Dissolution Kinetics of CuSiO$_3$ (Chrysocolla)

MSE 413: Phase Equilibria in Materials

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**Dissolution Kinetics of CuSiO₃ (Chrysocolla)**

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**Abstract:** Chrysocolla is a primary mineral source of copper for the copper leaching industry that contains approximately 34% copper by weight. The present study analyzed the dissolution of copper in sulfuric acid. Chrysocolla was placed in a controlled reactor in a water bath to control the temperature. Multiple trials were run at varying concentrations, then at varying temperatures. The reaction order and activation energy were determined. The activation energy was found to be 10.53 kcal/mol and the reaction order was found to be 0.99, very near 1.

I. INTRODUCTION

Copper leaching as a source of primary copper has increased significantly in the past twenty years. The increase is due in part to the adoption of solvent extraction and electrowinning as a low cost method to recover copper. Mines abundant in copper minerals such as chrysocolla provide a large source for this method of copper recovery.

Chrysocolla is a hydrated copper cyclosilicate mineral. It was initially used as solder for gold by early Romans, and was attributed the name Chrysocolla from the Greek words chryso, "gold", and kolla, "glue". Chrysocolla has a distinct cyan color often noted for its beauty. This color is due to the copper content in the mineral ranging between 23% and 37%. Pohlman found chrysocolla to have a copper content of 34.2% by weight. Sullivan reported chrysocolla to be 36.14% copper by weight. It is generally agreed to have the chemical formula CuO·SiO₂·2H₂O, and is dominant in many oxide leaching operations.

The objective of the present study was to model the reaction kinetics for the dissolution of chrysocolla by sulfuric acid leach solutions. This study used atomic adsorption spectroscopy to analyze the concentration of copper present at periodic time intervals through the controlled reaction of sulfuric acid with chrysocolla. The general leaching reaction of chrysocolla by sulfuric acid is given by:

\[
\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} (s) + 2\text{H}^+ (aq) \rightarrow \text{Cu}^{2+} (aq) + \text{SiO}_2 \cdot n\text{H}_2\text{O} (s) + (3-n)\text{H}_2\text{O} (l)
\]

The chrysocolla reacts under acidic conditions and the silica precipitates out of solution. The copper is dissolved and is present in the solution. An introductory lab was performed to demonstrate the process and necessary importance of lab technique. However, to provide a useful discussion, the data from Dr. Steve Pohlman’s PhD thesis was used in place of student determined data.

The reaction rate is determinable via the copper present in the solution at any particular time. To analyze the copper content, a sample is drawn from the controlled reaction at some known time and diluted for processing. Atomic adsorption spectroscopy is performed and the copper content is found. The fraction reacted, \( \alpha \), can be found by taking the initial copper content and subtracting the current content divided by the initial content:

\[
\alpha = \frac{[\text{Cu}]_0 - [\text{Cu}]}{[\text{Cu}]_0}
\]

After sufficient samples are collected and analyzed, a representative graph displaying \( \alpha \) versus time can be shown. From that data, a model was constructed to fit the data. Three different models were observed for the dissolution of chrysocolla by sulfuric acid. The models were the Spencer-Topley model for a shrinking sphere, the Valency model for shrinking core, and the Wadsworth model for mixed kinetics.

A reaction can be either mass transfer controlled or reaction controlled. To determine the controlling factor, the activation energy must be determined. It is accepted that if the activation energy is less than 5 kcal/mol, the reaction is considered mass transfer controlled. If the activation energy is 5 kcal/mol or greater, the reaction is controlled by the reaction rate. The activation energy can be determined by observing the effects of varying temperature on a controlled reaction. Once the trials are completed, the activation energy can be found using the Arrhenius equation:

\[
k = Ae^{-\frac{E_a}{RT}}
\]

The Arrhenius equation relates the rate constant, \( k \), with the energy of the system. It can be rewritten into a more useful form using the property of logarithms:

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

This equation is written in the form of a line, where \( \frac{1}{T} \) is the independent variable and \( -\frac{E_a}{RT} \) is the slope. The activation energy, \( E_a \), can then be determined.

It can also be useful to determine the reaction order, given by the exponent above the concentration term in the rate equation. To determine the reaction order, trials are performed while varying concentration of acid. The results are then fit linearly to a model. The natural log of the slope of each trial is then plotted against the natural log of the acid concentration of each trial.

The mixed kinetics model presented by the Wadsworth equation takes into account both factors, implying that the activation energy is very near 5 kcal/mol and both mechanisms are equally limiting. The
Valency equation is used to model a shrinking core. In this model the limiting mechanism is diffusion that occurs through a product layer built up as the particle reacts.

II. EXPERIMENTAL PROCEDURE

99.3 mg of CuSiO₃ (chrysocolla) were placed in a solution containing 1 mL and diluted to a total volume of 100 mL with water. This solution was then placed inside a controlled reactor stirred at the maximum speed of 2400 rpm to ensure a minimum boundary layer thickness. The reaction was temperature controlled at 25 °C via a water bath.

Figure 1. Very detailed figure of experimental apparatus. The reaction is placed in the upper container that is well stirred. The lower container is a constant temperature water bath.

100 µL samples were drawn from the reactor at 0.5, 1.0, 1.5, 2.0, 2.5, 3.5, 4.0, and 5.0 minutes. The samples were taken using an Eppendorf pipettors to filter any precipitates. The samples were placed in vials marked according to reaction times. 9.9 mL of DI water was then added to each vial to achieve 100x dilution.

The samples were then processed with Varien AA-20 atomic adsorption spectrometer to analyze the copper fraction at each time step.

Figure 2. Fraction reacted, α, for four different acid concentrations plotted against time in minutes.

It can be seen from Figure 2 that as the concentration of acid increases (pH decreases), the reaction occurs faster.

The Spencer-Topley equation is given by

\[ 1 - (1 - \alpha)^{1/3} = k t \]  

(5)

The lack of linearity in Figure 3 demonstrates that the data is not accurately modeled by the shrinking sphere model.

III. RESULTS

The experimental results were calculated from Steve Pohlman’s Ph.D Thesis. To determine the reaction order, the concentration of sulfuric acid was varied from a pH of 0.20, 0.41, 0.62, and 0.84. The results of the experimental runs are can be seen in Figure 2.
mixed kinetics model seen in Figure 4. The mixed kinetics model is given by the Wadsworth equation:

$$1 - 2/3\alpha - (1 - \alpha)^{2/3} + \frac{\beta}{r_0} [1 - (1 - \alpha)^{1/3}] = \frac{\gamma c}{r_0} t$$ \hspace{1cm} (6)

The linearity of the system when plotted using the model demonstrates how good of a fit a particular model is. Since the shrinking sphere model was a poor fit, the next model attempted was the mixed kinetics model given by the Wadsworth equation. The linearity was quite good, with R squared values seen in Figure 5.

The Valency equation was the best fit of the three models tested. The corresponding r squared values for each increasing pH value are 0.9965, 0.9946, 0.9774, and 0.9972.
Figure 6. The natural log of the slope against the natural log concentration. The slope was determined to be 0.9858, which represents the reaction order.

Figure 7. Plot of the trials while varying temperature.

Figure 8. Varying temperature trials fit to Valency equation.

Figure 9. Natural log of the slopes in Figure 8 versus $1/T$. The resulting activation energy was determined to be 10.53 kcal.
IV. Results

The Valency equation was demonstrated to provide the best linear fit to the data. This can be seen by it having the lowest R-squared error for each of the different trials. The Valency equation is derived as follows:

\[
\frac{dn}{dt} = -DA \frac{dc}{dr}
\]

Knowing the area to be \(4\pi r^2\), we can separate and integrate.

\[
\int_{r_0}^{r} \frac{dr}{r^2} = -4\pi D \left( \frac{dn}{dt} \right)^{-1} \int_{C_b}^{C_s} dc
\]

After integration we obtain

\[
\frac{1}{r_0} - \frac{1}{r} = 4\pi D \left( \frac{dn}{dt} \right)^{-1} (C_s - C_b)
\]

The surface concentration is 0 if the reaction is diffusion controlled since the reaction occurs much faster than the diffusion process. This can be rearranged to

\[
\frac{dn}{dt} = -4\pi D \frac{Crr_0}{r_0 - r}
\]

We know that by definition \(n\) is the total volume divided by the specific volume:

\[
n = \frac{4/3\pi r^3}{v}
\]

Deriving this we see

\[
\frac{dn}{dt} = \frac{4\pi r^2}{v} \frac{dr}{dt}
\]

Since \(dn/dt\) must be equal, we can set (7) and (8) equal to obtain

\[
\frac{dr}{dt} = -\frac{vCDr_0}{r(r_0 - r)}
\]

The fraction reacted can be seen from Equation [1]. This is equivalent to

\[
\alpha = 1 - \frac{r^3}{r_0^3}
\]

We can see by rearranging this equation for \(r\):

\[
r = r_0(1 - \alpha)^{1/3}
\]

By taking the derivative of Equation [4] we obtain

\[
\frac{d\alpha}{dt} = -3r^2 \frac{dr}{dt} \frac{1}{r_0^3}
\]

By substituting \(dr/dt\) from Equation [4] and \(r\) from Equation [4]

\[
\frac{d\alpha}{dt} = -3\frac{(1 - \alpha)^{1/3}}{3vDC} \frac{1}{r_0^3} \frac{1}{1 - (1 - \alpha)^{1/3}}
\]

Separating and integrating we get

\[
\int_0^\alpha (1 - \alpha)^{1/3} [1 - (1 - \alpha)^{1/3}] d\alpha = \frac{3vDC}{r_0^3} \int_0^t dt
\]

By integrating and multiplying both sides by \(2/3\) we get our final solution:

\[
1 - (1 - \alpha)^{2/3} - \frac{2}{3} \alpha = \frac{2DvC}{r_0^2}t
\]

The assumptions made at the beginning of the derivation are that the particles are spherical, the stochiometric factor is 1, \(r_0\) is constant throughout the particles, and there is an initial bulk concentration, \(C_b\).

The activation energy was determined by varying temperature under a controlled reaction to be 10.53 kcal/mol. This results is greater than 5 kcal/mol and represents a rate controlled reaction.

The reaction order was determined to be close to 1. The numerical value can be seen in Figure 6 to be 0.99. This reaction order makes sense for diffusion through a product layer.

Error in this lab might have come from inaccuracies assumed in the model. It should be noted that the beginning of the model does not fit the line very well. This is in part due to the assumptions made in the model. It is assumed that the model is limited by the diffusion through the product layer. However, at the start of the reaction, there is no product layer to limit diffusion. The result is that the model cannot fit the beginning time very well.

V. Conclusion

The reaction kinetics of the dissolution of chrysocolla have been analyzed. It was determined that the best fit for the reaction was the shrinking core model. The precipitates formed by the reaction stay on the product surface and build up and the reactant core shrinks. This limits the reaction based on the diffusion through the product layer. The activation energy was determined to be 10.53 kcal, which implies the reaction is rate controlled. The reaction was also found to be a first order reaction. Laboratory techniques require sufficient practice and persistence.

References

(1) Pohlman, S.; Olson, F. Solutions Mining Symposium 1974, 446–460.
(2) Pohlman, S. Extractive Metallurgy of Copper, AIME 1976, 943–959.