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CYANIDE LEACHING OF CHALCOCITE

by

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TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

TABLE OF CONTENTS--Continued

LIST OF TABLES

LIST OF TABLES -- Continued

LIST OF TABLES -- Continued

LIST OF TABLES -- Continued

LIST OF ILLUSTRATIONS

Figure Page

LIST OF ILLUSTRATIONS--Continued

ABSTRACT

The leaching of chalcocite concentrates with sodium cyanide under nonoxidizing conditions is shown to have several advantages: the leaching rate is high, the cyanide does not react with the pyrite contained in most chalcocite concentrates, the copper remains in the lower oxidation state, and the sulfur reports as bisulfide. These considerations make a study of the process promising.

A literature search was performed to accumulate information on cyanide leaching of copper minerals and the aqueous chemistry of the copper-cyanide-sulfide system. Although a large amount of research has been reported for copper cyanide extraction, there have been no investigations reported for leaching chalcocite under nonoxidizing conditions. Values of the required thermodynamic data were given in the literature. However, the published equilibrium constants showed considerable variation from one report to another.

A series of equilibrium and mass balance equations were written to describe the concentrations of the aqueous species to be expected in the leaching system. A finite ionic radius form of the Debye-Hückel equation was used to calculate the activity coefficients. A numerical method for solving these equations is presented that is slow, but stable. These calculations show that the copper occurs as

the tetra- and tricyanide complexes and the sulfur primarily as the bisulfide ion. The coupling of the cyanide and sulfur systems through a common hydrogen ion dependence complicates the system considerably.

The material used in the study was a massive chalcocite from the New Cornelia Mine in Ajo, Arizona. After dry grinding and sizing, a detailed analysis was made which showed that the sample was approximately 97 percent chalcocite with minor amounts of quartz and hematite.

Various empirical rate equations were tested. Although there was considerable scatter in the data which may have concealed some minor effects, the following were found to be significant for a pH over 10 and a total cyanide concentration from 0.16 M to 0.6 M. The activation energy of 2.5 kcal/mole of copper suggests that the reaction is diffusion controlled. It is first order in free cyanide concentration and exhibits a low order inverse dependence on sulfide ion concentration. Microscopic examination of the leached particles showed a definite increase in the shape factor during the experiment. However, it was found that a shrinking core model based on perfect spheres gave an adequate approximation up to an extraction of about 80 percent. Thus, at 25°C, the empirical rate equation is:

$$R = \frac{7.5 \times 10^{-5} A \left[CN^{1-}\right]}{\left[S^{2-}\right]^{0.1}} \quad M/min$$

Several significant pH effects were noted. As a consequence of the large differences between the hydrogen cyanide and bisulfide dissociation constants and the high consumption of cyanide during the extraction, there is a pH above which pH increases during the leach and below which it decreases. There is also a maximum in the leaching rate at about the same point. Under the conditions used in this study, this pH was about 10.

The actual extraction data is presented so that the major variables to be encountered in a commercial process can be evaluated. Extractions as high as 90 percent in fifteen minutes were obtained on the -28, +35 mesh fraction when there was a large excess of free cyanide. In view of the difficulty in reducing copper from the higher complexes, it is doubtful that such high cyanide to copper ratios could be used in actual practice. The effects of the major process variables on extraction rate are discussed in some detail.

CHAPTER I

INTRODUCTION

The hydrometallurgical treatment of copper concentrates has received considerable attention in recent years as a result of the emission standards that have been imposed upon smelters. Furthermore, an increased awareness of resource conservation has prompted studies of methods that can produce higher recoveries or treat lower grade materials than can be economically treated at the present time. Hydrometallurgical processes are, in general, better suited for treating mineralogically complex ores. Finally, the development of processes that are optimal for particular ore types rather than treating all copper ores by a single process is becoming increasingly important. Thus, processes that offer an improved means of treating a limited group of concentrates with resultant lower pollution problems or higher overall copper recovery merit serious consideration. Such consideration should also be given to the recovery of by-products which may become economically important in the future.

The commercially important copper minerals may be divided into three distinct categories with regard to their hydrometallurgy: oxides, sulfides other than chalcopyrite, and chalcopyrite. The leaching of oxides with sulfuric acid is well established and will not be considered here. The separation of chalcopyrite from chalcocite, covellite, and bornite is based on its much lower leaching rate. A few mining operations produce other minerals such as enargite or concentrates containing impurities such as bismuth which seriously affect smelting. Despite the significant tonnages of chalcopyrite concentrates that are produced, the production of concentrates containing most of the copper values as chalcocite is sufficiently large to justify a process that is unable to directly treat chalcopyrite. It should be noted, however, that Hiskey and Wadsworth (1974) have reported a method of altering chalcopyrite to chalcocite which might enable many processes that will not treat chalcopyrite concentrates directly to be successfully adapted to such use. In Arizona and New Mexico alone the Tyrone, Morenci and Metcalf operations of the Phelps Dodge Corporation, the Chino Mines Division of the Kennecott Copper Corporation, and the Inspiration Branch of the Inspiration Consolidated Copper Company produce most of their copper from chalcocite. The daily concentrate tonnages are approximately 1500, 1600, 1000, 800, and 225 respectively. Before its recent closure, the Copper Queen Branch of the Phelps Dodge Corporation also produced a chalcocite concentrate.

In most ore bodies where chalcocite is the dominant copper mineral it occurs as a rim on pyrite grains. Figure 1 shows a typical section of a chalcocite-pyrite vein. Even considering that the final concentrates are typically finer than 50 percent minus 325 mesh, the difficulty in separating the chalcocite and pyrite by flotation is readily seen. Partly as a consequence of this intimate association of chalcocite and pyrite, most concentrators treating such ores have copper extractions as low as 80 percent with the pyrite in the final concentrate as high as 70 percent. Because pyrite is 53 percent sulfur, the load imposed on the sulfur removal facilities at a smelter is considerable. Furthermore, since the iron must be removed as a iron silicate slag, a high flux usage and large copper loss in the slag result. These major effects on smelter economics often require the adjustment of concentrator operating conditions to produce a concentrate grade that is suitable for smelting at the expense of copper extraction. Consequently, alternatives to smelting that do not affect pyrite would probably allow a higher copper extraction in the concentrator.

Since cyanide leaching of chalcocite does not produce atmospheric pollution and cyanide does not attack pyrite, the topic of this dissertation is relevant to an important environmental and resource conservation need. The following sections of this chapter give a brief outline of the proposed process for producing copper by

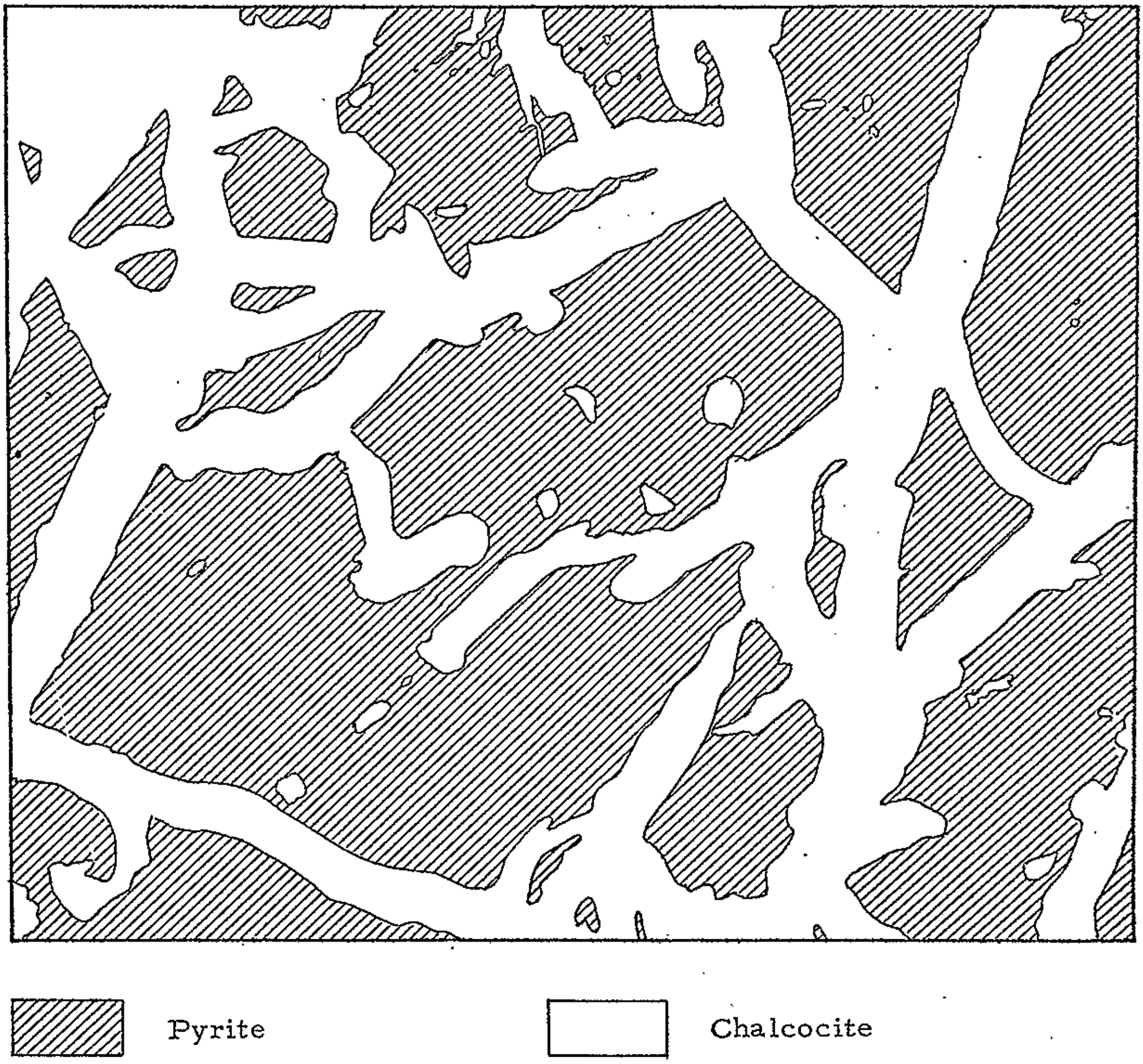

Figure 1. Polished Section of a Vein from a Typical Chalcocite Ore Body (125X)

cyanidation and a description of the topics covered by this dissertation. A more detailed discussion of previous work with the pertinent references is given in Chapter 2.

Leaching with Cyanide

The general response of the copper minerals to cyanide leaching has been reported in the literature. For the present time it is sufficient to note that the oxides and sulfides, with the exception of chalcopyrite, are readily soluble. However, those minerals such as covellite, cuprite, and azurite having copper in the higher oxidation state cause the oxidation of cyanide to cyanogen and consequently consume significant quantities of cyanide. There has been some unreported work by the Treadwell Company using sulfur dioxide as a reductant to circumvent this problem but no definite results are available. Because of the loss of cyanide to cyanogen with many minerals, the relative insolubility of chalcopyrite, the ready solubility of the oxides in acid, and the large tonnages of chalcocite concentrates available for possible treatment, this dissertation considers only the leaching of chalcocite. In the presence of oxygen numerous side reactions occur which considerably complicate the system and consume cyanide. As will be shown later, chalcocite dissolves rapidly in cyanide solutions under nonoxidizing conditions. These facts indicate that the optimum commercial approach will probably be leaching under nonoxidizing conditions. As a consequence of these considerations, only the leaching of chalcocite under nonoxidizing conditions was studied.

There are several advantages to leaching chalcocite in a cyanide solution. First is the major advantage associated with all hydrometallurgical methods: the elimination of atmospheric pollution. Considering that a recent report indicates that 82 million dollars was spent on pollution control equipment at the Hidalgo smelter of the Phelps Dodge Corporation alone (Cousland, 1975), the potential capital savings could be very significant for this reason by itself. Furthermore, cyanide does not react with the pyrite that is commonly associated with chalcocite. Consequently, a cyanide leach does not liberate the sulfur from the pyrite as smelting does thus reducing the quantity of sulfur oxides that must be treated. Modification of mill practice to maximize extraction of copper almost without regard to concentrate grade may thus become feasible in many operations since the economic penalty for the increased pyrite in the concentrate would be much less with cyanide leaching than with smelting. Unlike many other hydrometallurgical processes, cyanide leaching will recover the precious metal values except those locked in either the pyrite or the gangue. Because copper enters the solution as cuprous ion, only half as much reductant is required for a cyanide off-solution compared to acid or ammonia leach solutions.

Since the extraction rate is high, it might be possible to treat the coarse, rougher concentrate directly thus eliminating the regrind and cleaner flotation stages in the concentrator resulting in a major capital and power savings.

The pyrite concentrate that could be easily produced from the leach residue is a potential source of both iron and sulfur. Habashi (1969) describes the Duisburger Kupferhütte plant which has treated pyrite cinder from sulfuric acid production since 1876. Pyrite concentrates are purchased worldwide from sources as far as Canada and shipped to sulfuric acid plants throughout Germany. The resulting cinder is then treated at Duisburg to recover the nonferrous metal values and produce iron oxide pellets for blast furnace feed. Guccione (1965) outlines practices at Montecatini's plant at Follonica, Italy, which produces sulfuric acid, magnetite pellets, and electrical power from pyrite concentrates. A similar process at Kokkola by Outokumpu Oy produces elemental sulfur and iron oxide pellets (Guccione, 1966). Finally, Remirez (1968) describes a Japanese plant for producing sulfuric acid and iron oxide pellets. The Tyrone concentrator alone could produce about one thousand tons per day of pyrite concentrates as residue from a cyanide leach. Consequently, the values obtained from the production of by-product iron obtainable with cyanide leaching but not smelting might offset much of the higher operating costs of the cyanide leach.

The following are the primary drawbacks to cyanide leaching. First, the recovery of the metal from the cyanide complexes formed during the leach appears to be difficult. The high free energies of the complexes lead to high voltages and low current efficiencies during electrowinning while direct acidification reprecipitates cuprous sulfide. The latter approach would allow rejection of the pyrite in the feed even though it would require smelting of the synthetic chalcocite so produced. Upgrading the leach solution by solvent extraction has not been investigated although some reports indicate that it should be possible. The direct reduction of copper by hydrogen or other reductants has likewise not been reported. Cyanide losses in the presence of oxidants including Cu(II) could be significant with some concentrates. Air introduction into the system could result in the formation of a series of polythionates which would react with cyanide to form cyanate. No studies have been made on removing the sulfide ion produced during the leach. Finally, the toxicity of cyanide solutions requires care in handling and special precautions to prevent the discharge of cyanide-bearing solutions from the plant. If these difficulties can be overcome, cyanide leaching of chalcocite concentrates could be a very attractive process.

Development of the Dissertation

In the original proposal for the dissertation topic a comprehensive study of leaching copper sulfides in alkaline cyanide solution was envisioned. As the work progressed, an improved knowledge of the complexities of the system and the difficulties involved in dealing with them made it apparent that the study needed to be considerably more limited. An examination of the literature indicated that chalcocite would dissolve in cyanide solutions without oxidation of the sulfide ion. However, when air was introduced into the system numerous poorly defined but demonstrable side reactions resulted in the loss of cyanide by cyanate formation (Coghill, 1912; Hedley and Kentro, 1945; Lower and Booth, 1965a and 1965b; Hedley and Tabachnick, 1968). Since cyanide loss would be an additional expense in a commercial operation, and enclosed reactors could easily be used to prevent air oxidation, a detailed study of cyanide leaching of chalcocite under oxidizing conditions appeared to be of little practical interest and was therefore not attempted. In view of the oxidation of cyanide by Cu(II) a study of leaching a cupric mineral under reducing conditions would probably be a more reasonable next step.

The chemistry of the system was investigated and was found to be dominated by the equilibria among the copper cyanide complexes, free cyanide ion, and hydrogen cyanide. The cyanide ion-hydrogen cyanide equilibria couples with the sulfide-bisulfide-hydrogen sulfide system through their common hydrogen ion dependence. Consequently several interesting pH effects were found. Since significant pH changes were noted during the leach as a result of the hydrolysis of the sulfide ion produced by the dissolution of chalcocite, a system of nine simultaneous nonlinear equations was required to describe the concentrations of the ionic species. During the data analysis it became apparent that the concentrations could not be used directly for activities of the solution strengths of practical interest. Consequently, Debye-Hückel equations of the following form

$$-\ln\gamma_i = \frac{Az_i^2\mu^{\frac{1}{2}}}{1 + Ba_i\mu^{\frac{1}{2}}}$$

were introduced. This improvement led to an additional seven simultaneous nonlinear equations for the required activity coefficient ratios. These equations contained nine ionic size parameters which were estimated but not optimized. The values of the thermodynamic constants obtained from the literature showed considerable variation. Since the literature clearly indicated that these variations resulted from the inherent difficulties in determining the equilibrium constants, and consequently, that a major research effort would be necessary to improve upon the reported values, no effort was made to experimentally determine these constants during this study. The author believes that the improvements in the calculations of the concentrations that would result from improved equilibrium constants would be of minor importance from a practical standpoint since such variables as the particle geometry of actual concentrates would contribute significantly larger errors.

Since the system described above could not be solved and integrated analytically to obtain an expression for total copper as a function of time, a derivative method had to be used to study the kinetics. To accomplish this, the total copper versus time curve was fitted with an exponential equation and the rate at each sampling point calculated by the derivative of the fitted curve. The solution of the sixteen simultaneous equations for the concentrations of the ionic species at each sample point during the leach together with the rates obtained as described above allowed determination of an experimental rate law that adequately describes the data in the range of cyanide concentration from 0.01M to 0.5M, pH from 9 to 13, sulfide ion concentration from 0.00001M to 0.1M, and temperature from 3°C to 70°C. The uncertainties in the above data made it clear that a precise mechanism of reaction could not be verified. Consequently, a general explanation of the reaction rate in terms of the solution chemistry was developed. The author believes that such treatment is adequate at this point in the development of the process and that the immediate need is for work on other process steps.

Finally, for the benefit of those who could utilize the results of the leach tests for rough approximations in studies of proposed processes, a discussion of copper extraction in terms of the process variables is presented in Chapter 7. The raw data from the leach tests are given in Appendix III should anyone wish to attempt a different analysis of them.

CHAPTER 2

REVIEW OF THE LITERATURE

This chapter will trace the major developments in the understanding of copper cyanide chemistry and its application to copper metallurgy. Because most of the early experimental work was concerned with obtaining a reasonable leaching rate with precious metal ores containing copper rather than the leaching of the copper minerals themselves, the early work will be sketched only briefly.

Copper as a Cyanacide in Precious Metal Cyanidation

A fairly comprehensive review of previous experience with copper in cyanide leach solutions is given by Virgoe (1901). Virgoe states that the high cyanide consumptions in such solutions is a result of the formation of the double and triple salts, $KCu(CN)_2$ and $K_2Cu(CN)_3$, and the oxidation of cyanide to cyanogen by any cupric salts present. In addition, Virgoe explains the low precious metal extractions commonly reported as resulting from errors in determining the free cyanide concentration by the classical silver nitrate titration. Virgoe (1901) elaborates on his previous paper indicating that it is his opinion that the double and triple salts are the only ones of concern to the cyanide plant operators and that the double salt exists only in the absence of free cyanide. Coghill (1912), after proposing several possible reactions, concludes that sulfides may lead to the formation of thiocyanate and that the cyanide consumption may range from 2.0 to 3.6 parts per part of copper depending on the particular copper mineral involved. Halferdahl (1929) describes many methods including acidification and electrowinning that had been proposed or used to regenerate cyanide from solutions fouled by copper. Halferdahl's paper is fairly comprehensive and covers most of the reagents or methods that have been proposed recently for copper recovery from cyanide solutions. In this respect it is also interesting to note that Richmond (1907) reports commercial electrowinning of copper and precious metals at the San Sebastian Mine, San Salvador. The copper and gold were first electrowon together then separated in an electrorefining operation. In all, 24,391 pounds of copper cement were produced between May, 1905, and April, 1906. Several more recent papers including McLachlan, Ames, and Morton (1946), Hedley (1946), and Hedley and Tabachnick (1968) also discuss the role of copper in the cyanidation of precious metal ores.

Leaching Copper Minerals With Cyanide

Leaver and Woolf (1931) reported the results of a series of tests run on artificial ores made by mixing crushed copper minerals with sea sand. The tests were made with varying amounts of cyanide under oxidizing conditions. The results of a few of their experiments are presented in Table 1. The leach time was twenty-four hours. Lower and Booth (1965a, 1965b) report results of another series of tests on various copper minerals. Their results are presented in Table 2. The leach times were six hours except as noted. These tests clearly indicate that all commercially important copper minerals except chalcopyrite leach readily in the presence of adequate cyanide.

The Nature of the Copper Complexes

The early investigators of cyanide chemistry proposed various copper cyanide salts on the basis of the cyanide loss in precious metal leach solutions with the molar ratio of cyanide to copper usually being given as two or three to one. Based on measurements of vapor pressure, pH, and conductivity, Britton and Dodd (1935) state that the species formed is $Cu(CN)_3^{2-}$. A study of the silver nitrate titration of cyanide solutions by Willis and Woodcock (1950) showed that $Cu(CN)_2^{1-}$ and $Cu(CN)_3^{2-}$ exist in equilibrium. It was their opinion that typical precious metal cyaniding solutions contain a negligible concentration of $Cu(CN)_4^{3-}$. An infrared absorption study by Penneman and Jones (1956) identified peaks which they assigned to $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. While the dicyanide complex was observed, its low extinction coefficient made its measurement difficult. In the following years other authors also identified these complexes. In studies of the Raman spectra of the copper cyanides both Chantry

TABLE 1

SOLUBILITY OF COPPER MINERALS FROM LEAVER AND WOOLF (1931)

Name of Mineral	Extraction (%)
Azurite	100.
Bornite	94.
Chalcocite	100.
Chalcopyrite	8.4
Chrysocolla	16.9
Cuprite	100.
Enargite	98.9
Malachite	100.
Tetrahedrite	40.3
Metallic Copper	100.

TABLE 2

SOLUBILITY OF COPPER MINERALS FROM LOWER AND BOOTH (1965a)

Mineral	Cyanide Ratio[a]	Extraction (%)
Chalcocite	2.76	92.6
Cuprite	4.94	96.6
Malachite	4.48	99.7
Azurite	3.62	91.8
Covellite[b]	5.15	95.6
Chalcopyrite[c]	2.79	5.8
Bornite[b]	5.13	96.0

[a] Grams NaCN per gram of contained copper.

[b] Four hour leach in these tests only.

[c] Minus 325 mesh mineral used in this test.

and Plane (1960) and Cooper and Plane (1966) reported identification of the three complexes. Rothbaum (1957) used the ultraviolet absorption spectra and static electrode potentials at 20°C and at 80°C to determine both the nature and equilibrium constants of the system. Simpson and Waind (1958) studied the system by ultraviolet absorption spectra as did Baxendale and Westcott (1959). The latter authors also described the kinetics of the reaction of Cu(II) and cyanide. Brenner (1965) studied the equilibria of the complexes calorimetrically and reported values for the equilibrium constants. Finally, Izatt et al. (1967) reported log K, ΔH^o, and ΔS^o values for the Cu(I) complexes of cyanide. It has therefore been rather clearly established that the complexes $Cu(CN)_2^{1-}$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$, coexist in cyanide solutions and that the relative dominance of any particular species is a function of the cyanide to copper ratio, pH, and the values of the equilibrium constants. Since cuprous cyanide is essentially insoluble, there is a low solubility of copper for the lower cyanide to copper ratios. The values of the equilibrium constants will be discussed in detail in Chapter 3.

Dissolution of Chalcocite and Covellite in Cyanide Solution

Potashnikov and Kakovskii (1962) made a preliminary study of the dissolution of chalcocite in a cyanide solution in the presence of oxygen. They observed both sulfur and covellite films on their rotating disk and reported confirmation of the following reactions.

$$2Cu_2S + 6CN^{1-} + H_2O + \tfrac{1}{2}O_2 = 2CuS + 2Cu(CN)_3^{2-} + 2OH^{1-} \qquad (2.1)$$

$$2CuS + 6CN^{1-} + H_2O + \tfrac{1}{2}O_2 = 2S^{o} + 2Cu(CN)_3^{2-} + 2OH^{1-} \qquad (2.2)$$

They indicate that thiocyanate formed but did not determine the reaction by which it formed. In addition, their experiments demonstrated that in the absence of oxygen the sulfide entered the solution as sulfide ion.

In a later paper, Kakovskii and Potashnikov (1964) determined the kinetics of the dissolution of covellite in cyanide solution with a rotating disk. The existence of the following two competing reactions was reported and the predominance of one or the other related to the oxygen partial pressure.

$$2CuS + 8CN^{1-} + O_2 + 2H_2O = 2Cu(CN)_3^{2-} + 2S^{o} + (CN)_2 + 4OH^{1-} \qquad (2.3)$$

$$2CuS + 7CN^{1-} = 2Cu(CN)_3^{2-} + S^{2-} + CNS^{1-} \qquad (2.4)$$

These authors also state that covellite, chalcocite, and argentite all exhibit first order kinetics with regard to cyanide ion, that the kinetics are reaction controlled for covellite and argentite but diffusion controlled for chalcocite, and that the rate of dissolution decreases with increasing time for the copper sulfides in the presence of oxygen. No report was made of studies under nonoxidizing conditions. A special note was made that the increase in reaction rate with temperature was markedly less for chalcocite than for the other minerals.

These reports clearly indicate that oxygen will lead to thiocyanate formation during the leaching of chalcocite. In view of the high extraction rates reported later in this dissertation for chalcocite under nonoxidizing conditions, the economic advantage of excluding air or other oxidants is clear.

Electrowinning from Cyanide Solutions

Since it was anticipated that a study of electrowinning copper from the chalcocite leach solutions would be made later, a short literature search was made on the subject to determine whether or not any constraints would be imposed on the leach system by subsequent electrowinning. Richmond (1907) reported commercial-scale electrowinning but did not discuss either current efficiencies or energy consumption. Because the primary values involved were gold rather than copper, it is quite likely that low current efficiencies would have been tolerated. Glasstone (1929) reports current efficiencies ranging from 0 to 100 per cent, some of which are presented in Table 3. Glasstone further reports that current efficiencies increased with temperature. From Figure 2 and the reported cathode potential for hydrogen reduction in cyanide solution of -0.65 volt, one can readily see that molar ratios of cyanide to copper over about 3.2:1 result in formation of hydrogen and consequent low current efficiencies. Clevenger (1916) also reports low current efficiencies in experiments

TABLE 3

CATHODE POTENTIAL AND CURRENT EFFICIENCIES FROM GLASSTONE (1929) FOR SOLUTIONS 0.1 N IN KCN

Current Density		Solution 1[a]		Solution 2[b]	
(amps/cm^2) x10^4	(amp/ft^2)[c]	Cathode Potential (v)	Current Efficiency (%)	Cathode Potential (v)	Current Efficiency (%)
1.0	0.09	-0.29	---[d]	-0.77	---[d]
4.0	0.37	-0.34	100	-0.93	62
6.0	0.56	-0.39	81	-1.05	36
15.	1.4	-1.13	47	-1.27	21
100.	9.3	-1.41	22	-1.43	9

[a] Cyanide to copper ratio 2:1

[b] Cyanide to copper ratio 4:1

[c] Calculated from the original data

[d] Current efficiencies not reported in original article

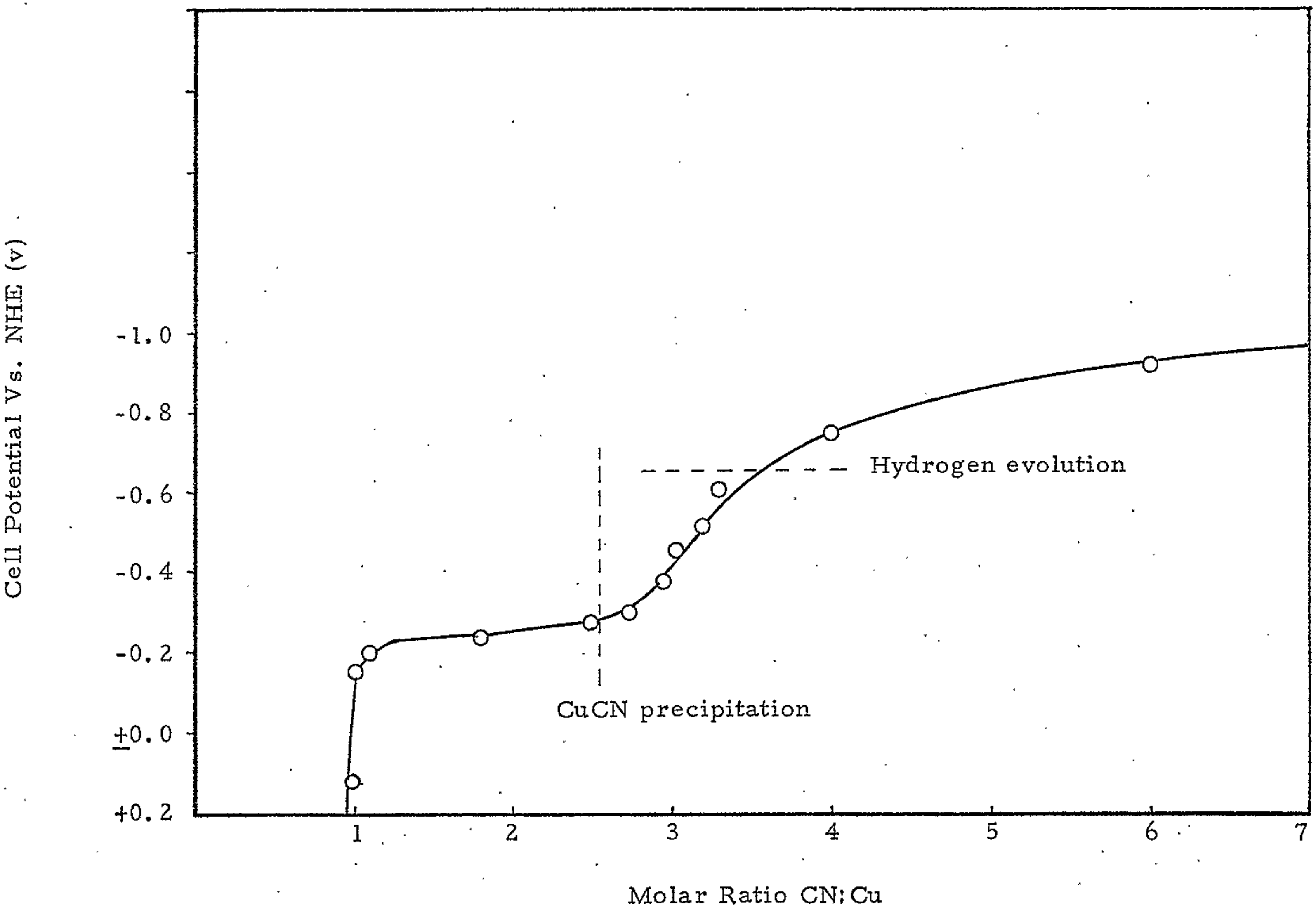

Figure 2. Electrode Potentials for the Cuprous Cyanides from Glasstone (1929)

on copper-bearing precious metal leach solutions. Thus, it appears that while high current efficiencies can be obtained under some conditions, the conditions most favorable for leaching will result in exceptionally low current efficiencies.

Proposed Processes for Cyanidation of Copper-Bearing Materials

With the exception of the previously noted work at San Sebastian (Richmond, 1907), no reference was found that reported commercial extraction of copper from cyanide solutions. Many processes involving cyanide leaching have been proposed, but none tested on any reasonable scale.

Lower and Booth (1965a and 1965b) describe a method that would use cyanide to leach a copper ore. Copper would then be precipitated as cuprous sulfide concurrently with recovery of the cyanide as hydrocyanic acid by the addition of sulfuric acid to the pregnant solution. The high-grade cuprous sulfide would then be treated by conventional methods. The major problems appear to be economic: the loss of cyanide by oxidation, complexation, and entrainment in the tailings, together with the high capital costs of leaching the entire low-grade feed. The Engineering and Mining Journal staff (1967) reviewed five inventions for the recovery of copper with cyanide. The first was the Treadwell process which essentially upgraded an acid solution of cupric sulfate by precipitating cuprous cyanide. A second Treadwell patent leaches the ore with cyanide, then precipitates cuprous sulfide by acidification. The other three are basically similar to those patents already described. Chamberlain, Newton, and Clifton (1969) have described a process for treating a copper-bearing silver leach residue. As in many of the preceeding processes, the copper is precipitated as cuprous sulfide which is then treated conventionally.

Summary of the Literature

The copper-cyanide complexes have been clearly shown to be $Cu(CN)_2^{1-}$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$. Reasonable values of the thermodynamic quantities for the equilibria have been reported. The kinetics of the dissolution of covellite have been reported as has some information for chalcocite under oxidizing conditions. There is general agreement that in the absence of oxygen chalcocite leaches with the formation of the cuprous complexes and sulfide ion. A short review of electrowinning indicates that the molar ratio of cyanide to copper in the leach off-solution will be critical in obtaining acceptable current efficiencies. The reported processes have been primarily aimed at upgrading other products rather than recovering copper metal directly from the cyanide leach solution.

CHAPTER 3

THE CHEMISTRY OF THE SYSTEM

The system that results from the dissolution of chalcocite in alkaline cyanide solution is fairly complex when conditions are such that few of the ionic species present can be neglected. Several attempts were made during the earlier stages of this study to avoid some of the complexities by carefully choosing initial conditions, but it soon became apparent from the experimental results that a simplified approach would be unacceptable. The following sections will describe the chemical species present in the leach solution and their interrelationships. The discussion of reaction rates will be presented in Chapter 5.

The Defining Equations for Ionic Concentrations

The reaction for the dissolution of chalcocite in cyanide solutions under nonoxidizing conditions is usually given as follows.

$$Cu_2S + 6CN^{1-} = 2Cu(CN)_3^{2-} + S^{2-} \tag{3.1}$$

However, the situation is in reality considerably more complicated. The many ionic species present are related to one another. The results of the literature survey reported in Chapter 2 clearly indicate that there are three cuprocyanide complexes present in solution that are in equilibrium. First, the dicyanide complex dissociates to cuprous ion and cyanide ion.

$$Cu(CN)_2^{1-} \overset{K}{\rightleftharpoons} Cu^{1+} + 2CN^{1-} \tag{3.2}$$

The equilibrium constant for this dissociation can be written as follows by substituting concentrations for activities.

$$K = \frac{\left[Cu^{1+}\right] \left[CN^{1-}\right]^2}{\left[Cu(CN)_2^{1-}\right]} \tag{3.3}$$

Izatt et al. (1967) report that the value of K is approximately 10^{-24}. Substituting this value of K into equation 3.3 and rearranging gives the next equation.

$$\frac{\left[Cu^{1+}\right]}{\left[Cu(CN)_2^{1-}\right]} = \frac{10^{-24}}{\left[CN^{1-}\right]^2} \tag{3.4}$$

Thus, at concentrations of free cyanide over 10^{-10}M cuprous ion is negligible, and hence will not be considered. It should also be noted that cuprous cyanide is insoluble and will precipitate at low cyanide to copper ratios.

The stepwise dissociation of the higher cuprocyanide complexes is given by the following reactions.

$$Cu(CN)_4^{3-} \overset{K_{4,3}}{\rightleftharpoons} Cu(CN)_3^{2-} + CN^{1-} \tag{3.5}$$

$$Cu(CN)_3^{2-} \overset{K_{3,2}}{\rightleftharpoons} Cu(CN)_2^{1-} + CN^{1-} \tag{3.6}$$

The respective equilibrium constants in terms of the ionic activities are then defined as follows.

$$K_{4,3} = \frac{a_{Cu(CN)_3^{2-}} \quad a_{CN^{1-}}}{a_{Cu(CN)_4^{3-}}} \tag{3.7}$$

$$K_{3,2} = \frac{a_{Cu(CN)_2^{1-}} \quad a_{CN^{1-}}}{a_{Cu(CN)_3^{2-}}} \tag{3.8}$$

Since significant amounts of copper can occur only as the three complexes, the copper mass balance may be written as follows where $\left[Cu_T\right]$ is the concentration of cuprous ion that would result if all the copper present in solution were in that form.

$$\left[Cu_T\right] = \left[Cu(CN)_4^{3-}\right] + \left[Cu(CN)_3^{2-}\right] + \left[Cu(CN)_2^{1-}\right] \tag{3.9}$$

The concentration of a particular copper complex may be very small at any given time during the test as a result of the test conditions. All, however, need to be considered as a result of the range of conditions used.

The stepwise dissociation of hydrogen sulfide can be treated in a similar manner. This treatment is required as a result of the hydrolysis of the sulfide ion formed during the leaching of the chalcocite. The stepwise hydrolysis can be represented by the following.

$$S^{2-} + H_2O = HS^{1-} + OH^{1-} \tag{3.10}$$

$$HS^{1-} + H_2O = H_2S + OH^{1-} \tag{3.11}$$

The first dissociation of hydrogen sulfide may be written as follows.

$$H_2S \overset{K_1}{=} HS^{1-} + H^{1+} \tag{3.12}$$

The equilibrium constant is then given by equation 3.13.

$$K_1 = \frac{a_{HS^{1-}} \quad a_{H^{1+}}}{a_{H_2S}} \tag{3.13}$$

Similarly, the second dissociation follows.

$$HS^{1-} \overset{K_2}{=} S^{2-} + H^{1+} \tag{3.14}$$

$$K_2 = \frac{a_{S^{2-}} \quad a_{H^{1+}}}{a_{HS^{1-}}} \tag{3.15}$$

A sulfur mass balance can then be written as shown below where $[S_T]$ is the total concentration of all sulfur species.

$$[S_T] = [H_2S] + [HS^{1-}] + [S^{2-}] \tag{3.16}$$

The relation between the total sulfur concentration and the copper extraction may be derived from the net reaction stoichiometry.

$$Cu_2S = 2Cu^{1+} + S^{2-} \tag{3.17}$$

Consequently, the total sulfur concentration is given by the sum of the initial concentration, $[S_I]$, and one-half the molar copper concentrataion resulting from the leaching of the chalcocite.

$$[S_T]=[S_I] + \frac{1}{2} \frac{\text{Moles}_{\text{Cu}}}{\text{Vol}} \{\alpha\} \tag{3.18}$$

In solutions below a pH of about 11 a significant amount of cyanide ion hydrolizes to hydrogen cyanide as illustrated by equation 3.19.

$$CN^{1-} + H_2O = HCN + OH^{1-} \tag{3.19}$$

The dissociation of the hydrogen cyanide may be expressed as follows.

$$HCN \overset{K_A}{\rightleftharpoons} CN^{1-} + H^{+} \tag{3.20}$$

$$K_A = \frac{a_{CN^{1-}}\, a_{H^{1+}}}{a_{HCN}} \tag{3.21}$$

The cyanide mass balance can then be written as indicated below where $[CN_T]$ is the concentration of free cyanide that would result if all the cyanide were present in this form.

$$[CN_T]=[CN^{1-}] + [HCN] + 2[Cu(CN)_2^{1-}] + 3[Cu(CN)_3^{2-}] + 4[Cu(CN)_4^{3-}] \tag{3.22}$$

Because it is computationally simpler to deal with the hydroxyl ion concentration than the hydrogen ion concentration in the higher pH range, the dissociation of water must be considered.

$$H_2O \overset{K_w}{=} H^{1+} + OH^{1-} \tag{3.23}$$

$$K_w = \frac{a_{H^{1+}} \; a_{OH^{1-}}}{a_{H_2O}} \tag{3.24}$$

The mass balance for the hydroxyl ion is somewhat more difficult to write since the dissociation of water is involved. In solutions whose pH is 8 or greater, the hydrogen ion concentration is less than 10^{-8} M. This concentration is much less than that required to hydrolize the sulfide ion formed during the leaching of the chalcocite under the test conditions that were used. Consequently, one may assume that the concentration of hydrogen ion is negligible and the following mass balance can be written where the subscript $\underline{j}$ refers to some time at which the concentrations of all species are known and $\underline{j} + 1$ to the time at which the concentrations are to be calculated.

$$\left[OH^{1-}\right]_{j+1} - \left[OH^{1-}\right]_j = \left[HCN\right]_j - \left[HCN\right]_{j+1} + 2\left\{\left[H_2S\right]_j - \left[H_2S\right]_{j+1}\right\} + \left[HS^{1-}\right]_j - \left[HS^{1-}\right]_{j+1} \tag{3.25}$$

Early attempts to determine a rate expression indicated that the use of concentrations for activities would be insufficient. Therefore, a finite ionic radius form of the Debye-Hückel equation was used to calculate activity coefficients. For species $\underline{i}$, the natural logarithm of the activity coefficient, γ, is given by equation 3.26 where A and B are Debye-Hückel constants, z_i is the charge on the ion, a_i is the ionic radius, and μ is the ionic strength.

$$-\ln\gamma_i = \frac{Az_i^2\mu^{\frac{1}{2}}}{1 + Ba_i\,\mu^{\frac{1}{2}}} \qquad (3.26)$$

The mean ionic strength, μ, is given by the following equation when the solution density is essentially the same as the density of water. The c_i are the concentrations of the ionic species.

$$\mu = \tfrac{1}{2}\sum_i c_i z_i^2 \qquad (3.27)$$

Substituting the product of concentration and activity coefficient for the activities in equation 3.7 and rearranging leads to the following equation for the tetracyanide dissociation constant, $K_{4,3}$.

$$K_{4,3} = \frac{\left[Cu(CN)_3^{2-}\right]\left[CN^{1-}\right]}{\left[Cu(CN)_4^{3-}\right]} \cdot \frac{\gamma_{Cu(CN)_3^{2-}}\,\gamma_{CN^{1-}}}{\gamma_{Cu(CN)_4^{3-}}} \qquad (3.28)$$

Defining an activity coefficient ratio, $F_{4,3}$, leads to the following equation.

$$F_{4,3} = \frac{\gamma_{Cu(CN)_3^{2-}}\,\gamma_{CN^{1-}}}{\gamma_{Cu(CN)_4^{3-}}} \qquad (3.29)$$

Equation 3.30 then follows by substitution into equation 3.28.

$$K_{4,3} = \frac{\left[Cu(CN)_3^{2-}\right]\left[CN^{1-}\right]}{\left[Cu(CN)_4^{3-}\right]} \cdot F_{4,3} \tag{3.30}$$

Similarly, the dissociation constant for the tricyanide, $K_{3,2}$, can be written as follows.

$$K_{3,2} = \frac{\left[Cu(CN)_2^{1-}\right]\left[CN^{1-}\right]}{\left[Cu(CN)_3^{2-}\right]} \cdot F_{3,2} \tag{3.31}$$

Solving equation 3.24 which gives the dissociation of water for the hydrogen ion activity, assuming that the activity of water is 1, and defining an activity coefficient ratio similar to the preceeding equations gives the following equation for the hydrogen ion concentration.

$$\left[H^{1+}\right] = \frac{K_w}{F_w\left[OH^{1-}\right]} \tag{3.32}$$

Substituting this result into those equations involving the hydrogen ion concentration, 3.13, 3.15, and 3.21, and defining activity coefficient ratios analogously to the preceeding gives the following equations for the sulfide and cyanide equilibrium constants.

$$K_1 = \frac{K_w \left[HS^{1-}\right]}{\left[H_2S\right] \left[OH^{1-}\right]} \cdot F_1 \qquad (3.33)$$

$$K_2 = \frac{K_w \left[S^{2-}\right]}{\left[HS^{1-}\right] \left[OH^{1-}\right]} \cdot F_2 \qquad (3.34)$$

$$K_A = \frac{K_w \left[CN^{1-}\right]}{\left[HCN\right] \left[OH^{1-}\right]} \cdot F_A \qquad (3.35)$$

Substituting equation 3.26 for the pertinent species into the definitions of the activity coefficient ratios gives the equations presented in Table 4. Equation 3.27 for the mean ionic strength can be written as shown in equation 3.36 by neglecting those species such as hydrogen ion whose concentrations are always negligible under the conditions used.

$$\mu = \tfrac{1}{2}\Big\{ 9\left[Cu(CN)_4^{3-}\right] + 4\left[Cu(CN)_3^{2-}\right] + \left[Cu(CN)_2^{1-}\right] + \left[HS^{1-}\right] + 4\left[S^{2-}\right] + \left[OH^{1-}\right] + \left[Na^{+}\right] + \left[CN^{1-}\right] \Big\} \qquad (3.36)$$

In order to run tests at higher hydrogen ion concentrations than those resulting from the hydrolysis of the cyanide and sulfide ions, several tests were made using acetic acid to adjust the pH. Acetic

TABLE 4

THE ACTIVITY COEFFICIENT RATIOS

$$F_{4,3} = \mathrm{EXP}\left\{A\mu^{\frac{1}{2}}\left[\frac{9}{1 + B\mu^{\frac{1}{2}}a_{Cu(CN)_4^{3-}}} - \frac{4}{1 + B\mu^{\frac{1}{2}}a_{Cu(CN)_3^{2-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{Cu(CN)_2^{1-}}}\right]\right\}$$

$$F_{3,2} = \mathrm{EXP}\left\{A\mu^{\frac{1}{2}}\left[\frac{4}{1 + B\mu^{\frac{1}{2}}a_{Cu(CN)_3^{2-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{Cu(CN)_2^{1-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{CN^{1-}}}\right]\right\}$$

$$F_{1} = \mathrm{EXP}\left\{A\mu^{\frac{1}{2}}\left[\frac{1}{1 + B\mu^{\frac{1}{2}}a_{OH^{1-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{HS^{1-}}}\right]\right\}$$

$$F_{2} = \mathrm{EXP}\left\{A\mu^{\frac{1}{2}}\left[\frac{1}{1 + B\mu^{\frac{1}{2}}a_{HS^{1-}}} + \frac{1}{1 + B\mu^{\frac{1}{2}}a_{OH^{1-}}} - \frac{4}{1 + B\mu^{\frac{1}{2}}a_{S^{2-}}}\right]\right\}$$

$$F_{A} = \mathrm{EXP}\left\{A\mu^{\frac{1}{2}}\left[\frac{1}{1 + B\mu^{\frac{1}{2}}a_{OH^{1-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{CN^{1-}}}\right]\right\}$$

$$F_{w} = \mathrm{EXP}\left\{A\mu^{\frac{1}{2}}\left[\frac{1}{1 + B\mu^{\frac{1}{2}}a_{H^{1+}}} + \frac{1}{1 + B\mu^{\frac{1}{2}}a_{OH^{1-}}}\right]\right\}$$

acid was used since it is nonoxidizing and does not form strong complexes with copper. In a manner similar to the previous sections the following equations result.

$$K_{Ac} = \frac{K_w \left[Ac^{1-}\right]}{\left[HAc\right] \left[OH^{1-}\right]} \cdot F_{Ac} \tag{3.37}$$

$$\left[Ac_T\right] = \left[Ac^{1-}\right] + \left[HAc\right] \tag{3.38}$$

$$F_{Ac} = EXP\left\{ \mu^{\frac{1}{2}} \cdot \left(\frac{1}{1 + B\mu^{\frac{1}{2}} a_{OH^{1-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}} a_{A_c{}^{1-}}} \right) \right\} \tag{3.39}$$

In addition, $\left[Ac^{1-}\right]$ must be added to equation 3.36 for the ionic strength and $\left[HAc_j\right] - \left[HAc_{j+1}\right]$ to equation 3.25 for the hydroxyl ion mass balance.

The Thermodynamic Quantities

Many authors reported widely varying values for the dissociation constants of the cuprocyanide complexes. The values for $K_{4,3}$, $K_{3,2}$, and some reports for the related enthalpies are given in Table 5. The values given by Izatt et al. (1967) were used for this dissertation since they appeared to be the most consistent. In particular, the difficulty in measuring the absorption of $Cu(CN)_2^{1-}$ caused significant problems for the spectrophotometric studies such as Penneman and Jones (1956) and Baxendale and Westcott (1959). Izatt et al. (1967)

TABLE 5

THERMODYNAMIC QUANTITIES FOR THE CUPROCYANIDE COMPLEXES AT 25°C

Source	$K_{4,3}$	$\Delta H_{4,3}$[a]	$K_{3,2} \times 10^5$	$\Delta H_{3,2}$[a]
Willis and Woodcock (1950)	0.01		1 to 10	
Penneman and Jones (1956)[b]	0.020	12	2.6	20
Rothbaum (1957)	0.0005		2.5	
Simpson and Waind (1958)			7.9	
Baxendale and Westcott (1959)	0.018		0.45	
Brenner (1965)	0.0023		1.0	
Izatt et al. (1967)[b]	0.032	11.2	0.50	11.1

[a] Kilocalories per mole.

[b] Values corrected to $\mu = 0$. All others were not reported.

determined their constants calorimetrically and, in addition, had the advantage of the previous study of hydrocyanic acid described below.

The values reported for the dissociation of hydrogen cyanide also show considerable variation. Cotton and Wilkinson (1966, p. 312) report 2.1×10^{-9}, Penneman and Jones (1956) obtained two averages from the literature: 4×10^{-10} and 7×10^{-10}, Hodgman, Weast, and Selby (1961, p. 1757) list 4.93×10^{-10}, and Izatt et al. (1962) report 6.2×10^{-10}. Since the experimental values reported by Izatt et al. were obtained by numerous experiments over a range of temperatures and were corrected to an ionic strength of zero, they were used in this study. Table 6 gives the values of K_A at various temperatures. The equilibrium data for the other species were obtained from a variety of sources. Data compiled by Sillén and Martell (1964) on the sulfide system are given in Table 7, the dissociation of water from Ackerman (1958) in Table 8, and the dissociation of acetic acid from Harned and Ehlers (1933) in Table 9. As can be readily seen by examining the tabulated data, a considerable amount of additional work needs to be done just defining the required equilibrium constants. Such work, however, is beyond the scope of this dissertation. Consequently, the best estimates of the constants were taken from the available data with the realization that considerable scatter would be introduced into the rate constant calculations. It is unlikely, however,

TABLE 6

K_A AND ΔH FOR HCN FROM IZATT ET AL. (1962)

Temperature, °C	$K_A \times 10^{10}$	ΔH, kcal/mol
8		11.3
10	2.34	
15	3.25	
20	4.37	
25	6.17	10.4
30	7.76	
35	10.2	
40	13.2	
45	16.6	

TABLE 7

EQUILIBRIUM CONSTANTS FOR THE SULFIDE SYSTEM FROM SILLÉN AND MARTELL (1964)

Temperature, °C	$-\log K_1$	$\Delta H_{1,2}$[a]	$-\log K_2$	ΔH_2[a]
0	7.57			
10	7.26	-5.10	12.60	-14.40
20	6.87		12.94	
25	6.99	-4.42	12.89	-7.60
25	7.07		12.20	
25	7.06			
30	6.66		12.76	
35	6.99	-3.65	12.05	-5.15
40	6.81		12.24	
45	6.59		12.43	
50	6.82	-1.80	12.43	
50	6.91		11.91	
60			12.28	
80	6.54		10.68	
90	6.52		10.32	
120	6.59		9.27	

[a] Units are Kcal/mole.

TABLE 8

DISSOCIATION CONSTANT OF WATER FROM ACKERMAN (1958)

Temperature, °C	$-\log K_w$
0	14.955
10	14.534
20	14.161
25	13.999
30	13.833
40	13.533
50	13.263
60	13.015
70	12.800
80	12.598
90	12.422
100	12.259

TABLE 9

DISSOCIATION CONSTANT OF ACETIC ACID FROM HARNED AND EHLERS (1933)

Temperature, °C	$-\log K_{Ac}$
0	4.7807
5	4.7696
10	4.7622
15	4.7582
20	4.7562
25	4.7560
30	4.7570
35	4.7625
40	4.7688
45	4.7773
50	4.7870
55	4.7989
60	4.8119

that erroneous conclusions as to the reaction order would result from the variation in these data.

Temperature Dependence of the Constants

The general temperature dependence of the equilibrium constants is given by the following expression.

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{3.40}$$

When ΔH is constant this equation can be integrated to give equation 3.41 where C is the constant of integration.

$$\ln K = -\frac{\Delta H}{RT} + C \tag{3.41}$$

When both ΔH and K are known at a given temperature, C can be found by solving equation 3.41. The equilibrium constant as a function of temperature can then be written as follows.

$$K = \mathrm{EXP}\left\{ C - \frac{\Delta H}{RT} \right\} \tag{3.42}$$

Using the values given by Izatt et al. (1967) of 0.0316 for $K_{4,3}$ and 5.02×10^{-6} for $K_{3,2}$ at 25°C together with 11.2 and 11.1 kcal/mole for $\Delta H_{4,3}$ and $\Delta H_{3,2}$ respectively, the following expressions were calculated for the cuprocyanide equilibrium constants.

$$K_{4,3} = \text{EXP}\left\{ 15.5 - 5636\left(\frac{1}{T}\right) \right\} \qquad (3.43)$$

$$K_{3,2} = \text{EXP}\left\{ 6.54 - 5586\left(\frac{1}{T}\right) \right\} \qquad (3.44)$$

Since the equilibrium constants for the other equilibria were available at several temperatures and the reported ΔH values often showed considerable variation with temperature, regression analysis was used to fit a straight line to an equation of the following form.

$$-\log K = a + b\left(\frac{1}{T}\right) \qquad (3.45)$$

Least squares analysis of the data in Table 7 gave the expressions for the sulfide equilibria. The data from Table 6 were used to generate an expression for the dissociation of hydrogen cyanide while that for the dissociation of water was obtained from data reported in Table 8. Finally, the data in Table 9 indicated that the acetic acid constant could be reasonably represented by a mean value. Furthermore, all the tests made with acetic acid as a buffer were run at 25°C. Consequently, K_{Ac} was taken as 1.75×10^{-5}. The equations obtained by these procedures are given below.

$$K_1 = \text{EXP}\left\{ -10.1 - 1790\left(\frac{1}{T}\right) \right\} \qquad (3.46)$$

$$K_2 = \text{EXP}\left\{ -19.8 - 2717\left(\frac{1}{T}\right) \right\} \qquad (3.47)$$

$$K_A = \mathrm{EXP}\left\{-4.36 - 5031\left(\frac{1}{T}\right)\right\} \qquad (3.48)$$

$$K_w = \mathrm{EXP}\left\{-11.2 - 6288\left(\frac{1}{T}\right)\right\} \qquad (3.49)$$

The Debye-Hückel Constants

The constants for the finite ionic size form of the Debye-Hückel equation were obtained as follows. Bockris and Reddy (1970, pgs. 211-212) list the values of A and B presented in Table 10. Least squares analysis of these data gave the following equations for A and B as functions of temperature.

$$A = 0.3519 + 1.808 \times 10^{-6} \cdot T^2 \qquad (3.50)$$

$$B = (0.2578 + 2.40 \times 10^{-4} \cdot T) \times 10^8 \qquad (3.51)$$

The ionic radius a is difficult to define theoretically since it represents a distance of closest approach. Bockris and Reddy (1970, p. 226) state: "To circumvent the uncertainty in the quantitative definition of $\mathring{a}$, it is best to regard it as a parameter in Eq. (3.106), i.e., a quantity, the numerical value of which is left to be calibrated or adjusted on the basis of experiment." Izatt et al. (1962) used 4 Å for the cyanide ion, Izatt et al. (1967) used 4 Å for all species since they reported that it gave the least variation with the ionic strength, and Penneman and Jones (1956) used 3.7 Å for cyanide ion and 6.6 Å

TABLE 10

DEBYE-HÜCKEL CONSTANTS FROM BOCKRIS AND REDDY (1970)

Temperature, °C	A	$10^{-8}B$
0	0.4918	0.3248
10	0.4989	0.3264
20	0.5070	0.3282
25	0.5115	0.3291
30	0.5161	0.3301
35		0.3312
40	0.5262	0.3323
50	0.5373	0.3346
60	0.5494	0.3371
80	0.5767	0.3426
100	0.6086	0.3488

for the cuprocyanide complexes. The computations required to adjust the ionic radii were beyond the range of the present research and only a cursory attempt at adjusting them was made. Those values that seemed to agree best with the experimental results, especially the pH, are given in Table 11. This subject would obviously be worth considerably more attention in future work.

Discussion

On the basis of the equations presented in the preceding sections, the following general trends can be expected. As chalcocite leaches to produce cuprous ion and sulfide ion, cyanide will be rapidly consumed to produce the tetracyanide complex. As the reaction proceeds, the free cyanide ion concentration will eventually drop resulting in the stepwise formation of the tri- and dicyanide complexes. If sufficient chalcocite is leached, the formation of a cuprous cyanide precipitate could be expected. The free cyanide ion concentration will decrease rapidly as the molar ratio of cyanide to copper drops below 4:1 with a resultant decrease in the reaction rate. However, some free cyanide will be present and a high specific reaction rate could offset the very low cyanide ion concentrations. The sulfide ion formed during the leach will hydrolize to bisulfide ion with a resultant increase in pH as the reaction proceeds. The concentration of sulfide ion will be significant only in solutions of high pH while that of

TABLE 11

IONIC RADII USED IN THIS STUDY

Species	Ionic Radii, Å
CN^{1-}	4
$Cu(CN)_4^{3-}$	4
$Cu(CN)_3^{2-}$	5
$Cu(CN)_2^{1-}$	6
HS^{1-}	4
S^{2-}	20
OH^{1-}	20
H^{1+}	20
$C_2H_3O_2^{1-}$	20

hydrogen sulfide only in the nearly neutral solutions. At lower pH, a significant quantity of hydrogen cyanide will be present. As the chalcocite leaches, the formation of the cuprocyanide complexes will result in the dissociation of the hydrogen cyanide at a rate faster than that at which the sulfide ions formed will consume hydrogen ions. Consequently, there exists some pH above which the pH will increase during the leach and below which the pH will decrease during the leach. Since the cuprocyanide equilibrium constants decrease with increasing temperature and the free cyanide ion concentration is approximately proportional to the constants, the reaction rate will not increase as rapidly with temperature as one might otherwise expect.

The preceding sections have clearly demonstrated the need for better thermodynamic values if the system is to be clearly defined. For example, a spread of over 200 percent is observed in the values reported for $K_{4,3}$ in Table 5 even neglecting the two extreme results. When the concentration of $Cu(CN)_2^{1-}$ can be neglected, the free cyanide ion concentration is approximately proportional to $K_{4,3}$ and the rate expressions that depend on this concentration will be subject to considerable error. Many of the other constants are, if anything, subject to even greater error. While the expressions used for the activity coefficients were sufficient for this study, the use of other expressions might give better results. For the more concentrated solutions, further work in this area would be fruitful.

CHAPTER 4

EXPERIMENTAL EQUIPMENT AND PROCEDURES

The rapid leach rates encountered required the development of test equipment and procedures that differed significantly from those commonly used to study hydrometallurgical systems. Several approaches were tried before the approach described below was adopted.

Equipment

The leach study was carried out in a specially built three-liter reactor that was made from a seven-inch length of six-inch diameter acrylic plastic tubing. The top was secured to the reactor body with nylon bolts and wing nuts and sealed with a neoprene O-ring. A 1/70 horsepower motor was mounted on the reactor giving a direct drive to the stainless steel impeller through a doubly-sealed ball bearing. A Variac was used to control motor speed. Numerous ports through the top of the reactor allowed the mounting of a sampling probe and return line, thermometer, nitrogen inlet and exhaust lines, and a sample introduction funnel.

A sample stream was drawn continuously from the reactor through two filters by a variable-speed positive displacement pump. The first filter, which was located inside the reactor, was simply a

200 mesh nylon screen secured to the end of a 3/8 inch diameter glass tube with rubber bands. The second filter, in-line between the reactor and pump, consisted of a fine stainless steel screen supporting a glass-wool mat. These filters insured that a clean sample was delivered to the sample vials. The in-line filter was changed often during a test as it tended to plug with fine, unreacted material composed principally of hematite. Since the filters were made from quick-disconnect couplings, a new filter could be installed with about ten seconds downtime. The pump discharge passed through a three-way stopcock and then returned to the reactor. The samples were taken at the desired time by turning the stopcock to direct the stream into a vial. Normally, about one second was required to take a fifteen milliliter sample. During sampling the mean residence time of solution in the sampling system was about two seconds. A schematic diagram of the system is given in Figure 3.

Several items of additional equipment were utilized. A Corning Model 12 pH meter was used to measure the initial and final pH of the solutions and, during a few tests, to continuously monitor the pH of the solution. Various atomic absorption spectrophotometers (AAS) were used to measure the copper concentrations of the solutions after suitable dilution. These included Perkin-Elmer models 403 and 360 and a Varian Model 1250. The temperature was controlled by

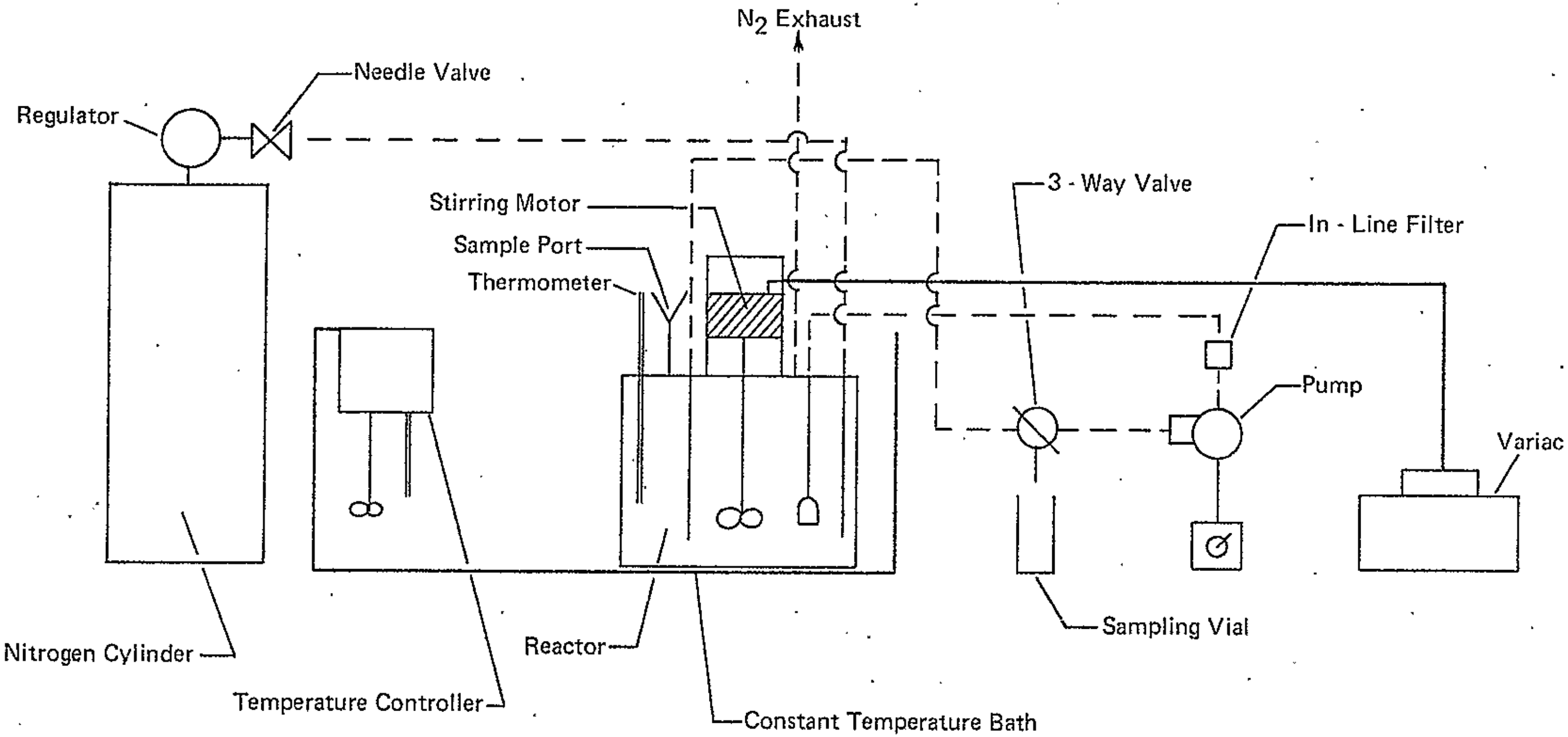

Figure 3. Schematic Diagram of the Cyanide Leaching System

partially submerging the reactor in a large bath. The bath temperature was controlled to a tenth of a degree Celcius by a combination heat-stirrer-controller. The reaction was sufficiently exothermic to cause a reactor temperature rise of one to two degress Celcius during a test.

Chemicals

All chemicals used in the test were Matheson, Coleman and Bell reagent grade. The sodium cyanide analyzed 98.5 percent NaCN by silver nitrate titration and the cuprous cyanide analyzed 100 percent CuCN by copper determination on an AAS. Sodium hydroxide and glacial acetic acid were used for pH adjustment. Additional sulfide was produced by adding sodium sulfide as required.

The Chalcocite Sample

The chalcocite used in this study was obtained from the New Cornelia Mine of the Phelps Dodge Corporation at Ajo, Arizona. The chalcocite occurred as a vein of high grade chalcocite between four and six inches thick. Approximately thirty pounds was obtained for this study. The chalcocite was broken into one-half inch pieces on a screw-type cleaving press, ground dry in a ceramic pebble mill, and screened to obtain various size fractions. The larger fractions whose use in the study was anticipated were upgraded on a high-tension separator to remove some of the nonconductor quartz impurities.

Since it was expected that the -35, +48 mesh fraction or one close to it would be used for most tests, a detailed chemical analysis was made on this fraction. All other fractions used in the study were analyzed for copper only. The detailed analysis of the -35, +48 mesh fraction is given in Table 12. The copper analyses of the other fractions are given in Table 13. The copper and iron analyses were run by AAS and the sulfur analyses by the standard barium sulfate precipitation. A microscopic examination of polished sections of the sample indicated that it was predominately chalcocite with some small quartz inclusions. A minor amount of very fine hematite was observed which accounted for the fine, reddish-brown residue formed during the leach tests. X-ray diffraction analysis was used to confirm the results of the microscopic examination of both the feed and residue. Table 14 gives a listing of the principal diffraction peaks of the sample along with their assignments.

Test Procedure

The required amount of sodium cyanide, cuprous cyanide, and sodium sulfide were dissolved in distilled water and diluted to 2.5 liters. The pH was adjusted to the desired initial level with either sodium hydroxide or acetic acid as required. The solution was transferred to the reactor which was then sealed and placed in the temperature bath. A stream of nitrogen was used to purge oxygen

TABLE 12

COMPOSITION OF THE -35, +48 FRACTION

Material	Percent	Number of Determinations
Cu	77.34	6
Fe	0.46	6
S	19.9	2
Insoluble	2.19	6
Cu_2S	96.85	[a]
Hematite	0.66	[a]
Insoluble	2.19	6
Total	99.70	

[a] Calculated from the Cu and Fe assays.

TABLE 13

COPPER CONTENT OF THE SIZE FRACTIONS

Tyler Mesh	Percent Copper	Number of Determinations
-28, +35	73.87	6
-35, +48	77.24	6
-48, +65	76.29	5
-65, +80	75.87	3
-80, +100	75.91	3
-100, +150	74.33	5
-150, +200	73.40	5

TABLE 14

MAJOR X-RAY DIFFRACTION LINES ARRANGED IN ORDER OF DECREASING INTENSITY

$2\theta_{Cu}$ Angle	Assignment
46.05	Chalcocite
48.58	Chalcocite
31.43	Chalcocite
37.59	Chalcocite
38.78	Quartz
36.40	Chalcocite
26.75	Quartz

from the system for approximately an hour while the solution reached temperature equilibrium with the bath.

The leach test was initiated by pouring twenty-five grams of chalcocite into the reactor through one of the ports. Sample introduction required about two seconds. The port was then resealed. About fifteen milliliters of sample was collected at several times during the test for copper analysis. Normally, ten samples were taken at intervals estimated to give reasonable differences in copper concentration. The leach times varied from ten minutes to several hours depending on initial cyanide concentration. The impeller speed was adjusted to keep all particles in suspension without introducing excess gas which would cause problems in sampling.

The temperature was noted at the beginning and end of the test on a thermometer immersed in the leach solution. Observation of the temperature during some tests indicated that in general it could be approximated by a linear function of time without introducing significant error. Consequently, its variation with time was not routinely noted. The final pH was noted in all tests, as was the pH variation during the test for one series.

The copper analyses were run by pipetting ten milliliters of each sample into a one hundred milliliter flask and diluting to volume. This solution was then diluted 5:500 to give an overall dilution of

1:1000. The final solution whose concentration ranged from 0.5 to 15 parts per million copper was analyzed by AAS.

In general the reproducibility between tests was good. A comparison of three replicates at an initial concentration of thirty grams per liter sodium cyanide is given in Table 15. Because of the short sampling intervals, these results show what should be the extreme variation. Consequently, later tests were not replicated more than twice and many were not replicated.

TABLE 15

REPRODUCIBILITY OF COPPER CONCENTRATIONS AMONG REPLICATE TESTS

	Measured Copper Concentration, gpl		
Time, min	1	2	3
0.5	0.73	1.03	0.93
1.0	1.39	1.71	1.57
1.5	1.96	2.33	2.10
2.0	2.49	2.90	2.66
3.0	3.33	3.45	3.46
4.0	4.14	4.44	4.11
5.0	4.74	4.98	4.63
6.0	5.15	5.39	5.02
8.0	5.74	6.08	5.47
10.0	6.22	6.66	5.95

CHAPTER 5

COMPUTATIONAL TECHNIQUES

The solution of the equations required for this study posed many serious problems. Numerous approaches were tried before a method that gave acceptable results was finally developed. Should the studies of later steps in the process indicate that the overall process has economic potential, additional work on the mathematical solution of the system would be justified. However, it is believed that the current system is adequate for the study at this preliminary level. The required calculations are described in the following sections. A more detailed derivation of the major equations is given in Appendix I.

The Calculation of the Ionic Concentrations

The system of simultaneous, nonlinear equations required to describe the ionic concentrations cannot be solved analytically. The wide range in values of the individual concentrations and constants together with changes of many orders of magnitude in concentration for some ions during a test led to serious difficulties in the numerical solution of the system. Direct solution by the Newton-Raphson or similar methods was prevented by the spread in values of the resultant matrices. The range in concentration during a test prevented the arrangement of the equations to give a system that was stable for iterative methods. After much trial and error a system was arrived at that converged in an acceptable length of time. The following approach makes no pretense of being the optimum method of solution. For ease of reference, the pertinent equations from Chapter 3 are listed in Table 16. A glossary of the symbols used is given in Table 17.

The general approach used was to solve first for those species whose concentrations changed most rapidly during the leach while assuming that all other concentrations could be adequately represented by their previous values. An initial set of concentrations was supplied to begin the iteration for the initial concentrations. The first step, then, was to solve for the concentrations of the copper complexes, free cyanide, and hydrogen cyanide. Next, these values were used to solve for the sulfur containing ions, hydroxide ion, free cyanide, and hydrogen cyanide. Finally, the activity coefficient ratios were recalculated. The entire process was then repeated until the change relative to the previous value for every species was less than the convergence criteria of 0.01 percent. The following sections describe these calculations in more detail.

TABLE 16

THE EQUATIONS THAT DESCRIBE THE CONCENTRATIONS

$$K_{4,3} = \frac{\left[Cu(CN)_3^{2-}\right]\left[CN^{1-}\right]}{\left[Cu(CN)_4^{3-}\right]} \cdot F_{4,3} \qquad (5.1)$$

$$K_{3,2} = \frac{\left[Cu(CN)_2^{1-}\right]\left[CN^{1-}\right]}{\left[Cu(CN)_3^{2-}\right]} \cdot F_{3,2} \qquad (5.2)$$

$$\left[Cu\right]_T = \left[Cu(CN)_4^{3-}\right] + \left[Cu(CN)_3^{2-}\right] + \left[Cu(CN)_2^{1-}\right] \qquad (5.3)$$

$$K_1 = \frac{K_w\left[HS^{1-}\right]}{\left[H_2S\right]\left[OH^{1-}\right]} \cdot F_1 \qquad (5.4)$$

$$K_2 = \frac{K_w\left[S^{2-}\right]}{\left[HS^{1-}\right]\left[OH^{1-}\right]} \cdot F_2 \qquad (5.5)$$

$$\left[S\right]_T = \left[H_2S\right] + \left[HS^{1-}\right] + \left[S^{2-}\right] \qquad (5.6)$$

Table 16, Continued. The Equations That Describe the Concentrations

$$K_A = \frac{K_w\left[CN^{1-}\right]}{\left[HCN\right]\left[OH^{1-}\right]} \cdot F_A \tag{5.7}$$

$$\left[CN\right]_T = \left[CN^{1-}\right] + \left[HCN\right] + 2\left[Cu(CN)_2^{1-}\right] + 3\left[Cu(CN)_3^{2-}\right] + 4\left[Cu(CN)_4^{3-}\right] \tag{5.8}$$

$$\begin{aligned}\left[OH^{1-}\right]_{j+1} - \left[OH^{1-}\right]_j = {} & \left[HCN\right]_j - \left[HCN\right]_{j+1} + \left[HS^{1-}\right]_j - \left[HS^{1-}\right]_{j+1} \\ & + 2\left[H_2S\right]_j - \left[H_2S\right]_{j+1} + \left[HAc\right]_j - \left[HAc\right]_{j+1} .\end{aligned} \tag{5.9}$$

$$F_{4,3} = EXP\left\{A\mu^{\frac{1}{2}}\left[\frac{9}{1 + B\mu^{\frac{1}{2}}a_{Cu(CN)_4^{3-}}} - \frac{4}{1 + B\mu^{\frac{1}{2}}a_{Cu(CN)_3^{2-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{CN^{1-}}}\right]\right\} \tag{5.10}$$

$$F_{3,2} = EXP\left\{A\mu^{\frac{1}{2}}\left[\frac{4}{1 + B\mu^{\frac{1}{2}}a_{Cu(CN)_3^{2-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{Cu(CN)_2^{1-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{CN^{1-}}}\right]\right\} \tag{5.11}$$

$$F_1 = EXP\left\{A\mu^{\frac{1}{2}}\left[\frac{1}{1 + B\mu^{\frac{1}{2}}a_{OH^{1-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{HS^{1-}}}\right]\right\} \tag{5.12}$$

Table 16, Continued. The Equations That Describe the Concentrations

$$F_2 = \mathrm{EXP}\left\{A\mu^{\frac{1}{2}}\left[\frac{1}{1 + B\mu^{\frac{1}{2}}a_{HS^{1-}}} + \frac{1}{1 + B\mu^{\frac{1}{2}}a_{OH^{1-}}} - \frac{4}{1 + B\mu^{\frac{1}{2}}a_{S^{2-}}}\right]\right\} \tag{5.13}$$

$$F_A = \mathrm{EXP}\left\{A\mu^{\frac{1}{2}}\left[\frac{1}{1 + B\mu^{\frac{1}{2}}a_{OH^{1-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}}a_{CN^{1-}}}\right]\right\} \tag{5.14}$$

$$F_w = \mathrm{EXP}\left\{-A\mu^{\frac{1}{2}}\left[\frac{1}{1 + B\mu^{\frac{1}{2}}a_{H^{1+}}} + \frac{1}{1 + B\mu^{\frac{1}{2}}a_{OH^{1-}}}\right]\right\} \tag{5.15}$$

$$\begin{aligned}\mu = \tfrac{1}{2}\ & 9\left[Cu(CN)_4^{3-}\right] + 4\left[Cu(CN)_3^{2-}\right] + \left[Cu(CN)_2^{1-}\right] + \left[HS^{1-}\right] \\ & + 4\left[S^{2-}\right] + \left[OH^{1-}\right] + \left[Na^{1+}\right] + \left[CN^{1-}\right] + \left[Ac^{1-}\right]\end{aligned} \tag{5.16}$$

$$K_{Ac} = \frac{K_w\left[Ac^{1-}\right]}{\left[HAc\right]\left[OH^{1-}\right]} \cdot F_{Ac} \tag{5.17}$$

Table 16, Continued. The Equations That Describe the Concentrations

$$[\mathrm{Ac}]_T = [\mathrm{Ac}^{1-}] + [\mathrm{HAc}] \qquad (5.18)$$

$$F_{Ac} = \mathrm{EXP}\left\{ A\mu^{\frac{1}{2}} \left[\frac{1}{1 + B\mu^{\frac{1}{2}} a_{OH^{1-}}} - \frac{1}{1 + B\mu^{\frac{1}{2}} a_{Ac^{1-}}} \right] \right\} \qquad (5.19)$$

TABLE 17

GLOSSARY OF SYMBOLS

$[C_i]$	Molar concentration of the ith species.
$[Cu]_T$	Total concentration of all copper species.
$[S]_T$	Total concentration of all sulfur species.
$[CN]_T$	Total concentration of all cyanide species referenced to free cyanide.
$[Ac]_T$	Total concentration of all acetate species.
$K_{4,3}$	Dissociation constant of the cuprotetracyanide ion.
$K_{3,2}$	Dissociation constant of the cuprotricyanide ion.
K_1	Dissociation constant of hydrogen sulfide.
K_2	Dissociation constant of the bisulfide ion.
K_A	Dissociation constant of hydrocyanic acid.
K_w	Dissociation constant of water.
K_{Ac}	Dissociation constant of acetic acid.
μ	Mean ionic strength of the solution.

Table 17, continued.

$F_{4,3}$	Activity coefficient ratio for the dissociation of the cuprotetracyanide ion.
$F_{3,2}$	Activity coefficient ratio for the dissociation of the cuprotricyanide ion.
F_1	Activity coefficient ratio for the dissociation of hydrogen sulfide.
F_2	Activity coefficient ratio for the dissociation of the bisulfide ion.
F_A	Activity coefficient ratio for the dissociation of hydrocyanic acid.
F_w	Activity coefficient ratio for the dissociation of water.
F_{Ac}	Activity coefficient ratio for the dissociation of acetic acid.
A	A constant for the Debye-Hückel equation.
B	A constant for the Debye-Hückel equation.
a_i	The ion size parameter for the <u>ith</u> species in the Debye-Hückel equation.
$[C_i]_{j+1}$	Molar concentration at the time for which the concentrations are being calculated.
$[C_i]_j$	Molar concentration at a previous, and hence known, time.

Solution of the Copper and Cyanide Systems

Equations 5.1, 5.2, 5.3, 5.7, and 5.8 may be solved analytically as described in Appendix I by assuming that all other variables are essentially constant. The following equations then result.

$$\left[Cu\right]_T - 4\left[Cu(CN)_4^{3-}\right] - 3\left[Cu(CN)_3^{2-}\right] - 2\,\frac{K_{3,2}F_{4,3}\left[Cu(CN)_3^{2-}\right]^2}{K_{4,3}F_{3,2}\left[Cu(CN)_4^{3-}\right]} - \frac{K_{4,3}\left[Cu(CN)_4^{3-}\right]}{F_{4,3}\left[Cu(CN)_3^{2-}\right]}\left\{1 + \frac{F_A K_w}{K_A\left[OH^{1-}\right]}\right\} = 0 \tag{5.20}$$

$$\left[Cu(CN)_3^{2-}\right] = \frac{-\left[Cu(CN)_4^{3-}\right] + \sqrt{\left[Cu(CN)_4^{3-}\right]^2 - 4\,\frac{K_{3,2}F_{4,3}}{K_{4,3}F_{3,2}}\left\{\left[Cu(CN)_4^{3-}\right]^2 - \left[Cu\right]_T\left[Cu(CN)_4^{3-}\right]\right\}}}{2\,\frac{K_{3,2}F_{4,3}}{F_{3,2}K_{4,3}}} \tag{5.21}$$

Substituting equation 5.21 for the tricyanide concentration and assuming that the activity coefficient ratios and hydroxide ion concentrations are known and constant allows one to treat equation 5.20 as a nonlinear equation in one unknown. The solution can then be approached in steps since the value of the function is positive for concentrations of the cuprotetracyanide ion less than the solution to the equation and negative for greater values. After using this technique to approach the solution, the final result to the desired relative degree of accuracy can be obtained by a regula-falsi method as outlined in Carnahan, Luther, and Wilkes (1969, p. 179). In general, the solution was considered satisfactory when successive values converged to 0.005 percent relative to the preceding value.

Using the value of the cuprotetracyanide ion concentration calculated from equation 5.20, the concentration of the cuprotricyanide ion can be calculated directly from equation 5.21. Note that the sign of the radical must be positive since the concentration of the cuprotetracyanide ion, the lead term in equation 5.21, is always positive. Using these two values and rearranging equation 5.1 gives the following equation for the concentration of the free cyanide ion.

$$\left[CN^{1-}\right] = \frac{K_{4,3}\left[Cu(CN)_4^{3-}\right]}{F_{4,3}\left[Cu(CN)_3^{2-}\right]} \qquad (5.22)$$

Similarly, a rearrangement of equation 5.7 gives equation 5.23 for the hydrogen cyanide concentration.

$$\left[HCN\right] = \frac{F_A K_w \left[CN^{1-}\right]}{K_A \left[OH^{1-}\right]} \qquad (5.23)$$

Finally, from equations 5.1 and 5.2 and the preceding values the cuprodicyanide concentration can be calculated.

$$\left[Cu(CN)_2^{1-}\right] = \frac{K_{3,2}F_{4,3} \quad \left[Cu(CN)_3^{2-}\right]}{K_{4,3}F_{3,2} \quad \left[Cu(CN)_4^{3-}\right]} \tag{5.24}$$

Since the copper concentrations experienced the greatest changes throughout the leach and proved most difficult to handle in preliminary attempts to solve the system, this subsystem was solved first.

The Sulfur, Hydroxide, Cyanide, and Hydrogen Cyanide Concentrations

Once an approximation for the copper complex concentrations has been made, the next most unstable subset of equations requiring solution is the sulfide equilibria and hydroxide ion concentration. As shown in Appendix I, equations 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 5.17, and 5.19 can be solved analytically by assuming that the activity coefficient ratios and the copper complex concentrations are known. Since the hydroxide ion concentration is strongly dependent upon all the acid species present, the hydrogen cyanide ion concentration was also recalculated. The following equation for the hydroxide ion concentration then results where the subscript _j_ refers to the previous sample point and _j + 1_ to the point being calculated.

$$\begin{aligned}
\left[OH^{1-}\right]_{j+1} = {} & \left[OH^{1-}\right]_j + \left[HCN\right]_j + \left[HS^{1-}\right]_j + 2\left[H_2S\right]_j + \left[HAc\right]_j \\
& - \frac{\left[S\right]_T \left\{ 1 + \dfrac{2K_wF_1}{K_1\left[OH^{1-}\right]_{j+1}} \right\}}{1 + \dfrac{K_wF_1}{K_1\left[OH^{1-}\right]_{j+1}} + \dfrac{K_2\left[OH^{1-}\right]_{j+1}}{K_wF_2}} \\
& - \frac{K_wF_A}{K_A\left[OH^{1-}\right]_{j+1}} \cdot \frac{\left[CN\right]_T - 4\left[Cu(CN)_4^{3-}\right] - 3\left[Cu(CN)_3^{2-}\right] - 2\left[Cu(CN)_2^{1-}\right]}{1 + \dfrac{K_wF_A}{K_A\left[OH^{1-}\right]_{j+1}}} \\
& - \frac{\dfrac{\left[Ac\right]_T K_wF_{Ac}}{K_{Ac}\left[OH^{1-}\right]_{j+1}}}{1 + \dfrac{K_w F_{Ac}}{K_{Ac}\left[OH^{1-}\right]_{j+1}}}
\end{aligned} \tag{5.25}$$

With the hydroxide ion concentration known, equations 5.17 and 5.19 can be solved to give the acetate ion concentration.

$$\left[Ac^{1-}\right] = \frac{\left[A_c\right]_T}{1 + \dfrac{K_w\, F_{Ac}}{K_{Ac}\left[OH^{1-}\right]}} \tag{5.26}$$

Then from equation 5.17 one can obtain the acetic acid concentration by rearrangement.

$$\left[HAc\right] = \frac{K_w F_{Ac}\left[Ac^{1-}\right]}{K_{Ac}\left[OH^{1-}\right]} \tag{5.27}$$

These calculations for the acetate containing species were made only for those tests where acetic acid was used for pH adjustment. Solving equations 5.7 and 5.8 then gives the following equation for the free cyanide ion concentration.

$$\left[CN^{1-}\right] = \frac{\left[CN\right]_T - 4\left[Cu(CN)_4^{3-}\right] - 3\left[Cu(CN)_3^{2-}\right] - 2\left[Cu(CN)_2^{1-}\right]}{1 + \dfrac{K_w F_A}{K_A\left[OH^{1-}\right]}} \tag{5.28}$$

Substituting this result for the free cyanide concentration and rearranging equation 5.7 gives the hydrogen cyanide concentration.

$$\left[HCN\right] = \frac{K_w F_A \left[CN^{1-}\right]}{K_A \left[OH^{1-}\right]} \tag{5.29}$$

Solving equations 5.4, 5.5, and 5.6 gives the bisulfide ion concentration.

$$\left[HS^{1-}\right] = \frac{\left[S\right]_T}{1 + \dfrac{K_w F_1}{K_1 \left[OH^{1-}\right]} + \dfrac{K_2 \left[OH^{1-}\right]}{K_w F_2}} \tag{5.30}$$

The substitution of this result into equations 5.4 and 5.5 and rearranging gives the sulfide ion and hydrogen sulfide ion concentrations.

$$\left[S^{2-}\right] = \frac{K_2 \left[OH^{1-}\right] \left[HS^{1-}\right]}{K_w F_2} \tag{5.31}$$

$$\left[H_2S\right] = \frac{K_w F_1 \left[HS^{1-}\right]}{K_1 \left[OH^{1-}\right]} \tag{5.32}$$

The Activity Coefficient Ratios and Mean Ionic Strength

Equations 5.10 through 5.16 and 5.19 can be ordered to give a system of nonlinear equations whose coefficient matrix of partial derivatives for Newton-Raphson solution is diagonally dominant. Consequently, the augmented matrix can be solved by the Gauss-Seidel method and the Newton-Raphson iteration converges rapidly. Choosing identical ionic radii for several species would allow considerable simplification of this subsection. However, the major computer time requirements were in the other subsections and the generality allows this subsection to be used for future optimization of the ionic radii parameters.

After modification of the test equipment to continuously monitor pH, a series of tests was made in which the pH at each point was known. The hydroxide ion concentration could then be calculated by equation 5.33.

$$\left[OH^-\right] = \frac{K_w}{10^{-pH} F_w} \qquad (5.33)$$

This result was then used in place of the solution to equation 5.25 for all other calculations.

Thus, the solution of the equations that describe the concentrations is complete. The normal execution time for runs on the IBM 360 Model 44 computer was about twenty seconds.

Curve Fitting for Copper Concentration Versus Time

In order to obtain estimates of the reaction rate at various times during the leach it was necessary to find a model to express the concentration of copper as a function of time. This equation could then be differentiated to give estimates of the reaction rate. The general relationship can be represented by equation 5.34.

$$\left[\mathrm{Cu}\right]_T = F\ (t) \tag{5.34}$$

In a batch system the following rate equation applies.

$$R = \frac{d\left[\mathrm{Cu}\right]_T}{dt} = \frac{d}{dt} F\ (t) \tag{5.35}$$

A typical curve from experimental data is shown in Figure 4. The shape suggests an exponential curve with the boundary conditions that F(0) equal the initial copper concentration and F(t) approach a constant equal to the sum of the initial concentration and extractable copper with increasing time. An equation of the following form was proposed.

$$\left[\mathrm{Cu}\right]_T = ae^{F(\frac{1}{t})} \tag{5.36}$$

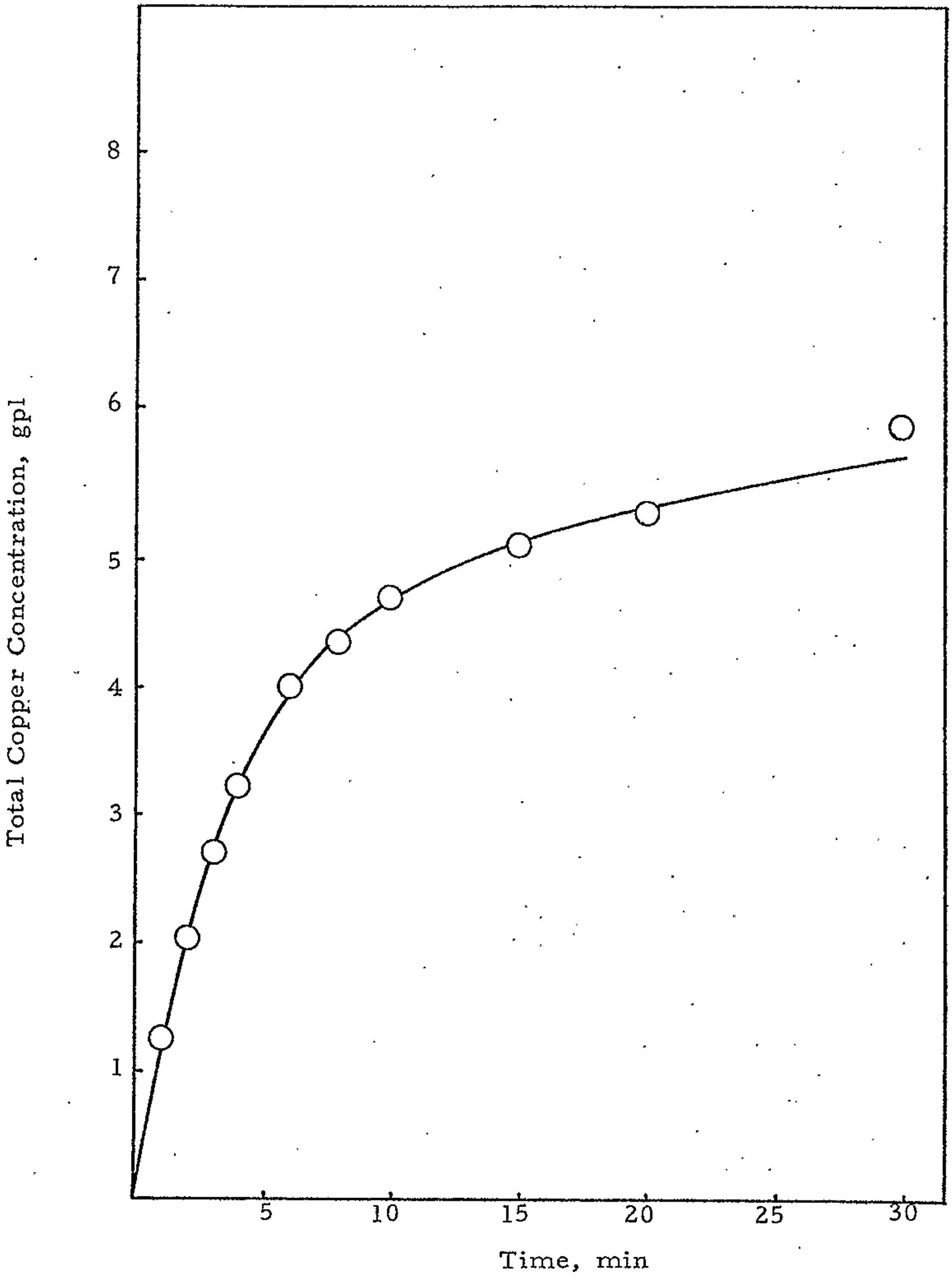

Figure 4. A Typical Graph of Total Copper Concentration Versus Time

If $F(\frac{1}{t})$ is negative, then the copper concentration approaches a with increasing time and 0 at time zero. Several forms of $F(\frac{1}{t})$ were tried before the following equation was adopted.

$$[Cu]_T = ae^{\left\{\frac{b_1}{t^{\frac{1}{2}}} + \frac{b_2}{t} + \frac{b_3}{t^2}\right\}} \tag{5.37}$$

Taking the natural logarithm of both sides gives equation 5.38 which is linear in the coefficients.

$$\ln [Cu]_T = \ln a + \frac{b_1}{t^{\frac{1}{2}}} + \frac{b_2}{t} + \frac{b_3}{t^2} \tag{5.38}$$

A multiple regression program was used to evaluate the constants and their t-values. The coefficients were determined by calculating the corrected sums of squares and cross products to form a matrix which was then inverted by Gauss-Jordan reduction. The methods are outlined by Carnahan, Luther, and Wilkes (1969). The intermediate results allowed the calculation of the t-values as outlined by Wine (1964, pp. 516-526). Any variable not meeting the 90 percent confidence level, which was approximately 1.44, was rejected. The other coefficients were then recalculated. Table 18 shows typical comparisons of the calculated and measured concentrations.

TABLE 18

TYPICAL EXPERIMENTAL AND CALCULATED COPPER CONCENTRATIONS IN GPL

Test No. 6			Test No. 23			Test No. 13		
Time, min	Measured gpl	Calculated gpl	Time, min	Measured gpl	Calculated gpl	Time, min	Measured gpl	Calculated gpl
½	0.73	0.73	1	1.22	1.22	1	.43	.43
1	1.39	1.36	2	2.10	2.07	6.	1.50	1.49
1	1.96	1.99	3	2.71	2.76	10	2.07	2.10
2	2.49	2.53	4	3.22	3.27	15	2.47	2.45
3	3.33	3.40	6	4.01	3.94	20	2.61	2.65
4	4.14	4.08	8	4.36	4.37	30	2.91	2.86
5	4.74	4.62	10	4.69	4.67	46	3.04	3.01
6	5.15	5.07	15	5.16	5.12	60	3.06	3.06
8	5.74	5.78	20	5.38	5.39	90	3.12	3.12
10	6.22	6.33	30	5.65	5.69	120	3.12	3.15

Calculating the Reaction Rates

Differentiating equation 5.37 leads to the equation for the reaction rate.

$$R = \frac{d\left[Cu\right]_T}{dt} = \frac{a}{63.54}\left\{\frac{b_1}{2t^{\frac{3}{2}}} + \frac{b_2}{t^2} + \frac{2b_3}{t^3}\right\} e^{\left\{\frac{b_1}{t^{\frac{1}{2}}} + \frac{b_2}{t} + \frac{b_3}{t^2}\right\}} \qquad (5.39)$$

The atomic weight of copper, 63.54, corrects the rate to moles per liter per minute. As can be noted in Table 19, a listing of typical regression coefficients, many of the calculated coefficients were positive. Consequently, the calculated curve approaches infinity as the time goes to zero and some initial rates had to be rejected. The approach used was to reject all negative reaction rates and any rate that was not at least 10 percent greater than the following rate. Examples of typical rate calculations and the points that were rejected are given in Table 20.

A major problem introduced into the later calculations of the rate constant by using derivatives of a fitted curve to calculate the reaction rate was the serial correlation of the differences between the measured curve and the fitted curve. That is, the fitted curve generally fell above the measured curve at the ends and below it at the middle. Consequently, there was a distinct tendency for the initial

TABLE 19

TYPICAL REGRESSION CONSTANTS USED FOR RATE CALCULATIONS

Test Number	a	b_1	b_2	b_3
1	2.16	-0.55	-2.95	1.57
6	2.61	-2.43	0	0.13
9	1.80	-2.27	0	0
16	1.65	-0.60	-1.04	0.28
18	2.53	-1.90	-0.49	0
19	1.63	0	-1.43	0.28
24	1.90	-0.62	-1.77	0.72
26	2.06	-1.65	0	0.42
34	1.90	0	-2.59	0.92

The constants were rounded for this table only.

TABLE 20

TYPICAL CALCULATED REACTION RATES IN MOLES PER LITER PER MINUTE

Test No. 6		Test No. 23		Test No. 13	
Time, min.	$Rx10^2$[b]	Time, min.	$Rx10^2$[b]	Time, min.	$Rx10^2$[b]
½	1.61[a]	1	1.10[a]	1	-1.11[a]
1	2.06	2	1.26	5.75	.31
1½	1.82	3	.93	10	.16
2	1.58	4	.69	15	.081
3	1.20	6	.41	20	.048
4	.95	8	.28	30	.022
5	.77	10	.20	46	.009
6	.65	15	.11	60	.005
8	.48	20	.07	90	.002
10	.38	30	.03	120	.001

The results were rounded for this table only.

[a] These points were deleted from the rate constant analysis.

[b] Units are moles copper per liter per minute.

calculated rates to be too low while later ones were too high. Thus the calculated rate constants tended to increase with time. It is probable that the problems in calculating the individual rates is a major source of error in the calculation of the rate constants.

Surface Area

The surface area of the particles was calculated by assuming that the particles were perfect spheres that reacted at a uniform rate. The geometric mean of the upper and lower screen opening was used as the average starting diameter for each mesh size. These values are listed in Table 21.

The weight of the chalcocite can be calculated by the following equation.

$$\mathrm{Wt}_{\mathrm{Cu_2S}} = \mathrm{Wt}_{\mathrm{sample}} \cdot \frac{\%\ \mathrm{Cu}}{100} \cdot \frac{\mathrm{Mol.\ Wt.}_{\mathrm{Cu_2S}}}{2\ \mathrm{At.\ Wt.}_{\mathrm{Cu}}} \qquad (5.40)$$

Assuming that the chalcocite is completely liberated from gangue material, the number of initial particles is given by equation 5.41.

$$N = \frac{\mathrm{Wt}_{\mathrm{Cu_2S}}}{\rho_{\mathrm{Cu_2S}}} \bigg/ \frac{d_o^{\,3}}{6} = \frac{6\,\mathrm{Wt}_{\mathrm{Cu_2S}}}{d_o^{\,3}\rho_{\mathrm{Cu_2S}}} \qquad (5.41)$$

TABLE 21

GEOMETRIC MEAN DIAMETERS FOR THE SIZE FRACTIONS

Size Fraction, Tyler Mesh	Mean Diameter, cm
-28, +35	0.0500
-35, +48	0.0353
-48, +65	0.0250
-65, +80	0.0193
-80, +100	0.0163
-100, +150	0.0125
-150, +200	0.00881

Using 5.6 g/cm^3 as the density of chalcocite and combining all other constants gives the number of particles in the sample.

$$N = \frac{0.341\ Wt_{Cu_2S}}{d_o^{\ 3}} \qquad (5.42)$$

With the total number of particles known, the diameter at any later time is given by equation 5.43 where $(1-\alpha)$ is the fraction of unreacted chalcocite.

$$d = \left\{\frac{0.341\ Wt_{Cu_2S}\ (1-\alpha)}{N}\right\}^{\frac{1}{3}} \qquad (5.43)$$

The surface area then, after simplification, is given by the following equation. The roughness factor is assumed to be one.

$$A = 1.53N^{\frac{1}{3}}\left\{Wt_{Cu_2S}\ (1-\alpha)\right\}^{\frac{2}{3}} \qquad (5.44)$$

Copper Extraction

The copper extraction can be calculated by multiplying the difference between the initial and measured weight concentrations by the volume of solution to obtain the weight of copper extracted. Because a significant volume is taken for samples, the total weight of copper so lost must be accounted for. The extraction of the ith sample is thus given by equation 5.45.

$$\alpha = \frac{(\text{Vol.})_i \left\{(\text{Cu})_i - (\text{Cu})\right\} + \sum_{j=1}^{i-1} \frac{\left\{(\text{Cu})_j - (\text{Cu})_1\right\}\left(\text{Vol.}_{\text{sample}}\right)_j}{(\text{Vol.})_j}}{\text{Wt}_{\text{Cu}_2\text{S}}\,(\%\ \text{Cu})\,/100} \tag{5.45}$$

Summary

The general methods used to calculate the rates, concentrations, and areas have been outlined. Serious problems arise from differentiating a fitted curve, using poorly established equilibrium constants, and using a model for activity coefficients that is known to exhibit error at the concentrations involved. As will be shown in Chapter 6, however, these computational techniques do give a reasonable approximation to the system which allows the determination of the practical relationships. In view of the difficulty of applying this method to the much more complex and poorly defined flotation concentrates that would be encountered in actual practice, it is believed that this treatment is adequate for its purposes.

CHAPTER 6

THE EMPIRICAL RATE EQUATION

The methods given in Chapter 5 for solving the equations that describe the system were used to calculate the rates, areas, and ionic concentrations for all the experiments. Typical results of the area calculations are given in Table 22. The range of values for the surface areas used to evaluate the rate constant was 76 to 2460 square centimeters. Likewise, typical results for the concentrations are given in Appendix II. One can especially note from these tables that pH rather than the added sodium sulfide is the dominant factor in determining the sulfide ion concentration.

Cyanide Dependence

By assuming that only the surface area and free cyanide ion concentration have a significant effect on the reaction rate, and that the area dependence is first order, a rate equation of the following form may be postulated.

$$R = KA\left[CN^{1-}\right]^{n} \qquad (6.1)$$

Dividing by the area and taking the natural logarithm of both sides of this equation gives the following linear equation.

TABLE 22

TYPICAL CALCULATED AREAS IN SQUARE CENTIMETERS FOR AN INITIAL SAMPLE WEIGHT OF 25 GRAMS

Test No. 2[a]		Test No. 42[b]		Test No. 20[c]	
Percent Copper Extraction	Area, cm^2	Percent Copper Extraction	Area, cm^2	Percent Copper Extraction	Area, cm^2
0	496	0	1025	0	1993
10	461	18	894	13	1823
19	430	32	793	26	1626
26	405	41	720	39	1430
32	383	48	663	47	1301
42	347	50	624	52	1227
48	322	56	589	58	1126
52	303	61	547	61	1061
60	276	64	514	62	1054
65	248	71	450	63	1021
70	223	71	450	69	955

[a] Size Fraction, Tyler Mesh: -28, +35

[b] Size Fraction, Tyler Mesh: -48, +65

[c] Size Fraction, Tyler Mesh: -100, +150

$$\ln\left(\frac{R}{A}\right) = \ln K + n \ln \left[CN^{1-}\right] \tag{6.2}$$

Thus, one would expect that a plot of $\ln\left(\frac{R}{A}\right)$ versus $\ln\left[CN^{1-}\right]$ would give a straight line of slope n and intercept ln K. Figure 5 shows such a plot made from a few data points representing the experimental range of free cyanide ion concentrations. The points used in this figure are listed in Table 23. A least squares fit was made from the calculated concentrations, rates, and areas from all tests made at 25°C except those points eliminated as explained under the rate calculation section in Chapter 5. The result was a slope of 0.92. Since this slope agreed well with a slope of one that could be expected, the free cyanide ion dependence was taken to be first order.

Sulfide Ion Dependence

After developing an estimate of the free cyanide ion dependence as outlined above, the sulfide ion dependence can be ascertained as follows. The empirical rate equation is postulated as equation 6.3 where it is assumed that the effect of the other variables is negligible.

$$R = KA\left[CN^{1-}\right]\left[S^{2-}\right]^{n} \tag{6.3}$$

Dividing by the area and free cyanide concentration and taking the natural logarithm of both sides gives the next equation.

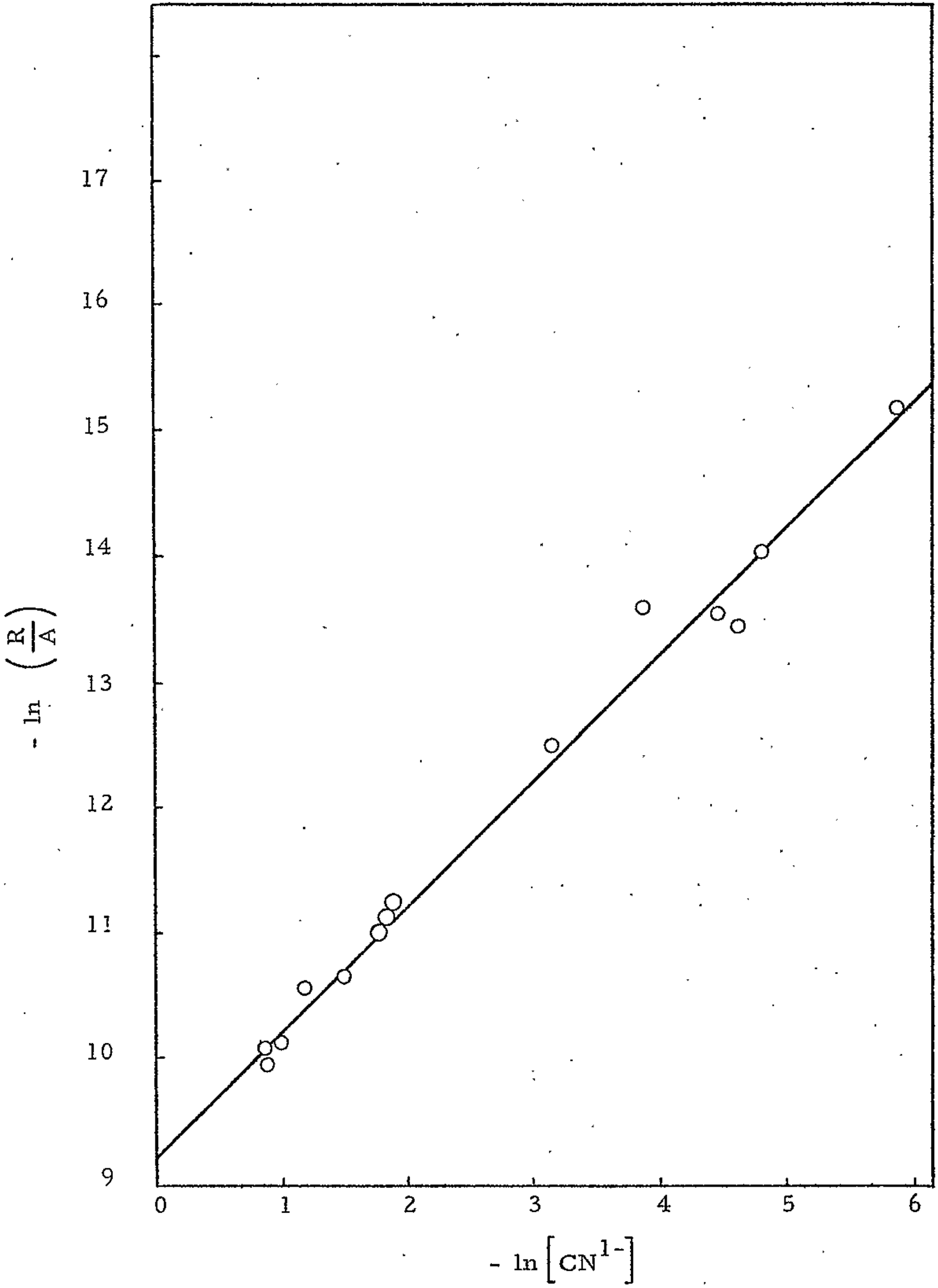

Figure 5. Reaction Order for Free Cyanide Ion Dependence

TABLE 23

POINTS USED TO PREPARE FIGURE 5

Test Number	Point Number	$\left[CN^{1-}\right]$ mol/l	Area cm^2	Rate x 10^3 mol/min	$-\ln\left(\frac{R}{A}\right)$	$-\ln\left[CN^{1-}\right]$
2	5	0.1708	383	6.47	10.99	1.77
2	9	0.0420	270	1.01	12.50	3.17
4	9	0.0207	318	.401	13.59	3.88
6	3	0.4131	431	20.6	9.95	0.88
6	8	0.3036	257	6.50	10.59	1.19
6	10	0.2134	162	3.80	10.67	1.54
8	5	0.3673	370	14.7	10.14	1.00
9	10	0.0098	299	.436	13.44	4.63
11	3	0.3983	437	17.9	10.11	0.92
11	10	0.1500	221	3.02	11.21	1.90
13	6	0.0111	372	.44	13.56	4.50
13	8	0.0028	351	.089	15.19	5.87
16	3	0.1516	1159	16.5	11.16	1.85
16	10	0.0079	794	.636	14.04	4.84

$$\ln \frac{R}{A\left[CN^{1-}\right]} = \ln K + n \ln\left[S^{2-}\right] \qquad (6.4)$$

A least squares regression analysis of all the experimental points at 25°C gave a slope of -0.088 that was significantly different from zero at the 99.95 percent confidence level on the t-test. The 80 percent confidence interval was ±0.012 and the 90 percent interval ±0.018. Regression analyses of the calculated concentrations from tests 10, 11, 56, 57, 58 and 59, which represent a range of pH and hence a large variation in sulfide ion concentration, and on data from tests 23, 24, 41, 56, 57, 58 and 59, which include those tests with sodium sulfide added, were made to determine the effect of sulfide ion concentration on the reaction rate without the regression being dominated by the large number of tests that were made at a high pH. The resulting slopes were -0.073 and -0.039 respectively. These slopes were likewise significantly different from zero at the 99.95 percent confidence level. A multiple linear regression analysis using the following equation was then made on all experimental values, except as previously noted.

$$\ln\left(\frac{R}{A}\right)=\ln K + n \ln\left[CN^{1-}\right] + m \ln\left[S^{2-}\right] \qquad (6.5)$$

The resulting values for $\underline{n}$ and $\underline{m}$ were 0.90 and -0.10 respectively.

The 80 percent confidence interval for the sulfide ion concentration coefficient was ±0.011. In view of these results and the general scatter in the data, the order for the sulfide ion concentration dependence was taken as -0.10.

The Rate Constant

Equation 6.6 was used to calculate the rate constant at each experimental point not eliminated as previously described. Typical results are shown in Table 24. The conditions used for each test are listed in Appendix III.

$$K = \frac{R\left[S^{2-}\right]^{0.1}}{A\left[CN^{1-}\right]} \qquad (6.6)$$

The tests were grouped to make comparisons of the mean rate constants at different levels of the operating variables. No significant trends were found, although the large standard deviations associated with some groups might conceal a minor trend. The rate constants are expressed in units of (mol. Cu^{1+}/ min.) (mol. $S^{2-})^{0.1}$ / mol. CN^{1-}/ cm^2/ l.

TABLE 24

TYPICAL RATE CONSTANTS[a] X 10^5 SHOWING THE VARIATION THROUGHOUT A TEST

Point Number	Test No. 2	Test No. 7	Test No. 12
1	b	6.4	b
2	5.7	7.6	5.4
3	6.0	7.5	6.1
4	6.1	7.4	5.4
5	6.4	6.4	5.6
6	6.6	6.9	5.6
7	7.1	7.8	4.7
8	8.7	7.8	4.2
9	11.8	9.3	1.9
10	7.7	12.3	1.5
Mean:	8.5	7.9	4.4

[a] Units are (mol. Cu^{1+}/min.)(mol. $S^{2-})^{0.1}$/mol. CN^{1-}/cm^2/l.

[b] These rates dropped for reasons explained in the text.

Initial Cyanide Addition

Table 25 lists the mean rate constants from those tests where the only change in initial conditions was the amount of sodium cyanide added. On the tests using an initial concentration of 0.16 M, the last two points were dropped because the slight change in measured copper concentrations made the concentration calculations doubtful. The points used in calculating this table represent a range in cyanide concentration of 0.0004 to 0.5 M. Given the standard deviations of these results there is no significant trend with initial cyanide addition. Since a model using first order free cyanide ion dependence was used to calculate these constants, the lack of any trends with initial sodium cyanide concentration supports the first order model.

Sodium Sulfide Addition

Four tests were made with the -35, +48 mesh fraction with only the amount of initial sodium sulfide added as a variable. The mean rate constants for these tests are given in Table 26. These rate constants are somewhat higher than those without the initial sulfide addition. However, considering the large deviations involved and the negligible differences in the reported extractions, the increase is not seen as significant.

TABLE 25

RATE CONSTANTS IN RELATION TO INITIAL SODIUM CYANIDE CONCENTRATION

Initial NaCN Concentration mol/l	Rate Constant[a] x 10^5			
	1[b]	2[b]	3[b]	Average
0.61	6.8	7.9	6.0	6.9
0.41	6.7	6.1		6.4
0.33	8.4	6.6	8.3	7.8
0.24	6.1	6.2		6.1
0.16	5.1	6.6		5.9

Overall Mean: 6.7

Standard Deviation: 1.0

[a] Units are (mol. Cu^{1+}/min.)(mol. $S^{2-})^{0.1}$/mol. CN^{1-}/cm^2/l.

[b] The column headings indicate the replicate number at each concentration, not the test number.

TABLE 26

RATE CONSTANTS IN RELATION TO INITIAL SODIUM SULFIDE ADDITION

Initial Sodium Sulfide Concentration mol/l	Rate Constant[a] x 10^5	Percent Copper Extraction
0	8.0	70
0.05	11.0	71
0.10	11.6	71
0.50	10.3	68

[a] Units are (mol. Cu^{1+}/min.)(mol. $S^{2-})^{0.1}$/mol. CN^{1-}/cm^2/l.

Initial Conditions: Sodium Cyanide Concentration, 0.33M

Size Fraction, Tyler Mesh, -35, +48

Temperature, 25°C

Initial Size Effects

Several different initial particle sizes were leached in this study. To keep the rates within a range that could be measured in the system, most tests were run with the -28, +35 mesh fraction. Table 27 lists mean reaction rate constants by initial size. Only those tests with initial sodium cyanide concentrations similar to the concentrations used for the other size fractions were chosen from the mass of the data on the -28, +35 mesh fraction. The extractions during these tests ranged from 50 to 70 percent. The rate constants for the larger fractions through -65, +80 mesh are fairly constant. Those for the last three are significantly higher. This increase in the rate constant may be due to sampling problems arising from the small particle size. Since the size range from -28, +35 mesh to -65, +80 mesh represents a change of a factor of about three in the initial area, the calculations used are consistent over a reasonable range. This consistency in the calculated rate constants gives additional support to the first order dependence on area that was used in the model. A better approximation, perhaps even an empirical fit, might be useful for modeling an actual process.

Initial Copper Additions

The results of several tests with cuprous cyanide added to the initial solution are presented in Table 28. The results of these tests

TABLE 27

RELATION OF THE RATE CONSTANT TO THE INITIAL PARTICLE SIZE

Size Fraction, Tyler Mesh	Rate Constant[a] x 10^5	Number of Determinations	$\left[CN^{1-}\right]_T$ mol/l
-28, +35	7.8	21	b
-28, +35	7.8	3	0.33
-35, +48	6.7	3	0.24
-48, +65	8.1	2	0.33
-65, +80	6.3	1	0.24
-80, +100	14.3	1	0.24
-100, +150	21.1	1	0.24
-150, +200	8.3	1	0.20

[a] Units are (mol. Cu^{1+}/min.)(mol. $S^{2-})^{0.1}$/mol. CN^{1-}/cm^2/l.

[b] This rate constant is the average of tests made at several different concentrations.

TABLE 28

RELATION OF THE RATE CONSTANT TO INITIAL CUPROUS CYANIDE ADDITION

Initial Copper Concentration mol/l	Sodium Cyanide Initially Added mol/l	Rate Constant[a] x 10^5
0.022	0.31	7.3
0.045	0.41	6.5[b]
0.067	0.45	9.9
0.112	0.57	8.7

Overall Mean: 8.1

Standard Deviation: 1.5

[a] Units are (mol. Cu^{1+}/min.)(mol. $S^{2-})^{0.1}$/mol. CN^{1-}/cm^2/l.

[b] Size Fraction, Tyler Mesh: -35, +48. All others were -28, +35 mesh.

are quite scattered, perhaps as a result of the increasing significance of the dissociation of the cuprotricyanide ion for which the dissociation constant, $K_{3,2}$, showed considerable variation in the literature. There is no indication that there is a change in the rate constant as a result of increased initial copper concentration.

Agitation

A series of tests was run to insure that the agitation was sufficiently high to remove it as a variable during the tests. Table 29 lists the extractions at various impeller speeds and Figure 6 shows a graph of extraction versus impeller speed. As can be seen from Figure 6, the extraction curve begins to level at about 900 rpm. Consequently, most tests were run at about 1000 rpm to eliminate bulk diffusion as a variable without having the impeller induce an excessive amount of gas into the system. All these tests were made with the coarsest size fraction used: -28, +35 mesh.

pH Effects

The changes resulting from variation in pH were the most difficult to measure since the concentration calculations did not fit tests well that had large changes in pH. However, the marked changes in sulfide ion concentrations which result from pH changes were in general agreement for these tests compared to the overall sulfide

TABLE 29

EFFECT OF IMPELLER SPEED ON PERCENT COPPER EXTRACTION

	Copper Extraction, Percent				
	Impeller Speed, rpm				
Time, min	600	700	900[a]	1100	1600
1	3.7	4.2	8.3	10.1	10.7
2	7.3	11.3	15.9	18.9	19.4
3	10.4	16.5	21.8	25.5	27.5
4	13.5	21.0	28.8	31.2	33.8
6	19.6	28.4	37.2	39.7	42.9
8	24.6	33.6	43.4	45.9	49.0
10	28.5	39.1	48.0	50.0	53.6
15	36.8	48.4	56.4	57.2	60.4
20	43.6	54.8	61.6	62.0	64.4
30	52.7	61.7	66.0	66.6	69.0

[a] Average of two tests. All other columns are the result of a single test.

Test Conditions: Initial Sodium Cyanide Concentration, 16 gpl
Size Fraction, Tyler Mesh, -28, +35
Temperature, 25°C

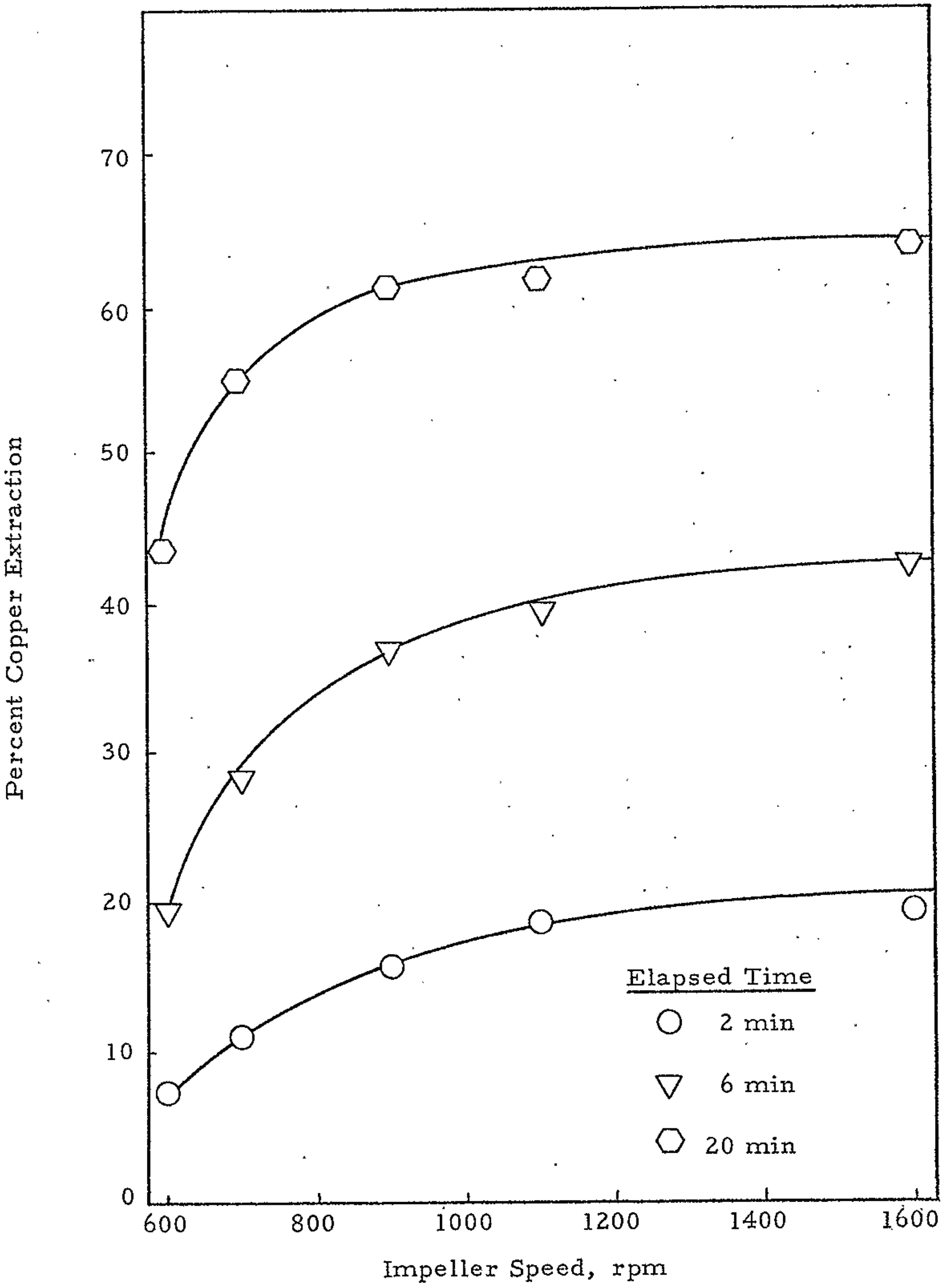

Figure 6. Effect of Agitation on Percent Copper Extraction

dependence. The most significant result was the demonstration that a critical pH exists above which the solution becomes more basic as a result of the leach reaction and below which it becomes more acidic. Table 30 lists the measured pH changes and the calculated pH changes for these tests. On one test the measured pH did not change, consequently, the program used to calculate the concentrations was modified to use this pH. When the equipment became available, a series of tests was run with a pH probe immersed in the reactor to continuously monitor pH. A comparison of the pH values measured during the test with those calculated by the previously described method is given in Table 31. As can be seen, the model predicts the trends in pH, but not the magnitude of the changes. Table 32 presents the rate constant values for the series of acid addition tests where the pH was continously monitored. The computer algorithm was modified to use the measured pH to calculate the hydroxide ion concentration. There are no important trends with pH in the range studied.

Temperature

Table 33 presents the results of several tests at different temperatures. The rate constant increases with temperature, with the increase more marked than might be expected. This results from the shifts in equilibrium constants with temperature which increase the free cyanide ion concentration. The Arrhenius equation, 6.7, indicates

TABLE 30

pH CHANGES DURING LEACH TESTS

		Final pH	
Test Number	Initial pH[a]	Measured	Calculated
45	8.9	6.8	7.8
46	9.5	8.5	8.4
44	9.9	9.9	9.9[b]
47	10.4	11.4	12.1
10	12.0	12.5	12.4

[a] The model that was used to calculate the ionic concentrations requires the calculated initial pH to agree with the measured value.

[b] A modification was made to the model to hold the pH constant during the calculations for this test.

TABLE 31

RESULTS OF MONITORING pH

	Test No. 57		Test No. 58		Test No. 59	
Time, min	Measured pH	Calculated pH	Measured pH	Calculated pH	Measured pH	Calculated pH
½	9.34	9.35	10.36	10.34	9.54	9.54
1	9.28	9.31	10.46	10.42	9.52	9.50
2	9.17	9.24	10.50	10.66	9.46	9.45
3	9.05	9.18	10.80	11.08	9.40	9.39
4	8.92	9.11	11.11	11.41	9.32	9.34
5	8.79	9.06	11.54	11.61	9.24	9.28
6	8.67	9.02	11.71	11.73	9.15	9.24
8	8.40	8.92	12.00	11.84	8.98	9.12
10	8.18	8.81	12.15	11.91	8.80	9.06
15	7.86	8.58	12.21	12.00	8.46	8.75

Test Conditions: Initial Sodium Cyanide Concentration, 24 gpl
Size Fraction, Tyler Mesh, -28, +35
Temperature, 25°C

TABLE 32

pH EFFECTS ON THE RATE CONSTANT

pH Range	Rate Constant[a] x 10^5
12.0 - 12.5	6.4
10.3 - 12.2	6.2
10.1 - 9.8	6.5
9.6 - 8.5	6.6
9.4 - 7.9	8.1

[a] Units are (mol. Cu^{1+}/min) (mol. $S^{2-})^{0.1}$/mol. CN^{1-}/cm^2/l.

TABLE 33

RATE CONSTANTS IN RELATION TO TEMPERATURE

Temperature, °C	Rate Constant[a] x 10^5			
	1	2	3	Mean
3	4.9	4.9	5.0	4.9
25	8.4	7.0	8.4	7.9
50	9.7	8.9	8.9	9.2
69	14.7	14.2	12.6	13.6

[a] Units are (mol. Cu^{1+}/min.)(mol. $S^{2-})^{0.1}$/mol. CN^{1-}/cm^2/1 .

Test Conditions: Initial Sodium Cyanide Concentration, 0.41M

Size Fraction, Tyler Mesh, -28, +35

Initial pH, 12.0

that a plot of ln K versus $\frac{1}{T}$ should yield a straight line of slope $-\frac{E^*}{R}$ where E^* is the activation energy.

$$\frac{d \ln K}{dT} = \frac{E^*}{RT^2} \tag{6.7}$$

Figure 7 shows a plot of the temperature data given in Table 33. The points used for this graph are given in Table 34. A least squares fit of the data gives a slope of -1.24 corresponding to an activation energy of 2.5 kilocalories per mole. The low activation energy probably indicates that the reaction is controlled by diffusion through the limiting boundary layer.

Alternate Models for Surface Area

A microscopic examination of the feed and leached particles showed that the particles developed a frosted appearance in contrast to the original conchoidal fractures as a result of surface etching during the test. This etching is attributed to preferential leaching along the cleavage planes. Microscopic examination of a polished section of chalcocite that was leached for a short time with sodium cyanide further supported this explanation. Consequently, there is an initial increase in area as the reaction proceeds followed by a steady decrease in area as the size of the particle is drastically reduced.

Several attempts were made to change the model for the surface area as a function of extraction. These included a zero order model

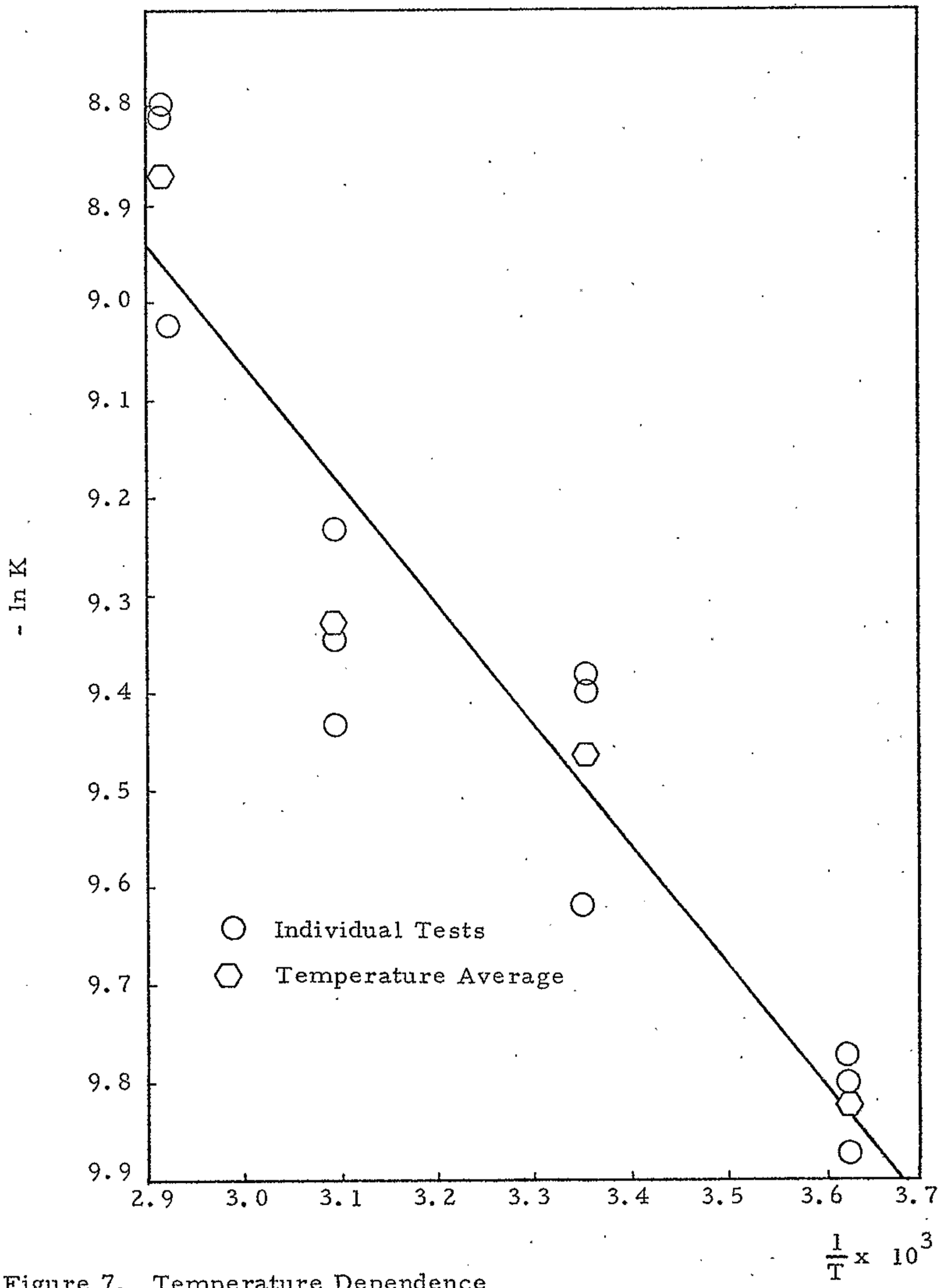

Figure 7. Temperature Dependence
of the Rate Constant From 3°C to 69°C

TABLE 34

POINTS USED TO PREPARE THE ARRHENIUS PLOT

Temperature, °C	$\left(\frac{1}{T}\right)_{°C^{-1}} \times 10^3$,	- ln K	Mean K $\times 10^5$	-ln(Mean K)
3	3.623	9.87		
		9.80		
		9.77	5.46	9.82
25	3.356	9.38		
		9.62		
		9.39	7.80	9.46
50	3.096	9.23		
		9.43		
		9.34	8.86	9.33
69	2.924	8.79		
		8.80		
		9.02	14.1	8.87

and a regression analysis to fit the area exponent in a manner analogous to that used to develop the free cyanide ion concentration dependence. A very small improvement in the consistency of the calculated rate constants resulted from the use of an order dependence of 0.7 for area, but the improvement was not sufficient to justify the use of a new model. The improvement appeared to be more a result of having an additional constant with which to fit the data rather than a result of an improved understanding of the leaching mechanism.

Effects of Other Ions

Because many point-by-point calculations of the rate constant showed a definite tendency to increase during the leach, various changes to the model were attempted. No significant correlations were found for the higher copper complexes or hydrogen ion. Considering the scatter in the data and the range of conditions chosen, it cannot be definitely stated that there is no dependence on other ions, but only that whatever dependence exists is slight compared to the free cyanide ion and sulfide ion concentrations under the conditions used in this study.

Summary

The dissolution of chalcocite in alkaline cyanide solutions under nonoxidizing conditions has been shown to be a diffusion controlled reaction that is first order with respect to free cyanide concentration. The rate was also shown to be inversely proportional to the sulfide ion concentration to a small power, the best present estimate of which is 0.1. The area effect is adequately represented by a shrinking core model based on perfect spheres. At 25°C the overall average rate constant was 7.5×10^{-5} (mol. Cu^{1+}) (mol. $S^{2-})^{0.1}$/ (mol. CN^{1-})/ cm^2/ l. The calculated activation energy was 2.5 kilocalories per mole. Consequently, at 25°C the empirical rate equation is as follows.

$$R = \frac{7.5 \times 10^{-5} A\left[CN^{1-}\right]}{\left[S^{2-}\right]^{0.1}} \quad \text{mol /l/ min} \qquad (6.8)$$

CHAPTER 7

EFFECTS OF THE PROCESS VARIABLES ON EXTRACTION

The preceeding chapter dealt primarily with the kinetics of the dissolution of chalcocite. This chapter contains a discussion of the actual extraction data generated during the study with the goal of giving some estimate of the leaching rates and total extractions that could be expected in practice. The conditions used in the investigation were chosen to aid the kinetic study rather than to simulate plant operating conditions. However, sodium cyanide additions as high as thirty grams per liter and copper concentrations as high as fifteen grams per liter were used in some tests. Consequently, the following data probably represent the low end of the operating range. It is anticipated that future work will develop data from leaching actual plant concentrates to produce higher copper concentrations. The following, then, demonstrates percent extraction as a function of the process variables one at a time with the others held relatively constant. It should be noted that many initial conditions were not replicated since early tests, as shown in Table 35, gave fairly consistent results.

TABLE 35

EXPERIMENTAL REPRODUCIBILITY OF REPLICATE TESTS

	Percent Copper Extraction			
Time, min	Test No. 2	Test No. 3	Test No. 5	Mean
1	10.3	10.3	8.9	9.8
2	19.1	18.6	17.8	18.5
3	26.2	25.5	25.0	25.6
4	32.2	31.5	31.0	31.6
6	41.6	40.1	40.1	40.6
8	47.6	46.4	47.4	47.1
10	52.3	51.0	51.9	51.7
15	59.7	58.6	59.6	59.3
20	64.6	62.9	64.1	63.8
30	69.8	67.6	69.8	69.1

Initial Sodium Cyanide Concentration: 16 gpl

Size Fraction, Tyler Mesh: -28, +35

Temperature: 25°C

Initial pH: 12.0

Initial Cyanide Concentration

Table 36 gives the percent extractions as a function of time for several tests run under similar conditions except for the initial amount of sodium cyanide added. These data are also presented in Figure 8. As can be seen, the dissolution of the coarse -28, +35 mesh fraction is extremely rapid in the presence of excess free cyanide. Whether or not such high molar ratios of cyanide to copper could be used in plant practice would depend on the later requirements of the copper recovery step.

Initial Size

Leaching tests were performed on size fractions from -28, +35 mesh to -150, +200 mesh. The averaged data for similar tests is given in Tables 37 and 38. The results for the -35, +48 mesh fraction leached with sixteen grams per liter sodium cyanide include those tests with initial sulfide addition. Figures 9 and 10 show the relations for those tests with identical initial cyanide addition. While the variation in test conditions limits the comparison of extractions by initial size, the data presented do give a rough idea of the increase in reaction rate with decreasing size.

TABLE 36

EFFECT OF INITIAL SODIUM CYANIDE CONCENTRATION ON PERCENT COPPER EXTRACTION

	Percent Copper Extraction				
	Initial Sodium Cyanide Concentration, gpl				
Time, min	30	24	16	12	8
½	12.1	8.9			
1	21.0	16.7	9.8	8.4	5.3
1½	28.6				
2	36.0	29.4	18.5		
2½				17.2	
3	45.5	38.6	25.6		
4	56.1	46.8	31.6	23.2	
5	63.3	53.5			
6	68.4	55.9	40.6	30.7	19.8
8	75.7	65.7	47.1	35.4	
10	82.1	72.2	51.7	39.1	26.9
15		81.3	59.3	45.4	32.0
20		89.0	63.8	48.8	34.2
30		94.3	69.1	52.7	37.7
45		99.1			39.6
50				55.7	
60					40.5
90					40.9
120					41.4

Size Fraction, Tyler Mesh: -28, +35

Temperature: 25°C

Initial pH: 12.0

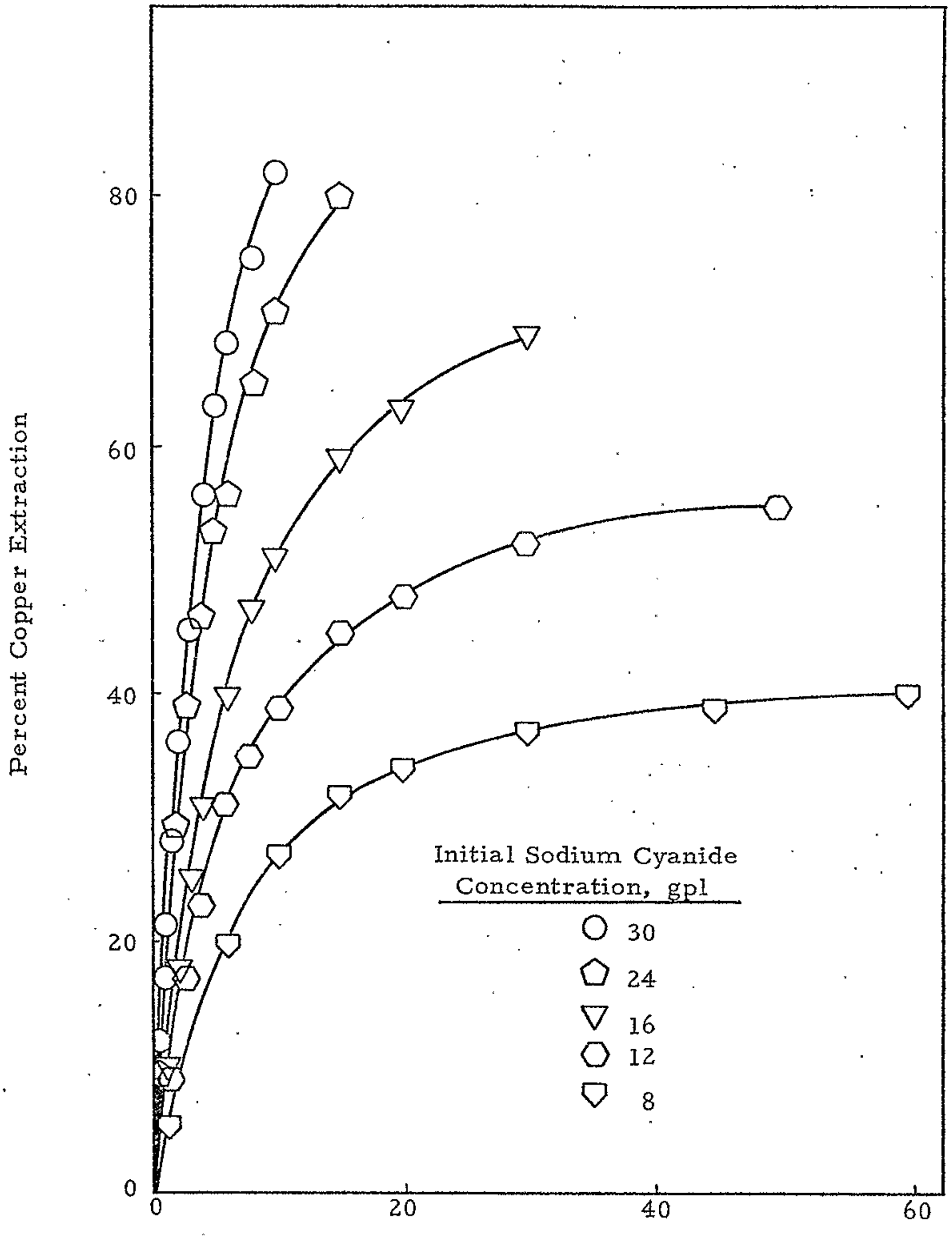

Figure 8. Copper Extraction as a Function of Time for Several Initial Sodium Cyanide Concentrations

TABLE 37

EFFECT OF INITIAL PARTICLE SIZE ON PERCENT COPPER EXTRACTION FOR TESTS WITH AN INITIAL SODIUM CYANIDE CONCENTRATION OF 16 GPL

	Percent Copper Extraction		
	Size Fraction, Tyler Mesh		
Time, min	-28, +35	-35, +48	-48, +65
1	9.8	15.4	18.5
2	18.5	26.7	31.7
3	25.0	35.0	42.3
4	31.6	40.6	47.4
5			52.5
6	40.6	49.6	55.8
8	47.1	55.1	60.8
10	51.7	58.7	64.1
15	59.3	64.4	70.3
20	63.8	67.3	71.3
30	69.1	70.1	

Initial Sodium Cyanide Concentration: 16 gpl

Temperature: 25°C

Initial pH: 12.0

TABLE 38

EFFECT OF INITIAL PARTICLE SIZE ON PERCENT COPPER EXTRACTION FOR TESTS WITH AN INITIAL SODIUM CYANIDE CONCENTRATION OF 12 GPL

	Percent Copper Extraction				
	Size Fraction, Tyler Mesh				
Time, min	-28, +35	-35, +48	-65, +80	-80, +100	-100, +150
½			11.1	11.6	12.5
1	8.4	11.1	17.1	21.5	26.3
2		18.5	27.9	35.0	39.3
2½	17.2				
3		24.2	34.8	42.1	47.3
4	23.2	29.1	39.1	46.4	51.7
5			45.8		
6	30.7	35.5	49.0	52.5	57.6
8	35.4	40.2	51.0	56.1	61.1
10	39.1	43.7	53.3	58.1	61.5
15	45.4	48.3	55.0	60.0	63.3
20	48.8	50.0		60.3	66.8
30	52.7	52.4			
50	55.7				

Initial Sodium Cyanide Concentration: 12 gpl

Temperature: 25°C

Initial pH: 12.0

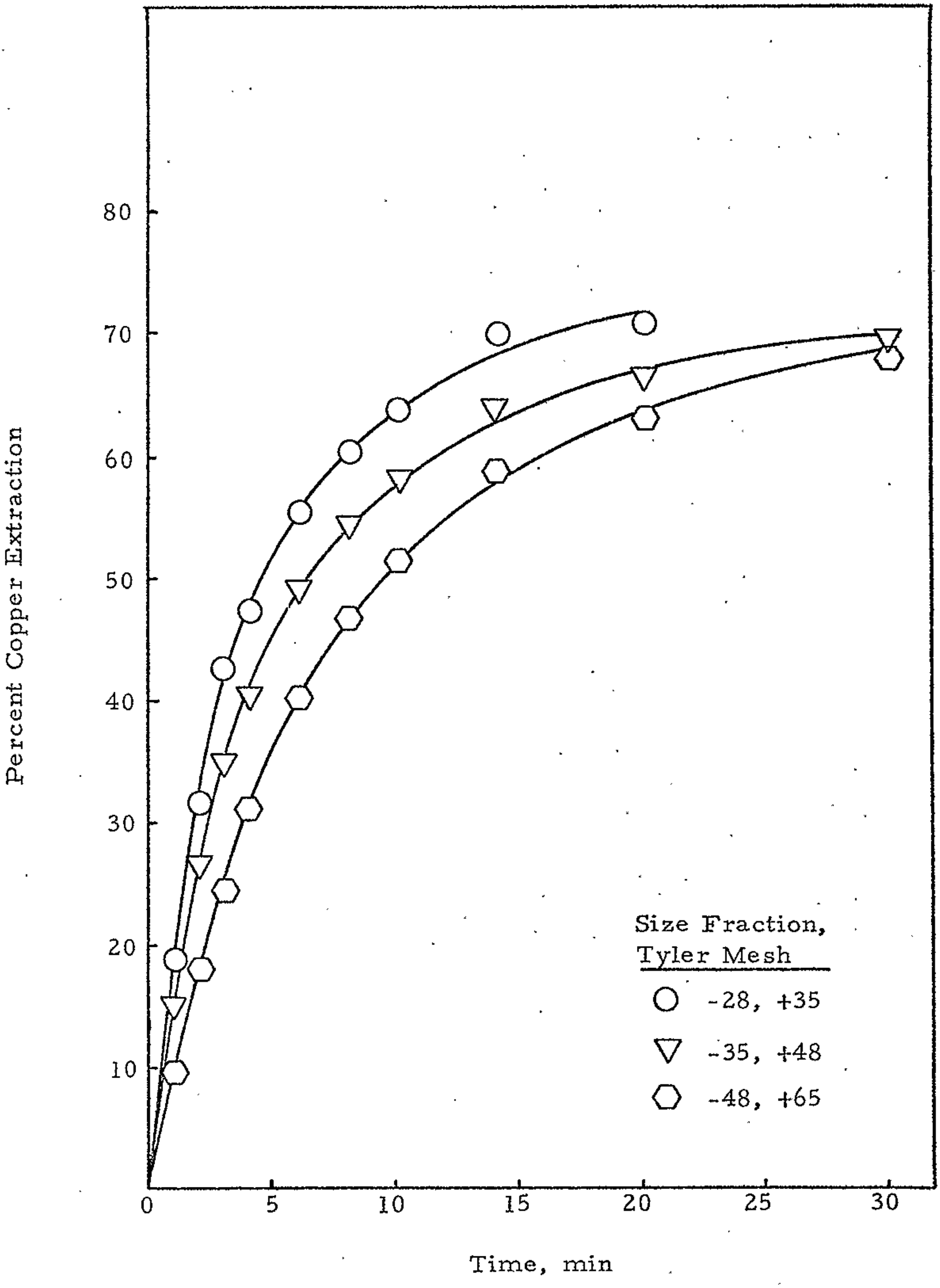

Figure 9. Effect of Initial Size on Percent Copper Extraction in Solutions with an Initial Sodium Cyanide Concentration of 16 gpl

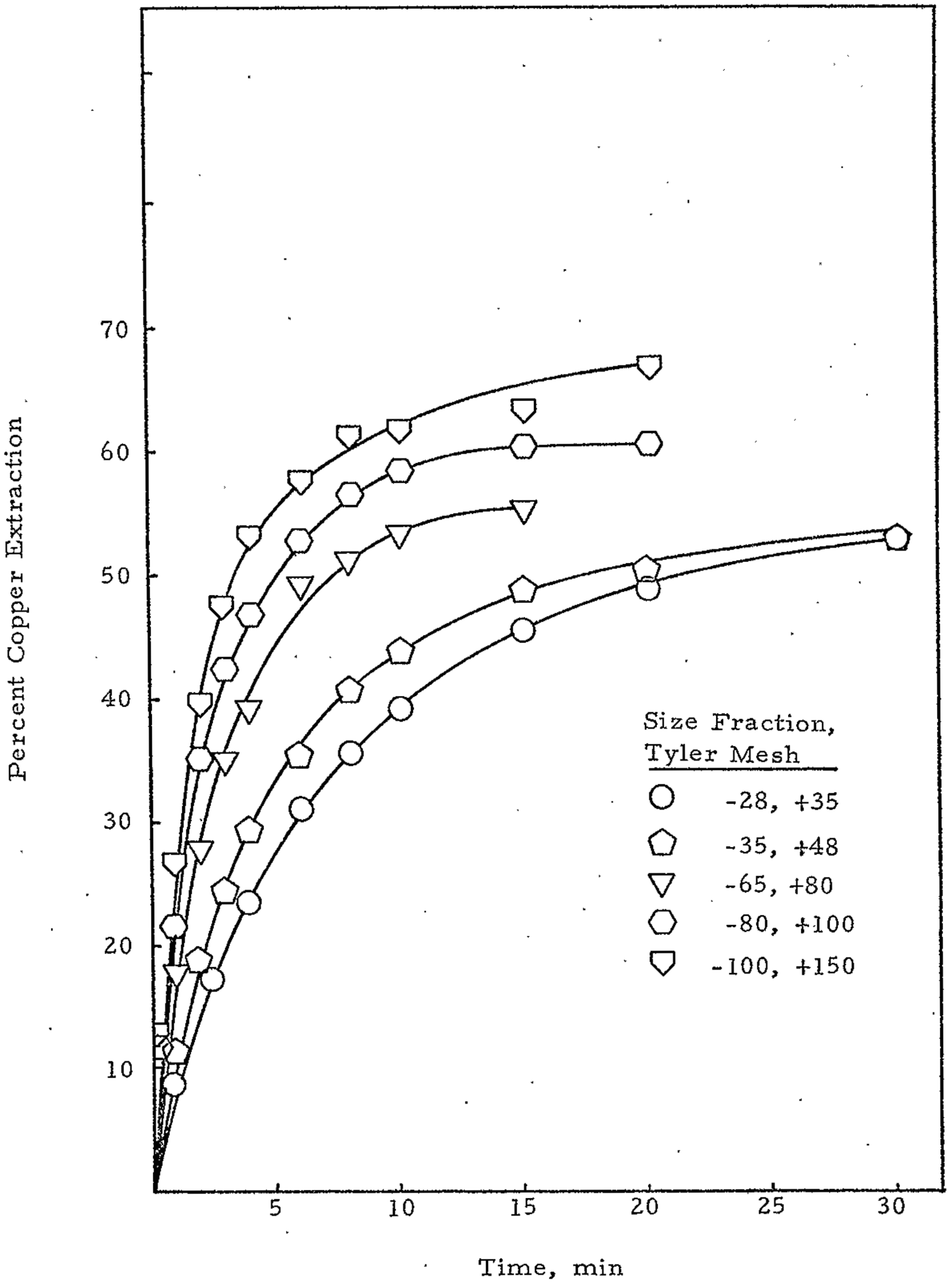

Figure 10. Effect of Initial Particle Size on Percent Copper Extraction in Solutions with an Initial Sodium Cyanide Concentration of 12 gpl

Initial Sulfide Addition

As shown in Table 39, there is no significant difference in the percent extraction as a result of adding sodium sulfide to the initial leach solution. This results from the relatively small change in initial sulfide concentration in relation to the low order sulfide dependence of the reaction rate that was demonstrated in Chapter 6. The large sulfide concentration changes that result from pH changes will be discussed in a later section.

Temperature

Three replicates were run under identical conditions at each of four temperatures: 3°, 25°, 50°, and 69°C. As expected, the rate of extraction increased with temperature. The temperature dependence results, at least in part, from the changes in equilibrium constants which raise the free cyanide ion concentration as the temperature increases. The results of these tests are listed in Table 40 and plotted in Figure 11.

Initial Copper Concentration

Several tests were run by adding cuprous cyanide to the initial solution. The results are presented in Table 41 only as a matter of interest since the leach conditions were not the same in any two tests.

TABLE 39

EFFECT OF INITIAL SODIUM SULFIDE ADDITION ON PERCENT COPPER EXTRACTION

	Percent Copper Extraction			
	Initial Concentration of Sodium Sulfide, gpl			
Time, min	0	3.9	7.8	39.0
1	13.6	15.8	16.4	16.0
2	24.5	27.1	27.8	27.3
3	32.7	34.8	36.2	36.4
4	38.6	41.3	42.0	40.5
6	47.3	51.2	50.4	49.6
8	53.4	55.6	55.9	55.3
10	57.0	59.7	59.6	58.7
15	63.3	65.4	65.0	64.0
20	66.8	68.1	67.9	66.4
30	70.4	71.4	70.8	68.0

Initial Sodium Cyanide Concentration: 16 gpl

Size Fraction, Tyler Mesh: -35, +48

Temperature: 25°C

Initial pH: 12.0

TABLE 40

EFFECT OF TEMPERATURE ON PERCENT COPPER EXTRACTION

	Percent Copper Extraction			
	Temperature, °C			
Time, min	3	25	50	69
1	7.4	9.8	12.5	18.1
2	12.8	18.5	25.1	32.9
3	18.2	25.6	33.8	43.1
4	22.7	31.6	40.5	50.0
6	30.6	40.6	50.0	60.3
8	36.7	47.1	55.7	65.9
10	41.6	51.7	60.6	69.5
15	50.3	59.3	66.8	75.2
20	55.6	63.8	70.2	77.0
30	62.1	69.1	73.0	78.6

Initial Sodium Cyanide Concentration: 16 gpl

Size Fraction, Tyler Mesh: -28, +35

Initial pH: 12.0

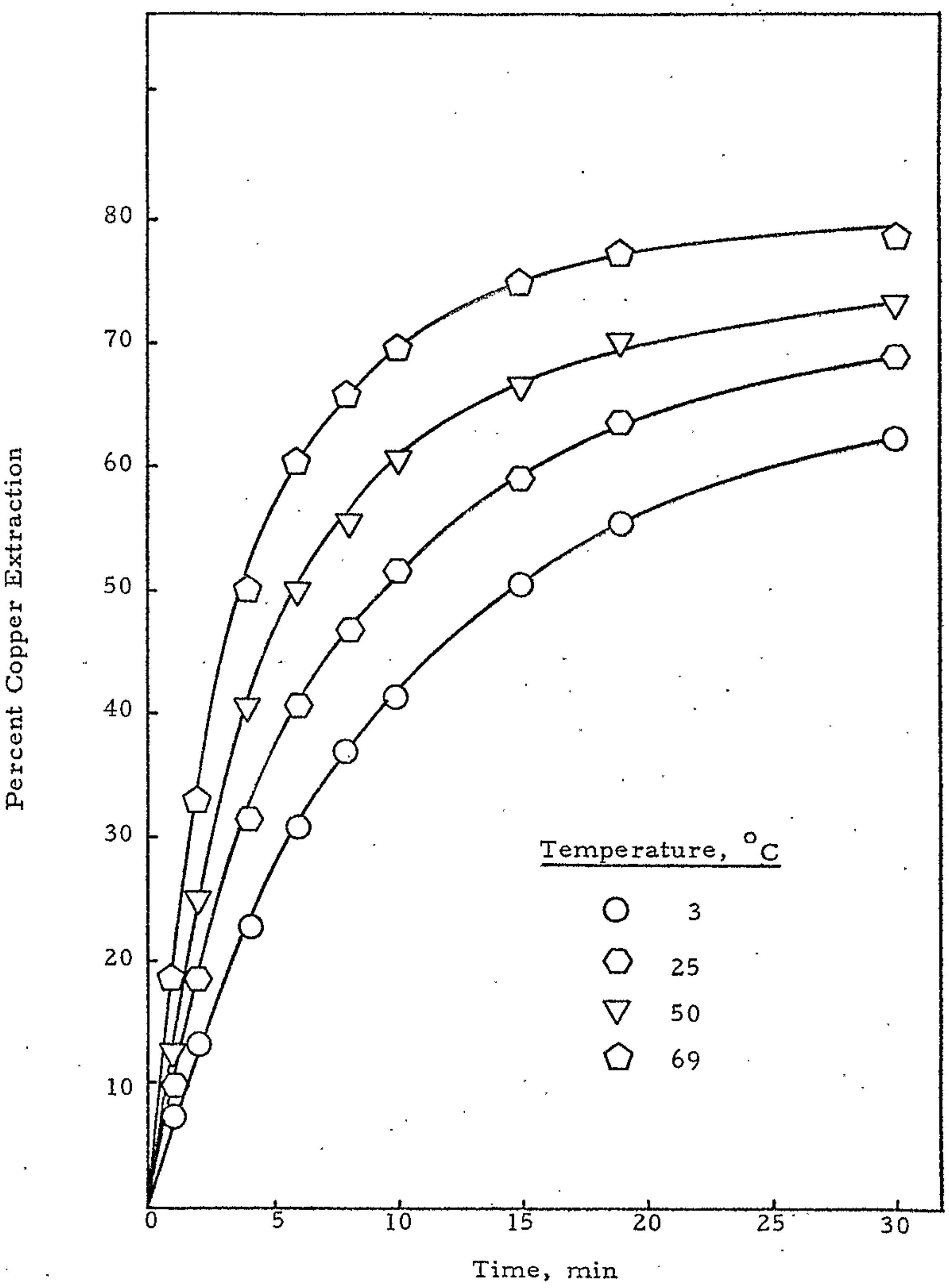

Figure 11. Effect of Temperature on Percent Copper Extraction in Solutions with an Initial Sodium Cyanide Concentration of 16 gpl

TABLE 41

EFFECT OF INITIAL COPPER CONCENTRATION ON PERCENT COPPER EXTRACTION

	Percent Copper Extraction				
	Initial Copper Concentration, gpl				
	1.4	2.9	4.3	7.1	14.3
	Initial Sodium Cyanide Concentration, gpl				
Time, min	16	20	22	28	32
1	11.7	8.7	11.7	9.3	1.8
2	17.7	19.7	20.1	17.1	1.8
3	23.2	26.8	26.1	22.5	2.8
4	27.1	34.0	30.9	26.4	5.5
6	34.6	41.9	37.4	34.0	7.4
8	40.2	47.8	43.3	38.6	10.9
10	43.8	51.3	46.9	41.7	10.7
15	49.0	56.4	54.3	48.5	13.2
30	57.8	65.0	60.0	56.0	15.8
45	60.2	70.3		59.9	18.3

Size Fraction, Tyler Mesh: -28, +35

Temperature: 25°C

Initial pH: 12.0

pH Effects

The variation in extraction as a function of pH is one of the more interesting facets of this study. As was shown in Chapter 6, the reaction rate is proportional to the free cyanide concentration and inversely proportional to the sulfide ion concentration to the 0.1 power.

$$R = \frac{KA\left[CN^{1-}\right]}{\left[S^{2-}\right]^{0.1}} \quad M/min \tag{7.1}$$

The changes in free cyanide concentration with pH is dominated by the cyanide ion-hydrogen cyanide equilibria.

$$\frac{\left[CN^{1-}\right]}{\left[HCN\right]} \sim \frac{K_A}{\left[H^{1+}\right]} \sim \frac{10^{-9}}{\left[H^{1+}\right]} \tag{7.2}$$

Thus, at a pH over eleven the concentration of hydrogen cyanide is negligible while at a pH of nine the concentrations of the two species are roughly equal. The second dissociation constant for hydrogen sulfide dominates the sulfide ion concentration.

$$\frac{\left[S^{2-}\right]}{\left[HS^{1-}\right]} \sim \frac{K_2}{\left[H^{1+}\right]} \sim \frac{10^{-13}}{\left[H^{1+}\right]} \tag{7.3}$$

Thus, the sulfide ion does not account for a significant portion of the total sulfur until a pH over eleven is reached. Consequently, at a pH below twelve essentially all the sulfide produced by the dissolution of the chalcocite hydrolizes with concurrent dissociation of water since there is insufficient hydrogen cyanide present to provide the required hydrogen ion. Therefore, the reaction is essentially as follows and the pH of the solution increases during the leach.

$$Cu_2S + 8CN^{1-} + H_2O \;=\; 2Cu(CN)_4^{3-} + HS^{1-} + OH^{1-} \tag{7.4}$$

At a pH of nine, however, the cyanide ion and hydrogen cyanide have roughly the same concentration and the following reaction approximates the events in solution. Consequently, there is an increase in pH during the leach.

$$Cu_2S + 4CN^{1-} + 4HCN \;=\; 2Cu(CN)_4^{3-} + HS^{-} + 3H^{1+} \tag{7.5}$$

Thus, there is some initial pH for a given set of conditions above which the pH will increase during the leach and below which it will decrease. Table 42 shows this situation where the pH was adjusted with acetic acid.

Another facet in this pH dependence is its effect on the reaction rate. Because of a difference of four orders of magnitude between the hydrogen sulfide and hydrogen cyanide dissociation constants, the initial result of decreasing the pH from the neighborhood of

TABLE 42

EFFECT OF INITIAL pH ON THE pH CHANGE AS A FUNCTION OF TIME

	Measured pH			
Time, min	Test No. 57	Test No. 59	Test No. 56	Test No. 58
0	9.39	9.56	9.96	10.27
½	9.34	9.54	9.96	10.36
1	9.28	9.52	9.95	10.46
2	9.17	9.46	9.93	10.50
3	9.05	9.40	9.92	10.80
4	8.92	9.32	9.91	11.11
5	8.79	9.24	9.90	11.54
6	8.67	9.15	9.89	11.71
8	8.40	8.98	9.87	12.00
10	8.18	8.80	9.85	12.15
15	7.86	8.46	9.80	12.21

Initial Sodium Cyanide Concentration: 24 gpl

Size Fraction, Tyler Mesh: -28, +35

Temperature: 25°C

twelve is to rapidly decrease the sulfide concentration without significantly affecting the free cyanide concentration. Consequently, by equation 7.1, the reaction rate and hence the copper extraction increase with decreasing pH. As the pH enters the nine to ten range, the free cyanide concentration begins to decrease rapidly. Since the order of the free cyanide dependence is much greater than that of the sulfide ion, the effect of the decrease in free cyanide concentration rapidly dominates the effect of the decrease in sulfide ion concentration and the reaction rate and copper extraction decrease with decreasing pH. Table 43 lists the copper extractions for several initial pH values. The calculated free cyanide and sulfide ion concentrations are presented in Tables 44 and 45 respectively. The copper extractions for the various tests are plotted in Figure 12.

Summary

The dissolution of chalcocite in alkaline cyanide solution is a rapid reaction compared to most hydrometallurgical processes. As would be expected, the reaction rate increases with increasing cyanide concentration and temperature and with decreasing particle size. Under the conditions used in these tests, the reaction rate undergoes a maximum with respect to initial pH at about a pH of ten.

TABLE 43

EFFECT OF INITIAL pH ON PERCENT COPPER EXTRACTION

Time, min	Initial pH 12.0	10.4	9.9	9.5	9.4	8.9
½	8.9	8.3	10.6	10.0	10.0	11.9
1	16.6	18.0	20.8	19.4	18.4	20.4
2	29.4	28.6	36.7	33.5	31.8	26.5
3	39.1	39.4	47.7	45.2	41.4	31.3
4	46.8	46.9	56.2	53.4	49.1	35.4
5	53.2	53.6	63.8	60.5	53.7	38.5
6	55.9	59.2	68.9	65.9	57.6	43.6
8	65.6	67.1	76.6	73.4	63.6	47.5
10	71.5	73.4	82.3	77.8	69.0	53.2
15	80.4	83.0	90.8	87.7	76.9	56.2

Initial Sodium Cyanide Concentration: 24 gpl

Size Fraction, Tyler Mesh: -28, +35

Temperature: 25°C

TABLE 44

EFFECT OF INITIAL pH ON CYANIDE ION CONCENTRATION AS A FUNCTION OF TIME

	Cyanide Ion Concentration, mol/l				
	Initial pH				
Time, min	12.0	10.4	9.9	9.5	9.4
$\frac{1}{2}$	0.435	0.424	0.406	0.358	0.315
1	0.400	0.404	0.362	0.318	0.272
2	0.344	0.335	0.297	0.262	0.212
3	0.297	0.292	0.252	0.212	0.165
4	0.261	0.260	0.218	0.174	0.126
5	0.230	0.238	0.181	0.142	0.098
6	0.220	0.201	0.162	0.117	0.076
8	0.170	0.163	0.121	0.078	0.043
10	0.144	0.135	0.100	0.057	0.025
15	0.097	0.087	0.060	0.022	0.011

Initial Sodium Cyanide Concentration: 24 gpl

Size Fraction, Tyler Mesh: -28, +35

Temperature: 25°C

TABLE 45

EFFECT OF INITIAL pH ON SULFIDE ION CONCENTRATION AS A FUNCTION OF TIME

	Sulfide Ion Concentration x 10^5, mol/l				
	Initial pH				
Time, min	12.0	10.4	9.9	9.5	9.4
½	164	4.45	1.83	0.60	0.47
1	342	9.85	3.54	1.21	0.76
2	682	19.3	6.17	1.82	1.02
3	974	52.1	7.94	2.20	1.01
4	1220	124.	9.17	2.21	0.88
5	1430	358.	10.4	2.11	0.72
6	1520	554.	11.0	1.86	0.58
8	1860	1060.	11.9	1.42	0.34
10	2065	1489.	12.2	0.98	0.22
15	2380	1842.	12.2	0.52	0.11

Initial Sodium Cyanide Concentration: 24 gpl

Size Fraction, Tyler Mesh: -28, +35

Temperature: 25°C

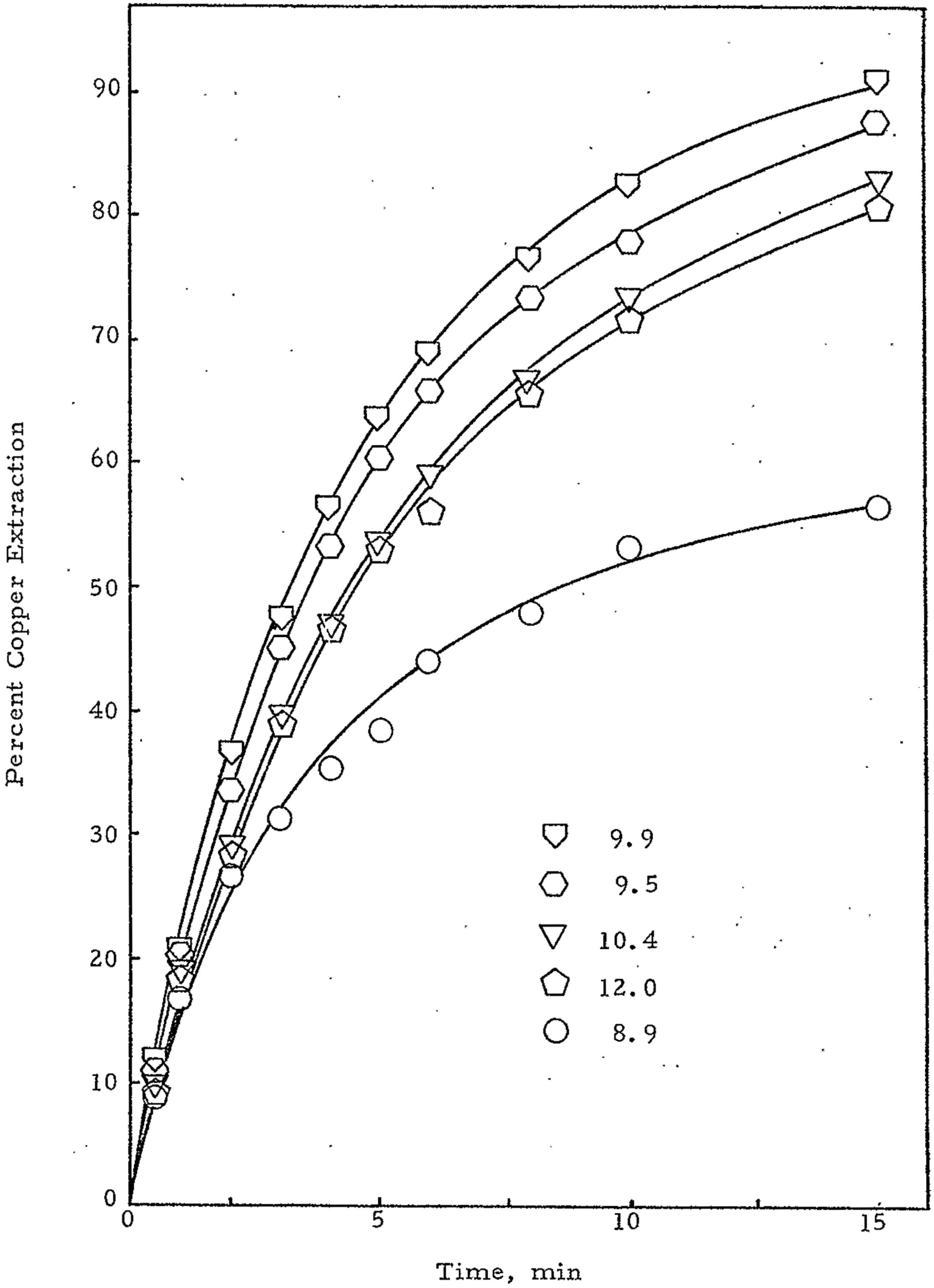

Figure 12. Effect of Initial pH on Percent Copper Extraction in Solutions with an Initial Sodium Cyanide Concentration of 24 gpl

If an economic means of recovering the copper from the leach solution can be demonstrated, the extraction curves presented in this chapter clearly demonstrate that the process would be attractive.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

Chalcocite can be extracted very rapidly in an alkaline cyanide solution when the free cyanide concentration is above approximately 0.1 molar. For example, extractions as high as 90 percent were obtained in fifteen minutes on -28, +35 mesh material. This rate is considerably higher than most hydrometallurgical processes and thus might make cyanide leaching an attractive process if other process problems can be solved. The major products of the leaching reaction are the di-, tri-, and tetracyanide copper complexes, bisulfide and sulfide ion, and either hydroxide or hydrogen ion depending upon the initial pH.

The concentrations of these species are related by a series of equilibrium and mass balance equations. The finite ionic size form of the Debye-Hückel equation for activity coefficients provides an acceptable means of relating the activities and concentrations. This system of simultaneous equations can then be solved by numerical techniques to give the ionic concentrations at each sampling time during the leach test. Continuous monitoring of pH during the test considerably simplifies the required calculations and is recommended for future work. Two additional improvements could be made in the concentration calculations: optimizing the ion size parameters in the Debye-Hückel equation and improving the estimates of the equilibrium constants.

A perfect sphere approximation was used for the particle surface area and was found to be satisfactory at this stage of the investigation. The area correlation worked reasonably well in the size range from 28 to 80 mesh with extractions as high as 80 percent. However, microscopic examination of the leached particles showed that there is a roughening of the surface as a result of preferential leaching on the cleavage planes leading to an increase in area during the early part of the experiment. An empirical area correlation should be developed for future studies, especially for the leaching of the smaller size fractions.

The reaction rate during an experiment was approximated by the derivative of an exponential curve fitted to the measured copper concentration data by a least squares regression. The agreement between the measured and calculated concentrations was quite good. However, taking the derivative led to several problems and some initial data points in each test could not be used in the calculation of the rate constant. Additional work on obtaining a better estimate of the rates would be desirable, especially for the initial rates.

By using the calculated values of the reaction rates, areas, and concentrations several models of the rate law were tested. The free cyanide ion dependence and the area dependence were shown to be first order. A low order inverse dependence on sulfide ion concentration was also demonstrated. The best current estimate of this order is 0.1, but the scatter in the data make the exact value uncertain. The average rate constant calculated during this study, at 25°C, was 7.5×10^{-5} (mol. Cu^{1+})(mol. $S^{2-})^{0.1}$/(mol. CN^{1-})/cm^2/l. Consequently, the empirical rate equation is as follows.

$$R = \frac{7.5 \times 10^{-5} A \left[CN^{1-}\right]}{\left[S^{2-}\right]^{0.1}} \text{ M/min}$$

A study of the variation of the rate constant with temperature indicated that the reaction is probably diffusion controlled with an activation energy of about 2.5 kilocalories per mole of copper.

The effects of pH were especially interesting. As a result of the opposite effects of the hydrogen cyanide and bisulfide dissociations, there is a pH above which pH increases during the reaction and below which it decreases. The resulting changes in cyanide and sulfide ion concentrations with pH cause a maximum leaching rate to occur with respect to pH. Under the conditions used in this study, the maximum rate was obtained at a pH of about ten.

It should be emphasized that solutions having an initial pH below about ten may become acid as a result of the leach reaction.

Particular caution should be exercised in such tests to prevent the evolution of hydrogen cyanide gas during the latter part of the test.

The present work has clearly demonstrated the high leaching rates and defined the important process variables for leaching chalcocite with cyanide. Better models would improve the correlations, however, it is the author's opinion that such work should not be undertaken until the economic recovery of copper from cyanide solution is demonstrated. The approach to this problem that seems most promising at present is electrowinning, although low current efficiencies pose a serious problem. It seems doubtful to the author that an improved model in one field alone, such as area, would make a sufficiently large improvement in the final results to justify the effort: that is, future work should either consider improvements in all areas or none at all.

The possibilities of improving extraction in the concentrator, recovering important by-products, and eliminating atmospheric pollution make this process worthy of further study.

APPENDIX I

DERIVATION OF SELECTED EQUATIONS

The equations that describe the system are given as Table 16 in Chapter 5. Solving equation 5.1 for the free cyanide ion concentration and defining X and Y as the concentrations of the tetra- and tricyanide complexes respectively gives the following equation.

$$\left[CN^{1-}\right] = \frac{K_{4,3}\, X}{F_{4,3}\, Y} \qquad \text{(I-1)}$$

Substituting this value of the free cyanide ion concentration into equation 5.2 and solving for the concentration of the cuprodicyanide ion gives the next result.

$$\left[Cu(CN)_2^{1-}\right] = \frac{K_{3,2}\, F_{4,3}}{K_{4,3}\, F_{3,2}} \cdot \frac{Y^2}{X} \qquad \text{(I-2)}$$

The copper mass balance, equation 5.3, can be written as follows by substituting the value of the cuprodicyanide ion concentration from equation I-2 and rearranging.

$$\frac{K_{3,2}\, F_{4,3}}{K_{4,3}\, F_{3,2}} \cdot Y^2 + X\,Y + X^2 - X\left[Cu\right]_T = 0 \qquad \text{(I-3)}$$

By using the quadratic formula to solve for the cuprotricyanide ion concentration Y and noting that the sign of the radical must be positive since X is a concentration and cannot be negative, the concentration of the cuprotricyanide ion is given as follows.

$$Y = \frac{-X + \sqrt{X^2 - 4\dfrac{K_{3,2}\,F_{4,3}}{K_{4,3}\,F_{3,2}}\left\{X^2 - X\left[Cu\right]_T\right\}}}{2\dfrac{K_{3,2}\,F_{4,3}}{K_{4,3}\,F_{3,2}}} \qquad \text{(I-4)}$$

Equation 5.7 for the cyanide equilibria can be solved for the hydrogen cyanide concentration.

$$\left[HCN\right] = \frac{K_w\,F_A}{K_A} \cdot \frac{\left[CN^{1-}\right]}{\left[OH^{1-}\right]} \qquad \text{(I-5)}$$

Substituting the free cyanide ion concentration from equation I-1 into equation I-5 gives the following.

$$\left[HCN\right] = \frac{K_w F_A K_{4,3}}{K_A F_{4,3}} \cdot \frac{X}{Y\left[OH^{1-}\right]} \qquad \text{(I-6)}$$

The cyanide mass balance, equation 5.8, can then be rewritten using the free cyanide ion concentration from equation I-1, the cuprodicyanide ion concentration from I-2, and the hydrogen cyanide concentration from I-6.

$$\left[CN\right]_T - 4X - 3Y - 2\frac{K_{3,2}F_{4,3}}{K_{4,3}F_{3,2}}\frac{Y^2}{X} - \frac{K_{4,3}X}{F_{4,3}Y}\left(1 + \frac{K_wF_A}{K_A\left[OH^{1-}\right]}\right) = 0 \tag{I-7}$$

If one substitutes the value of the cuprotricyanide ion concentration from equation I-4 into equation I-7, the latter can be treated as a nonlinear equation in one unknown. Successive back substitution of the calculated values gives the equations presented in Chapter 5.

Solving equation 5.4 and 5.5 for the hydrogen sulfide and bisulfide ion concentrations respectively gives the following equations.

$$\left[S^{2-}\right] = \frac{K_2\left[OH^{1-}\right]\left[HS^{1-}\right]}{K_wF_2} \tag{I-8}$$

$$\left[H_2S\right] = \frac{K_wF_1\left[HS^{1-}\right]}{K_1\left[OH^{1-}\right]} \tag{I-9}$$

Substituting these values into the sulfur mass balance, equation 5.6, and solving for the bisulfide ion concentration gives the next equation.

$$\left[HS^{1-}\right] = \frac{\left[S\right]_T}{1 + \dfrac{K_wF_1}{K_1\left[OH^{1-}\right]} + \dfrac{K_2\left[OH^{1-}\right]}{K_wF_2}} \tag{I-10}$$

Back substituting this result into equation I-9 and multiplying by two leads to the next equation.

$$2\left[H_2S\right] = \frac{2K_wF_1}{K_1\left[OH^{1-}\right]}\left(\frac{\left[S\right]_T}{1 + \dfrac{K_wF_1}{K_1\left[OH^{1-}\right]} + \dfrac{K_2\left[OH^{1-}\right]}{K_wF_2}}\right) \qquad \text{(I-11)}$$

Adding equations I-10 and I-11 and factoring gives the following.

$$\left[HS^{1-}\right] + 2\left[H_2S\right] = \frac{\left[S\right]_T\left(1 + \dfrac{2K_wF_1}{K_1\left[OH^{1-}\right]}\right)}{1 + \dfrac{K_wF_1}{K_1\left[OH^{1-}\right]} + \dfrac{K_2\left[OH^{1-}\right]}{K_wF_2}} \qquad \text{(I-12)}$$

Solving equation 5.7 for the hydrogen cyanide concentration gives equation I-13.

$$\left[HCN\right] = \frac{K_wF_A\left[CN^{1-}\right]}{K_A\left[OH^{1-}\right]} \qquad \text{(I-13)}$$

Substituting this value into the cyanide mass balance, equation 5.8, and solving for the free cyanide ion concentration by factoring gives the following for the free cyanide concentration.

$$\left[CN^{1-}\right] = \frac{\left[CN\right]_T - 4\left[Cu(CN)_4^{3-}\right] - 3\left[Cu(CN)_3^{2-}\right] - 2\left[Cu(CN)_2^{1-}\right]}{1 + \dfrac{K_w F_A}{K_A\left[OH^{1-}\right]}} \qquad \text{(I-14)}$$

Back substituting this result into equation I-13 gives the value of the hydrogen cyanide concentration.

$$\left[HCN\right] = \frac{K_w F_A}{K_A\left[OH^{1-}\right]} \cdot \frac{\left[CN\right]_T - 4\left[Cu(CN)_4^{3-}\right] - 3\left[Cu(CN)_3^{2-}\right] - 2\left[Cu(CN)_2^{1-}\right]}{1 + \dfrac{K_w F_A}{K_A\left[OH^{1-}\right]}} \qquad \text{(I-15)}$$

Equation 5.17 can be solved for the concentration of acetic acid.

$$\left[HAc\right] = \frac{K_w F_{Ac}\left[Ac^{1-}\right]}{K_{Ac}\left[OH^{1-}\right]} \qquad \text{(I-16)}$$

Substituting this concentration into the acetate mass balance, equation 5.18, gives the acetate ion concentration.

$$\left[Ac^{1-}\right] = \frac{\left[Ac\right]_T}{1 + \dfrac{K_w F_{Ac}}{K_{Ac}\left[OH^{1-}\right]}} \qquad \text{(I-17)}$$

This result can then be back substituted into equation I-16 to give the concentration of acetic acid.

$$\left[HAc\right] = \frac{K_w F_{Ac} \left[Ac\right]_T}{K_{Ac}\left[OH^{1-}\right]} \Bigg/ \left(1 + \frac{K_w F_{Ac}}{K_{Ac}\left[OH^{1-}\right]}\right) \qquad \text{(I-18)}$$

Substituting the results of equation I-12, I-15, and I-18 into the hydroxide ion mass balance, equation 5.9, and rearranging yields equation I-19 which is a nonlinear equation in one unknown. Back substitution of this concentration into the previous equations gives those equations listed in Chapter 5.

$$\left[OH^{1-}\right]_{j+1} = \left[OH^{1-}\right]_j + \left[HCN\right]_j + \left[HS^{1-}\right]_j + 2\left[H_2S\right]_j + \left[HAc\right]_j - \frac{\left[S\right]_T \left(1 + \dfrac{2K_w F_1}{K_1\left[OH^{1-}\right]_{j+1}}\right)}{1 + \dfrac{K_w F_1}{K_1\left[OH^{1-}\right]_{j+1}} + \dfrac{K_2\left[OH^{1-}\right]_{j+1}}{K_w F_2}} \qquad \text{(I - 19)}$$

$$
- \frac{K_w F_A}{K_A \left[OH^{1-}\right]_{j+1}} \left(\frac{\left[CN\right]_T - 4\left[Cu(CN)_4^{3-}\right] - 3\left[Cu(CN)_3^{2-}\right] - 2\left[Cu(CN)_2^{1-}\right]}{\left(1 + \dfrac{K_w F_A}{K_A \left[OH^{1-}\right]_{j+1}}\right)} \right)
$$

$$
- \frac{\left(\dfrac{K_w F_{Ac} \left[Ac\right]_T}{K_{Ac} \left[OH^{1-}\right]_{j+1}}\right)}{\left(1 + \dfrac{K_w F_{Ac}}{K_{Ac} \left[OH^{1-}\right]_{j+1}}\right)} \qquad \text{(I-19, cont.)}
$$

APPENDIX II

TABULATION OF CONCENTRATIONS AND ACTIVITY COEFFICIENT RATIOS FOR THE IMPORTANT AQUEOUS IONS

The primary purpose of the detailed calculations of concentrations and activity coefficient ratios was to define the aqueous chemistry of the copper-cyanide-sulfide system so that a more complete analysis of the kinetic data could be made. A complete listing of all the calculated concentrations and activity coefficient ratios used in the kinetic analysis would require about 180 pages. The following thirteen tables are presented to show the typical results and also to demonstrate some of the effects of the process variables. The concentration of all aqueous species is given in molarity. The extraction represents the fraction extracted with 1.0 corresponding to complete dissolution. A glossary of the symbols used is given in Table 17, Chapter 5.

A comparison of the sulfide ion concentrations in Tables II-2, II-5, and II-11 shows that pH rather than sulfide addition is primarily responsible for large changes in sulfide ion concentration. Table II-7 demonstrates the ability of the higher complexes to tie up the available cyanide with a resultant marked decrease in the leaching rate. One can also note that the concentration of the dicyanide complex remains quite low even at fairly high copper concentrations.

TABLE II-1

FREE CYANIDE ION AND COPPER COMPLEX CONCENTRATIONS FOR TEST NUMBER 11

	Molar Concentrations					
Time, min	$[CN^{1-}]$	$[Cu]_T$ x 10^2	$[Cu(CN)_4^{3-}]$ x 10^2	$[Cu(CN)_3^{2-}]$ x 10^2	$[Cu(CN)_2^{1-}]$ x 10^7	Percent Copper Extraction
0	0.48	0.	0.	0.	0.	0.
½	0.43	1.1	1.1	0.011	0.0056	9.5
1	0.40	2.0	2.0	0.021	0.012	17.1
2	0.34	3.5	3.5	0.042	0.027	29.9
3	0.30	4.7	4.6	0.062	0.047	39.5
4	0.26	5.6	5.5	0.084	0.072	47.3
5	0.23	6.3	6.2	0.11	0.10	53.3
6	0.22	6.8	6.6	0.12	0.12	56.9
8	0.17	7.7	7.6	0.17	0.22	64.8
10	0.15	8.4	8.2	0.21	0.32	70.3
15	0.10	9.6	9.2	0.36	0.83	79.5

TABLE II-2

SULFIDE ION CONCENTRATION AND OTHER VARIABLES FOR TEST NUMBER 11

			Molar Concentrations			
Time, min	pH	Mean Ionic Strength	$[HCN]$ x 10^4	$[H_2S]$ x 10^7	$[HS^{1-}]$ x 10^2	$[S^{2-}]$ x 10^2
0	12.0	0.49	4.8	0.	0.	0.
½	12.1	0.52	3.3	0.16	0.38	0.17
1	12.2	0.55	2.6	0.24	0.65	0.35
2	12.3	0.60	1.8	0.32	1.1	0.69
3	12.3	0.64	1.4	0.36	1.4	0.98
4	12.3	0.67	1.1	0.39	1.6	1.2
5	12.4	0.69	0.93	0.41	1.7	1.4
6	12.4	0.70	0.84	0.42	1.8	1.5
8	12.4	0.74	0.63	0.44	2.1	1.8
10	12.4	0.76	0.52	0.46	2.2	2.0
15	12.4	0.79	0.33	0.49	2.5	2.3

TABLE II-3

ACTIVITY COEFFICIENT RATIOS FOR TEST NUMBER 11

Time, min	$F_{4,3}$	$F_{3,2}$	F_A	F_2	F_1	F_w
0	6.7	2.1	0.75	0.99	0.75	0.75
$\frac{1}{2}$	6.9	2.2	0.75	0.99	0.75	0.74
1	7.1	2.2	0.75	1.0	0.75	0.74
2	7.5	2.2	0.74	1.0	0.74	0.74
3	7.7	2.2	0.73	1.0	0.73	0.74
4	7.9	2.2	0.73	1.0	0.73	0.74
5	8.1	2.3	0.73	1.0	0.73	0.74
6	8.2	2.3	0.73	1.0	0.73	0.74
8	8.4	2.3	0.72	1.0	0.72	0.74
10	8.5	2.3	0.72	1.0	0.72	0.74
15	8.8	2.3	0.72	1.0	0.72	0.74

TABLE II-4

FREE CYANIDE ION AND COPPER COMPLEX CONCENTRATIONS FOR TEST NUMBER 24

	Molar Concentrations					
Time, min	$[CN^{1-}]$	$[Cu]_T$ x 10^2	$[Cu(CN)_4^{3-}]$ x 10^2	$[Cu(CN)_3^{2-}]$ x 10^2	$[Cu(CN)_2^{1-}]$ x 10^6	Percent Copper Extraction
0	0.32	0.	0.	0.	0.	0.
1	0.24	2.0	2.0	0.03	0.003	16.4
2	0.19	3.4	3.3	0.07	0.008	27.8
3	0.15	4.4	4.3	0.11	0.02	36.2
4	0.12	5.2	5.0	0.16	0.03	42.1
6	0.08	6.2	5.9	0.28	0.08	50.4
8	0.05	6.9	6.4	0.47	0.20	55.9
10	0.03	7.4	6.7	0.71	0.45	59.6
15	0.01	8.1	6.5	1.6	2.4	65.0
20	0.009	8.5	5.9	2.5	6.4	67.9
30	0.005	8.8	5.1	3.7	16.	70.8

TABLE II-5

SULFIDE ION CONCENTRATIONS AND OTHER VARIABLES FOR TEST NUMBER 24

			Molar Concentrations			
Time, Min	pH	Mean Ionic Strength	$[HCN]$ x 10^5	$[H_2S]$ x 10^7	$[HS^{1-}]$ x 10^2	$[S^{2-}]$ x 10^2
0	13.0	0.54	3.3	0.13	2.2	8
1	13.0	0.61	2.4	0.14	2.4	8
2	13.0	0.65	1.8	0.15	2.6	9
3	13.0	0.69	1.4	0.15	2.7	9
4	13.0	0.71	1.1	0.15	2.8	10
6	13.0	0.75	0.72	0.16	2.9	10
8	13.0	0.77	0.47	0.16	3.0	10
10	13.0	0.78	0.32	0.17	3.0	10
15	13.0	0.78	0.14	0.17	3.1	11
20	13.0	0.78	0.08	0.18	3.2	11
30	13.0	0.77	0.05	0.19	3.3	11

TABLE II-6

ACTIVITY COEFFICIENT RATIOS FOR TEST NUMBER 24

Time, min	$F_{4,3}$	$F_{3,2}$	F_A	F_2	F_1	F_w
0	7.0	2.2	0.75	1.0	0.75	0.74
1	7.5	2.2	0.74	1.0	0.74	0.74
2	7.8	2.2	0.73	1.0	0.73	0.74
3	8.0	2.3	0.73	1.0	0.73	0.74
4	8.2	2.3	0.73	1.0	0.73	0.74
6	8.4	2.3	0.72	1.0	0.72	0.74
8	8.5	2.3	0.72	1.0	0.72	0.74
10	8.6	2.3	0.72	1.0	0.72	0.74
15	8.6	2.3	0.72	1.0	0.72	0.74
20	8.6	2.3	0.72	1.0	0.72	0.74
30	8.6	2.3	0.72	1.0	0.72	0.74

TABLE II-7

FREE CYANIDE ION AND COPPER COMPLEX CONCENTRATIONS FOR TEST NUMBER 30

	Molar Concentrations					
Time, min	$[CN^{1-}]$	$[Cu]_T$	$[Cu(CN)_4^{3-}]$	$[Cu(CN)_3^{2-}]$	$[Cu(CN)_2^{1-}]$ x 10^4	Percent Copper Extraction
0	0.013	0.22	0.18	0.04	0.06	0.
1	0.011	0.23	0.18	0.05	0.08	1.8
2	0.011	0.23	0.18	0.05	0.08	1.8
3	0.010	0.23	0.18	0.05	0.10	2.8
4	0.008	0.23	0.17	0.06	0.15	5.5
6	0.007	0.23	0.16	0.07	0.20	7.4
8	0.005	0.24	0.15	0.08	0.33	10.9
10	0.005	0.24	0.15	0.08	0.31	10.7
15	0.005	0.24	0.14	0.09	0.43	13.2
30	0.004	0.24	0.14	0.11	0.58	15.8
45	0.003	0.25	0.13	0.12	0.77	18.3

TABLE II-8

SULFIDE ION CONCENTRATIONS AND OTHER VARIABLES FOR TEST NUMBER 30

			Molar Concentrations			
Time, min	pH	Mean Ionic Strength	$[HCN]$ x 10^5	$[H_2S]$ x 10^8	$[HS^{1-}]$ x 10^3	$[S^{2-}]$ x 10^3
0	12.0	1.2	1.1	0.	0.	0.
1	12.0	1.2	0.89	0.35	0.75	0.28
2	12.0	1.2	0.89	0.35	0.75	0.28
3	12.0	1.2	0.79	0.54	1.2	0.46
4	12.1	1.2	0.58	0.97	2.3	0.94
6	12.1	1.2	0.48	1.2	3.1	1.3
8	12.1	1.2	0.34	1.7	4.5	2.1
10	12.1	1.2	0.35	1.6	4.4	2.0
15	12.1	1.2	0.28	1.9	5.3	2.6
30	12.1	1.2	0.23	2.2	6.3	3.2
45	12.2	1.2	0.19	2.4	7.3	3.8

TABLE II-9

ACTIVITY COEFFICIENT RATIOS FOR TEST NUMBER 30

Time, min	$F_{4,3}$	$F_{3,2}$	F_A	F_2	F_1	F_w
0	11	2.5	0.69	1.1	0.69	0.73
1	11	2.5	0.69	1.1	0.69	0.73
2	11	2.5	0.69	1.1	0.69	0.73
3	11	2.5	0.69	1.1	0.69	0.73
4	11	2.5	0.69	1.1	0.69	0.73
6	11	2.5	0.69	1.1	0.69	0.73
8	11	2.5	0.69	1.1	0.69	0.73
10	11	2.5	0.69	1.1	0.69	0.73
15	11	2.5	0.69	1.1	0.69	0.73
30	11	2.5	0.69	1.1	0.69	0.73
45	11	2.5	0.69	1.1	0.69	0.73

TABLE II-10

FREE CYANIDE ION AND COPPER COMPLEX CONCENTRATIONS FOR TEST NUMBER 57

	Molar Concentrations					
Time, min	$[CN^{1-}]$	$[Cu]_T$ x 10^2	$[Cu(CN)_4^{3-}]$ x 10^2	$[Cu(CN)_3^{2-}]$ x 10^2	$[Cu(CN)_2^{1-}]$ x 10^6	Percent Copper Extraction
0	0.36	0.	0.	0.	0.	0.
$\frac{1}{2}$	0.31	1.2	1.1	0.01	0.001	10.0
1	0.27	2.1	2.1	0.03	0.003	18.4
2	0.21	3.7	3.7	0.07	0.007	31.8
3	0.17	4.9	4.8	0.11	0.02	41.4
4	0.13	5.8	5.6	0.17	0.03	49.1
5	0.10	6.3	6.1	0.23	0.05	53.7
6	0.08	6.8	6.5	0.31	0.09	57.6
8	0.04	7.6	7.0	0.59	0.31	63.6
10	0.03	8.2	7.2	1.0	0.93	69.0
15	0.01	9.2	6.9	2.3	4.7	76.9

TABLE II-11

SULFIDE ION CONCENTRATION AND OTHER VARIABLES FOR TEST NUMBER 57

			Molar Concentrations			
Time, min	pH	Mean Ionic Strength	$[HCN]$	$[H_2S]$ x 10^3	$[HS^{1-}]$ x 10^2	$[S^{2-}]$ x 10^4
0	9.4	0.68	0.13	0.	0.	0.
½	9.3	0.72	0.12	0.01	0.6	0.05
1	9.3	0.74	0.12	0.03	1.1	0.08
2	9.2	0.79	0.12	0.06	1.9	0.10
3	9.1	0.81	0.12	0.11	2.4	0.10
4	8.9	0.84	0.13	0.18	2.9	0.09
5	8.8	0.85	0.13	0.26	3.1	0.07
6	8.7	0.86	0.14	0.36	3.4	0.06
8	8.4	0.87	0.14	0.74	3.7	0.03
10	8.2	0.88	0.14	1.3	4.0	0.02
15	7.9	0.89	0.13	3.0	4.3	0.01

TABLE II-12

ACTIVITY COEFFICIENT RATIOS FOR TEST NUMBER 57

Time, min	$F_{4,3}$	$F_{3,2}$	F_A	F_2	F_1	F_w
0	8.0	2.3	0.73	1.0	0.73	0.74
$\frac{1}{2}$	8.3	2.3	0.73	1.0	0.73	0.74
1	8.4	2.3	0.72	1.0	0.72	0.74
2	8.7	2.3	0.72	1.0	0.72	0.74
3	8.9	2.3	0.72	1.0	0.72	0.74
4	9.0	2.3	0.71	1.0	0.71	0.74
5	9.1	2.3	0.71	1.0	0.71	0.73
6	9.1	2.3	0.71	1.0	0.71	0.73
8	9.2	2.4	0.71	1.0	0.71	0.73
10	9.2	2.4	0.71	1.0	0.71	0.73
15	9.3	2.4	0.71	1.0	0.71	0.73

TABLE II-13

ACETATE ION CONCENTRATION FOR TEST NUMBER 57

Time, min	F_{Ac}	$[HAc] \times 10^4$	$[Ac^{1-}]$
0	0.73	0.07	0.52
$\frac{1}{2}$	0.73	0.08	0.52
1	0.72	0.09	0.52
2	0.72	0.11	0.52
3	0.72	0.15	0.52
4	0.71	0.20	0.52
5	0.71	0.26	0.52
6	0.71	0.35	0.52
8	0.71	0.65	0.52
10	0.71	1.1	0.52
15	0.71	2.2	0.52

APPENDIX III

THE EXPERIMENTAL DATA

The following listing of the raw test data for the experiments in this study is given should anyone wish to attempt an evaluation of them based on a different model. Only those values which were lost during chemical analysis have been omitted: several values of doubtful validity are embedded in the following tables. All tests were run using a twenty-five gram sample. The assays of the different size fractions are given in Table 13, Chapter 4. The analyses of the other materials are also given in Chapter 4. The impeller speed was 1000 rpm, the initial volume 2.5 liters, and the feed size -28, +35 mesh (Tyler) unless otherwise noted.

TABLE III-1

TEST NUMBER 1

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.25	22
3	2.85	23
5	4.02	22
7½	4.92	17
10	5.50	20
15	6.24	22
20	6.62	23
30	7.11	20
45	7.49	19
60	7.72	20

Initial Conditions: 60 g NaCN, 25°C, pH 12.0

Final Conditions: 26°C

TABLE III-2

TEST NUMBER 2

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.76	23
2	1.42	23
3	1.95	35
4	2.41	23
6	3.13	28
8	3.60	23
10	3.97	23
15	4.56	23
20	4.95	23
30	5.38	23

Initial Conditions: 40 g NaCN, 25°C, pH 12.0

Final Conditions: 26°C

TABLE III-3

TEST NUMBER 3

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.76	20
2	1.38	20
3	1.90	20
4	2.35	20
6	3.01	20
8	3.49	20
10	3.85	20
15	4.44	20
20	4.78	20
30	5.16	20

Initial Conditions: 40 g NaCN, 25°C, pH 12.0

Final Conditions: 26°C

TABLE III-4

TEST NUMBER 4

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.54	23
$2\frac{1}{2}$	1.22	23
4	1.74	23
6	2.26	23
8	2.64	23
10	2.92	23
15	3.41	23
20	3.69	23
30	3.99	23
50	4.26	23

Initial Conditions: 30 g NaCN, 25°C, pH 12.0

Final Conditions: 26°C

TABLE III-5

TEST NUMBER 5

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.66	23
2	1.32	28
3	1.86	20
4	2.32	20
6	3.02	28
8	3.58	30
10	3.94	23
15	4.55	23
20	4.91	20
30	5.37	20

Initial Conditions: 40 g NaCN, 25°C, pH 12.0

Final Conditions: 26°C, pH 12.54

TABLE III-6

TEST NUMBER 6

Time, min	Copper Concentration, gpl	Sample Volume, ml
$\frac{1}{2}$	0.73	20
1	1.39	20
$1\frac{1}{2}$	1.96	20
2	2.49	20
3	3.33	20
4	4.14	20
5	4.74	20
6	5.15	30
8	5.74	20
10	6.22	20

Initial Conditions: 75 g NaCN, 25°C, pH 12.02

Final Conditions: 26°C

TABLE III-7

TEST NUMBER 7

Time, min	Copper Concentration, gpl	Sample Volume, ml
$\frac{1}{2}$	1.03	18
1	1.71	18
$1\frac{1}{2}$	2.33	18
2	2.90	18
3	3.45	22
4	4.44	22
5	4.98	18
6	5.39	28
8	6.08	18
10	6.66	18

Initial Conditions: 75g NaCN, 24°C, pH 11.98

Final Conditions: $26\frac{1}{2}$°C

TABLE III-8

TEST NUMBER 8

Time, min	Copper Concentration, gpl	Sample Volume, ml
$\frac{1}{2}$	0.93	22
1	1.57	22
$1\frac{1}{2}$	2.10	22
2	2.66	22
3	3.46	19
4	4.11	19
5	4.63	22
6	5.02	22
8	5.47	25
10	5.95	19

Initial Conditions: 75 g NaCN, 24°C, pH 11.99

Final Conditions: $26\frac{1}{2}$°C, pH 12.56

TABLE III-9

TEST NUMBER 9

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.70	21
2½	1.34	21
4	1.71	22
6	2.34	19
8	2.68	22
10	2.97	21
15	3.46	19
20	3.72	21
30	4.03	21
50	4.88	21

Initial Conditions: 30 g NaCN, 24°C, pH 11.98

Final Conditions: 26°C, pH 12.45

TABLE III-10

TEST NUMBER 10

Time, min	Copper Concentration, gpl	Sample Volume, ml
½	0.61	23
1	1.20	22
2	2.15	23
3	2.90	23
4	3.48	23
5	4.01	23
6	4.15	26
8	5.06	24
10	5.56	21
15	6.26	23

Initial Conditions: 60 g NaCN, 23½°C, pH 12.03

Final Conditions: 26½°C, pH 12.5

TABLE III-11

TEST NUMBER 11

Time, min	Copper Concentration, gpl	Sample Volume, ml
$\frac{1}{2}$	0.70	21
1	1.27	23
2	2.23	23
3	2.96	23
4	3.56	22
5	4.02	22
6	4.30	22
8	4.92	23
10	5.36	24
15	6.10	23

Initial Conditions: 60 g NaCN, 24°C, pH 12.00

Final Conditions: $26\frac{1}{2}$°C, pH 12.57

TABLE III-12

TEST NUMBER 12

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.36	21
5.75	1.45	24
10	1.94	22
15	2.31	21
20	2.51	22
30	2.75	21
45	2.92	22
60	3.04	22
90	3.04	14
120	3.13	19

Initial Conditions: 20 g NaCN, $23\frac{1}{2}$°C, pH 12.00

Final Conditions: $26\frac{1}{2}$° C, pH 12.26

TABLE III-13

TEST NUMBER 13

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.43	21
5.75	1.50	22
10	2.07	23
15	2.47	24
20	2.61	19
30	2.91	20
46	3.04	18
60	3.06	19
90	3.12	19
120	3.12	16

Initial Conditions: 20 g NaCN, $23\frac{1}{2}^{\circ}$C, pH 11.97

Final Conditions: $26\frac{1}{2}^{\circ}$C, pH 12.58

TABLE III-14

TEST NUMBER 14

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.86	24
2	1.43	21
3	1.89	24
4	2.29	21
6	2.80	22
8	3.19	20
10	3.46	21
15	3.85	22
20	4.01	24
30	4.24	21

Initial Conditions: 30 g NaCN, 24°C, pH 12.02, -35, +48 mesh

Final Conditions: $26\frac{1}{2}^{\circ}$C, pH 12.68

TABLE III-15

TEST NUMBER 15

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.85	24
2	1.44	21
3	1.88	23
4	2.26	22
6	2.78	23
8	3.15	23
10	3.45	28
15	3.82	22
20	3.94	22
30	4.12	21

Initial Conditions: 30 g NaCn, 24°C, pH 12.29, -35, +48 mesh

Final Conditions: 27°C, pH 12.75

TABLE III-16

TEST NUMBER 16

Time, min	Copper Concentration, gpl	Sample Volume, ml
½	0.84	20
1	1.35	20
2	2.13	21
3	2.67	18
4	3.01	21
6	3.54	21
8	3.79	17
10	3.95	22
15	4.14	20
20	4.28	20

Initial Conditions: 30 g NaCN, 25°C, pH 12.10, -65, +80 mesh

Final Conditions: 27°C

TABLE III-17

TEST NUMBER 17

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.53	21
5	3.54	16
10	4.18	17
30	4.59	21
60	4.66	18
120	4.73	18
180	4.64	18
240	4.67	18
300	4.71	15
360	5.48	13

Initial Conditions: 30 g NaCN, 24°C, pH 11.98, -35, +48 mesh

Final Conditions: 25°C, pH 12.68

TABLE III-18

TEST NUMBER 18

Time, min	Copper Concentration, gpl	Sample Volume, ml
0	9.18	10
5	9.25	20
30	9.83	21
60	10.28	19
90	10.94	18
120	10.51	19
180	10.73	21
270	11.60	18
390	11.59	17
935	10.75	20
1260	10.41	13

Initial Conditions: 50 g NaCN, 30 g CuCN, 25°C, pH 11.94, -35, +48 mesh

TABLE III-19

TEST NUMBER 19

Time, min	Copper Concentration, gpl	Sample Volume, ml
½	0.88	20
1	1.64	22
2.1	2.68	20
3	3.23	20
4	3.57	19
6	4.05	21
8	4.34	22
10	4.50	21
15	4.66	20
20	4.68	20

Initial Conditions: 30 g NaCN, 24°C, pH 11.98, -80, +100 mesh

Final Conditions: 26°C, pH 12.68

TABLE III-20

TEST NUMBER 20

Time, min	Copper Concentration, gpl	Sample Volume, ml
½	0.93	17
1	1.96	20
2	2.94	19
3	3.55	21
4	3.88	15
6	4.34	20
8	4.62	18
10	4.65	19
15	4.79	20
20	5.07	21

Initial Conditions: 30 g NaCN, 24°C, pH 11.97, -100, +150 mesh

Final Conditions: 26°C, pH 12.66

TABLE III-21

TEST NUMBER 21

Time, min	Copper Concentration, gpl	Sample Volume, ml
$\frac{1}{2}$	1.27	19
1	2.03	17
2	2.94	19
3	3.34	17
4	3.49	13
6	3.75	15
8	3.86	18
10	3.91	21
15	3.93	18
20	3.97	17

Initial Conditions: 25 g NaCN, 24°C, pH 12.04, -150, +200 mesh

Final Conditions: 26°C, pH 12.65

TABLE III-22

TEST NUMBER 22

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	3.45	21
2	3.90	19
4	4.64	21
6	5.21	18
8	5.65	20
10	6.18	21
15	7.16	19
20	7.43	18
30	7.78	20
45	8.01	21

Initial Conditions: 50 g NaCN, 10 g CuCN, 25°C, pH 11.97, -35, +48 mesh

Final Conditions: 25°C, pH 12.68

TABLE III-23

TEST NUMBER 23

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.22	18
2	2.10	18
3	2.71	19
4	3.22	17
6	4.01	15
8	4.36	19
10	4.69	19
15	5.16	18
20	5.38	19
30	5.65	21

Initial Conditions: 40 g NaCN, 30 g $Na_2S \cdot 9H_2O$, 25°C, pH 12.68, -35, +48 mesh

Final Conditions: 26°C, pH 12.89

TABLE III-24

TEST NUMBER 24

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.27	19
2	2.16	20
3	2.82	19
4	3.28	20
6	3.95	19
8	4.39	20
10	4.69	20
15	5.13	20
20	5.37	19
30	5.61	21

Initial Conditions: 40 g NaCN, 30 g $Na_2S \cdot 9H_2O$, pH 12.68, 25°C, -35, +48 mesh

Final Conditions: 26°C, pH 13.11

TABLE III-25

TEST NUMBER 25

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.59	20
2	2.75	20
3	3.49	21
4	4.00	21
6	4.65	20
8	5.07	22
10	5.33	20
15	5.72	19
20	5.95	21
30	6.16	20

Initial Conditions: 40 g NaCN, 20 ml conc. perchloric acid, 24°C, pH 9.58, -35, +48 mesh

Final Conditions: 26°C, pH 7.7

TABLE III-26

TEST NUMBER 26

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	2.28	18
2	2.72	20
3	3.15	26
4	3.44	20
6	4.01	16
8	4.44	18
10	4.72	21
15	5.13	22
30	5.82	17
45	6.01	18

Initial Conditions: 40 g NaCN, 5 g CuCN, 26°C, pH 12.0

Final Conditions: $26\frac{1}{2}$°C, pH 12.5

TABLE III-27.

TEST NUMBER 27

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	3.98	19
2	4.30	21
3	4.83	18
4	5.38	20
6	5.98	17
8	6.43	16
10.2	6.70	18
15	7.10	22
30	7.78	22
45	8.20	18

Initial Conditions: 50 g NaCN, 10 g CuCN, 25°C, pH 12.0

Final Conditions: 27°C, pH 12.65

TABLE III-28

TEST NUMBER 28

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	5.12	20
2	5.75	22
3	6.20	19
4	6.56	18
6	7.06	17
8	7.51	20
10	7.79	35
15	8.37	18
30	8.82	16
45	-	22

Initial Conditions: 55 g NaCN, 15 g CuCN, 24°C, pH 12.0

Final Conditions: 26°C, pH 12.6

TABLE III-29

TEST NUMBER 29

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	7.78	19
2	8.36	22
3	8.77	21
4	9.06	18
6	9.64	17
8	10.00	21
10	10.24	21
15	10.77	17
30	11.36	18
45	11.67	22

Initial Conditions: 70 g NaCN, 25 g CuCN, 25°C, pH 12.2

Final Conditions: 27°C, pH 12.7

TABLE III-30

TEST NUMBER 30

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	14.32	23
2	14.32	23
3	14.40	16
4	14.60	17
6	14.75	20
8	15.02	22
10	15.00	22
15	15.20	24
30	15.40	21
45	15.60	23

Initial Conditions: 80 g NaCN, 50 g CuCN, 25°C, pH 12.0

Final Conditions: 26°C, pH 12.4

TABLE III-31

TEST NUMBER 31

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.42	21
2	1.96	23
3	2.61	21
4	3.10	21
6	3.83	21
8	4.27	17
10	4.66	16
15	5.12	20
20	5.43	16
30	5.62	16

Initial Conditions: 40 g NaCN, 50°C, pH 12.0

Final Conditions: 51°C

TABLE III-32

TEST NUMBER 32

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.93	18
2	1.85	19
3	2.48	16
4	3.00	16
6	3.74	16
8	4.16	20
10	4.50	18
15	5.01	17
20	5.25	19
30	5.47	16

Initial Conditions: 40 g NaCN, 48°C, pH 12.0

Final Conditions: 48°C

TABLE III-33

TEST NUMBER 33

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.91	20
2	1.77	18
3	2.44	17
4	2.95	17
6	3.64	17
8	4.09	18
10	4.50	20
15	4.97	18
20	5.24	20
30	5.47	16

Initial Conditions: 40 g NaCN, 50°C, pH 12.0

Final Conditions: 49°C

TABLE III-34

TEST NUMBER 34

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.26	17
2	2.30	16
3	3.13	17
4	3.66	17
6	4.48	20
8	4.93	20
10	5.20	21
15	5.69	20
20	5.80	20
30	5.65	21

Initial Conditions: 40 g NaCN, 69°C, pH 12.0

Final Conditions: 67°C, pH 12.6

TABLE III-35

TEST NUMBER 35

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.36	19
2	2.48	16
3	3.21	16
4	3.74	15
6	4.53	15
8	4.98	18
10	5.25	16
15	5.73	20
20	5.94	18
30	6.00	22

Initial Conditions: 40 g NaCN, 67°C, pH 12.0

Final Conditions: 66°C, pH 12.65

TABLE III-36

TEST NUMBER 36

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.40	20
2	2.53	20
3	3.27	21
4	3.76	17
6	4.51	16
8	4.90	18
10	5.19	21
15	5.56	16
20	5.65	18
30	5.84	20

Initial Conditions: 40 g NaCN, 70°C, pH 12.0

Final Conditions: 68°C, pH 12.6

TABLE III-37

TEST NUMBER 37

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.61	17
2	0.97	21
3	1.38	20
4	1.74	19
6	2.35	17
8	2.81	22
10	3.22	17
15	3.85	17
20	4.29	19
30	4.76	17

Initial Conditions: 40 g NaCN, 5°C, pH 12.0

Final Conditions: 5°C, pH 12.4

TABLE III-38

TEST NUMBER 38

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.50	16
2	0.90	17
3	1.29	20
4	1.64	17
6	2.24	19
8	2.72	18
10	3.08	20
15	3.78	20
20	4.22	21
30	4.71	18

Initial Conditions: 40 g NaCN, 3°C, pH 12.3

Final Conditions: 3°C, pH 12.4

TABLE III-39

TEST NUMBER 39

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.53	22
2	0.98	20
3	1.38	19
4	1.71	18
6	2.30	18
8	2.76	16
10	3.13	17
15	3.82	18
20	4.21	18
30	4.78	18

Initial Conditions: 40 g NaCN, 3°C, pH 12.2

Final Conditions: 2°C, pH 12.5

TABLE III-40

TEST NUMBER 40

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.05	20
2	1.90	22
3	2.55	17
4	3.01	19
6	3.71	16
8	4.20	17
10	4.49	17
15	5.00	16
20	5.29	17
30	5.59	19

Initial Conditions: 40 g NaCN, 26°C, pH 12.0, -35, +48 mesh

Final Conditions: 28°C, pH 12.4

TABLE III-41

TEST NUMBER 41

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.24	20
2	2.12	17
3	2.83	17
4	3.16	16
6	3.88	15
8	4.34	18
10	4.61	21
15	5.04	21
20	5.24	23
30	5.37	20

Initial Conditions: 40 g NaCN, 300 g $Na_2S \cdot 9H_2O$, 26°C, pH 12.8
-35, +48 mesh

Final Conditions: 28°C, pH 13.2

TABLE III-42

TEST NUMBER 42

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.41	17
2	2.44	20
3	3.15	28
4	3.69	32
5	4.04	23
6	4.37	20
8	4.74	18
10	5.02	23
15	5.55	18
20	5.55	18

Initial Conditions: 40 g NaCN, $25\frac{1}{2}$°C, pH 12.0, -48, +65 mesh

Final Conditions: $26\frac{1}{2}$°C, pH 12.4

TABLE III-43

TEST NUMBER 43

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	1.41	18
2	2.41	16
3	3.34	17
4	3.60	15
5	5.22	14
6	4.25	16
8	4.67	17
10	4.93	17
15	5.40	16
20	5.57	20

Initial Conditions: 40 g NaCN, 25°C, pH 12.0, -48, +65 mesh

Final Conditions: 26°C, pH 12.4

TABLE III-44

TEST NUMBER 44

Time, min	Copper Concentration, gpl	Sample Volume, ml
$\frac{1}{2}$	0.88	16
1	1.73	18
2	2.99	17
3	3.85	18
4	4.55	16
5	5.06	18
6	5.47	17
8	6.00	16
10	6.49	17
15	7.10	16

Initial Conditions: 60 g NaCN, 10 ml glacial acetic acid, 25°C, pH 9.92, 2.51 liter

Final Conditions: 27°C, pH 9.9

TABLE III-45

TEST NUMBER 45

Time, min	Copper Concentration, gpl	Sample Volume, ml
1	0.86	23
2	1.48	18
3	1.93	18
4	2.29	17
5	2.59	17
6	2.83	16
8	3.21	21
10	3.51	21
15	3.95	21
20	4.18	18

Initial Conditions: 60 g NaCN, 50 ml glacial acetic acid, 26°C, pH 8.9, 2.55 liters

Final Conditions: 27°C, pH 6.8

TABLE III-46

TEST NUMBER 46

Time, min	Copper Concentration, gpl	Sample Volume, ml
$\frac{1}{2}$	0.86	22
1	1.58	22
2	2.75	22
3	3.63	18
4	4.24	16
5	4.76	16
6	5.24	22
8	5.76	20
10	6.19	22
15	6.87	20

Initial Conditions: 60 g NaCN, 20 ml glacial acetic acid, 26°C, pH 9.5

Final Conditions: 28°C, pH 8.5

TABLE III-47

TEST NUMBER 47

Time, min	Copper Concentration, gpl	Sample Volume, ml
$\frac{1}{2}$	0.54	20
1	1.46	23
2	2.12	21
3	2.94	17
4	3.52	20
5	4.01	23
6	4.46	17
8	5.12	20
10	5.60	20
15	6.35	21

Initial Conditions: 60 g NaCN, 5 ml glacial acetic acid, 25°C, pH 10.4

Final Conditions: 27°C, pH 11.9

TABLE III-48

TEST NUMBER 48

Time, min	Copper Concentration, gpl	pH	Temperature °C	Sample Volume, ml
1	0.27	12.25	25.0	16
2	0.54	12.32	25.5	18
3	0.77	12.39	25.5	18
4	1.01	12.44	26.0	17
6	1.47	12.54	26.0	17
8	1.85	12.57	26.0	22
10	2.15	12.63	26.0	20
15	2.80	12.72	26.5	17
20	3.33	12.76	27.0	18
30	4.05	12.82	27.0	18

Initial Conditions: 40 g NaCN, 25°C, pH 12.10, 600 rpm

TABLE III-49

TEST NUMBER 49

Time, min	Copper Concentration, gpl	pH	Temperature, °C	Sample Volume, ml
1	0.79	12.28	28.0	16
2	1.44	12.53	28.0	18
3	2.04	12.55	28.5	18
4	2.52	12.65	28.5	19
6	3.21	12.69	29.0	18
8	3.68	12.67	29.0	20
10	4.03	12.69	29.0	18
15	4.56	12.76	29.0	20
20	4.86	12.75	29.0	23
30	5.24	12.79	29.0	20

Initial Conditions: 40 g NaCN, 27°C, pH 12.05, 1600 rpm

TABLE III-50

TEST NUMBER 50

Time, min	Copper Concentration, gpl	pH	Temperature, °C	Sample Volume, ml
1	0.72	12.43	26.0	20
2	1.37	12.55	26.5	20
3	1.47	12.62	27.0	19
4	2.29	12.68	27.0	22
6	2.93	12.73	27.0	17
8	3.03	12.76	27.5	18
10	3.28	12.78	27.5	18
15	3.62	12.78	28.0	18
20	3.96	12.80	28.0	18
30	4.34	12.85	28.0	24

Initial Conditions: 40 g NaCN, 26°C, pH 12.20, 1300 rpm

TABLE III-51

TEST NUMBER 51

Time, min	Copper Concentration, gpl	pH	Temperature, °C	Sample Volume, ml
1	0.57	12.28	27.5	22
2	1.10	12.38	28.0	20
3	1.53	12.44	28.0	21
4	2.20	12.49	28.0	20
6	2.84	12.54	28.0	14
8	3.35	12.64	28.0	20
10	3.66	12.67	28.5	23
15	4.33	12.70	28.5	19
20	4.70	12.73	28.5	19
30	4.13	12.77	28.0	22

Initial Conditions: 40 g NaCN, 27°C, pH 11.97, 900 rpm

TABLE III-52

TEST NUMBER 52

Time, min	Copper Concentration, gpl	pH	Temperature, °C	Sample Volume, ml
1	0.38	12.32	24.5	20
2	0.96	12.42	24.5	20
3	1.39	12.48	25.0	23
4	1.78	12.53	25.0	20
6	2.48	12.58	25.0	12
8	2.45	12.66	25.5	30
10	3.35	12.69	26.0	24
15	3.92	12.74	26.0	22
20	4.37	12.77	26.0	20
30	4.85	12.79	26.0	25

Initial Conditions: 40 g NaCN, 24.5°C, pH 12.05, 1100 rpm

TABLE III-53

TEST NUMBER 53

Time, min	Copper Concentration, gpl	pH	Temperature, °C	Sample Volume, ml
1	0.31	12.10	25.0	25
2	0.84	12.18	25.0	22
3	1.23	12.24	25.0	21
4	1.57	12.28	25.0	22
6	2.14	12.36	25.5	20
8	2.54	12.40	26.0	22
10	2.97	12.42	26.0	19
15	3.70	12.48	26.0	20
20	4.21	12.52	26.0	19
30	4.76	12.55	26.0	16

Initial Conditions: 40 g NaCN, 24.5°C, pH 11.98, 700 rpm

TABLE III-54

TEST NUMBER 54

Time, min	Copper Concentration, gpl	pH	Temperature, °C	Sample Volume, ml
1	0.66	12.24	25.5	23
2	1.26	12.34	26.0	20
3	1.72	12.41	26.0	17
4	2.10	12.44	26.0	15
6	2.74	12.50	26.5	20
8	3.19	12.54	27.0	20
10	3.60	12.56	27.0	20
15	4.24	12.60	27.0	17
22	4.68	12.64	27.5	22
30	5.04	12.64	27.5	20

Initial Conditions: 40 g NaCN, 25°C, pH 12.05, 900 rpm

TABLE III-55

TEST NUMBER 55

Time, min	Copper Concentration, gpl	pH	Temperature, °C	Sample Volume, ml
1	0.74	12.27	25.0	22
2	1.40	12.38	25.0	22
3	1.90	12.45	25.0	20
4	2.33	12.50	26.0	20
6	2.98	12.57	26.0	15
8	3.46	12.62	26.0	20
10	3.78	12.65	26.5	20
15	4.34	12.69	27.0	22
20	4.72	12.72	27.0	21
30	5.08	12.74	27.0	18

Initial Conditions: 40 g NaCN, 25°C, pH 12.09, 1100 rpm

TABLE III-56

TEST NUMBER 56

Time, min	Copper Concentration, gpl	pH	Temperature, °C	Sample Volume, ml
$\frac{1}{2}$	0.68	9.96	26.0	20
1	1.35	9.95	26.0	20
2	2.47	9.93	26.0	18
3	3.26	9.92	26.5	20
4	3.86	9.91	26.5	15
5	4.50	9.90	27.0	20
6	4.88	9.89	27.0	17
8	5.54	9.87	27.0	23
10	5.95	9.85	26.5	20
15	6.69	9.80	26.0	20

Initial Conditions: 60 g NaCN, 10 ml glacial acetic acid, 25°C, pH 9.96, 1600 rpm, 2.51 liter

TABLE III-57

TEST NUMBER 57

Time, min	Copper Concentration, gpl	pH	Temperature, °C	Sample Volume, ml
½	0.74	9.34	26.5	17
1	1.36	9.28	26.5	17
2	2.37	9.17	27.0	19
3	3.09	9.05	27.0	17
4	3.68	8.92	27.0	21
5	4.03	8.79	27.0	16
6	4.33	8.67	26.5	21
8	4.80	8.40	26.5	20
10	5.22	8.18	26.0	20
15	5.85	7,86	26.0	23

Initial Conditions: 60 g NaCN, 30 ml glacial acetic acid, 26°C, pH 9.39, 1600 rpm

TABLE III-58

TEST NUMBER 58

Time, min	Copper Concentration, gpl	pH	Sample Volume, ml
½	0.68	10.36	20
1	1.20	10.46	20
2	2.15	10.50	19
3	2.95	10.80	17
4	3.52	11.11	16
5	4.06	11.54	22
6	4.48	11.71	17
8	5.06	12.00	20
10	5.58	12.15	20
15	6.34	12.21	18

Initial Conditions: 60 g NaCN, 5 ml glacial acetic acid, 25°C, pH 10.27, 1600 rpm

TABLE III-59

TEST NUMBER 59

Time, min	Copper Concentration, gpl	pH	Sample Volume, ml
½	0.61	9.54	20
1	1.28	9.52	21
2	2.22	9.46	23
3	3.10	9.40	20
4	3.75	9.32	23
5	4.32	9.24	17
6	4.67	9.15	18
8	5.32	8.98	22
10	5.58	8.80	23
15	6.48	8.46	16

Initial Conditions: 60 g NaCN, 20 ml glacial acetic acid, 25°C, pH 9.56, 1600 rpm, 2.52 liter

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