ml, was added to the reaction flask with 15 ml of distilled water and 10 grams of aluminum chips. The flask was then assembled as shown in Figure 2 and 30 ml of 1:6 HCl solution was added. The flask was then submerged in a water bath at 50°C and the H₂S, swept out by the evolving hydrogen, reacted with the lead acetate forming a lead sulfide stain in the adsorption column. In this manner the lead acetate coated sand was standardized and from the known amount of sulfur in the standard solution the calibration for adsorbed sulfur was made. The results indicate that 1 ml of sand is equivalent to 0.169 mg of sulfur. The calibration curve for milligrams of adsorbed sulfur vs. milliliters of lead sulfide stain may be found in Appendix 2, Figure 8.

Samples sulfidized and dried were analyzed for the small quantity of sulfur adsorbed on the chrysocolla surface by fusing them with metallic calcium to form calcium sulfide. Calcium sulfide would then release the sulfur in the form of H₂S when the unstable compound was reacted with a dilute solution of HCl. The procedure of fusion and evolution was as outlined in reference 24.

**SULFIDIZATION**

Sulfidization was accomplished in 450 ml beakers with constant magnetic stirrer agitation. The sulfidizing solution was prepared by adding a weighed amount of fused Na₂S chips to a 1000 ml volumetric flask and diluting with distilled water. Fresh solution was used for each series of three sulfidizations. The solution was adjusted to the
FIGURE 2

ADSORBED SULFUR DETERMINATION

APPARATUS

The adsorption of sulfur could be measured by adding a solution of sodium bisulphide to a solution containing the adsorbed sulfur. The activity of the sulfur was determined by measuring the change in the density of the solution. After adding the sodium bisulphide, the solution was allowed to react for 15 minutes. Subsequently, the solution was filtered and the filtrate was analyzed for sulfur content.
desired pH using a dilute solution of HCl. Once a desired pH level was reached, if further base was needed to maintain the pH, sodium sulfide solution of the same concentration as used in the particular experiment was added. The sulfide ion electrode was then used to measure the sulfide ion activity of the solution.

It was determined by repeated experiments that 1200 ml of sulfidizing solution was needed per gram of chrysocolla to effect sulfidization with no more variation than six millivolts in the measurement of sulfide ion activity. A six millivolt variation in readings, equivalent to a change in sulfide ion activity of 2% of the total range covered during experimentation, was tolerated during a ten minute sulfidization period because this is the normal variation during a ten minute period of solution agitation without a chrysocolla sample. Approximately 0.250 gram of chrysocolla was used in each sulfidization and this was added to 300 ml of adjusted solution. Readings of pH and sulfide ion activity were then made at two minute intervals throughout the ten minute sulfidization period.

After decantation of the sulfidizing solution, the sulfidized sample was washed with three 100 ml portions of distilled water, decanting between washings. After the final decantation the sample was either transferred immediately to the pur cell for non-aged flotation, or was dried for 25 minutes at 40°C and then placed in the cell for dry-aged flotation.

**MICRO FLOTATION**

Many micro flotation techniques have been used with success. In the present study a pur cell was assembled as shown in Figure 3 for all flotation tests. The cell was filled to within one
FIGURE 3
PUR CELL MICRO FLOTATION APPARATUS

(1) reservoir
(2) volume controller
(3) three-way stopcock
(4) air trap
(5) rate control valve
(6) pur cell, loading position
   a, conditioning position
   b, floating position

The pur cell was calibrated and optimized before any micro flotation tests were made. The procedure for calibration outlined in Reference 27 was used. This indicates that the highest contact angle was achieved for chrysanthemum U-8 with a concentration of 50 milligrams per liter of Na3PO4. Table 3 shows the results of the calibration run. The results may be found in Appendix 3. Figure 7 illustrates the variation of recovery with flotation time.

![Diagram of PUR CELL MICRO FLOTATION APPARATUS](image-url)

The flow rate at constant flotation conditions is 0.783 cm/sec. It indicates that a flow rate of 0.783 cm/sec is sufficient to achieve recovery that is nearly 100% maximum. Each value reported in this investigation is an average of triplicate runs using 30 milligrams per liter of collector with complete drying of the sample, at 40°C, after sulfonation and before flotation. These results confirm the flow rate of 0.783 cm/sec of air and a flotation time of one minute as optimum for sulfides in this flotation in the...
inch of the top with a 30 mg per liter collector solution of potassium n-amyl xanthate, (Aero xanthate 350). Care was taken to eliminate all bubbles from the filled cell. A sulfidized sample of chrysocolla was then added to the cell, time noted, cell filled completely and clamped to insure no air entrapment. The sample was then conditioned in the cell for 15 minutes by agitation of the cell by hand. The clamp was removed and a 5 ml portion of the collector solution was pipetted off before adjusting the cell in the flotation position (see Figure 3). The air was then admitted at a metered rate for one minute and the floated product was collected, dried and weighed.

The pur cell was calibrated and optimized before any micro flotation tests were made. The procedure for calibration outlined in reference 27 was used. Chen indicates that the highest contact angle was achieved for chrysocolla sulfidized at pH 4.0 with a concentration of 400 milligrams per liter of Na₂S chips. These conditions were used in the pur cell optimization. The results of this optimization may be found in Appendix 3. Figure 9 illustrates the variation of flotation recovery with gas flow rate at constant flotation time. It indicates that a flow rate of 0.788 cc/sec is sufficient to obtain nearly the maximum recovery in one minute. Figure 10 shows the variation of recovery with flotation time at a constant air flow rate of 0.788 cc/sec. It indicates that a flotation time of one minute is sufficient to obtain a recovery that is nearly the maximum. Each value reported in this optimization is an average of triplicate runs using 30 milligrams per liter of collector with complete drying of the sample, at 40°C, after sulfidization and before flotation. Thus a flow rate of 0.788 cc/sec of air and a flotation time of one minute is an optimum for sulfidized chrysocolla flotation in the
pur cell because nearly maximum recovery is obtained without an excessive air rate or flotation time.

The recovery between areas of collusable and uncollectable surfaces of sulfidized chrysocolla was studied by Sowark and then using a constant angle apparatus. Three flotation techniques were employed in the study to try to confirm this geometry and to further the understanding of the sulfidization mechanism in chrysocolla flotation.

The sulfidation procedure then used is illustrated. An isometric angle sketch shows the sulfidated chrysocolla with three 500-ml portions of distilled water, alternating between washings and transferring after the two decantations immediately to the flotation tank. In washing the sulfidated samples, Cahn used a direct stream of tap water. Experiments indicate that the length of time for washing and the velocity of water were not defined by them. To further indicate that the washing procedure for non-aged flotation should produce a close approximation of the sulfidated surface used by them in flotation single measurements.

Flotation tests were made on samples sulfidated, washed and dried without drying, which was both collectable and non-collectable surfaces as defined by Cahn's index of separability. This index is shown in Figure 4, with the percent indicating the sulfidation conditions tested. The results of these flotation tests, as presented in Table IV, show that there is essentially no flotation at one of the points tested. At the 95% confidence level all the recoveries reported may be considered, within the limits of experimentation, to be equal with an average recovery of 93.2%. The recovery results for uncollectable chrysocolla using a similar sample and stirring it in the same manner.
RESULTS

NON-AGED FLOTATION

The boundary between areas of collectable and non-collectable surfaces of sulfidized chrysocolla was defined by Bowdish and Chen using a contact angle apparatus. Micro flotation techniques were adopted in this study to try to confirm this boundary and to further the understanding of the sulfidization mechanism in chrysocolla flotation.

The sulfidization procedure Chen used in his contact angle study followed somewhat that which is called non-aged flotation here: washing the sulfidized chrysocolla with three 100 ml portions of distilled water, decanting between washings and transferring after the last decantation immediately to the flotation cell. In washing the sulfidized sample Chen used a direct stream of tap water. Bowdish indicates that the length of time for washing and the velocity of the running water were not defined by Chen. He further indicates that the washing procedure for non-aged flotation should produce a close approximation of the sulfidized surface used by Chen in contact angle measurements.

Flotation tests were made on samples sulfidized, washed and floated at once without drying, which had both collectable and non-collectable surfaces as defined by Chen's island of bubble contact. This island is shown in Figure 4 with the points indicating the sulfidization conditions tested. The results of these flotation tests, as presented in Table IV, show that there is essentially no flotation at any of the points tested. At the 95% confidence level all the recoveries reported may be considered, within the limits of experimentation, to be equal with an average recovery of 5.43%. The recovery found for unsulfidized chrysocolla using a washed sample and floating it in the same manner
FIGURE 4

CHEN'S BUBBLE CONTACT ISLAND
WITH NON-AGED FLOTATION EXPERIMENTAL COVERAGE

CONCENTRATION, MG/LITER 63% Na₂S

pH

uncertain contact

no bubble contact

bubble contact

4.0 5.0 6.0

300 400 500 600 700

COnCENTrATION, MG/LITER 63% Na₂S
# RESULTS OF NON-AGED FLOTATION TESTS ON CHRYSOCOLLA SULFIDIZED FOR 10 MINUTES, WASHED, AND FLOATED AT ONCE IN 30 MG/LITER OF POTASSIUM N-AMYL XANTHATE

## TABLE IV

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TABLE IV (continued)

SULFIDIZATION CONDITIONS

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with 50 milligrams per liter as sulfide ion added. Thus, regardless of the concentration of sulfur in the solution, activity of the sulfide ion at the sulfidized sample before flotation was found to yield floatable chalcopyrite. With the optimum recovery being 29% for the flotation procedure, an alternate procedure, dry-aging flotation, was adopted for some of the sulfidized chalcopyrite to determine flotation yield. In dry-aging flotation experiments, after the chalcopyrite had been sulfidized, the sample was transferred to a watch glass and allowed to dry for 24 minutes at 40°C. This procedure is similar to that described by Moos and Stahlman on their treatment of sulfidized chalcopyrite before determination of the dissolved sulfur. During all of the dry-aged flotation experiments, as in the air-aged flotation experiments, Na₂S concentration, temperature, pH, sulfide ion activity, and elapsed time of sulfidation were evaluated as well as drying time and temperature. The results of the dry-aged flotation experiments, presented in Table 5, also demonstrating the effect of pH in the range from 4.00 to 4.40. In this range the recovery is apparently independent of sodium sulfide concentration, over the range of Na₂S concentrations from 300 to 700 mg/liter, and is only dependent upon the pH of the sulfidizing solution. This result is shown graphically in Figure 3 where recovery is plotted as a function of sulfidization pH only.
with 30 milligrams per liter of collector was 4.31%. Thus, regardless of the concentration of Na$_2$S, sulfide ion activity, or pH, no appreciable flotation could be realized on sulfidized chrysocolla which was washed, left wet, and floated at once. It may be concluded from these results that Chen's island of bubble contact is not reproducible by micro flotation experiments performed in this manner.

**DRY-AGED FLOTATION**

During the calibration of the pur cell apparatus, drying of the sulfidized sample before flotation was found to yield floatable chrysocolla with the optimum recovery being 77%. This alternate procedure, dry-aged flotation, was adopted for some of the sulfidized chrysocolla micro flotation work. In dry-aged flotation experiments, after the final wash decantation, the sample was transferred to a watch glass and allowed to dry for 25 minutes at 40°C. This procedure is similar to that described by Bowdish and Stahmann as their treatment of sulfidized chrysocolla before determination of the adsorbed sulfur.

During all of the dry-aged flotation experiments, as in the non-aged flotation experiments, Na$_2$S concentration, temperature, pH, sulfide ion activity, and elapsed time of sulfidization were recorded as well as drying time and temperature. The results of the dry-aged flotation experiments, presented in Table V, show decreasing recovery values as the pH increases from 4.00 to 5.40. In this region the recovery is apparently independent of sodium sulfide concentration, over the range of Na$_2$S concentrations from 250 to 700 mg/liter, and is only dependent upon the pH of the sulfidizing solution. This result is shown graphically in Figure 5 where recovery is plotted as a function of sulfidization pH only.
Table V

RESULTS OF DRY-AGED FLOTATION TESTS ON CHRYSOCOLLA
SULFIDIZED FOR 10 MINUTES, WASHED, DRYED AT 40°C
FOR 25 MINUTES AND FLOATED IN 30 MG/LITER OF
POTASSIUM N-AMYL XANTHATE

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FIGURE 5

RECOVERY OF CHRYSOCOLLA VS SULFIDIZATION pH

An experiment was designed to verify the dependence of flotation recovery on aging. A sample was selected as a possible mechanism of aging. In this experiment, a sample was sulfidized, washed, and split in half; one half was floated using the non-aged flotation technique and one half was aged in distilled water. The water was decanted from the aging sample at time intervals and analyzed for sulfur content. When no sulfur was detected in the decanted water, indicating no further sulfur dissociation, the aged sample was floated without being allowed to go out. The results of these tests may be found in Table VI. They support the conclusion that aging of the sulfidized sample is a significant factor in the flotation recovery of sulfidized chrysocolla, and it may be concluded also that sulfur, in some form, is eliminated during aging and through the elimination the sulfidized sample becomes floatable.
SOLUTION AGING

The difference in the recovery by flotation between that obtained on non-aged and dry-aged sulfidized chrysocolla was believed to be caused by a difference in the surfaces resulting from aging of the sulfidized sample. In drying the sulfidized sample the attainment of a surface that is stable under the changed conditions was accelerated and achieved by forcing an equilibrium shift through the heating process.

An experiment was designed to verify the dependance of flotation recovery on aging and to indicate a possible mechanism of aging. In this experiment a sample was sulfidized, washed, and split in half; one half was floated using the non-aged flotation technique and one half was aged in distilled water. The water was decanted from the aging sample at time intervals and analysed for sulfur content. When no sulfur was detected in the decanted water, indicating no further sulfur dissociation, the aged sample was floated without being allowed to dry out. The results of these tests may be found in Table VI. They support the conclusion that aging of the sulfidized sample is important to the flotation recovery of sulfidized chrysocolla. It may be concluded also that sulfur, in some form, is eliminated during aging and through its elimination the sulfidized sample becomes floatable.
TABLE VI
EFFECT OF SOLUTION AGING ON SULFIDIZED
CHRYSOCOLLA FLOTATION

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</tbody>
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Mg S desorbed 0.01 0.03 0.01 0.00

3.75 Mg S cumulative 0.01 0.04 0.05 0.05

81.2

SAMPLE SIZE 0.2278

CONCENTRATION 500 Mg/Liter

63% Na₂S pH 4.30

SULFUR ADSORPTION

The results of Bowdish and Stahmann indicated that the amount of sulfur adsorbed on chrysocolla in the pH region of 4.20 to 6.00 was constantly decreasing with increasing pH. It was believed that a direct relationship between recovery, pH, and adsorbed sulfur could be established using their technique for the analysis.

Determinations were made of the amount of sulfur adsorbed from solutions containing 300 and 600 mg of 63% Na₂S per liter at pH values of 4.20, 4.60, and 5.00. The results presented in Table VII show an average decrease of 20.5 percent in adsorption for this range of pH increase. The data also show the effect of mass action of the dissolved sulfide; doubling the sulfide solution strength caused an average 60.2 percent increase in sulfur adsorption.
TABLE VII
CONCENTRATION AND pH EFFECTS ON ADSORBED SULFUR

Mg S Adsorbed/Mg Sample

<table>
<thead>
<tr>
<th>pH</th>
<th>300 Mg/Liter 63% Na₂S</th>
<th>600 Mg/Liter 63% Na₂S</th>
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<tr>
<td>4.20</td>
<td>0.0132</td>
<td>0.0202</td>
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<tr>
<td>4.60</td>
<td>0.0120</td>
<td>0.0193</td>
</tr>
<tr>
<td>5.00</td>
<td>0.0105</td>
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MINIMUM SODIUM SULFIDE CONCENTRATION FOR SULFIDIZATION

In the application of sulfidization to chrysocolla and its flotation, (30) a minimum concentration of sodium sulfide in solution is important. (11) Chen in his thesis has made all his results a function of sodium sulfide concentration.

Sodium sulfide is a salt of a strong base and a weak acid; in an aqueous solution its reactions may be visualized as starting with hydrolyses, thus:

\[ \text{Na}_2\text{S} + 2\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + \text{H}_2\text{S} + 2\text{OH}^- \]

As a result of hydrolysis, hydroxide ions and hydrogen sulfide appear in solution. The latter is dissociated with the formation of the bisulfide ion,

\[ \text{H}_2\text{S} \rightarrow \text{H}^+ + \text{HS}^- \]

which in turn dissociates into hydrogen and sulfide ions,

\[ \text{HS}^- \rightarrow \text{H}^+ + \text{S}^2^- \]

It is thus seen that the activities of sulfide ion, bisulfide ion, and hydrogen sulfide in solution are dependant on pH also, and that a given concentration of Na₂S could produce different activities of each of these depending on the pH. In the present study activities of the sulfide ion were measured with the sulfide ion electrode, and thus in
conjunction with pH the activities of the bisulfide ion and hydrogen sulfide could be calculated.1 (Values of $K_{HS^{-}}$ and $K_{H_{2}S}$ as a function of temperature are presented in Appendix 4)

Chen, as seen in Figure 4, indicates an area of uncertain contact below his island of bubble contact. In this area the effect of $Na_{2}S$ concentration and pH on the sulfidizing of chrysocolla could not be determined definitely. Below a concentration of 100 mg/liter of $Na_{2}S$ (4) Chen has reported a region of no bubble contact. In the present study, with the aid of the sulfide ion electrode, an attempt was made to measure the minimum sodium sulfide concentration for sulfidization. The results of these measurements are shown in Figure 6. In this figure the concentration of 63% $Na_{2}S$ is plotted as a function of pH at constant sulfide and bisulfide activities. Above an $Na_{2}S$ concentration of 250 mg/liter the sulfide and bisulfide ion activity is nearly independent of concentration and is controlled entirely by pH. This was also verified for concentrations of 400, 500, 600, and 700 mg/liter

$H^{+} + S^{=} = HS^{-}$

$$K_{HS^{-}} = \frac{(a_{HS^{-}})/(a_{H^{+}})(a_{S^{=}})}{a_{H^{+}}^{2}} = 7.94 \times 10^{12} \text{ (at 25°C)}$$

$$\log a_{HS^{-}} = \log K_{HS^{-}} + \log a_{S^{=}} + \log a_{H^{+}}$$

$$\text{pH} = - \log a_{H^{+}}$$

thus

$$\log a_{HS^{-}} = \log K_{HS^{-}} + \log a_{S^{=}} - \text{pH}$$

Also

$$2H^{+} + S^{=} = H_{2}S$$

$$K_{H_{2}S} = \frac{(a_{H_{2}S})/(a_{H^{+}}^{2})(a_{S^{=}})}{a_{H^{+}}^{2}} = 8.92 \times 10^{19} \text{ (at 25°C)}$$

and

$$\log a_{H_{2}S} = \log K_{H_{2}S} + \log a_{S^{=}} - 2\text{pH}$$
Near 150 mg/liter of Na₂S the activity of the sulfide and bisulfide ion is more dependent upon small changes in concentration than upon pH. At pH values from 4.00 to 6.10, the range in which chrysocolla may be sulfidized for flotation, concentrations of Na₂S below about 200 mg/l will give rapidly decreasing sulfide and bisulfide ion activities as a function of pH and concentration. In this range of pH the activities of both the sulfide and bisulfide ions are very low and extremely difficult to control. It was concluded that the activities of both the sulfide and bisulfide ions below about 200 mg/l of 63% Na₂S appear to be too low to effect sulfidization and this establishes a minimum sodium sulfide concentration for sulfidization.
**Figure 6**

Minimum Sodium Sulfide Concentration for Sulfidization

- **Activity** $\text{HS}^-$
- **Activity** $\text{S}^-$

**Graph Details:**
- **Concentration, mg/liter $63\%$ Na$_2$S**
- **pH Range:** 4.0 to 9.0
- **Concentration Values:**
  - 300 mg/l
  - 250 mg/l
  - 200 mg/l
  - 150 mg/l

**Scaling:**
- pH axis
- Concentration axis

**Data Points:**
- various pH and concentration values

**Notes:**
- This graph illustrates the minimum sodium sulfide concentration required for sulfidization under different pH conditions.
DISCUSSION OF RESULTS

GENERAL

The results of the electrokinetic measurements of chrysocolla in the range of pH from 6.10 to 10.40 can be explained by examining the electrokinetics of CuO and SiO$_2$ independently, using the theory of Parks (19). This theory states that by using the electrokinetic measurements of SiO$_2$ and CuO separately the electrokinetic charge of the combined CuO SiO$_2$ may be calculated at any pH by applying a weighted equation similar to the ZPC$_{AB}$ equation in footnote 1 page 7. From pH 4.30 to pH 3.70 the measurements may be interpreted as being those for SiO$_2$, the copper oxide being soluble. In the pH range from 6.10 to 4.30, however, the electrophoretic charge on chrysocolla increases negatively, and this can be explained by the formation of polynuclear complexes of copper with water at the surface which decreases the effective plus charge, thus causing an overall increase in the negative charge on the surface.

Another explanation of the increasing negative charge in this pH range may be found in examining the principle hydroxo-aquo Cu (II) species in water at 25°C. In Appendix 5, Figure 11, the concentrations of hydrolyzed and other Cu (II) species in equilibrium with solid Cu(OH)$_2$ are represented as functions of pH. The literature values of stability constants for these species are summarized in Table IX of Appendix 5, and although the polynuclear complexes of water with copper are present in the system, more evident is the fact that at pH 6.10 copper becomes soluble and forms cupric ions in solution. This then suggests another reason for the increase in the negative charge on chrysocolla in the pH
range from 6.10 to 4.30. It is believed that at pH 6.10 incipient leaching of copper begins, leaving vacated sites on the surface causing the increase in negative charge. At pH 4.30 the surface begins to behave as an SiO$_2$ surface and this results in an electrophoretic mobility curve comparable to that of SiO$_2$.

This incipient leaching range of pH is nearly identical to the range in which chrysocolla can be sulfidized and floated, which extends to pH 4.00. The recovery of chrysocolla as well as the amount of sulfur adsorbed on the surface from solutions of the same concentration increases as the pH decreases to 4.00. The increase in recovery as pH is lowered is believed to be due to the increased incipient leaching of the chrysocolla at these pH values and the increased availability of copper ions on the surface. Sulfidization can and does take place below pH 4.00; however, the copper ions are removed from the surface at lower pH values and a detachable copper sulfide surface film, as described by Chen, is formed which will not aid in flotation.

The fused sodium sulfide chips used in this study were not all of the same percent Na$_2$S. In selecting chips to prepare sulfidizing solutions the most uniform and even colored ones were used. The chips were kept in an air tight glass container throughout the experimental study. Errors caused by the use of low Na$_2$S content chips would result in extremely small variations in sulfide ion activities during sulfidization which would have little or no effect on the recoveries reported.

The concentrations of bisulfide ion and hydrogen sulfide as well as sulfide ion in solution are functions of temperature as evidenced by the equilibrium constants in Appendix 4. There were some temperature variations during the course of this investigation. The temperatures
ranged from 22° to 25°C recorded as the room temperature during the sulfidization. No actual measurement of the temperature of the sulfidizing solution was made. All the solution make-up distilled water was at room temperature and its temperature was assumed to be unaffected by the stirring during sulfidization.

The measured sulfide ion activities were checked against the calculated sulfide ion concentrations for each solution using the pH and the concentration of sodium sulfide used to make-up the sulfidizing solution. It was found in these calculations that the difference between the calculated sulfide ion concentrations and the actual measured sulfide ion activities can be attributed to the activity coefficients, found in reference 23, needed to convert from concentration to activity.

It may be noted that the optimum recovery of 77% was achieved during the optimization of the pur cell. This recovery is low compared to the 89% obtained for samples sulfidized at pH 4.00 and dry-aged; this may be the result of using low grade chrysocolla samples for the cell optimization. These samples were used to conserve the more pure sample and the results of the optimization with them are assumed to apply to all of the samples used. A conditioning time of 15 minutes was recommended by Chen (11) and is assumed to be adequate. Chen also recommended the use of 30 mg/liter of collector potassium n-amyl xanthate. Rogers (31) and Wark (32) state that high collector concentrations may inhibit mineral flotation and that if on a given mineral surface there is an effective depressant, the concentration of the collector does not greatly influence the mineral's response to the collector (33). Knowing these facts, coupled with the results of Chen's testing, the use of 30 mg/liter of potassium n-amyl xanthate is assumed adequate.
The use of micro flotation techniques, in particular the Pur cell, is limited by the condition of the collector, the cleanliness of the cell, the adequacy of the flotation time and the experimenter’s ability in collecting the products. The temperature and pH of the collector were not controlled nor recorded throughout the entire study. Room temperature can be assumed a good measure of the temperature and is recorded in the sulfidization experiments. The pH of the 30 mg/liter xanthate collector solution was 5.90. Both temperature and pH were eliminated as variables in the flotation experiments because of similar conditions in all the experiments. Fresh xanthate solutions were prepared for each series of eight tests. This eliminated the effect of collector deterioration as proven by experimentation. Each cell was thoroughly cleaned following each test and the Tygon flexible joints were replaced after each series of tests. The conditioning of the sulfidized chrysocolla was accomplished in the cell in a gas free media, and immediately following conditioning the sample was floated. The one minute flotation time appeared to be adequate for this system; however, slightly greater recoveries would have been realized by using longer flotation times. The flotation time is relative, however, and it was assumed that all the recoveries vary in the same proportion.

Due to the limitations of the micro flotation technique a within sample variation of \( \pm 3.2\% \) recovery was realized for dry-aged flotations and \( \pm 1.7\% \) recovery for non-aged flotations. This measure of experimental error can explain the range of recoveries reported at each pH in Table V and Figure 5 and limits the use of this technique. These errors in the micro flotation technique make it impossible to determine the small effect, if any, of sodium sulfide concentration on recovery.
over the range of concentrations tested.

The adsorption experiments indicated dependency of the amount of sulfur adsorbed on the sodium sulfide concentration (see Table VII). The increase in the amount of sulfur adsorbed with a two-fold increase in the concentration of sodium sulfide of 60.2% may not be enough to effect greater recoveries.

The experimental evidence from the microflotation tests and the adsorption tests is not completely adequate to prove the dependency or non-dependency of recovery on the sodium sulfide concentration.

There is a 5 fold difference between the adsorbed sulfur reported by Bowdish and Stahmann and that reported in this investigation. Bowdish and Stahmann's low values are believed to have been caused by their failure to maintain a minimum sulfidizing solution to sulfidized material weight ratio of 100 to 1. It was found, as explained in the sulfidization section of this thesis, that a depletion of the sulfide and bisulfide ion activities could be detected during agitation without a chrysocolla sample, due to the evolution of \( \text{H}_2\text{S} \) gas and equilibrium shift to maintain the \( \text{H}_2\text{S} \) concentration, and that the minimum weight ratio of 100 to 1 is needed during sample sulfidization. Bowdish reported the approximate weight ratio of 70 to 1 in their study. Tests on this ratio have yielded depletion of the sulfide and bisulfide ion activities. A low sulfide and bisulfide ion activity in the sulfidizing solution would then give rise to low adsorption, as demonstrated by the mass action effect of concentration change in Table VII, and would explain the differences in the adsorbed sulfur reported.

The fusion technique for measuring the adsorbed sulfur on the surface of chrysocolla was investigated as to its effectiveness. It
was believed and verified that during the fusion of the sample with calcium some sulfur is eliminated and lost. A column of lead acetate coated sand was placed above the sulfidized sample and calcium before fusion. During the heating to effect fusion a trace of sulfur, in amount unmeasurable, was detected, perhaps indicating incomplete aging of the sample.

The results of the aging studies in water could explain the difference between Chen's island of collectable and non-collectable surfaces and the non-floatable surfaces reported in the present investigation. Chen washed the sulfidized samples under a stream of tap water and then rinsed them in distilled water. This washing could have accelerated the solution aging process and as a result his island of collectable and non-collectable surfaces may represent a partially aged surface condition.

Aging was controlled in the present study by an adequate 40°C, 25 minute drying period to accelerate the aging rate after which flotation of the sample resulted as a function of sulfidization pH only. The effect of aging was demonstrated by the dissolution of sulfur into a water solution as a function of time (see Table VI). The elimination of sulfur during aging suggests a possible mechanism for sulfidization and explains why aging is important and what is accomplished.

**PROPOSED MECHANISM**

From the electrophoretic mobility, non-aged flotation, dry-aged flotation and solution aging study results it is proposed that the mechanism of sulfidization of chrysocolla and subsequent flotation is related to the amount of copper ions present on the mineral surface and
to the extent to which the elimination of H$_2$S from the sulfidized surface takes place during aging.

If in the pH range of 6.10 to 4.30 the increase in the negative charge on the chrysocolla is caused by vacated copper sites and by copper's incipient leaching, it is believed that hydroxylated copper ions begin to leave the surface of the mineral at pH 6.10, where copper becomes soluble (see Appendix 5, Figure 11). This may be shown as:

\[
\begin{align*}
\text{CuOH}^+ + \text{CuOH}_2^- & \rightarrow \text{CuOH}^+ + \text{CuOH}_2^- \\
\text{CuOH}_2^- & \rightarrow \text{CuOH}^+ + \text{H}_2^+ 
\end{align*}
\]

As the pH is lowered more copper vacates the surface and the concentration of Cu(OH)$^+$ increases as the concentration of the hydrogen increases until pH 4.40 where Cu(OH)$^+$ becomes soluble (see Appendix 5, Figure 11). The Cu(OH)$^+$ ions are then free to move into solution and at this pH the chrysocolla begins to behave as if no copper were present or as if only a quartz surface were present.

If the sulfidizing mechanism results in the formation of non-collectable sites as indicated by non-aged flotation experiments, the reaction between chrysocolla and the HS$^-$ ion would be;
The formation of a collectable surface as demonstrated by dry-aged flotation and solution aging studies may then be a non-collectable surface made collectable by $H_2S$ elimination.

The surface thus formed is then collectable and forms a suitable site for collector anions as Chen suggests. (xanthate ion is...
The representation of the copper on the surface as a hydroxylated ion is dictated by chrysocolla's behavior, in the pH range from 6.10 to 10.40, as an oxide mineral whose potential determining ions are H\(^+\) and OH\(^-\). This accounts for the immediate pH rise on the addition of chrysocolla to an unbuffered solution in the pH range from 4.00 to 8.00,

\[
\begin{align*}
&\text{CuOH}_2 + \text{H}_2\text{O} \rightarrow \text{CuOH}^+ + \text{OH}^- \\
&\text{CuOH}_2 + \text{S} + \text{K}^+ + \text{Z}^- \rightarrow \text{CuOH}_2\text{S K} + \text{CuOH}_2\text{Z}
\end{align*}
\]

It has been shown that a sulfide surface can become collectable with xanthate under proper conditions, and that the presence of more than a certain concentration of bisulfide ion will form a non-collectable surface on a sulfide surface. These facts lead to the deduction that collectable sites on chrysocolla should be copper sulfide sites while non-collectable sites should be copper bisulfide sites.

It has been indicated that if the concentration of the bisulfide ion in a solution is very much larger than the concentration of the sulfide ion, the bisulfide ions could combine with copper to form...
an unstable intermediate which breaks down to form copper sulfide and liberate \( \text{H}_2\text{S} \). Such processes are known in the formation of oxides by precipitation. (Intermediate \( \text{Cu(OH)}_2 \) changing to \( \text{CuO} \) on heating).

Since sulfur and oxygen are in the same group in the periodic system, and hydrogen sulfide is therefore the analogue of water, it could be expected that an unstable bisulfide could be formed first with the breakdown of this bisulfide to a sulfide and the elimination of \( \text{H}_2\text{S} \).

As can be seen in Tables IV and V, the concentration of bisulfide ion is approximately \( 10^6 \) times greater than the concentration of the sulfide ion in all the sulfidizing solutions. Thus the sulfidization of chrysocolla could be expected to proceed by the above bisulfide mechanism.

The extent of formation of non-collectable sites is dependent upon the hydroxylated copper ions on the surface which is dependent upon the pH of the sulfidizing solution and has not been measured.
CONCLUSIONS

From the results of this investigation it can be concluded that:

1. Sulfidized chrysocolla, washed but not dried, could not be floated using microflotation techniques.

2. Chen's island of collectable and non-collectable surfaces of sulfidized chrysocolla was not reproduced by microflotation experiments.

3. Activities of both the sulfide and bisulfide ions below 200 mg/l of 63% Na₂S appear to be too low to effect sulfidization of chrysocolla.

4. A minimum ratio of sulfidizing solution to mineral sulfidized of 100 to 1 must be used during sulfidization to maintain a constant sulfide ion concentration.

5. Flotation recoveries of up to 89% were obtained on samples of sulfidized chrysocolla aged by drying or by extended soaking in water.

6. Solution aging of sulfidized chrysocolla resulted in the loss of sulfur from chrysocolla to the water.

7. Flotation recovery of aged sulfidized chrysocolla depended upon the pH of sulfidization and not upon the concentration of the solution, provided it was above 200 mg/l.
RECOMMENDATION FOR FUTURE STUDY

It was made evident from the results of this study that the attainment of a stable surface of sulfidized chrysocolla is necessary before flotation can take place. This would suggest further aging studies on sulfidizable minerals. The rate at which more stable surfaces are formed may be measured and controlled by using the sulfide ion electrode coupled with adsorbed sulfur studies. The length of time for sulfidization may be important and related to chrysocolla recovery. Further studies of this variable are suggested.

Further studies also suggested are the investigation of other sulfidizable oxide minerals and the surface charge on their particles as a function of pH. It may be found that similar electrokinetic curves exist for these minerals which would explain their regions of collectable and non-collectable surfaces resulting from sulfidization. Also studies on the electrophoretic mobility of sulfidized particles might indicate other approaches to chrysocolla flotation.

The region of incipient leaching, pH 4.30 to 6.10, should be studied to determine the extent and rate of this phenomena.


34. Bowdish, F. W., Personal Communication.


38. Fuerstenau, D. W., and Aplan, F., Froth Flotation, ibid, Chapter 5.


40. Sutherland, K. L., and Wark, I. W., Principles of Flotation, ibid, pp. 113-1533.


FIGURE 7
CHRYSOCOLLA ORE PURIFICATION

Lumps
- crush to -3 mesh
- screen at 8 mesh
- -8 mesh reject 3 to 8 mesh hand pick
- rolls to 10 mesh blue particles
- screen into fractions
- hand pick to +2 8 mesh
- reject
- blue particles
- Frantz isodynamic separation of fractions
- non-magnetic reject
- magnetic chrysocolla
- hand pick unliberated particles
- reject chrysocolla
- rod mill, stage screen to pass 4 8 mesh
- screen into fractions
- Frantz separation of fractions
- non-magnetic light chrysocolla 33.4 % Cu
- magnetic chrysocolla ultra-pure 352 % Cu
FIGURE 2

LEAD ACETATE SAND STANDARDIZATION

Appendix 2
FIGURE 8

LEAD ACETATE SAND STANDARDIZATION

MILLILITER LEAD SULFIDE STAIN

MILLIGRAM ADSORBED SULFUR
APPENDIX 3

Figure 9
Flotation Cell Optimization
Flotation Time: 1 Minute

Chrysocolla sulfided at
pH 4.00 and 400 mg/l
63% Na₂S
10% Na₂S

% Recovery

Air Flow Rate, SCFM

Graph showing the relationship between air flow rate and percent recovery.
Figure 9

Chrysoberyl sulfidized at
pH 4.00 and 400 mg/l
63% Na₂S

Pur Cell Optimization
Air Flow Rate 0.7 cc/sec
Flotation Time 1 Minute

% Recovery

Air Flow Rate, cc/sec

Flotation Time, sec
FIGURE 10
PUR CELL OPTIMIZATION
AIR FLOW RATE 0.788 cc/sec

chrysocolla sulfidized at
pH 4.00 and 400mg/l
63% Na₂S

% RECOVERY

30 60 90

FLOTATION TIME, SEC.
<table>
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<tr>
<th>TEMPERATURE, °C</th>
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<th>$\log K_{HS^-}$</th>
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