

SULFIDE FILMING AND FLOTATION OF CHRYSOCOLLA

by

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CHAPTER I - INTRODUCTION

The porphyry ore-bodies in the Southwest contain both copper sulfide and oxidized copper minerals. The sulfide minerals are readily concentrated by flotation. Although concentration of oxidized minerals by flotation methods by the Kennecott Copper Company in Alaska was successful, many other large and small scale attempts have failed. Chapman¹ has stated that, "present recoveries of oxide copper contained in feeds to flotation plants range from 15 to 60 per cent, most mills reporting a recovery of less than 40 per cent for 1929 and 1930." The general failure of flotation methods to solve the copper oxide problem led to adoption of other methods by the large copper companies for the recovery of oxidized copper, namely, leaching by the New Cornelia Company at Ajo, Arizona, and leaching followed by precipitation and flotation of the cement copper by the Miami Copper Company at Miami, Arizona.

Sulfidizing of oxidized minerals for the recovery of copper and lead by flotation methods has been the basis of considerable experimental work, and in the case of lead,

1. Chapman, T. G., Concentration of Copper Ores in North America, Bull. 392, U. S. Bureau of Mines, 1936, p. 13.

used commercially in the past. A survey of the literature by the writer shows the current situation with respect to these investigations to be as follows.

Rickard and Ralston² did considerable work with sulfidizing reagents and found that hydrogen sulfide was the sulfide most naturally suggested as a reagent for the sulfidizing of oxidized minerals. The amount of this gas necessary for sulfidizing was much less when it was applied to the wet ore as compared to the dry ore. The addition of sulfuric acid was found to be necessary during the flotation operation to decompose the freshly formed iron sulfide in order to render it non-floatable. As most oxidized ores contain considerable amounts of acid-soluble constituents a high consumption of acid was usually encountered. One serious objection to the use of hydrogen sulfide, outside of the cost of the chemicals used for its production, was the effect of the gas on workmen due to its poisonous nature.

Considering sodium sulfide, the same investigators chose it as a more promising reagent than hydrogen sulfide for commercial sulfidizing of minerals. If the ore was conditioned with sodium sulfide in a Pachuca tank the air oxidized the sodium sulfide to sodium sulfate with but little sulfidizing of the oxidized minerals, and on further treatment the sulfidized minerals were oxidized. Hence it seemed imperative

2. Rickard, T. A. and Ralston, O. C., Flotation, 1917, McGraw-Hill Book Co., New York, pp. 360-378.

that treatment of oxidized minerals with sodium sulfide solutions must be done without large admixtures of air. Ores high in acid-soluble alumina, or those containing either manganese dioxide or basic sulfates of iron, consumed sodium sulfide without allowing sulfidizing of the oxidized minerals. Excess sodium sulfide in the flotation pulp had an injurious effect on the character of the froth, either greatly toughening it or eliminating it entirely.

Rickard and Ralston further stated that the polysulfides of sodium did not prove as effective as sodium sulfide, whereas the sulf-hydrate of sodium, NaSH , seemed to be somewhat more effective. The normal sulfide of sodium hydrolyzes to sodium sulf-hydrate and sodium hydroxide, and the activity of sodium sulfide is, for that reason, probably exactly the same as that of the sulf-hydrate, although the presence of sodium hydroxide from hydrolysis might have some effect on the effectiveness of sulfidizing. Calcium sulfides were slower in their action than the corresponding sulfides of sodium. Again it was found that the sulf-hydrate of calcium was more active than the sulfide, which in turn was more active than the polysulfide.

Rickard and Ralston concluded that for oxidized copper ores hydrogen sulfide seemed to be by far the best medium for sulfidizing previous to flotation, and they quoted J. M. Callow to the effect that it is unnecessary to blacken the

mineral to be floated and as little as one half pound per ton of sulfur (as hydrogen sulfide) gave satisfactory results at the test plant of the Magma Copper Company on malachite. Sodium sulfide has been tested at the concentrators of a number of the larger copper companies, having been added to the flotation machines or to conditioning tanks before flotation as tests showed that better sulfidizing of the minerals resulted if some little time of preliminary contact was allowed before flotation was effected.

Upon the subject of sulfidizing Gaudin³ stated that successful sulfidizing flotation of an oxidized mineral depends upon its preliminary sulfidizing, in order to convert at least the surface of the mineral to the sulfide form. This film on the mineral must be continuous, or else the mineral may exhibit, in part, the original instead of the sulfide surface. The discontinuous film may be due to the difference in specific volume of the coating and the mineral. This freshly formed sulfide coating is in an eminently reactive state and will readily oxidize. The poor results obtained in floating oxidized minerals, therefore, may be due to the oxidizability of the coating or its discontinuous character. It would seem that oxidized copper minerals ought to be readily sulfidized because of the relative insolubility of copper sulfides. However, the sulfidizing

3. Gaudin, A. M., Flotation, 1932, McGraw-Hill Book Co., New York, pp. 292-308.

of copper silicate is practically impossible. This last statement is in disagreement with Rickard⁴ and Ralston who said that although chrysocolla will blacken when treated with a sulfidizing reagent, it still resists flotation, possibly because it still presents a silicate rather than a sulfide surface.

Realizing the value of a concentration method for the recovery of the oxidized copper minerals, the Southwestern Experimental Station of the United States Bureau of Mines in 1936 started experimental work on the flotation of chrysocolla. This experimentation⁵ indicated that soap flotation of chrysocolla was possible on a laboratory scale, but the selectivity of soaps was poor and the reagent consumption was almost prohibitive.

The writer continued the experimental work started by Leininger and presents in this paper the results of further experimental work on the flotation of chrysocolla, employing sulfidizing of the copper silicate and its subsequent flotation by copper sulfide collectors.

4. Rickard, T. A., and Ralston, O. C., Flotation, 1917, McGraw-Hill Book Co., New York, p. 375.

5. Leininger, G. W., Experimental Work on the Flotation of Chrysocolla-Part II, Thesis U. of A., 1937, p. 18.

CHAPTER II - PROCEDURES, MATERIALS, AND APPARATUS

The experimental procedure involved in this problem comprised: (1) The determination of a suitable method for sulfidizing chrysocolla after trials with various sulfidizing reagents. (2) The determination of a suitable method for floating the sulfidized mineral employing a synthetic chrysocolla-pegmatite mixture. (3) The results obtained from these data to be applied to ores.

Materials

The material used for sulfidizing tests was minus 100-mesh chrysocolla, containing 28.5 percent of copper, furnished by the Inspiration Consolidated Copper Company.

The synthetic mixture employed in flotation testing consisted of two grams of the above minus 100-mesh chrysocolla and 98 grams of a pegmatite from the Oracle district, ground to pass a 100-mesh screen.

All reagents used in sulfidizing and flotation tests were dissolved in distilled water unless otherwise noted.

The pH value of all solutions was determined by colorimetric comparison.

Sulfidizing Procedure

The degree of sulfidizing of a mineral may be judged by the color change produced but it was decided that the best

index of the effectiveness of sulfidizing was the amount of reagent abstracted from solution by chrysocolla. All sulfidizing tests were made by the procedure which follows. A sample of chrysocolla weighing two grams was agitated in a beaker or stoppered flask with 300 c.c. (capacity of 100-gram flotation machine later used) of distilled water for five minutes to insure complete wetting of the material. After wetting, the sulfidizing agent and other reagents were added and the mixture agitated for ten minutes. The mixture was then filtered, the pH value of the solution determined, and sulfur in the filtrate estimated by colorimetric comparison. The first method of comparison was the reaction (in test tubes) between copper sulfate and the soluble sulfide which produced colors ranging from dark blue to brown, depending on the concentration of sulfur. This method was not sufficiently accurate or reliable and was abandoned in favor of the procedure described below.

Estimation of Sulfur

The method used consisted of a colorimetric comparison of the products of the reaction between lead acetate and the soluble sulfide not abstracted by chrysocolla. After various trials gum acacia was found to be the best dispersor for the freshly formed lead sulfide. The color produced varied from no color to a very dark brown with increasing strengths of sulfide.

A twenty c.c. sample of the filtrate from the sulfidizing test was diluted to 100 c.c. with distilled water, two c.c. of a saturated gum acacia solution added and the solution stirred vigorously. One c.c. of a 20 per cent lead acetate solution was then added and the solution again mixed. The depth of color of the solution was then measured by putting it in a flat-bottomed glass cylinder over a six-volt bulb. The amount of light passing through the solution was measured by a photoelectric cell which actuated a delicate galvanometer. The galvanometer reading was then compared with figures for solutions of known concentrations in order to get the amount of sulfur left in solution. Turbidity in the filtrate was taken care of by adjusting a rheostat in the six-volt light circuit. Results by this method were quite accurate and reliable.

Flotation Procedure

All flotation tests were made by the procedure outlined below which follows as closely as possible that used in the previous soap flotation in order to get comparative results.

A hundred-gram sample of the chrysocolla-pegmatite mixture or of an ore was charged into a 100-gram capacity flotation machine of the mechanical sub-aeration type. The sample was agitated in the cell with approximately an equal amount of distilled water for five minutes for wetting before the addition of any reagents. This wetting was done in order to conform to the condition of an ore after ball mill grinding.

After wetting, the necessary reagents were added and the mixture was conditioned the required length of time. The pulp level in the machine was then raised by adding water and the froth removed. The time of flotation was usually ten minutes, unless it could be seen that chrysocolla was still being recovered after ten minutes of floating, in which event the operation was continued until no more chrysocolla was apparent in the froth. The pulp level in the machine was maintained at such a height that the froth overflowed the lip by gravity. After flotation, the pH value of the tailings solution was determined.

The concentrate and tailing were filtered in an ordinary suction filter. When the excess liquid was removed, a small amount of ethyl alcohol was poured upon the residue and allowed to drain. The residue was then put in a pan, dried and weighed.

A five-gram sample was then taken from each tailing for analysis. The sample was decomposed with 10 c.c. of concentrated nitric acid by heating in a beaker. The solution was then diluted and filtered, and five c.c. of concentrated sulfuric acid added to the filtrate, which was then analyzed by electrolysis.

Reagent Quantities

All reagent quantities referred to in the chapters which follow are in pounds per ton of solids on the basis of 100 grams of solids. In the case of sulfidizing tests using two grams of chrysocolla, reagents were added in quantities equal to those required for 100 grams of solids.

CHAPTER III - EXPERIMENTAL WORK ON SULFIDIZING

Sodium Sulfide

The normal sodium sulfide was used as the sulfidizing reagent in tests 1 to 12 inclusive. The sulfidizing power of the sodium sulfide was determined in both alkaline and acid solutions. The experimental results are given in table I.

Preliminary blank tests on sodium sulfide solutions, one maintaining an atmosphere of nitrogen above the solution and the other in an open beaker, showed no appreciable consumption of sodium sulfide by oxygen in dissolved air in the water or air in contact with the surface of the solution. Another test on a sodium sulfide solution showed that this reagent was not abstracted from solution by adsorption on a filter paper.

(1) Referring to the results given in table I, it was found that if acid or base was not added the amount of chryso-colla sulfidized increased as the concentration of the sulfidizing reagent in the solution was raised, but the percentage of sodium sulfide effectively used for sulfidizing decreased.

(2) The pH value of the solution after sulfidizing was raised as the residual sodium sulfide in the solution increased.

(3) From (1) and (2) it was therefore believed that the lowering of the effectiveness of sulfidizing as indicated in (1) was due to the greater alkalinity (pH value).

(4) In order to overcome the low efficiency of sodium sulfide due to alkalinity, sulfuric acid was added to tests 7 to 12 inclusive as in table I. The results of these tests showed that when the pH value was lowered the consumption of sodium sulfide increased considerably, but the amount of acid necessary was considered prohibitive. As explained later in this chapter the writer believes that it is a fair assumption that the chrysocolla would react with any hydrogen sulfide liberated by the reaction between sulfuric acid and sodium sulfide.

(5) The coating formed on the chrysocolla by sodium sulfide was brown in color and appeared to be firmly adherent.

Sodium Sulfide with Ammonium Salts

In tests 13 to 27 inclusive, various ammonium salts were used together with sodium sulfide in an effort to increase the amount of sodium sulfide consumed by chrysocolla.

The two reagents were added at the same time in all tests. The ammonium salts did not interfere with the determination of residual sulfide. Referring to the results presented in table I the conclusions which follow are given.

(1) All the ammonium salts tested increased the amount of sodium sulfide used by chrysocolla. As the concentration of the ammonium salt was increased, the consumption of sodium

sulfide increased. For every unit quantity of sodium sulfide added, a definite quantity of ammonium salt was found necessary in order to get 100 per cent abstraction of sodium sulfide by the chrysocolla.

(2) As the amounts of sodium sulfide and ammonium salt were increased the chrysocolla became progressively darker.

(3) Ammonium fluoride was the most effective of the salts tried, followed by ammonium sulfate and ammonium carbonate. Since ammonium sulfate is the cheapest of these salts it suggested itself as the best reagent for further work. A suitable coating on the chrysocolla was obtained by using 0.5 pound of sodium sulfide per ton of solids and 0.75 pound of ammonium sulfate per ton of solids.

(4) The effectiveness of ammonium salts as conditioning agents in sulfidizing was probably due to the fact that they hydrolyzed to form a strong acid and a weak base, permitting sulfidizing at a lower pH value. Since, however, the pH value of the entire solution was not measurably lowered, an adsorption of the ammonium salt at the surface of the chrysocolla was suggested.

Sodium Bisulfide

Sodium bisulfide was used for sulfidizing in tests 28 through 30.

The sodium bisulfide for this series of tests was made by bubbling a stream of hydrogen sulfide through a solution of sodium sulfide until there was no further lowering of the

pH value of the solution. The experimental work indicated the conclusions which follow.

(1) Sodium bisulfide formed a very dark coating on the chrysocolla.

(2) Referring to table I, the amount of unused reagent could not be measured since the solutions were colored dark brown by some of the reaction products, but tests with lead acetate paper showed some sulfur left in the filtrate.

(3) The pH value of the solutions after sulfidizing was high, being between 9.1 and 9.5, and becoming higher with increasing amounts of the reagent added.

(4) No definite conclusions can be made as to the effectiveness of sodium bisulfide as a sulfidizing reagent from the above data inasmuch as all attempts to measure the amount of unused reagent failed.

Hydrogen Sulfide

In this series of tests, numbered 31 to 39 inclusive, water saturated with hydrogen sulfide was used as the sulfidizing reagent. The hydrogen sulfide was prepared from iron sulfide and acid. The sulfur content of the hydrogen sulfide solution was estimated by the same method as used for sodium sulfide and described on page 7, but the results were not very reliable due to the constant oxidation of the hydrogen sulfide by air during the determination. All tests were run in stoppered Erlenmeyer flasks in order to keep losses of

sulfur by oxidation at a minimum. These tests using hydrogen sulfide indicated the statements which follow.

(1) Referring to the results as given in table I, these tests showed that if hydrogen sulfide was added to chrysocolla and water the chrysocolla reacted with all the hydrogen sulfide present, providing not more than one pound of hydrogen sulfide per ton of solids was used.

(2) A dark brown coating was formed on the chrysocolla by hydrogen sulfide, which coating showed well-developed cleavage faces in bright sunlight. This coating became darker with higher concentrations of hydrogen sulfide.

(3) About 0.25 pound per ton of hydrogen sulfide was necessary to form a fairly dark brown coating on the chrysocolla. The coating formed rapidly and all the hydrogen sulfide was consumed almost immediately.

(4) Satisfactory sulfidizing of chrysocolla by hydrogen sulfide was obtained if the pH value of the solution was below 7.6. At higher pH values the amount of sulfidizing was less and at a pH of 9.4 the sulfidizing reaction apparently ceased.

Table I - Sulfidizing Data

Test Number	Sulfidizing Reagent		Conditioning Reagent		Sulfidizing Reagent	pH after Reaction
	Kind	Lbs. per ton	Kind	Lbs. per ton	abstracted, per cent ¹	
1	Na ₂ S	0.10	-	-	75	8.8
2	do.	0.25	-	-	72	8.9
3	do.	0.50	-	-	70	9.0
4	do.	0.06	-	-	65	9.1
5	do.	0.75	-	-	57	9.2
6	do.	1.00	-	-	46	9.4
7	do.	0.50	H ₂ SO ₄	1.00	96	6.8
8	do.	0.75	do.	1.00	65	7.6
9	do.	0.75	do.	3.00	93	7.2
10	do.	1.00	do.	1.00	51	8.6
11	do.	1.00	do.	3.00	77	8.4
12	do.	1.00	do.	4.00	95	8.1
13	do.	0.50	NH ₄ F	0.25	88	9.2
14	do.	0.50	do.	0.60	100	9.1
15	do.	1.00	do.	0.50	70	9.2
16	do.	1.00	do.	1.00	79	9.2
17	do.	1.00	do.	2.00	100	9.1
18	do.	0.50	(NH ₄) ₂ SO ₄	0.25	86	9.2
19	do.	0.50	do.	0.75	100	9.1
20	do.	1.00	do.	0.50	67	9.3
21	do.	1.00	do.	1.00	77	9.2
22	do.	1.00	do.	2.10	100	9.1
23	do.	0.50	(NH ₄) ₂ CO ₃	0.25	80	9.2
24	do.	0.50	do.	0.85	100	9.1
25	do.	1.00	do.	0.50	60	9.4
26	do.	1.00	do.	1.00	75	9.2
27	do.	1.00	do.	2.40	100	9.1
28	NaHS	0.50	-	-	-	9.1
29	do.	1.00	-	-	-	9.2
30	do.	1.50	-	-	-	9.5
31	H ₂ S	0.10	-	-	100	5.9
32	do.	0.25	-	-	100	5.9
33	do.	0.50	-	-	100	5.9
34	do.	1.00	-	-	100	5.9
35	do.	0.25	NaOH	(2)	100	7.0
36	do.	0.25	do.	(2)	100	7.5
37	do.	0.25	do.	(2)	75	8.5
38	do.	0.25	do.	(2)	50	9.0
39	do.	0.25	do.	(2)	0	9.4

1. Accuracy within one per cent.

2. NaOH was not measured as the pH value was the essential variable.

CHAPTER IV - EXPERIMENTAL WORK ON FLOTATION

The experimental work described in this chapter is classified according to the sulfidizing reagent used.

Sodium Sulfide

Flotation tests numbered 1 to 5 inclusive were made on the chrysocolla-pegmatite mixture described in chapter II using sodium sulfide as the sulfidizing reagent followed by the addition of xanthate to float the sulfidized copper silicate. The results are given in table IIa, and may be interpreted as follows:

(1) If the amount of potassium ethyl xanthate, the collector, was held constant and the amount of sodium sulfide increased, the recovery decreased with larger quantities of sodium sulfide, with no appreciable effect upon the copper content of the concentrate.

(2) The most satisfactory results were obtained when part of the xanthate was added before the sodium sulfide.

(3) The generally low recoveries may have been due to the buffer effect of the sodium sulfide, which held the pH at 8.8 to 9.0 in all tests. In the sulfidizing tests described in chapter III it was pointed out that the quantities of acid necessary to lower the pH sufficiently would have been prohibitive, so this plan was not tried.

(4) No difficulty was met in obtaining a stable froth provided that 0.1 pound of GNS No. 5 pine oil per ton of solids was employed.

(5) The chrysocolla was rather slow-floating in all tests.

(6) Tests 5 to 7 inclusive were made omitting the sulfidizer in order to show the effect of xanthate alone in floating chrysocolla, and the results indicated that a sulfidizing reagent was necessary in order to obtain a fair recovery of copper. With the sulfidizer recoveries as high as 90 per cent were effected whereas without the sulfidizer the maximum recovery was 47 per cent when using amyl xanthate, which proved to be much more effective than ethyl xanthate. The pH values of the tailing solutions were considerably lowered if sodium sulfide was omitted.

Sodium Sulfide with Ammonium Sulfate

In this series of tests, numbered 8 to 15 inclusive, sodium sulfide and ammonium sulfate were added together in the proper proportions to give complete consumption of the sodium sulfide. After a 10-minute conditioning period with the sulfidizer and ammonium sulfate conditioner, the collector and frother were added, the pulp conditioned another five minutes and the froth collected. The results of this series of tests led to the observations which follow.

(1) If the amount of collector was kept constant and the amounts of sulfidizer and ammonium sulfate conditioner

increased, the recovery increased. A satisfactory recovery of copper was made using 0.2 pound of amyl xanthate, 0.5 pound of sodium sulfide and 0.75 pound of ammonium sulfate per ton of solids. The pH was 7.8 when using this combination of reagents, in the amounts specified, with distilled water.

(2) Any increase in the copper content of the concentrate made for slightly lower recovery.

(3) Substituting aerofloat for xanthate and pine oil showed that approximately the same quantity of reagent and a much longer conditioning time were necessary in order to approximate the results made when xanthate was used.

(4) When an ethyl thio-xanthate was used in place of potassium amyl xanthate as the collector for the sulfidized chrysocolla the results were poor. However, if used in large quantities without a sulfidizer and with a 30-minute conditioning period, the thio-xanthate gave a satisfactory recovery but the concentrate had a very low copper content. The ethyl thio-xanthate was prepared by F. S. Wartman of the United States Bureau of Mines Experiment Station, Tucson, Arizona, by the regular xanthate synthesis substituting ethyl mercaptan for ethyl alcohol.

(3) The substitution of tap water for distilled water in sodium sulfide-ammonium sulfate flotation lowered the recovery 20 per cent when amyl xanthate was used and 10 per cent when aerofloat was employed. The pH when tap water was used was one unit higher than when distilled water was employed. The drop in recovery when tap water was used was probably due to the soluble salts in the tap water.

rather than the slightly increased pH, since lowering the pH value by adding sulfuric acid did not affect the results.

Sodium Bisulfide

A series of flotation tests numbered 16 and 17 was made in which sodium bisulfide as the sulfidizing reagent and amyl xanthate as the collector were used. The following statements are presented from an examination of the results as given in table IIa.

(1) The recoveries of copper in all tests were quite low and the recovery decreased with increasing amounts of sodium bisulfide.

(2) Since the sodium bisulfide decomposes to form hydrogen sulfide and sodium sulfide the low recoveries may have been due to the presence of unreacted sodium sulfide.

Hydrogen Sulfide

In the first tests of this series, numbered 18 to 21 inclusive, the hydrogen sulfide was added first and the pulp conditioned for five minutes, the xanthate and pine oil were added and conditioned for another five minutes, after which the froth was removed. From a consideration of the results as given in table IIa, the following statement is presented.

(1) The recoveries and copper contents of concentrates obtained by the procedure described were uniformly low regardless of the amounts of hydrogen sulfide and xanthate used.

A second set of tests, numbered 22 to 27 inclusive, was run wherein the xanthate was added before the hydrogen sulfide. The results of these tests as recorded in table IIA, may be summarized in the following observations.

(1) When 0.1 pound of amyl xanthate per ton of solids was used and the amount of hydrogen sulfide added was varied it was found that a fair recovery of copper was effected but the recovery decreased if more than 0.3 pound of hydrogen sulfide per ton of solids was used.

(2) Further tests with 0.2 pound of amyl xanthate per ton of solids showed that the recovery increased to 100 per cent with about 0.3 pound of hydrogen sulfide per ton of solids and decreased if more hydrogen sulfide was used.

(3) In tests using more xanthate the copper content of the concentrate was not improved.

(4) In all cases the copper content of the concentrate was low when maximum recoveries were obtained.

(5) The fact that the most satisfactory flotation results were obtained when xanthate was present to react with the freshly formed copper sulfide would indicate that the sulfide coating was very readily oxidized and that the sulfidized chrysocolla should be floated immediately.

(6) Several attempts were made to raise the copper content of the concentrates in hydrogen sulfide-xanthate flotation tests, and it was found that if xanthate was added first followed by the stage additions of small amounts of hydrogen

sulfide higher grade concentrates were produced but with some sacrifice in recoveries. A test on a low-grade xanthate-hydrogen sulfide concentrate containing 2.5 per cent copper indicated that a concentrate containing 10 per cent copper could be made by one cleaning.

(7) Tests numbered 28 and 29 were run substituting Minerec A for xanthate as the collector for the sulfidized chrysocolla. In all of these tests it was necessary to add sulfuric acid to the pulp as Minerec A will function as a collector only in an acid circuit. Referring again to table IIIa, the recovery with the use of Minerec A increased slightly as the pH value of the pulp was lowered, but in no case was over 65 per cent of the copper floated.

Hydrogen Sulfide with Tap Water or Soluble Salts

The laboratory tap water contained a fairly high concentration of soluble salts, mainly calcium bicarbonate and sodium chloride, with minor amounts of magnesium, sodium and calcium sulfates, carbonates and nitrates. The floatability of chrysocolla when tap water was substituted for distilled water was determined and found to be considerably reduced and frothing to be much more difficult. The effect of the salts found in the tap water and other soluble salts was then investigated by using distilled water together with such salts in flotation pulps in the approximate concentrations as found in tap water. In all tests, numbered 1 to 12 inclusive in

table IIb, constant quantities of xanthate and hydrogen sulfide were used in order to get comparative results. Referring to the results as given in table IIb, the following conclusions are given.

(1) The results of these tests showed that if used in the approximate concentrations as found in tap water, sodium chloride, sodium bicarbonate and potassium sulfate had very little effect on the recovery of copper or the frothing power of pine oil.

(2) Calcium chloride acted as a serious depressant for chrysocolla but a stable froth could be maintained with pine oil.

(3) Magnesium sulfate, magnesium chloride and ferrous sulfate practically prevented the formation of a froth. Although magnesium chloride and ferrous sulfate depressed chrysocolla considerably, magnesium sulfate had only a slight effect upon recovery.

(4) Ferrous sulfate lowered the pH considerably but the addition of lime did not improve the copper recovery by increasing the pH value when ferrous sulfate was used.

(5) Greatly increasing the hydrogen sulfide added raised the recovery considerably in the case of ferrous sulfate and magnesium chloride.

(6) The addition of a proprietary frother known as Duponol WA Paste improved the recovery when calcium chloride

or magnesium sulfate were present. This reagent is a commercial sulfated alcohol, possibly sodium lauryl sulfate.

(7) In general it may be said that the presence of soluble salts necessitated an increase in the amounts of sulfidizer and frother found necessary for the successful flotation of chrysocolla.

Hydrogen Sulfide as Applied to Ores

Since the most satisfactory results on the synthetic chrysocolla-pegmatite mixture were obtained when using xanthate and hydrogen sulfide, this combination suggested itself as the best to try on ores. A series of tests numbered 30 to 33 inclusive in table IIa, was run on Miami mixed ore which had been ground through 100-mesh, partially deslimed, and the sulfides removed by regular xanthate flotation. From the results of the above tests the following observations may be made.

(1) A satisfactory recovery of copper was not effected in any of the tests and the copper content of the concentrate was uniformly low.

(2) If the amount of hydrogen sulfide was kept constant the copper content of the concentrate increased slightly with an increase in the quantity of xanthate, but the addition of over 0.4 pound of xanthate per ton of solids was not warranted considering both expense and results.

(3) The use of hydrogen sulfide was found necessary in order to effect any recovery since green-colored copper minerals did not appear in the froth until after the addition of hydrogen sulfide.

(4) The slime in the ore was blackened rapidly by the hydrogen sulfide and the poor results may have been due to contamination with this slime.

(5) Assuming that the oxidized copper minerals in this ore were properly liberated by the degree of grinding employed, the recovery by hydrogen sulfide-xanthate flotation was unsatisfactory. Testwork to determine the exact nature of the occurrence of chrysocolla in this ore is being carried on at present by the United States Bureau of Mines Experiment Station, Tucson.

Miscellaneous Flotation Tests

Experiments numbered 35 to 37 inclusive were run on the synthetic chrysocolla-pegmatite mixture in order to test the possible application to flotation of chrysocolla of a new reagent known as DLT 698, a modified soap of a fatty acid in which the alkaline earth base has been replaced by an organic base. The results of the above tests indicated the statements which follow.

(1) Chrysocolla was not noticeably floated by using DLT 698 alone in any quantities up to 0.5 pound per ton of solids.

(2) The addition of hydrogen sulfide to a pulp previously conditioned with DLT 698 did not result in the flotation of any copper.

(3) The addition of DLT 698 to a pulp conditioned with xanthate and hydrogen sulfide gave the usual recovery for this type of flotation, showing that DLT 698 did not inhibit the flotation of chrysocolla.

(4) The use of DLT 698 with xanthate and pine oil gave very satisfactory recoveries when the DLT 698 was added before the xanthate, the copper content of the concentrates being essentially the same as that obtained from xanthate-hydrogen sulfide flotation.

(5) Laboratory tap water did not interfere with flotation when using DLT 698 and xanthate.

Table IIa - Flotation Data

Test Number	Sulfidizing Reagent		Collector		pH value: of water: after flota- tion	Weight of Products		Copper in Concentrate, per cent:	Per cent: of total: copper floated:
	Kind	Lbs. per ton	Kind	Lbs. per ton		Concen- trate, grams	Tail- ings, grams		
1	Na ₂ S	0.35	KEX ¹	0.20	8.8	11.5	88.5	4.48	87.2
2	do.	0.50	do.	0.20	8.8	11.0	86.0	4.09	84.0
3	do.	0.75	do.	0.20	8.9	9.0	91.0	4.63	73.4
4	do.	1.00	do.	0.20	9.0	15.0	85.0	2.48	65.6
5	do.	1.00	do.	0.20 ²	9.0	11.5	88.5	4.41	89.1
6		-	do.	0.20	7.5	10.0	90.0	2.18	34.6
7		-	KAX ³	0.20	7.5	6.5	93.5	4.09	46.8
8	Na ₂ S	0.25	KAX	0.20	7.8	9.5	90.5	5.36	89.0
	(NH ₄) ₂ SO ₄	0.35							
9	Na ₂ S	0.50	do.	0.20	7.8	10.5	89.5	5.94	95.3
	(NH ₄) ₂ SO ₄	0.75							
10	Na ₂ S	0.75	do.	0.20	7.9	8.5	91.5	7.21	93.6
	(NH ₄) ₂ SO ₄	1.00							
11	Na ₂ S	0.50	Aero.31	0.25	7.8	6.0	94.0	9.70	92.0
	(NH ₄) ₂ SO ₄	0.75							
12	Na ₂ S	0.50	Thio.X	0.20	7.9	5.5	94.5	4.04	21.7
	(NH ₄) ₂ SO ₄	0.75							
13		-	Thio.X ⁴	0.50	7.5	16.5	83.5	3.20	89.9
14 ⁵	Na ₂ S	0.50	KAX	0.20	8.8	5.5	94.5	9.00	75.0
	(NH ₄) ₂ SO ₄	0.75							
15 ⁵	Na ₂ S	0.50	Aero.31	0.25	8.8	6.0	94.0	9.70	85.5
	(NH ₄) ₂ SO ₄	0.75							
16 & 17	NaHS	0.50	KAX	0.20	8.8	12.0	88.0	3.12	62.4
	NaHS	1.00	KAX	0.20	9.0	7.0	93.0	3.17	37.6
18	H ₂ S ⁶	0.20	KAX	0.20	7.5	7.0	93.0	4.83	47.7
19	do.	0.40	do.	0.20	7.5	9.0	91.0	3.45	47.1
20	do.	1.00	do.	0.20	7.4	13.0	87.0	1.88	43.2
21	do.	1.00	do.	0.50	7.4	9.0	91.0	3.60	51.8
22	do.	0.20	KAX ⁷	0.10	7.4	7.0	93.0	7.05	87.0
23	do.	0.30	do.	0.10	7.4	9.0	91.0	6.50	88.8
24	do.	0.50	do.	0.10	7.5	7.0	93.0	6.91	85.3
25	do.	0.30	do.	0.20	7.4	16.0	84.0	3.54	100.0
26	do.	1.00	do.	0.20	7.6	10.5	89.5	4.63	85.9
27	do.	0.40	do.	0.40	7.5	16.5	83.5	3.44	100.0
28	do.	0.50	MIN.A ⁷	0.50	6.9	11.0	89.0	1.68	32.6
29	do.	0.50	do.	0.50	6.1	11.0	89.0	2.81	54.4
30 ⁸	do.	0.30	KAX ⁷	0.20	7.4	16.0	84.0	2.22	54.0
31 ⁸	do.	1.10	do.	0.30	7.4	14.0	86.0	2.69	62.7
32 ⁸	do.	1.00	do.	0.40	7.4	10.0	90.0	3.57	59.4
33 ⁸	do.	1.00	do.	0.60	7.3	11.0	89.0	3.15	57.8
34 ⁵	do.	0.30	do.	0.20	7.9	12.0	88.0	4.13	87.7
	Modified Soap								
	Lbs. per ton								
	of solids								
35	0.1		KAX	0.20	7.3	9.0	91.0	5.09	80.9
36	0.2		do.	0.20	7.3	15.5	84.5	3.55	97.1
37 ⁵	0.2		do.	0.20	8.0	14.0	86.0	3.92	97.0

1. Potassium ethyl xanthate
2. One-half of xanthate added ahead of sodium sulfide
3. Potassium amyl xanthate
4. Thirty minute conditioning period
5. Tap water substituted for distilled water
6. Hydrogen sulfide added first
7. Xanthate added first
8. Miami ore

Table IIb - Data on Xanthate-Hydrogen Sulfide Flotation
in the Presence of Soluble Salts

Test Number:	Soluble Salts			KAX ¹ :Lbs. per :ton of :solids	H ₂ S :Lbs. per :ton of :solids	pH value: :of water: : after :flota- :tion	Weight of :Products :Concen- :trate, :grams	Tail- :ings, :grams	Copper :in :Concen- :trate, :per cent:	Per cent: :of total: :copper :floated
Ion	Parts :per :million	Formula								
1	Cl	50	NaCl	0.20	0.30	7.7	13.0	87.0	4.30	98.7
2	HCO ₃	125	NaHCO ₃	0.20	0.30	7.6	7.0	93.0	7.30	90.2
3	SO ₄	150	K ₂ SO ₄	0.20	0.30	7.7	11.5	88.5	4.70	95.4
4	Cl	150	CaCl ₂	0.20	0.30	7.1	4.5	95.5	3.38	26.8
5 ²	Cl	150	CaCl ₂	0.20	0.30	7.3	5.0	95.0	6.98	61.6
6	SO ₄	150	MgSO ₄	0.20	0.30	7.3	6.0	94.0	7.56	80.1
7 ²	SO ₄	150	MgSO ₄	0.20	0.30	7.4	8.5	91.5	5.70	85.6
8	Cl	150	MgCl ₂	0.20	0.30	7.1	4.5	95.5	3.59	28.6
9	Cl	150	MgCl ₂	0.20	1.00	7.3	18.0	82.0	2.61	83.0
10	SO ₄	150	FeSO ₄	0.20	0.30	6.6	7.0	93.0	4.78	59.2
11 ³	SO ₄	150	FeSO ₄	0.20	0.30	8.0	6.5	93.5	2.68	30.8
12	SO ₄	150	FeSO ₄	0.20	1.00	6.9	8.5	91.5	5.49	82.3

1. Potassium amyl xanthate
2. 0.01 lbs. per ton Duponol frother
3. Lime added

CHAPTER V - CONCLUSIONS

From the results of the experimental work on the sulfidizing and flotation of chrysocolla as described in this paper the conclusions which follow were indicated.

(1) Pure chrysocolla was satisfactorily sulfidized by the use of sodium sulfide together with an ammonium salt or by hydrogen sulfide alone.

(2) Satisfactory flotation of chrysocolla from a synthetic chrysocolla-pegmatite mixture was attained by flotation of the sulfidized mineral when the usual collectors for copper sulfides were used.

(3) Successful flotation of chrysocolla was also obtained by the use of a combination of xanthate and a modified soap without resorting to preliminary sulfidizing.

(4) The results of tests on Miami mixed ore were unsatisfactory from the standpoint of recovery of oxidized copper minerals.

CHAPTER V - CONCLUSIONS

From the results of the experimental work on the oxidation and reduction of chrysochroite as described in this paper the conclusions which follow were indicated.

(1) Pure chrysochroite was satisfactorily oxidized by the use of sodium nitrate together with an ammonium salt or by hydrogen nitrate alone.

(2) Satisfactory reduction of chrysochroite from a synthetic chrysochroite-pyrite mixture was obtained by flotation of the sulfidized mineral when the usual collectors for copper sulfides were used.

(3) Satisfactory reduction of chrysochroite was also obtained by the use of a combination of xanthate and a modified soap without resorting to preliminary sulfidizing.

(4) The results of tests on blast sizes are given in the accompanying table. The results of recovery of oxidized copper minerals.

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