GALVANIC INTERACTION BETWEEN CHALCOPYRITE
AND PYRITE DURING ATMOSPHERIC LEACHING

by

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ABSTRACT

Chalcopyrite is the most abundant copper minerals, yet one of most difficult to leach due to a passive layer which forms under a variety of oxidative leaching conditions. For this reason, chalcopyrite has traditionally been processed by pyrometallurgical routes. However, due to a host of environmental and economic issues there has been increased interest in developing a hydrometallurgical process to treat primary copper sulfides. A novel process was developed at UBC in which pyrite was added intentionally to chalcopyrite to provide a galvanically-assisted leach. The ground minerals were subjected to an acidified ferric sulfate solution at atmospheric pressure, and excellent copper recovery was achieved. The present study continued this work, applying the technology to several chalcopyrite concentrates in order to determine optimal conditions for the leach. Leaching experiments were conducted in a sealed 3-liter jacketed glass stirred-tank reactor.

Initial work with a concentrate from Zambia was conducted using pyrite from the Huanzala region of Peru. It was determined that a pyrite-to-chalcopyrite ratio of 2.7 was optimal. The solution potential should be controlled above 455 mV vs Ag/AgCl, although it is difficult to comment on the optimal range due to gas liquid mixing limitations at higher potentials. Initial acid content of 1.8 kg per kg concentrate and a leach temperature of 80°C were also selected for best results. Pyrite remained an effective catalyst when recycled wet as very little was oxidized during the leach.

A second chalcopyrite concentrate from Mongolia was obtained, along with a pyrite concentrate from the same mine. The optimal conditions from the previous study were used. Initial experiments showed a significant induction period, but the induction period deceased substantially when a second charge of concentrate was used with the wet-recycled residue. It was believed that reagents used in the flotation circuit may have fouled the surface of the pyrite, thus reducing its effectiveness as a galvanic catalyst. Attempts were made to 'activate' the pyrite concentrate prior to use, but these proved unsuccessful. It remains unclear why the pyrite becomes more reactive when recycled.
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CHAPTER 1 INTRODUCTION

In recent years, there has been an intense effort to find a hydrometallurgical alternative to traditional pyrometallurgy processes to treat primary copper concentrates. While excellent copper and precious metal recoveries are readily obtainable by smelting, \( \text{SO}_2 \) emissions, sulfuric acid market saturation, high capital cost and impurity limitations (As, Sb, Bi) are driving the shift in technology. Dreisinger (2006) presented a review of chemical and biological processes for copper recovery from concentrates. The process under development can be divided into sulfate and chloride process (although halide and ammonia processes have been investigated). Within this grouping, the processes can be divided further based on pressure (atmospheric or super-atmospheric) and based on the leaching mechanism (chemical or biological).

Hydrometallurgical treatment of chalcopyrite has been hindered greatly by the formation of a passive layer on the surface. Initial kinetics are rapid, but soon slow and result in poor copper recovery. Although the passivation of chalcopyrite has been the focus of considerable research in the past half century, the exact mechanism of passivation is still under considerable debate. In spite of this, many processes have been proposed that overcome the reluctant nature of chalcopyrite.

Many of the newly developed process employ special conditions to increase the rate of copper recovery from chalcopyrite; however, in all cases there are drawbacks to the technologies. The Placer Dome process (total pressure oxidation) uses high temperature (220°C) oxidative conditions to decompose copper minerals. Although high copper extraction and fast kinetics are obtained, oxygen consumption is high because all the sulfur is converted to sulfate and high lime consumption is required for neutralization.

Processes such as Activox and Nenatech employ fine grinding (>20 \( \mu \text{m} \)) to increase leach kinetics, but the cost associated with fine grinding is high. The Anglo American Corporation and UBC have also developed a process that uses fine
grinding (sub 20 μm), moderate temperature (150°C), and moderate pressure. Do
to the temperature range used in this process, surfactants need to be added to
disperse molten sulfur (Peacey et al., 2003)

Currently, a lot of attention has been paid to two chloride–based processes: the
CESL process and Hydrocopper. The CESL process was developed by Teck–
Cominco. The chemistry of the process is an oxidizing pressure leach using a
mixture of cupric sulfate and cupric chloride operating at 150°C and 200 psi,
followed by acid leaching to dissolve the antlerite. Iron is precipitated as hematite
and sulfur yield is between 75% to 90%. Outokumpu recently developed the
HydroCopper process. In this process, chalcopyrite concentrates are leached at
atmospheric pressure with cupric chloride–brine solution. Copper is recovered from
the purified leach solution by precipitating cuprous oxide using caustic soda.
Hydrogen gas is used to reduce the cuprous oxide to copper. Reagents are
regenerated using a chlor–alkali cell technology. Both of these chloride–based
processes are currently in pilot plant testing (Peacey et al., 2003). Although the
chloride media allows for rapid chalcopyrite dissolution kinetics, severe corrosion of
equipment serves as a major technical issue to overcome.

In 2004, Tshilombo presented a novel process for treating chalcopyrite in ferric
sulfate at low temperatures and atmospheric pressure in his Ph.D. thesis. He
examined the galvanic interaction between ground chalcopyrite and pyrite minerals
(particle size fraction of 38–75 μm) and found the combined effects of low solution
potential, high temperature, pyrite addition and high acidity are desirable for the
complete conversion in a relatively short time. As part of his recommendations,
Tshilombo suggested that the technology should be tested on high grade primary
copper concentrates.

The early work performed at UBC on the galvanically assisted chalcopyrite shows
significant promise in that it eliminates many of the drawbacks of other
hydrometallurgical processes. The ‘low-temperature’ (>80°C) and atmospheric
pressure leach remove the problems associated with molten sulfur, formation of
sulfate, and high capital costs of autoclaves. Furthermore, the sulfate-based solution allows for conventional construction materials and SX/EW technology to be used, an advantage over the chloride systems. For these reasons, it was decided to investigate the feasibility of using the galvanic effect of pyrite to leaching chalcopyrite concentrates.

Two chalcopyrite concentrates were obtained from Kansanshi Mines, in Zambia, and Erdenet Mines, in Mongolia. The aim of the investigation was to determine the optimal operation conditions for the atmospheric leach. Parameters such as temperature, solution potential, initial acid content, and pyrite-to-chalcopyrite ratio (Py:Cp) were examined. The source of the pyrite was also investigated; more specifically, the difference in leach behavior between pure pyrite and a pyrite concentrate. The viability of recycling pyrite for multiple copper concentrate charges was also investigated.
CHAPTER 2 LITERATURE REVIEW

Chalcopyrite is regarded as the most abundant source of copper, but due to its recalcitrant nature, chalcopyrite is almost exclusively treated by smelting. However, tougher environmental regulations and impurity penalties have brought renewed interest in hydrometallurgical processing. While a variety of hydrometallurgical processes have been developed at the lab and pilot plant scales, only one technology, the CLEAR process, reached commercial production (although for only a brief period of time) in 1976.

Hydrometallurgical processes can be grouped according to the media used: sulfate processes, sulfate/chloride processes, and chloride processes. Within these groups, processes can further be classified by the leach temperature, pressure, and the use of bacteria. Sulfate processes are an attractive option because the leach chemistry is well understood and SX/EW technology is easily inserted into a sulfate leach circuit. Chloride processes have the advantage of faster leach kinetics, but corrosion issues tend to make chloride processes less attractive.

A survey of the literature was conducted to describe the chemistry of chalcopyrite in ferric sulfate leaching at ambient temperatures. A summary of research on the attempts to accelerate chalcopyrite leaching using additives and galvanic interactions is given in the following sections, as well as a detailed description of the proposed passivation models.

2.1 Leach Chemistry

It is generally accepted that chalcopyrite breaks down as follows during acidic ferric sulfate leaching under atmospheric conditions (i.e. below 100°C):

\[
\text{CuFeS}_2 + 2 \text{Fe}(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 5 \text{FeSO}_4 + 2 \text{S}^0
\]  

\[2.1\]

Ferrous is then oxidized back to ferric in the bulk solution, consuming oxygen and sulfuric acid:

\[
\text{CuFeS}_2 + 2 \text{Fe}(\text{SO}_4)_3 + \text{O}_2 \rightarrow \text{CuSO}_4 + 5 \text{FeSO}_4 + 2 \text{S}^0
\]
Combining [2.1] and [2.2] yields the overall reaction for the leaching of chalcopyrite by ferric sulfate. For every mole of chalcopyrite leached, one mole of oxygen and two moles of sulfuric acid are required:

\[ \text{CuFeS}_2 + 2 \text{H}_2\text{SO}_4 + \text{O}_2 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2 \text{S}_0 + 2 \text{H}_2\text{O} \]  \[ \text{2.3} \]

The dissolution of chalcopyrite can also be described as an electrochemical reaction with both the anodic and cathodic reactions occurring simultaneously on the mineral surface:

**Anodic:** \[ \text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2 \text{S}_0 + 4 \text{e}^- \]  \[ \text{2.4} \]

**Cathodic:** \[ 4 \text{Fe}^{3+} + 4 \text{e}^- \rightarrow 4 \text{Fe}^{2+} \]  \[ \text{2.5} \]

When these two half cell reactions are combined, they give the same reaction shown in [2.1].

### 2.2 Attempts to Accelerate Leaching of Chalcopyrite

Over the past few decades many researchers have investigated numerous methods for increasing the leaching rate of chalcopyrite. The following section describes and highlights the results of their work.

#### 2.2.1 Chalcopyrite Activation

Warren *et al.* (1968) examined the effect of two thermal pretreatments to activate chalcopyrite prior to leaching. Roasting in the absence of oxygen at 825°C and treatment with elemental sulfur at 425°C both resulted in significantly faster copper recovery compared to untreated samples. Further research was conducted on activating chalcopyrite by sulfidization, but poor selectivity of copper over iron halted continued examination [Subramanian, 1973].
2.2.2 Catalysts and Surfactants

A wide array of materials has been investigated as possible promoters for chalcopyrite leaching. Iron powder was shown to promote the leaching of chalcopyrite concentrate in HCl solution (Sanchez et al., 1996). Hydrogen gas is generated when iron reacts with HCl. The concentrate also reacts with HCl, forming FeCl₂, CuCl₂ and H₂S. The following reactions are then believed to occur:

\[
\text{CuCl}_2 + \text{H}_2\text{S} \rightarrow \text{CuS} + 2 \text{HCl} \quad [2.6]
\]

\[
2\text{CuS} + \text{H}_2 \rightarrow \text{Cu}_2\text{S} + \text{H}_2\text{S} \quad [2.7]
\]

These researchers also examined the effect of hematite (as a source of iron for H₂ generation) on chalcopyrite leaching (Sanchez et al., 1997). Misra (2005) investigated the effect of nanosize silica on chalcopyrite leaching at moderate temperature and ambient pressure. Leaching was conducted at 75°C in the presence of 0.5 N H₂SO₄ and 40 g/L FeCl₃. The addition of 17.5 g/L nanosilica increased chalcopyrite dissolution by about 25% compared to experiments conducted in the absence of nanosilica. No mechanism was offered to explain the enhanced leaching by silica.

The catalytic influence of soluble silver salts has been of interest for several decades. Miller and Portillo (1981) investigated the mechanism of silver catalysis on ferric sulfate leaching of chalcopyrite and concluded that Ag₂S formed crystallites on the surface of the mineral. They reported the initial stoichiometry of the reaction as follows:

\[
\text{CuFeS}_2 + 4 \text{Ag}^+ \rightarrow 2 \text{Ag}_2\text{S} + \text{Cu}^{2+} + \text{Fe}^{2+} \quad [2.8]
\]

Elemental sulfur replaces the crystallites forming a porous, non-protective layer, while the liberated Ag⁺ acts as a transfer agent, thus:

\[
\text{Ag}_2\text{S} + 2 \text{Fe}^{3+} \rightarrow 2 \text{Ag}^+ + \text{S}^0 + \text{Fe}^{2+} \quad [2.9]
\]
Several researchers investigated the amount of silver required for the catalytic effect to occur. Silver content varied from 0.004% (Snell and Sze, 1977), to 0.05% (McElroy and Duncan, 1975), to 0.75% (Pawlek, 1976).

Activated carbon has also received attention. Wan et al. (1984) demonstrated that the leaching of chalcopyrite in acidified ferric sulfate solution was enhanced by the formation of chalcopyrite/carbon aggregates. They suggested that the carbon particles alter the conductivity of the reaction product layer and the increased conductivity attributed to the increase in leaching rate. Nakazawa et al.(1998) studied the interaction between activated carbon and chalcopyrite concentrate during bioleaching. It was determined that copper recovery increases with the amount of carbon and with the decrease in carbon particle size. They also suggested that the enhanced rate of dissolution was due to a galvanic effect between activated carbon and chalcopyrite.

Duncan (1964) first investigated the use of surfactants in the leaching of chalcopyrite with Thiobacillus ferrooxidans. Accelerated leaching was observed in shake tests when a non–ionic surfactant was added. They attributed the enhanced leaching rates to the surfactant increasing the contact angle between the organism and the mineral surface.

Sandoval (1990, 1991) later demonstrated that the surface of chalcopyrite becomes hydrophobic as the leach proceeds. He suggested that the passivation of the mineral was due to the alteration in the surface properties from hydrophilic to hydrophobic and that non–ionic surfactants could be used to enhance the leaching rate.

2.2.3 Galvanic Interactions

When two metal sulfides of different rest potentials are in contact with each other in an acid solution, the mineral with the higher rest potential acts as the cathode and is galvanically protected. Conversely, the mineral with the lower rest potential acts as the anode. This is shown schematically is Figure 2- 1. The galvanic interaction
may also greatly increase the leaching kinetics of the anodic mineral by effectively removing most of the cathodic surface area. By doing so, the majority of the minerals surface area can now be anodic. This phenomenon has been observed by various researchers.

![Diagram showing galvanic interaction between chalcopyrite and pyrite](image)

**Figure 2-1** Illustration of galvanic interaction between chalcopyrite and pyrite

Electrochemical investigations of corroding electrodes are difficult because the properties of the electrodes change during the experiment due to alterations of the electrode surface, as well as during imposed polarization. In light of this, Nowak et al. (1984) examined four mineral couples (including chalcopyrite-pyrite) and attempted to characterize the galvanic action in terms of Tafel slopes and ratios of galvanic current to total corrosion current. They concluded that the magnitude of the galvanic effect in the anodic dissolution depends mainly on the difference in rest potentials of the mineral. They also noted a significant self-corrosion in the chalcopyrite-pyrite couple, stating that the galvanic current attributed only a third of the total corrosion current.

Gottschalk and Beuhler recognized that the solubility of mineral sulfides greatly increased in the presence of pyrite [Gottschalk, 1912]. Dutrizac et al. performed a systematic study on the galvanic interactions of sulfide minerals and found that pyrite, low iron sphalerite, and molybdenite increase chalcopyrite dissolution, while the addition of galena and high iron sphalerite retard leaching of chalcopyrite [Dutrizac, 1973]. Linge (1977) also showed that sphalerite slowed chalcopyrite dissolution.
slightly, along with bismuthinite. Magnesium dioxide has also been shown to form a galvanic couple with chalcopyrite [Gantayat, 2000]. SEM images of the residue showed that there were no major changes to the pyrite surfaces. Hiskey and Wadsworth (1975) examined the kinetics associated with the galvanic interaction between chalcopyrite and copper, finding rapid conversion of CuFeS$_2$ to Cu$_2$S.

Most of the interest in galvanic interaction between sulfide minerals has been in bioleaching processes. Berry et al. examined the galvanic interaction between chalcopyrite and pyrite during bacterial leaching of low-grade waste. The results showed that when pyrite and chalcopyrite were in contact, the resulting galvanic interaction caused chalcopyrite to corrode more rapidly than pyrite, which was effectively protected. This effect was accelerated in the presence of bacteria, and at elevated temperature. It was also demonstrated that when the pyrite and chalcopyrite were not in contact, the pyrite reacted more rapidly. Mehta et al. also found the presence of pyrite in optimized quantities considerably enhanced the rate of copper dissolution, which was increased by a factor of 2 to 15 [Mehta, 1983]. Maximum copper extraction was observed at a CuFeS$_2$:FeS$_2$ ratio of 1:1 and a particle size of -200 mesh at pH of 2.3. Leaching rates were enhanced in the presence of bacteria. Attia and El-Zeky (1990) also examined the effect of pyrite during the leaching of complex sulfide ores and tailings using *Thiobacillus ferrooxidans*. The results showed that galena, sphalerite and chalcopyrite were all leached preferentially over pyrite. Excellent precious metal recovery was also obtained.

However, to date there are no industrial processes that intentionally exploit the galvanic couple to recover copper from chalcopyrite concentrates.

### 2.3 Passivation of Chalcopyrite

The formation of a passive layer on the surface of chalcopyrite is a problem that has plagued hydrometallurgists over the last half century. Initially, the reaction proceeds rapidly, but soon slows. Many researchers have suggested theories describing this phenomenon, but the exact mechanism is still a matter of considerable debate.
The main theories of chalcopyrite passivation are the following, each of which is described in the following section.

- Limitation of reactant
- Formation of elemental sulfur layer
- Formation of defect structure
- Precipitation of iron compounds

### 2.3.1 Limitation of Reactant

Possibly the easiest place to start when determining the rate limiting step or mechanism in chalcopyrite passivation is to examine the transport of reactants, or more specifically, the limitation of ferric diffusion to the mineral surface. Hiroyoshi (1997) and Third (2000) reported that an increase in the concentration of ferric does not result in a corresponding increase in leaching rate. Hirato (1987) observed a first-order dependence of the leaching rate of chalcopyrite on increasing ferric concentration up to 0.1 M Fe$_2$(SO$_4$)$_3$. However, the rate declined with further ferric addition. Jones and Peters (1976) observed similar trends. Increasing the ferric concentration from 0.03 to 0.1 M Fe$_2$(SO$_4$)$_3$ increased the leaching rate of chalcopyrite slightly, but further increases in ferric concentration yielded rates lower than those found at 0.03 M. Since decreasing leaching rates were observed above a ferric concentration of 0.1 M, another factor must become rate controlling.

Hirato [1987] examined the distribution of iron species as a function of ferric sulfate concentration in 0.2 M H$_2$SO$_4$. A rapid decline in Fe$^{3+}$ and FeHSO$_4^{2+}$ was observed at higher Fe$_2$(SO$_4$)$_3$ concentrations ($10^{-1}$ M). A thirty-fold increase in ferric sulfate concentration resulted in only a six-fold increase in Fe$^{3+}$ activity, while FeSO$_4^{+}$ concentration increased linearly. He concluded that Fe$^{3+}$ and/or FeHSO$_4^{2+}$ are the most significant ions in ferric leaching. Crundwell (1987) observed similar results for sphalerite dissolution.
Kametani and Aoki (1985) examined the role of ferrous on chalcopyrite oxidation. They reported that ferric concentration has little effect on the oxidation of chalcopyrite from 50°C to 90°C and suggested that copper extraction is mainly controlled by the redox potential (i.e., the Fe$^{3+}$/Fe$^{2+}$ ratio). Their results also showed that there is a critical potential at which copper extraction is maximized. Above this critical point (~0.43 V vs. SCE) there is a sudden decrease in leaching rate. The critical point also corresponded to the onset of oxidation of the pyrite which was present in the concentrate tested.

A method of “ferrous promoted” leaching was proposed by Hiroyoshi (1997), where ferrous acts as a reductant. Chalcopyrite is initially reduced by ferrous in the presence of cupric to form chalcocite:

\[
\text{CuFeS}_2 + 3 \text{Cu}^{2+} + 3 \text{Fe}^{2+} \rightarrow 2 \text{Cu}_2\text{S} + 4 \text{Fe}^{3+} \tag{2.10}
\]

The chalcocite is then oxidized by either ferric or oxygen to form cupric and elemental sulfur:

\[
2 \text{Cu}_2\text{S} + 8 \text{H}^+ + 2 \text{O}_2 \rightarrow 4 \text{Cu}^{2+} + 2 \text{S}^0 + 4 \text{H}_2\text{O} \tag{2.11}
\]

\[
2 \text{Cu}_2\text{S} + 8 \text{Fe}^{3+} \rightarrow 4 \text{Cu}^{2+} + 8 \text{Fe}^{2+} + 2 \text{S}^0 \tag{2.12}
\]

The enhanced copper recovery by ferrous occurs only at low potentials when cupric is present. Furthermore, Cu$_2$S does not form with cupric or at higher potentials (above 0.7 V vs SHE). This theory is contrasted by the work of Dutrizac (1981) who observed small amounts of FeSO$_4$ added to 0.1 M ferric sulfate and 0.3 M sulfuric acid at 80°C caused the rate of chalcopyrite leaching to fall by up to 30%.

2.3.2 Formation of Elemental Sulfur

Anodic dissolution of chalcopyrite in acidic medium indicates elemental sulfur formation on the surface. This elemental sulfur layer has received the most attention as the cause of passivation, and is thought to provide a barrier to diffusion. Sulfur enjoys extraordinary stability under a wide range of conditions at temperatures as high as its melting point (Peters, 1976). Dutrizac (1989) noted that elemental sulfur
is the major reaction product of ferric sulfate leaching of chalcopyrite with some sulfate formed at 95°C. He reported 94% elemental sulfur and 6% sulfate formation regardless of leach time, ferric concentration, or particle size.

Several authors report parabolic leaching kinetics with respect to ferric concentration. They conclude that this result is indicative of diffusion control through the sulfur layer. Linge (1976) contests this finding, stating that ferric diffusion through an elemental sulfur film is four times greater than the chalcopyrite leaching rate. Instead, it is proposed that the rate limiting step is electron transport through the sulfur layer (Munoz, 1979).

Leaching experiments were conducted in the presence of finely ground graphite to act as a conductor. These graphite particles were found to be embedded in the sulfur coatings surrounding the chalcopyrite particles and resulted in enhanced leaching rates. This observation is in good agreement with the proposed mechanism by Munoz. However, the high activation energy of the process is not usually associated with mass transfer limited reactions.

Peters (1973, 1984) determined that the oxidation of one mole of chalcopyrite (42.65 cm$^3$) to produce 100% elemental sulfur (31 cm$^3$), produces a significant negative volume change. Consequently, it would be impossible for the sulfur layer to be without cracks or porosity. This may be an oversimplified approach in that it assumes that all the sulfur forms directly, and not from precipitates from the aqueous phase.

Lu (2000) used CS$_2$ solvent to remove the sulfur coating from partially leached chalcopyrite particles. After the CS$_2$ wash, he did not observe any significant change in the leaching rate, leading to speculation that the passivation is due to a metal-deficient structure. Similar results were obtained by Buttinelli et al. (1992). However, conflicting observations were presented by Wan (1984).

Parker also supports the concept of a metal-deficient, copper-rich polysulfide causing passivation by slowing the transport of cupric and ferric, as well as slowing
electron transfer to and from electro-active species in solution. Reddy (1984) confirmed the formation of a semi-conducting, metal-deficient polysulfide film using ESCA and microscopic analysis. The exact nature of the intermediate layer below the sulfur layer is difficult to identify due to the extremely thin layers formed (Dutrizac, 1989).

2.3.3 Formation of a Defect Structure

The dissolution of chalcopyrite can be viewed as an electrochemical process in which the anodic and cathodic reactions (as given by Eqns. [2.4] and [2.5], respectively) occur simultaneously on the mineral surface.

Polarization curves of chalcopyrite show three distinct regions: active, passive, and trans-passive. The passive regime reflects a region in which a progressively thickening surface film is forming (Warren, 1982; Jones, 1976).

Several researchers believe that the anodic reaction of chalcopyrite occurs through a series of intermediate steps (Holliday, 1990; Warren, 1982; Hiskey, 1981). Warren suggested that the reaction proceeds as follows:

\[
\text{CuFeS}_2 \rightarrow \text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z} + x\text{Cu}^{2+} + y\text{Fe}^{2+} + z\text{S}^0 + 2(x + y)e^- \quad [2.13]
\]

where \(y > x\) initially.

The defect structure \(\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}\) releases ferrous much faster than cupric initially. Both Baur (1972) and Linge (1976) observed Fe:Cu ratios higher than one in solution at low potentials during the initial stages of leaching.

The defect structure further decomposes to form a second intermediate phase in the region of 700 to 750 mV (SHE):

\[
\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z} \rightarrow 2(y - x)\text{CuS}_{(n-s)} + (1 - y)\text{Cu}^{2+} + (1 - y)\text{Fe}^{2+} + (2 + x - y - z)\text{S}^0 + 4(1 - y)e^- \quad [2.14]
\]
Warren (1982) and Baur (1972) validated reaction [2.14]; they found the ferrous to cupric ratio to be one after extended leaching times.

The two intermediate phases \( \text{Cu}_{1-x}\text{Fe}_{1+y}\text{S}_{2-z} \) and \( \text{CuS}_{(n-s)} \) have been labelled S1 and S2, respectively. Based on potential-pH diagrams for the Cu-Fe-S-H\(_2\)O system, Warren suggested that S1 and S2 are bornite (\( \text{Cu}_5\text{FeS}_4 \)) and covellite (\( \text{CuS} \)). Theses two phases serve as a passive layer by limiting ionic transport to the covered chalcopyrite surface.

McMillan et al. (1982) performed electrochemical oxidation of \( \text{CuFeS}_2 \) in both sulfate and chloride media under chemical leaching conditions. The results of his experiments indicate a surface layer that has the properties of covellite, which slows the rate of electron transfer. Biegler and Horne (1984) used cyclic voltammetry to propose the formation of covellite by the following reaction:

\[
4 \text{CuFeS}_2 \rightarrow 3 \text{CuS} + \text{Cu}^{2+} + 4 \text{Fe}^{2+} + 5 \text{S}^0 + 10 \text{e}^- [2.15]
\]

Holliday and Richmond (1990) also reported the formation of covellite during anodic dissolution of chalcopyrite by the following sequence at low potentials.

\[
\text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{FeS}_2 + 2 \text{e}^- [2.16]
\]

\[
\text{Cu}^{2+} \rightarrow x \text{Cu}^{2+} \text{(ads)} + (1-x) \text{Cu}^{2+} \text{(aq)} [2.17]
\]

\[
\text{Cu}^{2+} \text{(ads)} + \text{FeS}_2 \rightarrow \text{CuS} + \text{Fe}^{2+} + \text{S}^0 [2.18]
\]

However, Hackl (1995a and 1995b) rejected the theory that bornite and covellite passivate chalcopyrite on the knowledge that these two minerals dissolve much faster than \( \text{CuFeS}_2 \) in acidic sulfate media. He proposed that the passive layer was a polysulfide, \( \text{CuS}_n \) (\( n > 2 \)).

Koch and McIntyre (1976) observed the formation of metastable phases during the electrochemical oxidation of chalcocite to covellite, given as follows, in order from the lowest rest potential to the highest rest potential:
It is possible that similar intermediate products are formed during the oxidative leaching of chalcopyrite. Since the intermediates are believed to be semiconductors and are in contact with CuFeS₂, a galvanic couple may be formed. Further investigations of this possible galvanic interaction are necessary to determine its significance.

### 2.3.4 Precipitation of Iron Compounds

Several researchers theorize that iron precipitates form impermeable layers on the surface of chalcopyrite (Hiroyoshi et al., 1999; Stott et al., 2000). As acid is consumed by the leach, ferric sulfate begins to hydrolyze and precipitate as ferric hydroxide:

\[
Fe_2(SO_4)_3 + 6 H_2O \rightarrow 2 Fe(OH)_3 + 3 H_2SO_4 \quad [2.19]
\]

Iron can also precipitate as ferric hydroxysulfate, goethite, and jarosite, respectively:

\[
Fe_2(SO_4)_3 + 2 H_2O \rightarrow 2 Fe(OH)SO_4 + H_2SO_4 \quad [2.20]
\]

\[
Fe_2(SO_4)_3 + 4 H_2O \rightarrow 2 FeOOH + 3 H_2SO_4 \quad [2.21]
\]

\[
3 Fe_2(SO_4)_3 + 12 H_2O + A_2SO_4 \rightarrow 2 AFe_3(SO_4)_2(OH)_6 + 6 H_2SO_4 \quad [2.22]
\]

where \( A = K, Na, NH_4, H_3O, Ag, \) or \( \frac{1}{2} Pb. \)

Ferric is mainly present in solution at pH < 2. As the pH rises above this level, jarosites begin to precipitate in the presence of suitable cations. Jarosite formation can not be avoided during ferric leaching that operates within the temperature range of 20°C to 100°C, provide sufficient acid content is present. Complete ferric precipitation occurs above pH 3, forming highly stable iron compounds such as Fe(OH)₃, FeOOH, and Fe₂O₃ (although Fe₂O₃ only forms at temperatures greater than 100°C). The formation of jarosite and other iron precipitates may retard
leaching by restricting reaction products from reaching the bulk solution and preventing ferric access to the mineral surface.

Scott (2000) observed extensive jarosite precipitation on the surface of chalcopyrite particles during ferric and microbial leaching. The removal of the majority of this layer (70%) did not significantly increase the leaching rate. A thin layer of jarosite remained strongly bound to the mineral surface. This small layer was believed to be sufficient to diminish copper recovery significantly. Parker (1981) detected basic ferric sulfate compounds on chalcopyrite. The results indicated that polysulfide products did not play any role in inhibiting chalcopyrite dissolution. The slow kinetics was mainly due to the formation of jarosite.

In practice, most ferric leaching operates at pH < 1.8 to limit the extent of ferric precipitation. This makes it doubtful that iron compounds alone are responsible for the passivation of chalcopyrite.
CHAPTER 3 SCOPE AND OBJECTIVES

The scope of this study is to continue the work conducted by Alain Tshilombo on the galvanic interaction between pyrite and chalcopyrite. In his thesis, he examined the interaction between pure mineral samples. The present work will examine the feasibility on applying galvanically assisted leaching to chalcopryite concentrates. Two concentrates were obtained for the study: one from Kansanshi Mines in Zambia and one from Erdenet Mines in Mongolia.

The objectives of the study are to answer the following questions:

- Can the galvanic couple between chalcopyrite and pyrite be exploited during the atmospheric leaching of chalcopyrite concentrates in acidic ferric sulfate solutions?
- What are the optimal leach conditions?
- Can a pyrite concentrate be used and if so, how effective is it as compared to a pure pyrite?
- Can the pyrite be recycled and used again to leach chalcopryite?
- What is the extent of pyrite oxidation?
CHAPTER 4 EXPERIMENTAL METHODOLOGY

This chapter describes in detail the experimental setup used in the atmospheric leaching experiment, the reagents used, and experimental procedures.

4.1 Apparatus

A schematic of the experimental setup is shown in Figure 4-1. Chemical leaching experiments are conducted in a sealed 3-liter jacketed glass reactor. The reactor is heated by a Haake P14 circulating hot water bath. A stirring assembly with a 6-bladed Rushton turbine impeller and three baffles is fitted to the underside of the top plate. The stirring assembly is attached to an exterior motor, which is controlled to 1200 rpm by a controller (not shown).

Three probes are inserted into the reactor: a thermocouple, a 235 mm glass pH probe from AppliSens, and a solution redox potential probe from Analytical Sensors, Inc (labeled T, pH, and Eh, respectively). These three probes are attached to a digital ADI 1030 Biocontroller. The outputs of the three electrodes are recorded by a laptop computer.

The ADI 1030 Biocontroller allows a solution potential setpoint to be specified. When the solution potential measured by the electrode inside the reactor drops below the setpoint, an analogue signal is sent to an Aalborg gas mass flow meter. The mass flow meter allows oxygen to flow into the reactor via a sparger from the compressed gas cylinder. The oxygen flow is slowly decreased as the potential approaches the setpoint. Once the setpoint is reacted, the oxygen flow is turned off. Excess oxygen exits the reactor through a condenser to limit the amount of water loss by evaporation.
4.2 Reagents

Deionized water and reagent grade chemicals were used to prepare the test solutions. The chemicals were used as received with no additional purification.

- Iron(III) sulfate heptahydrate $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]$ (100% purity)
- Iron(III) sulfate pentahydrate $[\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}]$ (97% purity)
- Sulfuric Acid $[\text{H}_2\text{SO}_4]$ (98% purity)
- Cupric sulfate pentahydrate $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ (100% purity)
4.3 Procedure

The reactor is filled with 1500 g of DI water and the desired mass of sulfuric acid and sealed. Next, the oxygen line, condenser, and stirring motor are installed. The solution is mildly agitated while heating to the operating temperature. Prior to use, the redox probe is immersed in Light's solution to ensure good working condition before being inserted into the reactor. Similarly, the pH probe is calibrated using buffer solutions of pH 1.68 and pH 4.00 before being placed into the reactor; the biocontroller thermocouple is placed into a temperature reference (DI water) to ensure the pH measurements are corrected to the actual temperature of the standard buffer solutions. Once the solution has reached the desired temperature, iron salts (and copper salts if desired) are added using a funnel. Agitation is increased to 1200 rpm and the ore is introduced to the reactor, all by a funnel. All open ports on the lid are plugged with rubber stoppers to seal the reactor.

Samples of the solution are withdrawn from the reactor periodically using a 20-mL syringe. Approximately 8 mL of slurry is transferred to a centrifuge tube. Any slurry remaining in the syringe is put back into the reactor. The samples are labeled, filtered, and stored in 2-mL micro-centrifuge tubes. Copper content is measured using standard atomic absorption spectroscopy (AAS).

Once the test is complete, the contents of the reactor are emptied into a large flask. The walls of the reactor are washed with DI water to ensure that all solids are removed. The entire solution (including wash water) is passed through a 5-μm vacuum filter and then washed. The filter is allowed to dry in air for a day or two. The filter paper and solids are weighed and then the solids are ‘coned and quartered’ to obtain a representative sample for chemical analysis. Solid samples were sent to International Plasma Labs for determination of total copper content by wet titration.
CHAPTER 5 RESULTS AND DISCUSSION

5.1 Kansanshi Leaching Experiments

A primary copper sulfide concentrate was obtained from Kansanshi Mine in Africa to study the galvanic couple between chalcopyrite and pyrite during atmospheric leaching of concentrates. Unfortunately at the time of the study, there was no local pyrite source that could be supplied and therefore massive pyrite samples from Huanzala, Mexico were used. Mineralogy and elemental composition of the copper concentrate and pyrite sample are summarized in Table I and Table II, respectively.

Table I XRD-Rietveld Analysis of Kansanshi Concentrate and Huanzala Pyrite

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mass %</th>
<th>Kansanshi Concentrate</th>
<th>Huanzala Pyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (SiO₂)</td>
<td>2.9</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Muscovite (KAl₂AlSi₃O₁₀(OH)₂)</td>
<td>0.9</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Plagioclase (NaAlSi₃O₈ – CaAl₂Si₂O₈)</td>
<td>5.2</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Gypsum (CaSO₄·2H₂O)</td>
<td>1.1</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Talc (Mg₃Si₄O₁₀(OH)₂)</td>
<td>–</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Fluorite (CaF₂)</td>
<td>–</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>Sphalerite (Zn₁Fe)S</td>
<td>–</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Marcasite (FeS₂)</td>
<td>–</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Pyrite (FeS₂)</td>
<td>9.7</td>
<td>92.3</td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite (CuFeS₂)</td>
<td>63.1</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Anilite (Cu₇S₄)</td>
<td>17.0</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>
Table II  Elemental Analysis of Kansanshi Concentrate and Huanzala Pyrite

<table>
<thead>
<tr>
<th>Element</th>
<th>Kansanshi Concentrate</th>
<th>Huanzala Pyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>35.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>26.3</td>
<td>46.7</td>
</tr>
<tr>
<td>S</td>
<td>29.1</td>
<td>49.2</td>
</tr>
<tr>
<td>Al</td>
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<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>0.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Pb</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>Mg</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>P</td>
<td>0.3</td>
<td>-</td>
</tr>
</tbody>
</table>

The copper concentrate was used in the as-received condition. The massive pyrite samples were crushed in a series of cone crushers and then pulverized in 150 g lots for five minutes.

Five variables were studied in the leaching of Kansanshi copper concentrate: initial acid content, solution potential, pyrite-to-chalcopyrite (Py:Cp) ratio, temperature, and the effect of pyrite recycle. Only one variable was changed at a time in each experiment. Table III contains a “test-matrix” and summarizes the conditions for all the experiments.

Results and Discussion
### Table III Experimental Conditions and Selected Results of All Kansanshi Tests

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Kansanshi Concentrate Mass (g)</th>
<th>Huanzala Pyrite Mass (g)</th>
<th>Initial Acid Content (g)</th>
<th>Delonized Water Mass (g)</th>
<th>Total Iron Content (g)</th>
<th>Potential Setpoint</th>
<th>Temperature, °C</th>
<th>Final Copper Recovery (AAS)</th>
<th>Final Copper Recovery (Solids) %</th>
<th>Pyrite Oxidation (XRD) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>50</td>
<td>0</td>
<td>65</td>
<td>1500</td>
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<td>470</td>
<td>2.7</td>
<td>80</td>
<td>84.00</td>
</tr>
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<td>450</td>
<td>2.7</td>
<td>80</td>
<td>81.33</td>
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<td>80</td>
<td>84.70</td>
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<td>470</td>
<td>3.8</td>
<td>80</td>
<td>91.85</td>
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<td>80</td>
<td>92.81</td>
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<td>81.56</td>
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<td>K20</td>
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<td>1500</td>
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<td>K22</td>
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<td>1500</td>
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<td>80</td>
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<td>K25</td>
<td>50+50</td>
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<td>90</td>
<td>1500</td>
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<td>0.25</td>
<td>470</td>
<td>2.7</td>
<td>80</td>
<td>99.02</td>
</tr>
</tbody>
</table>

A K16 (in boldface type) is the baseline test
B K23 used the residue from K8 as the pyrite source (after sampling)
C K24 used the residue from K5 as the pyrite source (after sampling)
D 7.5 g Cu was added to the initial solution for test K24

*Results and Discussion*
5.1.1 Pyrite Addition Experiments

In order to determine the galvanic effect of pyrite addition to the Kansanshi Copper concentrate, an experiment was conducted in which only the copper concentrate was present. A solution of 1500 g of deionized water and 65 g of sulfuric acid, containing 25 g of total iron was produced. The ferric to ferrous ratio was 0.25. This yielded an initial solution potential of 490 mV (Ag/AgCl) at 80°C. Subsequent tests were performed with increasing amounts of Huanzala pyrite. All other test conditions were kept constant. The results of these experiments are shown in Figure 5-1.

![Figure 5-1](image)

**Figure 5-1** Effect of Huanzala pyrite addition on copper extraction from Kansanshi concentrate: 65 g H$_2$SO$_4$; 25 g Fe total; 80°C; 470 mV setpoint, 1200 rpm

Clearly, there is a large effect on copper extraction with the addition of pyrite. The pyrite deficient test achieved 57% extraction in 47 hours. The addition of 25 g of pyrite (Py:Cp ratio of 0.8) dramatically increased the recovery of copper; however, a significant induction period was observed. This induction period was also observed
in the test in which 50 g of pyrite were added, although the length of the induction period was substantially diminished. Additions of 100 g and 150 g of pyrite (Py:Cp ratios of 2.7 and 3.8, respectively) displayed similar behavior. There was no increase in the rate of copper extraction by increasing the Huanzala pyrite content above 100 g. Both tests achieved 95% copper extraction in less than 10 hours with no discernable induction period. In an effort to conserve the pyrite sample, all further tests were conducted using 100 g of Huanzala pyrite.

A second set of experiments were conducted in which the acid content was increased from 68 g to 90 g. The extraction curves are similar, showing little dependence on acid content (Figure 5-2).

![Figure 5-2](image)

**Figure 5-2** Effect of Huanzala pyrite addition on copper extraction from Kansanshi concentrate: 90 g H$_2$SO$_4$; 25 g Fe total; 80°C; 470 mV setpoint, 1200 rpm

*Results and Discussion*
5.1.2 Potential Experiments

Tests were conducted at various solution potentials between 425 mV and 485 mV (Ag/AgCl). The results are shown in Figure 5-3. Increasing the solution potential from 425 mV to 470 mV results in increasingly improved copper extractions. The two highest potentials test (470 mV and 485 mV) showed very similar results, although, in the 485 mV test the copper recovery decreased from a maximum of 99% after 7.83 hours to a final recovery of 96%. However, it is believed that this is an analytical artifact of pyrite dissolution. Solid assays confirm the higher extraction value.

![Graph showing copper recovery vs. time and potential](image)

**Figure 5-3** Effect of solution potential on copper recovery from Kansanshi copper concentrate: Py:Cp = 2.7; 90 g H₂SO₄; 25 g Fe total; 80°C; 1200 rpm

The potential behavior is shown in Figure 5-4 and Figure 5-5. All of the tests begin at a potential close to 495 mV. Within minutes of the concentrate being added to the solution, the potential drops abruptly (Figure 5-4). This decline in solution potential is due to the rapid consumption of ferric from the dissolution of chalcopyrite. The
rate of ferrous oxidation with oxygen cannot keep up with the consumption of ferric during this period.

![Graph showing initial potential behavior of potential experiments](image)

**Figure 5-4** Initial potential behavior of potential experiments

After roughly one hour of oxygen addition, the potential slowly approaches the higher setpoints of 470 mV and 485 mV. However, before the setpoint is reached, a second drop in solution potential occurs. It is believed that once a critical potential is reached, either anilite (Cu₇S₄) or chalcopyrite begins to leach rapidly. The 470 mV setpoint was not achieved until 4.1 hours into the test, while the 485 mV setpoint was not achieved until 6.6 hours into the test. Interestingly, the potential behavior of the 470 and 485 mV tests were identical for the first four hours, even though the oxygen flow rate was greater in the higher potential experiment. As a result, the extraction curves for those two tests are virtually identical. This indicates that the rate of leaching was limited by the rate of oxygen mass transfer into the solution during this period.
Figure 5-5  Solution potential behavior of potential experiments
5.1.3 Acid Experiments

The results of the initial acid experiments are shown in Figure 5-6. Assuming that the copper minerals leach completely to form elemental sulfur and that all other minerals present are inert, the stoichiometric requirement of sulfuric acid is 42.21 g for a 50 g charge of Kansanshi concentrate. The lowest acid content tested (45 g) is near the stoichiometric requirement. Initial copper recovery is similar to as the other acid tests, but the copper extraction begins to slow after two hours, resulting in a final copper recovery of 87% after 24 hours. This suggests that 45 g of acid is below the true stoichiometric requirement.

![Graph showing copper recovery vs. time for different acid contents.]

**Figure 5-6** Effect of initial acid content on copper recovery from Kansanshi copper concentrate: Py:Cp = 2:7; 470 mV setpoint; 25 g Fe total; 80°C; 1200 rpm

Increasing the initial acid content to 60 g improved copper recovery significantly. When the solution potential data was examined for the 65 g and 70 g experiments it was discovered that the potential was controlled to 450 mV, not 470 mV, for both experiments. For this reason, the copper recovery curve for the 65 g and 70 g
experiments were not included in Figure 5-6. Removing these two data sets for the plot shows a clear trend with initial acid content for the initial 6 hours of the experiment. Increasing the initial acid increases the copper recovery. The most rapid copper recovery was obtained in the experiment with the highest initial acid. For that reason all subsequent tests were conducted using an initial acid content of 90 g. The higher acid concentration also has the added benefit of suppressing iron from hydrolyzing.

There is a good correlation between the measured pH and the extraction of copper. The rise in pH nearly mirrors the recovery of copper. This observation is shown in test K17 and K20 (shown in Figure 5-7 and Figure 5-8, respectively). Hence, a plateau in measured pH indicates when copper extraction has ceased.

![Graph showing pH and copper recovery](image)

**Figure 5-7** Test K17 – correlation between pH and copper recovery

The plateau in the recorded pH also indicates that in the final stages of leaching, very little (if any) pyrite was oxidized. When pyrite is oxidized, ferric is consumed and ferrous and sulfuric acid are produced as follows:
The extent to which the reaction proceeds is dependent on a combination of solution potential and acidity. Typically, $\beta \approx 0.6 - 0.7$ (Bouffard et al., 2006). Therefore, if pyrite were to leach significantly, the pH would also drop noticeably.

![Graph showing copper recovery and pH over time](image)

**Figure 5-8** Test K20 – correlation between pH and copper recovery
5.1.4 Temperature Experiments

Figure 5-9 shows extraction curves for the three temperature tests. Experiments were conducted at 60°C, 70°C, and 80°C. A significant induction period was observed in the 60°C experiment. The length of the induction period decreased with increasing temperature. However, the final copper recovery was nearly the same for all the temperatures examined. These experiments show that higher temperatures (at least 80°C) are desirable for rapid copper recovery.

![Graph showing copper recovery at different temperatures](image).

**Figure 5-9** Effect of solution temperature on copper recovery from Kansanshi copper concentrate: Py:Cp = 2:7; 470 mV setpoint; 25 g Fe total; 90 g H$_2$SO$_4$ 1200 rpm
5.1.5 Pyrite Recycle Experiments

Test solutions identical to those for K16 (baseline conditions) were prepared to examine the viability of recycling pyrite for subsequent charges of Kansanshi concentrate. 100 g of filtered and dried residue from tests K8 and K5 were used as the recycled pyrite source. Test K23 used the residue from K8, and test K24 used the residue from K5 with the addition of 5 g/L of copper to the initial solution. Fifty grams of Kansanshi copper concentrate were added in both tests. The results of these experiments as well as the recovery curve from the baseline experiment are shown in Figure 5-10.

![Figure 5-10 Effect of recycling dried residue on copper recovery from Kansanshi copper concentrate: Py:Cp = 2:7; 470 mV setpoint; 25 g Fe total; 90 g H₂SO₄; 80°C; 1200 rpm](image)

Clearly, the experiment in which copper was initially added to the solution out-performed the pyrite recycle experiment in the absence of initial copper. The results of test K24 were very similar to the baseline test, demonstrating the effectiveness of pyrite recycling (in the presence of copper in the initial solution). The addition of
copper sulfate appears to have a beneficial effect on the leaching rate. Figure 5-10 also shows that a significant induction period is present in the experiment in which no copper sulfate is added (test K23) to the initial solution. The marked difference between these two experiments can possibly be attributed to an alteration of the pyrite surface during drying or storage. It appears that this altered surface (an oxide coating, perhaps) diminishes the effectiveness of pyrite as a galvanic catalyst for chalcopyrite. However, it is worth noting that both pyrite recycle tests finished with complete copper recovery within 24 hours' of retention time.

A final experiment was devised to determine the effectiveness of recycling pyrite while the pyrite was still wet. A baseline test was performed for 24 hours at which point the agitation was stopped and the solids were allowed to settle. 500 mL of the leach liquor were removed from the reactor using a peristaltic pump. 500 g of deionized water were then added along with 70 g of sulfuric acid to make up for the removed solution and consumed acid. A second charge of Kansanshi copper concentrate was added once the solution reached 80°C and the experiment was run for another 24 hours. The results are shown in Figure 5-11.
Although the first charge appears not to have recovered all the copper from the concentrate, the final recovery is most likely around 98% (the AAS results could not be corrected from the residue assay). Based on the leaching curves all three experiments behaved very similarly, indicating that adding fresh copper concentrate to the recycled pyrite is as effective as the first copper concentrate charge. Therefore, the pyrite may be easily and effectively recycled.
5.2 Determination of a Rate Expression

Due to the nature of the experiments, a detailed kinetic study based on first principles is not possible at this time. However, a simplified rate expression can be obtained by using a power law fit of the conversion data.

The initial data for the leaching curves fits very well to the following power-law form:

\[ X = bt^a \]  \[5.2\]

A self imposed criterion of an \( R^2 \geq 0.95 \) was imposed. Typically, this allowed the curve fit to capture the data accurately up to 75% copper recovery. Beyond this, the power law fit diverged significantly from the data.

Taking the derivative of \[5.2\] with respect to time gives the following:

\[ \frac{dX}{dt} = abt^{a-1} \]  \[5.3\]

Rearranging \[5.2\] and substituting into \[5.3\], a rate expression in terms of copper recovery is obtained:

\[ \frac{dX}{dt} = ab^{\gamma_s}X^{1-\gamma_s} \]  \[5.4\]

This may be re-expressed in simpler power-law form as follows:

\[ \frac{dX}{dt} = \beta X^\alpha \]  \[5.5\]

where \( \beta = ab^{\gamma_s} \) and \( \alpha = 1 - \gamma_s \)

The benefit of characterizing the data and rate by a power law fit is that all the results can be summarized by two constants, \( \alpha \) and \( \beta \) (or \( a \) and \( b \)), as given in Table IV.
Table IV  Power law rate constants for the Kansanshi experiments

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
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<td>K1</td>
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<td>K3</td>
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<td>-1.30</td>
<td>0.0572</td>
</tr>
<tr>
<td>K13</td>
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<td>0.999</td>
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<td>0.0488</td>
</tr>
<tr>
<td>K14</td>
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<td>0.434</td>
<td>1.000</td>
<td>-1.12</td>
<td>0.0799</td>
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<td>K15</td>
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<td>0.997</td>
<td>-1.39</td>
<td>0.0470</td>
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<td>K16</td>
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<tr>
<td>K17</td>
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<td>-2.40</td>
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<td>K18</td>
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<td>0.999</td>
<td>-1.15</td>
<td>0.0827</td>
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<tr>
<td>K20</td>
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<td>0.454</td>
<td>0.995</td>
<td>-1.13</td>
<td>0.0870</td>
</tr>
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<td>K21</td>
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<tr>
<td>K22</td>
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<td>-2.01</td>
<td>0.0105</td>
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<tr>
<td>K23</td>
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<td>0.366</td>
<td>0.995</td>
<td>-3.48</td>
<td>0.0025</td>
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<tr>
<td>K24</td>
<td>0.408</td>
<td>0.362</td>
<td>0.996</td>
<td>-1.45</td>
<td>0.0338</td>
</tr>
<tr>
<td>K25-1</td>
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<td>0.404</td>
<td>0.996</td>
<td>-1.03</td>
<td>0.0789</td>
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<tr>
<td>K25-2</td>
<td>0.423</td>
<td>0.413</td>
<td>0.982</td>
<td>-1.36</td>
<td>0.0523</td>
</tr>
</tbody>
</table>

Figure 5-12 and Figure 5-13 illustrate the typical fit using the power law expression. As stated above, the predicted copper recovery is valid up to a copper extraction of approximately 75%.
Figure 5-12 Log-log plots of the temperature experiments

Figure 5-13 K9 and K17 actual data and predicted results using power law fit

Results and Discussion
5.2.1 Effect of Solution Potential

The leaching rate curves for the solution potential experiments are shown in Figure 5-14. The rate curves are congruent with the leaching curves in that the highest calculated rates were observed for the high potential experiments. In all cases the rates fell in an exponential fashion. It should be noted that the high potential experiments (455 mV, 470 mV, and 485 mV) all behaved very similarly. This is in very good agreement with the leaching curves shown in Figure 5-3 where the three curves were nearly identical for the first 4 hours (or up to approximately 80% copper recovery).

![Leaching rates for potential experiments](image)

**Figure 5-14** Leaching rates for potential experiments
Figure 5-15 shows the leaching rates normalized to the rate of the 455 mV experiment. As expected, the 425 mV and 440 mV experiments had rates much lower than the 455 mV experiment. Moreover, the rates of the 425 mV and 440 mV experiments decrease steadily with respect to the 455 mV experiment.

The leaching rates at higher potentials (470 mV and 485 mV) showed very little variation from the 455 mV leaching rate. It is difficult to conclude any meaningful information from this since the potential history of the three highest potential experiments were nearly identical. Therefore, the effect of high potential on the leaching rate could not be determined for most of the experiment. However, a slight increase in the leaching rate relative to the 455 mV experiment was noted for the 470 mV and 485 mV tests (2% and 4%, respectively).

The leaching curves and calculated leaching rates both suggest that a potential greater than 455 mV would be desirable for rapid copper recovery; however, due to gas-liquid mixing shortcomings in the laboratory reactor, such high solution potentials were not obtained until > 80% copper extraction had been achieved.
5.2.2 Effect of Initial Acid

The leaching rates of the initial acid tests are shown in Figure 5-16. These results show similar trends to the leaching curves. Again, the 60 g and 75 g leaching curves have been omitted from the data set due to lower than expected solution potentials. As with the potential experiments there is a clear trend in the rate data. The highest leaching rates were observed at the highest initial acid levels.

![Figure 5-16 Leaching rates for initial acid experiments](image)

Figure 5-16 shows the leaching rates of the initial acid experiment normalized to the rate of the 45 g acid experiment. Both the 55 g and 68 g experiments show a significant improvement in leaching rate when normalized to the 45 g experiment. While the 68 g experiment remains 20% to 24% faster than the baseline experiment throughout the leach, the 55 g experiment shows a decreasing rate as the leach continues. This suggests that 55 g of acid may not have been sufficient to leach all of the chalcopyrite in the concentrate, as some of the initial acid was consumed by gangue minerals in the concentrate.

Results and Discussion
Figure 5-17 Leaching rates for the initial acid experiments relative to the 45 g acid experiment

The two highest initial acid experiments (80 g and 90 g) start with normalized rates much faster than the 55 g and 68 g experiments. The high initial acid experiments show increasing normalized rates as the leach continues. By the end of the leach (85% extraction), the 80 g and 90 g experiment leaching rates were 63% and 74% higher than the 45 g experiment, respectively. The high leaching rates of the 90.0 g experiment further supports the conclusion that 90.0 g of initial acid is optimal.

5.2.3 Effect of Pyrite-to-Chalcopyrite (Py:Cp) Ratio

The leaching rates for the Py:Cp ratio tests are shown in Figure 5-18. As expected, the fastest rate was observed at the highest Py:Cp ratio (3.8); The leaching rates decreased as the Py:Cp ratio decreased. The rapid decline in leaching rates of the tests at Py:Cp = 0.2 and Py:Cp = 0.8 is attributed to the observed induction periods in the leaching experiments (Figure 5-1). These results clearly show that the best leaching results are obtained with a high Py:Cp ratio (greater than 1.4).
Figure 5-18 Leaching rates for the Py:Cp ratio experiments with 65 g initial acid

Figure 5-19 Leaching rates for the Py:Cp ratio experiments with 90 g initial acid

Results and Discussion
Similar rate results were obtained from the set of Py:Cp experiments conducted with an initial acid content of 90 g (Figure 5- 19). However, it should be noted that the best rates were observed for the Py:Cp ratio of 2.7, not Py:Cp of 3.8. It is unclear why the highest ratio did not have the highest calculated rate. It may be that the optimum Py:Cp ratio is a decreasing function of initial acidity, but more experiments would be required to test this hypothesis.

5.2.4 Effect of Temperature

Both the 60°C and 70°C experiments began with much lower leaching rates than the 80°C experiment (Figure 5- 20). The leaching rate of the 60°C experiment continued to fall rapidly in a similar fashion to the experiment at Py:Cp = 0.2; the rapid decrease in leaching rate is indicative of an induction period. There was no indication of an induction period in the 70°C and 80°C tests.

![Figure 5-20 Leaching rate for temperature experiments](image)

Initially, the rate of the 80°C test was approximately two times that of the 70°C experiment. This observation is congruent with the findings from the leaching
experiments where there is a clear advantage in increasing the temperature for copper recovery.

5.2.5 Effect of Pyrite Recycle

The leaching rates of the three recycle experiments are shown in Figure 5-21, as well as the leaching rate of K16 for comparison. The second charge of the recycle experiment and the “baseline” experiment (K16) have comparable rates, suggesting that the recycled pyrite is just as effective as fresh pyrite when it is kept wet.

Comparing the two experiments in which dried residue was used, the rate data clearly shows that the presence of cupric in solution greatly increases the leaching rate. However, the rates of these two experiments were much less than the baseline and wet-recycle experiments.

![Figure 5-21 Leach rate for recycle experiments](image-url)

\[ \text{Leaching Rate} = \frac{dX}{dt} \]
5.3 Analysis of Leach Residues

Three residues were selected at random to determine the mineralogy after leaching. Samples from K8 (Py:Cp = 3.8 experiment), K10 (Py:Cp = 0.8 experiment), and K17 (425 mV solution potential experiment) were prepared for XRD Rietveld analysis. These results were compared to the mineralogy of the head samples to determine how much of the pyrite was oxidized during the leaching process as well as to determine the form of any remaining copper.

Table V shows the chalcopyrite and pyrite content for the three samples. Pyrite oxidation ranged from 9% to effectively 0%. This result is particularly pleasing in that it shows that pyrite is nearly inert in the leaching process and that very little pyrite would have to be added in a continuous circuit to make up for losses. In fact, the pyrite oxidation could be lowered even more by reducing the leaching time, since the laboratory experiments ran much longer than required for most of the tests. Reducing the retention time would limit the time during which the pyrite could react.

Table V Chalcopyrite and pyrite content in leach residues

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>Initial Mass (g)</th>
<th>Final Mass (g)</th>
<th>Percent Oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>K8</td>
<td>FeS₂</td>
<td>143.30</td>
<td>134.12</td>
<td>6%</td>
</tr>
<tr>
<td></td>
<td>CuFeS₂</td>
<td>31.55</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>K10</td>
<td>FeS₂</td>
<td>27.93</td>
<td>25.44</td>
<td>9%</td>
</tr>
<tr>
<td></td>
<td>CuFeS₂</td>
<td>31.55</td>
<td>0.51</td>
<td>98%</td>
</tr>
<tr>
<td>K17</td>
<td>FeS₂</td>
<td>97.15</td>
<td>100.55</td>
<td>-3%</td>
</tr>
<tr>
<td></td>
<td>CuFeS₂</td>
<td>31.55</td>
<td>5.45</td>
<td>83%</td>
</tr>
</tbody>
</table>

5.4 Erdenet Material

A second concentrate was obtained from Erdenet Mining in Mongolia, to ascertain the sensitivity of the process to different copper concentrates as well as whether if local pyrite sources were amenable to the process. Bulk samples of a copper concentrate and a pyrite concentrate were delivered to UBC. Mineralogy and
The elemental composition of the two concentrates are summarized in Table VI and Table VII, respectively.

**Table VI**  
Erdenet Concentrate Mineralogy

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mass %</th>
<th>Copper Concentrate</th>
<th>Pyrite Concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (SiO₂)</td>
<td>7.2</td>
<td>20.6</td>
<td></td>
</tr>
<tr>
<td>Muscovite (KAl₂AlSi₃O₁₀(OH)₂)</td>
<td>4.6</td>
<td>11.9</td>
<td></td>
</tr>
<tr>
<td>Plagioclase (NaAlSi₃O₈)</td>
<td>2.3</td>
<td>9.3</td>
<td></td>
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<tr>
<td>Clinochlore ((Mg,Fe²⁺)₅Al(Si₃Al)O)</td>
<td>-</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Pyrite (FeS₂)</td>
<td>28.9</td>
<td>54.4</td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite (CuFeS₂)</td>
<td>49</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Covellite (CuS)</td>
<td>5.8</td>
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<tr>
<td>Tennantite ((Cu,Ag,Fe,Zn)₁₂As₄S₁₃)</td>
<td>2.1</td>
<td>-</td>
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<tr>
<td>Molybdenite (MoS₂)</td>
<td>0.2</td>
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**Table VII**  
Erdenet Concentrate Composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass Percent</th>
<th>Copper Concentrate</th>
<th>Pyrite Concentrate</th>
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<td>S</td>
<td>34.3</td>
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<td>Al</td>
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<td>As</td>
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<td>Ca</td>
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<tr>
<td>Cu</td>
<td>25.7</td>
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<tr>
<td>Fe</td>
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<td>Mg</td>
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</tr>
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<td>0.3</td>
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</tr>
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<td>K</td>
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<tr>
<td>Zn</td>
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A single experiment was conducted using Huanzala pyrite for ease in comparing results to the Kansanshi study described above. The optimal conditions from the Kansanhsi tests were used as a starting point for the Erdenet trial.

Some attention should be paid to the floatation circuit employed at Erdenet mines to produce the two concentrates. A diagram illustration the floatation circuit is shown in Figure 5-22. Reagent use in the circuit is as follows:

- Collector: 24 g/t
- Diesel Fuel: 55 g/t
- CaO: 644 mg/L

![Floatation Circuit Diagram]

**Figure 5-22** Flowsheet of bulk concentration separation section for Erdenet material

### 5.4.1 Leaching Experiments

Similar to the final Kansanshi experiment (test "K25"), a baseline experiment was performed in which 45.12 g of Erdenet copper concentrate and 104.88 g of Erdenet pyrite concentrate were charged into a solution of 1500 g of DI water with 90 g of 98%
H₂SO₄ at 80°C. This combination of copper and pyrite concentrates corresponded to a Py:Cp ratio of 3. The solution potential was controlled to 470 mV.

After 46.5 hours of leaching, the agitation and oxygen supply were shut off and the solids were allowed to settle. Using a peristaltic pump, 500 mL of the leach liquor were removed from the reactor. A make up solution containing 45g of 98% H₂SO₄ and 455 g DI H₂O was added to the reactor and the solution was reheated to 80°C. Finally, a second charge of Erdenet copper concentrate (45g) was introduced to the reactor.

Two separate experiments were conducted in this manner: one with no initial copper, and a second with 10g of copper (as 39.29 g of CuSO₄:5H₂O) added to the initial solution. The results of these experiments are shown in Figure 5-23 and Figure 5-24.

The addition of copper sulfate to the initial solution had no effect on the copper recovery. However, in both of the experiments shown in Figure 5-23 and Figure 5-24, the second charge of copper concentrate was leached significantly faster than the first charge.
In order to determine what causes the pyrite concentrate to become more reactive after the first charge, a set of four experiments were conducted. In two experiments pyrite was allowed to soak at 80°C in acidified ferric sulfate solution for nearly 20 hours with no oxygen supplied to the reactor. The only difference between the two tests was that one test contained 10g of copper in solution (as 39.29 g of CuSO₄·5H₂O), while the other contained no copper salt. The addition of copper to one reactor was to simulate the copper that would be present after a typical experiment.

Figure 5-23 Baseline Erdenet experiment including second charge of copper concentrate
The other two experiments were designed at determining the effect of solution potential on the activation of the pyrite concentrate. The pyrite was charged into acidified ferric sulfate solution at 80°C and maintained at an elevated solution potential (500 mV) for 3.4 hours. Similar to the acid soak experiments, one test initially contained copper (as 29.47 g CuSO₄·5H₂O). Figure 5-25 shows the results for the set of four experiments.

**Figure 5-24** Erdenet experiment with 10g initial copper in solution and second charge of copper concentrate
The results clearly show that none of the pretreatments were able to activate the pyrite. In fact, the four tests behaved very similarly to the baseline test in which no additional pyrite was added to the copper concentrate. This result is very surprising since the first charge of the recycle tests where the pyrite concentrate and copper concentrate were added to the reactor at the same time out-performed the baseline test (Figure 5-26). It therefore appears that the attempts to activate the pyrite concentrate hindered the galvanic interaction between chalcopyrite and pyrite.
The final leaching experiment conducted on the Erdenet copper concentrate used Huanzala pyrite instead of the Erdenet pyrite concentrate. 65g of Huanzala pyrite was added to 45g of Erdenet copper concentrate, giving a Py:Cp ratio of 3.30:1. The results of this experiment, along with the results of the second charge results of the recycle experiments, are shown in Figure 5-27. For comparison, the leaching curve for the baseline experiment is also included in Figure 5-27.
The test conducted with Huanzala pyrite shows excellent results. Complete copper recovery is obtained within 12 hours’ of retention time. Although the second charges from both the recycle experiments also leached in 12 hours, a significant induction period of six hours was observed. Only once the induction period was complete did the leaching rate of the recycle tests improve.

5.4.2 Leaching Rates

A simple power law fit was applied to the leaching data as described above. Figure 5- 28 shows all the leaching rate curves for the Erdenet experiments.
Figure 5-28 Erdenet leaching rates

The power law fit data constants $\alpha$ and $\beta$ (or $a$ and $b$) for the Erdenet experiments is presented in Table VIII.
Table VIII  Power law rate constants for the Kansanshi experiments

<table>
<thead>
<tr>
<th>Test</th>
<th>$a$</th>
<th>$B$</th>
<th>$R^2$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$X_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM1-1</td>
<td>0.257</td>
<td>0.242</td>
<td>0.999</td>
<td>-2.90</td>
<td>0.00101</td>
<td>45%</td>
</tr>
<tr>
<td>EM1-2</td>
<td>0.367</td>
<td>0.259</td>
<td>0.996</td>
<td>-1.73</td>
<td>0.00921</td>
<td>50%</td>
</tr>
<tr>
<td>EM2-1</td>
<td>0.367</td>
<td>0.224</td>
<td>0.981</td>
<td>-1.73</td>
<td>0.00620</td>
<td>57%</td>
</tr>
<tr>
<td>EM2-2</td>
<td>0.286</td>
<td>0.307</td>
<td>0.988</td>
<td>-2.50</td>
<td>0.00460</td>
<td>52%</td>
</tr>
<tr>
<td>EM5</td>
<td>0.241</td>
<td>0.261</td>
<td>0.991</td>
<td>-3.15</td>
<td>0.00091</td>
<td>49%</td>
</tr>
<tr>
<td>EM6</td>
<td>0.272</td>
<td>0.234</td>
<td>0.965</td>
<td>-2.68</td>
<td>0.00131</td>
<td>46%</td>
</tr>
<tr>
<td>EM8</td>
<td>0.233</td>
<td>0.274</td>
<td>0.995</td>
<td>-3.30</td>
<td>0.00089</td>
<td>50%</td>
</tr>
<tr>
<td>EM9</td>
<td>0.270</td>
<td>0.259</td>
<td>0.988</td>
<td>-2.71</td>
<td>0.00181</td>
<td>66%</td>
</tr>
<tr>
<td>EM10</td>
<td>0.271</td>
<td>0.242</td>
<td>0.992</td>
<td>-2.69</td>
<td>0.00145</td>
<td>60%</td>
</tr>
<tr>
<td>EM11</td>
<td>0.581</td>
<td>0.320</td>
<td>0.985</td>
<td>-0.72</td>
<td>0.08194</td>
<td>76%</td>
</tr>
</tbody>
</table>

In order to facilitate the comparison of rate data, the data are normalized to the baseline experiment (the test that involved only Erdenet copper concentrate). The rates are then expressed as a percent change from the baseline experiment at a given copper recovery.

Figure 5-29 shows the four pyrite pretreatment experiments normalized to the baseline rate. Both of the oxidative pretreatments of the pyrite increase the leaching rate as compared to the baseline experiment initially. The experiment that did not contain copper showed a greater increase in leaching rate; however, the magnitude of this increase decreased as the chalcopyrite was converted. Once 45% copper recovery was obtained, the leaching rates were comparable to the baseline test. The increase in leaching rate by the oxidative pretreatment with copper remained more or less constant at an increase of 27% over the baseline experiment.
A similar trend was observed in the acid soak pretreatment. The acid soak pretreatment that did not contain copper initially started much faster than the baseline experiment; however, the increase in the rate diminished as the chalcopyrite was leached until the baseline rate was matched at about 35% extraction. Again, the pretreatment that contained copper demonstrated a constant rate with respect to the baseline experiment, but in the case of the acid soak experiment, the rate was less than the baseline experiment.

Figure 5-29 Pyrite pretreatment rates normalized to baseline experiment
Figure 5-30 Best leaching results normalized to baseline experiment

Figure 5-30 shows the normalized rates for the three best experiments conducted on the Erdenet material. The recycle tests showed an increased leaching rate between 66% and 225% over the baseline experiment. Moreover, the experiment conducted using Huanzala pyrite showed a dramatic increase in leaching rate of the baseline experiment. Initially the rate was 267% larger than the baseline experiment after 25% extraction. The rate continued to rise with respect to the baseline test; after 50% extraction, the leaching rate was over 1300% larger than the baseline experiment.

5.4.3 Pyrite Activation

It is clear based on the leaching tests that the local pyrite source from Erdenet mines requires activation before it becomes an effective galvanic catalyst for chalcopyrite. During the course of a regular leach experiment, an induction period of up to ten
hours occurs before the copper recovery rate picks up. The induction period is reduced to six hours when the pyrite is recycled wet. However, there is no significant induction period when Huanzala pyrite is employed.

This abnormal behavior was investigated in the previous sections by attempting a series of pretreatments on the Erdenet pyrite concentrate. It was believed that the surface of the pyrite became fouled during flotation, either by the diesel fuel, or, more likely, by the lime. (Previous experiments not reported here suggest that the reagents used during bulk flotation do not affect the catalytic properties of pyrite.) Therefore, it seemed plausible that soaking the pyrite in acid, exposing the pyrite to copper in solution, and/or oxidizing the pyrite would remove the fouling species and activate the pyrite. However none of these pretreatments improved leaching significantly.

It therefore seems to be a complex interaction between the pyrite and the copper concentrate that activates the pyrite during the leaching process itself. Further investigation is required to determine the mechanism of pyrite activation, and how to make the Erdenet pyrite concentrate as effective as Huanzala pyrite in leaching chalcopyrite. Of course, the most obvious solution is not to subject the pyrite to anything more than bulk flotation, which would avoid exposing the pyrite to any potentially harmful reagents. This solution is particularly satisfying, given that any pyrite in the ore is best left with the chalcopyrite. This would also have the added benefit of reducing the complexity and the cost of any flotation circuit associated with this particularly leaching technology.
CHAPTER 6 CONCLUSIONS

The addition of sufficient quantities of pyrite to chalcopyrite concentrates greatly improves copper recovery during atmospheric leaching in acidic ferric sulfate solutions. Chalcopyrite and pyrite form a galvanic couple when they come into contact. In the resulting electrochemical system, chalcopyrite acts as the anode and releases ferrous and cupric into solution, while pyrite acts as the cathode and provides a catalytic surface for ferric reduction.

Normally the leaching of chalcopyrite is hindered by passivation, which drastically reduces leaching rates and results in poor copper recoveries. It is possible that the passive layer on the surface of chalcopyrite greatly reduces the rate of ferric reduction, causing the overall leach reaction to slow down, and that pyrite provides an alternative surface for the reduction reaction to occur.

The rest of this chapter will summarize findings of this study in two parts: first the Kansanshi experiments, and then the Erdenet experiments.

Kansanshi Experiments

A total of twenty five leaching experiments were conducted on the Kansanshi copper concentrate using pulverized Huanzala pyrite. The experiments examined the effect of pyrite–to–chalcopyrite ratio, initial acid content, solution potential, temperature, and pyrite recycling.

Without the addition of pyrite to the copper concentrate, the typical chalcopyrite leaching response was observed. The chalcopyrite was passivated and only 57% of the copper was extracted after 48 hours’ of retention time (note that approximately 35% of the copper was in the form of secondary sulfides, which are readily leached in acidic ferric sulfate solutions). Experiments were conducted in which 25 g, 50 g, 100 g, and 150 g of Huanzala pyrite were added to 50 g of Kansanshi copper concentrate. While there was a marked increase in copper recovery with the addition only 25 g of pyrite, a significant induction period was observed. The
induction period diminished with further increase in pyrite and was all but absent when 100 g or more of pyrite was added. A pyrite-to-chalcopyrite ratio of at least 2.7:1 was optimal.

Initial acid had little effect on overall copper recovery provided that sufficient acid was present to satisfy stoichiometric requirements. Although complete copper recovery occurred within 24 hours, stoichiometric acid was not sufficient for rapid recovery. Increasing the acid content to 1.1 g of acid per g of copper concentrate resulted in complete extraction in less than 12 hours. Further increase in acid content did not show significant improvement in the leach response; however, increasing initial acid did not inhibit leaching, either. Hence, an initial acid content of 1.8 g of acid per g of concentrate (90 g) was taken to be optimal. The elevated acid content also has the benefit of ensuring that ferric remains soluble.

Solution potential is an important variable in the galvanically assisted leaching of chalcopyrite. Maintaining the solution potential at 425 mV and 440 mV resulted in significant induction periods and poor copper recoveries (copper recovery was better in the case of the 440 mV experiment). Increasing the solution potential to 455 mV resulted in the disappearance of the induction period. Further increases in solution potential did not have a significant effect; however, the two highest potentials tested (470 mV and 485 mV) were unable to reach their setpoints until nearly complete extraction was attained. Hence, the 455 mV, and 470 mV, and 485 mV potential histories were practically identical while copper was being extracted. This shows that the process was limited by the rate of gas-liquid mixing above 455 mV. As a result of this, a solution potential set point of 470 mV was selected as being optimal.

As with most chemical reactions, temperature has a significant effect on the rate. Experiments conducted at 60°C and 70°C showed significant induction periods (although the induction period was less in the 70°C experiment). An operating temperature of 80°C was chosen as optimal. Increasing the temperature further would result in severe evaporation losses from the hot water bath which is used to heat the reactor, but would undoubtedly increase the leaching rate.
Using filtered and dried leach residue as the pyrite source gave mixed results. When the dried residue was used, a significant induction period was observed. However, in the presence of 7.5 g of copper in solution initially, the results were comparable with experiments conducted with fresh Huanzala pyrite. The pyrite is equally effective when used in successive experiments without removal. XRD of selected leach residues showed that roughly 6% to 9% of the pyrite was oxidized during the leach. This shows that the leach residue can be effectively recycled with very little pyrite makeup. This may be important for those deposits which are deficient in pyrite.

**Erdenet Experiments**

The results of the Erdenet experiments demonstrated that the local pyrite concentrate is capable of providing a galvanic couple for chalcopyrite leaching. Although the first leach response is slow for the first charge, the pyrite appears to become activated allowing the second charge to leach much more rapidly. Copper recoveries of 90% were obtained after 12 hours' retention time, with full recovery (>95%) after 24 hours. These results show that pyrite has a very significant effect on chalcopyrite leaching. Without the addition of pyrite, the copper concentrate requires 48 hours to leach completely (96% recovery).

Similar retention times were also required when the Erdenet concentrate was leached using Huanzala pyrite. The Huanzala pyrite experiment showed improved leaching rates as well as a decreased induction period.

Attempts to activate the Erdenet pyrite concentrate by various pretreatments proved unsuccessful. Soaking the pyrite at temperature in acidified ferric sulfate solution and mildly oxidizing the pyrite for a few hours at 500 mV did not change the leach response. For the most part, the pretreatment experiments behaved very similarly to the baseline experiment, which contained only copper concentrate.
CHAPTER 7  FUTURE WORK AND RECOMMENDATIONS

Several variables of the leaching process were not investigated during this study, but are still worthy of examination:

- the effect of alternate massive pyrite mineral sources
- the effect of natural pyrite particle size
- the effect of agitation speed
- the effect of a local pyrite source for Kansanshi concentrate to ascertain any differences in leach response from Huanzala pyrite
- the possibility using air instead of oxygen
- the separate effects of lime and diesel fuel on the catalytic effectiveness of pyrite
- the effect of using a bulk concentrate from Erdenet mines which contains high amounts of both pyrite and chalcopyrite, but which has not been exposed to lime or diesel fuel

The final recommendation from this study of galvanic interaction between chalcopyrite and pyrite is to complete a mass and heat balance around the process flowsheet and then proceed to pilot plant testing. Pilot plant testing should answer several technical questions surrounding the process, such as the true feasibility of pyrite recycling, iron removal, and copper solvent extraction and electrowinning.
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