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Copper Silicate Mineral Flotation by Activation with Organic Copper-Avid Reagents

By

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Synopsis

In order to collect the copper silicate, chrysocolla, a method in which the mineral is activated by a copper-avid organic reagent and then floated by using amyl xanthate was investigated. The copper-avid reagents used were salicylaldehyde, 8-hydroxyquinoline and α -benzoin oxime.

The adsorption amounts of amyl xanthate on chrysocolla by the addition of each organic reagent in xanthate solutions were measured. The organic copper-avid reagent coadsorbed with amyl xanthate onto the chrysocolla surface.

Fundamental tests for the attachment of chrysocolla particles to the air bubble were carried out to clarify the effect of such factors as the pH of the solution, conditioning time, the addition of a copper-avid reagent and the xanthate addition on the floatability of chrysocolla particles.

The pH region for the chrysocolla collection by activation with a copper-avid reagent and subsequent flotation using amyl xanthate is closely related to that for the formation of a copper-organic reagent complex, which can be obtained from thermodynamic data for the related stability constants.

Flotation tests on the synthetic and natural ores were performed. As a result, it was confirmed that chrysocolla could be floated sufficiently and selectively by its activation with copper-avid reagent like 8-hydroxyquinoline or salicylaldehyde, and also by its subsequent collection with amyl xanthate.

Experiments

Froth flotation is one of the most important methods for the separation of mineral particles, and has been successfully adapted for many kinds of minerals. Its application to copper silicate minerals is still a difficult problem, although investigations on copper silicates have been conducted in various countries.

There are three main reasons why the adaption of froth flotation to copper silicates is difficult. First copper silicates are themselves extremely hydrophilic. Second they are hardly sulfidized by sulfidizing agents, and even if sulfidizable,

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the conditions of sulfidization followed by flotation are severely limited. Third no sufficient collection of copper silicates can be obtained with conventional collectors. Even though a favorable collection might occur, selective separation of the copper silicates from the gangue minerals would be impossible. Therefore, for the flotation of copper silicate, it is necessary to find a new selective and powerful collector. It is also necessary to develop a new flotation process based on a unique concept for collecting silicate minerals. Some reports along this line have been published¹⁻⁵.

As one method for collecting copper silicates sufficiently and selectively in flotation, the authors tried to use some copper-avid organic reagents in order to activate the minerals, and then tried to float them by the higher xanthate. As a consequence, the copper silicate minerals were successfully floated. Hence, some fundamental results on the copper silicate flotation based on this concept are described in this paper.

Experimental

The silicate mineral tested was chrysocolla from Live Oak Pit, Gila County, Arizona, U.S.A., obtained through Nippon Chikagaku-sha Co.. It contained 31.6% Cu, and was identified as chrysocolla by a comparison of its X-ray diffraction results and DTA data with those reported for chrysocolla by other researchers⁶⁻⁷.

High grade coarse pieces of the material were selected, ground in an agate mortar, then screened to obtain a -48+100 mesh (Tyler) fraction and a -200 mesh fraction. The -48+100 mesh fraction was used to measure the amount of mineral particles picked up by air bubbles. The -200 mesh fraction was used for flotation tests in a laboratory flotator, and deslimed at 5 microns to measure the adsorption of xanthate.

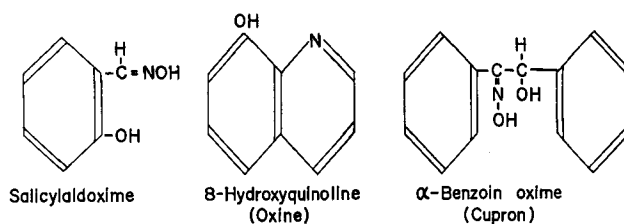
In measuring the amount of mineral particles picked up by air bubbles, the bubble pick-up method of Cooke⁸ was employed. One hundred milliliters of solution, made up to the desired condition, and a 0.5 g mineral sample were placed in a bubble pick-up tube. The tube was immersed in a thermostatically controlled water bath ($25 \pm 0.1^\circ\text{C}$) for ten minutes. An air bubble was introduced by a glass tube having a 10 mm inner diameter and was pressed against the mineral particles for a few seconds. The particles picked up by the air bubble were dried and weighed. The recorded results are the total weight in mg of six pick-ups.

Flotation tests were carried out with an MS type of laboratory flotation machine. Flotation feeds were a mixture of -200 mesh chrysocolla and -200 mesh quartz and a sample of natural chrysocolla ore.

Adsorption experiments for xanthate and the other organic reagents were

carried out in a 500 ml flask, in which 0.2 g of chrysocolla particles and 400 ml of the reagent solution were combined and gently stirred at a fixed temperature, $25 \pm 0.1^\circ\text{C}$. After the desired interval, the reagent concentration of the bulk solution was measured. The amount adsorbed was determined from the difference in the concentration of the adsorbate before and after adding the chrysocolla particles. The concentrations of xanthate and the other organic reagents in the solution were determined by ultraviolet spectrophotometry.

The organic reagents used to activate the chrysocolla were salicyldoxime, 8-hydroxyquinoline and α -benzoin oxime. They have the structural formulas:



All three reagents are used as the precipitating agent in copper analysis, reacting with the copper atom to form insoluble copper chelate compounds. Each reagent was dissolved in methyl alcohol when used in the experiments.

Potassium amyl xanthate was used as the collector. It was prepared synthetically and purified in the authors' laboratory. To adjust the pH of the solutions, hydrochloric acid and caustic soda were used. All inorganic and organic chemicals, except xanthate, were of an "extra pure" grade. The conductivity water, obtained by an ion exchange resin treatment, followed by a double distillation in a quartz still, was used for the adsorption and the bubble pick-up studies.

Results and Consideration

Coadsorption of the Organic Precipitating Agent with Xanthate on Chrysocolla

Figure 1 shows the xanthate adsorption on chrysocolla as a function of time, which varies with the addition of 8-hydroxyquinoline as none, 5 mg/l, 10 mg/l and 20 mg/l, at a constant addition of amyl xanthate (20 mg/l) and natural pH*, 6.7~7.8. This figure shows that the xanthate adsorption on chrysocolla increases with an increase of the reaction time, and was especially remarkable in the first 20 minutes. Xanthate can be adsorbed on chrysocolla to some extent without the

* In this paper, "natural pH" means the pH value which a solution naturally has when mineral particles are suspended in it.

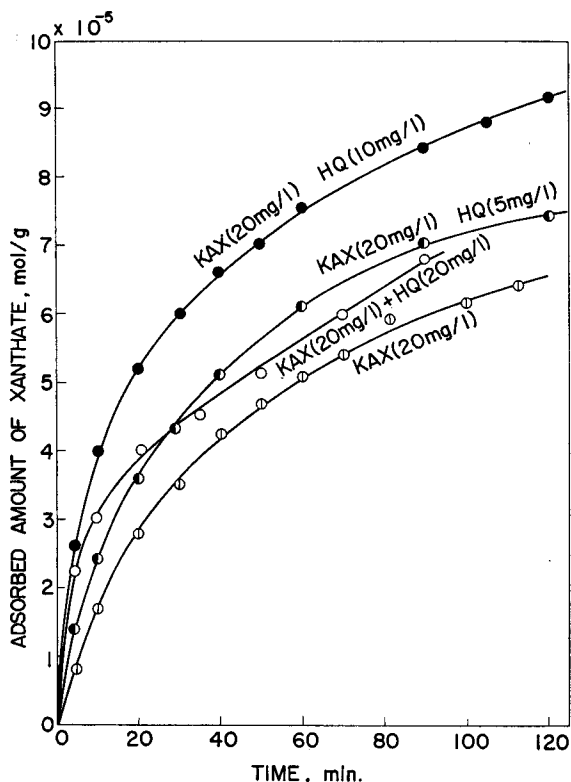


Fig. 1. Xanthate adsorption on chrysocolla as a function of time, with the addition of 8-hydroxyquinoline (HQ) as none, 5 mg/l, 10 mg/l, and 20 mg/l, at a constant addition of amyl xanthate (KAX), 20 mg/l.

addition of 8-hydroxyquinoline, but with the addition of 8-hydroxyquinoline, xanthate is adsorbed much more.

Figure 2 shows how hydroxyquinoline adsorbs on chrysocolla with reaction time under the same conditions used in the xanthate adsorption experiments. Hydroxyquinoline adsorption also increases with an increase of both the reaction time and the reagent addition. Figures 1 and 2 show that in the presence of hydroxyquinoline, xanthate tends to coadsorb on chrysocolla together with hydroxyquinoline.

Similarly, Figure 3 shows xanthate adsorption on chrysocolla as a function of time at a 10 mg/l addition of salicylaldoxime and α -benzoin oxime, respectively. In this experiment, the addition of amyl xanthate was held at a constant value of 20 mg/l, and the pH of the solution was also natural (pH 7.0~7.8 for salicylaldoxime and pH 6.7~7.6 for benzoin oxime). Figure 3 indicates that the xanthate

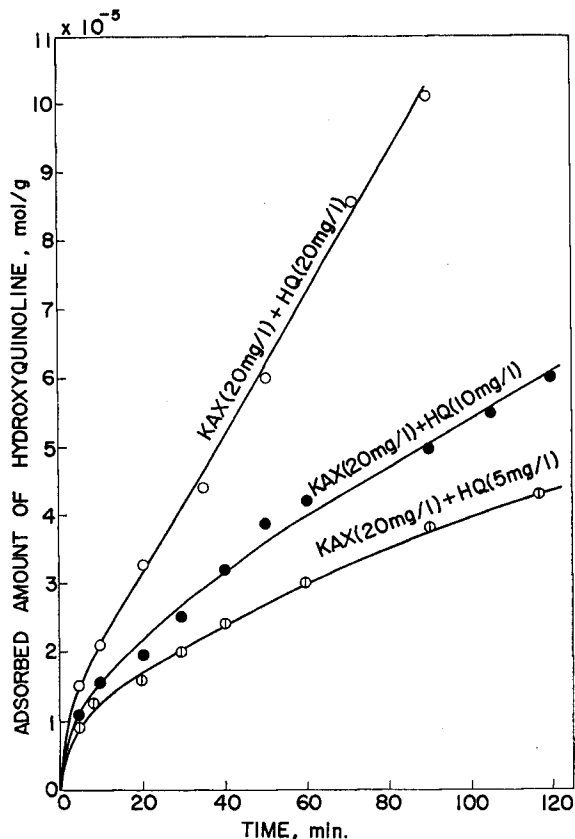


Fig. 2. Hydroxyquinoline adsorption on chrysocolla as a function of time, with addition of 8-hydroxyquinoline (HQ) as 5 mg/l, 10 mg/l, and 20 mg/l, at a constant addition of amyl xanthate (KAX), 20 mg/l.

adsorption in both cases increases with an increase of the reaction time, and is markedly notable in the first interval of minutes. When each precipitating agent is added, xanthate adsorbs on chrysocolla much more than when there is no addition of the agent. A comparison of the three precipitating agents, as to the extent of xanthate coadsorption, shows that hydroxyquinoline is best, salicylaldehyde is second, and benzoin oxime comes last.

From these results, it can be concluded that xanthate adsorption increases with the addition of the above organic precipitating agents, and that xanthate clearly tends to coadsorb on chrysocolla with the reagents.

Attachment of Chrysocolla to the Air Bubble Using the Organic Precipitating Agent Alone

Figure 4 shows the amount of chrysocolla particles picked up by air bubbles

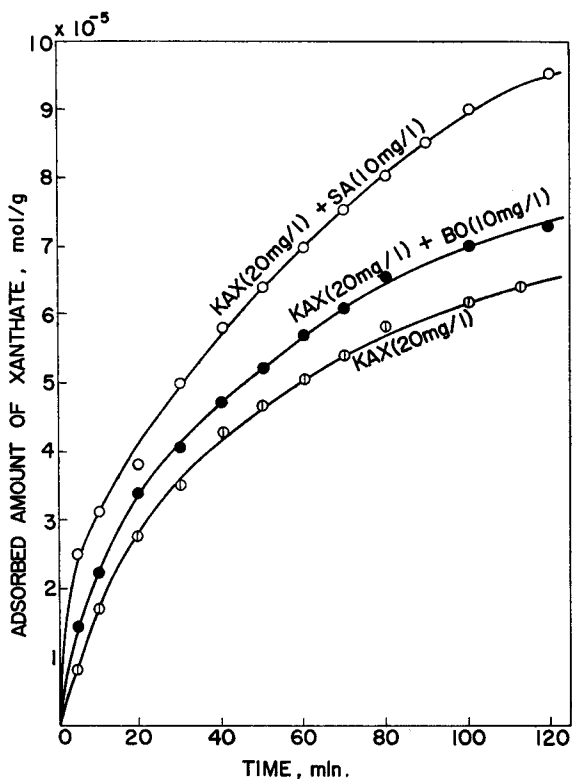


Fig. 3. Xanthate adsorption on chrysocolla as a function of time, at a 10 mg/l addition of salicylaldoxime (SA) and α -benzoin oxime (BO) and at a constant addition of amyl xanthate (KAX), 20 mg/l.

as a function of the conditioning time using benzoin oxime, salicylaldoxime and hydroxyquinoline by themselves. The result for amyl xanthate alone is also given as a reference. In these experiments the pH of the solutions was natural. The amount of chrysocolla particles picked up by the air bubbles increase with an increase in conditioning time. The order in which chrysocolla attaches to the air bubble at a 50 mg/l reagent addition is hydroxyquinoline, salicylaldoxime and benzoin oxim. It should be noted that the amyl xanthate used as the reference cannot cause an attachment between the chrysocolla particle and the air bubble at any time during conditioning, in spite of the existence of xanthate adsorption, as shown in Figure 1.

Attachment of Chrysocolla to the Air Bubble Using both Amyl Xanthate and an Organic Precipitating Reagent

Figure 5 shows the amount of chrysocolla particles picked up by air bubbles,

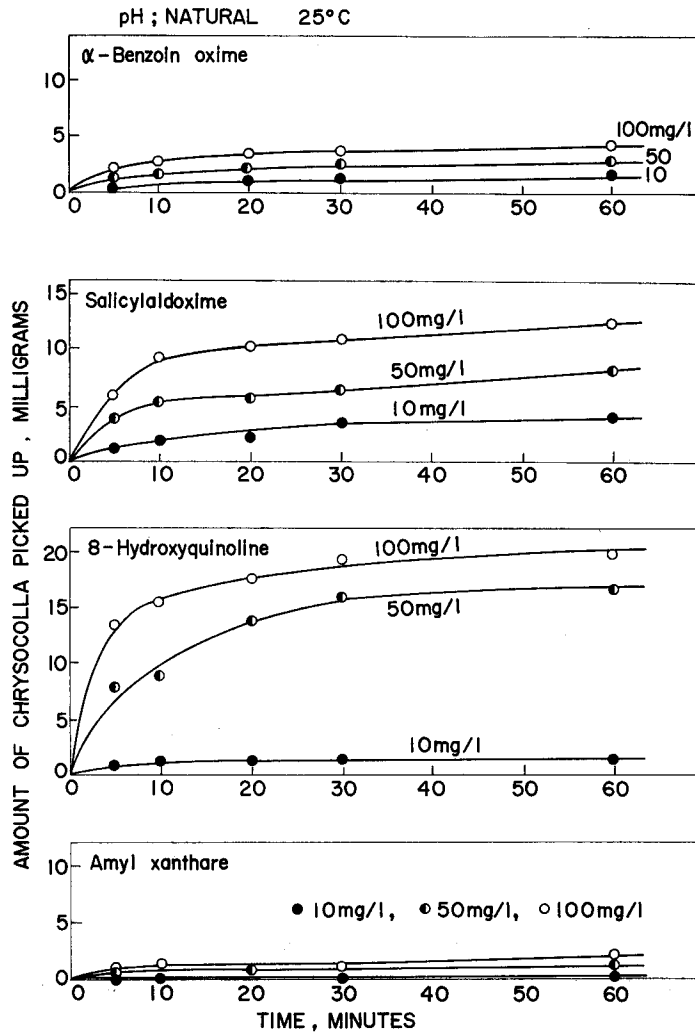


Fig. 4. Amount of chrysocolla particles picked up by air bubbles as a function of the conditioning time, using benzoin oxime, hydroxyquinoline, and amyl xanthate, by themselves.

using each of the three precipitating agents and amyl xanthate at 25 mg/l, as a function of the precipitating agent addition. The conditioning time was ten minutes.

When the results of Figure 5 are compared with those of Figure 4, it is clear that the xanthate addition causes an increase in chrysocolla attachment to the air bubble. The amount of chrysocolla picked up using a 25 mg/l xanthate addition and a 50 mg/l addition of each precipitating agent is several times that

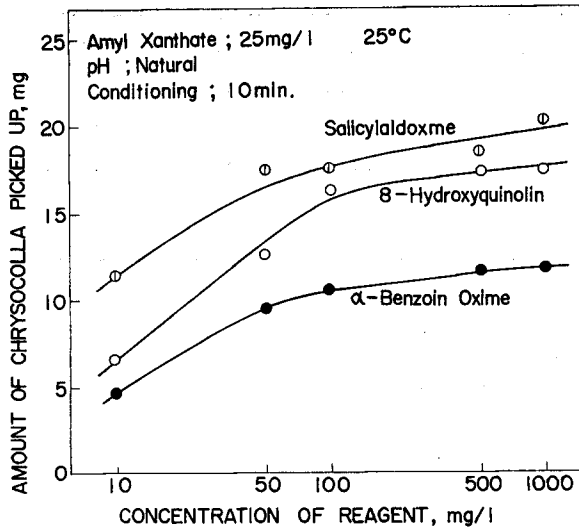


Fig. 5. Amount of chrysocolla particles picked up by air bubbles, using each of three precipitating agents and amyl xanthate (25 mg /l), as a function of the precipitating addition.

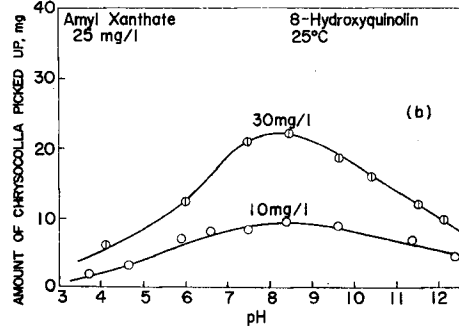
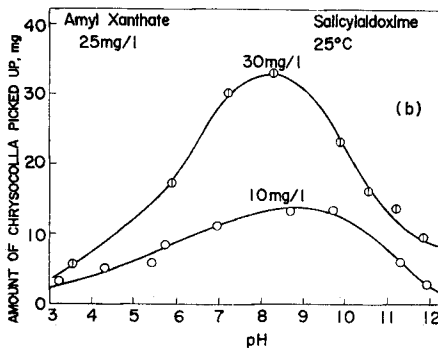
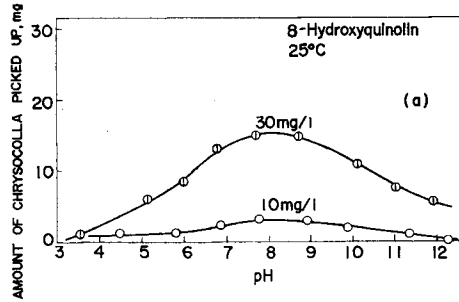
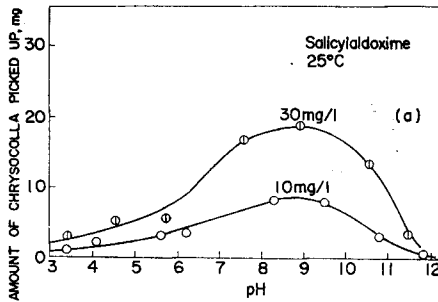


Fig. 6. Amount of chrysocolla attachment to air bubble as a function of pH, using salicylaldoxime, in the absence of xanthate (a) and in the presence of 25 mg/l xanthate (b).

Fig. 7. Amount of chrysocolla attachment to air bubble as a function of pH, using 8-hydroxyquinoline, in the absence of xanthate (a) and in the presence of 25 mg/l xanthate (b).

of its pick-up using a 50 mg/l addition of each precipitating agent alone, i.e., about five times higher with benzoin oxime, about two times higher with hydroxyquinoline, and about three times higher with salicylaldoxime.

Thus, it can be said from the above facts that the successful collection of chrysocolla by xanthate flotation is possible if the mineral surface is activated by the precipitating agents.

The pH Dependence of the Chrysocolla Attachment to an Air Bubble Using both Amyl Xanthate and an Organic Precipitating Agent

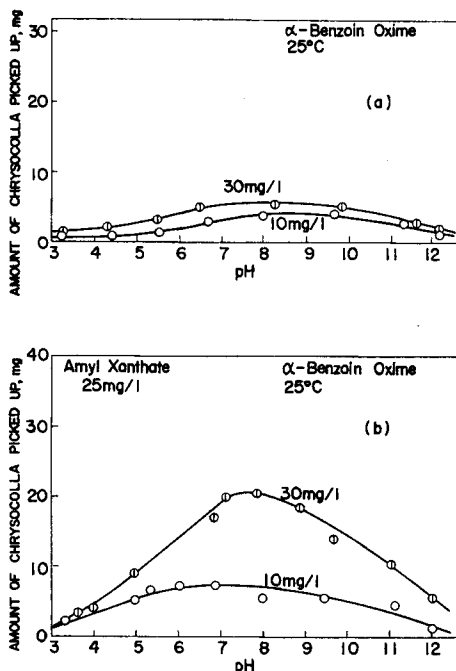


Fig. 8. Amount of chrysocolla attachment to air bubble as a function of pH, using α -benzoin oxime, in the absence of xanthate (a) and in the presence of 25 mg/l xanthate (b).

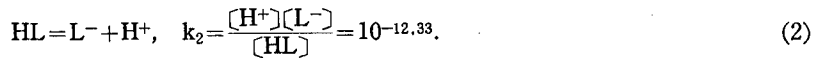
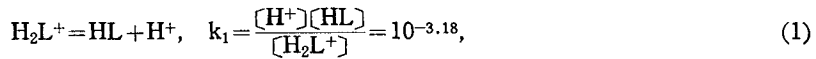
Figures 6, 7 and 8 present the pH dependence of the chrysocolla attachment to air bubbles using both amyl xanthate and each of the precipitating agents: salicylaldoxime, hydroxyquinoline and benzoin oxime. The amounts of chrysocolla picked up by the air bubbles after 10 minutes of conditioning in the precipitating agent additions of 10 mg/l and 30 mg/l are plotted against the pH of the solution. Each figure has two kinds of results: one for no addition of xanthate as the reference (a), the other with the xanthate addition (b). The data, with and without an addition of xanthate, clearly show that the chrysocolla attachment to the air

bubbles depends on the pH of the solution. There is an optimum pH range giving a maximum attachment for each precipitating reagent, i.e., pH 8~9 for hydroxyquinoline; pH 7~8 for benzoin oxime and pH 8~9 for salicylaloxime. When the maximum amounts of chrysocolla picked up at a 30 mg/l addition of each precipitating agent and a 25 mg/l addition of amyl xanthate are compared among the three precipitating agents, salicylaloxime has the highest value while benzoin oxime has the lowest.

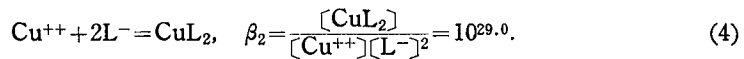
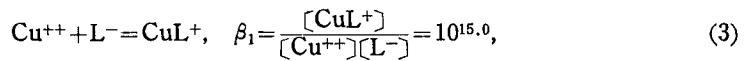
The pH Region of the Chrysocolla Attachment to an Air Bubble in Relation to the Conditional Stability Constant of a Complex Formed between the Copper Atom and the Precipitating Agent

To determine in what pH range a principal reaction concerned proceeds to completion, the conditional stability constant introduced by Schwarzenbach has been often employed in analytical chemistry using chelate compounds. In this section, the pH dependence of the conditional stability constant of a complex formed in the copper-hydroxyquinoline system is obtained in order to discuss the pH region of the chrysocolla attachment to the air bubble.

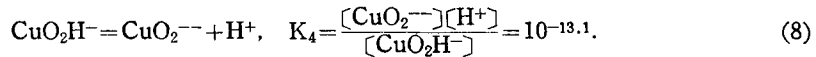
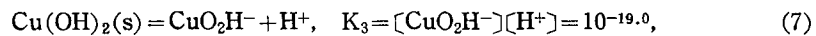
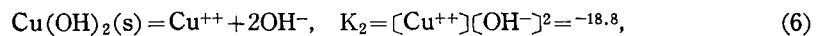
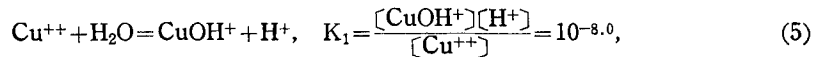
L^- represents the ionic form of hydroxyquinoline from which one proton has been removed. Then, the dissociation equilibria for the reagent in an aqueous solution are as follows⁹⁾:



The formation of the copper-hydroxyquinoline complex is:



The formation of the copper hydroxide complexes is also important:



The existence of the other hydroxide complexes, e.g. $\text{Cu}_2\text{OH}^{+++}$ and Cu_2O^{++} , is known, but they are neglected here because they occur in such small quantities.

β_2 in Equation (4) is the stability constant of CuL_2 . If β_2' is the conditional stability constant, there is the following relation between β_2 and β_2' .

$$\beta_2' = \frac{[\text{CuL}_2]'}{[\text{Cu}^{++}]'[\text{L}^-]'^2} = \frac{A_{MY2}}{A_M \cdot A_Y^2} \beta_2 \quad (9)$$

where

$$\begin{aligned} [\text{Cu}^{++}]' &= [\text{Cu}^{++}] + [\text{CuOH}^+] + [\text{Cu}_2\text{OH}^-] + [\text{CuO}_2^{--}] \\ &= [\text{Cu}^{++}] \left\{ 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_3K\omega}{K_2[\text{H}^+]^3} + \frac{K_3K_4K\omega}{K_2[\text{H}^+]^4} \right\} \\ &= [\text{Cu}^{++}] A_M, \quad (K\omega \text{ is the ion product of water}) \end{aligned} \quad (10)$$

$$\begin{aligned} [\text{L}^-]' &= [\text{L}^-] + [\text{HL}] + [\text{H}_2\text{L}^+] \\ &= [\text{L}^-] \left\{ 1 + \frac{[\text{H}^+]}{k_2} + \frac{[\text{H}^+]^2}{k_1k_2} \right\} \\ &= [\text{L}^-] A_Y, \end{aligned} \quad (11)$$

$$\begin{aligned} [\text{CuL}_2]' &= [\text{CuL}_2] \\ &= [\text{CuL}_2] A_{MY2} \quad (\text{In this case } A_{MY2}=1). \end{aligned} \quad (12)$$

From Equation (9), the conditional stability constant β_2' is determined by the values of β_2 , A_{MY2} , A_M and A_Y . A_{MY2} , A_M and A_Y are expressed in terms of pH as shown in Equations (12), (10) and (11), respectively. Accordingly, the con-

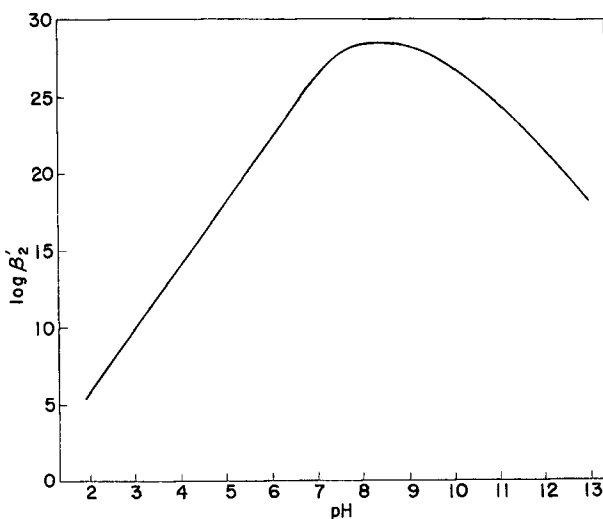


Fig. 9. The pH dependence of the conditional stability constant of Cu-hydroxyquinoline complex.

dional stability constant β_2' can eventually be obtained as a function of pH.

Figure 9 shows the plot of $\log \beta_2'$ against pH for the copper-hydroxyquinoline system.

Note that in Figure 9, $\log \beta_2'$ depends markedly on pH and that the pH range between 7 and 10 is the region where the values of $\log \beta_2'$ are very high, i.e., the copper-hydroxyquinoline complex is extremely stable. As can be seen from a comparison of the results in Figures 9 and 7, the pH region, where the chrysocolla attachment to the air bubble is large, coincides fairly well with that where the values of $\log \beta_2'$ are high.

It can be concluded from the above results that, when such a precipitating reagent is used, an optimum pH range for flotation can be presumed by determining the pH dependence of the conditional stability constant for the principal compound formation conceivable in the system concerned.

Flotation Tests

Flotation tests for two kinds of ore, synthetic and natural, were carried out, using hydroxyquinoline as an organic activator and potassium amyl xanthate as the collector in an MS laboratory cell (250 cc capacity). The flotation conditions, i.e., the pH of the pulps, the addition of the organic activator, the xanthate addition and the conditioning time, were set on the basis of the fundamental results of chrysocolla attachment to the air bubble and the coadsorption of xanthate on chrysocolla with hydroxyquinoline.

(1) Flotation tests for synthetic ore

The synthetic ore was a mixture of -200 mesh chrysocolla and -200 mesh quartz. The ore particles were put in a beaker and stirred with 30 mg/l of hydroxyquinoline and 10 mg/l of xanthate at pH 8.26. After 15 minutes of conditioning they were transferred to the flotation cell. Flotation tests were performed according to the flowsheet shown in Figure 10.

In the first stage of flotation (Roughing), hydroxyquinoline and xanthate were added stepwise to recover as much chrysocolla as possible. The total ad-

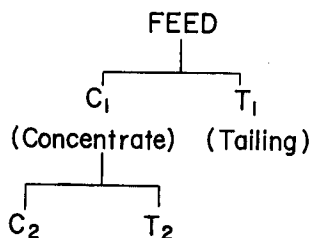


Fig. 10. Flowsheet of copper ore flotation.

ditions of hydroxyquinoline and xanthate amounted to 40 mg/l and 24 mg/l, respectively, including their additions in the conditioning stage. The frother was pine oil. A few drops of pine oil were given from a fine injection needle. The flotation time for the first stage was about 6 minutes. The froth concentrate in this stage of flotation was repulped for a second flotation, that of cleaning. In the cleaning the second froth could be recovered very rapidly with a few drops of pine oil alone. The metallurgical results are shown in Table 1.

Table 1. Flotation results for synthetic ore.

	Weight (g)	Assay Cu (%)	Recovery of Cu (%)	Conditions
Feed	9.234	2.13	100.0	Conditioning: Time; 15 min., pH; 8.26 Hydroxyquinoline; 30 mg/l Amyl xanthate; 10 mg/l 1st flotation: Time; 6 min. Hydroxyquinoline; 10 mg/l Amyl xanthate; 14 mg/l Pine oil; A few drops 2nd flotation: Time; 2 min., pH; 7.59 Pine oil; A few drops
T ₁	6.373	0.06	1.99	
C ₁	2.861	6.72	98.1	
C ₂	0.868	20.8	92.0	
T ₂	1.993	0.6	6.1	

As can be seen from Table 1, the recovery of chrysocolla in the first roughing flotation was as high as 98.1%, and the 20.8% Cu concentrate in the cleaning flotation could be successfully recovered.

(2) Flotation tests for natural ore

A natural oxide copper ore from Peru, South America, was used in the flotation tests. Most of the copper in the ore existed as chrysocolla. Malachite was detectable but in a small quantity. X-ray diffraction data showed that the gangue minerals were quartz and andradite.

The copper ore was ground to -200 mesh and then deslimed by decantation until it was free from -5 microns. Flotation tests for the natural ore were carried out according to the flowsheet shown in Figure 10.

Typical results are presented in Tables 2 and 3. The major differences in the flotation conditions of Table 3 as compared with those of Table 2 are: an increased addition of hydroxyquinoline during conditioning, decreased conditioning time, no addition of hydroxyquinoline in the first flotation, and the addition of xanthate in the second flotation.

Tables 2 and 3 indicate that the recovery of chrysocolla from the natural ore is appreciably high through the roughing flotation, 94.92% or 96.79%, and

Table 2. Flotation of natural ore (I).

	Weight (g)	Assay Cu (%)	Recovery of Cu (%)	Conditions
Feed	10.735	6.12	100.0	Conditioning : Time ; 15 min., pH ; 7.94 Hydroxyquinoline ; 30 mg/l Amyl xanthate ; 20 mg/l 1st flotation : Time ; 7 min. Hydroxyquinoline ; 10 mg/l Amyl xanthate ; 10 mg/l Pine oil ; A few drops 2nd flotation : Time ; 2 min., pH ; 7.20 Pine oil ; A few drops
T ₁	4.763	0.77	5.58	
C ₁	5.972	10.38	94.42	
C ₂	3.158	16.38	78.78	
T ₂	2.814	3.65	15.64	

Table 3. Flotation of natural ore (II).

	Weight (g)	Assay Cu (%)	Recovery of Cu (%)	Conditions
Feed	9.350	6.14	100.0	Conditioning : Time ; 2 min., pH ; 8.28 Hydroxyquinoline ; 40 mg/l Amyl xanthate ; 20 mg/l 1st flotation : Time ; 7 min. Amyl xanthate ; 20 mg/l Pine oil ; A few drops 2nd flotation : Time ; 2 min., pH ; 7.90 Pine oil ; A few drops Amyl xanthate ; 10 mg/l
T ₁	4.006	0.46	3.21	
C ₁	5.344	10.40	96.79	
C ₂	2.301	21.75	87.19	
T ₂	3.043	1.81	9.60	

and that a concentrate with a high grade of copper and sufficient recovery can be obtained through a cleaning flotation in each test.

The results of this study show that chrysocolla can be recovered sufficiently and selectively by flotation, using amyl xanthate as the collector after activation with a copper-avid precipitating agent like hydroxyquinoline. Further, other tests have shown that salicylaldehyde may act similarly to hydroxyquinoline with respect to chrysocolla activation, while benzoin oxime is inferior.

Conclusion

In order to collect the copper silicate mineral, chrysocolla, a method in which the copper silicate mineral is activated by a copper-avid organic reagent, then floated by using amyl xanthate was investigated. The copper-avid organic reagents used were salicylaldehyde, 8-hydroxyquinoline and α -benzoin oxime.

The adsorption amounts of amyl xanthate on chrysocolla were measured

under various conditions in the presence of each organic reagent. The addition of an organic reagent caused a markedly increased adsorption of xanthate on chrysocolla. The adsorption studies showed that xanthate coadsorbed on chrysocolla with the copper-avid organic reagents used.

Fundamental tests on the attachment of chrysocolla particles to the air bubble were carried out. Conditions such as the pH of the pulp, the conditioning time, the addition of an organic activator and the xanthate addition, where chrysocolla particles could attach to the air bubble were ascertained.

The pH region for the chrysocolla collection by activation with a copper-avid reagent and subsequent flotation using amyl xanthate is closely related to that for the formation of a copper-organic reagent complex, which can be obtained from thermodynamic data for the related stability constants.

In addition, flotation tests for synthetic and natural ores were performed. As a result, it was confirmed that chrysocolla could be floated sufficiently and selectively by activation with a copper-avid reagent like hydroxyquinoline or salicylaldoxime and by the collection with amyl xanthate.

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