CHRYSOCOLLA FLOTATION BY THE FORMATION OF INSOLUBLE SURFACE CHELATES

by H. D. Peterson, M. C. Fuerstenau, R. S. Rickard and J. D. Miller

Pure chrysocolla is floated with chelating agents that form insoluble complexes with copper at ambient temperature. Complete flotation is obtained with potassium octyl hydroxamate as collector at pH 6. Flotation response is enhanced with increased temperature when low additions of hydroxamate are involved. A natural ore was floated with 0.4 lb per ton octyl hydroxamate at pH 6.5 and 58°C, and a flotation recovery of 76% was obtained with a concentrate grade of 31.6% copper.

The flotation characteristics of the oxide copper minerals, malachite, azurite, and cuprite, have not presented the difficulty for concentration as have those of the copper silicate, chrysocolla. The copper carbonates and oxides respond reasonably well to flotation with conventional collectors, whereas chrysocolla will not respond to flotation with fatty acids or xanthates under normal flotation conditions.

In this view then, other reagents will have to be devised to function as collectors for chrysocolla. The most obvious general class of reagents for this purpose would seem to be the organic copper chelating compounds. The utility of chelating agents as collectors in flotation systems has already been demonstrated. For example Vivian[1] has floated cassiterite using ammonium nitrosophenylhydroxylamine. Holman[2] studied the flotation of nickel oxide ores with dimethylglyoxime and also suggested the use of taurine on oxidized lead ores.

A rather detailed study on the application of certain chelating agents to some flotation systems was presented by Gutzeit.[3] This work indicated that the formation of surface insoluble chelates is probably responsible for flotation in many cases. The role that soluble chelating agents assume was also presented, that is with effective removal of polyvalent cations by complex formation, effective depression of quartz can be obtained.

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DeWitt and Batchelder[4,5] have shown that oximes function well as collectors for chalcocite, malachite, azurite, and cuprite. Ludt and DeWitt[6] have presented the possibility of using dyes, such as octyl malachite green, as a collector for chrysocolla. These works presented by DeWitt et al suggest that organic copper chelating compounds offer considerable promise for concentrating chrysocolla, but that the most suitable chelating reagent from the standpoint of cost and flotation response has yet to be determined.

The present investigation was undertaken to study the flotation response of chrysocolla to selected copper chelating compounds, that is ethylenediamine, hexamethylenetetramine, potassium octyl hydroxamate, dimethylglyoxime, and benzoin α-oxime.

EXPERIMENTAL MATERIALS

Chrysocolla: The chrysocolla used in the microflotation studies was from New Mexico and analyzed 20.8% copper. X-ray diffraction showed this material to be amorphous in character, but some faint lines of quartz were noted.

A natural oxide copper ore from Utah was also used in the investigation. This ore contains malachite principally but also contains chrysocolla and tenorite together with some sulfide copper. The sulfide copper comprises from 15 to 20% of the total copper content of the ore.

Water: Conductivity water was used in the microflotation experiments, while Golden tap water was used in the experiments with the natural ore.

Reagents: Reagent grade n-amyl alcohol was used as frother in the experiments with pure mineral, while MIBC was used in the work with the ore.

Ethylenediamine, hexamethylenetetramine, dimethylglyoxime and benzoin α-oxime were reagent grade in quality. Pure potassium octyl hydroxamate was prepared as follows: 1) 1.0 mole of KOH in 140 cc of methanol was combined with 0.6 mole of hydroxylamine hydrochloride in 240 cc of methanol at 40°C (KCl precipitates under these conditions and to effect complete removal of KCl, the system was cooled to 10°C and filtered), 2) a light methanol wash was then given the KCl cake, 3) the filtrate was agitated at room temperature and 0.33 mole of the methyl ester of the organic acid (i.e. methyl octanoate) was

added, 4) agitation was maintained for a period up to 48 hours (over 90% conversion will occur in approximately 4 hours), 5) the potassium alkyl hydroxamate was filtered and then washed with methanol and 6) as potassium alkyl hydroxamate is soluble in methanol, recrystallization was effected by heating, with subsequent cooling of the methanol.

EXPERIMENTAL PROCEDURE

The microflotation experiments were conducted with the equipment and technique described previously[7,8] with 3-g charges of 48 × 150 mesh chrysocolla at ambient and elevated temperature.

Experiments with the natural ore were conducted with the following procedure: 1) the ore was ground in a porcelain mill with porcelain balls with tap water at 60% solids and screened through 48 mesh, 2) the ground ore was deslimed by decanting until relatively free from slimes, 3) the pulp was heated to about 70°C by bubbling steam into the Fagergren cell and the pH was adjusted to the desired value, 4) a given amount of potassium octyl hydroxamate and frother were added to the cell and the pulp was conditioned for 3 min, 5) the pH was measured (termed flotation pH) and the temperature was measured (termed flotation temperature) and 6) the froth was collected until depleted.

EXPERIMENTAL RESULTS

Microflotation experiments with pure chrysocolla were performed first with potassium octyl hydroxamate,*

$$R - \underset{\underset{HO}{|}}{C} = \underset{\underset{OK}{|}}{N} ,$$
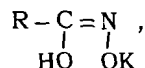
*In this and other structural formulas, R represents the hydrocarbon chain.

as collector, and the experimental results are shown in Fig. 1. It can be seen that a recovery of 35% was obtained with 5 × 10⁻⁵ mole per liter at pH 6 at ambient temperature. Doubling the collector addition resulted in doubling the recovery under the same conditions. With an addition of 3.3 × 10⁻⁴ mole per liter, complete flotation was achieved at about pH 6 at ambient temperature and recovery was noted to decrease markedly above and below this value of pH.

When the pulp temperature was increased to 50°C, a maximal recovery of about 65% was obtained with an addition of 5 × 10⁻⁵ mole per liter hydroxamate at pH 6 as compared to a recovery of about 35% with the same pH and level of addition of collector at ambient temperature.

As it is known that the alkyl hydroxamates form insoluble complexes with copper,[9] experiments were conducted with other chelating agents that are also known to form insoluble complexes to establish
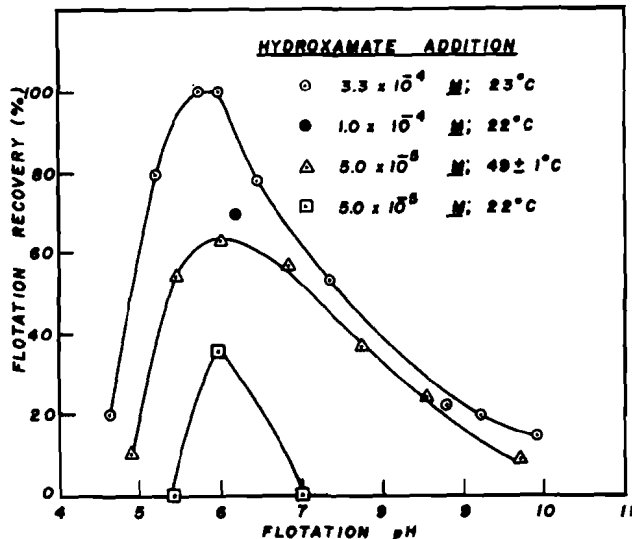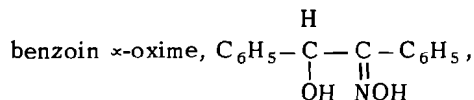

Fig. 1 — Relationship between flotation recovery of chrysocolla and flotation pH with three constant additions of potassium octyl hydroxamate at two different temperatures (Separate Experiments).

whether this is the criterion necessary for chrysocolla flotation. In this regard,

$$\text{benzoin } \varkappa\text{-oxime, } C_6H_5 - \underset{\underset{OH}{|}}{C} - \underset{\underset{NOH}{\|}}{C} - C_6H_5 ,$$

was added as collector at ambient and elevated temperature at various values of pH (Table I).

Similar experiments were also conducted with dimethylglyoxime,

$$HC - \underset{\underset{HON}{\|}}{\underset{H}{C}} - \underset{\underset{NOH}{\|}}{\underset{H}{C}} - CH ,$$
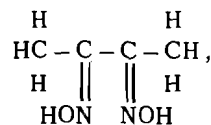
as collector. No flotation was obtained with additions as high as 1 × 10⁻³ mole per liter from pH 5.1 to 7.8 at 68°C.

Experiments were also conducted with two reagents that form soluble complexes with copper. These reagents were ethylenediamine

$$\begin{matrix} H & H & H & H \\ N - C & - C & - N \\ H & H & H & H \end{matrix}$$
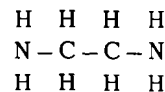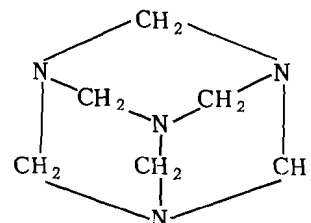
and hexamethylenetetramine..

Table I. Experimental Results Obtained with Pure Chrysocolla with Two Levels of Addition of Benzoin ∝-Oxime at Various Values of pH at Various Temperatures

Benzoin ∝-Oxime Addition (mole per l)	Flotation Temperature (°C)	Flotation pH	Flotation Recovery (%)
1×10^{-4}	69	5.35	0
1×10^{-4}	64	7.18	0.8
1×10^{-4}	65	7.32	35.3
1×10^{-4}	66	7.32	29.0
1×10^{-4}	66	8.10	2.7
1×10^{-4}	66	8.80	3.6
5×10^{-4}	66	7.40	58.2
5×10^{-4}	22	7.70	7.9

Table II. Experimental Results Obtained with 0.14 lb per ton Octyl Hydroxamate and 0.12 lb per ton Amyl Xanthate at pH 5.9 and 23° C.

Product	Weight (gm)	% Cu	Cu Weight (gm)	Flotation Recovery (%)
Concentrate	7.7	25.7	1.98	37
Tailing	411.0	0.83	3.41	

Table III. Experimental Results Obtained with 0.096 lb per ton Octyl Hydroxamate and 0.12 lb per ton Amyl Xanthate at pH 6.4 and 61° C.

Product	Weight (gm)	% Cu	Cu Weight (gm)	Flotation Recovery (%)
Concentrate	10.0	31.3	3.13	58
Tailing	405.0	0.54	2.29	

Table IV. Experimental Results Obtained with 0.41 lb per ton Octyl Hydroxamate and 0.15 lb per ton Amyl Xanthate at pH 6.5 and 58° C.

Product	Weight (gm)	% Cu	Cu Weight (gm)	Flotation Recovery (%)
Concentrate	15.2	23.7	3.60	73
Tailing	318.0	0.428	1.36	

Table V. Experimental Results Obtained with 2.4 lb per ton Octyl Hydroxamate and 0.12 lb per ton Amyl Xanthate at pH 5.8 and 58° C.

Product	Weight (gm)	% Cu	Cu Weight (gm)	Flotation Recovery (%)
Concentrate	110.5	4.47	4.95	79
Cleaner Tailing	24.4	0.546	0.13	
Final Tailing	281.7	0.442	1.24	

No flotation was obtained with additions of 1×10^{-4} and 5×10^{-4} mole per liter hexamethylenetetramine from pH 5 to 8 at ambient and elevated temperatures.

Two levels of addition of ethylenediamine were also tried, that is 1×10^{-4} mole per liter at pH 7.7 at 62°C and 2×10^{-3} mole per liter at pH 7.2 at 62°C. No flotation was obtained under either of these two conditions.

When octyl hydroxamate, benzoin ∝-oxime and dimethylglyoxime were used as collectors, chrysocolla changed from blue in color to malachite green during the 3-min conditioning period. No change in color of chrysocolla was noted when ethylenediamine or hexamethylenetetramine were involved.

Natural Ore: Experiments were also conducted with a natural ore to determine if octyl hydroxamate is sufficiently selective for practical use. The experimental results obtained with various levels of addition of potassium octyl hydroxamate at ambient and elevated temperature are listed in Tables II, III, IV, and V. In this first series of experiments, a nearly constant amount of amyl xanthate was added to collect the sulfide copper.

Experiments were also conducted with only octyl hydroxamate added in one system and amyl xanthate in another at elevated temperature and pH 6.5 for a comparison with the flotation response determined when both collectors were added to the same system. Compare Tables VI and VII with Table IV.

The concentrate obtained with octyl hydroxamate alone looked very similar to that obtained when hydroxamate and xanthate were added together. That is, all of the four copper minerals floated when only octyl hydroxamate was employed as collector.

When 0.12 lb per ton amyl xanthate was added to a separate system, only the sulfide copper and tenorite were noted to float. Neither the chrysocolla nor malachite responded under these conditions.

Precipitation of Copper Hydroxamate from Solution: Experiments were also conducted to determine the number of moles of hydroxamate consumed per mole of copper in the precipitation of cupric hydroxamate

Table VI. Experimental Results Obtained with 0.4 lb per ton Octyl Hydroxamate at pH 6.5 and 55° C.

Product	Weight (gm)	% Cu	Cu Weight (gm)	Flotation Recovery (%)
Concentrate	12.4	31.6	3.92	76
Tailing	337.0	0.38	1.28	

Table VII. Experimental Results Obtained with 0.12 lb per ton Amyl Xanthate at pH 6.5 and 58° C.

Product	Weight (gm)	% Cu	Cu Weight (gm)	Flotation Recovery (%)
Concentrate	5.5	42.9	2.36	35
Tailing	488.0	0.91	4.44	

to gain some insight into the mechanism of adsorption of this reagent on the chrysocolla surface. In this work, a constant amount of Cu^{++} (2.5×10^{-4} mole per liter) was combined with excess octyl hydroxamate at pH 4, 7 and 10. At each of these values of pH, complete precipitation of copper as copper hydroxamate occurred. The residual hydroxamate concentrations were then determined by combining the filtrate with ferric iron and analyzing the soluble ferric chelate colorimetrically. The experimental results showed that one mole of copper and one mole of hydroxamate are present in one mole of precipitated copper hydroxamate.

DISCUSSION OF RESULTS

The experimental results obtained with pure chrysocolla in the presence of various copper chelating reagents as collectors suggests that flotation collection is due to the formation of an insoluble complex between surface copper ions and chelating agent. This premise appears to be substantiated by the fact that a change in color of the chrysocolla was observed after 3 min of conditioning with any of the three complex formers used, which shows positive adsorption of the reagent on the surface. Further it has been reported that the copper salts of mono-hydroxamic acids are green in color and very insoluble in water.[9]

The configuration of copper hydroxamate might be[10]

$$R\text{---}C\text{==}N$$
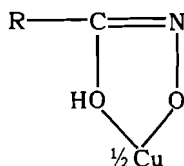
in which a coordinate bond is present with the hydroxyl.

However, since one mole of octyl hydroxamate is consumed with one mole of copper in the precipitation of cupric hydroxamate, the configuration of the precipitate is probably as follows:
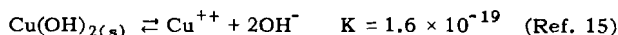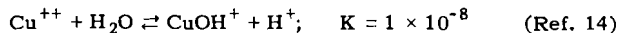
$$R\text{---}C\text{==}N$$
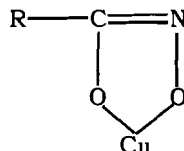
This configuration is similar to that presented for a chelate of cupric ion and benzoin oxime.[11]

Combination of octyl hydroxamate and cupric chloride in solution showed that complete precipitation of copper hydroxamate occurs from pH 4 to 10. Adsorption of the insoluble complex formers was physically evident from pH 4 to 9 and flotation was possible in this range when moderate additions of

Table VIII. Concentrations of Various Cu^{++} Ion Species as a Function of pH for a Nominal Addition of 1×10^{-3} mole per liter Cupric Chloride to Water

| | Species | | |
pH	Cu^{++}	$CuOH^+$	$Cu(OH)_{2(s)}$
5.0	1.0×10^{-3}	1.0×10^{-6}	0
5.2	1.0×10^{-3}	1.6×10^{-6}	0
5.4	1.0×10^{-3}	2.5×10^{-6}	0
5.6	1.0×10^{-3}	4.0×10^{-6}	0
5.8	1.0×10^{-3}	6.3×10^{-6}	0
6.0	9.9×10^{-4}	9.9×10^{-6}	0
6.1	9.9×10^{-4}	1.2×10^{-5}	0
6.2	6.4×10^{-4}	1.0×10^{-5}	3.5×10^{-4}
6.4	2.5×10^{-4}	6.4×10^{-6}	7.4×10^{-4}
6.6	1.0×10^{-4}	4.0×10^{-6}	9.0×10^{-4}
6.8	4.0×10^{-5}	2.6×10^{-6}	9.6×10^{-4}
7.0	1.6×10^{-5}	1.6×10^{-6}	9.8×10^{-4}

These calculations were made utilizing the following equilibria:

$$Cu^{++} + H_2O \rightleftarrows CuOH^+ + H^+; \quad K = 1 \times 10^{-8} \quad \text{(Ref. 14)}$$

$$Cu(OH)_{2(s)} \rightleftarrows Cu^{++} + 2OH^- \quad K = 1.6 \times 10^{-19} \quad \text{(Ref. 15)}$$

Note that activity coefficients of unity were assumed in these calculations.

octyl hydroxamate were involved. However, the optimum flotation pH with this collector is pH 6, with marked reductions in recovery occurring both above and below this pH. As the monohydroxamic acids are reported to function as weak acids in aqueous solution,[12] it might be assumed that system depression observed below about pH 4 is due to hydrolysis of hydroxamate to hydroxamic acid, if the hydroxamate is functioning as the collector.
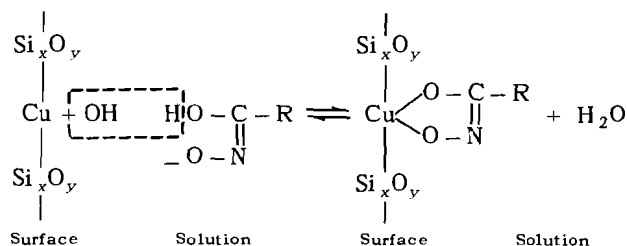
Another explanation for system depression in this pH region might be the fact that chrysocolla is soluble under these conditions.

Although both of the phenomena just discussed may contribute to depression of chrysocolla in acid media, data obtained in similar systems[13] indicate that depression may also be due to the lack of chemisorbed hydroxyl ion at the surface. That is, with reference to Table VIII, it can be noted that the maximal concentration of $CuOH^+$ in solution occurs from about pH 6.0 to 6.2 for an addition of 1×10^{-3} mole per liter Cu^{++} to water. At pH 6.2 and above, copper hydroxide will precipitate and essentially complete hydrolysis of Cu^{++} ion will occur above pH 6.5.

By analogy, some of the surface copper ions of chrysocolla should also have hydrolyzed to $CuOH^+$ at pH 6 and above. If dissolved hydroxamate ion

$$R\text{--}C\text{=}N$$
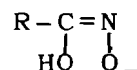
is functioning as the collector, adsorption on the surface might occur in the following manner:

$$Si_xO_y \quad \begin{array}{c} | \\ Cu + OH \quad H \overset{|}{O} - \overset{O}{\underset{\|}{C}} - R \\ | \\ Si_xO_y \\ | \end{array} \rightleftharpoons \begin{array}{c} Si_xO_y \\ | \\ Cu < \overset{O - C - R}{\underset{O - N}{\|}} \\ | \\ Si_xO_y \\ | \end{array} + H_2O$$

Surface Solution   Surface Solution

x and y have been used as subscripts since the ratio of silicon to oxygen in this mineral is not known.

The effect of temperature in these systems is probably due to thermodynamic considerations rather than adsorption kinetics. That is, it was quite evident that adsorption of the three insoluble copper chelate formers occurred during the 3-min conditioning period even at ambient temperature. If the hydrolysis reaction of Cu^{++} to $CuOH^+$ is endothermic, then the addition of heat to the system will favor the formation of $CuOH^+$, or in the flotation system, surface hydroxide complexes, which are apparently necessary for a favorable flotation response.

The depression of chrysocolla at pH values above 10 (Fig. 1) may be due to the complete hydrolysis of surface copper ions to copper hydroxide.

Although dimethylglyoxime was seen to adsorb on the surface of chrysocolla, no flotation was obtained which may be due to the lack of hydrocarbons in its configuration. Sufficient hydrophobicity was apparently lacking with only methyl groups contained in the hydrocarbon chains.

Concerning chain length, preliminary experiments indicated that octyl hydroxamate is a suitable collector for chrysocolla. A detailed study of the effect of chain length was not undertaken at this time, but surely this is an area for investigation in the future.

The experimental conditions for a favorable flotation response that evolved from the work with pure chrysocolla were also employed with a natural ore. The fact that the ore sample used is actually drill cuttings from a deposit accounts for the variation in total copper present in the four charges of flotation feed. Flotation recoveries of 58, 73 and 79% were obtained with 0.096, 0.41 and 2.4 lb per ton of octyl hydroxamate and 0.12 lb per ton amyl xanthate at elevated temperature, and the grades of the concentrates were 31.3, 23.7 and 4.47% copper, respectively.

Microscopic inspection of the tailings from the experiments in which the higher levels of addition of hydroxamate (e.g. 0.4 lb per ton) were used, showed these products to be almost entirely free of malachite and chrysocolla. A detailed mineralogical examination of the tailings was not undertaken to determine

what constituted the remaining 20 to 25% of the copper that was not floated, as the intent of this experimental work was simply to establish whether the technique devised with pure chrysocolla was amenable to natural ore systems.

The data also show that as the hydroxamate addition is increased, selectivity is decreased. This may be explained by normal chelation phenomena, that is with small concentrations of chelater, the most stable chelates are formed first, which in this case is copper hydroxamate. With higher concentration levels, metal chelates of lower stability are also formed, accounting for the relatively large amount of the feed that was floated with an addition of 2.4 lb per ton hydroxamate.

Similar to the observations of DeWitt and Batchelder,[4] good flotation of sulfide copper is also obtained with octyl hydroxamate which will preclude the necessity of adding xanthate for this purpose.

ACKNOWLEDGMENTS

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