A KINETIC STUDY OF ENARGITE DISSOLUTION
IN AMMONIACAL SOLUTIONS

by

Soliman Younes Gajam

A Thesis Submitted to the Faculty of the
DEPARTMENT OF METALLURGICAL ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE
WITH A MAJOR IN METALLURGY

In the Graduate College
THE UNIVERSITY OF ARIZONA

1 9 8 1

STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: _____

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

S. Raghavan

S. RAGHAVAN
Assistant Professor
Metallurgical Engineering

2/2/87

Date

ACKNOWLEDGMENTS

The author expresses his gratification to the faculty and staff of the Department of Metallurgical Engineering of The University of Arizona.

Special thanks go to Dr. S. Raghavan for his valuable suggestions and technical advice in the progress of this study and in the preparation of this work.

The author is greatly indebted to Mountain States Research and Development Company for its help in the analysis of solutions and for its financial assistance.

I would, in particular, like to extend special thanks to Frank Tyndall for his unfailing help in the analysis of the leach solution.

Special thanks are extended to Robert Young for his aid during the work.

Finally, I am grateful to my wife Aisha and my daughter Esra for their sacrifices and patience during my academic years.

TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	vi
LIST OF TABLES	viii
ABSTRACT	ix
INTRODUCTION	1
BACKGROUND AND LITERATURE REVIEW	2
Thermodynamic Considerations on Enargite	2
Eh-pH Diagrams	4
Thermodynamic Data on Copper Ammonia Complexes	5
Previous Work on Enargite	9
Vapor Pressure of Ammoniacal Solutions	12
EXPERIMENTAL MATERIALS AND METHODS	14
Experimental Materials	14
Experimental Methods	16
EXPERIMENTAL RESULTS AND DISCUSSION	18
Effect of Speed of Rotation on the Leaching Process	18
Effect of Temperature on the Leaching of Enargite	18
Effect of Oxygen Pressure	21
Effect of pH of the Ammoniacal Solution	23
Effect of Total Ammonia Concentration	26
Effect of Particle Size	29
DISCUSSION	31
Electrochemical Mechanism for Enargite Leaching	31
Leaching Models	35
As-Cu Ratio in Solution	37
CONCLUSIONS	41

TABLE OF CONTENTS--Continued

	Page
APPENDIX A: EXPERIMENTAL DATA	42
REFERENCES	49

LIST OF ILLUSTRATIONS

Figure		Page
1.	Crystal structure of enargite	3
2.	Potential-pH diagram for the Cu-S-NH ₃ -H ₂ O system	6
3.	Potential-pH diagram for the As-H ₂ O system at 25°C	7
4.	Potential-pH diagram for the S-H ₂ O System at 25°C	8
5.	Leach extraction as a function of time on three concentrates of different mineralogy	11
6.	Vapor pressure of ammoniacal solutions at different temperatures	13
7.	Schematic diagram of the experimental apparatus	17
8.	Leaching of enargite at different speeds of rotation	19
9.	Leaching of enargite at different temperatures	20
10.	Arrhenius plot for the enargite dissolution	22
11.	Leaching of enargite at different oxygen pressure	24
12.	Plot of rate of extraction versus square root of oxygen pressure	25
13.	Leaching of enargite at different pH value	27
14.	Leaching of enargite at different ammonia concentration	28
15.	Leaching of enargite at different particle size	30

LIST OF ILLUSTRATIONS--Continued

Figure	Page
16. Plot of rate of extraction versus square root of hydroxide ion concentration	36
17. Plot of time for 25% copper extraction versus log particle size	38

LIST OF TABLES

Table	Page
1. Thermodynamic data for enargite	2
2. The log of equilibrium constants for reaction at different temperatures	4
3. Vapor pressure of ammonia at different temperatures	12
4. Chemical analyses for different particle sizes of enargite	14
5. X-ray diffraction analyses of the enargite sample	15
6. Enargite leaching	40

ABSTRACT

A detailed investigation of the kinetics of dissolution of natural enargite in ammoniacal solution has been carried out. Unlike other copper sulfide minerals, the dissolution of copper from enargite is very slow and only 60% of the copper is extracted after 24 hours. The rate of dissolution is favored by high temperatures and high oxygen pressures. The experimental data seem to fit an electrochemical mechanism.

INTRODUCTION

Many copper sulfide ores contain arsenic in the form of the mineral enargite. Preconcentration of enargite containing ores by froth flotation techniques invariably concentrates enargite along with the other copper sulfides. Treatment of such copper concentrates for the recovery of copper will depend on the relative dissolution rates of the various copper sulfide minerals. Because available information on the hydrometallurgical treatment of enargite is scarce, it was decided to investigate the dissolution of enargite in ammonical solution under oxygen pressure. In particular, this investigation was directed towards elucidating the kinetics of dissolution of enargite in ammonical solutions with a view to finding optimal conditions for its dissolution.

BACKGROUND AND LITERATURE REVIEW

Crystal Structure of Enargite

Enargite (Cu_3AsS_4) has an orthorhombic crystal structure with each arsenic or copper atom being surrounded by four sulfur atoms at the corners of a nearly regular tetrahedron, and each sulfur atom being similarly surrounded by a tetrahedron of one arsenic atom and three copper atoms. The AsS_4 groups are discrete, sharing no sulfur atoms with one another. The atomic arrangement for enargite is shown in Figure 1.

Thermodynamic Considerations on Enargite

The heat capacity, enthalpy, and entropy of enargite are given in Table 1.

Table 1. Thermodynamic data for enargite

$$H^\circ = -42.78 \text{ kcal/gfw}$$

$$S^\circ = 85.17 \text{ cal/degrees}$$

$$\text{Cp coefficients: } a = 0.0, b = 0.0, c = 0.0$$

Knight (1977) studied the hydrothermal chemistry of enargite on the basis of the following equation:

Figure 1. Crystal structure of enargite. -- Pauling and Weinbaum (1930).

where K is the equilibrium constant for reaction (1). He determined these values of the equilibrium constant K at different temperatures from thermodynamic data. These K values are tabulated in Table 2.

Table 2. The log of equilibrium constants for reaction (1) at different temperatures

Temperature °C	Log K
25	- 74.55
60	- 66.25
100	- 58.54
150	- 50.99
200	- 45.19
250	- 40.27
300	- 34.95

Eh-pH Diagrams

The feasibility of dissolution of sulfide minerals in ammonical solutions can be understood by a careful construction of potential pH diagrams. An excellent compilation

of Eh-pH diagrams for sulfide minerals has been made by Peters (1976). The key observations that can be made from the Eh-pH diagrams for copper sulfide systems such as the one shown in Figure 2 for chalcocite are as follows:

1. For dissolution in ammoniacal solution an oxidative atmosphere is necessary (Eh value of 0.64 volt).
2. The pH value should be in the range of 7 to 10.5.
3. The most stable copper ammonium complex is $\text{Cu}(\text{NH}_3)_4^{+2}$.
4. Under oxidizing conditions sulfur in the metal sulfide lattice is converted to aqueous sulfate ions.

The presence of arsenic in enargite adds complexity to the Eh-pH diagram for enargite. The Eh-pH diagram for arsenic water system at 25°C is presented in Figure 3. This shows that arsenic can exist in different oxidation states in aqueous solutions. However, in ammoniacal solutions HAsO_4^{-2} is the most stable species if an oxidative atmosphere prevails. The Eh-pH diagram for sulfur water systems at 25°C presented in Figure 4 shows that $\text{SO}_4^{=}$ is the most stable species in the leaching condition.

Thermodynamic Data on Copper Ammonia Complexes

The dissolution of copper concentrates in ammoniacal solution leads to the formation of the following copper amine complexes:

Figure 2. Potential-pH diagram for the Cu-S-NH₃-H₂O system. -- From Peters, 1976.

Figure 3. Potential-pH diagram for the As-H₂O system at 25°C. -- From Encyclopedia of Electrochemistry of the Elements (1972).

Figure 4. Potential-pH diagram for the S-H₂O system at 25°C. -- From Forward, Peters, and Majima (1976).

are the equilibrium constants of
 ; Butler, 1964). The tetra-amine
 most stable species in aqueous
 a pH range of 7.5 to 11.

Previous Work on Enargite

Hydrometallurgical treatment of enargite has not received much attention to date. Dutrizac and MacDonald (1972) investigated the dissolution of synthetic enargite in acidified ferric sulfate solutions, which take place according to the following equation:

They found that copper and arsenic dissolve at approximately the same rate and that the residual solid is not substantially

depleted of either element. From their experimental results they concluded that the dissolution process in the temperature range 60°C was controlled by a surface chemical reaction. The rate of copper dissolution was found to increase with the 0.55 power of the ferric ion concentration and 0.20 power of the hydrogen ion concentration.

Kuhn, Arbiter, and Kling (1973) investigated the dissolution of copper concentrates containing different copper sulfides in ammoniacal solutions under conditions of intense agitation. This process, known as the Arbiter process, was designed to improve the extraction rates by removing the surface products that might form during the leaching reaction. They found that in ammoniacal solutions, under low oxygen pressure (5 psi), enargite exhibits the least rapid reaction in comparison to other copper sulfides. The extractability of copper from different sulfides was found to follow the order.

This is also shown in Figure 5.

Enargite leaching in ammoniacal solutions can be represented by the following equation:

Figure 5. Leach extraction as a function of time on three concentrates of different mineralogy

According to equation (3), enargite dissolution in ammoniacal solutions will result in a higher arsenic content in the pregnant solution. This important feature must be borne in mind in devising schemes for the recovery of copper from pregnant solutions obtained from the enargite leaching process.

Vapor Pressure of Ammoniacal Solutions

Kracek (1930) studied the vapor pressure of ammoniacal solutions at different temperatures and found the vapor pressure to increase considerably with temperatures. His data are presented in Figure 6 and Table 3.

At the highest temperature used in the experiments (viz., 82°C) the ammonia vapor pressure is only of the order 6.88 psi. This is small compared to the oxygen pressure used in the experiments.

Table 3. Vapor pressure of ammonia at different temperatures

Temperature °C	Vapor Pressure (psi)
0	0.0884
10	0.17778
20	0.3390
30	0.6143
40	1.0703
50	1.80
60	2.891
70	4.522
80	6.88
90	10.2
100	14.7

Figure 6. Vapor pressure of ammoniacal solutions at different solutions

EXPERIMENTAL MATERIALS AND METHODS

Experimental Materials

The enargite sample used in the investigations was donated by Hussein Salek of the Anaconda Research Center in Tucson. The enargite sample was crushed and ground in a porcelain mortar and pestle and sieved into various sized fractions. The chemical analyses of the different sized fractions used in the investigation is tabulated in Table 4. The purity of the samples was tested using an x-ray diffractometer and a polarizing microscope. Limited tests with the polarizing microscope indicated very small amounts of arsenopyrite and chalcocite inclusions.

Table 4. Chemical analyses for different particle sizes of enargite

Particle Size (wash)	Cu (%)	As (%)	Fe (%)	Ag (oz/ton)
100 x 150	15.82	10.5	15.5	0.72
150 x 270	28.15	13.12	12.2	1.23
270 x 400	30.07	17.2	---	1.63

The peaks obtained in the x-ray diffraction patterns are summarized in Table 5. X-ray diffraction analysis also indicates a small amount of arsenopyrite and chalcocite present in the samples.

Reagent grade $(\text{NH}_4)_2\text{SO}_4$ and NH_4OH were used to make leach solutions. The NH_4OH solution contained 58 percent by weight NH_4OH . Sodium hydroxide and sulfuric acid were used for pH adjustment.

Table 5. X-ray diffraction analyses of the enargite sample

d	Expected Mineral
3.3510	Cu_2S
3.2090	Cu_3AsS_4 and Cu_2S
3.0686	Cu_3AsS_4 and Cu_2S
2.8400	FeAsS and Cu_3AsS_4
2.7063	FeAsS and Cu_2S
2.2116	Cu_3AsS_4 and Cu_2S
1.8519	Cu_3AsS_4 and FeS_2
1.7277	Cu_3AsS_4
1.6079	Cu_3AsS_4

The mineral is not pure enargite but also contains Cu_2S , FeAsS , and FeS_2 . The impurity content follows the sequence $\text{Cu}_2\text{S} > \text{FeAsS} > \text{FeS}_2$.

Experimental Methods

The leaching reactions were conducted in a 1-gallon stainless steel reactor made by the Bench Scale Equipment Company. This reactor is rated for 150 psi over pressure. The speed of the reactor shaft was measured with a frequency counter. Temperatures higher than the ambient temperature were obtained by: (1) a heating jacket surrounding the reactor and (2) an internal cooling coil through which water at a given temperature was circulated. The water to the cooling coil was supplied by a Forma scientific, 7-gallon, constant-temperature bath. The internal cooling coil and the reactor were made of 316 stainless steel to prevent corrosion. The reactor also contained an inside filter to prevent solids from escaping during the withdrawal of samples for analysis.

A schematic sketch of the reactor setup is shown in Figure 7. A typical experimental run was as follows. The reactor was charged with 2,000 cc of a solution containing NH_4OH and $(\text{NH}_4)_2\text{SO}_4$ in a predetermined ratio. The reactor was then sealed and heated to the required temperature of 82°C . Once the required temperature was reached, 1 gram of a given sized fraction of the enargite sample was added to the leach solution and the system pressurized to the required value. Agitation was then started and samples were taken at regular time intervals for copper and arsenic analysis by atomic absorption spectrometry.

Figure 7. Schematic diagram of the experimental apparatus

EXPERIMENTAL RESULTS AND DISCUSSION

Effect of Speed of Rotation on the Leaching Process

The possibility of mass transfer through the boundary layer around particles being the rate-controlling step in the leaching reaction was first investigated by conducting experiments at different degrees of agitation. Three different rotation speeds of the agitation, namely, 1,000, 750, and 500 rpm were chosen for the investigations. The results of these experiments are plotted in Figure 8 along with the conditions used for these sets of experiments. It can be concluded from the data in the figure that increasing the speed of rotation within the range investigated produced no significant improvement in the rate of extraction.

Effect of Temperature on the Leaching of Enargite

Valuable information on the leaching reaction can be obtained by changing the reaction temperature and by calculating the activation energies from the leaching data. The leaching of 150 x 270-mesh enargite was investigated at temperatures of 30, 55, 70, and 82°C at a rotation speed of 1,000 rpm, an oxygen pressure of 50 psi, and a pH value of 10. The results obtained are shown in Figure 9. A

Figure 8. Leaching of enargite at different speeds of rotation

Figure 9. Leaching of enargite at different temperatures

striking observation can be made from Figure 9 is that the rate of extraction of copper from enargite increases significantly with an increase in temperature. From the extractions versus time data obtained at these four temperatures a rough calculation of activation energy for the leaching reaction was made using the following equation:

$$\frac{d(\ln k)}{dt} = \frac{E}{RT^2}$$

where K is a reaction rate, E is the activation energy, T is a reaction temperature, and R is a gas constant.

According to this equation, a plot of $\log k$ vs. $\frac{1}{T} \times 10^3 \text{ } ^\circ\text{K}^{-1}$ should yield a straight line of slope E/R . Such plot is shown in Figure 10. The activation energy calculated from the slope of the plot in Figure 10 is 7.0 kcal/mole. It should be mentioned at this point that this value for activation energy is a little on the low side for a chemical reaction to be the rate-controlling step in the leaching process.

Effect of Oxygen Pressure

The dissolution of enargite in ammoniacal solution takes place by transfer of arsenic from the lattice to the solution as arsenate and the transfer of sulfur from the lattice in solution as sulfate. As depicted in equation (3), oxygen is essential to the leaching reaction.

Figure 10. Arrhenius plot for the enargite dissolution

Hence, it was decided to investigate the role of oxygen pressure in the kinetics of the leaching reaction. The oxygen pressure was varied between 5 and 50 psi during the leaching of 150 x 270-mesh enargite particles at a temperature of 82°C and a pH of 10. The results obtained are shown in Figure 11. It can be discerned from this figure that the rate of dissolution increases with an increase in oxygen pressure. The data in Figure 11 were replotted in Figure 12 as rate of extraction versus square root of partial pressure of oxygen. The slope of this plot is equal to 1, indicating that the rate of leaching reaction is proportional to the square root of oxygen partial pressure. As will be discussed later, this feature strongly indicates that the leaching takes place by an electrochemical mechanism.

Effect of pH of the Ammoniacal Solution

The leaching process is likely to depend on not only the total ammonia concentration but also on the ammonia-ammonium ion ratio in the leach solution. For the dissolution of copper the pH of the leach solution should be maintained in the pH range of 9 to 11, where the $\text{Cu}(\text{NH}_3)_4^{+2}$ amine complex is the most stable species. Experiments were carried out at pH values of 8.5, 9.4, 10, and 11, with the total ammonia concentration maintained at a fixed value of 0.3044 moles. The results of this experiment, which are

Figure 11. Leaching of enargite at different oxygen pressure

Figure 12. Plot of rate of extraction versus square root of oxygen pressure

given in Figure 13, show that a pH value of 10 yields the best extraction. Increasing the pH above 10 drastically decreases the extraction of copper from enargite.

Effect of Total Ammonia Concentration

Free ammonia and ammonium ions are consumed during the leaching process by conversion of Cu to $\text{Cu}(\text{NH}_3)_4^{+2}$ and As to arsenate. Hence, it is only natural that the rate of leaching reaction, if chemically controlled, will depend on the ammonia concentration. To investigate, the experiments were carried out with 150 x 270-mesh samples at 82°C, 150 psi oxygen pressure, and a pH value of 10. Three different total ammonia concentrations were used for these experiments:

1. Total ammonia concentration = 0.3044 moles.
2. Total ammonia concentration = 0.6088 moles.
3. Total ammonia concentration = 0.1522 moles.

It should be noted that case (1) is a concentration level used for most of the experiments. The results of these tests are presented in Figure 14. This figure indicates that increasing the ammonia concentration above a value of 0.3044 moles of ammonia does not improve the rate or the extent of an extraction. However, a decrease in the total ammonia to copper molar ratio below a value of 0.3044 moles decreases the rate as well as the extent of extraction of copper from enargite.

Figure 13. Leaching of enargite at different pH value

Figure 14. Leaching of enargite at different ammonia concentration

Effect of Particle Size

Particle size plays a key role in the rate of dissolution of many sulfide and oxide ores. The rate of dissolution of copper from enargite was investigated with enargite samples of 100 x 150 mesh, 150 x 270 mesh, and 270 x 400 mesh. The results of experiments carried out with these three samples are presented in Figure 15. As is obvious from these data, a decrease in particle size enhances the rate and extent of extraction of copper from enargite. For example, at the end of 8 hours of leaching time, only 24 percent of the copper was extracted from the 100 x 150 mesh sample whereas almost 51 percent of the copper is extracted from the 270 x 400 mesh sample.

Figure 15. Leaching of enargite at different particle size

DISCUSSION

A recapitulation of some of the results is pertinent at this stage. These are: (1) the rate of the leaching reaction in proportion to the square root of oxygen partial pressure and (2) the activation energy is about 7.23 kcal/mole.

An interpretation of the experimental results will now be made in terms of an electrochemical model. An electrochemical mechanism is indicated by the half-order dependence on the oxygen partial pressure and the hydroxide ion concentrations. It is also well known that many metal sulfides dissolve in oxygenated ammoniacal solutions by an electrochemical mechanism.

Electrochemical Mechanism for Enargite Leaching

The ammonia oxidation leaching of enargite can be considered to take place by two electrochemical reactions:

Anodic reaction

Cathodic reaction

The Butler-Volmer equation can be used for the interpretation of the kinetic data under these conditions. The general Butler-Volmer current density equation for a half-cell reaction is:

$$i = nF\vec{k}\vec{C} \exp(\beta zFE_m/RT) - [nF\hat{k}\hat{C} \exp[(1-\beta)zFE_m/RT]]$$

where

i = current density

F is the Faraday constant,

$\vec{k}_a$ and $\hat{k}_c$ are the rates for the anodic and cathodic directions respectively in the absence of potential,

Z is the number of electrons transferred in the rate determining step,

β is the transfer coefficient, or symmetry factor,

T is the absolute temperature,

E_m is the mixed potential of the overall reaction,

and

R is the gas constant

$\vec{C}$, $\hat{C}$ = concentrations of the reacting species for the forward and reverse directions, respectively.

n = number of electrons.

Applying this equation to the anodic and cathodic reactions of enargite:

1. $i_a = 35 F (OH^-) k_a \exp\left[\frac{\beta_a FE}{RT}\right]$
 $- 35 F (Cu^{+2}) (HAS_4^{-2}) (SO_4^{-2}) k_a \exp\left[\frac{-(1-\beta_a) FE}{RT}\right]$
2. $i_c = 4 F (OH^-) k_c \exp\left[\frac{\beta_c FE}{RT}\right]$
 $- 4 F (O_2) k_c \exp\left[\frac{-(1-\beta_c) FE}{RT}\right]$
3. If $i_a = i_c$ and $\beta_a + \beta_c = 1$,

and assuming that both i_a and i_c fall within their corresponding Tafel region, it can be shown that:

$$\begin{aligned}
 & 35 F (OH^-) k_a \exp\left[\frac{\beta_a FE}{RT}\right] \\
 & = 4 F (O_2) k_c \exp\left[\frac{-(1-\beta_c) FE}{RT}\right] \\
 4. \quad & \exp\left[\frac{\beta_a FE}{RT}\right] = \frac{4 F [O_2] k_c \exp\left[\frac{-(1-\beta_c) FE}{RT}\right]}{35 F (OH^-) k_a}
 \end{aligned}$$

By raising the two parts of (4) to the mth power where

$$m = \frac{\beta_a}{1 + \beta_a - \beta_c}$$

$$\exp\left[\frac{\beta_a FE}{RT}\right]^m = \left[\frac{4 [O_2] k_c}{35 (OH^-) k_a}\right]^m \exp\left[\frac{-(1-\beta_c) FE}{RT}\right]^m$$

$$\begin{aligned}
&= \left[\frac{4[\text{O}_2]k_c}{35(\text{OH}^-)k_a} \right]^m \left[\exp \frac{-m(1-\beta_c)FE}{RT} \right] \\
&= \left[\frac{4[\text{O}_2]k_c}{35(\text{OH}^-)k_a} \right]^m \exp \left[\beta_a \frac{(m-1)}{RT} FE \right] \\
\exp \left[\frac{\beta_a FE}{RT} \right] &= \left[\frac{4(\text{O}_2)k_c}{35(\text{OH}^-)k_a} \right]^m
\end{aligned}$$

$$i_a = 35F(\text{OH}^-) k_a \exp \left[\frac{\beta_a FE}{RT} \right]$$

$$i_a = 35F(\text{OH}^-) k_a \left[\frac{4(\text{O}_2)k_c}{(\text{OH}^-)k_a} \right]^m$$

$$i_a = 35F[\text{OH}^-]^{1-m} k_a^{1-m} [4(\text{O}_2)k_c]^m$$

The rate of leaching is

$$\frac{-d_{nM_s}}{dt} = \frac{i_a}{35F} = \frac{35F[\text{OH}^-]^{1-m} k_a^{1-m} [4(\text{O}_2)k_c]^m}{35F}$$

where n_{M_s} is the number of moles of metal sulfides and

$$m = \frac{\beta_a}{1 + \beta_a - \beta_c}$$

For the special case $\beta_a = \beta_c = 0.5 \Rightarrow m$ the above equation reduces to:

$$\frac{-d_{nM_s}}{dt} = (\text{OH}^-)^{0.5} k_a^{0.5} (4(\text{O}_2)k_c)^{0.5}$$

If the proposed mechanism is valid, a plot of rate of leaching against (1) $(P_{O_2})^{\frac{1}{2}}$ at constant pH and (2) $(OH^-)^{\frac{1}{2}}$ at constant oxygen pressure should yield straight lines. The plots for case (1) and (2) are shown in Figures 12 and 16, respectively. The straight-line nature of these plots yields strong support for the electrochemical mechanism.

Leaching Models

An attempt will be made at this stage to explain the role of particle size in the leaching kinetics. The classical solid-fluid reaction model, i.e., the shrinking-core model can be invoked to explain the experimental data. The shrinking-core model can be applied to particles of unchanging size as well as to particles of decreasing size. The time needed to achieve the same fractional conversion for particles of different but unchanging sizes is given by:

1. Time for a given percent of extraction $\propto r^{1.5}$ to 2.0 for film diffusion control.
2. Time for a given percent of extraction $\propto r^{2.0}$ for product layer control.
3. Time for a given percent of extraction $\propto r$ for chemical reaction control.

For particles ($> 10 \mu m$) that change in size during the leaching process the following relationships hold:

Figure 16. Plot of rate of extraction versus square root of hydroxide ion concentration

1. Time for a given percent of extraction $\propto r^{3/2}$ for film diffusion control.
2. Time for a given percent of extraction $\propto r_0$ for chemical reaction control.

The above sets of relationships can be used to decipher the rate-controlling step in the leaching process. Because the time for conversion versus radius relationship is of the same functional form for a chemical reaction-controlled process, the choice of the model is rather arbitrary.

In Figure 17 a plot of time for 25% copper extraction from particles of different sizes is plotted as a function of particle size on a log-log scale. The slope of this plot is very close to one. This strongly suggests that a surface chemical reaction is the rate-controlling step.

In the leaching of enargite copper, arsenic and sulfur go into solution simultaneously; this strongly indicates that particle size is decreasing during the leaching step. However, no attempt was made to characterize the size distribution of the leached product.

As-Cu Ratio in Solution

There is some discrepancy between the As-Cu ration in solution and the As-Cu ratio in pure enargite. The As-Cu ratio in pure enargite is 0.39, and hence, if the leaching

D^* = particle size

t_{25} = time for 25% copper extraction (taken from Figure 15)

Figure 17. Plot of time for 25% copper extraction versus log particle size

reaction takes place according to equation (4), the As-Cu in solution should also be 0.39. However, the As-Cu in solution has almost a constant value of 0.24 at different leach times as summarized in Table 6. This behavior is not easy to explain because both copper and arsenic are soluble in ammoniacal solution under oxidizing conditions. The low value of the As-Cu ratio may rise from two factors:

1. The part of the copper in solution could be from another copper mineral in the solid. This copper mineral is most likely Cu_2S , which is known to dissolve, readily in ammoniacal solutions.
- (2) The arsenate in solution may precipitate with iron from iron-bearing sulfides forming ferric arsenate, which will cause a decrease in the ratio of As to Cu.

Kuhn et al. (1973) observed that if chalcopyrite is being leached along with enargite the level of aqueous arsenic reporting to the pregnant solution is minimized.

Table 6. Enargite leaching. -- Temperature
82°C; pH = 10, and 150 x 270 mesh.

Time (hr)	Cu ppm	As ppm	As/Cu Solution
0:20	13	3	0.231
0:40	15	4	0.27
1:00	18	5	0.28
1:30	25	6	0.24
2:00	31	7	0.28
2:30	37	9	0.24
3:00	40	10	0.25
3:30	45	11	0.244
4:00	50	13	0.25
5:00	60	14	0.233
6:00	69	16	0.232
7:00	80	18	0.23
8:00	88	20	0.23
9:00	97	24	0.25

CONCLUSIONS

1. The dissolution of enargite exhibits a half-order dependence on both the oxygen concentration and hydroxide concentration.

2. The rate of dissolution increases with increase of temperature, oxygen pressure, and a decrease in particle size. The apparent activation energy for the leach reaction is 7.0 kcal/mole.

3. Dissolution is independent of stirring speed in the range of 500-1,000 rpm.

4. Dissolution is pH dependent, and the optimum pH value is around 10.

5. In the range of the experimental conditions used only 60 percent of copper can be extracted from enargite.

6. From the experimental data it can be concluded that enargite dissolution in ammoniacal solutions is a chemical reaction-controlled process.

APPENDIX A

EXPERIMENTAL DATA

Table A-1. Summary of data presented in Figure 8

Experimental conditions:

Temperature: 82°C Initial pH value: 10
 Pressure: 50 psi Variable: Stirring speed
 Feed Size: 150 x 270 mesh
 Total NH₃ concentration: 0.3044 moles

Speed	500 rpm	Speed	750 rpm	Speed	1,000 rpm
Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)
0:20	8.0	0:20	9.0	0:20	9.5
0:40	9.0	0:40	10.0	0:40	10.74
0:60	10.0	0:60	11.8	0:60	12.6
1:30	12.0	1:30	14.0	1:30	15.4
2:00	14.0				
2:30	15.0		16.0		17.7
3:00	18.0	2:30	19.7	2:30	20.7
3:30	19.0	3:00	20.0	3:00	23.01
4:00	22.0				
5:00	25.0	3:30	21.0	3:30	24.0
6:00	30.0	4:00	26.0	5:00	30.7
7:00	34.0	5:00	28.0	6:00	34.4
8:00		6:00	31.8	7:00	38.7
9:00				8:00	42.8
11:00				9:00	45.2
				11:00	52.0

Table A-2. Summary of data presented in Figure 9

Experimental conditions:

Pressure: 50 psi
 Stirring speed: 1,000 rpm
 Feed Size: 150 x 270 mesh

Total NH₃ concentration: 0.3044 moles
 Initial pH value: 10
 Variable: Temperature

Temperature 30°C		Temperature 55°C		Temperature 70°C		Temperature 82°C	
Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)
0:20	2.0	0:20	4.3	0:20	5.7	0:20	9.5
0:40	3.8	0:40	5.63	0:40	7.02	0:40	10.74
0:60	4.0	0:60	7.00	0:60	8.34	0:60	12.6
1:30	5.8	1:30	7.5	1:30	10.3	1:30	15.4
2:00	6.4	2:00	7.6	2:00	12.2	2:0	17.7
2:30	7.0	2:30	8.12	4:00	18.03	2:30	20.7
3:00	7.8	3:00	8.71	5:00	21.03	3:00	23.01
4:00	8.0	4:00	9.30	6:00	22.6	3:30	24.0
5:00	8.4	5:00	10.4	7:00	25.4	5:00	30.7
6:00	8.7	6:00	10.84	8:00	27.0	6:00	34.4
7:00	9.0	7:00	11.9			7:00	38.7
8:00	9.5	8:00	13.0			8:00	42.8
9:00	9.8	9:00	17.11			9:00	45.2
						11:00	52.0

Table A-3. Summary of data presented in Figure 11

Experimental conditions:

Temperature: 82°C	Total NH ₃ concentration: 0.3044 moles
Stirring speed: 1,000 rpm	Initial pH value: 10
Feed size: 150 x 270 mesh	Variable: Pressure

Pressure = 5 psi		Pressure = 5 psi		Pressure = 50 psi	
Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)
0:20	5.2	0:20	6.3	0:20	9.5
0:40	5.8	0:40	7.9	0:40	10.74
0:50	7.2	0:60	8.5	0:60	12.6
1:30	7.8	1:30	10.4	1:30	15.4
2:00	9.7	2:00	11.6	2:00	17.7
2:30	10.9	3:00	14.8	2:30	20.7
3:00	12.1	3:30	16.5	3:00	23.01
3:30	13.2	4:00	18.13	3:30	24.0
5:00	15.6	5:00	21.00	5:00	30.7
6:00	17.1	6:00	23.8	6:00	24.4
7:00	18.0	7:00	26.8	7:00	28.7
8:30	20.0	8:00	29.3	8:00	42.8
9:00	24.5	9:00	31.2	9:00	45.2
	26.0			11:00	52.0

Table A-4. Summary of data presented in Figure 13

Experimental conditions:

Temperature: 82°C

Pressure: 50 psi

Stirring speed: 1,000 rpm

Feed size: 150 x 270 mesh

Total NH₃ concentration: 0.3044 moles

Variable: pH value

pH = 8.5		pH = 9.4		pH = 10.0		pH = 11.0	
Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)
0:20	4.3	0:20	5.3	0:20	9.5	0:20	4.3
0:40	4.52	0:40	5.6	0:40	10.74	0:40	6.4
1:30	6.5	0:60	8.8	0:60	12.6	1:00	9.8
2:00	7.1	1:30	10.74	1:30	15.4	1:30	12.4
2:30	8.1	2:30	15.5	2:30	17.7	2:30	17.0
3:00	8.6	3:00	18.7	3:00	20.7	3:00	19.5
4:00	10.4	3:30	19.8	3:30	23.0	3:30	21.3
5:00	14.03	4:00	22.0	5:00	24.0	4:00	23.0
6:00	14.4	4:30	24.1	6:00	30.7	5:00	24.42
7:00	15.3	5:00	25.5	7:00	24.4	6:00	25.0
8:00	16.4	6:00	30.0	8:00	38.7	7:00	25.2
9:00		7:00	32.2	9:00	42.8	8:00	25.4
		8:00	36.2	11:00	52.0	9:00	30.94

Table A-5. Summary of data presented in Figure 14

Experimental Conditions:

Temperature: 82°C

Pressure: 50 psi

Feed size: 150 x 270 mesh

Initial pH value: 10

Stirring speed: 1,000 rpm

Variable: Total NH_3 concentrate

<u>NH_3 Conc. = 0.1522 mole</u>		<u>NH_3 Conc. = 0.3044 mole</u>		<u>NH_3 Conc. = 0.6088 mole</u>	
Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)
0:20	5.0	0:20	8.014	0:20	10.7
0:40	5.9	0:40	8.5	0:40	11.2
0:60	7.1	0:60	9.8	0:60	11.8
4:00	12.0	1:30	12.4	1:30	13.1
5:00	13.1	2:00	15.0	2:00	15.0
6:00	15.0	2:30	16.6	2:30	16.8
7:00	14.0	3:00	19.0	3:00	19.14
8:00	14.0	4:00	22.5	4:00	22.8
9:00	14.0	5:00	26.6	5:00	25.7
		6:00	30.3	6:00	29.02
		7:00	33.4	7:00	32.4
		8:00	37.3	8:00	36.4
		9:00	41.0	9:00	42.0

Table A-6. Summary of data presented in Figure 15

Experimental conditions:

Temperature: 82°C

Pressure: 50 psi

Stirring speed: 1,000 rpm

Total NH₃ concentration: 0.3044 moles

Initial pH value: 10

Variable: Feed size

Feed Size (100 x 150) Mesh		Feed Size (100 x 270) Mesh		Feed Size (270 x 400) Mesh		Feed Size (270 x 400) Mesh	
Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)	Time (hour)	Cu Extracted (%)
0:20	6.8	0:20	9.5	0:20	8.4	0:20	3.5
0:30	8.0	0:40	10.74	0:40	10.0	0:40	4.7
0:40	9.2	0:60	12.6	0:60	11.9	0:60	5.7
0:60	11.01	1:30	15.4	1:30	16.3	1:30	6.8
2:00	14.12	2:00	17.7	2:00	20.0	2:00	7.85
2:30	15.13	2:30	20.7	2:30	23.5	2:30	9.9
3:00	16.2	3:0	23.01	3:00	25.1	3:00	10.95
4:00	18.5	3:30	24.0	3:30	28.0	3:30	11.92
5:00	19.3	5:00	30.7	4:00	30.8	4:00	14.00
6:00	21.4	6:00	34.4	5:00	36.10	5:00	14.7
7:00	23.3	7:00	38.7	6:00	41.0	6:00	16.6
8:00	24.1	8:0	42.8	7:00	47.0	7:00	18.5
9:00	22.8	9:00	45.2	8:00	51.1	8:00	20.3
		11:00	52.0	9:00	55.4	9:00	23.9

REFERENCES

- Bjerrum, J., Metal Ammine Formation on Aqueous Solution, Copenhagen: P. Haase and Son (1957).
- Butler, J. N., Ionic Equilibrium-A Mathematical Approach, Massachusetts: Addison Wesley Publishing Company, (1964).
- Dutrizac, J. E., "The Kinetics of Dissolution of Enargite in Acidified Ferric Sulphate Solutions," Canadian Metallurgical Quarterly, Vol. 11, No. 3, (1972).
- Encyclopedia of Electrochemistry of the Elements, Vol. 11, Part 11-2, Bard, A. J. (Ed.), 1972, pp. 22-24.
- Knight, J. E., "A Thermodynamic Study of a Lunite, Enargite, Luzonite, and Tennantite Deposits," Economic Geology, Vol. 72, pp. 132-136, (1977).
- Kracek, F. C., "Vapor Pressure of Solution and the Ramsey-Young Rule: Application to the Complete System Water Ammonia," J. of Physical Chemistry, Vol. 34, pp. 499-521, (1930).
- Kuhn, M. C., Arbiter, N., and Kling, H., "Anaconda's Arbiter Process for Copper," a paper presented to the Hydro-metallurgy Section of the CIM (October 1, 1973).
- Pauling, L., and Weinbaum, S., "The Crystal Structure of Enargite, $\text{Cu}_3\text{As}_5\text{S}_4$," Z. Kristallogr., Vol. 88, pp. 48-53, (1930).
- Peters, E., "Direct Leaching of Sulphides: Chemistry and Applications," Metallurgical Transactions, AIME, Vol. 7B, pp. 505-517 (1976).
- Peters, E., Forward, F. A., and Majima, H., "The Physical Chemistry of Sulphating Reactions in Aqueous Solution," a paper presented at the AIME Annual Meeting, February (1976).

642
5930 8