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Leaching of Chalcopyrite with Sodium hypochlorite

Ravinder Kumar Garlapalli

**Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Chemical Engineering**

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2010

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Leaching; Reagent consumption ratio.**

Abstract

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Ravinder Kumar Garlapalli

Chalcopyrite is the most important copper mineral source and also a refractory mineral for leaching. Several processing routes have been proposed to overcome the environmental problems related to copper extraction from chalcopyrite. In this study, the leaching of chalcopyrite has been investigated with a new reagent sodium hypochlorite (NaOCl). Experiments were carried out in two stages: conversion of chalcopyrite to cupric oxide with NaOCl solution in the first stage, followed by dissolution of the cupric oxide to cupric ion with 1 normal sulfuric acid at room temperature in the second stage. In the first stage leaching, the initial pH varied from 12.5 to 13.7; the temperature, from 35 to 75°C; NaOCl concentration, from 0.2 to 0.85 molar; and the chalcopyrite dosage, from 1 to 10 grams/500 ml. The leaching conversion showed a maximum (68.3%) around pH 13.2 at 0.5 molar of hypochlorite concentration and 65°C in 1 hour. The reagent consumption ratio, defined as the number of moles of hypochlorite consumed to leach one mole of chalcopyrite is found to be much higher than its stoichiometric ratio of 8.5. It reached 57.6 when the solid dosage was 1 gram/500 ml and decreased to 12.9 when the solid dosage was increased to 10 grams/500 ml. It was found that the leaching rate of chalcopyrite in the first stage was controlled by chemical reaction with the activation energy of 50.2 kJ/mol (12.0 kcal/mol). A leaching scheme was identified in which 98% chalcopyrite was leached by adding hypochlorite stock solution stepwise in less than three hours.

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1. Introduction

Chalcopyrite (CuFeS_2) is the most abundant copper mineral and an important raw material source for copper production. Chalcopyrite is processed by both pyrometallurgical and hydrometallurgical processes to extract the copper metal. In the conventional pyrometallurgical smelting processes, chalcopyrite ore is concentrated by flotation to produce a high grade ore which is smelted in a furnace at high temperatures for recovery of copper. The Hydrometallurgical process involves crushing, leaching and other treatment steps such as solvent extraction and electrowinning usually at low temperatures. Currently, the majority of the tonnages of copper extraction from chalcopyrite are produced by pyrometallurgical processes.

Pyrometallurgical processes produce sulfur dioxide (SO_2) emissions which are then either converted to sulfuric acid or released to the atmosphere. However, the conversion of sulfur dioxide to sulfuric acid needs sufficient market demand for acid¹. Venting of SO_2 gases to the atmosphere causes acid rain; the United States government has tightened regulations on the emission of sulfur oxide gases under title IV of the 1990 Amendments of the Clean Air Act (CAA)² which demands complete SO_2 capture.

To overcome the environmental and economic drawbacks of SO_2 emissions, sulfuric acid market saturation and high operational costs of pyrometallurgical processes, constant efforts have been made to switch to hydrometallurgical processes. Hydrometallurgy offers alternatives for producing copper from sulfide concentrates without producing SO_2 and to recover most of the sulfur in the solid state³. Numerous processes have been developed in the past; still only few operate at full scale commercially. These processes used various reagents like ferric sulfate,

ferric chloride, nitric oxide, ammonia and oxygen. Except for the process using oxygen and ammonia, all the other processes produce an elemental sulfur layer which inhibits the leaching rate. Research on the leaching of chalcopyrite with ferric sulfate or ferric chloride has been studied extensively in the past and a vast number of papers are available in the literature. The general problem with these processes is that the leaching kinetics of chalcopyrite is slow.

The purpose of this study is to investigate the leaching of chalcopyrite with a new reagent sodium hypochlorite to propose an economical and environmentally friendly industrial process for recovery of copper.

The objectives are:

1. To determine the effects of following parameters on the leaching rate/ conversion of chalcopyrite with sodium hypochlorite.
 - Temperature,
 - Initial pH,
 - Sodium hypochlorite concentration and
 - Chalcopyrite dosage.
2. To establish a reaction kinetic model to explain the leaching rate of chalcopyrite with sodium hypochlorite solution.

2. Literature Review

Copper has been in use for over five thousand years. With a sharp increase in the global copper production in the past 25 years (Figure 2.1), the availability of high grade copper ores is bound to decline⁴.

Figure 2. 1 World copper production since 1981-2005 (Data from Edeltein⁵ for the years 1981-2000 and from the International Copper Study Group⁶ for the years 2001- 2005).

According to the International Copper Study Group (ICSG), during the last decade world copper mineral production from mines increased by 30% from 11.5 million metric tons in 1997 to 15 million metric tons in 2006. During this period the production of copper by the

pyrometallurgical methods rose by 24% while by the hydrometallurgical processes rose by as high as 63%⁷. Furthermore, world copper mineral production from mines is expected to increase by 9% to 17.9 million metric tons by 2009 owing to mine developments and increased demand capacity of the copper metal. Therefore, it is considered essential to develop new alternative processes to the traditional pyrometallurgical processes one of which may be the hydrometallurgical process.

The hydrometallurgical copper processing generally consists of three fundamental operations⁸:

- Leaching of copper ore preferably with weak acid.
- Solvent extraction, in which the leach solution is mixed with an organic solvent, to recover copper from being acidic. The copper is then stripped from the organic solution with a strong acidic solution to obtain a highly concentrated copper rich solution.
- Electrowinning, where the copper rich solution is passed through a series of electrolytic cells to deposit copper on the cathodes.

There may arise, a question as to why first leaching in weak acid is followed by solvent extraction and again stripping using strong acid. When chalcopyrite is leached with sulfuric acid large amounts of iron enter into the solution which has to be precipitated before copper is recovered in the electrowinning process⁹. The presence of iron causes problems during the operation of the electrolytic cells in the electrowinning process, leading to a poor quality product and reduction of current efficiency.

2.1 Research Work

Much research work has been conducted on leaching of chalcopyrite using various reagents such as sulfate, chloride, nitric acid, ammonia and biological systems. Some of them are discussed below.

Sulfate Processes

The leaching of chalcopyrite with acidic ferric sulfate solution has been studied by Munoz *et al.*³ and Dutrizac¹⁰. The leaching of chalcopyrite in ferric sulfate system occurs by the reaction,

Munoz *et al.*³ observed that the leaching of 12 μm chalcopyrite particles in 0.25 M $\text{Fe}_2(\text{SO}_4)_3$, 1 M H_2SO_4 at 90 °C took 100 hours to reach a conversion of 60%. Similar results were also observed by Dutrizac¹⁰ when chalcopyrite was leached at 90°C in 0.2 M $\text{Fe}(\text{SO}_4)_{1.5}$, 0.3M H_2SO_4 . These authors suggested that the slow conversions are due to the formation of an elemental sulfur layer on the chalcopyrite surface which becomes a diffusion barrier and hence the rate is limited by the diffusion of ferric ion through the sulfur product layer.

Chloride Processes

The leaching of chalcopyrite with chloride solutions has gained importance over the last 30 years. The chloride processes have several distinct advantages over sulfate processes which include faster reaction kinetics of chalcopyrite leaching with chloride solutions than sulfate

solutions, high solubility of copper and ferric ion, and the formation of porous elemental sulfur product¹¹.

Leaching of chalcopyrite in chloride solutions was investigated by several investigators. Ferric chloride leaching of chalcopyrite was studied by Dutrizac¹⁰ and Palmer *et al.*¹². Palmer *et al.* observed that their leaching rate followed the chemical reaction controlled kinetics model at 0.5 to 1 M ferric chloride. Dutrizac observed that the ferric chloride system is 3 times more aggressive than the ferric sulfate system. These authors attributed that the reaction was under mixed electrochemical control and electron transfer occurring from iron chloride complexes.

Bonan *et al.*¹³ and Lundstrom *et al.*¹⁴ reported that the leaching of chalcopyrite by CuCl₂ takes place as shown

Bonan *et al.*¹³ studied the chalcopyrite leaching rates by CuCl₂ in strong NaCl solutions in the temperature range from 75 °C to 104 °C, chloride ion concentration of 4 mol/dm³ NaCl and the ratio of Cu²⁺/Cu⁺ from 0.5 to 7. It was observed that the leaching rates were much faster when the Cu²⁺/Cu⁺ ratio was increased and also when the Cl⁻ ion concentration was increased. It took 4 hours at 90 °C, 4 mol/dm³ NaCl and Cu²⁺/Cu⁺ ratio of 1 to reach a conversion of 62%. They found that the reaction was controlled by diffusion above 85 °C.

Lundstrom *et al.*¹⁴ studied the effect of temperature (70 °C to 90 °C), pH (1 to 3) and the concentration of cupric ion (0.09 to 26.6 g/L) on the dissolution of chalcopyrite. The authors observed that for pH between 2 and 2.5, and with increasing cupric ion concentration above 9 g/L the dissolution rates increased. They also proposed that with cupric ion concentrations above

9 g/L, at pH 2 and at a temperature of 85 °C, the rate is controlled by diffusion, but with lower cupric ion concentration, the reaction is under mixed or chemical control.

Lu *et al.*¹⁵ have studied the effect of chloride ions on the leaching rate of chalcopyrite using oxygenated solutions. They found that when the chloride ion was absent, only 30% of copper was extracted, but with the presence of chloride 98% of the copper was extracted over a period of 9 hours. The authors also observed that chloride concentration above 0.5 M does not increase the leaching rates. Similar results have been obtained by Palmer *et al.*¹². They found that the rate increases until the chloride concentration reaches 0.5 M but becomes independent of concentration for values greater than 1 M.

2.2 Industrial Process

Based on the electrochemical dissolution of chalcopyrite in the presence of ammonia, chloride and sulfate solutions, various processes have been developed but have not progressed beyond laboratory or pilot scale. Some of the processes are abandoned and few are currently operating at pilot scale.

Abandoned processes

1. Cymet process
2. Arbiter process
3. Clear process

Current processes

1. Outokumpu
2. Galvanox
3. Intec process

Cymet process:

Cyprus metallurgical corporation developed the Cymet process at the pilot plant scale^{16,17}.

In this process chalcopyrite ore is partially leached according to the reaction 2.3 and the slurry is separated in a thickener and is introduced to a diaphragm electrolytic cell. The underflow goes to the anode side for further dissolution of unreacted chalcopyrite with hydrochloric acid.

The overflow (CuCl) goes to the cathode side for reduction to Cu^0 , according to reaction 2.4. The solution from the cathode of the copper electro-cell is purified and then goes to the iron electro cell for reduction of iron at the cathode and regeneration of FeCl_3 at the anode. The overall reaction for the entire process showing the products as elemental copper, iron and sulfur is

Problems encountered with the Cymet process are the operation of electrolytic cells, coupled with poor quality product needing further refining.

Clear process:

This process also uses ferric chloride as reagent similar to Cymet process. Leaching takes place in two stages. In the first stage chalcopyrite ore is oxidized to cupric chloride upon reaction with ferric chloride according to the reaction 2.6

In the second stage the cupric ions which are produced from the first stage are used as an oxidizing reagent in the second stage as shown

The cuprous chloride thus obtained is mixed with NaCl to form CuCl_2^- anion and electrolyzed in a diaphragm cell to produce copper. The purity of the copper powder produced was poor due to the lack of leach solution purification¹⁸.

Arbiter/ Ammonia process:

This process was developed in 1970 by Arbiter. The process is based on leaching of chalcopyrite concentrates with ammonia at 75 - 80 °C in presence of oxygen to form copper ammine sulfate and iron hydroxide¹⁹.

After filtering the solids, copper from the pregnant leach solution is recovered by solvent extraction, stripped by sulfuric acid, and then copper is removed by electrowinning. The ammonia is recovered by treating the ammonium sulfate with calcium oxide and steam to produce calcium sulfate (gypsum). Gypsum is not a desirable waste and has a limited market.

This ammonia recovery step as well as the residue washings proved to be technically difficult and economically unsound and was the main reason for the shut down.

Most recently, novel processes in chloride media promoted by Intec, Galvanox and Outokumpu addressed the problem of purity and developed new processes.

Outokumpu HydroCopper process:

In this process, copper concentrate is leached into a strong sodium chloride solution containing CuCl_2 , in agitated reactors at a temperature 85-90 °C. Air is blown to precipitate iron as the oxide or hydroxide at pH of 1.2- 2.5. Chalcopyrite is leached in the chloride solution with the help of Cu^{2+} according to the reaction

Ferrous iron is oxidized as

The pregnant leach solution contains Cu^+ , Cu^{2+} and other metals which are purified. Copper is recovered from the purified leach solution by precipitating cuprous oxide. The pure, solid copper is melted and cast directly into shapes. The main key of this process is the regeneration of reactants using chlor-alkali electrolysis technology from the spent brine: caustic soda, chlorine for oxidation of the leach solution; and hydrogen to reduce the cuprous oxide to copper²⁰.

Galvanox process:

This process is based on leaching by making a galvanic couple between the more “electrochemically noble” pyrite, and chalcopyrite thus enhancing the leaching rate under

atmospheric, medium temperature (80 °C) conditions in acidic iron sulfate solution. The presence of pyrites provides the catalytic effect for the leaching of chalcopyrite without passivation²¹.

3. Theory

Hypochlorous acid and Hypochlorite leaching

The solution chemistry of chlorine is characterized by the following equilibria:

The above equilibrium constants are those at 25°C and obtained from Reference 22.

Hypochlorite (OCl^-) is predominant at high solution pH such as above 10. As pH decreases, hypochlorous acid (HClO) becomes predominant. The pH where the concentrations of the two species are the same falls in at 7.5. As the pH further decreases, hypochlorous acid turns to aqueous chlorine which will ultimately escape from the solution as gaseous chlorine.

Cho studied the leaching of chalcopyrite with hypochlorous acid (HClO), the predominant chlorine derivative in concentration at acidic conditions (pH 3-7)²². It was found that the leaching of -65 + 100 mesh sized particles with 0.23 molar concentration of hypochlorous acid at room temperature achieved about 90% conversion in 1 hour at room temperature. The pH was maintained at 4 by adding NaOH solution.

In the present study chalcopyrite is leached with sodium hypochlorite (NaOCl), the predominant chlorine derivative in concentration at high pH levels. The leaching takes place in

two separate stages. In the first stage, the mineral is converted to cupric oxide with hypochlorite which is subsequently dissolved in an acid solution in the second stage.

The leaching of chalcopyrite with hypochlorite may take place by electrochemical reaction. The anodic reaction may be written as

And the cathodic reaction is

The E° value of reaction 3.5 is for the reduction reaction. The difference in E° between the anodic and cathodic reactions is large, suggesting that the overall reaction will be thermodynamically feasible under normal conditions. The overall reaction will be written as

It can be seen that 8.5 moles of hypochlorite are required to leach one mole of chalcopyrite or the stoichiometric ratio of hypochlorite is 8.5. Since the first stage leaching is carried at high pHs, the converted CuO may be dissolved to oxy-anion, CuO_2^{2-} . The reaction is written as

It is seen from the equilibrium constant of reaction 3.8 that the oxy-anion concentration is essentially zero unless the pH becomes very high (e.g., 13). The oxy-anion concentration in the ppm range was observed in the first stage leaching in this study.

In the second stage, CuO is leached with sulfuric acid. The leaching reaction is written as

In the study, chalcopyrite ore is partially leached with sodium hypochlorite in the first stage in which the Cu is converted to $\text{CuO}_{(s)}$, Fe is converted to $\text{Fe}(\text{OH})_{3(s)}$ and sulfur is liberated into the solution which is removed as sulfate. The slurry is separated by filtration. In the second stage the copper oxide is leached with sulfuric acid to cupric sulfate.

The advantage of using sodium hypochlorite is, in the second stage the leaching of copper oxide at a constant pH with sulfuric acid (e.g., $\text{pH} > 3$) may prevent the dissolution of iron content, which will benefit the subsequent processes of solvent extraction and electrowinning.

4. Experimental Methods

4.1 Materials

Chalcopyrite samples purchased from Wards Mineral (Rochester, NY) were used in this study. Lumps of samples were crushed and screened to give a fraction of 200 x 270 mesh size. This sized fraction was further concentrated by a conventional flotation technique using amyl xanthate as a collector and MIBC (methyl isobutyl carbinol) as a frother. Chemical analyses were conducted by dissolving the sized fraction with aqua-regia solution and analyzing the leach solution with an atomic absorption unit (Perkin Elmer model) in order to determine the purity of chalcopyrite. The results showed that the average composition was 88.62% CuFeS_2 and 4.7% ZnS .

Hypochlorite solutions used for the leaching experiments were prepared by diluting the hypochlorite stock solution, which was purchased from a chemical supplier (VWR). The hypochlorite concentration was about 1.8 molar. As soon as it was received, extra NaOH pellets of 7 g/liter were added and stored in a refrigerator to minimize the loss due to evaporation.

4.2 Leaching experiments with hypochlorite

The leaching experiments with chalcopyrite were conducted in a one-liter reactor placed in a constant-temperature paraffin-oil bath. Figure 4.1 shows the schematic diagram of the experimental setup. The reactor has four necks. The central neck is equipped with a stirrer connected to a motor running at 500 rpm. One of the side necks is fitted with a reflux condenser which is used to prevent excessive evaporation at high temperatures. The next one is equipped with a thermometer which is used to measure the temperature of the solution. And the last one is

used for charging the mineral sample, and pipetting out solution for analysis of chlorine and sulfate concentrations.

Figure 4. 1 Schematic diagram of leaching apparatus.

1. Temperature controller
2. Reflux condenser
3. Stirrer
4. Sampling pipette
5. Glass cover
6. Glass reaction vessel
7. Paraffin oil bath

Five hundred milliliters of hypochlorite solution at the desired concentration were charged into the reactor. When the leach solution reached the desired temperature, a 2-5 ml solution was withdrawn from the reactor and analyzed for hypochlorite. It was found that the original concentration did not decrease during the heating period for all the experiments conducted in this study. Then a predetermined amount of chalcopryrite sample was added to the reactor. The leaching continued for up to 1 hour. Twenty-milliliter liquid samples were withdrawn from the reactor at 15, 30 and 60 minutes. Shortly before each sample was taken (about 10 seconds), the stirring was momentarily stopped in order to minimize the solid content in the sample. Treatment of the samples will be described later under section 4.4. After leaching, the chalcopryrite slurry was vacuum filtered and washed three times, each time with a 150-200 ml 0.5 molar NaOH solution to remove remnant hypochlorite. Then the solid was similarly washed with deionized water three times to remove sodium hydroxide. Finally the filtered and washed chalcopryrite was dried under infrared light, and was used for acid leaching in the second stage.

4.3 Leaching Experiments with Sulfuric Acid

The filtered and dried chalcopryrite from the first stage was repulped in 500 ml of 1 normal sulfuric acid. In this second stage, the converted cupric oxide was leached with the sulfuric acid. The same reactor was used. The temperature was room temperature. The stirring speed was 500 rpm. The leaching continued for 90 minutes. These conditions were found to be rigorous enough to completely leach cupric oxide through preliminary experiments. At the end of the leaching, the slurry was vacuum filtered and the filtrate was diluted properly before analyzing for copper by atomic absorption.

4.4 Analyses

The chlorine concentration of the hypochlorite solution was analyzed according to American Society for Testing and Materials (ASTM) method D2022-64. Solid potassium iodide was added to the chlorine-containing solution and dissolved. The solution was acidified by adding concentrated acetic acid. The aqueous chlorine oxidizes the iodide to iodine, which was titrated by sodium thiosulfate solution, using starch as an indicator.

In the preliminary study, three separate experiments were conducted to complete one leaching curve during the first stage at three different times such as 1, 2 and 3 hours. The largest disadvantage of this method was that since different solid samples were used each time, the leaching curve might produce some errors that could not be specified. Thus, a new method was designed in this study. Approximately 20 ml of solution was withdrawn from the reactor using a 20-ml pipette each time at 15, 30 and 60 minutes, and filtered using a Whatman No.42 filter paper. A 10-ml solution was pipetted from the filtrate and used to analyze the sulfate content; a 2-5-ml solution was used to analyze the hypochlorite concentration; and the rest was returned to the reactor. The conversion of chalcopyrite during the first stage at each 15 and 30 minutes was determined using the concentration of sulfate ion and the molar ratio of sulfate to cupric at 60 minutes. This ratio at 60 minutes was determined later by the cupric concentration from the second stage leaching. This method is based on the assumption that the molar ratio of sulfate to cupric is maintained throughout the first stage, which is reflected on reaction 2.18. The average ratio was observed to be about 2.5. Since the theoretical ratio is 2 as shown in reaction 2.18, the higher value may be due to other sulfate sources such as ZnS. However, this experimental ratio of 2.5 may verify that the sulfur product from the leaching of chalcopyrite is sulfate rather than elemental sulfur.

Sulfate was analyzed by ASTM D 3177-84 which is designed to analyze total sulfur in coal. This method is based on precipitation of sulfate as barium sulfate by adding barium chloride solution, followed filtration and ignition. The pH of the filtrate before adding barium chloride was adjusted to 2.2 by using a pH meter instead of using methyl orange because it was decolorized by hypochlorite.

Only once, chloride ion in the hypochlorite stock solution was analyzed using ASTM D 2361-85 which is designed to analyze chlorine in coal. This method is based on the back titration of silver ion after precipitating chloride ion with excessive silver nitrate with potassium thiocyanate using ferric ammonium sulfate as an indicator.

Copper Analysis by Atomic Absorption

Atomic absorption spectrophotometry is a standard laboratory technique for solution analysis in which the concentration of an element in the solution is determined by measuring the absorption of radiation in the atomic vapor produced from the sample at a wavelength that is specific and characteristic of the element. According to Beer's law the absorbance should be linear function of concentration. At high concentrations of absorbing species deviation from linearity is observed. Therefore, strong solution should be diluted so that the concentration is in linear working range. The linear working range of copper is up to 5 ppm (mg/ liter). 100 ml of standard copper solutions of 1, 2, 3, 4 and 5 ppm are prepared by diluting 1000 ppm copper stock solution.

5. Results

5.1 XRD patterns:

Figure 5.1 X-Ray diffraction spectra of the unleached chalcopyrite mineral sample.

The XRD pattern for the unleached chalcopyrite mineral sample is shown in Figure 5.1. As seen in Figure 5.1, the chalcopyrite (CuFeS_2) is characterized by two-theta peak values of 29.4, 49.1 and 57.9 degrees. Figure 5.2 shows the XRD patterns for the leached/converted chalcopyrite sample. The leaching experiment conducted at 55°C, 0.5 molar of hypochlorite, pH

13.15 and 1 hour. The leached sample washed with sodium hydroxide solution and deionized water, as described previously. The leaching conversion found to be about 67%.

Figure 5.2 X-Ray diffraction spectra of the leached chalcopryrite sample after first stage of leaching (55°C, 0.5molar OCl⁻, 3grams chalcopryrite, initial pH 13.15).

The two-theta peak values of 29.4, 49.1 and 57.9 are maintained as shown in Figure 5.2, representing the unleached chalcopryrite. As demonstrated in figure 5.2, the two two-theta peaks at 35.6 and 38.8 degrees coincided with CuO pattern, verifying that the leach product is CuO.

5.2 Effect of stirring speed:

Figure 5.3 shows the results of a series of experiments conducted to determine the effect of stirring speed²⁴. Experimental conditions were temperature at 85°C, pH 13 and hypochlorite concentration 0.5 molar. The results reveal that the leaching rate increases as the stirring speed increases from 265 to 500 rpm. Nonetheless, the stirring speed of 500 is used for all the subsequent experiments.

Figure 5.3 Effect of stirring speed on leaching conversion of chalcopyrite (85 °C, hypochlorite concentration 0.5 M, pH - 13.00).

5.3 Effect of pH:

Figure 5.4 Effect of initial pH on chalcopyrite leaching conversion (55°C, 0.5 molar OCl⁻, 3 grams chalcopyrite, 60 minutes reaction time).

Figure 5.4 shows the effect of initial pH on leaching conversion of chalcopyrite to cupric oxide at 1 hour during the first stage of leaching. The leaching conversion is defined as the fraction of chalcopyrite leached into cupric oxide. The initial pH varied from 12.5 to 13.7, at a temperature of 55°C, hypochlorite concentration of 0.5 molar, with chalcopyrite dosage of 3 grams in 500 ml. It is observed from the experimental results that the leaching conversion shows

a maximum at pH 13.15-13.20. Figure 5.5, shows the depletion of hypochlorite concentration as a function of time during the first stage leaching for the same experiments as for Figure 5.4.

Figure 5.5 Effect of pH on hypochlorite depletion (55°C, 0.5 molar OCl-, 3 grams chalcopryrite).

It can be seen in Figure 5.5 that the pH values yielding the maximum conversion coincide with curves of the least hypochlorite depletion, with the exception for pH 12.99, and that the lower conversions at both pH ends in Figure 5.4 coincide with the curves of higher reagent depletion.

Table 5. 1 Effect of pH on Leaching of Chalcopyrite in First Stage (55 °C, 0.5 molar OCl⁻, 3grams chalcopyrite).

NaOH added (grams)	0	2	4	8	12	20
Initial pH	12.5	12.99	13.15	13.20	13.25	13.70
Final pH	11.9	12.55	12.88	12.91	12.99	13.2
Concentration of Cu ⁺⁺ (ppm) in the first stage	0.19	0.21	0.3	0.77	3.24	26.54
Hypochlorite consumption*	33.09	28.15	25.23	25.18	27.30	40.45

*Hypochlorite consumption is defined as the number of moles of hypochlorite consumed to the number of moles of chalcopyrite leached.

Table 5.1 gives numerical data for this effect. The soluble cupric concentration (the cupric oxy-anion) increases as pH increases and reaches 26.54 ppm at pH 13.7. Table 5.1 also gives hypochlorite consumption ratio at various pHs. This is calculated by dividing the number of moles of hypochlorite depleted by the number of moles of chalcopyrite leached. The ratio shows the minimum value of 25.18 at pH 13.2 which yields the maximum leaching conversion.

A question arises as to the mechanism(s) which leads to the pattern of hypochlorite depletion as shown in Figure 5.5. The fast depletion at pH 12.5 is because hypochlorite is not stable at lower pHs. However, this is not the case for high hypochlorite depletion at pH 13.7. It is assumed first that the fast depletion at pH 13.7 is due to the catalysis by cupric oxy-anion. However, this could not be proven due to the inability of hypochlorite depletion from an experiment where 0.5 molar of hypochlorite in the presence of 0.5 ppm of cupric oxy-anion at 55°C and pH 13.7 was allowed to react up to 1 hour without the solid sample.

It is particularly interesting to note the effect of initial pH at 11.9. This pH is adjusted by adding 5 ml 10% sulfuric acid in 500 ml of 0.5 molar of hypochlorite. The rest of the conditions were the same as for Figure 5. The results showed that the final pH decreased to 8.3 and the cupric concentration reached 1161 ppm (63.3% conversion equivalent) and the conversion to solid cupric oxide was 18.4%. It may be surmised that at the final pH of 8.3 a significant amount of hypochlorous acid (HClO) is produced and able to leach chalcopyrite to cupric-chloride complexes.

If the hypochlorite stock solution is prepared by dissolving chlorine gas into sodium hydroxide solution, chloride concentration will be the same as that of hypochlorite. In this experiment cupric ion could be in solution at this pH because it could form complexes with chloride ions. Chloride ion was analyzed in the hypochlorite stock solution. From the result it is found that the chloride concentration (1.63 molar) was 9.4% lower than that of hypochlorite (1.8 molar). This disparity may be due to the loss of both species as gaseous chlorine during the acidification of the solution. It is concluded then from this experiment that the leaching at the initial pH of 11.9 gives completely different mechanism from experiments conducted at initial pH of 12.5 or larger.

5.4 Effect of temperature:

The effect of temperature on leaching conversion of chalcopyrite examined by varying the temperatures from 35°C to 75°C, with 3 grams of chalcopyrite and at 0.5 molar of hypochlorite. Figure 5.6 shows the results of the experiments.

Figure 5.6 Effect of temperature on chalcopyrite leaching conversion (0.5 molar OCl^- , 3 grams chalcopyrite, pH 13.15).

The leaching conversion increased with increasing temperature up to 65°C not much upon further increasing the temperature to 75°C. Experiments above 75°C could have been performed to verify the trend; however, difficulty existed in analyzing hypochlorite concentration because of its fast depletion rate. The cupric oxy-anion concentration was also

detected during this series, and was found to be 2.14 ppm at 35°C, 0.3 ppm at 55°C, and 0.23 ppm at 75°C. From this trend, it can be verified on the basis of Le Chatelier's principle that reaction 3.8 is an exothermic reaction.

Figure 5.7 Effect of temperature on hypochlorite depletion (0.5 molar OCl-, 3 grams chalcopyrite, pH 13.15)

Figure 5.7 demonstrates the depletion of hypochlorite concentration from the same series of experiments as for Figure 5.6. The solid lines in Figure 5.6 are the fitting lines for a kinetic model which will be discussed later. Also, the solid lines in Figure 5.7 are the fitting lines with a rate equation which will be discussed later as well.

Using the data of Figures 5.6 and 5.7, the hypochlorite consumption ratio at 1 hour was calculated and is presented in Figure 5.8. This ratio is defined as the number of moles of hypochlorite consumed to leach one mole of chalcopryrite.

Figure 5.8 Effect of temperature on reagent consumption ratio (55°C, 3 grams chalcopryrite, initial pH 13.15).

As shown in Figure 5.8, the consumption ratio is rather insensitive to temperature. It may be due to the fact that the hypochlorite depletion increases as the temperature increases, but the number of moles of chalcopryrite leached also increases, maintaining the ratio at roughly the same level. From Figure 5.8, the average consumption ratio is found to be around 25 which is about 3 times more than the stoichiometric ratio, if the reaction were to take place according to reaction 3.7 for which the stoichiometric ratio is 8.5.

5.5 Effect of Hypochlorite concentration:

The effect of initial concentration of hypochlorite on leaching conversion of chalcopyrite is shown in Figure 5.9. The experimental conditions are hypochlorite concentration 0.2-0.85 molar and 3 grams chalcopyrite at a temperature of 55°C and pH 13.15.

Figure 5.9 Effect of hypochlorite concentration on chalcopyrite leaching conversion (55°C, 3 grams chalcopyrite, pH 13.5).

The leaching conversion increases with increasing initial hypochlorite concentration up to 0.5 molar and then not much upon further increase. The conversion is 36.4% at 0.2 molar of hypochlorite and increases to 76.4% at 0.85 molar in 1 hour. The cupric oxy-anion concentration was also detected during this series, and was found to be 0.21 ppm at 0.2 molar and 0.44 ppm at 0.85 molar. Figure 5.10 demonstrates the depletion of hypochlorite concentration from the same series of experiments as for Figure 5.9.

Figure 5.10 Depletion of hypochlorite concentration at various initial concentrations (55 °C, 3 grams chalcopyrite, initial pH 13.15).

Figure 5.11 Effect of initial hypochlorite concentration on reagent consumption ratio at 60 minutes (55 °C, 3 grams chalcopryrite, initial pH 13.15).

Using the data of Figures 5.9 and 5.10, the hypochlorite consumption ratio at 1 hour is calculated and plotted in Figure 5.11. As shown in Figure 5.11, the consumption ratio is an almost linear function with respect to the initial hypochlorite concentration. It varies from 13.7 at 0.2 molar of hypochlorite to 38.2 at 0.85 molar. When the concentration is 0.2 molar, much of the hypochlorite depletion may be due to the leaching of the mineral; however, as the concentration increases to 0.85 molar, the depletion of hypochlorite increases disproportionately to the number of moles of chalcopryrite leached. The reason is not known at this time.

5.6 Effect of Chalcopyrite dosage:

The next series of experiments conducted to study the effect of chalcopyrite dosage with 1-10 grams of chalcopyrite in 500 ml solution at 55°C, initial pH 13.15 and 1 hour. The results are demonstrated in Figure 5.12. The leaching conversion of chalcopyrite to cupric oxide is 78.6% with 1 gram of the mineral but decreases to 40.0% with 10 grams of the mineral

Figure 5.12 Effect of chalcopyrite dosage on leaching conversion at 60 minutes (55 °C, 0.5 molar OCl-, initial pH 13.15).

Figure 5.13 Effect of chalcopyrite dosage on hypochlorite consumption ratio at 60 minutes (55 °C, 0.5 molar OCl^- , initial pH 13.15).

. Figure 5.13 shows hypochlorite consumption ratio from the same series of experiments as for Figure 5.12. The consumption ratio is as high as 57.6 with 1 gram of the mineral and decreases to 12.9 with 10 grams of the mineral.

5.7 Discussion:

A. Optimum Leaching Conditions

As shown in Figure 5.11, hypochlorite consumption ratio varies from 13.7 at 0.2 molar of hypochlorite to 38.2 at 0.85 molar. The ratio of available hypochlorite to leach one mole of chalcopyrite at 0.2 molar is 6.12 and that at 0.85 molar is 27.53. These values correspond to 0.72 and 3.24 times as much as the stoichiometric factor, respectively. Thus, in order to minimize the hypochlorite consumption ratio, the available concentration should be lower or equal to its stoichiometric value. Again, as shown in Figure 5.13, the hypochlorite consumption ratio is as high as 57.6 with 1 gram of the mineral and decreases to 12.9 with 10 grams of the mineral. The ratio of available hypochlorite to leach one mole of chalcopyrite with 1 gram mineral is 45.88 and that with 10 grams is 4.59. These values correspond to 5.4 and 0.54 times as much as the stoichiometric factor, respectively.

Again, in order to minimize the hypochlorite consumption ratio, the solid dosage should be increased so that hypochlorite concentration should become lower than its stoichiometric value. However, in determining the optimum conditions in terms of hypochlorite concentration and solid dosage, the leaching conversion of chalcopyrite to cupric oxide also should be considered because it is directly related to how many leaching stages should be applied to complete the leaching. Thus, it is not a simple matter to determine the optimum conditions because there should be compromise between these two factors. However, a first approximation is possible as follows: The temperature could be 55°C because the conversion is near the maximum value at this temperature and the cupric oxy-anion concentration is small at 0.3 ppm. The pH should be 13.2. The optimum conditions in terms of hypochlorite concentration and solid

dosage could be determined with the same stoichiometric factor of 0.54 when the solid dosage was 10 grams. If this stoichiometric factor is adopted and the concentration of hypochlorite is 1.8 molar, the solid percent is determined to be 7.2.

B. Step wise addition:

A new leaching scheme was devised in this study to achieve complete conversion. An experiment was carried out in the same way as other experiments in this study, but its reaction time was extended by adding hypochlorite stock solution stepwise every 40 minutes for three times. The experiment was initiated with 10 g chalcopryrite at 0.5 molar hypochlorite, pH 13.2 and 55°C. At 40 minutes, a 50-ml sample was withdrawn from the reactor and filtered, and immediately 100 ml hypochlorite stock solution was withdrawn from the separate 1-liter reactor maintained at 55°C and poured into the leaching reactor. This addition continued for two more times. The conversions were determined as before. The result is depicted in Figure 5.14.

Figure 5. 14 Leaching conversion of chalcopryrite with stepwise addition of hypochlorite (55°C, pH 13.2, 10 grams chalcopryrite).

It is observed that the conversion is almost completed in 160 minutes. However, a problem seems to come from application of excessive reagent amounts of hypochlorite and sodium hydroxide. In this experiment, the amounts of hypochlorite and sodium hydroxide at 1.9 and 2.6 times, respectively, as much as stoichiometric amounts according to reaction 2.18 were used. The hypochlorite consumption ratio was calculated at 160 minutes and it was 16.8 which are almost twice as much as the stoichiometric amount. Thus, this leaching scheme with stepwise addition should be optimized on the concentrations of hypochlorite and sodium hydroxide, and solid dosage to achieve the complete conversion and, at the same time, to reduce the hypochlorite consumption ratio as small as possible toward its stoichiometric value of 8.5 in order to determine the technical feasibility.

C. Kinetic Models

In this study, the leaching rate of chalcopyrite was analyzed by fitting the rate curves using a shrinking core model based on chemical reaction control. According to the model the leaching rate of chalcopyrite may be given as

$$\frac{dn}{dt} = - \frac{4\pi r^2}{\phi} C^p k \quad (5.1)$$

Where, n = number of moles of unleached chalcopyrite in a particle at time t,

r = radius of unreacted core in a particle (m),

C = concentration of hypochlorite at time t (mol/m³),

k = rate constant ((m^{3p}/mol^{p-1}).sec),

p = reaction order with respect to C, and

φ = sphericity of chalcopyrite particle.

Equation (5.1) may be further simplified as:

$$\frac{dF}{dt} = \frac{3VC^p k_1}{r_0} (1 - F)^{2/3} \quad (5.2)$$

Where, F = fraction of chalcopyrite leached or leaching conversion into cupric oxide,

V = chalcopyrite molar volume (m³/mol),

k₁ is k/φ and

r₀ = original radius of chalcopyrite particle (m).

The hypochlorite concentration is a time-dependent term, and should be available for numerical integration of Equation (5.2). A mathematical relationship for the depletion of hypochlorite concentration vs time was obtained by fitting the experimental data as shown in Figure 5.7 with an integrated equation of a q^{th} order rate equation, which is given by

$$\frac{dC}{dt} = -k_2 C^q \quad (5.3)$$

Where, q is the reaction order with respect to hypochlorite concentration and

k_2 is the rate constant.

Equation (5.3) is integrated to

$$\frac{1}{C^{q-1}} - \frac{1}{C_0^{q-1}} = (q - 1)k_2 t \quad (5.4)$$

where C_0 is the initial concentration of hypochlorite (mol/m^3).

The values of q and k_2 were selected by fitting the experimental data at 35 to 75 °C as shown in Figure 5.7, and are given in Table 5.2 together with k_1 values which will be obtained later. One can see that from the figure that the fitting for the depletion of hypochlorite with Equation (5.4) is generally good with the exception at 35 °C.

The numerical integration of Equation (5.2) was carried out using the Matlab ode45 function. The value of p , the reaction order with respect to hypochlorite concentration was determined by a trial-and-error method. Two values of p were tried. They were 1 and 0.5, or of first and half order reactions. The values of q and k_2 at 55 °C from Table 5.2 were used in the computation. Then k_1 values were selected for their best fitting by a trial-and error method.

Table 5. 2 k_1 , q and k_2 values.

Temperature	35°C	45°C	55°C	65°C	75°C
$k_1,$ $m^{-0.5}mol^{0.5}s$	1.48×10^{-6}	3.54×10^{-6}	5.7×10^{-6}	8.5×10^{-6}	9.12×10^{-6}
q	0.95	0.95	0.95	0.95	0.95
$k_2,$ $(mol/m^3)^{1-q}s^{-1}$	0.0002	0.00065	0.0012	0.002	0.0024

Figure 5.15 Comparison of surface reaction control model fitting for first and half orders with respect to hypochlorite concentration (55°C, 3 grams chalcopryite, initial pH 13.15).

Figure 5.15 compares the experimental data with each computed leaching curve using the two models of first and half order reactions. One can see that the model with the half order

reaction better fits the experimental data than that with the first order dependence. Then the model with the half order dependence was used to fit the experimental data at other temperatures of 35, 45, 65, and 75 °C. The k_1 values at these temperatures were selected for their best fitting of the experimental data by a trial-and error method. The fitting including that of 55 °C is shown in Figure 5.6. It appears that the fitting is generally good.

This model resembles those of ferric chloride leaching¹² and ammonia leaching¹⁹ in that the three models are based on the surface reaction control and also half-order dependence with respect to the reagent concentrations. The half-order reaction is frequently observed on electrochemical reactions when the rate is controlled by chemical reaction. This half-order dependence on the hypochlorite concentration may verify that this leaching reaction is an electrochemical reaction as previously presented.

An Arrhenius plot is made with the k_1 values and shown in Figure 5.16. Only four k_1 values from 35 to 65 °C given in Table 5.2 were used to calculate the activation energy. However, the k_1 value at 75 °C does not seem to be on the straight line. It appears that at this temperature, the rate controlling step may change to diffusion controlling step or mixed kinetics where the diffusion is a great part of it.

Figure 5.16 Arrhenius plot for chalcopryrite leaching with hypochlorite (0.5 molar OCl^- , 3grams chalcopryrite, initial pH 13.15)

However, more experiments above this temperature are needed to verify this trend, and as mentioned previously, those experiments are difficult to conduct because the hypochlorite concentration tended to decrease too fast to analyze accurately. From the slope of the straight line in the Arrhenius plot (Figure 5.16), the activation energy was calculated and this was found to be 50.2 kJ/mol (12.0 kcal/mol). The magnitude of this activation energy verifies the chemical reaction controlling mechanism previously assumed²⁵.

6. Conclusions

The present study reveals that the chalcopyrite can be leached much faster with sodium hypochlorite than with the conventional reagents such as ferric sulfate or ferric chloride. The leaching conversion reaches about 68% in 1 hour at 65 °C and 0.5 molar of hypochlorite. The conversion shows a maximum at pH 13.15-13.20 and also at 65 °C in their respective series.

Hypochlorite consumption ratio reached 57.6 when the solid dosage was 1 gram in 500 ml at 55 °C and 0.5 molar of hypochlorite which is much higher than its stoichiometric value of 8.5. The ratio decreased to 12.9, when the chalcopyrite weight was increased to 10 grams.

The optimum leaching conditions were proposed considering primarily the hypochlorite consumption ratio and leaching conversion. The optimum conditions are 55 °C, pH 13.2, 7.2 solid weight% and 1.8 molar of hypochlorite.

Leaching curves were fitted well by a shrinking core model based on chemical reaction control. A half order reaction with respect to hypochlorite concentration was determined in the model. The activation energy of 50.2 kJ/mol (12.0 kcal/mol) was found.

A leaching scheme was identified in which 98% of chalcopyrite was leached with adding hypochlorite stock solution stepwise in less than three hours.

Areas requiring additional study:

As seen from the above discussion, many aspects of the reaction between chalcopryrite and hypochlorite are fairly resolved, or require only moderate clarification. However, there are still some important topics which need to be addressed. The following areas require additional study,

1. It would be appropriate to conduct kinetic studies at higher temperatures to confirm the reaction mechanism.
2. In order to enhance the leaching rate of chalcopryrite with hypochlorite it would be appropriate to conduct more experiments in presence of copper ions, ferrous ions or other catalysts and promoters.
3. Conduct more experiments to study the reagent loss by other side reactions.
4. To study the economics of this process compared with other process.

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