Leaching of Chrysocolla with Ammonia-Ammonium Carbonate Solutions

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Chrysocolla was leached in solutions of ammonium hydroxide and ammonium carbonate as a function of the variables: temperature (25 to 55 °C), ammonia-ammonium ratio (0.0:1.0 to 1.0:0.0), total ammonia concentration (0.25 to 6.0 M), and particle size (100 to 400 mesh). A model of the leaching behavior was deduced based on: (1) the activation energy of 60.75 kJ/mole (14.51 kcal/mole) for 3 M total NH_3 which was dependent on both total ammonia concentration and temperature; (2) first-order dependence of rate on $[(NH_4)_2CO_3]$; (3) dependence of initial reaction rate on reciprocal of particle diameter; and (4) morphological evidence from SEM and EDAX measurements of diffusion and leaching occurring primarily in surface microcracks and not in the submicroscopic pores. In addition to the importance of diffusion through microcracks in rate control chemical reaction at active surface sites to produce the species, $CuNH_3^{2+}$, is also important. Only a fraction of the Cu atoms react that are exposed to lixiviant. Higher ammonia-ammonium ion concentrations, higher temperatures, or much longer times are required for more refractory Cu atoms to dissolve.

I. INTRODUCTION

CHRYSOCOLLA, a hydrous copper silicate, $CuO \cdot SiO_2 \cdot 2H_2O$, found in the upper oxidation zones of copper deposits, is commonly associated with malachite, azurite, and limonite.[1] Samples vary widely in composition, but using the above formula chrysocolla has a copper content of 36.18 pct as compared to 34.62 pct for chalcopyrite. Large ore deposits of chrysocolla are found throughout the world, some of which are presently being mined.[2] Unfortunately, chrysocolla is not easily concentrated for froth flotation like chalcopyrite. The direct smelting of high grade oxide ores has been reported,[3] but such an alternative would not be applicable to a majority of oxide ore deposits which are low grade. Hydrometallurgy, however, opens the possibilities of exploiting such deposits.

Chrysocolla has been leached with various agents like EDTA[5] and NTA,[6] cyanide solutions,[7,8] and ammoniacal solutions.[8,9,10] Although the sulfuric acid leaching of chrysocolla has been generally accepted as practical, the preponderance of carbonates in certain ore deposits can cause tremendous increases in acid consumption, thus creating the need for a more selective reagent for such deposits. Ammonia is an attractive reagent because it does not react with carbonates, and because of its ease of handling, low inventory cost, and amenability to regeneration. The NH_3-CO_2-H_2O system was therefore chosen in the investigation of the kinetics of copper dissolution from chrysocolla. The variables studied were ammonia-ammonium ratio, total ammonia concentration, temperature, and initial particle size. The roles of these variables in terms of leaching rate are interpreted using the residue analyses: SEM and EDAX. Surface area and infrared measurements as well as X-ray studies were also conducted.

II. EXPERIMENTAL

A. Materials

The chrysocolla samples were from an upgraded ore from Globe, Arizona. The mineral was ground using a Fisher Mortar Grinder into five size fractions between 100 mesh and 400 mesh. Each size fraction was analyzed for copper using an atomic absorption spectrophotometer, and the copper content of the samples varied from 33.01 pct to 36.16 pct, with a slight tendency for the chrysocolla to concentrate in the finer size fractions. The composition and purity of the samples were determined using combined gravimetric and atomic absorption techniques. The chemical formula $CuO \cdot SiO_2 \cdot \frac{1}{2}H_2O$ was obtained and based on this formula, the samples contained 91 pct chrysocolla, with the remaining 9 pct being free silica. Both X-ray and infrared spectrophotometric studies confirmed the presence of these minerals.

The leaching solutions were prepared from reagent-grade ammonium hydroxide and ammonium carbonate, dissolved in distilled deionized water, according to the desired total ammonia concentration and ammonia-ammonium ratio. The total ammonia concentration ($NH_3 + NH_4^+$) of the leaching solution was varied from 0.25 to 6.00 M. The ammonia-ammonium ratio was changed from 1:0 (pure ammonium hydroxide carbonate in solution) to 0:1 (pure ammonium carbonate in solution). The ammonia-ammonium ratio was defined as above on the basis of mole ratio of ammonium hydroxide to ammonium carbonate initially added into the leaching solution. A 0.5:0.5 ammonia-ammonium ratio is a ratio of unity, i.e., equimolar ratio.

B. Apparatus and Technique

The leaching experiments were conducted in a reactor vessel system consisting of a one liter, unbaffled reaction kettle with a glass cover having openings for reflux condenser, thermometer, closed-system stirrer, and a sampling device with a fritted glass end for the withdrawal of 2.5 ml aliquot samples for solution analysis. The whole system was immersed in a water bath equipped with a Haake E2 stirrer-heater capable of maintaining the bath at a selected temperature to within ±0.03 °C. Experiments were conducted

at temperatures between 25 and 60 °C. Initial studies showed that the agitation rate had no effect on the leaching rate above 600 rpm. All subsequent experiments were performed with an agitation rate of 800 rpm.

Each experimental run was started by pouring 750 ml of freshly prepared leaching solution of desired strength and ammonia-ammonium ratio into the reaction vessel and allowing it to reach process temperature. Leaching was initiated by the addition of 1 gm of the mineral of desired mesh size. Aliquot samples withdrawn at predetermined time intervals were analyzed for copper content using an Instrument Laboratory, Inc., Model 351, Atomic Absorption Spectrophotometer.

Internal and external (or commercial) standards were both used in the atomic absorption analysis. Internal standards were prepared by dissolving known amounts of chrysocolla in aqua regia. The internal standards were diluted at the same dilution ratio used for the sample solutions to eliminate any systematic error that the Hyperion Variable Ratio Diluter may have introduced. The use of the internal standards allowed the direct calculation from absorbance units of the fraction of copper extracted, α. The external or commercial standards were in turn used to check for any decomposition of the internal standards.

C. Logarithmic Kinetics

The data as shown by the typical leaching curves in Figure 1 for α vs time at temperatures from 25 to 55° fit only an empirical α vs $\log_e$ time plot, and this is used to interpret all of the leaching rate data. The results hereafter are presented on that basis. All other known topochemical leaching rate models were tried unsuccessfully; thus, it is good now to consider the analytical approach used before further results are presented and discussed.

To appreciate the reason why the fraction extracted vs time curves would fit only a logarithmic plot, note from Figure 1 an initial very rapid extraction rate with leveling off after some time. In most experiments, about half of the maximum amount of copper extracted after 30 minutes was leached out in 15 minutes while the remaining half took 285 minutes to dissolve. The decrease in the reaction rate is not due to a decrease in the surface area of the particles. The large surface area of 255 m²/g (determined using the BET N₂ adsorption technique) remained virtually constant throughout the reaction.

The equation which fits the data of Figure 1 is

$$\alpha = (1/\beta) \log_e (\beta \delta t + 1) \qquad [1]$$

where t = time and β and δ are equation parameters which will be explained subsequently.

Although the logarithmic rate law is commonly encountered in chemisorption and oxidation,[11] it has also been used to explain the leaching of chrysocolla in nitrilotriacetic acid (NTA),[6] the conversion of chalcopyrite into copper sulfides,[12] and the thermal dehydration of muscovite.[13] Several different models which may lead to the logarithmic rate law expression have been presented in the literature. The models developed by Evans[14] for the oxidation of zinc and the strain model developed by Cook and Oblad[15] seem to fit the experimental results in this work best. Neither of these models, however, can explain all aspects of ammoniacal leaching of chrysocolla. Prosser[16] explained the leveling off
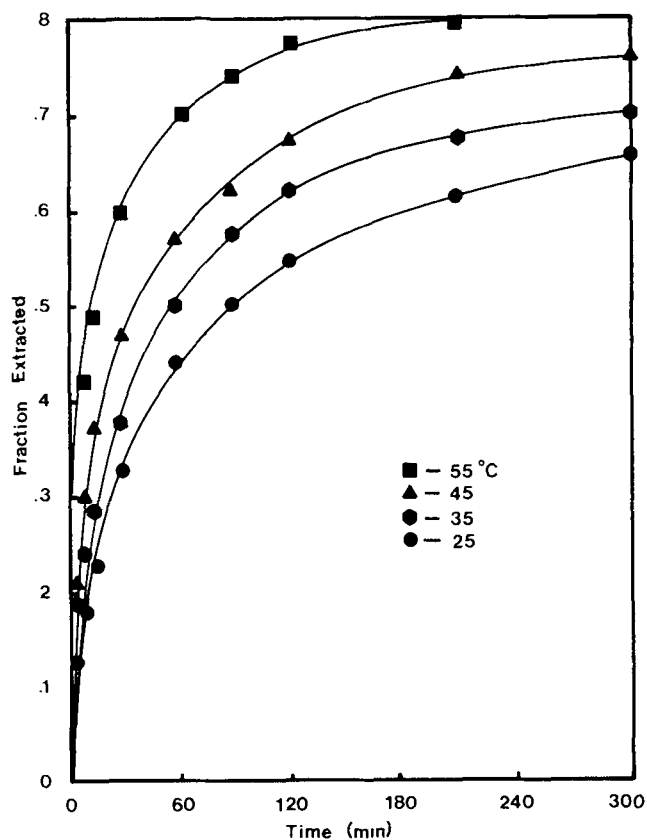

Fig 1 — Typical leaching curves.

of the leaching curves as being indicative of the presence of a continuum of copper forms in chrysocolla, some of which are soluble and some are refractory at a particular temperature and concentration of ammonia.

Assuming an asymmptotic case of Eq. [1], that is, when t is large such that $\beta \delta t > 1$, the logarithmic rate law expression simplifies into:

$$\alpha = (1/\beta) \log_e(\beta \delta t) \qquad [2]$$

which predicts a linear dependence of the fraction of copper extracted on the logarithm of time, as shown in Figure 2. Equation [2], however, is no longer valid as t approaches zero and Eq. [1] must be used. When differentiated with respect to time, Eq. [1] becomes:

$$\frac{d\alpha}{dt} = \delta \exp(-\beta\alpha) \qquad [3]$$

wherein the leaching rate, $d\alpha/dt$, may be calculated for any value of α, knowing the values of β and δ. In this study, these parameters were estimated from Eq. [1] using a Simplex Search Minimization Algorithm.[17]

D. Simplex Algorithm

The simplex method is a derivative-free technique of minimization of a nonlinear function through the use of regular search patterns involving simplexes. For two parameters, an equilateral triangle is the regular simplex used. The method consists of evaluating the values of the objective function, ϕ, at the vertices of the simplex, as described by Kuester and Mize.[18] For the minimization routine used on
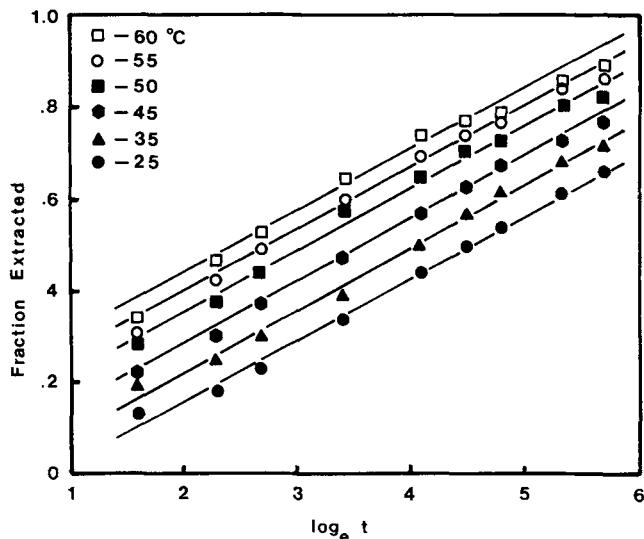
Fig. 2—Linear dependence of fraction extracted on $\log_e t$ for $-100 + 150$ mesh particles at $(NH_3)_T = 3.00$ M.

Eq. [1], the objective function was

$$\phi = \sum \frac{(\text{predicted } \alpha - \text{experimental } \alpha)^2}{\text{experimental } \alpha} \qquad [4]$$

The values of β and δ were used to predict α values using Eq. [1], which were then compared to the experimental values of α. Figure 3 is a plot of the predicted values of α (line) against experimental α values (data points) for temperature as a variable, and the fit is very good. Similar plots were also done for the three other variables, ammonia-ammonium ratio, total ammonia concentration, and initial particle size, and they fit equally well giving confidence in the logarithmic rate law expression (Eqs. [1] and [2]).

As presented in Eq. [3], the value of $d\alpha/dt$ may be calculated for any value of α and at $\alpha = 0$, Eq. [3] simplifies to:

$$\frac{d\alpha}{dt} = \delta \qquad [5]$$

The value of δ, therefore, is a measure of the initial kinetics of the system. The value of β, on the other hand, is a measure of the resistive forces that slow down the leaching rate from an initial value of δ, with its maximum effect being evident at $\alpha = 1$.

With this understanding of Eq. [1] and the two empirical parameters δ and β which will now be used, the experimental data can be presented and interpreted.

III. RESULTS

A. Effect of Ammonia-Ammonium Ratio

Leaching experiments were performed to investigate the effect of various ammonia-ammonium ratios on the behavior of chrysocolla. The results for initial rate are summarized in Figure 4, which shows a maximum at an ammonia-ammonium ratio of unity. The recovery after 300 minutes of leaching was also measured and it maximized similarly at unity ratio of ammonia-ammonium (ratio of 0.50:0.50) with very little extracted when pure am-
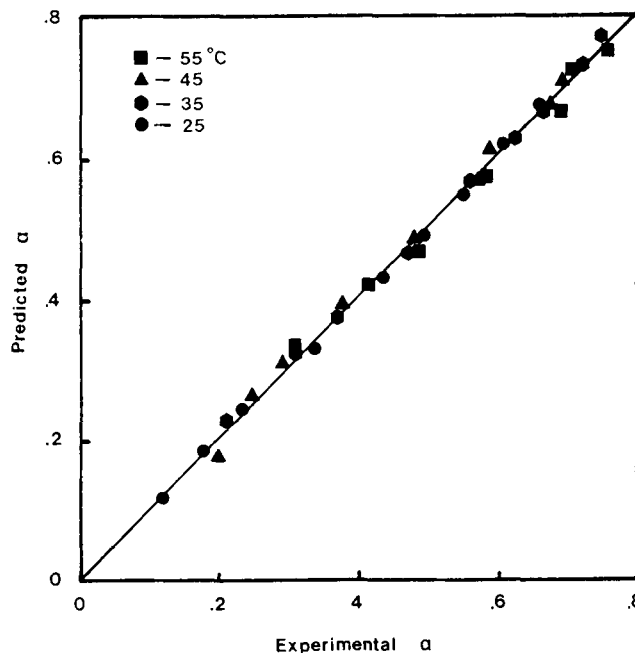

Fig. 3—Comparison of leaching model against experimental data as a function of temperature
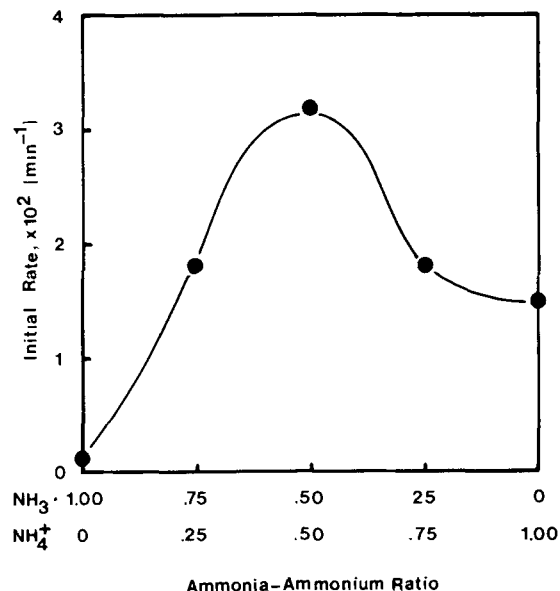

Fig 4—Effect of the ammonia-ammonium ratio on the initial leaching rate, δ, of $-100 +150$ mesh particles at $(NH_3)_T = 3$ 00 M and 25 °C.

monium hydroxide was used. The slowest leaching rate, as well as the lowest recovery, were both observed at an ammonia-ammonium ratio of $1:0$ (pure ammonium hydroxide). Complex equilibria calculations (Figure 5) on the NH_3-CO_2-H_2O system reveal that at this ratio, the predominant species is free ammonia. This suggests that free ammonia is not the active species in the ammoniacal leaching of copper from chrysocolla, but most probably it is ammonium ion.

A $\log_e \delta - \log_e[NH_4^+]$ plot (Figure 6) for experiments with an ammonia-ammonium ratio of unity gives the dependence of the initial rate on the ammonium ion concentration. The results show a good fit, especially at 25 °C,

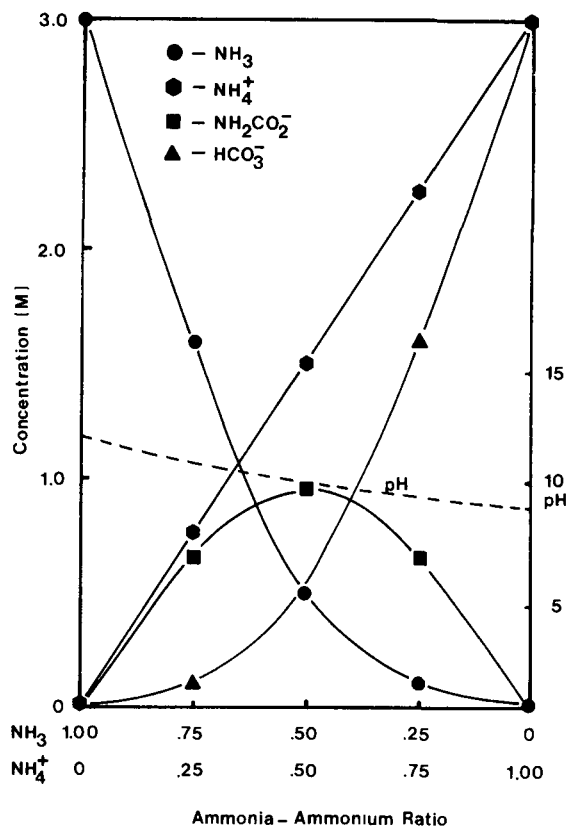Fig 5—Distribution of predominant species in the NH_3-CO_2-H_2O system at $(NH_3)_T = 3.00$ M.

with a slope of 0.9537 and a regression correlation coefficient of 0.9981. The slopes for the higher temperatures are 1.0539, 1.0785, and 1.2840 for 35, 45, and 55 °C, respectively. The linear fit is not as good at 55 °C, probably due to the volatilization of some components in the lixiviant. These results, therefore, point to a first-order dependence of the initial rate on the ammonium ion concentration as given by the equation:

$$CuO \cdot SiO_2 \cdot nH_2O + NH_4^+$$
$$= Cu(NH_3)^{2+} + OH^- + SiO_2 + (n)H_2O \qquad [6]$$
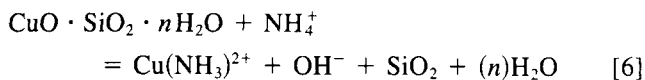
This would explain the increases observed in both the leaching rate and recovery as the ammonia-ammonium ratio is changed from 1:0 to 0.50:0.50 (unity) wherein the concentration of the ammonium ion increases as shown in Figure 5. Equation [6], however, cannot explain the decreases in both the recovery and the initial leaching rate as the ammonia-ammonium ratio is changed from 0.50:0.50 to 0:1, where solution equilibria predicts a continuous increase in the ammonium ion concentration (Figure 5).

B. Surface Adsorption

Consider that the leaching reaction given by Eq. [6] occurs in two steps, adsorption followed by chemical reaction. The adsorption step involves the adsorption of the ammonium ion and its appropriate counter ion as represented by the reaction
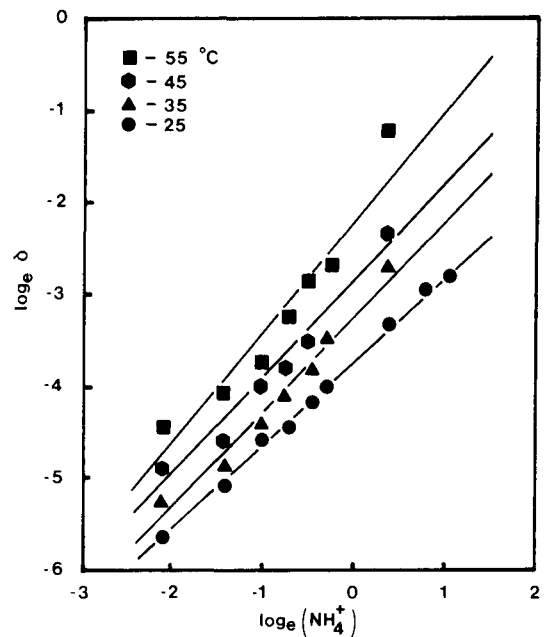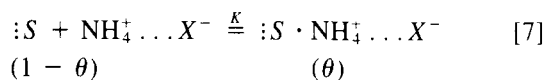
$$\underset{(1 - \theta)}{:S + NH_4^+ \ldots X^-} \overset{K}{=} \underset{(\theta)}{:S \cdot NH_4^+ \ldots X^-} \qquad [7]$$

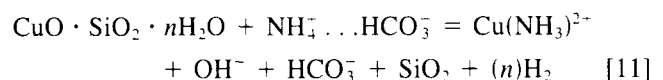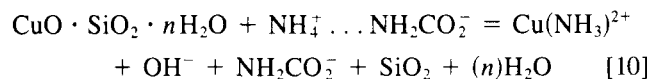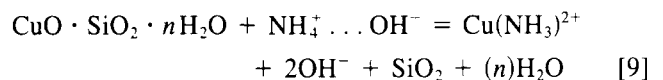Fig 6—Dependence of the initial rate, δ, on the ammonium ion concentration

where
$:S$ = surface active site
θ = fraction of active sites covered
K = adsorption equilibrium constant
X^- = ammonium counter ion.

Using this reaction and single site Langmuir adsorption of $NH_4^+ \ldots X^-$ a Langmuir equation may be obtained[18] in terms of δ and $NH_4^- \ldots X^-$ concentration. From this the enthalpy and entropy of activation may be calculated.[19] This was done and yielded respective values of -28.22 kJ/mole $(-6.74$ kcal/mole) and -101.47 J/mole·K $(-24.23$ e.u.). This is a rather small enthalpy of adsorption, only moderately greater in absolute value than that for physical adsorption (5 kcal/mole or less). The very negative entropy of adsorption indicates that the adsorbed state is extremely low in entropy compared to the nonadsorbed state.

The introduction of the concept of surface adsorption thus modifies the chemical reaction presented in Eq. [6] to:

$$CuO \cdot SiO_2 \cdot nH_2O + NH_4^- \ldots X^- = Cu(NH_3)^{2-}$$
$$+ OH^- + X^- + SiO_2 + (n)H_2O \qquad [8]$$
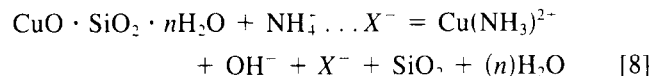
In the NH_3-CO_2-H_2O system, the possible reactions in terms of species X^- are:

$$CuO \cdot SiO_2 \cdot nH_2O + NH_4^+ \ldots OH^- = Cu(NH_3)^{2+}$$
$$+ 2OH^- + SiO_2 + (n)H_2O \qquad [9]$$

$$CuO \cdot SiO_2 \cdot nH_2O + NH_4^+ \ldots NH_2CO_2^- = Cu(NH_3)^{2+}$$
$$+ OH^- + NH_2CO_2^- + SiO_2 + (n)H_2O \qquad [10]$$

$$CuO \cdot SiO_2 \cdot nH_2O + NH_4^- \ldots HCO_3^- = Cu(NH_3)^{2-}$$
$$+ OH^- + HCO_3^- + SiO_2 + (n)H_2 \qquad [11]$$

Assuming that the adsorption constant K of Eq. [7] does not vary with ammonia-ammonium ratio and that it is the same for the three ion pairs* given above, an empirical fit is

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* This is an approximation and is used due to the unavailability of actual K values for each species. It must be considered as a first step toward a more detailed study of the systems
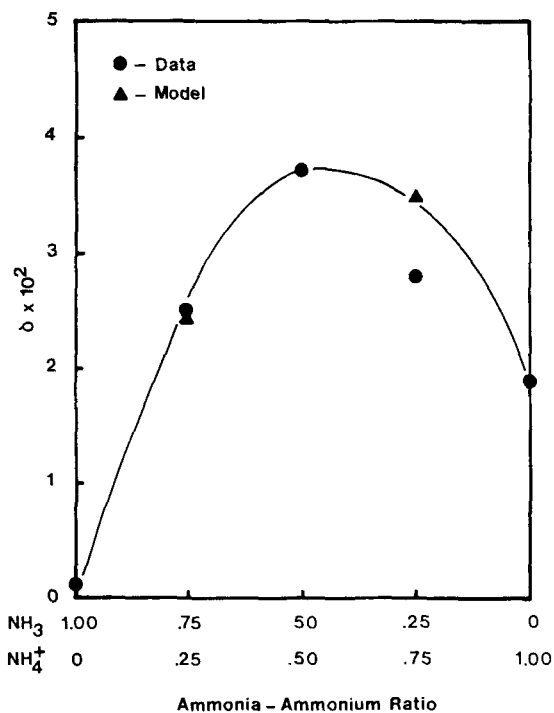
Fig. 7—Comparison of model (Eq [12]) against experimental data

Fig. 8—Leaching of chrysocolla as a function of total ammonia concentration at 25 °C for $-100 +150$ mesh particles.

obtained using the experimental data given in Figure 4 which yields the expression:

$$\hat{\delta} = 4.82\text{E-}1\left[\frac{K(\text{NH}_4^+\ldots\text{OH}^-)}{1 + K(\text{NH}_4^+\ldots\text{OH}^-)}\right]$$
$$+ 1.20\text{E-}1\left[\frac{K(\text{NH}_4^+\ldots\text{NH}_2\text{CO}_2^-)}{1 + K(\text{NH}_4^+\ldots\text{NH}_2\text{CO}_2^-)}\right]$$
$$+ 3.37\text{E-}2\left[\frac{(K\text{NH}_4^+\ldots\text{HCO}_3^-)}{1 + K(\text{NH}_4^+\ldots\text{HCO}_3)}\right] \qquad [12]$$

where $\hat{\delta}$ is the empirical estimate of the rate, δ. Equation [12] is plotted against the experimental data, and the results (Figure 7) show good agreement between $\hat{\delta}$ and δ except at an ammonia-ammonium ratio of 0.25:0.75. At this ratio, the difference between $\hat{\delta}$ and δ, (1.16E-2), is equivalent to the contribution of the ammonium ion-bicarbonate ion pair (1.22E-2), which suggests that the bicarbonate species may not be contributing significantly in the presence of the carbamate ion, NH_2CO_2^- (Figure 5). It is even possible that the carbamate ion is participating directly in the leaching of chrysocolla by acting as a chelate. Its sulfur analog, the dithiocarbamate ion (NH_2CS_2^-), is a known chelating agent[20] for metals and is an important constituent in fungicides, although not much information is available on the carbamate ion itself.

C. Temperature and Concentration Effects

The results of the ammonia concentration experiments are given in Figure 8 for the 25 °C data where the fraction of copper extracted as a function of time is plotted for different ammonia concentrations. This was repeated at 35, 45, and 55° to produce similar curves except that increase in temperature increased the rate and the final amount of copper removed. These results are summarized in terms of copper
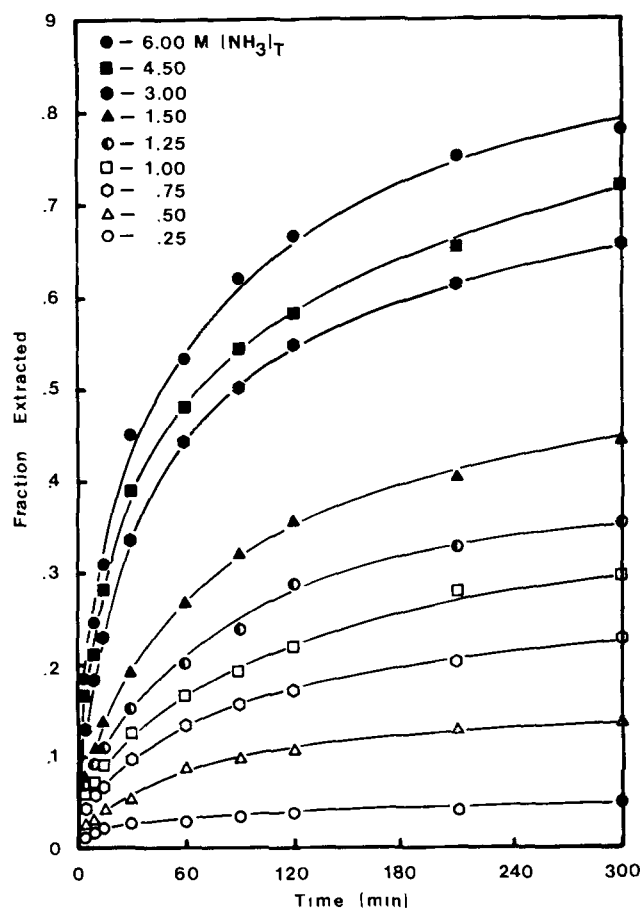
recovery at 300 minutes of extraction as a function of temperature and ammonia concentration in Figure 9 which shows that changing the total ammonia concentration has a greater effect on the recovery than variations in temperature.

The effect of temperature and concentration on the initial rate may be considered[18,19] in terms of initial activation energy, E_a, giving for (Eq. [2])

$$\delta = C\theta \exp(-E_a/RT) \qquad [13]$$

where C = constant containing the terms, surface area, number of active sites per unit area, and a term containing the entropy of activation

R = gas constant

T = absolute temperature

From Eq. [13] E_a was obtained using an Arrhenius-type plot of $\log_e \delta$ against $1/T$; a value of 60.74 kJ/mole (14.51 kcal/mole) for $[\text{NH}_3] = 3.00$ M was obtained. E_a was also calculated for the other ammonia concentrations used, and the results are plotted in Figure 10 which shows that the activation energy is not a constant with respect to total ammonia concentration. It has been shown[18] that changes in the state of solvation of either the reactant or the activated complex can cause a change in the activation energy, but it is not certain whether this mechanism or something else caused the variation in the initial activation energy for the ammoniacal leaching of chrysocolla.

Experiments were also conducted in which the ammonia concentration was increased during the leaching process
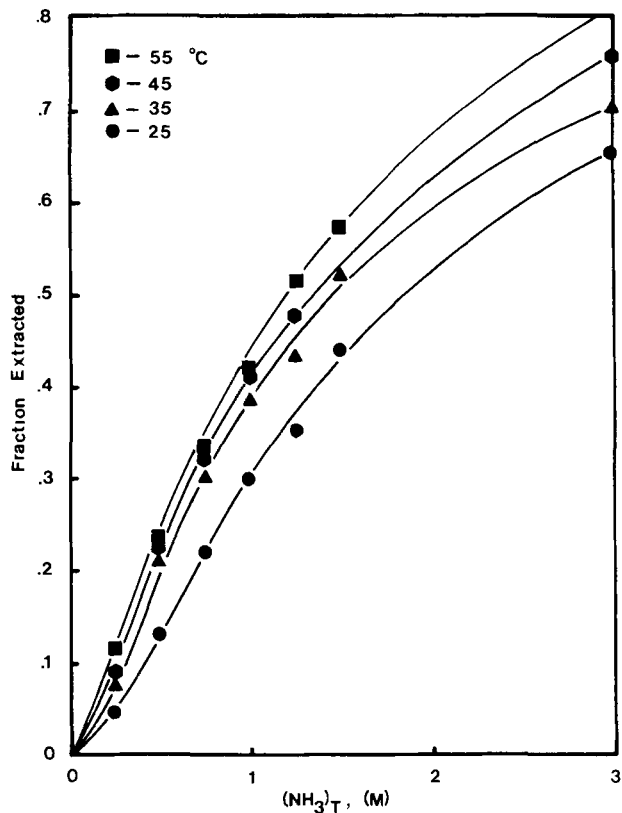
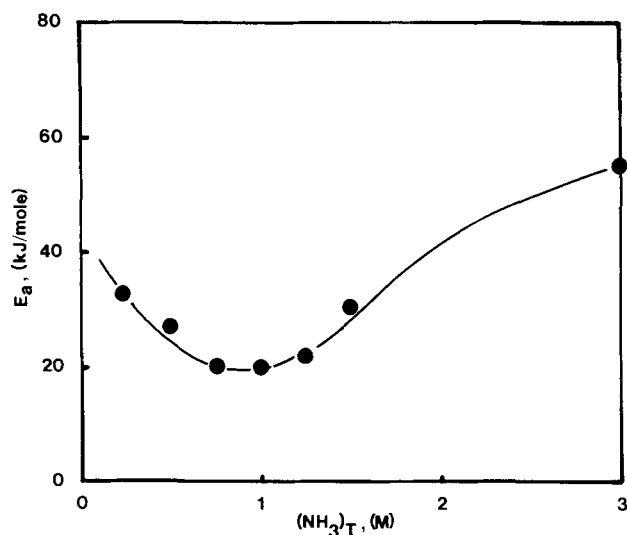Fig. 9 — Recovery after 300 min of leaching as a function of temperature and total ammonia concentration.

Fig. 11 — Results of leaching experiments wherein the total ammonia concentration was increased during the reaction

Fig. 10 — Variation of the energy of activation with total ammonia concentration

Fig. 12 — β and δ as a function of particle size

(Figure 11), and an increase in ammonia concentration caused an increase in the amount of copper leached. Furthermore, the leaching curve of the experiment wherein the ammonia concentration was increased approached the curve in which the leaching was started with a higher value of ammonia concentration. These results support Prosser's[16] hypothesis that chrysocolla is composed of a continuum of copper forms. Increasing the ammonia concentration has made some forms of copper soluble which were refractory at the lower concentration.
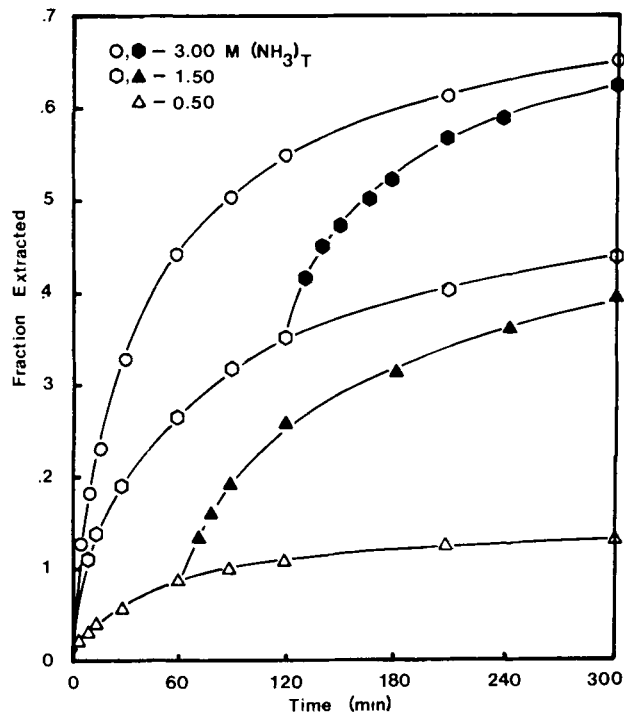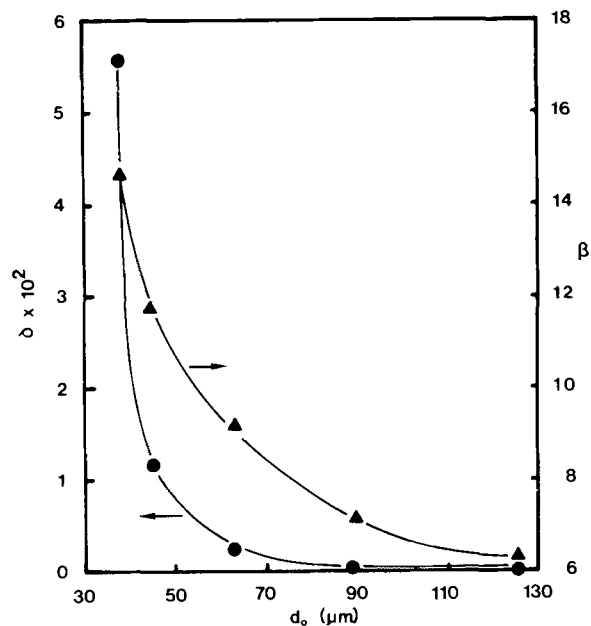
D. Particle Size Effect

Variation of initial particle size showed that the finer chrysocolla particles leached faster initially but yielded almost the same fraction of copper extracted as the coarser particles after extended leaching periods (300 minutes). This suggests the involvement of a diffusional process in the leaching of copper from chrysocolla. Figure 12 shows the effect of particle size on δ and β. Grinding the particles from 126 μm to 68 μm did not seem to have much effect on the initial leaching rate (δ). As the particles were ground
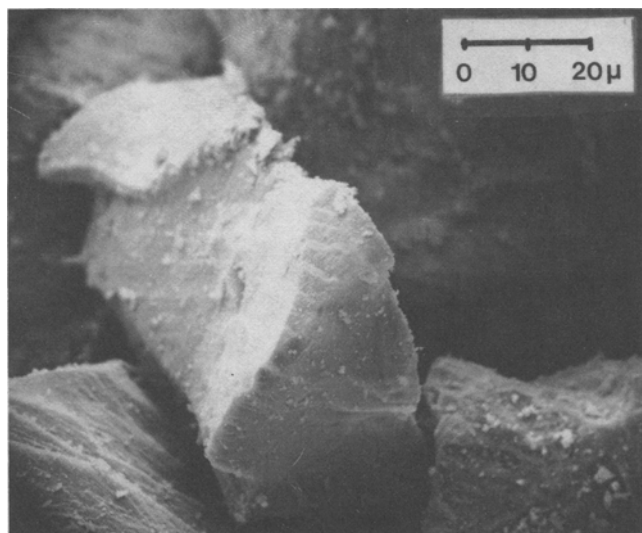
(a)
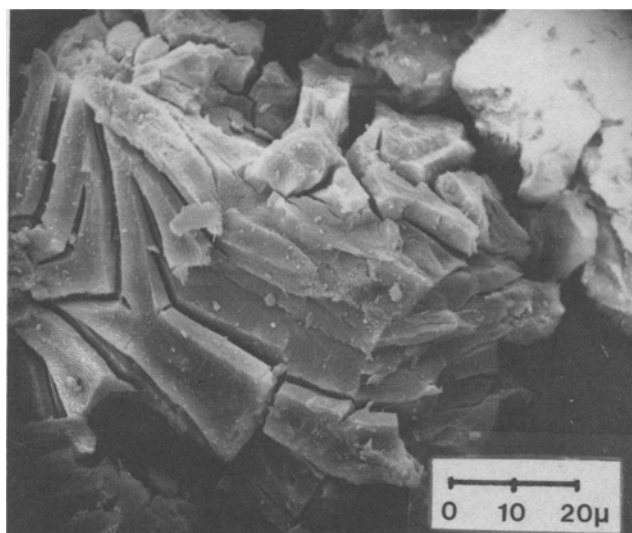
(b)

Fig. 13 — SEM photomicrographs of unleached (a) and partially leached (α = 0.83) (b) chrysocolla. Magnification 415 times.

below 63 μm, a tremendous increase in the initial rate is observed. This effect is possibly due to the activation of chrysocolla during grinding through the generation of microcracks as postulated by Horlick.[21] The microcracks activate the surface of chrysocolla by creating unsaturated bonds and allowing the lixiviant to penetrate into the interior of the particle. As the particle size gets smaller, the crack depth starts to approach the particle diameter, such that the application of a small amount of stress (impeller action, for example) causes the particles to break up as was noted from photomicrographs. This action exposes more of the chrysocolla to the leaching solution. As the extraction proceeds, the more soluble forms of copper are consumed, and the leaching rate becomes much slower when the more refractory forms of copper are leached. Diffusion is no longer rate controlling. The extraction then becomes insensitive to particle size, and the recovery for all size fractions converges as was found experimentally.

E. *Residue Analysis*

The leach residues (−100 +150 mesh) were also subjected to SEM and EDAX analysis. The SEM micrographs at 415 magnification (Figure 13) show that as the extraction proceeded, cracks developed in the remaining silica residue. The density of the cracks increased and the cracks widened as α increased. The cracks may have grown from microcracks as described by Horlick.[21]

The copper contents of the cross-sections of three samples at different amounts of copper extracted were measured by EDAX, and the results are summarized in Figure 14. The unleached sample shows a uniform distribution of copper. The partially leached samples show the expected average reduction in copper, but it is nonsystematic. Unlike sulfuric acid leaching,[4,22] no shrinking core was observed.

IV. DISCUSSION

The results obtained in this study suggest that the important processes controlling the kinetics of leaching of chrysocolla in ammonia-ammonium carbonate solutions are:
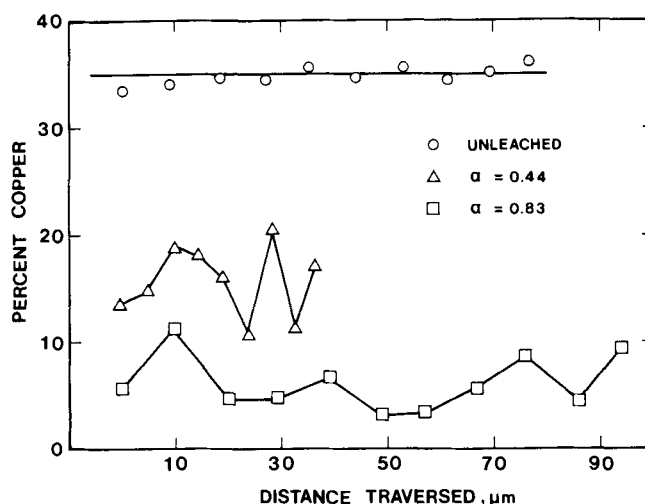

Fig. 14 — EDAX analyses of unleached and partially leached samples.

1. diffusion through microcracks and some pores,
2. adsorption of ion pairs on surface-active sites, and
3. chemical reaction at the active surface sites.

Leaching of chrysocolla with ammonia-ammonium carbonate solutions is more complex than was found for acid leaching as reported by Pohlman[4] and by Pohlman and Olson.[22] With acid leaching the submicroscopic 0.8 nm (8 angstrom) average radius pores are diffusion paths; leaching is topochemical and obeys a mixed kinetics model with both pore diffusion and surface chemical reaction being rate controlling. Also, leaching is very rapid, about 30 times as fast as with the ammonia-ammonium system. With the ammonia-ammonium system, however, diffusion is also important but in a rather different way.

The particle size effect points to the importance of diffusion on the initial kinetics, although rate does not show an inverse second order dependence on initial particle diameter as would be expected if the leaching were topochemical. This is possibly because of the effect the microcracks have on the diffusional process. The cracks act as flow-paths through which the active species is able to penetrate the
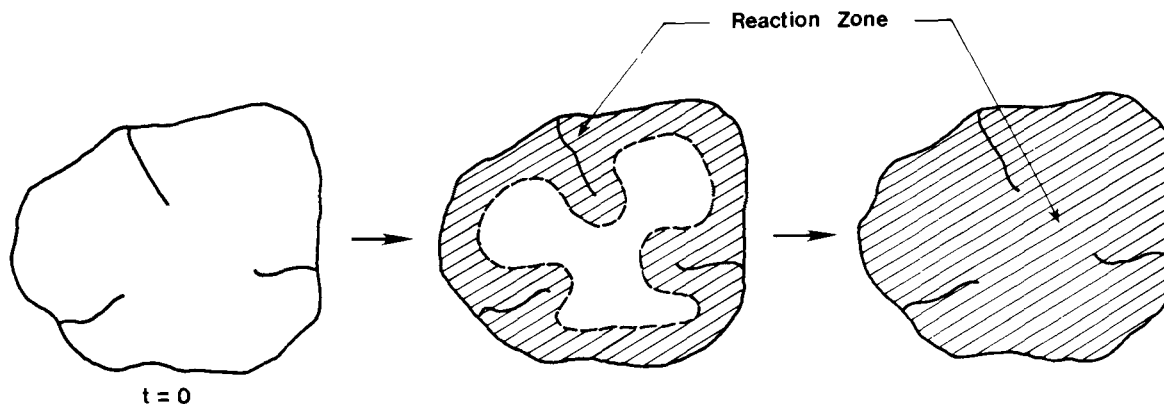
Fig. 15 — Diagrammatic sketch of particle undergoing reaction.

interior of the particle at a much faster rate than through the 0.8 $nm^{4,22}$ pores of chrysocolla which are too small to allow much diffusion of ion pairs.

A rather simple diagrammatic sketch of a particle undergoing reaction with only three cracks instead of the numerous cracks that would actually be present is given in Figure 15. It shows the presence of a broad reaction zone and a model of how the cracks affect penetration into the particle. The nontopochemical EDAX results of Figure 14 support the finding that the dependence of rate on particle size is not $1/d_0^2$. This dependence would be expected for a topochemical pore diffusion process as was found by Pohlman and Olson[4,22] with acid leaching. However, in this study a $1/d_0$ dependence results because the microcrack density (number per unit area) has a $1/d_0$ dependence, i.e., they penetrate only the surface. Thus, once the surface microcracks are fully utilized particle size dependence disappears.

Some adsorption does occur throughout the entire surface area. A limitation here is that this is where only reactive species can penetrate. However, only those that adsorb on to forms of copper soluble at the given temperature and concentration (Prosser concept) cause chemical reaction. The activation energy of 60.75 kJ/mole is consistent with chemical reaction at the surface being important. This value is also a reasonable activation energy for diffusion through microcracks.

The leveling off of the leaching curves is consistent with Prosser's[16] model. As leaching progresses, the more refractory forms of copper take longer to dissolve. The logarithmic rate law expression typifies this behavior.

The chemical species which seems to be important in controlling the reaction rate is $CuNH_3^{2+}$ as found by Oudenne and Olson[23] for leaching of malachite with ammonia-ammonium carbonate. This conclusion is based on the first-order dependence of the reaction rate on ammonium ion concentration and hence on $[NH_3]$ as shown by Eq. [8]. Once $CuNH_3^{2+}$ is formed, the species $Cu(NH_3)_4^{2+}$, which is stable at the bulk pH of this system, 8.8 to 12, would form.

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