ELECTROCHEMICAL AND LEACHING STUDIES OF ENARGITE AND CHALCOPYRITE

by

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Abstract

The oxidative behavior of chalcopyrite and enargite in acidic ferric solutions was studied using surface characterization methods, leaching experiments and electrochemical techniques with massive electrodes and single fine particles.

Results demonstrate that chalcopyrite oxidation displays classical active-passive behavior, as often observed in passivating metals. Values predicted electrochemically on massive samples for the passivation potential $E_{pp}$ are in excellent agreement with leaching experiments in batch reactors. A transpassive regime was observed to appear after the passive regime and total dissolution of chalcopyrite was observed at potentials higher than 1.2 V vs. SCE. Passivated surfaces at low potentials between 300 and 550 mV showed non-stoichiometric chalcopyrite compounds and some isolated areas covered by sulfur. Passivated particles of chalcopyrite were reactivated with the addition of pyrite. At high potentials > 600 mV vs. SCE a dense sulfur layer was detected on particle surfaces and is assumed to be responsible for passivation at these potentials.

Electrochemical studies of fine particles of enargite also showed active-passive behavior. The anodic active dissolution of enargite began at 300 mV and became passive at 700 mV vs. SCE. A compact sulfur layer on the surface of enargite particles was detected at potentials higher than 700 mV and caused passivation. Based on these electrochemical studies, enhancement of enargite leaching by addition of pyrite was proposed and validated. Leaching tests in batch reactors demonstrated that enargite can be dissolved effectively at atmospheric conditions producing elemental sulfur. Total extraction of copper was achieved within 24 h with a pyrite-to-enargite mass ratio of 4:1. Solid residues consisted entirely of porous elemental sulfur and all arsenic was found in the solution phase, predominantly as As(III).

The implementation of this process at an industrial scale to leach
chalcopyrite-enargite concentrates will be significant, since there is no process operating at moderate temperatures and atmospheric conditions that is able to efficiently leach high-arsenic copper concentrates.
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Co-Authorship Statement

This thesis presents research conducted by Mr. Berny Fernando Rivera Vasquez in collaboration with Dr. Gonzalo Viramontes Gamboa and Dr. David G. Dixon.

Chapter 2: The active-passive behavior of chalcopyrite: Comparative study between electrochemical and leaching responses. Dr. Gonzalo Viramontes proposed the electrochemical tests and Berny F. Rivera Vasquez was responsible for conducting both electrochemical tests and leaching tests, and for interpretation of the results. Preparation of the manuscript was a joint effort by Dr. Gonzalo Viramontes and Mr. Berny F. Rivera Vasquez. Dr. David G. Dixon provided guidance and editorial input.

Chapter 3: Electrochemical characterization of single micron-size particles of sulfides in acidic solutions. The primary investigator and author of the manuscript was Mr. Berny F. Rivera Vasquez, who was responsible for conducting the research, analyzing the results, and writing the manuscript. Dr. David G. Dixon provided guidance and editorial input.

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CHAPTER 1
INTRODUCTION

1.1. THE PROBLEM

A growing world population, and an increasing standard of living, especially in emerging countries, is causing an increase in the global consumption of resources. Metals, being a major part of these resources, are a part of almost everything that people need, either by necessity or just for convenience. One the most commonly used metals is copper, and its demand has been constantly increasing over the last decade. During 2008 total mined copper production and global copper use were over 15 and 23.9 million metric tonnes respectively (Group, 2009). Copper is used for a variety of purposes, especially in the sectors of equipment manufacture, building construction, and infrastructure. This is basically due because copper has the second highest conductivity of all the elements ($59.6 \times 10^6$ S/m), an exceptional ductility, strength, and resistance to corrosion and creeping. Based on data from the International Copper Study Group, its demand has been increasing at a rate of 4% per year for the last 15 years (Group, 2009). Thus, it is important to know where copper comes from and the difficulties that the copper mining industry will face in the near future due to the high demand of the red metal.

Copper oxides, and secondary and primary copper sulfides constitute the important ores of copper. Oxides are the easiest to be dissolved, requiring only dilute sulfuric acid solution. Up to 90% copper extraction can be obtained in only a few weeks of leaching in heaps. With the depletion of copper oxide reserves, the leaching process has begun to be applied to secondary copper sulfides such as chalcocite ($\text{Cu}_2\text{S}$) and covellite ($\text{CuS}$). These ores are dissolved with ferric sulfate as shown in Eq. 1.1 and Eq. 1.2.

\begin{align*}
\text{Cu}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 & \rightarrow \text{CuSO}_4 + 2 \text{FeSO}_4 + \text{CuS} \\
\text{Eq. 1.1}
\end{align*}
Eq. 1.2 \[ \text{CuS} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 2 \text{FeSO}_4 + \text{S}^0 \]

The leaching of secondary copper sulfides in heaps is usually improved with the use of iron-oxidizing microbes and the injection of air at the base of the heap. Few months are needed to obtain similar copper extractions as copper oxides.

On the other hand, the dissolution of primary copper sulfides has been demonstrated to be slow and incomplete under the same leaching conditions applied for secondary copper sulfides. This implies a considerable problem since primary copper sulfides are the main source of copper. Indeed, chalcopyrite alone accounts for 70% of total copper reserves. Fortunately, there are alternative routes for recovering copper from primary copper sulfides. The most common method is to obtain copper concentrates by using froth flotation of fine mineral particles, and then to smelt this concentrate at high temperatures to obtain copper matte. This matte is then converted to copper anodes which are then electro-refined to finally obtain high purity cathodes assaying over 99.99% copper. In the past, copper pyrometallurgy had a big disadvantage over copper hydrometallurgy, since the former produced large amounts of gases and consumed large amounts of energy to smelt chalcopyrite concentrates. Nowadays, modern smelters have largely overcome this problem with the use of more efficient reactors. Compared with the old reververatory technology, modern smelters use flash fusion, autogenous bath fusion or oxy-fuel burner technology, which give much lower energy consumption. These new techniques also generate much less off-gas, which can now be treated efficiently in an acid plant to capture most of the SO\(_2\) and produce H\(_2\)SO\(_4\) as a byproduct. This sulfuric acid is then sold back to copper leaching operations.

Despite the fact that pyrometallurgy offers a proven treatment for chalcopyrite concentrates, there are other factors that keep researchers active in the search for an affordable method to treat chalcopyrite concentrates hydrometallurgically. One possibility is that the number of smelters will be insufficient in the near future to meet increasing copper demand. The capital investment required for the
construction of a smelter is very large. Thus, smelters are designed to treat a large quantity of materials. This is a disadvantage compared with hydrometallurgical plants that can be built on a smaller scale, with far less capital. Additionally, the emission of gases, and storage capacity and transport difficulties associated with on-site production of sulfuric acid could become a problem. Finally, the presence of impurities such as arsenic and antimony in concentrates is a growing concern, as these render chalcopyrite concentrates less attractive for smelting, and are considered as penalties to be avoided.

Arsenic occurs in copper concentrates as copper bearing minerals such as tennantite (Cu₁₂As₄S₁₃) and enargite (Cu₃AsS₄). These sulfides are present in minor quantities in many ore deposits but their presence is steadily increasing due to the depletion of clean deposits worldwide. Thus, arsenic will be more common in copper concentrates in a near future and an effective, environmental and economical route for processing these concentrates will be required. Preliminary studies of enargite dissolution have demonstrated that enargite does not leach easily, requiring much longer leaching times than chalcopyrite (Balaz et al., 1999). In short, copper from chalcopyrite and enargite ores is poorly extracted in ferric sulfide media, and the possible reasons for their poor dissolution, based on previous studies, are summarized in the following sections.

1.1.1. Leaching of Chalcopyrite

Combining chalcopyrite and ferric ion leaching, many investigations have been carried out to elucidate the reaction kinetics and to outline the leaching variables. In spite of much work carried out over past decades, leaching kinetics and other fundamentals aspects of chalcopyrite leaching are still poorly understood. There are some doubts and many details that have not been resolved or commonly accepted among investigators.

Acid ferric sulfate solutions are not generally an effective lixiviant for copper
extraction from chalcopyrite, as it leaches extremely slow. Sullivan and Brown (1934) were among the first to investigate the ferric sulfate leaching of chalcopyrite. When they tried to leach finely ground (<45 μm) chalcopyrite with a 1% Fe$_2$(SO$_4$)$_3$ solution at 35°C, only 38% of the copper was extracted after 57 days of leaching. The extraction of copper was improved when the temperature was increased close to the boiling point. The same amount of copper went into solution in only five hours. After this, they tried to increase the concentration of ferric sulfate to 5%, but the dissolution rate decreased rapidly with time. Since then, a diverse literature has been written on this topic, including studies during the 1970s by Wadsworth (1972), Dutrizac and McDonald (1973) and Jones and Peters (1976). Important studies in the 1980s include those by Munoz et al. (1979), Majima et al. (1985) and Kametani and Aoki (1985). Recent studies include those by Hiroyoshi et al. (1997; 2000) and Hackl et al. (1995).

Reactions involving the dissolution of chalcopyrite are generally agreed to include:

Eq. 1.3  \[ \text{CuFeS}_2 + 2 \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 5 \text{FeSO}_4 + 2 \text{S}^0 \]

Eq. 1.4  \[ \text{CuFeS}_2 + 8 \text{Fe}_2(\text{SO}_4)_3 + 8 \text{H}_2\text{O} \rightarrow \text{CuSO}_4 + 17 \text{FeSO}_4 + 8 \text{H}_2\text{SO}_4 \]

Most of the copper dissolves according to Eq. 1.3 and the rest according to Eq. 1.4. Sullivan and Brown (1934) found that around 75% of the oxidized sulfur ended up in elemental form. Munoz et al. (1979) reported that 90% of the sulfur formed elemental sulfur during leaching. Jones and Peters (1976) leached pure chalcopyrite in 1 M ferric sulfate at 90°C for 38 days and found that around 82% of the oxidized sulfur reported to the elemental form. Dutrizac (1989) leached chalcopyrite with ferric sulfate at 95°C and reported about 94% elemental sulfur formation. This was observed regardless of the leaching time (up to 70 hours), ferric sulfate concentration, or chalcopyrite particle size. The relative amounts of elemental sulfur and sulfate did not vary systematically when any of these
variables were changed.

Dutrizac (1989) also leached polished chalcopyrite surfaces and chalcopyrite grains. The polished surfaces (~1 cm²), showed the formation of discrete elemental sulfur globules on a roughened chalcopyrite surface after leaching. By contrast, chalcopyrite grains < 40 μm quickly became enveloped in a compact layer of elemental sulfur which was likely sufficiently protective to be responsible, from his point of view, for the non-linear leaching kinetics observed. Continuation of the leaching process resulted in the progressive thickening of the sulfur layer and the agglomeration of the individual chalcopyrite particles into larger masses. Munoz et al. (1979) also observed partially reacted chalcopyrite particles surrounded by a dense and tenacious sulfur layer. They assumed that the elemental sulfur layer is formed almost instantaneously, and that control by an electrochemical surface reaction represents a negligible contribution to the overall reaction kinetics. The elemental sulfur layer passivates the surface and the reaction rate switches to a transport control mechanism. They suggested that the rate limiting process may be the transport of electrons through the sulfur layer. This theory is supported with the evidence that the experimental activation energy determined in that study (20 kcal/mol) is approximately the same as the apparent activation energy for the transfer of electrons through elemental sulfur reported in the literature (23 kcal/mol). They also found that the leaching rate is dependent on the inverse square of the particle diameter, and independent of initial ferrous and cupric concentrations. All this work was conducted at very low pulp densities, in the range of 0.3 to 0.5% solids.

Majima et al. (1985) studied the leaching of chalcopyrite using ferric sulfate and ferric chloride. He found that ferric chloride produced a porous elemental sulfur layer and ferric sulfate resulted in the formation and peeling-off of an aggregate of plate-like crystals of elemental sulfur. Kinetics were found to be linear over an extended period of time, followed by an acceleration stage resulting from an increase in reaction surface area. Although Hackl (1995) only studied kinetics at
temperatures at or above 110°C, he claims that chalcopyrite is passivated by a thin (<1 μm) copper-rich surface layer which forms as a result of solid state changes to the mineral during leaching. He assumed this layer is a copper polysulfide, which determines the leaching kinetics as the copper polysulfide leaches. Wan (1984) showed that if the leaching is interrupted and the elemental sulfur layer is removed, the initial reaction kinetics would be restored. Conversely, Buttinelli et al. (1992) noted that chalcopyrite still leaches slowly even when the elemental sulfur layer is removed.

It has been reported repeatedly that increasing the concentration of ferric sulfate does not increase the leaching rate in the same proportion. Jones (1974) observed that increasing the concentration of ferric sulfate over the range from 0.03 to 0.1 M increased the leaching rate only slightly. However, increasing the ferric concentration to 1 M showed a slower leaching rate than was found at 0.03 M. Hirato et al. (1987) found that the dissolution rate of chalcopyrite increased with an increase of ferric sulfate concentration up to 0.1 M, showing a first order dependency, but decreased at higher concentrations. In contrast, Hiroyoshi et al. (1997) observed that ferrous sulfate was more efficient than ferric sulfate in chalcopyrite oxidation. They showed that the amount of copper that was extracted in the presence of ferrous ions was larger than in the absence of ferrous ions, by a factor of five. By adding ferrous sulfate, the consumption of dissolved oxygen increased, the proton consumption increased and the pH decreased. Later, the same authors (Hiroyoshi et al., 2000) proposed a model where two reaction steps are considered: first, the reduction of chalcopyrite to chalcocite (Cu₂S) by ferrous ions in the presence of cupric ions, and then the oxidation of Cu₂S to cupric ions and elemental sulfur by dissolved oxygen and/or ferric ions. The study also stipulates the existence of a critical potential below which it is possible to find the conditions for the reactions mentioned in the model.

Kametani and Aoki (1985) reported that ferric sulfate concentration has little effect on the oxidation of chalcopyrite. They concluded that the ratio of ferric to ferrous
(i.e., the redox potential) is what determines the leaching rate. They also found a critical range of potential from 0.445 to 0.475 V vs. Ag/AgCl. The rate increased rapidly up to 0.475 V, after which there was a marked decrease at around 0.495 V. At this point it was observed that leaching of pyrite present in the concentrate took place. These workers also noted the same behavior in independent experiments using relatively pure chalcopyrite. Hence, they assumed that the critical potential does not seem to be due to the simultaneous oxidation of pyrite but rather to either a change in the nature of the chalcopyrite or the chemical reaction. An analysis of solid residues showed that when the suspension potential was below 0.475 V, only the chalcopyrite in the concentrate was oxidized, but when the suspension potential was above 0.515 V, there was simultaneous oxidation of chalcopyrite and pyrite. Chalcopyrite yielded stoichiometric amounts of elemental sulfur in the range from 0.345 to 0.695 V, whereas pyrite oxidation took place only above 0.515 V and yielded sulfate ions. Below 0.375 V, CuS was found in the residue. They assume that copper sulfide may have formed by the reaction between cupric ions and elemental sulfur, or directly from chalcopyrite. In the same study they reported an induction period during chalcopyrite leaching. As confirmed in other studies, the induction period could be decreased with increasing temperature and also, interestingly, by adding a second load of fresh chalcopyrite to a used solution. They did not offer an explanation for this, but it may be because of a catalytic effect of copper in solution on chalcopyrite oxidation.

1.1.2. Effect of Pyrite on Chalcopyrite Leaching

It has been seen in past studies that impurities present during chalcopyrite leaching can play an important role, sometimes even being the key determinant for the performance of the system. Dutrizac and MacDonald (1973) studied the effect of other sulfides such as bornite, cubanite, galena and pyrite on the performance of chalcopyrite dissolution. They concluded that the presence of galena retards dissolution of chalcopyrite. Sintered pellets were used in these experiments.
Microscopic examination of these pellets showed distinct phases of each sulfide, in this case cubanite and bornite, in intimate contact with the chalcopyrite when the impurity was present in amounts equal to or greater than 5%. Bornite in contact with chalcopyrite produced a substantial increase in the total amount of dissolved copper, but the presence of cubanite had little effect. They saw that extrapolating the extraction curves to 100%, impurities produce dissolution values that are approximately equal to those of pure bornite or pure cubanite for each case. The chalcopyrite-bornite mixture appeared to dissolve slightly more rapidly than the weighted sum of the dissolution rates of the pure sulfides. For the chalcopyrite-cubanite mixtures the weighted sum of the dissolution rates equaled that of the two pure sulfides. The presence of pyrite accelerated the dissolution of chalcopyrite by a factor of three. A pellet containing 25% pyrite dissolved twice as fast as pure chalcopyrite.

In a mixture of two different sulfides, significant oxidation may occur in one of the sulfides while galvanic protection is observed in the other. This occurs due to the difference of potential between the two sulfide minerals. The mineral with the lower rest potential will take the role of anode, whereas cathodic behavior may be imposed on the mineral possessing the higher rest potential. Pyrite possesses the highest rest potential of the mineral sulfides. If pyrite makes electrical contact with another sulfide mineral, the oxidation of the other sulfide mineral will be accelerated under oxidative leaching conditions. On the surface of pure chalcopyrite, certain regions such as impurity atom sites, dislocations, grain boundaries, etc., become anodic and the remainder of the surface is cathodic. The actual dissolution occurs in the anodic regions, while oxidant is reduced at the cathodic sites. The electron transfer is completed through the conducting chalcopyrite. If chalcopyrite is in contact with a mineral with a more positive potential, that mineral would become cathodic and the chalcopyrite would become the anode forming in this way a mini galvanic cell. Under these conditions the dissolution of chalcopyrite would be favored because the reduction step can occur.
easily on the surface of the second sulfide. The reactions to occur are:

Eq. 1.5 \[ 4 \text{Fe}^{3+} + 4 \text{e}^- \rightarrow 4 \text{Fe}^{2+} \] (pyrite surface)

Eq. 1.6 \[ \text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2 \text{S}^0 + 4 \text{e}^- \] (chalcopyrite surface)

The flow of electrons is completed through the sulfides. On the other hand when chalcopyrite is in contact with a mineral that has a lower rest potential, the dissolution of chalcopyrite is retarded while that of the second mineral is accelerated.

Mehta and Murr (1983) studied the contribution of galvanic interactions of mixed metal sulfides under an acid-bacterial leaching system. It was found that the rate of chalcopyrite dissolution increases as the amount of pyrite in contact with chalcopyrite increases. A mass ratio of 1:1 and a particle size of –200 mesh was found to be the most preferable when leaching was carried out in the presence of \( T. \text{ferrooxidans} \). Under these conditions the dissolution of copper from chalcopyrite was considerably enhanced, by a factor of 2 to 15 times. Under these experimental conditions, \( E_h \) increased from 338 to 580 mV vs. Ag/AgCl while pH dropped from 2.30 to 1.56. Linge (1977) compared different chalcopyrite concentrates containing pyrite. This research showed that concentrates with mass ratios of pyrite to chalcopyrite of 0.6 and 0.45 were more reactive than concentrates with only traces of, or no, pyrite. Those concentrates containing pyrite were about 10 times more reactive than pure chalcopyrite. These results confirm the beneficial effect of pyrite for the leaching of chalcopyrite concentrates showed before by Dutrizac and MacDonald (1973), but it was not agreed that the galvanic interaction between sulfides was the cause of this dissolution enhancement. It was concluded that the reason for this phenomenon may be because the minerals associated with chalcopyrite in the concentrates changed the dissolution rate by altering the diffusivity or concentration, or both, of the rate
controlling species within the chalcopyrite lattice.

Mishra (1973) examined the effect of mixing pyrite with chalcopyrite expecting to observe galvanic interaction between them. The mixture consisted of equal proportions of chalcopyrite and pyrite having a total weight of 150 g. Leaching at 80°C with sulfuric acid, he observed three stages: a first stage of very rapid dissolution, where it was believed that the galvanic interaction between chalcopyrite and pyrite was occurring; a second stage where, evidently, a product layer formed which insulated the particles, thus blocking the galvanic effect and decreasing the dissolution rate; and, finally, a third stage where pyrite was assumed to leach forming sulfuric acid which acted to dissolve iron salts deposited on the chalcopyrite surfaces, thus increasing the rate. The total copper released was twice as much as pure chalcopyrite when pyrite was present. More recently, Abraitis et al. (2004) investigated mechanisms of dissolution of major base metal sulfide minerals such as pyrite, chalcopyrite, galena and sphalerite in acidic chloride media. They mainly studied the galvanic effects between pyrite and the other minerals. The dissolution rates for chalcopyrite, galena and sphalerite in the presence of pyrite were determined respectively as 18, 31 and 1.5 times faster than in single mineral experiments. Mineral powders were used with pH control at 2.5 with additions of HCl. No data for the amounts of mineral or ratios used in those mixtures was provided, but they conclude that it was clear evidence of galvanically promoted chalcopyrite leaching in pyrite-chalcopyrite pulps.

1.1.3. Treatment of Enargite

Enargite is a copper/arsenic sulfide mineral \( \text{Cu}_3\text{AsS}_4 \) that belongs to the family enargite/luzonite/famatinite whose composition can be \( \text{Cu}_3(\text{As,Sb})\text{S}_4 \) being the enargite the most common. Deposits of enargite have been identified in regions of Peru, Chile, Argentina, Philippines and the United States. It is usually found associated with pyrite, chalcocite, covellite and in some locations with gold minerals such as Pascua Lama, El Indio and Valadero in Chile (Deyell, 2001), and
Yanacocha (Bell et al., 2004) and Pierina (Marsden and House, 2006) in Peru.

Enargite has been used as a copper source as early as 900 A.D. Ancient tools were found in the central Andes of Peru that contained high–arsenic copper alloys. These enargite-arsenopyrite raw materials were treated in smelting-refining furnaces at that time (Lechtman, 1991), and since then arsenic has remained a nuisance in the smelting process. The presence of arsenic in a final copper cathode adversely affects metal properties. Arsenic tends to form compounds in the grain boundaries during the solidification of copper which affects its workability by causing cracks, and also diminishing the electrical conductivity of copper (Fabian et al., 1997). Thus, the maximum arsenic content permitted in copper metal is 1 ppm.

When arsenic containing ores enter a smelting/converting circuit, the arsenic is divided into several streams. Around 75% of the arsenic reports to the vapor phase and is captured as dust in boilers, or in water during the wet gas cleaning process. The dust is leached, and waste water from this process together with the water from the gas cleaning step are treated for arsenic precipitation. Around 20% of the arsenic reports to the final slag. The low concentration of arsenic in slag is due to the low solubility of arsenic oxides in silicate slag (Yasawa and Takeda, 1986). Only 2% of the arsenic reports to the anode slime after electrorefining the copper anodes. Any remaining arsenic reports to the H₂SO₄ produced from the SO₂ off-gas (<1ppm As), and by mass balance the rest reports to final gases. As a result a number of outputs containing arsenic are generated, and each one requires treatment for a friendly release to the environment. These different streams are (Castro, 2008): arsenic in volatilized As₄O₆ vapors, As₂O₃ dusts from electrostatic precipitators, electrorefining electrolyte bleed, electrorefining anode slimes, copper cathodes, final slag, sulfuric acid, and off-gases from the sulfuric acid plant. As one can see, the treatment of all these outputs, when possible, bears a high cost, both economically and environmentally. It is here where hydrometallurgical processes can take the advantage since all of the arsenic
contained in the materials to be treated will remain in solution. Thus, arsenic can be precipitated and released in a safe form as a scorodite (FeAsO$_4$.2H$_2$O) from only one output stream.

Hydrometallurgical treatments have been proposed to enable the processing of enargite-containing ores and concentrates. Previous studies propose the separation of enargite from other valuable minerals such as chalcopyrite during flotation using electrochemical control and other means (Fornasiero et al., 2001; Guo and Yen, 2005; Mihajlovic et al., 2007). The purpose of this separation is to obtain a clean chalcopyrite concentrate containing only traces of enargite in order to avoid penalties and to facilitate separate treatment of the various minerals.

Dutrizac and MacDonald (1972) investigated the dissolution of enargite in acidic ferric sulfate media. They observed very slow leaching kinetics, with the formation of a compact elemental sulfur, later also observed in another study (Kantar, 2002). The proposed reaction is as follows:

\[
\text{Cu}_3\text{AsS}_4 + 11 \text{Fe}^{3+} + 4 \text{H}_2\text{O} \rightarrow 3 \text{Cu}^{2+} + \text{AsO}_4^{3-} + 4 \text{S}_0 + 8 \text{H}^+ + 11 \text{Fe}^{2+}
\]

Any physical barrier formed by the sulfur layer could be responsible for the slow dissolution of enargite. Leaching enargite with chlorine also gave very slow dissolution kinetics (Herreros et al., 2002; Padilla et al., 2005; Riveros and Dutrizac, 2008). Biological leaching of enargite has also been investigated (Acevedo et al., 1998; Canales et al., 2002; Escobar et al., 1997; Munoz et al., 2006). All investigators noted that mesophiles were unable to break down enargite. When thermophiles were used, surface modification occurred with formation and later oxidation of sulfur to sulfate. The dissolution was slightly faster compared with abiotic sulfate media but complete dissolution of enargite was difficult to achieve. An inhibitory effect of arsenic in solution on bacterial viability was also observed, but this effect was less apparent when ferric was present. Another inconvenience using thermophiles was the limitation on the amount of suspended solids (Batty and Rorke, 2006). A limit of approximately 12.5% was
proposed to avoid shearing the microbial cells and accelerating their death rate.

Passivation of enargite has been proposed to be caused by sulfur layers (Dutrizac and Macdonald, 1972; Herreros et al., 2002; Padilla et al., 2005), or iron compounds (Munoz et al., 2006). Although enargite has been less studied compared with other copper sulfides, there are a number of electrochemical studies (Asbjoernsson et al., 2003; Asbjornsson et al., 2004a; Asbjornsson et al., 2004b; Cordova et al., 1997; Córdova et al., 1996; Elsener et al., 2007; Munoz et al., 2006; Pauporte and Schuhmann, 1996; Velasquez et al., 2000), under various conditions, but none have applied the results obtained to improve the performance of enargite leaching. In general, little emphasis has been put into the determination of active zones within which enargite leaching might be accelerated.

1.2. SUMMARY AND PROJECT MOTIVATION

In summary, various studies of chalcopyrite dissolution conducted in sulfate media have observed a passivation mechanism that seems to depend on the solution potential, but little emphasis has been placed on determining solution potentials to avoid passivation. In addition, the inhibitory role of elemental sulfur on chalcopyrite dissolution is unclear. Finally, similar studies on enargite are simply non-existent in the literature. Thus, electrochemical techniques combined with surface analysis techniques are promising tools that could provide answers to these questions. In previous electrochemical studies, the working electrode was conventionally constructed by mounting a large cubic specimen of solid sulfide into epoxy resin. However, there is significant evidence that the source, prior history, impurities, and preparation method of the electrodes influence the results. Hence, in order to avoid these problems, single-particle working electrodes were used for most of the present work.
1.3. OBJECTIVES AND SCOPE

The focus of this thesis was to investigate for chalcopyrite and enargite: their active and passive behavior, formation and role of sulfur during dissolution of the sulfides, and explore possible solutions to avoid passivation for chalcopyrite and enargite; all of this using original electrochemical and surface characterization techniques.

The specific research objectives were to:

1. Determine the real active-passive anodic behavior of chalcopyrite on massive samples (CHAPTER 2).

2. Determine the active-passive behavior on leaching of chalcopyrite concentrates at controlled potentials. (CHAPTER 2).

3. Construct a cell and evaluate the feasibility of the microelectrode technique to be used for the electrochemistry of chalcopyrite and enargite single particles. (CHAPTER 3)

4. Evaluate the active-passive behavior of microelectrodes of chalcopyrite and enargite, and explore the possibility of using pyrite to enhance the dissolution of enargite galvanically (CHAPTER 3).

5. Evaluate the formation of sulfur and the dissolution of chalcopyrite at high potentials in presence of H₂SO₄ and NaCl (CHAPTER 4).

6. Evaluate the controlled potential leaching of enargite in reactors applying the best possible parameters found in the previous objectives (CHAPTER 5).
1.4. OVERVIEW

This dissertation is presented in six chapters. The core of the dissertation consists of Chapters 2, 3, 4, and 5 which comprises materials published and ready to be submitted to refereed journals. Chapter 1 provides the overall introduction to the thesis including research background, the research objectives, and the description of the organization of this dissertation. A brief description of the Chapters 2-6 is provided below.

Chapter 2 presents an electrochemical study of massive specimens of chalcopyrite from different sources showing the true active-passive behavior. Electrochemical tests evaluated the effect of acidity and temperature on the passivation of the samples. The active-passive behavior was also studied for the case of chalcopyrite concentrates leached at controlled potentials. In Chapter 3, the adaptation of the microelectrode technique to be used on sulfide particles is discussed. Open circuit potentials of pyrite, chalcopyrite and enargite are measured, and possible mechanisms of dissolution at various conditions of acid and temperature are studied for chalcopyrite and enargite. In Chapter 4, anodic polarizations, high potential electro-dissolution, and batch reactor leaching experiments were done on chalcopyrite samples. Sulfur morphologies formed during dissolution of chalcopyrite in the presence and absence of pyrite were studied by near-surface characterization techniques. The effect of NaCl on sulfur morphology was studied. In Chapter 5, the effect of pyrite addition on the dissolution of enargite is studied considering results of electrochemical studies obtained in previous chapters. Morphologies of residues, effect of solution potential, temperature, iron, acid, and arsenic behavior during enargite dissolution were studied. Finally, Chapter 6 summarizes the original contributions, the application of research findings, and suggestions in future research.
1.5. REFERENCES


JD Sullivan, (1934). USBM RI 3228.


CHAPTER 2.
THE ACTIVE-PASSIVE BEHAVIOR OF CHALCOPYRITE: COMPARATIVE STUDY BETWEEN ELECTROCHEMICAL AND LEACHING RESPONSES*

2.1. INTRODUCTION

When chalcopyrite is leached in H₂O-H₂SO₄-Fe₂(SO₄)₃-FeSO₄ media at atmospheric pressure the leaching rate increases with increasing solution potential up to a certain value \( E_{pp} \), generally known as the passivation potential. At higher potentials the leaching rate decreases and remains low within a narrow range of potential. A passive-transpassive transition can also be observed at even higher potentials, around 700 mV (potentials in this paper are referred to the KCl-saturated calomel electrode (SCE)). In this context, chalcopyrite leaching exhibits the classical active-passive behavior of passivating metals. The passivation potential is key for chalcopyrite leaching, since it determines the maximum solution potential to be used in any hydrometallurgical process designed to dissolve this mineral, which accounts for ~70% of the world’s copper reserves (Davenport et al., 2002). Many authors have studied the transition from the active to the passive state through the leaching of suspended powders in order to establish the most effective range of potentials for leaching chalcopyrite. Kametami and Aoki (1985) reported \( E_{pp} \) to be around 450 mV. Pinches et al. (2001a) suggested a value of around 450 mV in the absence of bacteria, and a significantly higher value in their presence (Pinches et al., 2001b): 555 to 605 mV for *Leptospirillum* and 405 to 455 mV for *Acidithiobacillus ferrooxidans*. They recognized that \( E_{pp} \) depends on the source of the mineral and recommended not exceeding 405 mV if pyrite is present.

* A version of this chapter has been published.
Third et al. (2002) found that chalcopyrite leaching is inhibited at potentials higher than 375 mV. Ballester and Cordoba (2005) found that the active-to-passive transition occurs between 355 and 455 mV.

The significant discrepancies in the values of $E_{pp}$ reported by different authors, the disparity of the experimental conditions used, and the lack of strict potential control render it nearly impossible to quantify the dependence of $E_{pp}$ on acidity and temperature using data from the literature. Moreover, it is possible that $E_{pp}$ depends on the source of the mineral as well.

The passivation of chalcopyrite has also been studied with electrochemical techniques, mostly with relatively fast linear potential sweeps. Unfortunately the true active-passive behavior commonly observed in leaching tests, regardless of the source of the mineral, has rarely been observed using conventional polarizations with fast linear potential sweeps. Instead, the current increases monotonically with potential to a certain value, while at higher potentials the current experiences low sensitivity to potential and remains essentially constant. The portion of the curve where the current does not increase, or increases only slightly with increasing potential, is usually referred to as the “passive” region, even though it does not resemble true passivation at all. Electrodes become active again in the transpassive region, which begins at potentials around 630 mV or in some cases much higher. This behavior is typical of potentiodynamic polarizations made with ordinary scanning rates ranging from 0.1 to 50 mV/s in a wide variety of oxidizing media (Peters, 1977; Parker et al., 1981a; Parker et al., 1981b; Warren et al., 1982; Gomez et al., 1996; Devi et al., 2000; Tshilombo et al., 2002; Tshilombo, 2002). The existence of a pre-wave associated with the formation of a nanometer-scale passive layer has also been reported by Biegler et al. (1979; 1984), but unfortunately it is not always observed and its characteristics depend on the method of electrode preparation and the scanning rate. As happens with passivating metals and alloys, the measured oxidation currents of chalcopyrite strongly depend on the scanning rate and the content of impurities.
Electrochemical studies reported in the literature have had problems not only predicting true active-passive behavior, but in many other key electrochemical aspects of chalcopyrite leaching as well:

a) When fast linear potential sweeps are used the values of $E_{pp}$ (which is not well defined in most cases) and the size of the pseudo-passive window vary widely between electrodes made of specimens from different sources. In some cases wide variations are observed even using a single electrode, and results strongly depend on the source of the mineral (Peters, 1977; Warren et al., 1982; Gomez et al., 1996; Tshilombo et al., 2002) the prior history of the electrode (Parker et al., 1981a; 1981b), and the method of electrode preparation (Peters, 1977; Hiskey, 1993). As a result, the range of potentials where chalcopyrite leaching is active has been estimated through leaching tests to be between roughly 350 and 450 mV. The appropriate slurry potential for leaching chalcopyrite has also been reported to depend on the source of the mineral (Pinches et al., 2001a; 2001b).

b) The leaching kinetics of chalcopyrite have been reported to be essentially parabolic (Linge, 1976; 1977), but linear kinetics or a mix of linear and parabolic kinetics have also been reported (Wadsworth, 1972). More often a transition from a parabolic induction period to a faster linear kinetics is observed in leaching tests (Tshilombo, 2002; Hirato et al., 1987). The parabolic induction period can be very long; Hirato et al. (1987) showed a case where 4 to 5 days elapsed before linear kinetics appeared. This kinetic transition might be due to the presence of meta-stable phases or mineralogical transformations. Electrochemical techniques may help to elucidate the phenomena underlying this transition, but unfortunately the electrochemistry reported so far has made little effort in this direction.

c) The presence of added cupric in the leaching solution has a considerable effect on the leaching rate (Kametami and Aoki, 1985), but conventional linear sweeps are insensitive to dissolved copper (Warren et al., 1982).

These apparent inconsistencies between electrochemistry and leaching studies
have rendered the former a technique of diminished relevance for predicting the kinetics and the passivation potential of chalcopyrite leaching. Based only on the vast literature concerning chalcopyrite electrochemistry, one is unable to choose the proper conditions to leach this mineral.

The main reason why the results of electrochemical studies of chalcopyrite reported so far in the literature have not been as relevant to chalcopyrite leaching as they are for other minerals or metals is because of the complex way in which this mineral reacts upon oxidation. The precise nature of the passivating layer(s) remains unknown. The oxidation kinetics of chalcopyrite and the underlying chemical transformations are inordinately slow, and long periods of time are required to observe and study them. Finally, as massive electrodes of chalcopyrite dissolve through localized corrosion, the true active area is generally unknown and real oxidation rates are difficult to measure (Biegler and Swift, 1979).

Many studies of chalcopyrite leaching have reported a significant lack of reproducibility. Peters (1977) found that chalcopyrite electrochemistry varies significantly with the nature of the mineral specimen and its method of preparation, and reproducible polarization curves were difficult to obtain. He observed that carefully polished faces of chalcopyrite are nearly passive to an anodic potential, or to ferric ion oxidation, while rough, saw-cut specimens are reactive. Warren et al. (1982), working with six different sources of natural chalcopyrite, also found that their anodic polarization curves showed significant differences, particularly in the value of the passive current, which varied by up to two orders of magnitude. The presence of impurities was suggested as the reason for those considerable differences. The rest potentials reported by these authors were significantly different as well, varying between roughly 210 and 310 mV. Parker et al. (1981a; 1981b) found that freshly prepared electrodes exhibited rather different current-potential behavior, and lower currents over several weeks of electrolysis experiments, than extensively leached but well polished electrodes. Nowak et al. (1984) also reported considerable scattering in the currents resulting from galvanic
couples involving sulfide minerals. Considerable variations in the corrosion potentials for those minerals were observed after polishing as well.

Some other measurable properties of chalcopyrite that might affect polarization curves obtained experimentally vary widely between natural sources. Electrical resistivity, for example, varies over a range of up to three orders of magnitude. Studying natural chalcopyrite samples from 24 different sources, Primode and Shuey (1976) measured resistivities from $1.6 \times 10^{-4}$ to $3.0 \times 10^{-1}$ $\Omega \cdot m$, with a mean of $3 \times 10^{-3}$ $\Omega \cdot m$. As a consequence of this large variation in the bulk electrical resistance of different electrodes, variations of up to three orders of magnitude in the current density are to be expected when chalcopyrite samples from different sources are polarized. This in fact has been observed and reported (Warren et al., 1982). This huge difference in the current density does not reflect variations in the processes at the mineral-solution interface; however, it renders faithful estimations of the oxidation rate of powders very difficult. The leaching kinetics of powders also show considerable dependence on the source of the mineral (Linge, 1977).

The work of those authors and many others shows that the electrochemical behavior of massive natural chalcopyrite specimens should be interpreted carefully, and their interpretation is not at all straightforward. Some authors have reported that powder-based carbon paste electrodes give much more reproducible open circuit potentials and voltammetry curves than massive samples (Lazaro et al., 1995; Lu et al. 2000). However there is concern as to how paste electrodes work, and they are not free of experimental problems (Perdicakis et al., 1997). The binder used to bind graphite and mineral particles influences the results (Perdicakis et al., 1997) and the passivation potential they exhibit strongly depends on the scanning rate (Viramontes-Gamboa et al., 2006). Also, the hydrophobic nature of the binder makes its surface an excellent place for water vapor nucleation such that the results of long-duration experiments are very erratic, especially at high temperatures. Many researchers believe that the precipitation of ferric salts such as jarosite plays an important role in chalcopyrite
passivation (Parker et al., 2003; Sandstrom et al., 2005); carbon paste electrodes are especially inconvenient to study this phenomenon because the binder modifies the mineral surface.

Various authors disagree not only about the selection of the best electrochemical procedures with which to study chalcopyrite, but also about the nature and properties of the passive layer. Residual elemental sulfur, jarosite precipitates, and non-stoichiometric polysulfides have all been proposed as the passivating agent. However, removing the residual sulfur by chemical means does not reactivate the leaching kinetics (Tshilombo et al., 2002). Moreover, emerging technologies are leaching chalcopyrite to completion at atmospheric conditions in as little as 5 h, with only layers of elemental sulfur as the remaining product (Dixon and Tshilombo, 2005). This demonstrates that residual sulfur is unlikely to be the passivating agent. The fact that iron is released faster than copper during the initial stages of chalcopyrite leaching (Tshilombo, 2002; Hackl et al., 1995) supports the theory that a passivating layer of non-stoichiometric polysulfide is formed at the interface separating the mineral and the residual sulfur, according to the following reaction (Warren et al., 1982; Hackl et al., 1995):

\[
\text{Eq. 2.1} \quad \text{CuFeS}_2 \rightarrow \text{Cu}_{1-x^+} \text{Fe}_{1-y^+} + \text{S}_{2-z^+} + x\text{Cu}^{2+} + y\text{Fe}^{2+} + z\text{S}^0 + 2(x - y)\text{e}^- 
\]

at potentials between the corrosion potential and ~700 mV (with \( y > x \) and \( x + y = 1 \)). The thermodynamic instability of this layer is evident from the fact that chalcopyrite leaching, although slow, continues indefinitely over this range of potentials. The protective layer reaches a state where it is broken down at the solution interface and formed at the mineral interface at a constant rate. According to Biegler et al., (1979; 1984) it is only a few nanometers thick.

The stoichiometry of the reaction in Eq. 2.1 corresponds only to the passive layer, and does not indicate the final extraction of copper, which for this range of potentials (where elemental sulfur is stable) is generally given by
At potentials above the passive range, chalcopyrite experiences very active
dissolution; it can be decomposed to form different compounds of copper.
Recently the formation of CuS has been identified at potentials between 840 and
920 mV, where chalcopyrite experiences very fast oxidation, by Nava et al. (2006).
Those authors proposed the following reaction for this active range of potentials in
an attempt to explain the observed mineralogical transformation.

Eq. 2.3 \[ 2 \text{CuFeS}_2 + 13 \text{H}_2\text{O} \rightarrow 0.75 \text{CuS} + 1.25 \text{Cu}^{2+} + \text{Fe}_2(\text{SO}_4)_3(\text{s}) + 0.25 \text{SO}_4^{2-} + 26 \text{H}^+ + 28 \text{e}^- \]

As an alternative theory, Hiroyoshi and co-workers (1997; 2000; 2001; 2002;
2004) have claimed that many key aspects of chalcopyrite leaching, such as the
catalytic effect of silver, its active-passive behavior, and other important
phenomena can be explained considering that leaching takes place through the
reduction of chalcopyrite to Cu\textsubscript{2}S by ferrous ions in the presence of cupric ions.
Regarding the active-passive behavior, they affirmed, based on electrochemical
techniques, that this phenomenon occurs only when cupric and ferrous ions
coexist in solution at relevant concentrations (Hiroyoshi et al., 2004), and not
otherwise. They argued that the ferrous-promoted formation of a Cu\textsubscript{2}S
intermediate is a crucial step, since this mineral is more amenable to oxidation
than chalcopyrite and it only forms when the solution redox potential is below
some critical value, which is a function of ferrous and cupric concentrations. At
higher potentials the ferrous-promoted leaching ceases due to the thermodynamic
instability of Cu\textsubscript{2}S. Of course, ferrous and cupric ions always coexist in the vicinity
of the anodized electrode as a consequence of its own dissolution. However,
according to Hiroyoshi et al., these trace amounts were insufficient, and significant
amounts (0.1 M) of these ions were required initially in order to observe the active-
to-passive transition.
In contrast to their results, the present study succeeded in obtaining anodic polarization curves for chalcopyrite displaying true active-passive behavior without the addition of ferrous or cupric ions. These curves have been generated with aqueous solutions containing only sulfuric acid at different temperatures using massive electrodes mounted on epoxy resin. More important than the addition of ferrous and cupric ions was found to be the source of the mineral; some mineral specimens displayed the active-to-passive transition very easily while others were reticent and did not show passivation even under Hiroyoshi’s conditions.

This paper contributes to the knowledge of chalcopyrite electrochemistry by showing that some (but not all) chalcopyrite electrodes indeed display true active-passive behavior, as observed in leaching tests, under near steady-state potentiostatic conditions. From the curves showing a sharp transition to passivation, the dependence of $E_{pp}$ on acidity and temperature is systematically established. Additionally, it is shown that fast potential sweeps applied on massive electrodes do not display active-passive behavior because the time needed to passivate those electrodes ranges from roughly 4 to 24 hours. Any electrochemical technique with a shorter time scale will not reveal the true effect of the passive film on massive electrodes.

### 2.2. EXPERIMENTAL SETUP

The oxidative behavior of chalcopyrite is reported based on the results of two different kinds of experiments: electrochemical techniques and leaching of chalcopyrite concentrates.

A series of leaching tests were conducted at 80°C and 30 g/L of H$_2$SO$_4$ using an as-received concentrate of chalcopyrite (containing 68.4% chalcopyrite, 20.3% pyrite, 4.6% quartz, 2.9% sphalerite, 1.8% covellite, 1.6% gypsum, 0.4% molybdenite) in order to establish the effect of the solution potential on the leaching rate of chalcopyrite. The leaching tests were carried out in a well-sealed,
3-L jacketed glass reactor at a pulp density of 22.4 g/L of concentrate. 5 g/L of total iron were initially added into the solution as ferric and ferrous sulphate salts. The solution redox potential was controlled at pre-established set points ranging from 430 to 700 mV (SCE); a solution of 0.2 M KMnO$_4$ was used as the oxidant for ferric regeneration. The addition of KMnO$_4$ was totally automated. A computer controlled electronic device detected changes in the ORP (measured with a common ORP electrode) and sent the signal to a feedback mechanical system (essentially a software-controlled peristaltic pump), which fed KMnO$_4$ solution as required to maintain the potential at the desired value. Potential deviations were no greater than ± 3 mV from the desired set point.

In order to characterize electrochemically the oxidative behavior of chalcopyrite and to establish the dependence of $E_{pp}$, the transpassive potential, $E_{transpassive}$, the passive current, $i_{passive}$, and the critical current, $i_{cc}$, with temperature and acidity, a series of electrochemical experiments were conducted using a common three-electrode arrangement. A platinum wire was used as the auxiliary electrode (AE), the chalcopyrite sample as the working electrode (WE) and a KCl-saturated calomel electrode immersed in a Luggin capillary as the reference electrode (RE). The AE and WE were located in separate compartments joined by a Vycor porous frit. The AE compartment contained H$_2$SO$_4$ and Fe$_2$(SO$_4$)$_3$, while the WE compartment contained only H$_2$SO$_4$ at the same concentration. With this arrangement the chalcopyrite electrode was not in contact with ferric, ferrous or cupric ions, except those resulting from its own dissolution, so contributions from the Fe(III)/Fe(II) redox couple to the electrode potential were avoided. This arrangement maintained the solution pH and ORP surrounding the WE essentially constant, since reaction products coming from the AE were confined to their own compartment. Oxygen was purged from every solution prior to and during each experiment by sparging high purity N$_2$. Experiments were conducted under maximum magnetic agitation in a 700-mL electrochemical cell. The potentiostat was the PARSTAT 2273 Advanced Electrochemical Interface (Princeton Applied
Massive electrodes were prepared by cutting natural specimens of chalcopyrite from different sources into approximately cubic shapes with areas of roughly 0.7 to 0.9 cm$^2$ on each side. The electrical contact between a copper wire and the sample was made with silver-loaded epoxy resin (Mg Chemicals). The whole system was protected from the solution by mounting it in epoxy resin (LECO), leaving only one face of the chalcopyrite sample exposed to the solution. The exposed face of the electrode was polished with No. 600 carbide paper to begin each experiment with a fresh surface.

Current-potential curves obtained electrochemically require correction by the potential drops across both the solution and the body of the electrode. The potential applied by the potentiostat, $E_{\text{applied}}$, is not the potential at the working electrode surface, $E_{\text{chalcopyrite}}$, since some potential drops are caused by the electrical resistance of the solution between the tip of the Luggin capillary and the electrode, $R_{\text{solution}}$, and the resistance of the body of the electrode, $R_{\text{chalcopyrite}}$. Since chalcopyrite is a semiconductor its electrical resistivity can be very high; hundreds of ohms for a 1-cm$^3$ electrode, in our experience. For this reason the potential drop across the body of the electrode can be very significant, up to 100 mV. Assuming that both the electrode and the solution follow Ohm's law, these quantities are related by

$$\text{Eq. 2.4} \quad E_{\text{chalcopyrite}} = E_{\text{applied}} - i (R_{\text{solution}} + R_{\text{chalcopyrite}})$$

If $R_{\text{solution}}$ and $R_{\text{chalcopyrite}}$ are known, then the potential at the surface of the electrode can be estimated, since $E_{\text{applied}}$ and the measured current $i$ are recorded by the potentiostat. Eq. 2.4 was used to correct the potentials applied by the potentiostat in the electrochemical experiments reported in this paper.

The electrical resistances of the electrodes were obtained by two methods, first
Eq. 2.5 \[ R_{\text{chalcopyrite}} = \rho \frac{l}{A} \]

where \( \rho \), \( l \), and \( A \) are the electrical resistivity, the thickness, and the exposed surface area of the electrode, respectively. The initial values of \( l \), \( A \) and \( R_{\text{chalcopyrite}} \) were measured to establish the value of \( \rho \). After polishing the new value of \( R_{\text{chalcopyrite}} \) was given by Eq. 2.5 at the new value of \( l \). Electrodes were cut in such a way as to maintain \( A \) constant after successive polishes.

If the body of the electrode behaves as a resistor, then the electrical resistances \( R_{\text{solution}} \) and \( R_{\text{chalcopyrite}} \) are elements in series in the electrochemical circuit. Electrochemical impedance spectroscopy can be used to measure the sum of these two resistances; it is given by the high-frequency intersection of the Nyquist plot with the real impedance axis. However, the intersection obtained at frequencies of \( 2 \times 10^6 \) Hz was generally noisy. The value of \((R_{\text{solution}} + R_{\text{chalcopyrite}})\) used in Eq. 2.4 was estimated from both impedance spectroscopy, and by Eq. 2.5. Typical chalcopyrite impedance spectroscopies and how to obtain the correction from them can be consulted in (Viramontes-Gamboa et al., 2006). For the samples of chalcopyrite used in this study typical values for \( R_{\text{solution}} + R_{\text{chalcopyrite}} \) were 5.1 \( \Omega \) at 25°C and 2 g/L \( \text{H}_2\text{SO}_4 \); 4.56 \( \Omega \) at 40°C and 70 g/L \( \text{H}_2\text{SO}_4 \); 6.0 \( \Omega \) at 60°C and 100 g/L \( \text{H}_2\text{SO}_4 \); and 3.06 \( \Omega \) at 80°C and 100 g/L \( \text{H}_2\text{SO}_4 \).

2.3. RESULTS AND DISCUSSION

Figure 2.1 depicts schematically the anodic polarizations of a hypothetical system presenting active-passive behavior (curve a) and another presenting only pseudo-passive behavior (curve b). In the active-passive system, current increases with potential until the passivation potential, \( E_{pp} \), is reached. Next is a window of potential where the measured current \( i \) decrease sharply to a passive current,
$i_{\text{passive}}$, which is considerably smaller than the maximum critical current, $i_{cc}$, measured at $E_{pp}$. If the potential is increased even more, then a passive-transpassive transition is observed at the transpassive potential, $E_{\text{transpassive}}$. In the pseudo-passive system (curve b) the current does not decrease with increasing potential; instead there is a window of potential within which the current remains constant or increases only slightly, but usually it is difficult to define unambiguously the values for $i_{cc}$, $E_{pp}$, and $E_{\text{transpassive}}$ from such behavior. Passivation of many corroding materials (including chalcopyrite) is due to the formation of a thin, relatively un-reactive layer resulting from the initial reaction between the mineral and its environment. The kinetics of formation of this protective layer have a strong influence on the shape of anodic potentiodynamic curves, which are usually carried out at pre-defined scan rates. If the time taken to sweep the potential range where passivation may occur is shorter than the natural timescale characterizing the kinetics of passivation, then the resulting anodic curve will not show the active-to-passive transition.
Figure 2.1. Hypothetical anodic polarization curves showing active-passive (curve \textbf{a}) and pseudo-passive (curve \textbf{b}) behavior. $E_{pp}$ = passivation potential, $E_{\text{corr}}$ = open circuit (corrosion) potential, $i_{cc}$ = critical current, $i_{\text{passive}}$ = passive current.
The system simply will not have sufficient time to form a protective layer. The result of conducting a scan under such conditions gives a result much like curve b. If the time used to sweep the potential window where passivation is expected is much longer than the natural timescale required to obtain the protective layer, then the anodic curve will indeed show true passivation, as in curve a. However, the risk exists not to observe the active window and its accompanying “nose” since long immersion periods at or near the open circuit potential may modify and passivate the electrode surface before the active region can be seen. This situation is typical of some commercial nickel alloys, which fail to show active oxidation at low scanning rates (Morris and Scarberry, 1970). Another situation where curve b can be experimentally obtained is when the system is in fact only partially passivated, independent of the scan rate or the immersion time. That may happen when the protective layer does not cover the entire surface, or perhaps when the passivating layer is meta-stable and reacts with the environment at a rate independent of the electrode potential, but still rapidly enough not to be passivating. If experimental anodic curves such as curve b are obtained, as is typically the case for the reported electrochemistry of chalcopyrite, then it is of practical and fundamental importance to discern between these two possibilities.

So far the active-passive behavior of chalcopyrite has been observed only in leaching experiments, while chalcopyrite electrodes have been reported as partially passive, displaying only pseudo-passive behavior (the only exception is Hiroyoshi et al., 2004). Looking for an answer to this inconsistency, it is obvious that few researchers in the field of chalcopyrite electrochemistry have taken into account that the kinetics of oxidation and its underlying phenomena are different in the active and passive regions. Each region has its own timescale, which must be considered when experimental variables such as the scanning rate are chosen.

Figure 2.2 presents the most relevant characteristic features of chalcopyrite leaching in H₂O-H₂SO₄-Fe₂(SO₄)₃-FeSO₄ media. The chalcopyrite concentrate described in the experimental section was leached for up to 350 h at controlled
potentials ranging from 433 to 703 mV. Figure 2.2a shows the copper extraction kinetics at constant temperature and solution potential. Figure 2.2b shows the percentage of copper extracted after 50 h of leaching (abscissa) as a function of potential (ordinate). Figure 2.2c shows the accuracy of potential control and deviations from the potential set point. Figures 2.2a and b demonstrate that the leaching rate increases with increasing potential up to 511 mV. At potentials just above this value the rate falls sharply and remains low over a small range of potentials, between 511 and 577 mV. At or above 577 mV the rate increases again. These results show that the leaching of chalcopyrite concentrates indeed displays active-passive behavior with a very small passive window of only 60 to 70 mV. The transpassive region was easily reached in sulfate media with the redox couple Fe(III)/Fe(II). Figure 2.2b shows that the extraction of copper in the transpassive region (at 700 mV) did not increase as dramatically as would be expected from the classical passive-transpassive electrochemical transition of passivating metals. Attempts to explain this transpassive behavior are given below. Figure 2.2c shows that the control of solution potential was very satisfactory, except for the case labeled as 703 mV. The criterion for that experiment was to use only ferric in the solution. The fluctuations arose because the ORP probe was occasionally measuring the contribution of the redox couple Mn(VII)/Mn(II) to the solution potential in the virtual absence of Fe(II). With KMnO₄ as the ferric regenerator the behavior labeled as 703 mV was the maximum potential achievable.
Figure 2.2. Leaching results for a chalcopyrite concentrate and its active-passive behavior. 

a) Kinetics of copper extraction at the solution potentials indicated in the legends. 

b) Active-passive behavior after 50 h of leaching. 

c) Accuracy of potential control.
Consequences of the classical active-passive behavior shown in Figure 2.2b have been observed during chalcopyrite leaching by many in the field (Kametami and Aoki, 1985; Pinches et al., 2001a; Pinches et al., 2001b; Third et al., 2002; Ballester and Cordoba, 2005; Ahonen and Tuovinen, 1993; Okamoto et al., 2003). However, wide variations are reported for values of $E_{pp}$, which was $\sim 510$ mV for the concentrate discussed here. Values as low as 375 mV (Third et al., 2002) and as high as 550 mV (Ahonen and Tuovinen, 1993) have been suggested. The reason for such wide variations may be that $E_{pp}$ strongly depends on temperature, acidity and/or the source of the mineral, since different laboratories work with samples from different sources and at different temperatures and acidities. From the literature it is impossible to obtain systematic data to establish the dependence of $E_{pp}$ on those variables. The importance of $E_{pp}$ is that it delineates the dividing line where chalcopyrite can or cannot be leached effectively; the ability to predict its behavior is of extreme importance for the hydrometallurgical treatment of this mineral.

Figure 2.3 shows what is observed experimentally when different massive electrodes are polarized in the anodic direction at 80°C in H$_2$SO$_4$ solution using linear potential sweep chronoamperometry at a scanning rate of 10 mV/s. The legends in the figure make reference to the source of the mineral; Santa Eulalia and Chihuahua are mine sites in Mexico, Temagami is a mine site in Canada, and a fourth sample was obtained from an unknown source. Curves in Figure 2.3 do not show a true transition to passivation; instead, their behavior corresponds to what we have defined as pseudo-passivation as illustrated in Figure 2.1. A region of potential where currents are essentially constant follows the Tafel-like region. Wide variations in the corrosion potential, $E_{corr}$, and in the magnitude of the currents, as in Figure 2.3, are common when the electrochemistry of chalcopyrite from different sources is compared. The behavior observed in Figure 2.3 is typical of chalcopyrite when this electrochemical technique is used at fast scanning rates (from 0.1 to 100 mV/s), regardless of the source of the mineral, and has been
reported repeatedly in the literature (Peters, 1977; Parker et al., 1981a; Parker et al., 1981b; Warren et al., 1982; Gomez et al., 1996; Devi et al., 2000; Tshilombo et al., 2002; Tshilombo, 2002). The problem with the shape of these curves is that $E_{pp}$ is not well defined since the transition from the active potentials in the Tafel region to what looks like passivation at higher potentials has a high degree of uncertainty; quantitative and practical information cannot be obtained from these pseudo-passive curves.

Figure 2.3. Linear potential sweep chronoamperometry in the anodic direction for four different samples of chalcopryite. Conditions: 80°C, 40 g/L of H$_2$SO$_4$ (for Unknown: 20 g/L H$_2$SO$_4$), scanning rate 10 mV/s.
The scenario of Figure 2.3 changes dramatically if the anodic curves are obtained by potentiostatic techniques instead of potentiodynamic sweeps. As will be shown, potentiostatic experiments allow enough buildup of the protective layer to show a clear active-passive behavior on some of the electrodes represented in Figure 2.3. In the potentiostatic experiments, $E_{corr}$ was recorded first, and when steady state was reached (variations of $E_{corr} < 1$ mV/min) one impedance scan under open circuit potential conditions was conducted from 2.0 MHz to 1.0 Hz with a potential amplitude of 5 mV. Then the electrode was systematically polarized in increments of 10 or 20 mV every hour with the first polarization beginning at 30 mV above $E_{corr}$. Potential steps of 20 mV were used in the potential ranges $E_{corr} + 30 < E < 400$ mV and $600$ mV < $E$ < $E_{transpassive}$. In the range $400 < E < 600$ mV the potential steps were only 10 mV. This higher resolution is required because the active-to-passive transition takes place within this range of potential, as well as the approach from $i_{cc}$ to $i_{passive}$. The anodic potentiostatic curves were generated by plotting the potentials vs. the final (steady state) currents at each step. Impedance spectroscopy scans were also intercalated at 370, 440, 530, and 640 mV as a means to estimate the electrical resistance of the solution and the body of the electrode, and to identify changes in the properties of the double layer and reaction products with increasing potential.

Figure 2.4 shows the effect of temperature as given by potentiostatic techniques on the active-passive behavior of chalcopyrite at three concentrations of H$_2$SO$_4$: 2, 30, and 100 g/L in Figure 2.4a, b and c, respectively. Similar curves were generated at 10, 50, and 70 g/L H$_2$SO$_4$. In order to generate the whole set of experiments in Figure 2.4 two electrodes were required. They were cut from adjacent sections of the same massive mineral specimen, but even so their electrical resistivities were quite different. In the figure the legends indicate the temperature in °C; those accompanied by an asterisk correspond to experiments conducted with an electrode whose resistivity was 62.93 Ω-cm, and legends without an asterisk correspond to experiments conducted with an electrode whose
resistivity was 4.52 Ω-cm. This difference yields smaller currents for the high resistivity electrode even if the applied potential and any other variable are the same. Each curve has symbols and a solid line; the symbols represent $E_{\text{applied}}$ and the solid lines represent the corrected potentials, $E_{\text{chalcopyrite}}$. The correction factor assumed in Eq. 2.4 is proportional to $i$ and to $R_{\text{chalcopyrite}}$. Hence, the smaller $i$ or $R_{\text{chalcopyrite}}$, the smaller the correction factor. At any concentration of acid the correction factor at 25 and 40°C was smaller than 1 mV and the solid line overlaps the symbols in Figure 2.4a–c. At 50°C the correction factor was at most 2 mV, and symbols and lines overlap again. Correction factors were only significant for the electrode of higher resistivity (legends with the asterisk), by 15 mV at 60°C and 61 mV at 80°C (Figure 2.4c). Corrections for the electrode of low electrical resistivity were never larger than 3 mV at 60°C. The abnormal shape of the solid (corrected) line in Figure 2.4c at 80°C indicates that the assumptions supporting Eq. 2.4 are not valid under these conditions; potential drops across highly resistive electrodes should be corrected by a more accurate method.
Figure 2.4. Potentiostatic anodic polarizations of chalcopyrite. $\text{H}_2\text{SO}_4 = \text{a) 2, b) 30, and c) 100 g/L.}$ Symbols correspond to the potential applied and solid lines indicate the potential corrected with Eq. 2.4 to yield the potential of the chalcopyrite surface. Curves accompanied by an asterisk were obtained with an electrode of resistivity 62.9 Ω-cm, while those without an asterisk were obtained with an electrode of resistivity 4.52 Ω-cm. Note the two experiments at 80°C in Figure 2.4c, illustrating the inadequacy of Eq. 2.4 for correcting the potential of high resistivity electrodes.
From Figure 2.4a–c it can be seen that the oxidative current of chalcopyrite increases up to two orders of magnitude when the temperature increases from 25 to 80°C, regardless of the concentration of acid. Although the currents are much smaller at low temperature, the relative degree of passivation, given by the difference between $i_{\text{passive}}$ and $i_{\text{cc}}$, indicates that the passivation of chalcopyrite is relatively more significant at high temperatures. The difference factor was approximately 10 (one order of magnitude) at 80°C and only 2 or 3 at 25°C. $E_{\text{transpassive}}$ also increases with increasing temperature. At 2 g/L H$_2$SO$_4$ it increases from 630 mV at 25°C up to 900 mV at 80°C. $E_{pp}$ also depends strongly on temperature, with values of about 440 mV at 25 and 40°C, increasing to about 510 mV at 60 and 80°C. At 50°C a transition takes place; the shape of the active-passive “nose” is very different at this particular temperature. It is flat between 440 and 500 mV, which contrast with the sharp nose at low and high temperatures. This flatness is observed consistently at each concentration of acid (see Figure 2.7b) and reflects the transition between low and high temperatures. Whatever the nature of the passive layer, an important transition in its properties apparently takes place around 50°C.

Figures 2.5–2.9 show the effect of acidity at temperatures of 25, 40, 50, 60, and 80°C, respectively. Each figure includes an $i$-$t$-$E$ surface at a randomly chosen acid concentration to exemplify the comprehensive behavior of the potentiostatic experiments. All $i$-$t$-$E$ surfaces share the same general shape, including those not shown in the paper. The first potentiostatic polarization, which began at around 30 mV above $E_{\text{corr}}$, asymptotically shows a parabolic relationship between $i$ and $t$ (Figure 2.5a and Figure 2.6a). This parabolic relationship was only observed in the first polarization, and it changes as soon as the second potential step is initiated to a power low relationship $i = i_0 t^{-\beta}$, with $\beta$ showing a marked dependence on the potential. All $i$-$t$-$E$ surfaces show a region of potential where Tafel behavior is observed, and in this region the currents are essentially constant with time (except during initial transients) and $\beta = 0$. The Tafel slope of the potentiostatic anodic
curve is nearly the ideal value, ranging from 60 to 70 mV/decade.

The Tafel region is followed by the active-to-passive transition, where the critical currents are recorded at $E_{pp}$. At 25, 40, 60, and 80°C this transition is sharp; only at 50°C is it consistently flat at every concentration of acid over a potential range of ~70 mV (Figure 2.7a–b). The inset of Figure 2.7b shows that at 50°C the changes in acidity produce a shift in $E_{pp}$; at 2 and 10 g/L $\text{H}_2\text{SO}_4$ $i_{cc}$ is obtained at ~490 mV; at 30 and 50 g/L there are two maximum currents, at ~490 and ~440 mV; finally at 70 and 100 g/L $\text{H}_2\text{SO}_4$ $i_{cc}$ is obtained at ~440 mV. In a range of potentials approximately 100 to 150 mV above $E_{pp}$, currents consistently decrease with time with increasing potentials following the power law with $\beta > 0$. Finally a region of potential is reached where currents remain constant and independent of the applied potential. In many cases the electrode was polarized at potentials high enough to detect the onset of the passive-to-transpassive transition. When this happens the color of the electrode changes dramatically. According to the reaction of Eq. 2.3 this is due to the formation of covellite.

From the whole set of Figure 2.5 through Figure 2.9 it can be seen that acid essentially has no effect on $i_{\text{passive}}$. In the active Tafel-like region the oxidation currents show a slight trend to increase with increasing concentration of $\text{H}_2\text{SO}_4$, by a factor of 2 to 3. $E_{\text{transpassive}}$ increases with increasing temperature and acid concentration. Perhaps the most relevant information from this set of figures is the fact that acid has little effect on $E_{pp}$, except at 50°C where the acid-dependent transition from high to low $E_{pp}$ is detected. The number of experiments made between the maximum current and the passive state indicates the time required by these massive electrodes to reach the passive state, since each point represents one hour of oxidation. Figure 2.5 to Figure 2.9 show that 12 to 15 h are common for the sample from Chihuahua. However, passivation times as short as 4 h or as long as 24 h have been observed for other samples.
Figure 2.5. Potentiostatic anodic polarizations for chalcopyrite from Chihuahua, Mexico at 25°C. a) $i$-$t$-$E$ surface at 30 g/L H$_2$SO$_4$; b) Anodic potentiostatic behavior of chalcopyrite at various concentrations of H$_2$SO$_4$. No ferric, ferrous or cupric ions were added.
Figure 2.6. Potentiostatic anodic polarizations for chalcopyrite from Chihuahua, Mexico at 40°C. a) i-t-E surface at 50 g/L H₂SO₄; b) Anodic potentiostatic behavior of chalcopyrite at various concentrations of H₂SO₄. No ferric, ferrous or cupric ions were added.
Figure 2.7. Potentiostatic anodic polarizations for chalcopyrite from Chihuahua, Mexico at 50°C. 

a) i-t-E surface at 2 g/L H\textsubscript{2}SO\textsubscript{4}; b) Anodic potentiostatic behavior of chalcopyrite at the various concentrations of H\textsubscript{2}SO\textsubscript{4}. The arrows indicate the trends with increasing concentration of acid. The inset zooms in on the behavior between 420 and 520 mV. No ferric, ferrous or cupric ions were added.
Figure 2.8. Potentiostatic anodic polarizations for chalcopyrite from Chihuahua, Mexico at 60°C. a) $i$-$t$-$E$ surface at 30 g/L H$_2$SO$_4$; b) Anodic potentiostatic behavior of chalcopyrite at the various concentrations of H$_2$SO$_4$. No ferric, ferrous or cupric ions were added.
Figure 2.9. Potentiostatic anodic polarizations for chalcopyrite from Chihuahua, Mexico at 80°C. a) $i$-$t$-$E$ surface at 10 g/L H$_2$SO$_4$; b) Anodic potentiostatic behavior of chalcopyrite at the various concentrations of H$_2$SO$_4$. No ferric, ferrous or cupric ions were added.
Because of the scale of the potential axes and the 3D perspective of the $i$-$t$-$E$ surfaces of Figure 2.5 through Figure 2.7, it is not possible to appreciate from them another important phenomena, namely, the kinetics of the onset of corrosion pits and the onset of the active-transpassive transition. Figure 2.10 shows the current density vs. time behavior of the experiments made between 590 and 750 mV at 50°C and 2 g/L of $\text{H}_2\text{SO}_4$, zooming in on the first 200 seconds of the oxidative currents. The time axis has been broken to show the remaining time in log scale. The critical current under these conditions was obtained at 500 mV and is also included for reference. The figure shows that each curve between 590 and 750 mV has two oxidative waves, labeled A and B. Waves A are oxidation pulses at the beginning of the potentiostatic polarizations which last for $\sim$100 seconds and then gradually die out. Waves B represent a process taking place at longer times with a longer time scale, the amplitude and duration of which increase with increasing potential, becoming progressively larger until they turn into the transpassive regime. The appearance of waves B corresponds to a change in the color of the electrode surface from that of chalcopyrite to that of covellite. If the reaction of Eq. 2.3 is correct, then waves B can be associated with the oxidative transformation of chalcopyrite to covellite. In this work no further attempts were made to identify the nature of the transpassive region other than those reported in the literature (Nava and Gonzales, 2006) and leading to the reaction of Eq. 2.3. Waves A were observed for each sample of chalcopyrite studied at temperatures lower than 80°C (at this temperature only traces of the phenomenon are detected) and acid concentrations from 2 to 70 g/L. They are observed even in those electrodes showing only pseudo-passive behavior (see discussion below). This indicates the universality of the underlying phenomenon.

It is well known that localized corrosion pits produce a sharp rise in the corrosion rate when they break the passive film of active-passive metals, although corrosion pits are not always stable. In a recent study it was reported that short-lasting spikes of oxidative potentiostatic current in stainless steel are caused by the
appearance of localized meta-stable corrosion pits (Punckt et al., 2004). After a few seconds these meta-stable pits passivate and the current spike flattens out. This phenomenon in stainless steel presents the same characteristic waves as those waves A shown in Figure 2.10. Given this similitude it is plausible to suggest that the phenomenon behind the strongly increased oxidation of waves A is the appearance of localized metastable corrosion pits on the electrode surface. The formation of those pits at high potentials is visible without the help of a microscope, although microscopic studies of the density of these pits at different potentials have been reported by Biegler and Swift (1979).

Figure 2.10. Waves of potentiostatic current observed at short and long times at 50°C and 2 g/L H₂SO₄ between 590 and 750 mV. Waves A may indicate the beginning of unstable localized corrosion. Waves B result from the oxidative transformation of chalcopyrite to covellite.
It can be observed in Figure 2.2b that the size of the passive region given by leaching results is very small, only 60 to 70 mV. However, the size of the passive window obtained from the electrochemical results shown in Figure 2.5 through Figure 2.9 indicates a much wider range of passivation, roughly 200 to 300 mV. It would seem that electrochemical and leaching experiments disagree with respect to the size of the passive potential region. However the difference between the passivation potential and the potentials where waves A begin to appear is around 60 to 70 mV at low concentrations of acid. Each potentiostatic anodic curve in Figure 2.7b has only one black symbol (all others are white). That particular symbol indicates the potential where waves A began to appear for the experimental conditions of each curve. This might indicate that the phenomenon that initiates the appearance of waves A is more relevant and persistent when chalcopyrite is finely ground than it is for massive electrodes. If this hypothesis is valid, then waves A would last longer in powdered chalcopyrite and the onset of the transpassive region would be established at much lower potentials with a non-uniform preferential corrosion. In fact, Figure 2.11 compares leached particles and the residual elemental sulfur of the chalcopryte concentrate used in Figure 2.2 at potentials of 500 and 700 mV, which respectively correspond to the active and the transpassive regions of potential in Figure 2.2b.

The SEM images of Figure 2.11a show that at low (active) potentials the leached particles resemble “shrinking cores” with the residual elemental sulfur uniformly covering the particles. At high (transpassive) potentials Figure 2.11b shows that the particles of chalcopyrite have been corroded following certain crystallographic planes of the mineral. Moreover, it is a general observation that the remaining sulfur at transpassive potentials does not cover the surface uniformly, but is more localized. Crystallographically localized corrosion is a well-known phenomenon which leads to preferential oxidation on certain planes of the sample and has also been reported recently for powdered chalcopyrite at high potentials in ferric sulphate media by Al-Harahsheh et al. (2006). They showed that the dissolution of
finely ground chalcopyrite powder takes place on preferential planes while other non-corroding planes support cathodic reactions and do not accumulate elemental sulfur. These facts support the hypothesis that the phenomenon leading to waves A in Figure 2.10 might be due to the preferential oxidation of the mineral, which manifests as corroding pits in the massive electrode and as crystallographic-preferential dissolution in finely ground particles. Under this hypothesis the size of the passive window of leaching experiments shown in Figure 2.2b agrees well with the onset of waves A in Figure 2.10.
Figure 2.11. SEM micrographs showing the morphology of chalcopyrite particles partially leached under the following conditions at 80°C: a) 500 mV, 30 g/L H₂SO₄; b) 500 mV, 15 g/L H₂SO₄; c) 700 mV, 30 g/L H₂SO₄. Figures b and c show that chalcopyrite dissolves preferentially along certain crystallographic planes.
Moreover, the present authors have made many experiments with carbon paste electrodes of powdered chalcopyrite (Viramontes-Gamboa et al., 2006), and generally the onset of the passive-to-transpassive transition is observed in that type of electrode at potentials lower than those observed for massive electrodes.

Figure 2.12 summarizes the whole dependence of $E_{pp}$ on temperature and $\text{H}_2\text{SO}_4$ concentration. Symbols indicate the passivation potential at the temperature indicated by the legends, with the concentration of acid on the horizontal axis. The passivation potentials in this figure are the corrected ones, not the potentials applied by the potentiostat. For some experiments the currents were very high and Eq. 2.4 was not appropriate for correcting the potential (see the solid curve at 80°C and 100 g/L in Figure 2.4c, for example). In these problematic cases a new electrode was prepared and polished until its resistance was no higher than 4 $\Omega$, then the experiment was repeated to ensure an accurate measurement of $E_{pp}$, where differences between $E_{applied}$ and $E_{chalcopyrite}$ were never greater than 4 mV.

Figure 2.12 shows that the temperature affects significantly the passivation potential of chalcopyrite. At low temperatures (25 and 40°C) $E_{pp}$ is 440 mV. At high temperatures (60 and 80°C) it is around 515 mV. At those low and high temperatures acid has no significant effect. The transition between low and high $E_{pp}$ takes place at around 50°C; only at this temperature is a high sensitivity to the concentration of acid detected. The errors bars at 30 and 50 g/L $\text{H}_2\text{SO}_4$ at 50°C indicate the region where the anodic potentiostatic polarizations show a flat plateau of ~70 mV, and $E_{pp}$ is not mono-valued, but in fact two maximum currents may be observed, one at 440 mV and the other at 490 mV (see the inset of Figure 2.7b). The curve belonging to 50°C plots the potentials at the middle of the plateau and shows the acid-driven transition taking place between high and low passivation potentials. The figure also indicates the “active” and “passive” potential regions; each isotherm separates the two areas. At potentials below each curve chalcopyrite is in the active region and rapid leaching kinetics are predicted. At potentials above the curve chalcopyrite is in the passive region and low copper
recoveries are to be expected. The solid square symbol indicates the passivation potential obtained in the leaching experiments of Figure 2.2 in order to compare the results of electrochemistry and leaching tests. As can be seen the agreement between the two techniques is excellent. Unfortunately the potential controlled experiments shown in Figure 2.2a–c are very time consuming and only one leaching point could be included in Figure 2.12.

![Graph showing the dependence of $E_{pp}$ on temperature and concentration of $\text{H}_2\text{SO}_4$.](image)

Figure 2.12. The dependence of $E_{pp}$ on temperature and concentration of $\text{H}_2\text{SO}_4$. The errors bars at 30 and 50 g/L $\text{H}_2\text{SO}_4$ and 50°C indicate that in that zone the maximum of the anodic curve is a flat plateau and that $E_{pp}$ is not a mono-valued function of current (the symbols indicate the middle potential of the plateau. See inset in Figure 2.7b).
The potential applied to the electrode in an electrochemical experiment and the potential of mineral particles suspended in a solution with a redox potential given by the activities of ferric and ferrous ions are conceptually different. Those potentials are in general incomparable, because the potential of the mineral particles in the slurry (the mixed potential) depends on both the oxidation kinetics of the mineral itself and the partial currents for the oxidation of ferrous and the reduction of ferric. If the oxidation of the mineral is rapid, then the potential of the mineral is lower than the solution potential determined by the activities of the redox couple components. Only when the oxidation of the mineral is slow can the potential of the solution be compared with the potential of the mineral. While chalcopyrite has one of the slowest leaching rates of all the common base metal sulfides in Fe(III)/Fe(II) sulfate media, the authors have previously reported experimental values of the potential difference between the solution and various chalcopyrite samples (Viramontes-Gamboa et al., 2006). They found that for ferric-to-ferrous ratios up to 100, differences between the two potentials are never greater than 4 mV, regardless of the concentration of acid, which allows a direct correlation of potential between electrochemical and leaching experiments (at least for potentials up to ~580 mV). Significant differences were only noticed when the solution contained only ferric, with no ferrous present (Nicol and Lazaro, 2002). In this way the electrochemical results of Figure 2.12 can be applied directly to chalcopyrite leaching experiments, where the potential of the suspended particles is, for all practical purposes, equal to the solution potential.

Many of the leaching studies reported in the literature are made with chalcopyrite concentrates directly from operating mines. Pyrite is almost always present in these concentrates to some degree, because it is naturally associated with chalcopyrite in most geological deposits, and complete pyrite depression during froth flotation is difficult to achieve. It is well known that pyrite may affect chalcopyrite reactivity through the formation of galvanic couples, with chalcopyrite as the anode and pyrite as the cathode, if the experimental conditions are such
that pyrite has a higher potential than chalcopyrite. (This situation can be reversed at high solution potentials, where pyrite leaches much more rapidly than chalcopyrite, thereby lowering its surface potential.) In order to ascertain whether the passivation potentials of Figure 2.12 obtained electrochemically are applicable to leaching experiments on chalcopyrite concentrates containing pyrite, it is necessary to know to what extent pyrite affects chalcopyrite reactivity. Previous studies have established the effect of pyrite on chalcopyrite reactivity in leaching experiments, using various samples of both minerals in various proportions (Tshilombo et al., 2002). Based on these studies, 20% pyrite in a chalcopyrite concentrate would only be expected to increase the leaching rate of copper by 5% or less. Hence, such low concentrations of pyrite are not expected to change the passivation potentials predicted in Figure 2.12. As shown, the passivation potentials of leaching experiments containing roughly 20% pyrite agree very well with anodic polarization experiments on nearly pure chalcopyrite electrodes.

Most values reported for $E_{pp}$ in the literature and based on leaching experiments range between 440 mV and ~515 mV. According to the results of this study it is in this range of potentials that the shape of the curve flattens around $E_{pp}$ and $i_{cc}$ (being perfectly flat at 50°C and 30 to 50 g/L H$_2$SO$_4$). Acid and temperature tilt the plateau toward 440 or 515 mV. Below 440 mV Tafel behavior is practically ideal. Quantitative analysis of copper and iron dissolved into the solution (see the discussion below) demonstrates that chalcopyrite electrodes dissolve with the total stoichiometry given by Eq. 2.2, although an iron-deficient protective structure, as suggested by Eq. 2.1, is in fact established (Tshilombo, 2002).

The anodic potentiostatic response of chalcopyrite was tested using massive electrodes from three different sources: Santa Eulalia (Mexico), Chihuahua (Mexico), and Temagami (Canada). Electrodes made from the first two samples produced anodic curves with very well defined active-passive behavior, both of them with $E_{pp}$ values in excellent agreement with leaching tests. However, the samples from Temagami were reticent and only displayed pseudopassive
behavior when the same potentiostatic procedure was applied, as shown in Figure 2.13.

Figure 2.13. Anodic potentiostatic curve for chalcopyrite from Temagami at 80°C, 10 g/L H₂SO₄. Temagami samples display only pseudo-passive behavior.

To our knowledge the only other study that succeeded in showing the active-to-passive behavior of chalcopyrite through electrochemical techniques in sulfate media is that of Hiroyoshi et al. (2004). These authors associated the active-to-passive transition to the synergistic effect of cupric and ferrous ions, since this transition was only observed when these ions were present. In order to examine their theory, some experiments were conducted, with and without the addition of cupric and ferrous ions, using both reticent electrodes (from Temagami) and active ones (from Chihuahua). Figure 2.13 compares the response of Temagami
chalcopyrite at 80°C and 10 g/L H₂SO₄, with and without the addition of 0.1 M cupric and ferrous as sulfate salts (following the study of Hiroyoshi et al. 2001). The improvements claimed by Hiroyoshi when ferrous and cupric ions coexist were not observed in the present study; the pseudopassive shape of the curves remained the same and the transition to passivation was not observed. The only observable difference is the magnitude of the current densities, which are almost 2 orders of magnitude higher when ferrous and cupric are present. This increase is almost certainly due to the contribution of ferrous oxidation, as Warren et al. (1982) had already pointed out. These results clearly show that the coexistence of cupric and ferrous ions in solution neither guarantees, nor can be the reason for, the active-passive behavior of chalcopyrite.

In the experiments reported in Figure 2.4 through Figure 2.10, current densities range from only a few μA/cm² at 25°C to hundreds of μA/cm² at 80°C. Hence, even when the time involved was very long, the accumulation of cupric and ferrous ions resulting from the dissolution of the electrode was not significant, especially at low temperatures. Table 2.1 shows quantitative values for the electric charge involved in the electrochemical reactions and the accumulations of those ions at different temperatures. Values are given for both the entire experiment, and for the period up to the onset of passivation. Table 2.1 compares the values measured by atomic absorption spectrophotometry with the values estimated from the stoichiometry of Eq. 2.2 and Eq. 2.3 (the latter reaction was assumed only for the transpassive regime). The number of electrons involved in each experiment can be estimated from the total electric charge which is recorded by the potentiostat. At temperatures up to 50°C, the two values agree very well. Deviations are observed only at higher temperatures, possibly due to the contribution of sulfur oxidation to the total electric current or deviations from the stoichiometry of Eq. 2.2. Because current densities are not strongly influenced by acid, it has no significant effect on Table 2.1 values. The last two columns in Table 2.1 show the concentrations of copper and iron dissolved into the solution at the onset of
passivation, which were estimated using the stoichiometry of Eq. 2.2 and the measurement of the electric charge. It can be seen that the concentration of those ions in solution are as low as 1 µM at 25°C and 53 µM at 80°C. These negligible concentrations are four to five orders of magnitude lower than those used by Hiroyoshi et al. (2001) (0.1 M at 25°C).

It was attempted to establish the dependence of $E_{pp}$ on acidity and temperature using carbon paste electrodes (prepared as Lazaro et al., 1995) of either chalcopryite concentrates or freshly ground chalcopryite, using both potentiodynamic and potentiostatic techniques as described above. However, those attempts were unsuccessful because $E_{pp}$ was found to depend strongly on either the time step or the scanning rate (in fact, the classical active-passive “nose” defining $E_{pp}$ was undetectable for potentiostatic steps longer than 60 s). Another major drawback of carbon paste electrodes is that, at high temperatures, the hydrophobic nature of the binder (which is a nonconductive oil) causes rapid nucleation of water vapor bubbles on the exposed surface, thereby blocking the surface to electrochemical reactions. At 60 and 80°C the blockage can be total. However, those electrodes in fact also show the active-passive and passive-transpassive transitions in solutions containing only H$_2$SO$_4$, in the total absence of cupric and ferrous. A typical example is shown in Figure 2.14 for a concentrate of chalcopryite at 25°C and 50 g/L H$_2$SO$_4$. In those experiments, the electric charge involved at the onset of passivation is further reduced to minimum levels as low as 15 mC; considering a reaction involving four electrons for estimation purposes, this would correspond to concentrations of cupric and ferrous ions released into the solution on the order of 0.55 nM, which are virtually undetectable. This result further supports the view that the coexistence of cupric and ferrous ions in solution cannot be the cause of chalcopryite passivation, which disagrees with the theory of Hiroyoshi and co-workers.
Table 2.1. Concentrations of copper and iron due to the dissolution of the electrode. The electric charge involved in each experiment was recorded directly by the potentiostat.

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>Accumulation during the entire experiment</th>
<th>Accumulation up to ( E_{pp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>([\mathrm{Cu}]) (mg/L)</td>
<td>([\mathrm{Fe}]) (mg/L)</td>
</tr>
<tr>
<td>( T, {^\circC} )</td>
<td>([\mathrm{H}_2\mathrm{SO}_4]) (g/L)</td>
<td>Vol (mL)</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>700</td>
</tr>
<tr>
<td>40</td>
<td>2</td>
<td>670</td>
</tr>
<tr>
<td>50</td>
<td>2</td>
<td>650</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
<td>700</td>
</tr>
<tr>
<td>80</td>
<td>30</td>
<td>700</td>
</tr>
</tbody>
</table>

\(^a\) AA = Atomic absorption spectrophotometry assays.

\(^b\) Estimated = Values estimated with the stoichiometry of Eq. 2.2 and Eq. 2.3
Figure 2.14. Response of carbon paste electrodes to passivation. Chalcopyrite-graphite mixtures show an active-passive transition (albeit only at certain scanning rates) with no additional cupric and ferrous ions in solution. In these experiments the accumulation of those ions resulting from the dissolution of chalcopyrite is on the order of $10^{-10}$ M. The carbon paste was made by mixing 0.2 g of chalcopyrite concentrate, 0.8 g of graphite powder (Aldrich), and nonconductive silicon oil (Aldrich).

Figure 2.13 showed the effect of coexisting cupric and ferrous ions on samples of chalcopyrite reticent to passivation. Figure 2.15 shows their effect on active electrodes from Chihuahua at 25°C and 30 g/L H$_2$SO$_4$. The most notable effect observed is increased current density, for this sample roughly one order of magnitude higher than obtained in solutions containing only acid. However, the classical active-passive behavior of the sample and the shape of the curves remained essentially the same. Atomic absorption spectrophotometry assays for
copper taken into solution where cupric and ferrous sulfate salts were initially added at 0.1 M showed no detectable increase in copper content. As Table 2.1 shows, the dissolution of the electrode only increases the concentration of copper by a few parts per billion (~70 ppb at 25°C), which is indistinguishable from the copper initially added (6355 ppm). The conclusion is that the only significant effect of ferrous and cupric ions in solution is the detection of higher currents, which are due to the contribution of ferrous oxidation on the surface of the electrodes rather than to the oxidation of chalcopyrite. Furthermore, the passivation observed when those ions are present represents passivation to the oxidation of ferrous, which appears to begin at slightly lower potentials than chalcopyrite passivation. It may be worth noting that, while the passivation of Fe(II) oxidation and chalcopyrite oxidation may be related, they are not necessarily equal, and studying the former does not necessarily imply observation of the latter.

To the present author’s knowledge, the shape of the anodic curves for chalcopyrite presented in this study has not been reported elsewhere. The effects of temperature and acidity on the plateau between 440 and 500 mV may have major consequences for the accurate design of novel routes for copper extraction through chalcopyrite leaching. From the many theories proposed to explain chalcopyrite passivation mentioned in the introduction, none of them takes into account the existence of this plateau and its effects. The resemblance of our anodic curves with those for iron in H₂SO₄ media suggests that both systems may have common underlying phenomena. The plateau we observe for chalcopyrite is also commonly observed in iron passivation in sulfate media, and for that system it is believed to be due to the precipitation of iron sulfate salts on the surface of the electrode.
Figure 2.15. Effect of cupric and ferrous ions on the active-passive behavior of Chihuahua chalcopyrite. When those ions are present the active-passive shape of the anodic curve does not change dramatically; however, the measured currents are mainly due to the oxidation of ferrous to ferric rather than to the oxidation of chalcopyrite.

From the work conducted in our laboratory we have confirmed the preferential dissolution of iron during the initial stages of electrochemical leaching for some samples of chalcopyrite (Tshilombo, 2002), which is a well-known phenomenon (Warren et al., 1982; Biegler and Swift, 1979; Biegler and Horne, 1984; Hackl et al., 1995) and indicates that an iron-deficient protective layer in agreement with Eq. 2.1 may be the cause of passivation. At low temperatures and potentials between 450 and 550 mV dissolved Cu/Fe ratios around 1/3 are typical (exact values are sensitive to the particular sample). However, in light of this electrochemical study it seems that chalcopyrite oxidative behavior and its passivation are not only determined by the formation of iron-deficient protective
structures. Similitude with iron behavior in sulfate media suggests that the precipitation of sulfate salts may also play an important role in chalcopyrite passivation, which has already been observed (Parker et al., 2003).

The results of this study demonstrate that the active-passive behavior of chalcopyrite observed in leaching tests can be studied by electrochemical techniques and useful operational parameters can be obtained. However, the source of the mineral has a major influence on the shape of the anodic curves, and properly responding electrodes must be chosen to observe the active-passive behavior.

2.4. CONCLUSIONS

The active-passive behavior of chalcopyrite has been studied using electrochemical potentiostatic techniques with massive electrodes of chalcopyrite over the potential range from 300 to 700 mV (SCE). The application of this technique produces well-defined active-passive behavior and allows determination of the passivation potential for this mineral at all temperatures and H2SO4 concentrations. The passivation potential was found to be dependent on temperature, with a sharp acid-driven transition at 50°C. At temperatures lower and higher than 50°C, $E_{pp}$ does not depend on the concentration of H2SO4. In the active range of potentials the oxidation currents show a systematic slight increase, by a factor of 2 to 3, with increasing acidity from 2 to 100 g/L. The critical and passive currents increase with increasing temperature (from 25 to 80°C) up to two orders of magnitude. Within the experimental range of error the passive currents were insensitive to the concentration of acid at constant temperature. The onset of the transpassive region, which might indicate the oxidation of chalcopyrite to covellite, strongly depends on both acidity and temperature; the higher these variables, the higher the transpassive potential.

The application of anodic potentiostatic steps of 10 mV/h shows that the time
chalcopryte electrodes require to reach the passive state ranges from roughly 4 to 24 h, which means that in this type of electrode the passivating protective layer builds up very slowly. This time scale characterizes the passivation process and establishes appropriate scanning rates in order to observe the active-passive and passive-transpassive transitions. The addition of ferrous and cupric ions was not required to observe the active-to-passive transition. The source of the mineral was found to be much more important, as some sources are reticent and do not show the transition to passivation when the same technique is applied.

2.5. ACKNOWLEDGEMENTS

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2.6. REFERENCES


CHAPTER 3.
ELECTROCHEMICAL CHARACTERIZATION OF SINGLE MICRON-SIZE PARTICLES OF SULFIDES IN ACIDIC SOLUTIONS*

3.1. INTRODUCTION

Chalcopyrite is of primary interest in the metals industry because it accounts for roughly 70% of total world copper reserves. It is extremely difficult to leach because passivates in different leaching media, stopping the chemical leaching reactions. Ferric sulfate is considered the most convenient leaching medium because its chemistry is well known, corrosion of industrial equipment is minimal, and solvent extraction and electrowinning can be used to recover leached copper. Overcoming chalcopyrite passivation in this medium is the ultimate objective of many current research projects, both in academia and industry.

In approaching the problem of chalcopyrite passivation, one of the first steps undertaken was to establish, through small lab-scale leaching experiments, the range of potentials where chalcopyrite leaching is active and passive. Chalcopyrite concentrates were leached at controlled potentials (Rivera-Vasquez et al., 2006) (See Chapter 2), and electrochemical anodic potentiostatic techniques were used on massive samples from various sources (Viramontes-Gamboa et al., 2007) (See Chapter 2). Those studies demonstrated that electrochemical techniques have the potential to accurately predict operational parameters, such as the passivation potential, exactly as observed in leaching conditions. The predictive potential of the technique can be of great relevance for industrial practice. However, there are some discrepancies between leaching and electrochemical passivation; for example, in some cases chalcopyrite passivates at 440 mV according to leaching experiments, but at 510 mV according to electrochemistry (and vice versa). These

* A version of this chapter will be submitted for publication. BF Rivera-Vasquez and DG Dixon, (2010). Electrochemical Characterization of Single Micron-Size Particles of Sulfides in Acidic Solutions.
differences may be due to the massive nature of the working electrode used in those previous studies.

Electrochemical studies reported in the literature have presented dissimilar results concerning the potential range of the passive region. It has been determined that the causes for this irreproducibility could be the electrode preparation (Hiskey, 1993; Peters, 1977) and the source of the mineral specimens (Gomez et al., 1996; Peters, 1977; Tshilombo et al., 2002; Warren et al., 1982). For example, Peters (1977) reported the electrochemical response of chalcopyrite changes with the nature of the sample and the way in which it is prepared. Warren et al. (1982), working with different sources of chalcopyrite, observed different passive currents among the various samples. This difference was attributed to the occurrence of impurities in the samples.

One impurity that often occurs with chalcopyrite concentrates is enargite. This sulfide is the most common arsenic-bearing sulfide and is associated with chalcopyrite concentrates due to their similar flotation properties. A number of studies have been conducted electrochemically with the purpose of separating enargite from chalcopyrite during flotation to avoid the environmental and economic drawbacks associated with the smelting of high arsenic concentrates (Castro and Baltierra, 2005; Cordova et al., 1997; Fornasiero et al., 2001; Guo and Yen, 2005; Kantar, 2002; Mihajlovic et al., 2007; Pauponte and Schuhmann, 1996). Considerable research has also been conducted on the leaching of enargite concentrates (Munoz et al., 2006). However, massive samples were also used in most of these studies, potentially causing the same lack of reproducibility observed in chalcopyrite literature.

Thus, the objectives of this work are: to initiate a study of the electrochemical behavior of individual finely ground particles of chalcopyrite and enargite under similar conditions to leach, and to generate basic knowledge of chalcopyrite and enargite passivation which may facilitate successful leaching of these materials.
3.2. EXPERIMENTAL PROCEDURE

3.2.1. Single Particle Technique

One of the main goals is to adopt the microelectrode technique that was developed by Bursell and Bjornbom (1990), and Uchida et al. (1997) to study the electrochemical response of sulfide mineral particles. This technique has been used, for example, to measure the electrochemical and mass transport characteristics of nanoporous carbon (Bursell and Bjornbom, 1990), oxygen reduction and measuring transport parameters for hydrogen in metal hybrids (Johnsen et al., 2003), and the catalytic material properties of fuel cells, and to characterize materials in microbatteries (Nishizawa and Uchida, 1999). The use of this technique implies the use of capillary-type microelectrodes commonly used by biologists to study single living cells.

Based on previous studies mentioned above, a set of new techniques were developed for the precision micromanipulation of micron-size sulfide particles that includes a temperature controlled micro electrochemical cell and shielded glass capillary microelectrodes. A correct arrangement of these devices ensures a reliable particle current collector connection for applying various electrochemical techniques. Also, placing the entire apparatus under an optical microscope provides a convenient means of visual monitoring.

The single microelectrode technique consists of contacting a carbon fiber to a single particle of material to be investigated using a micromanipulator. A sketch of the final arrangement is shown in Figure 3.1.
The instrumental array involved in the assembly and characterization of single sulfide particles included a conventional stereo microscope (Meiji EMZ-13TR) equipped with a digital microscope eyepiece camera (Lumenera Infinity 1-3) connected to a PC via an USB interface. This system allowed acquisition of both pictures and real time video images for further processing. An XYZ motorized micromanipulator (Sutter Instruments MP-225) mounted on one side of the microscope provided the means for accurately positioning the working electrode.

The construction of the working microelectrode was made by joining together an electrochemically activated carbon fiber of 25 μm (WPI Carbon Wire) with a copper wire of approximately 0.5 mm in diameter using silver epoxy. Then, this assembly was inserted into a flame-pulled glass micropipette (WPI Glass Pipette) with an internal diameter of 0.68 mm and a tip of approximately the same diameter of the carbon fiber being used. Finally, both ends were sealed with an epoxy (ethyl cyanoacrylate). A sketch of the electrode is shown in Figure 3.2. Carbon fibers have traditionally been used as strengthening materials. However, because of
their good conductivity, non-toxicity, non-reactivity under different conditions, and small size, microelectrodes from carbon fibers have been applied in electrochemical detection of oxidizable compounds (Cahill et al., 1996; Cahill and Wightman, 1995).

Figure 3.2 Working microelectrode assembly

The tip of the working electrode was contacted with a single sulfide particle among several ones spread on a disk of glass frit immersed in electrolyte solution by handling the micromanipulator using a remote controller (See Figure 3.3). The glass frit was inside of a glass beaker of 0.1 L containing the electrolyte solution, the reference electrode, and the counter electrode. The reference electrode was a standard calomel electrode (SCE) with a potential of 0.245 V against the standard hydrogen electrode (SHE). A Luggin capillary was used in conjunction with the SCE. The counter electrode was a platinum wire with a length of 5 cm and a diameter of 1 mm. The electrolyte solution was temperature controlled with a
heating band. All electrochemical measurements were carried out with a potentiostat from Princeton Applied Research (PARSTAT 2273).

Figure 3.3 Photography under the microscope of chalcopyrite particles on the porous glass frit showing the electrode arrangement. Carbon fiber diameter (working electrode) 25 µm.

3.2.2. Single Sulfide Particles

In the course of this study, open circuit potential and cyclic voltammetry experiments were conducted on <100 µm particles of chalcopyrite (Cp), pyrite (Py), and enargite (En). XRD analysis was performed on all samples to determine the purity of the specimen. Details on the way this analysis was performed are explained in detail in Section 3.2.3. The particles were prepared from specimens of massive sulfides in all cases. The massive samples were first crushed using a
ring mill for 2 minutes. Then, the ground material was sieved to collect particles within a size range of +75 to –125 microns.

The chalcopyrite sample used in this study was from Chihuahua, Mexico; the pyrite was from Huanzala, Peru; and the enargite was from Butte, Montana. XRD analysis showed that chalcopyrite and pyrite samples were reasonably pure with 98.6% and 92.3% respectively; enargite purity was 62%. For the case of the Cp and Py, hand-picked samples were selected using an optical microscope to confirm purity of the particle by color and OCP measurements. But in the case of the enargite, due to its moderate purity, particles were chosen after an energy dispersive X-ray spectroscopy (EDX) analysis was performed under a scanning electron microscope (SEM). This extra analysis helped to avoid choosing any other similar mineral particles by mistake. XRD results for Cp, Py, and En are shown in Table 3.1, Table 3.2, and Table 3.3 respectively.

Table 3.1  XRD mineralogical analysis of the Chihuahua, Mexico chalcopyrite massive sample.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>98.6</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Table 3.2 XRD mineralogical analysis of the Huanzala, Peru pyrite massive sample.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
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</tr>
<tr>
<td>Talc</td>
<td>Mg₃Si₄O₁₀(OH)₂</td>
<td>0.9</td>
</tr>
<tr>
<td>Fluorite</td>
<td>CaF₂</td>
<td>4.6</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>(Zn,Fe)S</td>
<td>1.0</td>
</tr>
<tr>
<td>Marcasite</td>
<td>FeS₂</td>
<td>0.4</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>92.3</td>
</tr>
</tbody>
</table>

Table 3.3 XRD mineralogical analysis of the Butte, Montana enargite massive sample.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>7.9</td>
</tr>
<tr>
<td>Enargite</td>
<td>Cu₃AsS₄</td>
<td>62.0</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>16.1</td>
</tr>
<tr>
<td>Tennantite</td>
<td>(Cu,Ag,Fe,Zn)₁₂As₄S₁₃</td>
<td>6.5</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>(Zn,Fe)S</td>
<td>1.3</td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu₅FeS₄</td>
<td>2.7</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>2.3</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃</td>
<td>0.8</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg₃Si₄O₁₀(OH)₂</td>
<td>0.5</td>
</tr>
</tbody>
</table>
3.2.3. Characterization Techniques

X-Ray diffraction analysis (XRD) was conducted using a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer equipped with a diffracted beam with a Fe monochromator foil. The sulfide samples were reduced to fine powder to the optimum grain-size range for X-ray analysis (<10μm) by grinding under ethanol in a vibratory McCrone Micronising Mill for 7 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-80°2θ with CoKα radiation. The X-ray diffractogram was analyzed using the International Centre for Diffraction Database PDF-4 using the Search-Match software by Siemens (Bruker). X-ray powder-diffraction data were refined with the Rietveld program Topas 3 (Bruker AXS). The results produced by XRD in the course of this work represent the relative amounts of crystalline phases normalized to 100%.

Morphology and surface analyses were performed on a scanning electron microscope (SEM) (Hitachi S3000N) at a voltage of 20kV coupled with a energy dispersive X-ray analysis (EDX) (Quartz XOne). Samples were placed on a sample holder using a carbon sticker and placed inside the microscope without any sputtered layer in an effort to avoid any change in the morphology of the samples. The preparation of samples for SEM analysis as mentioned was performed under an optical microscope due to the minuscule size of the micron-size samples.

3.2.4. Solutions

All solutions where made with distilled water and analytical grade reagents. The chemicals used in the course of this work are listed in Table 3.4. The chemicals were used with no additional purification. Solutions were prepared at concentrations of 2, 10, 50 and 90 g/L of sulfuric acid (H₂SO₄) in distilled water. For the experiments with sodium chloride (NaCl), the solutions were prepared with 90 g/L of sulfuric acid and 60 g/L of NaCl. Electrochemical tests were performed
with solutions at two different temperatures, 20ºC and 60ºC. No attempt was made to eliminate dissolved oxygen and no agitation was applied to the solutions.

Table 3.4  List of reagents used to prepare the acidified solutions used in electrochemical tests.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Formula</th>
<th>Purity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric Acid</td>
<td>H₂SO₄</td>
<td>98</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>NaCl</td>
<td>99</td>
</tr>
</tbody>
</table>

3.3. RESULTS AND DISCUSSION

3.3.1. Open Circuit Potential Measurements

The study of open circuit potential on sulfide minerals has definitive importance in the hydrometallurgical field, particularly in the development of new processes where a key factor is the galvanic interaction between two different sulfide minerals. This was stated in the work of Tshilombo (2004) and later demonstrated its applicability to concentrates by Mayne (2006). Thus, open circuit potential (OCP) of micron-size single sulfide particles and the effect of some factors on the OCP of a mineral will give important information on the behavior of these particles in different processes.

The effect of sulfuric acid concentration on OCP at concentrations of 2, 10, 50 and 90 g/L was investigated in solutions at 20 and 60ºC. Also one point at 45ºC and 10 g/L was evaluated. To investigate the effect of sodium chloride on OCP, solutions containing 90 g/L of H₂SO₄ and 60 g/L of NaCl were also measured at both temperatures. The results are illustrated in Figure 3.4 for chalcopyrite particles and
Figure 3.5 for enargite particles. All potentials in this paper are referred to the KCl-saturated calomel electrode (SCE) unless otherwise noted.

Each symbol in both plots represents an average of five individual experiments (See Appendix A). A single sulfide particle was immersed in the solution to be evaluated and was allowed to rest for about 5 minutes before the measurement of OCP began. This rest time was applied because a drift in OCP was observed in some particles whose OCP was measured immediately after they were placed on the solution. On the other hand, those particles which were allowed to rest in solution showed an almost instantaneous steady state with a very small variation of OCP, in the range of ±2 mV during 2-to-5 minute duration of the test. Two other factors were also observed to have an effect on the measurement of the OCP in particles. One was the existence of impurity inclusions in the particles. Under the microscope it was observed that when a given particle had noticeable impurities attached to its surface, or forming part of it, this particle gave a very unstable OCP reading. These impurities were usually silica. Another aspect was the presence of oxygen as air at the surface of the particles. These oxygen bubbles had a strong effect during the measurements, increasing the OCP of the particles. Thus, the particles electrochemically evaluated in this work were chosen to avoid these factors.

Results in Figure 3.4 and Figure 3.5 for chalcopyrite and enargite respectively show that the OCP of both sulfides decreased with increasing sulfuric acid concentration. An initial rapid decline in OCP was observed up to 10 g/L of H₂SO₄, and then a slower decline with increasing acidity was observed. On the other hand, increasing solution temperature caused a decrease in the initial OCP. For example, the initial OCP of chalcopyrite at 2 g/L of sulfuric acid was 360 mV at 20°C and 272 mV at 60°C. The difference in OCP between these two temperatures was almost constant at the various acid concentrations measured. This pattern was observed for both sulfides with a gap that averaged 94 mV for chalcopyrite and 19 mV for enargite.
The addition of 1 M of sodium chloride to a solution containing 90 g/L of sulfuric acid caused a significant decline in OCP. For chalcopyrite the change was from 280 mV to 247 mV at 20°C and from 193 mV to 137 mV at 60°C. A similar OCP decreasing effect during the addition of NaCl was observed for enargite. At 20°C the enargite OCP decreased from 126 mV to 120 mV, and at 60°C the OCP decreased from 110 mV to 84 mV.

When the OCP values obtained during the sulfuric acid experiments were plotted against pH instead of acid concentration, a good straight line fit was obtained. For chalcopyrite slopes of 46 mV and 47 mV were found at 20 and 60°C respectively. Enargite gave slopes of 28 mV and 25 mV at 20 and 60°C respectively. It should be noted that the initial OCP measurements were performed in the absence of ferric, ferrous or cupric salts in solution. This was done to avoid any contribution from the ferric/ferrous couple to the measured potential of the electrodes (particles). The only possible presence of these ions was from the dissolution of the particles themselves. In any case, after a measurement was made, the solution was discharged and a new solution was used in each test to avoid the accumulation of any reaction products in solution.

Different results were presented when pyrite was studied under similar conditions as chalcopyrite and enargite. Figure 3.6 presents the OCP results for pyrite at various acid concentrations and temperatures. The OCP measurements at 20°C and 60°C did not change significantly with acid concentration. The variation of OCP for both temperatures was minimal compared with the other two sulfides, and the difference between the two temperatures was in the range of 25 mV for the different acid solutions. The temperature had also a different effect on the OCP of pyrite. Whereas the OCPs of chalcopyrite and enargite decreased with increasing temperature, the OCP of pyrite increased with increasing temperature. Pyrite showed an average OCP of 387 mV at 20°C and 412 mV at 60°C.

These OCP results of single sulfide particles, applied to processes which take
advantage of galvanic interaction among sulfides, in the presence only of sulfuric acid in solution, will suggest the following facts: enargite could be dissolved faster when pyrite is present in solution in an amount sufficient to allow them to interact galvanically; the potential region, where the dissolution of chalcopyrite and enargite in the presence of pyrite takes place, will increase with increasing acidity and temperature of the solution; and, enargite will dissolve preferentially over chalcopyrite, and chalcopyrite will dissolve preferentially over pyrite.

Figure 3.4 Variability of OCP of single particles of chalcopyrite (Cp) in solutions with sulfuric acid and sodium chloride at various concentrations and temperatures.
Figure 3.5  Variability of OCP of single particles of enargite (En) in solutions with sulfuric acid and sodium chloride at various concentrations and temperatures.
Figure 3.6  Variability of OCP of single particles of pyrite (Py) in solutions with sulfuric acid and sodium chloride at various concentrations and temperatures
3.3.2. Voltammetric Studies of Chalcopyrite (Cp)

Voltammograms were obtained by applying cyclic potential sweeps to single chalcopyrite particle microelectrodes from an initial potential ($E_0$) 0.0 V, anodic switching potential ($E_a$) of 0.8 V, and a cathodic switching potential of $-0.2$ V ($E_c$). A sweep rate of 20 mV/s was chosen for all the voltammograms reported in this study.

Figure 3.7 shows typical voltammograms for chalcopyrite at 90 g/L H$_2$SO$_4$ and at three different solution temperatures. Analyzing the curve at 60ºC, the first current response is detected at around 250 mV, where the current ($i$) begins to increase with potential. At around 464 mV a passivation potential ($E_{pp}$) and its respective current ($i_{pp}$) are detected. After $E_{pp}$ the current decreases to a passive current ($i_{passive}$) that is slightly smaller than $i_{pp}$. When the potential reaches 0.6 V a passive-transpassive transition is observed at the transpassive potential ($E_{tp}$). The peak observed at $E_{pp}$ is marked in the figure as A1, and the region observed after $i_{passive}$ is marked as A2. The cathodic side of the cycle from $E_a$ to the cathodic switching potential presents four cathodic peaks, at 425 mV (C1), 250 mV (C2), 80 mV (C3), and a large peak starting at 0.0 V.

Increasing solution temperature has a displacement effect on the anodic and cathodic peaks. The maximum current for peak A1 at 20ºC was observed at 400 mV whereas the same peak was at 439 mV at 45ºC and 464 mV at 60ºC. The same effect was observed for peak C2, where potentials became more electropositive with increasing temperature. Peak C1 was only observed at 45 and 60ºC. The same positive drift also affected the initiation of C4. In a contrary manner, increasing temperature made potentials at peak A2 more electronegative indicating that $E_{tp}$ decreases with temperature while $E_{pp}$ increases together with $i_{pp}$.

Figure 3.8 presents the influence of solution acidity on chalcopyrite voltammetry evaluated at 2, 10 and 50 g/L H$_2$SO$_4$. Solution acidity did not have a significant
effect on the potential location of the various anodic and cathodic reactions. Increasing sulfuric acid concentration showed an increase in the peak currents with a considerable increase in peak A1 from 2 g/L to 10 g/L H₂SO₄ and also peak C2 from 10 g/L to 50 g/L H₂SO₄. The passive region after peak A1 decreased with increasing acidity. The transpassive potential $E_{tp}$ was shifted to more electronegative potentials as acidity was increased in such a way that the transpassive regime (peak A2) began immediately after peak A1 at 50 g/L H₂SO₄. This indicates that increasing solution acidity increases the mineral electro-oxidation rate at lower potentials.

Usually, reactions that take place on mineral surfaces are in a relatively small scale and often the products of these reactions are difficult to detect and characterize. The aspects mentioned before also affected the nature of this work. In this study the solid and ionic products formed during the anodic and cathodic reactions of the single sulfide particles were difficult to determine. The only surface characterization technique used during the course of this work was the scanning electron microscope (SEM) coupled with EDX. Thus the characteristics of the reactions taking place on the chalcopyrite microelectrodes are summarized below.

The most important area of the chalcopyrite voltammogram with respect to the dissolution process is the region of peak A1 and where curiously the chalcopyrite also presents a passivation regime. It has been suggested in other investigations that, at those potentials, chalcopyrite may form an intermediate non-stoichiometric phase. For example, Warren (1986; 1982) suggested that this A1 peak corresponds to a pre-wave or partial oxidation of chalcopyrite in the following manner:

\[
\text{Eq. 3.1} \quad \text{CuFeS}_2 \rightarrow \text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z} + x \text{Cu}^{2+} + y \text{Fe}^{2+} + z \text{S}^0 + 2 (x+y) \text{e}^- 
\]

Thus, the new layer formed on the surface of chalcopyrite could be the one causing the passivation. Another study (Biegler and Horne, 1984) anticipated the
formation of covellite at those potentials with a release of $Cu^{2+}$ and $Fe^{2+}$ ions and the formation of elemental sulfur on the surface of chalcopyrite. It was also noticed that iron was released to solution in a higher rate than copper, especially during the initial stages of leaching. The following reaction stoichiometry was proposed:

$$\text{Eq. 3.2} \quad CuFeS_2 \rightarrow 0.75 \text{CuS} + 0.25 Cu^{2+} + Fe^{2+} + 1.25 S^0 + 2.5 \text{e}^-$$

In summary other researchers (Holliday and Richmond, 1990; Parker et al., 1981) have proposed that the chalcopyrite surface is coated and protected from leaching with a layer of non-stoichiometric compounds or $Cu_5FeS_4$, $CuS$ and $S^0$ at these potentials. In the course of this study chalcopyrite particles were polarized to potentials of 450 mV at 60°C for 10 minutes with the purpose to characterize by EDX the possible films that could form on the surface. The EDX results showed that a non-stoichiometric compound was present with an apparent preferential dissolution of iron over copper with atomic ratios $S/Cu/Fe$ of 2.18 / 1 / 0.8. Although EDX analysis is not the most adequate medium to analyze this kind of thin layer formation, it can give an estimate of the real atomic ratio present on the surface of the particle. Another possibility could be that this atomic ratio corresponds to the original arrangement of this particular chalcopyrite, considering that the thin layer that passivates chalcopyrite has been calculated to be in the order of nanometers (Biegler and Horne, 1984; Biegler and Swift, 1979). There is an other investigation (Parker et al., 1981) that claims that this passive film will grow until it reaches an equilibrium thickness and after that it will decompose. During the polarization of the chalcopyrite particles at 450 mV it was noticed under the optical microscope that the gold-yellow color of chalcopyrite turned slightly reddish-gold with the formation of tiny monticules. SEM analysis revealed that the reddish-gold surface corresponded to the $S/Cu/Fe$ atomic ratio indicated before, but that the tiny monticules were represented as dark regions on the mineral surface with an atomic ratio $S/Cu/Fe$ of 7.2 / 1 / 1. Clearly this represents regions of sulfur plus a background analysis of unleached chalcopyrite.
The region where peak A2 begins is considered as a transpassive region. At that point the current generated by the chalcopyrite particles increased very rapidly with potential. At high potentials chalcopyrite will dissolve by the combination of two different reactions:

Eq. 3.3 \[ \text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2 \text{S} + 5 \text{e}^- \]

and

Eq. 3.4 \[ \text{CuFeS}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ + 17 \text{e}^- \]

As indicated in Eq. 3.3, at potentials above 0.6 V, rapid dissolution of chalcopyrite is observed with a direct liberation of Cu$^{2+}$, Fe$^{3+}$ and S$^0$ without the formation of non-stoichiometric films. Calculations based on the total dissolved copper and total charge transferred at 1.2 V determined on average that a total of 88.7% of sulfur sulfide in chalcopyrite is oxidized to elemental sulfur and 11.3% to sulfate according to Eq. 3.4. These calculations and the experimental procedures behind them are presented in detail in Chapter 4 and Appendix B.

Chalcopyrite particles observed under an optical microscope during polarization at 1.2 V also presented the same color change from yellow to reddish gold as seen before for particles polarized at 450 mV. This color change effect was almost instantaneous, and occurred within the first 2 seconds after the overpotential was applied to the particle. After that time the particle returned immediately to its original color and a transparent film began to emerge on the surface of the particle. This layer covered the whole particle surface and become progressively thicker with time. Figure 3.9 shows a chalcopyrite particle covered completely by a sulfur layer with a composition of 97.9% S and 2.1% Fe. This sulfur layer apparently is a non-conductive layer because the carbon electrode needed to be maintained in direct contact with the undissolved chalcopyrite core in order for the
transpassive reaction to continue. The current generated by chalcopryite at 1.2 V during transpassive leaching was in the range of 120 μA at 20°C. Comparing this transpassive current with the normal current associated with peak A1 at the same temperature, the transpassive current is at least 100 times higher. Normally at 1.2 V a particle of approximately 75 microns was totally dissolved in about four minutes.

All of the information presented this far suggests that the dissolution of chalcopyrite over the potential range of approximately 300 to 550 mV, occurs at a rate determined by the dissolution of a passive film. At dynamic equilibrium, the passive film will grow at a rate equal to the rate at which it dissolves. Therefore the passive film will be present during the entire process of leaching until a compact sulfur layer forms according to Eq. 3.1 or Eq. 3.2 and this sulfur layer may or may not further retard the dissolution process. However another study has demonstrated that chalcopyrite presents passivation even when the particles do not present a layer of sulfur, and this passivation could be avoided with the addition of an external agent (Chapter 4). This is an indication that the dissolution of chalcopyrite in sulfuric acid is chemically controlled. To support the controlling rate assumption, the activation energy of the process at peak A1 can be calculated using the Arrhenius equation

\[ k = A \cdot e^{\frac{-E_a}{RT}} \]

Eq. 3.5

where \( k \) is the rate constant, \( A \) is the frequency factor, \( R \) the universal gas constant, \( E_a \) is the activation energy and \( T \) is the absolute temperature. Considering that the concentration of reactants and the surface area of the electrode are constant, \( k \) could be replaced by the peak current. Therefore the activation energy can be calculated from the currents of peak A1 at the three different temperatures from Figure 3.7.
The Arrhenius plot for peak A1 was found to be linear with a calculated activation energy of 43 kJ/mol. In similar fashion the activation energy of peak A2 in the transpassive leaching region was calculated using currents generated at 800 mV. The activation energy for this regime was estimated to be 28 kJ/mol (See Figure 3.10). Thus, the observed $E_a$ of 43 kJ/mol reconfirms the assumption that chalcopyrite dissolution in sulfuric acid solution is chemically controlled. On the other hand, the activation energy of 28 kJ/mol for peak A2 in the transpassive region may indicate mixed diffusion-reaction control with a higher importance of mass diffusion, most likely through the layer of compact sulfur as shown in Figure 3.9.

As mentioned before, during the reverse scan four different reduction processes were observed. Those cathodic reactions are not presented in detail since the main intention of this work is to elucidate the oxidation processes of chalcopyrite. However some details about these reactions are discussed.

Peak C1 could be associated with ferric reduction as follows:

\[ \text{Eq. 3.6 } \text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \]

The kinetics of this reaction are almost negligible on surfaces of p-type chalcopyrite but relatively fast in n-type chalcopyrite (Mcmillan et al., 1982). A study by Nava and Gonzalez (2006) also suggested that this peak could correspond to the reduction of jarosite that was formed at higher potentials. Peaks C2 and C3 have a close relation with the products formed during the previous anodic scan. Neither peak appeared when a negative-going scanning was applied to a fresh particle of chalcopyrite (data not shown). Particularly peak C2 was observed to increase its current when high charges were observed for peak A2. Thus C2 is related to the reduction of sulfur as follows:

\[ \text{Eq. 3.7 } \text{S}^0 + \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{CuS} \]
and peak C3 with:

\[
\text{Eq. 3.8} \quad \text{CuS} + \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}_2\text{S} + \text{H}_2\text{O}
\]

From Figure 3.8 it can be seen that the activation of peak C4 was influenced by the acid concentration in solution, thus suggesting the following reactions:

\[
\text{Eq. 3.9} \quad \text{S} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{S}
\]

\[
\text{Eq. 3.10} \quad 2 \text{CuS} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Cu}_2\text{S} + \text{H}_2\text{S}
\]

\[
\text{Eq. 3.11} \quad 2 \text{CuFeS}_2 + 6 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Cu}_2\text{S} + 2 \text{Fe}^{2+} + 3 \text{H}_2\text{S}
\]

In addition to these reactions, reduction of chalcopyrite to bornite, Cu^{2+} to Cu^0, H^+ to H2 may also occur. Finally, when the potential was reversed from the cathodic switching potential \((E_c)\) to the initial potential \(E_0\) no peaks were observed. A second sweep cycle applied to the microelectrode did not reveal any new peaks. The two anodic peaks and four cathodic peaks were present and their associated currents were approximately half of the current presented during the first cycle. Some authors found new anodic peaks during the second cycle sweep before the peak A1 (Gomez et al., 1996; Lu et al., 2000). These currents were associated to the oxidation of H2S to sulfur and Cu^0 to Cu^{+2} (Mcmillan et al., 1982; Price and Warren, 1986).
Figure 3.7  Effect of temperature on cyclic voltammograms (CV) of chalcopyrite at 90 g/L H₂SO₄ and a positive scanning rate of 20 mV/s.
Figure 3.8 Effect of acid concentration on cyclic voltammograms (CV) of chalcopyrite at 20°C and a positive scanning rate of 20 mV/s.
Figure 3.9  SEM micrograph of a chalcopyrite particle polarized during 30 seconds in a solution of 50 g/L $\text{H}_2\text{SO}_4$ at 1.2 V, completely encapsulated by a compact layer of elemental sulfur.
Figure 3.10  Arrhenius plot for the anodic dissolution of chalcopyrite for peak A1 at 450 mV (●), and peak A2 at 800 mV (■)
3.3.3. Voltammetric Studies of Enargite (En)

Various electrochemical studies of enargite have been conducted on massive enargite samples (Asbjörnsson et al., 2003; Asbjörnsson et al., 2004; Cordova et al., 1997; Córdova et al., 1996; Elsener et al., 2007; Munoz et al., 2006; Velasquez et al., 2000) and enargite mixed into carbon-paste electrodes (Asbjörnsson et al., 2004). In the present work, the voltammetric behavior of single micron-size enargite particles were studied in solutions with 2, 10, 50 and 90 g/L H₂SO₄ at 20°C and 90 g/L H₂SO₄ at 60°C. The cycles were started at 0.0 V and were scanned in a positive direction. Figure 3.11 and Figure 3.12 show voltammograms obtained at 20°C and 60°C, respectively. During the anodic sweep, up to three different peaks were identified, noted as 1A, 2A, and 3A. During the cathodic sweep three different peaks were also detected, noted as 1C, 2C, and 3C. As seen in Figure 3.11 and Figure 3.12, the anodic peaks are not clearly delineated one from each other, forming a single broad peak. This broad peak may indicate that more than one electrochemical process is taking place in the same potential region.

In Figure 3.11 the effect of solution acidity on the distribution of the peaks is small. The anodic and cathodic reactions shifted slightly towards positive or negative potentials without a clear pattern. On the other hand, the effect of acidity on intensity of peak currents is noticeable. At 2 and 5 g/L H₂SO₄, maximum currents of 10 µA and 18 µA are observed; when acid concentration is increased to 50 and 90 g/L a clear increase in current is noted. Although there is little difference in current between 50 and 90 g/L, maxima up to 120 µA were measured. The broad peak from peaks 1A and 2A began at around 200 mV and continued until a clear and sharp active-to-passive transition was observed. With a further increase in potential, a passive-to-transpassive region is observed (peak 3A). The beginning of this peak apparently depends on solution acidity. At 10 g/L H₂SO₄ this transition was observed at 1040 mV. At 90 g/L H₂SO₄, peak 3A begins at 950 mV.
Temperature appears to have an additional influence on the occurrence of the transpassive region. From Figure 3.12 it is observed that at 60°C for the same conditions of 90 g/L of H₂SO₄, the peak 3A is not observed at potentials up to 1100 mV. Increasing the temperature generated higher currents on the anodic peaks of up to 1.66 times relative to 20°C. The positive effect of temperature on enargite leaching is also observed in a separate study conducted at UBC (Chapter 5). In Figure 3.12A it is also observed that currents at peak 2A were higher than currents at peak 1A. The opposite condition is observed at 20°C (Figure 3.11).

During cathodic sweeps, reactions 1C and 2C were shifted to more electropositive potentials with increasing temperature. At 20°C, peaks 1C and 2C occur at 220 mV and 60 mV respectively; whereas at 60°C they have their maximum currents at 260 mV and 160 mV. When enargite reaches transpassive potentials as indicated by peak 3A, currents at peak 2C are increased. This indicates that peak 2C bears a close relation and depends strongly on the reaction taking place under peak 3A and the products formed therefore at transpassive potentials. Peak 3C was influenced by solution acidity but not by temperature. At 2 g/L H₂SO₄, peak 3C occurs at –225 mV. On the other hand, at acid concentrations higher than 50 g/L, this peak 3C occurs at –140 mV. At this potential, the reduction of enargite may occur as indicated in Eq. 3.12, and may also be accompanied by hydrogen production at more negative potentials.

Eq. 3.12 \[ 2 \text{Cu}_3\text{AsS}_4 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow 3 \text{Cu}_2\text{S} + \text{As}_2\text{S}_2 + 3 \text{H}_2\text{S} \]

At potentials < –250 mV, it was observed that a brown cloud begins to form around the enargite particles. This cloud formation soon changes to a fine dust that precipitates on the enargite surface and around the particle. This particle was analyzed by EDX immediately after being removed from the electrochemical cell. The brown dust had an atomic As/S ratio of 1.73 to 2. This clear evidence of As₂S₂ formation could confirm that the reaction in Eq. 3.12 was taking place at those
negative potentials. Figure 3.13 shows a particle of enargite being polarized at –250 mV and 20°C in a solution with 90 g/L H₂SO₄. The crusty brown precipitate layer is clearly observed.

The two anodic peaks that appear to be overlapping each other (1A and 2A) emerge at around 250 mV. Based on the potential-pH diagram proposed by Asbjornsson et al. (2004) the reaction responsible for peak 1A could be the dissolution of enargite as indicated in the following reactions:

Eq. 3.13 \[ \text{Cu}_3\text{AsS}_4 + 19 \text{H}_2\text{O} \rightarrow 3 \text{Cu}^{2+} + \text{H}_3\text{AsO}_3 + 4\text{HSO}_4^- + 31 \text{H}^+ + 33 \text{e}^- \]

Eq. 3.14 \[ \text{Cu}_3\text{AsS}_4 + 20 \text{H}_2\text{O} \rightarrow 3 \text{Cu}^{2+} + \text{H}_2\text{AsO}_4^- + 4\text{HSO}_4^- + 34 \text{H}^+ + 35 \text{e}^- \]

Eq. 3.15 \[ \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{AsO}_4^- + 2 \text{H}^+ + 2 \text{e}^- \]

The oxidation of arsenious acid to arsenic acid represented in Eq. 3.15 has been demonstrated to occur at these anodic potentials by Lazaro et al. (1997) and will add current to the wide peak 1A. Eq. 3.13 and Eq. 3.14 have HSO₄⁻ as a reaction product; however it has been reported that enargite dissolution forms elemental sulfur (Dutrizar and Macdonald, 1972; Padilla et al., 2005; Chapter 5). Therefore elemental sulfur could be attributed to form at peak 2A. To determine the formation of elemental sulfur, a particle or enargite was polarized at 750 mV for 20 minutes at 60°C and 90 g/L H₂SO₄. Figure 3.14A shows an SEM photograph of the particle after polarization. The enargite particle presents two different regions randomly distributed across the entire surface; EDX analysis was performed to determine their composition. The composition of the bright surface, on average, was close to the theoretical enargite stoichiometry for copper and arsenic with an atomic ratio S/Cu/As of 4.7 / 3 / 1. This indicates that at the bright areas of the particle, dissolution of copper and arsenic occurs at the same rate whereas an excess of sulfur is remaining on the surface of the particle. A different situation is observed
at the dark areas where the atomic ratio S/Cu/As was calculated to be 12.4 / 6.3 / 1. These areas can be considered as areas where the dissolution of copper and arsenic both occurred, but the dissolution of arsenic was two times faster than the dissolution of copper. Thus the non-stoichiometric enargite could be the reason why enargite presented a well-defined active-to-passive transition. The sulfur formation will re-enforce this passivation, but is not the determining factor for passivation. It has been demonstrated that the formation of porous layers of elemental sulfur during leaching of enargite does not passivate enargite by itself (Chapter 5). It has also been observed that enargite can be passivated without a visible sulfur layer being formed (Chapter 5). Therefore, the dissolution of enargite at potentials where peak 2A is present could be described by the following reaction:

\[
\text{Eq. 3.16} \quad \text{Cu}_3\text{AsS}_4 + 4y \text{H}_2\text{O} \rightarrow \text{Cu}_{3-x}\text{As}_{1-y}\text{S}_{4-z} + x \text{Cu}^{2+} + y \text{H}_2\text{AsO}_4^- + z \text{S}_0 + 6y \text{H}^+ + (2x + 5y) \text{e}^-
\]

where \( x < y \).

When the particle reaches the transpassive zone at potentials > 950 mV, at peak 3A, the same reaction as Eq. 3.16 will continue but the high potential will bring the enargite to dissolution without the formation of the non-stoichiometric compounds:

\[
\text{Eq. 3.17} \quad \text{Cu}_3\text{AsS}_4 + 4 \text{H}_2\text{O} \rightarrow 3 \text{Cu}^{2+} + \text{H}_2\text{AsO}_4^- + 4 \text{S}_0 + 6 \text{H}^+ + 11 \text{e}^-
\]

The polarization of an enargite particle at potentials of 1.4 V for 2 minutes revealed that almost the entire surface was covered by a surface layer with some small bright areas apparently consisting of enargite. This is in contrast to dissolution of enargite at low potentials, which shows localized areas of attack. A picture of the particle is shown in Figure 3.14B. The inset image in Figure 3.14B shows a bare region of enargite. EDX analysis at that bright point revealed an atomic ratio
S/Cu/As of 4 / 2.87 / 1. This confirms that enargite is underneath the observed dark layer. On the other hand, analysis of the dark layer near that spot revealed an atomic ratio S/Cu/As of 18.6 / 2.47 / 1. Considering that EDX measurements originate at around 1 μm depth, these surface measurements may indicate that the measured copper and arsenic levels, correspond to un-reacted enargite under a layer of elemental sulfur. As a consequence it can be said that the sulfur layer grew to less than 1 μm in thickness during the duration of polarization. This sulfur layer was strongly attached to the surface of the particle. Its visual appearance was like a red translucent coating, and it could not be removed from the particle by manipulation with the carbon fiber electrode. These characteristics differ from the sulfur layer formed at the same potentials on the surface of chalcopyrite as shown in Figure 3.9. The sulfur layer in that case had the appearance of a transparent film that was easily de-attached from un-dissolved chalcopyrite cores.

On the negative going potential scans, peaks 1C and 2C represent the reduction of products generated during the anodic scans. A voltammogram in the negative direction did not generate these two peaks. However, the presence of peak 3C was noted, indicating that this peak is related to the electrochemical reduction of the mineral as pointed out in Eq. 3.12. When the transpassive region was reached (peak 3A) in the voltammogram, as observed in Figure 3.11 at 50 and 90 g/L H₂SO₄, peak 2C was larger, but peak 1C was unaffected. Thus peak 1C is associated to peaks 1A and 2A according to the following reaction:

Eq. 3.18 \( \text{H}_3\text{AsO}_4 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \)

which is the reverse of Eq. 3.15. For the case of peak 2C, it is associated to the products of peaks 2A and 3A, which are liberated in a higher proportion according to Eq. 3.17, resulting in the reduction of elemental sulfur as follows:

Eq. 3.19 \( \text{S}^0 + \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{CuS} \)
Additionally, a new anodic peak was observed after the potential was switched back to the positive direction. This peak 4A is observed in Figure 3.12, and could be attributed to the oxidation of As$_2$S$_2$, a product generated during the previous cathodic sweep in peak 3C:

\[
\text{Eq. 3.20} \quad \frac{1}{2}\text{As}_2\text{S}_2 + 7\text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_3 + \text{HSO}_4^- + 10\text{H}^+ + 9\text{e}^- 
\]

The execution of a second voltammetric cycle on enargite particles gave no new peaks. As shown in Figure 3.12, upon a second scan, over the entire range of potential, the electrochemical response decreased to around half the currents obtained during the first sweep. The smaller active area of the particle, after the first cycle, will cause this smaller amount of charge in the peaks during the second scan. Furthermore, this smaller area indicates the irreversibility of the oxidizing reactions occurring on the surface of the enargite particles.
Figure 3.11  Effect of acid concentration on cyclic voltammograms (CV) of enargite at 20ºC and a positive-going scanning rate of 20 mV/s
Figure 3.12  Typical CV of enargite at 90 g/L H₂SO₄, 20 mV/s scanning rate, and 60°C showing the behavior of two cycles.
Figure 3.13 A single enargite particle polarized at –250 mV vs. SCE during 30 seconds. A) The beginning of the reaction, showing the formation of a cloud of fine suspended solids. B) After the reaction was stopped, the fine solids precipitate on the particle surface and the surrounding area. Carbon wire diameter was 25 μm.
Figure 3.14 SEM micrograph of an enargite particle polarized in a solution of 90 g/L H$_2$SO$_4$ and 60$^\circ$C at A) 750 mV for 20 minutes, and B) 1.4 V vs. SCE for 2 minutes.
3.4. CONCLUSIONS

This study demonstrates that the use of single particle microelectrodes can be effectively applied to the electrochemical study of sulfide minerals, giving good reproducibility and sensitivity. Single particles of pyrite (Py), chalcopyrite (Cp), and enargite (En) with sizes <100 μm were investigated with cyclic voltammetry (CV) and measurements of open circuit potential (OCP) under various conditions of temperature and acidity in the electrolyte.

For chalcopyrite and enargite, a decrease of OCP was observed with increasing concentration of acid in solution. The addition of NaCl further increased the potential drop. For pyrite the change in OCP was almost nil. Temperature had a favorable effect on dissolution of chalcopyrite and enargite at potentials below the passive region. In the case of chalcopyrite the passive zone was less significant with increasing temperature. The effect of H₂SO₄ concentration on dissolution rate was well defined at levels ≥10 g/L for chalcopyrite and ≥50 g/L for enargite. For both sulfides an evolving layer of elemental sulfur was observed to form at transpassive potentials, whereas oxidation of enargite at lower potentials exhibited localized sulfur formations.

The anodic currents measured during the oxidation of chalcopyrite at active potentials exhibited surface dissolution control, but at transpassive potentials the reaction was partially under mass diffusion control. The transition from active to passive behavior was less severe for chalcopyrite than for enargite, where the passivation was almost total. This behavior was even stronger with increasing temperature. As a result, the range of potentials where these particular sulfides are active can be estimated to be between 300 mV and 450 mV vs. SCE for chalcopyrite, and 300 mV to 700 mV vs. SCE for enargite.

Although this technique was only tested on micron size particles of pure mineral specimens, the technique may be more useful when being applied to particulate mineral concentrates, in order to improve conditions for leaching and flotation.
3.5. ACKNOWLEDGEMENTS

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3.6. REFERENCES


CHAPTER 4.
MORPHOLOGIES AND TRANSPASSIVE LEACHING OF CHALCOPYRITE PARTICLES

4.1. INTRODUCTION

Chalcopyrite is a mineral that displays active-passive and passive-transpassive transitions as a function of the potential applied to its surface. Such surface potentials can be applied using external sources of potential or through the use of chemical redox couples in the leaching solution. Between the open circuit potential of the mineral ($E_{OCP}$) and the evolution of oxygen it is possible to identify four distinct ranges of potential where chalcopyrite exhibits different behaviors, which are shown in Figure 4.1. In the first range of potentials $E_{OCP} < E < \sim 440$ mV vs. SCE, which is called the active range, the dissolution rate of the mineral follows Tafel behavior. In the second range, $\sim 440 < E < \sim 510$ mV, the dissolution rate stops following Tafel behavior, and a tilted current plateau is observed. In the third range of potentials, beginning at around 510 mV, chalcopyrite experiences passivation effects characterized by a gradual decrease of the dissolution current until it reaches a limit steady state value. That limit value can be up to 10 times lower than the maximum dissolution rates observed in the active range, although this is dependent on temperature.

The third, passive, range is the one to be avoided in any hydrometallurgical process, since the rates of copper recovery are exceptionally slow. The upper limit of the third range is the beginning of the transpassive regime, which is the fourth and, for the objectives of this paper, the most important range of potential. The third range can therefore be expressed as $\sim 510 < E < E_{\text{transpassive}}$ mV. The exact value of potential at which the transpassive behavior of chalcopyrite begins is

*A version of this chapter will be submitted for publication. BF Rivera-Vasquez and DG Dixon, (2010). Morphologies and Transpassive Leaching of Chalcopyrite Particles.*
strongly influenced by acidity and temperature (Viramontes-Gamboa et al., 2007) (See Chapter 2). Increasing the concentration of sulfuric acid from 2 to 100 g/L increases the onset of transpassive leaching from ~ 650 mV to ~ 1100 mV at room temperature. When acidity is maintained constant, increasing temperature also increases the onset of transpassive dissolution. In the transpassive regime, the oxidation rate of chalcopyrite increases abruptly by up to six orders of magnitude (one million times) with respect to typical values observed in the active or passive ranges. Unfortunately, transpassive potentials are not achievable using common redox couples available industrially. Hence, chemical leaching in the transpassive regime at economic industrial rates is virtually impossible. However, if there is no reason to restrict ourselves to chemical leaching, this extremely fast dissolution rate of chalcopyrite creates an opportunity to design innovative processes by applying transpassive external potentials to chalcopyrite concentrates using adequately designed electrochemical reactors.

Thus, the present work explored the behavior of individual chalcopyrite particles during the application of high potentials that fall in the transpassive regime. This was made possible by the application of single particle electrochemical techniques. Total dissolution of single particles was possible since the high potentials applied dissolved the tiny mass of chalcopyrite present in the particles in matter of minutes. During the dissolution process, the formation of sulfur was explored in detail, with a special emphasis on the effect of the sodium chloride addition on the morphology of the sulfur layer. A dissolution model and mass balances are also proposed for single particle dissolutions, which give the proportions of elemental sulfur and sulfate formed. This work also provides further information concerning the role of elemental sulfur as a factor in chalcopyrite passivation, offers a better explanation of the role of sodium chloride as an enhancer for chalcopyrite leaching, and demonstrates that near instantaneous dissolution of chalcopyrite is possible at high potentials without the addition of oxidizing agents.
4.2. EXPERIMENTAL PROCEDURE

4.2.1. Leaching Experiments

Three different types of experiments were conducted in this study: potentiostatic anodic polarization, transpassive electrochemical leaching, and batch reactor leaching experiments. Transpassive leaching and potentiostatic anodic polarization experiments of single sulfide particles were performed using the electrochemical single particle technique. This consists of a three electrode arrangement with a platinum wire as auxiliary electrode (AE), the couple formed by a sulfide single particle and a carbon wire as working electrode (WE), an a saturated calomel electrode with potassium chloride coupled with a Luggin capillary as the reference electrode (RE). Details of the single particle electrochemical cell and supporting apparatus are explain in detail elsewhere (Chapter 3). All potentials in this study are expressed with respect to the saturated calomel electrode (SCE). Experiments were conducted using solutions of sulfuric acid (H₂SO₄) and in some cases sodium chloride (NaCl) was also added. During the experiments no attempt was made to purge oxygen or to agitate the solution.

Sulfide particles used were prepared from massive specimens, which were ground using a ring mill and then sieved within a range of +75 to −125 microns. Chalcopyrite samples were obtained from Chihuahua, Mexico with a XRD mineralogical analysis of 98.6 % chalcopyrite (CuFeS₂), and 1.4% quartz (SiO₂). Selected particles were picked up with tweezers and placed on a glass frit submerged in an electrolyte solution under an optical microscope. The volume of the solution used in the electrochemical measurements was approximately 140 mL and a thermostatic heating band controlled the electrolyte temperature inside the cell when experiments were run at elevated temperatures.

Leaching experiments were conducted to study and compare the sulfur formation on the surface of partially leached chalcopyrite particles in the absence and
presence of pyrite (FeS$_2$), which was intentionally added to increase the dissolution rate of chalcopyrite as demonstrated in previous studies (Dixon et al., 2008; Rivera-Vasquez et al., 2007; Tshilombo, 2004). Batch reactor leaching experiments were conducted in a sealed, jacketed 2.7 L glass reactor. Solution containing 25 g total iron, and 70 g H$_2$SO$_4$ in 1.5 L of destilled water was maintained at 80°C, agitated at 1200 rpm. The solution potential was initially fixed at 470 mV vs. Ag/AgCl (425 mV vs. SCE) by the ratio of ferric to ferrous ions added as salts. During the course of the experiments this potential was maintained by the addition of oxygen through a digital mass flow valve. This digital valve, together with pH and redox potential probes inserted in the reactor, were connected to a digital controller. Two different sulfides were used during these experiments. A copper concentrate from Australia containing 60.2% of chalcopyrite, and a massive pyrite sample from Huanzala, Peru containing 92.3% pyrite (FeS$_2$), 4.6% fluorite (CaF$_2$), and traces of quartz, talc, and marcasite as determined by XRD analysis. The Australian concentrate was used as received without any further preparation. The pyrite was ground in a ring mill to a final P$_{80}$ of 70 μm. The morphological effect of the pyrite on chalcopyrite during the leaching process was studied by adding pyrite in a ratio of 2:1 vs. chalcopyrite.

### 4.2.2. Morphological Observations

Optical observations of sulfur formation and particle morphological changes were captured using a conventional stereo microscope equipped with a digital eyepiece camera. This configuration allowed capture of surface changes in-situ during the transpassive dissolution of single particles. Additionally, sulfur morphology and chemical characterization were performed on a scanning electron microscope (SEM) at a voltage of 20kV coupled with an energy dispersive X-ray analyzer (EDX). Samples of chalcopyrite leaching residues were filtered, rinsed with dilute sulfuric acid solution and filtered again, prior to being placed inside the SEM. Both, top views, and cross-sectional views were obtained. Residues from transpassive
leaching and reactor leaching were fixed in an epoxy bed and then slightly polished and examined under the microscope to observe the placement and interaction between the sulfur formed during leaching and the un-leached sulfide cores.

4.3. RESULTS AND DISCUSSION

4.3.1. Chalcopyrite Anodic Polarizations

Potentiostatic anodic polarization was applied to chalcopyrite particles to study their behavior at different conditions of temperature and acid concentration. Figure 4.1 shows the anodic profile of chalcopyrite particles over the potential range of 0.3 to 0.8 V vs. SCE with 90 g/L H₂SO₄. It can be seen that temperature plays an important role in the dissolution of chalcopyrite. In the active region of the particles at around 0.42 V, the anodic current at 60ºC was about three times higher than the anodic current at 45ºC, and the dissolution of chalcopyrite at 20ºC was virtually undetectable. The currents recorded by the potentiostat were 5.66, 1.93 and 0.64 µA for 60, 45 and 20ºC respectively. When potential was increased to more positive values, a transpassive regime began to appear depending on temperature. Apparently, temperature accelerates the process of dissolution at high potentials at values up to 1 V. Beyond that potential the dissolution current was similar for the three temperatures evaluated. In order to estimate the effect of acid concentration on the transpassive regime, the solution was maintained at 20ºC and the acid concentration was evaluated at 2, 10, 50 and 90 g/L H₂SO₄. Under these conditions the acid concentration did not seem to have any effect on the dissolution current at high potentials. The rapid increase in current at the beginning of the transpassive region was observed at around 0.7 V for all acid concentrations and the value of the dissolution current was similar in all cases.

Based in these findings it can be stated that temperature and acid concentration have no beneficial effect on the dissolution of chalcopyrite particles at potentials
higher than 1 V vs. SCE. Thus, 90 g/L H₂SO₄ in solution and temperature 20ºC were the conditions used in subsequent experiments at potentials of 1.2 V vs. SCE.

Figure 4.1 Potentiostatic anodic polarizations of single chalcopyrite particles at various temperatures in a solution of 90 g/L H₂SO₄ at a scanning rate of 20 mV/s.
4.3.2. Behavior of Chalcopyrite Particles in the Transpassive Regime

When transpassive potentials were applied to different chalcopyrite particles in a solution of 90 g/L H₂SO₄, some interesting phenomena were observed. Nearly instantaneous dissolution of the copper and iron from the particles was observed. Oxidation currents detected by the potentiostat were as high as 0.1 to 1 A/cm². If typical leaching rates of ground chalcopyrite in ferric sulfate media are transformed to current density, the values obtained are around 1 to 20 μA/cm². Hence, in the transpassive regime, chalcopyrite can be dissolved up to one million times faster than when it is dissolved in the active or passive regime at low solution potentials.

Copper and iron are entirely dissolved from the mineral. The only observable residue was a pure transparent sulfur, which had the same shape as the original particle and surrounded it completely. Contrary to what is reported in the literature, transformation of chalcopyrite to covellite or non-stoichiometric sulfides was not observed at these high potentials. The residual sulfur was an electrical insulator, with a very fragile jelly-like structure that was easily broken by poking with the microelectrode. The structure of this sulfur is obviously far from thermodynamic equilibrium, since, with the passage of time the sulfur gradually loses its original high plasticity and crystallizes to a more inflexible stable structure with a change of color from nearly transparent to pale-yellow. This equilibration process took as long as 24 hours, leaving a brittle structure with none of its original plastic bending properties.

When the carbon wire is touching only the formed sulfur, but not the unleached chalcopyrite core inside, the oxidation of the mineral ceases due to the insulating properties of the sulfur. However, the application of gentle pressure is enough to break apart the layer of plastic sulfur and reestablish electrical contact. This allows uninterrupted dissolution of the particles, and also demonstrates that with the continuous removal or breaking apart of this plastic sulfur by mechanical methods in such a way that electric contact with the source of potential is not lost, or lost
only momentarily, chalcopyrite leaching in the transpassive regime can be achieved in a continuous process. Measurements of electrical conductivity of the residual sulfur following the two-probe technique confirmed its insulating properties. Electrical resistivity was always higher than $10^9 \Omega \text{ cm}$.

The plastic sulfur formed from the beginning of the dissolution process forms an insulating sac, which not only prevents the free flux of electrons but also hinders the free diffusion of ions. As copper and iron ions are released from the chalcopyrite particle, most of them remain inside, gradually filling the space between the particle and the sulfur sac. As the osmotic pressure increases due to the gradual accumulation of positive charge in the interior, the sac swells and finally explodes, releasing concentrated amounts of iron and copper ions. This entire process was observed and recorded under a stereographic microscope. Figure 4.2 shows a sequence of pictures during the dissolution of a chalcopyrite particle at 1.2 V vs. SCE. In the figure it can be observed that after 30 seconds of constant applied voltage, a clear layer of sulfur covers the entire surface of the particle. After about 2.5 minutes almost the entire particle was dissolved, leaving only a tiny unleached core of chalcopyrite. This chalcopyrite core was etched smooth and bright with no visible angles. The transparent sulfur was treated with carbon disulphide but did not dissolve. This suggests that it is an amorphous and plastic form of sulfur as also suggested by Biegler and Swift (1979). On the other hand, sulfur that was left standing for a day or more was treated with CS$_2$, and this time the sulfur dissolved to some extent but not completely. This indicates that the initial plastic sulfur changed with time to the typical yellow rhombic form, a more stable structure of sulfur, which dissolves in CS$_2$.

The same rapid dissolution behavior was observed when chloride ions, in the form of sodium chloride (NaCl), were added to the solution and a potential of 1.2 V vs. SCE was applied to the particles. A group of pictures in sequence, showing the dissolution of a single chalcopyrite particle, are given in Figure 4.3. As before, the dissolution of the particle began forming an apparent thin sulfur layer. With time
this sulfur layer began to exhibit some differences from the previous sulfur layer. This sulfur was less dense, opaque and quite sticky being difficult to dislodge from the carbon wire electrode, and its morphology seemed to follow the shape of the original particle. This sulfur layer was difficult to break by mechanical means with the carbon wire electrode. Nevertheless the contact between the particle and the working carbon electrode did not seem to be effected by the sulfur layer growing.

This new sulfur formed in the presence of NaCl responded in a different way when it was treated with CS$_2$. Only a part of the sulfur layer was removed by the carbon disulfide when the particles were treated one hour after the sulfur layer was formed. However, after 24 hours, almost all of the sulfur was dissolved. This result suggests that the presence of chloride ions in solution results in a more crystalline form of sulfur being formed. More detailed SEM images presented later on in this work will confirm this observation.
Figure 4.2  Sequence of photographs at different times showing the formation of sulfur in a near instantaneous dissolution of chalcopyrite at transpassive potentials of 1.2 V vs. SCE. The solution contained 90 g H$_2$SO$_4$ at a temperature of 20°C.
Figure 4.3  Sequence of photographs at different times showing the dissolution of chalcopyrite particles in electrolytes containing 90 g/L H$_2$SO$_4$ + 1M NaCl at 20°C and at a transpassive potential of 1.2V vs. SCE. The diameter of the carbon wire is 25 µm.
4.3.3. Sulfur Nucleation and Formation

During the transpassive leaching of particles in solutions with sulfuric acid and sodium chloride, special emphasis was put in how the sulfur begins to form on the surface of the particles. The purpose of this special interest in the formation of sulfur was to develop a better understanding of the role of sulfur in the passivation of chalcopyrite during the leaching process.

Images of chalcopyrite particles during the first 10 seconds of leaching were captured by SEM photographs. Figure 4.4.A shows a particle leached for 10 seconds in a solution containing 90 g/L H₂SO₄ with no chloride. As observed in the figure, the particle was only attacked on certain parts of its surface. The attack occurred preferentially at dislocations and along grain boundaries. Most of the surface did not show clear evidence of attack, and the only manifestations of sulfur, as globules, were sparsely distributed on the chalcopyrite surface. When a larger piece of chalcopyrite was tested, the same sulfur deposition pattern was observed. Some initial sulfur globules were present on the surface of chalcopyrite, with a larger accumulation of sulfur globules close to mineral inclusions, in this case the impurity was silica. This can be observed in Figure 4.5A. Analyses by EDX of the two different materials observed in this picture give 99.4% sulfur for the dark brown spots, and pure chalcopyrite for the bright surfaces.

With time, and maintaining the transpassive potential (1.2 V vs. SCE) constant, the entire surface of the chalcopyrite particles began to be covered with the sulfur globules. These sulfur globules eventually formed a uniform and dense layer of sulfur around the surface of the particle. This layer completely surrounded the particle after only 20 seconds. Figure 4.6A presents an SEM image of a chalcopyrite particle that was leached for 20 seconds. Initially a plastic sulfur layer encapsulated the particle completely, but a part of this layer was broken by mechanical means to show the surface of the remaining sulfide core. This unleached surface of chalcopyrite did not exhibit any evidence of corrosion.
whichever. EDX analysis of the exposed chalcopyrite surface gave a S/Cu/Fe ratio of 2 / 1 / 1. This suggest that chalcopyrite at this high potential dissolves to Cu ions, Fe ions, and S directly without the formation of intermediate compounds. EDX analysis the sulfur layer gave 99.3% S with minute traces of copper and iron.

The addition of 1 M of sodium chloride to the sulfuric acid solution gave a totally different sulfur morphology on the chalcopyrite particles. In this case when transpassive potentials were applied, during the first few seconds of dissolution the particles exhibited some dark spots on their surfaces under the stereomicroscope. The same particles observed with the SEM showed a very curious pattern of well-defined holes. These corrosion pits formed triangular pores, and an overall attack on the mineral surface was observed. Figure 4.4B shows an SEM image of a particle leached for five seconds. The two different areas observed on this particle corresponded to chalcopyrite (bright areas), and sulfur (dark holes) as determined by EDX analysis. Apparently these triangular pits are formed in the first seconds of chalcopyrite dissolution at high potentials (1.2 V vs. SCE) and do not contain sulfur when they are formed. With time, however, these pits fill up with sulfur. Figure 4.5B shows a different particle of chalcopyrite with some triangular pores empty of sulfur, and other pores with some sulfur inside. These sulfur formations appear as dendritic structures, where the pores act as a seeding surface for the sulfur to emerge, and then the sulfur grows outward from the surface. After 20 seconds of dissolution, a porous sulfur layer covered the entire surface of the reacted particle. This sulfur layer did not change its morphological aspect even after the particle was completely leached. Figure 4.6B shows what remains of a chalcopyrite particle after dissolution in presence of sodium chloride at high potentials; now a porous sulfur formation in the shape of the original particle.

The formation of sulfur dendrites in well-defined locations such as the triangular pores could indicate the formation of elemental sulfur by precipitation from dissolved sulfur compounds such as H$_2$S. The formation of sulfur by precipitation
was also suggested in previous studies (Dutrizac, 1989; 1990; 1992). Based on the evidence from the SEM images an empirical morphological model can be formulated. In Figure 3.7 a three-step model is shown. The first step implies the formation of the well defined triangular pores by action of the sodium chloride as a corrosion accelerator. During the second step the presence of elemental sulfur is observed to form initially in the centre of the pits. Then the sulfur progressively spreads inside the lower surface of the pit, and after that the sulfur begins to grow perpendicularly to the surface of the particle in a dendrite-like formation by precipitation. Finally in the third step, these defined dendrites coalesce into a coherent layer over the surface of the shrinking particle core.

Although the function and effect of the sodium chloride is not entirely clear, based on the results of this part of the study one can conclude that NaCl promotes pitting corrosion of the chalcopyrite surface creating a porous layer of elemental sulfur that at the same time has a completely different structure and different physical properties from the sulfur formed in the absence of NaCl. As a consequence of this porous layer, the continuous chemical attack on the particle is observed. These two factors are associated with very rapid leaching of the mineral.
Figure 4.4  Single chalcopyrite particles after five to ten seconds of leaching in the transpassive regime (1.2 V vs. SCE) with A) 90 g/L H₂SO₄, and B) 1 M NaCl + 90 g/L H₂SO₄ at 20°C.
Figure 4.5  A) Evident preference of sulfur globule formations near grain boundaries and mineral inclusions. Solution of 90 g/L H$_2$SO$_4$. B) Formation of sulfur as dendrites during the dissolution of chalcopyrite particles in a solution containing 1 M NaCl + 90 g/L H$_2$SO$_4$ at 20ºC.
Figure 4.6 Chalcopyrite particles showing the sulfur layer formed at transpassive potentials after: A) 20 seconds in a solution of 90 g/L H₂SO₄, and B) 90 seconds in a solution of 1 M NaCl + 90 g/L H₂SO₄ at 20°C.
Figure 4.7  Cross-section sketch of a possible mechanism of sulfur formation in the surface of chalcopyrite in contact with an electrolyte containing NaCl at transpassive potentials (1.2 V vs. SCE). A) Fresh sulfide surface; B) triangular shape pits began to appear; C) seeding and growing of elemental sulfur at the bottom-center of the triangular pits; D) formation of a porous sulfur layer in the surface of the chalcopyrite by coalescence of elemental sulfur formations emanating from the corrosion pits.
4.3.4. Cyclic Voltammogram of a Generated Sulfur Layer and the Depassivation of Chalcopyrite

The atmospheric leaching of chalcopyrite in sulfuric acid media has been an active field of research for many years, with many researchers trying to understand the critical factor that inhibits the leaching process. It is widely held that the passivation is the result of a metal deficient film polysulfide (Ammou-Chokroum et al., 1977; Hackl et al., 1995), while other studies refer to the formation of a layer of elemental sulfur during the leaching of chalcopyrite as the cause for passivation (Dutrizac, 1981; Munoz et al., 1979). To determine if the sulfur layer is a passivating factor on the surface of chalcopyrite, cyclic voltammograms were generated on a particle of chalcopyrite, which was previously electro-dissolved at high potential (1.2 V vs. SCE) until an evident layer of sulfur encapsulated the particle. The test was executed at 20°C in a solution containing only 90 g H₂SO₄ at a scan rate of 20 mV/s in the positive direction. The single particle microelectrode technique was used for this experiment, and special care was put on touching only the sulfur layer generated on top of the particle instead of contacting the unleached particle core.

Figure 4.8A shows a cross-section picture of the particle used for the electrochemical characterization, and Figure 4.8B presents the resulting voltammogram for this particle of chalcopyrite. It is evident from this plot that the sulfur has a considerable blocking effect on chalcopyrite leaching. The particular oxidation anodic peak, which usually is observed under conditions in the potential range between 350 to 550 mV vs. SCE, is not present. This also demonstrates that the sulfur is forming a non-conductive layer. It is possible to observe two main peaks at the limits of the cycle at potentials of 1.0 V and -0.2 V. These peaks correspond to the beginning of the generation of oxygen and hydrogen respectively. A lone cathodic peak is observed at 0.1 V vs. SCE, and could be associated with the reduction of the sulfur layer covering the chalcopyrite particle.
(Gomez et al., 1996; Holliday and Richmond, 1990).

Eq. 4.1 \[ S^0 + Cu^{2+} + 2e^- \rightarrow CuS \]

The dissolved copper in Eq. 4.1 corresponds to the copper liberated from the particle during its dissolution at the time the sulfur layer was formed. Its concentration could be considerable near the particle surface due to the lack of agitation used during the dissolution, and the execution of the cyclic sweep. This voltammogram demonstrates that chalcopyrite is totally passive over a broad range of solution potentials which include the potential range governed by the Fe$^{3+}$/Fe$^{2+}$ couple. Thus it can be concluded that the dense layer of elemental sulfur covering the chalcopyrite particles is an important cause of passivation.

Passivation caused by the formation of a metal deficient polysulfide layer may not be dismissed. It has been observed in our laboratory that when experiments of chalcopyrite leaching are performed, SEM images of the passivated chalcopyrite residues show particles with little or no visible sulfur on their surfaces. Hence, one could conclude that metal deficient polysulfide layers passivated these particles (Hackl et al., 1995; Hiskey, 1993; Parker et al., 1981).

This kind of passivation, where no sulfur layer is evident, is more common. More than five copper concentrates from around the world have shown this passivation. However, the addition of pyrite intentionally to the reactor has overcome this passivation. The mechanism by which pyrite accelerates the dissolution of chalcopyrite has been assigned to the galvanic effect between those two sulfides (Dixon et al., 2008; Tshilombo, 2004). During previous experiments, pyrite and chalcopyrite were added to the reactor together at time zero. Under these conditions is was not possible to evaluate whether pyrite could reverse the passivation of chalcopyrite because it was assumed that chalcopyrite did not form a passive layer in the presence of pyrite. Thus an experiment was designed to evaluate the effect of pyrite after a passive layer had already been formed on the
surface of chalcopyrite. During the leaching test, 100 g of an Australian copper concentrate were leached for 24 hours without pyrite. Solution analyses after 24 hours gave copper dissolution of only 24%, and the chalcopyrite began to show signs of passivation after only 5 hours of leaching, as shown in Figure 4.9. The morphology of the particles after 21 hours of leaching show only selected areas on the surface with elemental sulfur, but most of the particles were without evident sulfur formation (See Figure 4.10). After 24 h, 100 g of pyrite from Huanzala was added, and a dramatic increase in the leaching rate was observed. After 19 hours in the presence of pyrite, copper extraction was complete (43 h total time).

Morphological studies by SEM of the leached chalcopyrite particles after the addition of pyrite at 35 and 43 h are presented in Figure 4.11A and B, respectively. Particles at both times present a very porous sulfur layer that is not compact. This layer has a brain-like morphology with a large number of open channels, and does not represent a significant barrier to the diffusion of ions. This effect of pyrite on chalcopyrite has been observed in different chalcopyrite concentrates, regardless of their provenance or impurity levels.

Thus it can be assumed that chalcopyrite passivation may be caused by the two possible factors evaluated in this study: the formation of a non-stoichiometric polysulfide layer, and the formation of a compact sulfur layer, which encapsulates the chalcopyrite particles. Both will cause passivation of chalcopyrite but something to have clear is that the compact sulfur layer will form only if the polysulfide layer passivation has been overcome. The latter is easily broken during transpassive leaching, with the inconvenient of using mechanical means to get rid of the plastic sulfur layer formed on the particles. On the other hand, chalcopyrite passivates when is leached at moderate potentials apparently by the non-stoichiometric layer, but overcomes passivation when pyrite is added. This observation will lead to the hypothesis that the non-stoichiometric polysulfide layer, observed and studied by different authors, is a consequence of a different mechanism that is the real foundation for passivation. Besides the galvanic effect
of pyrite over chalcopyrite, pyrite in some way induces to a different behavior of sulfur avoiding the presence of compact layers, and providing a different sulfur crystallization that is totally porous. Although research in more detail is needed to reveal a conclusion, the dissolution-precipitation-crystallization mechanism of sulfur may provide a better understanding of this subject matter.
Figure 4.8  A) SEM cross-section of a chalcopyrite particle used to evaluate the passivation behavior of sulfur deposited on the surface. B) Resulting cyclic voltammogram of the particle at 20°C, 90 g H₂SO₄ and 20 mV/s scan rate.
Figure 4.9 Copper dissolution of an Australian copper concentrate showing obvious passivation after a few hours of leaching. Re-activation leaching to complete copper dissolution is observed after 24h when ground pyrite was added to the slurry.
Figure 4.10  SEM cross-section of chalcopyrite particles leached in the absence of pyrite after 21 h. A) Some particles did not present clear signs of leaching or the occurrence of sulfur on their surfaces. B) Most particles have some sulfur covering only parts of their surfaces.
Figure 4.11  Particles of chalcopyrite reactivated after the addition of pyrite. A) By 35 h most of the particles have already developed a porous sulfur layer. B) 19 h after pyrite addition the only particles remaining in the residue were porous sulfur and pyrite.
4.3.5. Charge, Current and Particle Dissolution

During the electro-dissolution of chalcopyrite particles at 1.2 V vs. SCE in solutions with sulfuric acid and sodium chloride, it was possible to obtain at time intervals of one second the amount of current released until the particle was totally dissolved. By integrating this current, the total charge is obtained. This charge indicates the dissolution kinetics of the chalcopyrite particle. During the dissolution process the carbon wire electrode was in permanent contact with the particle. The growing layer of elemental sulfur did not interfere with the measurement since a constant pressure was applied with the carbon wire. When an unexpected decrease in current was observed, more pressure was applied to break the weak plastic sulfur layer and ensure an appropriate contact. On the other hand, the elemental sulfur layer formed during the dissolution of particles in a solution containing sodium chloride in addition to sulfuric acid was of a different nature. It had the consistency of a porous rubber, and was stronger and more difficult to penetrate than the sulfur formed in the solution containing only sulfuric acid. As a consequence, the experimental measurements using this solution were realized simply by pressing the carbon wire electrode strongly enough to ensure a constant current reading.

The experimental results for the dissolution of chalcopyrite in a solution of 90 g/L H₂SO₄ only are presented in Figure 4.12A. That figure shows the current for the complete dissolution of the particle and its respective charge. Charge is also represented on the graph as the fraction reacted of the particle, since this value is the same as the amount of copper released to the solution divided by the total copper contained in the particle. Knowing the fraction reacted of the particle for every second of dissolution, well-known particle dissolution models could be applied. The experimental values of the fraction reacted were applied to models of product-layer diffusion and surface reaction control for shrinking cores and spheres. The experimental results correlated best to the model represented by Eq. 4.2, corresponding to surface reaction control. This model represented the process for nearly the full duration of the test, giving an almost perfect fit up to
approximately 85% particle dissolution (See Figure 4.12B). After this point apparently there is a change in the dissolution mechanism, perhaps shifting the control towards diffusion.

Eq. 4.2 \[ \frac{t}{\tau} = 1 - (1 - X)^{1/3} \]

The current for the particles that were electro-dissolved in a solution of 90 g/L H₂SO₄ and 1 M NaCl showed a different behavior. As shown in Figure 4.13A, the maximum current at the beginning of dissolution was 120 \( \mu \)A, which is slightly smaller compared with the current of 150 \( \mu \)A from Figure 4.12A. Also the total time to dissolve the particle completely was 350 s, which was almost double the time required to dissolve a particle of similar size of 100 \( \mu \)m in H₂SO₄ alone. This same relative behavior was observed with more than fifty individual particles electro-leached in both solutions.

As before, the measured currents were integrated to obtain the charge expressed as fraction reacted and fitted to various kinetic models. The model that yielded the best fit was the mass transport control model for shrinking spheres:

Eq. 4.3 \[ 1 - X = \left(1 - \frac{t}{\tau}\right)^{3/2} \]

Figure 4.13B shows the resulting model fit. It was observed that a porous sulfur layer forms during the dissolution of chalcopyrite particles in the presence of sodium chloride (Figure 4.6B). This layer apparently did not offer any diffusion resistance to the transport of ions. The only resistance came from the stagnant film surrounding the particle during leaching. This stagnant film is significant because the dissolution of the particle was conducted without agitation, and the particles were stationary. Considering that the stagnant film can be minimized at agitated conditions, and the porous sulfur layer has demonstrated that is not an
impediment for a free diffusion of ions, it can be expected that a more realistic model for the dissolution of chalcopyrite in presence of sodium chloride can be a surface reaction control. This shift to a different mechanism will accelerate the dissolution of chalcopyrite particles to the same or even higher extent than particles dissolved in solution with sulfuric acid alone which is in consensus with literature where always the presence of chloride ion enhances the dissolution of chalcopyrite (Carneiro and Leao, 2007; Flett, 2002).
Figure 4.12  A) Current and charge passed expressed as fraction reacted of a particle dissolved at 1.2 V vs. SCE in a solution containing 90 g H₂SO₄ at 20ºC. B) Experimental data fitting the reaction control model.
Figure 4.13 A) Current and charge passed expressed as fraction reacted of a particle dissolved at 1.2 V vs. SCE in a solution containing 90 g H$_2$SO$_4$ + 1 M NaCl at 20ºC. B) Experimental data fitting the mass transfer model.
4.3.6. Sulfur and Sulfate Calculation at High Potentials

Mass balances were performed during the dissolution of chalcopyrite particles at constant high potentials of 1.2 V vs. SCE. Using the concentration of Cu\(^{+2}\) in solution, and the charge measured by the potentiostat, an approximate yield of sulfur to sulfate was calculated. The experiments were carried out using two different solutions, one containing 1 M H\(_2\)SO\(_4\), and the other one containing 1 M H\(_2\)SO\(_4\) + 1 M NaCl. The concentration of copper in both solutions was measured by atomic absorption (AA) and inductively coupled plasma (ICP). Both techniques were used in order to obtain more precise data, considering that the copper concentration was very small. An average of 50 particles between 75 and 100 \(\mu\)m diameter were dissolved completely in order to give an appreciable amount of copper in solution and to facilitate more accurate chemical analysis. The reactions that were considered to be taking place at high potential are:

Eq. 4.4 \[ \text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2 \text{S}^0 + 5 \text{e}^- \]

Eq. 4.5 \[ \text{CuFeS}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ + 17 \text{e}^- \]

Iron is assumed to enter the solution as ferric considering the high potential at which these experiments were performed. Three different tests were performed; the first and second in the solution with H\(_2\)SO\(_4\) only, and the third in the solution of H\(_2\)SO\(_4\) + NaCl.

Table 4.1 presents the results obtained for the calculation (See Appendix B) of elemental sulfur (S) and sulfate (SO\(_4^{2-}\)). The average elemental sulfur yield was 88.8% in the solution containing only H\(_2\)SO\(_4\), and of 76.8% in the solution containing NaCl. The average numbers of electrons involved in the reactions \(n\) were 6.34 and 7.79, respectively, for each solution. Direct analysis of sulfur and sulfate in solution were not attempted since the small amounts of these formed compounds would not be reliable. A mayor presence of sulfate was expected to
build up at this high potential, however based on data in Table 4.1 and SEM pictures, sulfur was the main specie formed under these conditions. A possible explanation for this result is that the discharge of water needed to form sulfate only occurs on conductive surfaces (Vetter, 1967), and given that the surface of the chalcopyrite particles are covered by a insulating and non-porous layer of sulfur, the formation of sulfate is less probable to occur.

Similar results were obtained by Warren et al. (1982) who measured an average of 90.3% elemental sulfur formation using an electrolyte with 1 M H₂SO₄. When he used 1 M HClO₄ the average sulfur yield dropped slightly to 82.53%. Biegler and Swift (1979), using similar calculations, also predicted a sulfur yield of 86% using a electrolyte containing 1 M H₂SO₄. Apparently the presence of chloride in solution increases the oxidation of sulfur to sulfate. It has also been pointed out that chloride promotes the formation of oxidized sulfur compounds such as thiosulfate and polythionates (Kinnunen and Puhakka, 2004). Additionally, the present study used higher potentials than that used by Warren et al. (849 mV vs. SCE). This factor contributed to the higher yield of sulfate measured in this study.
Table 4.1 Calculated sulfur and sulfate yields for chalcopyrite particles dissolved at 1.2 V vs. SCE.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>1 M H₂SO₄</th>
<th>1 M H₂SO₄</th>
<th>1 M H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>+ 1 M NaCl</td>
</tr>
<tr>
<td># Particles Dissolved</td>
<td>48</td>
<td>53</td>
<td>45</td>
</tr>
<tr>
<td>Charge (C)</td>
<td>1.1295</td>
<td>1.2467</td>
<td>1.2850</td>
</tr>
<tr>
<td>AA ICP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu (mol x 1000)</td>
<td>1.775</td>
<td>2.034</td>
<td>1.689</td>
</tr>
<tr>
<td>n (e⁻)</td>
<td>6.595</td>
<td>6.352</td>
<td>7.887</td>
</tr>
<tr>
<td>% S</td>
<td>86.7</td>
<td>88.7</td>
<td>75.9</td>
</tr>
<tr>
<td>% SO₄</td>
<td>13.3</td>
<td>11.3</td>
<td>24.1</td>
</tr>
<tr>
<td>Average S yield</td>
<td>88.8 %</td>
<td>76.8 %</td>
<td></td>
</tr>
<tr>
<td>Average SO₄ yield</td>
<td>11.2 %</td>
<td>23.2 %</td>
<td></td>
</tr>
</tbody>
</table>
4.4. CONCLUSIONS

This study has demonstrated that it is possible to dissolve chalcopyrite at high potentials in less than five minutes at room temperature. In a solution with sulfuric acid an amorphous, easily broken plastic sulfur was formed. On the other hand, the addition of sodium chloride to the sulfuric acid solution gave a porous, elastic, hardly broken sulfur layer that began to grow within well-defined triangular corrosion pits. During the first few seconds of dissolution in sulfuric acid solution had, the surface of chalcopyrite was attacked only in selected locations, while in the presence of sodium chloride, the entire surface was attacked uniformly.

The sulfur layer formed during transpassive leaching was shown to be an inhibiting factor for the dissolution of chalcopyrite under the conditions studied. Residual particles leached at moderate potentials showed passivation without the formation of sulfur layers, while the addition of pyrite was found to enhance and reactivate the dissolution of chalcopyrite even after it had been strongly passivated.

The dissolution rate of particles at high potentials in sulfuric acid appears to be controlled by the surface reaction; and in the presence of sodium chloride, mass transport was the controlling model for the studied conditions. The yield of elemental sulfur created was 88.8% in 1 M $\text{H}_2\text{SO}_4$ solution, and 76.8% when 1 M NaCl was added.

4.5. ACKNOWLEDGEMENTS

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4.6. REFERENCES


5.1. INTRODUCTION

Copper compounds containing arsenic such as enargite (Cu$_3$AsS$_4$) commonly occur in minor quantities in many ore deposits. But this presence has increased over the last few years due to the depletion of relatively clean deposits and the search for new sources of copper to supply the growing demand for this metal worldwide.

Various treatments have been proposed to enable the processing of enargite-containing ores and concentrates. Some past studies proposed the separation of enargite from other valuable minerals such as chalcopyrite during the flotation using electrochemical control and other means (Fornasiero et al., 2001; Guo and Yen, 2005; Mihajlovic et al., 2007). The purpose of these past studies was to obtain a clean chalcopyrite concentrate containing only traces of enargite in order to avoid smelter penalties and to facilitate separate treatment of the various minerals. In the past, copper concentrates containing considerable amounts of arsenic have been roasted before being treated in a smelter. At the El Indio smelter in Chile, this process was used to reduce the arsenic content from 10% in the concentrate to only 0.1% As in the roasted product, and the arsenic was captured as arsenic trioxide (As$_2$O$_3$) in bag filters (Smith, 1986). Another hydrometallurgical route to obtain concentrates suitable for smelting has been the application of alkaline leaching. Sodium sulfide (Na$_2$S) can be used to leach arsenic selectively from enargite as follows:

\[
\text{Eq. 5.1} \quad \text{Cu}_3\text{AsS}_4 + 3 \text{Na}_2\text{S} \rightarrow 3 \text{Cu}_2\text{S} + 2 \text{Na}_3\text{AsS}_4
\]

* A version of this chapter has been submitted for publication. BF Rivera-Vasquez and DG Dixon, (2010). Rapid Atmospheric Leaching of Enargite in Acidic Ferric Sulfate Media.
Balaz and Achimovicova (2006) found that the extent of arsenic extraction from enargite using sodium sulfide was only 5% after 10 minutes of leaching at 55°C. However, when the enargite was mechanically activated with a planetary mill, the arsenic extraction increased to 85% at 55°C and was nearly complete when the temperature was increased to 80°C.

Enargite dissolution in acid media has been shown to be much slower than chalcopyrite (Filippou et al., 2007). One of the first studies in acid sulfate media was conducted by Brown (Brown, 1931) in 1931. He found that leaching an almost pure specimen of enargite in a solution containing sulfuric acid and ferric sulfate extracted only 2% of copper after 60 days at 35°C, and only 0.5% after 30 days with sulfuric acid alone. A simple study by Sullivan (1933) working with an enargite sample containing 45.02% Cu and 13.22% As, extracted less than 3% of the copper after 146 days at 35°C with a solution containing 5% of iron by mass as ferric sulfate.

A more detailed study of natural and synthetic enargite dissolution by Dutrizac and MacDonald (1972) confirmed the slow kinetics of dissolution in acid sulfate media at temperatures from 60 to 70°C. They observed that the dissolution of copper and arsenic have the same leaching rate, and that the residue consists solely of elemental sulfur. They also determined that the dissolution of enargite follows linear kinetics, thus discarding a diffusion-controlled reaction mechanism for two reasons: the dissolution rate was independent of the rotation speed applied to the sample used, and the removal of the sulfur layer from enargite by grinding did not increase the dissolution rate. The activation energy was calculated to be 55.7 kJ/mol. The presence of Fe(III) in solution had a beneficial effect on the dissolution rate up to 0.2 M, above which higher concentrations were insensitive. They also observed that the oxidation of sulfur to sulfate was in the range of 5 to 50%, and thus suggested the following reaction for the dissolution of enargite as follows:

\[
\text{Eq. 5.2 } \quad \text{Cu}_3\text{AsS}_4 + 11 \text{Fe}^{3+} + 4 \text{H}_2\text{O} \rightarrow 3 \text{Cu}^{2+} + \text{AsO}_4^{3-} + 4 \text{S}^0 + 8 \text{H}^+ + 11 \text{Fe}^{2+}
\]
By this reaction, only 50% of the copper was extracted from finely ground enargite (-149 μm) after seven days at 85°C with 0.1 M H₂SO₄ and 0.1 M Fe(III) in solution.

When Flynn and Carnahan (1989) tried to leach enargite in a Fe₂(SO₄)₃-H₂SO₄ solution at the boiling point, they achieved extractions of only 8% Cu and 9% As after 6 h. Surprisingly, when these researchers added 0.25 g/L of Ag₂SO₄ the Cu and As extractions increased to 94 and 97%, respectively. They did not present a mechanism of dissolution for this catalytic effect of silver dissolving enargite, and also there was no information about the particle size for the sample used in their experiments. Hourn et al. (1999) leached a copper concentrate containing 20.9% enargite, 11.9% chalcocite and 50% pyrite as major sulfide species. They used a vertical mill to obtain an ultra-fine concentrate with a P₈₀ of 3.5 μm, at 90°C after 10 hours of leaching in ferric sulfate media obtaining 92% Cu extraction. This recovery represents total copper extraction, but if one considers that chalcocite leaches much faster than any other copper sulfides (Filippou et al., 2007; Kuhn et al., 1974; Peters and Loewen, 1973) and conducting a copper balance based on the initial mineralogy, the calculated copper extraction from enargite is only 85%. Additionally, they used oxygen to regenerate ferric ions in solution, and lignosol to reduce frothing during leaching. They presented no further information regarding the effect of solution potential that could have been modified by the addition of oxygen, or the effect of the pyrite-to-enargite ratio during leaching. The Py/En ratio in the sample was 2.4.

Chloride media has been studied for enargite leaching by several authors. Herreros et al. (2002) leached enargite using chlorine which was produced in-situ by the reaction between sodium hypochlorite and hydrochloric acid in the leaching reactor. They noticed that the dissolution of enargite occurred in two distinct stages. The first stage is very fast, and is controlled by diffusion in a liquid boundary layer. The second stage is slow, and is controlled by diffusion through a solid product layer. This solid product was estimated to be non-porous elemental sulfur. Leaching at 25°C for 40 minutes for fine particles (<15 μm) gave 38% Cu extraction, and only 4.8% Cu extraction for course particles (50 to 75 μm). The formation of sulfur coatings on the particles was
assumed to be the cause of the slow dissolution.

Padilla et al. (2005) used a combination of sulfuric acid, sodium chloride, and oxygen to dissolve enargite. At a temperature of 100°C with 0.25 M H₂SO₄, 1.5 M NaCl, and at an oxygen flow of 0.3 L/min, only 6% of the arsenic was dissolved after 7 h. Elemental sulfur was reported as the predominant sulfur product at 95%, but this elemental sulfur did not form passive layers on the surface of the particles. The predominant sulfide species in the sample were enargite and pyrite at 84.1 and 9.6% respectively. The average particle size was 58 μm. They suggested that the dissolution of enargite is linear, which agrees with another study by Riveros and Dutrizac (2008), who also noticed the slow dissolution of enargite, obtaining only 27% Cu extraction after 16 h of leaching at 100°C in a FeCl₃-HCl media.

Biological leaching of enargite has also been investigated (Acevedo et al., 1998; Canales et al., 2002; Escobar et al., 1997; Munoz et al., 2006). All investigators noted that mesophiles were unable to break down enargite. When thermophiles were used, surface modification occurred with formation and later oxidation of sulfur to sulfate. The dissolution was slightly faster compared with sulfate media, but complete dissolution of enargite was difficult to achieve. An inhibitory effect of arsenic in solution on bacterial viability was also observed, but this effect was less apparent when ferric was also present. Another inconvenience using thermophiles was the limitation on the amount of suspended solids (Batty and Rorke, 2006). A limit of approximately ~12.5% solids by mass was proposed to avoid shearing the microbial cells and accelerating their death rate.

In summary, previous studies have shown that oxidative leaching of enargite in sulfuric or hydrochloric acid media, with and without bacteria, is inefficient. Those studies in general agree that the dissolution of enargite forms majority elemental sulfur, but there is no consensus as to whether this sulfur layer is porous or non-porous, or whether this layer contributes to enargite passivation. In addition, no studies reported in literature investigated enargite leaching at controlled solution
potentials. A range of suitable potentials to be applied could be obtained by electrochemical studies of the sample to be leached. Even though there are a number of electrochemical studies of enargite, no study interconnects these studies with a way to improve enargite leaching.

However, in our laboratory, with a combination of simple electrochemical measurements on particles, an appropriate control of the solution potential, and the addition of a sulfide that is usually found in copper concentrates, we observed a catalytic effect of pyrite on the dissolution of enargite. This same effect has also been observed for the dissolution of chalcopyrite, resulting in the conception of a new process. The present study reveals how the addition of pyrite in solution creates a process that is capable of leaching enargite to completion, and is thus the only process capable of leaching copper-arsenic concentrates at atmospheric pressure in sulfate media without fine grinding or the use of bacteria, or chloride.

5.2. EXPERIMENTAL

5.2.1. Electrochemical Measurements

A single particle, three-electrode electrochemical cell was used. The instrumental array involved in the assembly and characterization of single sulfide particles of μm size included a conventional stereo microscope equipped with a digital microscope eyepiece camera connected to a PC via a USB interface. This system allowed acquisition of both pictures and real-time video images for further processing. An XYZ motorized micromanipulator mounted on one side of the microscope provided the means for accurate positioning of the working electrode and is thus a critical part of the assembly. The working microelectrode was made by joining together an electrochemically activated carbon fiber 25 μm in diameter with a copper wire approximately 0.5 mm in diameter using silver epoxy. This assemblage was inserted into a flame-pulled glass micropipette with an internal diameter of 0.68 mm and a tip of approximately the same diameter as the carbon fiber. Finally, both ends were
sealed with epoxy.

The tip of the working electrode was contacted with a single sulfide particle placed on a disk of glass frit immersed in electrolyte solution by remote control of the micromanipulator. The glass frit was inside a 100-mL glass beaker containing the electrolyte solution, the reference electrode, and the counter electrode. The reference electrode was a saturated calomel electrode (SCE) with a potential of 0.245 V versus the standard hydrogen electrode (SHE). A Luggin capillary was used in conjunction with the SCE. The counter electrode used during the experiments consisted of a platinum wire 5 cm long and 1 mm in diameter. The temperature of the electrolyte solution was maintained with heating tape. All electrochemical measurements were made with a potentiostat (Princeton Applied Research PARSTAT 2273). A sketch of the final arrangement is shown in Figure 5.1.

![Figure 5.1 Schematic representation of the experimental electrochemical cell](image-url)
5.2.2. Leaching Experiments

The experimental leaching apparatus is shown in Figure 5.2. Leaching experiments were conducted in a sealed, jacketed, 2.7-L glass reactor. The reactor was maintained at the desired temperature with a circulating hot water bath. The stirring speed was maintained at 1200 rpm. Three probes were inserted into the reactor: a thermocouple, a glass pH probe, and a redox potential probe. These three probes were attached to a digital controller. The outputs of the three electrodes were recorded by a computer. The controller allowed a redox potential setpoint to be specified. When the redox potential measured by the electrode inside the reactor fell below the setpoint, an analogue signal was sent to a gas mass flow valve. This valve allowed oxygen to flow into the reactor via a sparger from a compressed gas cylinder. Once the setpoint was reached, the oxygen flow was shut off.

Figure 5.2  Schematic diagram of the experimental apparatus.
5.2.3. Materials

Three different sulfide minerals were used in the present study: chalcopyrite (CuFeS$_2$) from Chihuahua, Mexico; enargite (Cu$_3$AsS$_4$) from Butte, Montana; and pyrite (FeS$_2$) from Huanzala, Peru. The Chihuahua chalcopyrite was only used in the electrochemical tests. The enargite sample was 62% enargite with a total copper content of 41.06%. The pyrite sample was 92.3% pyrite. These two sulfides were used in the leaching experiments. XRD-Rietveld analysis of the mineralogical composition of the Butte enargite is summarized in Table 5.1.

Table 5.1  XRD mineralogical analysis of the Butte, Montana enargite massive sample

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>7.9</td>
</tr>
<tr>
<td>Enargite</td>
<td>Cu$_3$AsS$_4$</td>
<td>62.0</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS$_2$</td>
<td>16.1</td>
</tr>
<tr>
<td>Tennantite</td>
<td>(Cu,Ag,Fe,Zn)$_{12}$As$<em>4$S$</em>{13}$</td>
<td>6.5</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>(Zn,Fe)S</td>
<td>1.3</td>
</tr>
<tr>
<td>Bornite</td>
<td>Cu$_5$FeS$_4$</td>
<td>2.7</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>2.3</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO$_3$</td>
<td>0.8</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg$_3$Si$<em>4$O$</em>{10}$(OH)$_2$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The reagents used to prepare the test solutions consisted of de-ionized water, ferrous sulfate (FeSO$_4$·7H$_2$O), ferric sulfate (Fe$_2$(SO$_4$)$_3$·5H$_2$O), and sulfuric acid (H$_2$SO$_4$). The oxygen used as primary oxidant during the leaching test had a purity of 99.5%.
5.3. RESULTS AND DISCUSSION

5.3.1. Electrochemical Characterization of Single Sulfide Particles

Electrochemical tests consisting of cyclic voltammetry (CV) and the measurement of open circuit potentials (OCP) were conducted on sulfide particles of approximately 100 μm diameter. The OCP of particles (Cp, Py, En) was measured in 10 g/L H₂SO₄ solution at 20°C (Figure 5.3).

![Figure 5.3](image)

Figure 5.3  Rest Potentials of sulfide particles in acidic solution (See Appendix A for reproducibility)

Increasing sulfuric acid concentration and increasing temperature both caused a significant decrease in the OCP of all of the sulfides. These results are explained in more detail by the author in Chapter 3. In spite of the clear effect of temperature and acid concentration, the differences in rest potential between the different sulfide minerals were always maintained. As shown in Figure 5.3, pyrite has the highest OCP...
at 398 mV whereas chalcopyrite and enargite have rest potentials of 335 mV and 164 mV, respectively.

Enargite is a highly refractory semiconductor that passivates during leaching to form a sulfur layer on its surface. To provide evidence for the formation of the sulfur layer, a cyclic voltammetry test was applied to a single particle of enargite. Figure 5.4 shows how rapidly and severely enargite is passivated. The cyclic voltammogram was initiated from the rest potential in a positive direction up to 1.1 V and returned to negative potentials down to –0.3V and then back to the starting point. Both cycles showed a wide peak on the anodic side from 0.2 V to 0.85 V. During the first cycle enargite began to become passivated at around 0.75 V, with a corresponding drastic decrease in its anodic current. In the second cycle, this passivation was almost total, giving currents near to zero above 0.8 V. Also the anodic current at the oxidation peak decreased by half. This could have been caused by a decrease in active enargite surface area which was partially covered by elemental sulfur after the first scan, as also observed in (Asbjørnsson et al., 2003). Figure 5.5 shows an SEM image of the enargite particle that was used for these cyclic voltammogram tests after two cycles. It can be seen that an appreciable portion of its surface is covered by sulfur, as identified by EDX analysis, while some other parts are totally uncovered, suggesting dissolution along preferential planes.
Figure 5.4  Cyclic voltammogram of Butte enargite with a positive-going potential scan at 90 g/L H₂SO₄ and a scanning rate of 20 mV/s

Figure 5.5  SEM picture of an enargite particle after 2 CV cycles showing a sulfur layer covering nearly the entire surface of the particle.
Considering that enargite is a semiconductor as well as chalcopyrite and many other sulfides, it can be stipulated that the dissolution of this mineral is a galvanic corrosion process. For this to occur, both cathodic and anodic sites must occur on the mineral surface. Often certain surface regions such as impurity atom sites, dislocations, grain boundaries, etc., become anodic, while the remainder of the surface becomes cathodic. The actual dissolution occurs at the anodic sites while oxidant is reduced at the cathodic sites. The electrical circuit is then completed through the conducting enargite. Apparently, during the first steps of leaching enargite presents both anodic and cathodic sites, but after the compact sulfur layer has formed, the dissolution rate begins to decrease. This leaves enargite particles with almost no cathodic sites with which to continue its electrochemical dissolution.

It has been demonstrated previously, in a mixture of two different sulfide minerals, that significant oxidation occurs on one of the sulfides while a measure of galvanic protection is conferred on the other (Abraitis et al., 2004; Mehta and Murr, 1983; Mishra, 1973). This phenomenon occurs due to the difference in potential between the two sulfide minerals. The mineral with the lower rest potential will assume the role of anode, while the mineral with the higher rest potential will assume the role of cathode. This principle has been successfully applied in a hydrometallurgical process for leaching of chalcopyrite concentrates (Dixon et al., 2008; Tshilombo, 2004) using pyrite as the cathodic material. As Figure 5.3 shows, enargite has a lower rest potential than pyrite, so the principle used in these previous studies could be also applied for the dissolution of this copper-arsenic sulfide.

Figure 5.6 shows how enargite could be dissolved in the presence of pyrite. The oxidation step will occur on the surface of enargite and the reduction step on the surface of pyrite according to the following reactions:

\[ \text{Eq. 5.3:} \quad \text{Cu}_3\text{AsS}_4 \rightarrow 3 \text{Cu}^{2+} + \text{As}^{3+} + 4 \text{S}^0 + 9 \text{e}^- \] (Anodic Reaction)
Eq. 5.4: \[ 9 \text{Fe}^{3+} + 9 \text{e}^- \rightarrow 9 \text{Fe}^{2+} \] (Cathodic Reaction)

Figure 5.6  Galvanically-assisted enargite leaching: cathodic reactions are translated to the pyrite surface, allowing faster enargite dissolution
5.3.2. Enargite Leaching Tests

5.3.2.1. Effect of Pyrite Addition

In order to demonstrate the effectiveness of pyrite addition during enargite leaching, a set of experiments were performed using the enargite sample from Butte (Montana) with additions of the Huanzala (Peru) pyrite. Seven tests were run in 1.6 L of solution under the following conditions: 480 mV vs Ag/AgCl redox potential controlled with oxygen gas, 80°C, 20 g/L total dissolved iron, 60 g total sulfuric acid, 1200 rpm agitation speed, and an initial ferric-to-ferrous ratio of 1:3. A total of 25 g of enargite was used in each test with different amounts of pyrite. The Py:En ratios evaluated were 0:1, 1:1, 2:1, 2.8:1, 3:1, 4:1, and 5:1. Slurry samples of 5 mL were withdrawn at predetermined intervals during the experiment for Cu analysis by atomic absorption spectroscopy. The solid residues were also analyzed by SEM-EDX. The results are shown in Figure 5.7.

![Figure 5.7](image_url)

Figure 5.7 Effect of pyrite addition (Py:En) on enargite leaching.
When enargite leaching was conducted in the absence of pyrite, the leach rate was very slow and apparently reached a plateau after 25 hours at a total copper extraction of only 30%. When residues from this test were characterized by SEM (See Figure 5.8), it was noticed that most of the enargite particles showed only localized sulfur formation, with some occurring deep within the particles. No particles completely surrounded by an elemental sulfur layer were observed. This could imply that enargite dissolves along preferential planes, as stipulated before, and that those different plane groups forming a single particle can behave differently as cathodic and anodic sites.

Adding pyrite to the system increased the dissolution rate. This increase was particularly dramatic at a Py:En ratio of 4:1 or more. When this Py:En ratio was used the enargite leaching was essentially complete after 24 hours. Additional pyrite above a ratio of 5:1 ratio showed no further improvement. Cross-sectional SEM analyses of partially leached particles catalyzed by pyrite (See Figure 5.9) also showed exposed enargite surfaces in most of the particles as shown in Figure 5.10A. This particular mode of enargite dissolution differs from chalcopyrite residues under the same conditions. When chalcopyrite is leached, a porous sulfur layer is observed to cover the entire particle surface (Rivera-Vasquez et al., 2007) and leaching proceeds at a centered shrinking core. Residues from fully leached enargite particles shown in Figure 5.10 reveal formations of porous sulfur similar to those observed in chalcopyrite Galvanox™ residues. EDX analysis performed on polished sections of completely leached enargite particles gave residue composition of 96.7% elemental sulfur, 3.2% iron (the latter presumably precipitated from solution), with less than 0.1% arsenic and copper representing tiny inclusions of unleached enargite. The sulfur layer formed around the enargite particles was very porous, facilitating the diffusion of reagents and products to and from the reaction sites. Pyrite particles show no obvious signs of chemical attack on their surfaces.
Figure 5.8  SEM cross-section of a enargite residue after ferric-acidic chemical leaching without addition of pyrite

Figure 5.9  SEM cross-section of a partially leached enargite residue at 80°C and 480mV in presence of pyrite.
Figure 5.10  SEM cross-section of a completely leached enargite residue leached at 80°C and 480 mV, also showing the external view of a residue particle.
5.3.2.2. Effect of Sulfuric Acid

To study the effect of sulfuric acid on enargite dissolution, three different experiments were performed with sulfuric acid concentrations of 120, 60, and 40 g of total acid. The test run at a Py/As ratio of 3 (Figure 5.7) was considered as the baseline for the study of this variable and for the leaching variables studied subsequently. The results of these experiments are shown in Figure 5.11. The three acid concentrations used were well beyond the stoichiometric acid requirement for the amount of enargite present. The concentration of acid had no significant effect on dissolution kinetics except for the 120g test, which presented a slightly diminished total copper extraction. This result differs from the study of Dutrizac and MacDonald (1972) where the rate of enargite dissolution in the presence of iron sulfates and sulfuric acid increased slightly with increasing acid concentration. Narita et al. (1983) reported that an increase of sulfate ions in an aqueous solution significantly decreases the oxygen solubility. This assumption was also corroborated by Tromans (1998). Therefore the slight decrease in dissolution observed for the test at 120 g of H₂SO₄ could be due to a decrease in oxygen solubility.

5.3.2.3. Effect of Pulp Density

The baseline test of this study was based on 25 g of enargite plus 75 g of pyrite. This renders a pulp density of 6.7 % considering that the entire set of tests were run in 1.5 L of solution. To evaluate the behavior of pulp density on enargite leaching with addition of pyrite, double the amount of solids were added to the reactor, comprising 13.4% solids. Figure 5.12 shows that a double amount of solids has no impact on the dissolution rate of enargite. The initial amount of acid was the same for both tests and no negative effect was observed for the lower acid ratio at high pulp density. This was because the amount of acid (60 g) was more than double the stoichiometric requirement. Also, with double the amount of solids, one might assume more interaction between pyrite and enargite particles, therefore increasing the galvanic
effect. However, the results shown in Figure 5.12 do not support this supposition.

Figure 5.11 Effect of initial sulfuric acid addition on the dissolution of enargite in the presence of pyrite.
Figure 5.12  Effect of pulp density on the dissolution of enargite in the presence of pyrite.
5.3.2.4. Effect of Total Iron in Solution and Pyrite Recycling

To study the effect of the total iron concentration on the dissolution of enargite, and also the effect of pyrite recycle, two different experiments with 7 and 20 g/L of total iron were conducted at 80°C, 480 mV and 60 g of initial acid. After a leaching time of 48 hours both tests were stopped. The solids were allowed to settle for 15 minutes until the solution was clear. Then, 750 mL of solution were extracted from the reactor. To make up for the removed solution, another 750 mL of deionized water with 50 g of H$_2$SO$_4$ and the matching amounts of iron (3.5 and 10 g/L for the corresponding test) were added to each test. After the desired temperature was reestablished, 25 g of new enargite ore were added and the tests were restarted.

The results of these four experiments are shown in Figure 5.13. It can be seen that decreasing total iron from 20 g/L to 7 g/L (or from 0.36 to 0.12 M) has no apparent effect on the leaching kinetics of enargite. Dutrizac and MacDonald (1972) pointed out that the total concentration of ferric had an evident effect on the dissolution rate for concentrations up to 0.2 M, but appeared to have no effect above that amount. In the present study, the concentration of ferric was in the range of 0.03 to 0.09 M (considering a Fe$^{3+}$/Fe$^{2+}$ ratio of 1 to 3) falling inside the range which ferric concentration was found to have an effect on enargite dissolution. However, no effect was seen. Thus, it could be concluded that enargite leaching in the presence of pyrite is insensitive to ferric concentration within this range.

Comparing both of the pyrite recycle experiments, it can be seen that total iron content also did not influence these test. On the other hand, copper extraction after 50 hours was only 73%. This result is significantly lower compared with 89% copper dissolution achieved for each test with freshly added pyrite. The marked difference between the non-recycled and recycled pyrite tests could be attributed to a decrease in the surface area of pyrite, decreasing in this way the effectiveness of the galvanic effect between enargite and pyrite. This decrease of pyrite surface can be attributed to both physical and chemical factors. The physical factor may be due to a blockage
of pyrite surface by arsenic-iron precipitates. To evaluate this assumption, solid pyrite residues of these tests were analyzed with SEM and EDX. As shown in Figure 5.14, pyrite particles have no apparent precipitates on their surfaces. Also EDX microanalyses done at different points on the pyrite particles confirmed that the surface was still comprised of only iron and sulfur with no traces of arsenic. Considering that X-rays from EDX penetrate to about 2 microns in depth, the results obtained from EDX cannot be considered as surface analysis. EDX analyses of the cross-sections of pyrite residue particles were also evaluated, again showing no presence of arsenic or other impurity elements, but only iron and sulfur. Chemical analysis of the solid residues by ICP also confirm the absence of arsenic, other than the small amount corresponding to unleached enargite. This is discussed in detail in the following sections.

Leaching caused the decrease in pyrite surface area. Apparently, the solution potential of these tests was high enough to cause pyrite leaching. ICP analysis showed an increase of iron in solution between the first and last samples of 9.96 g total iron (See Table 5.2). Assuming that all of this iron was generated from pyrite dissolution (iron from bornite is only 0.075 g), the total pyrite leached during the first 48 hours of the test was 21.4 g. This significant amount of pyrite loss changed the Py/En ratio from the initial 3:1 to 2.2:1. If an imaginary curve is plotted for this new ratio of 2.2:1 in Figure 5.7, the copper extraction of 73% for both pyrite recycling tests will fit in between the 2.8:1 and 2:1 curves. Thus, the decrease of copper dissolution observed in the pyrite recycle tests can be attributed to the loss of pyrite surface area by leaching at a solution potential of 480 mV vs. Ag/AgCl.
Table 5.2  ICP results for iron dissolution ($\text{Fe}_{\text{total}}$) during the enargite leaching test with pyrite recycling.

<table>
<thead>
<tr>
<th>Test #</th>
<th>A - 7 g/L Fe (75 g Py)</th>
<th>B - 20 g/L Fe (75 g Py)</th>
<th>C - 20 g/L Fe (150 g Py)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Sample Fe</td>
<td>10.701</td>
<td>28.732</td>
<td>28.032</td>
</tr>
<tr>
<td>Last Sample Fe</td>
<td>19.583</td>
<td>39.080</td>
<td>48.450</td>
</tr>
<tr>
<td>Iron Dissolved</td>
<td>8.881</td>
<td>10.347</td>
<td>20.418</td>
</tr>
<tr>
<td>Calculate Py Diss.</td>
<td>19.08</td>
<td>22.23</td>
<td>43.86</td>
</tr>
<tr>
<td>New Py/En Ratio</td>
<td><strong>2.24</strong></td>
<td><strong>2.11</strong></td>
<td><strong>2.13</strong></td>
</tr>
</tbody>
</table>
Figure 5.13  Effect of total Iron concentration on the dissolution of enargite in the presence of pyrite at 60 g H₂SO₄, 80°C, and 480 mV.
Figure 5.14  SEM micrograph of residue from an enargite leaching test with pyrite-recycle at 80°C and 480 mV showing pyrite particles with no apparent precipitates on their surfaces.
5.3.2.5. Effect of Solution Potential

To evaluate the effect of solution potential on the dissolution of enargite catalyzed by pyrite, four different tests were performed. Keeping the En/Py ratio constant at 3:1, with 60 g H$_2$SO$_4$, and 20 g/L Fe in solution, the only variable that changed was the solution potential. Oxygen was supplied through an electronic valve to the reactor to allow the oxidation of ferrous and to maintain tight control of the solution potential over the course of the experiments. The initial solution potential was about 490 mV vs Ag/AgCl. Within 10 minutes of adding solids to the reactor, the potential dropped 50 mV. This abrupt decline was due to the rapid consumption of ferric ions from the dissolution of tiny particles of enargite. After the solution potential reached 450 mV the algorithm for potential control was activated.

The results of copper extraction for solution potentials of 460, 470, 480 and 490 mV are shown in Figure 5.15. Comparing these four tests at 40 hours, it is observed that the best results were achieved by the tests at 460 and 470 mV, with a copper extraction of 87%. Increasing the solution potential by 10 and 20 mV resulted in the decrease of copper extraction to 83% and 78%, respectively. Analyzing these results with the anodic currents obtained in Figure 5.4, it can be seen that the solution potential range of 460 to 490 mV is inside the range where enargite is constantly increasing its dissolution current or leaching rate. Thus, the total extraction of copper was expected to be higher at 490 mV and lower at 460 mV. However, it is believed that the factor that determined the poor performance at 480 and 490 mV was the dissolution of pyrite. The dissolution of pyrite will affect the dissolution of enargite by decreasing the pyrite surface area, thus decreasing the ratio Py/En, and also by hindering the galvanic effect between the two sulfides. Once pyrite particles begin to dissolve, they generate anodic sites on their surfaces and the catalyzing effect over enargite is diminished.

The same Huanzala pyrite used in this work was used in a different study (Mayne, 2006) to dissolve chalcopyrite under similar conditions. In that study, there was no
difference in copper extraction between 470 and 485 mV vs. Ag/AgCl. These results imply that no dissolution of pyrite occurred. However, in the present investigation the presence of arsenic in solution could be enhancing the dissolution of pyrite. This was also observed by Blanchard et al. (2007) who concluded that the presence of arsenic could have an accelerating effect on pyrite dissolution by the formation of AsS groups on the surface of the pyrite, thus causing an accelerated formation of sulfur vacancies. This finding substantiates that not only the dissolution potential of enargite must be evaluated, but also the potential at which pyrite begins to dissolve under various conditions.

![Figure 5.15 Effect of solution potential on copper recovery from enargite in presence of pyrite.](image)
5.3.2.6. Effect of Particle Size

The experimental conditions for the study of enargite particle size effect were similar to those described above with a solution potential controlled at 480 mV vs. Ag/AgCl. In this case, however, the enargite sample was evaluated at two different particle sizes. One test was run with the same particle size used in all previous tests with a P_{80} of 78 microns, and another test used finer particles. An enargite sample with a P_{80} of 38 microns was prepared by regrinding the coarse enargite sample using a ring mill for three minutes. The P_{80} of pyrite for all tests was 70 microns. The particle size distributions of both enargite and pyrite samples were measured with a Malvern microsizer particle size analyzer as shown in Figure 5.16.

The effect of particle size on the oxidation of enargite is presented in Figure 5.17. As expected, the rate of enargite dissolution increased with increasing particle surface area. The reaction rate was observed to decrease with increasing particle size. Copper extraction of 96% was achieved after 30 hours with the fine enargite sample, while only 75% of the copper was extracted from the 78\textsubscript{P80} coarser enargite sample.
Figure 5.16  Particle size distribution of enargite and pyrite samples used in the present study.
Figure 5.17  Effect of enargite particle size on copper extraction in the presence of pyrite (60 g H₂SO₄, 80°C, and 480 mV).
5.3.2.7. Effect of Temperature

Four experiments were conducted to determine the effect of temperature on the rate of copper dissolution from enargite. The variables used in these experiments (480 mV vs. Ag/AgCl, 60 g H₂SO₄, 3 Py/En ratio) were the same for all the tests. The temperature was varied from 50 to 90°C. The results of these tests are shown in Figure 5.18.

Temperature had a strong effect on the leaching rate. About 35% of the enargite was leached after 45 hours at 50°C, while 59% was leached at 65°C, 86% was leached at 80°C, and 89% was leached at 90°C. This considerable temperature dependency is normally found in leaching systems where the controlling step is a surface chemical reaction. The dissolution rate decrease at 90°C is probably because the pyrite was leached quickly at that temperature, thus decreasing the catalytic effect over enargite.
Figure 5.18  Effect of temperature on copper extraction from enargite in presence of pyrite (60 g of $\text{H}_2\text{SO}_4$, 480 mV vs. Ag/AgCl, 3:1 Py/En ratio).
5.3.2.8. Determination of Activation Energy

Based on the previous results of temperature dependence and assuming surface chemical reaction as the rate-controlling step, the experimental data were analyzed using the shrinking core model:

\[ 1 - (1 - X)^{1/3} = kt \]

Where \( X \) is the fraction of enargite leached, \( t \) is the leaching time, and \( k \) is the linear kinetic constant. Figure 5.19 shows a plot of \( 1 - (1 - X)^{1/3} \) versus \( t \) for the experimental data obtained in the range 50 to 90 °C. This figure shows an excellent linear fit indicating the applicability of Eq. 5.5. Data corresponding to the first two hours of leaching were excluded. This is because the leaching curves showed an initial jump that can be attributed to the presence of fast-leaching traces of covellite and bornite in the enargite sample. To quantify the effect of temperature on the leaching rate, linear rate constants were obtained from the slopes of each leaching curve over the range of 50 to 80°C. The experiment at 90°C was not considered in this calculation for the reasons discussed in the previous section. The values obtained were used to draw an Arrhenius plot as shown in Figure 5.20.

The apparent activation energy was calculated as 48 kJ/mol, confirming that the process is controlled by surface chemical reaction. This activation energy is slightly lower than the value of 55.6 kJ/mol reported by Dutrizac and MacDonald (1972) in acidified ferric solutions. But when NaCl and FeCl₃ were added to the solution, higher activation energies of 65 kJ/mol (Padilla et al., 2005) and 64 kJ/mol (Riveros and Dutrizac, 2008) were reported. This confirms that the sulfur layer formed on the surface of the enargite particles during leaching in the presence of pyrite is porous enough to allow the unimpeded transport of reactants and products between the bulk solution and the surfaces of unreacted sulfide particles.
Figure 5.19  The effect of temperature on copper dissolution from enargite plotted according to the linear kinetic model.
Figure 5.20 Arrhenius plot for the leaching of enargite using pyrite as a catalyst in a H$_2$SO$_4$-Fe$_2$(SO$_4$)$_3$ solution.
5.3.2.9. Arsenic Behavior During Enargite Leaching

The objective of this section is to compare the dissolution of arsenic and copper during the leaching process, to determine the extent of arsenic precipitation, and to clarify the oxidation state of dissolved arsenic. Tests were run at 80°C and 480 mV vs. Ag/AgCl, with 60 g of sulfuric acid, 20 g of total iron, and a pyrite to enargite ratio of 3:1.

Solution samples were analyzed using induction-coupled plasma (ICP). The amounts of copper and arsenic calculated are presented in Figure 5.21. The dissolution rates of copper and arsenic showed similar patterns. After 48 hours of leaching, no arsenic precipitation was detected. The ratio of copper to arsenic in solution was also calculated and plotted in Figure 5.22. This ratio was obtained from three different tests showing an average Cu:As ratio of 3.3 which is close to the stoichiometric ratio of copper to arsenic in enargite. Traces of copper and arsenic were found in the solid residues. From these analyses, it was determined that all of the arsenic present in the residues belonged to un-leached enargite particles, based on the fact that the ratio between copper and arsenic in the residues was 3.21. To corroborate this by other means, scanning electron microscopy (SEM) characterization in combination with EDX was applied to the leaching residues. The results also confirm that no precipitates containing arsenic were found, either attached to the un-leached particles or forming free clusters of different compounds such as ferric arsenate precipitates. The only arsenic present in the solid residues was detected in tiny areas of enargite that were exposed upon polishing of residue samples fixed on epoxy beds.

The stoichiometric ratio of copper and arsenic in solution suggests that the dissolution of enargite occurs without the formation of intermediate sulfides or other compounds, which is in agreement with previous studies conducted under similar conditions (Dutrizac and MacDonald, 1972; Escobar et al., 1997). Thus, the oxidation of enargite by ferric occurs as follows:
Eq. 5.6 \[ 2 \text{Cu}_3\text{AsS}_4 + 9 \text{Fe}_2(\text{SO}_4)_3 + 6 \text{H}_2\text{O} \rightarrow 6 \text{CuSO}_4 + 18 \text{FeSO}_4 + 8 \text{S} + 2 \text{H}_3\text{AsO}_3 + 3 \text{H}_2\text{SO}_4 \]

Or, also:

Eq. 5.7 \[ 2 \text{Cu}_3\text{AsS}_4 + 9 \text{Fe}_2(\text{SO}_4)_3 + 8 \text{H}_2\text{O} \rightarrow 6 \text{CuSO}_4 + 22 \text{FeSO}_4 + 8 \text{S} + 2 \text{H}_3\text{AsO}_4 + 5 \text{H}_2\text{SO}_4 \]

Both reactions generate elemental sulfur which forms at the surface of the unreacted mineral particles as shown in Figure 5.9 and Figure 5.10. However, part of this sulfur could also be oxidized to higher sulfur species such as sulfates, as noted in previous studies where sulfur oxidation was observed to be between 10 and 30% (Dutrizac and MacDonald, 1972; Escobar \textit{et al.}, 1997).

The oxidation state of arsenic in solution is determined by the mechanism of enargite oxidation as given by Eq. 5.6 and Eq. 5.7. In this work this relation was determined by analyzing the final leaching solutions at room temperature by Electrospray Ionization Mass Spectrometry (ESI-MS). Leaching solution was analyzed in negative full scan mode, where only negative ions are detected. Mass scans between mass/charge (m/z) levels of 40 and 500 were recorded during 50 seconds with a scan speed of 5 s. Figure 5.23 shows the ESI-MS results of the analyzed solution. Although As is a mono-isotopic element, the spectra showed several lines due to the different isotopes of Cu, Fe, and S. These different patterns served to identify the various ions. Some of the peaks identified in the spectrum are listed in Table 5.3.
Table 5.3  Major m/z peaks and corresponding complexes identified in enargite leaching solution.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>97.2</td>
<td>$[\text{HSO}_4]^-$</td>
</tr>
<tr>
<td>168.9</td>
<td>$[\text{Fe}_2(\text{SO}_4)_2(\text{AsO}_3)_3\text{H}_3]^{4-}$</td>
</tr>
<tr>
<td>247.9</td>
<td>$[\text{Fe}(\text{SO}_4)_2]^-$</td>
</tr>
<tr>
<td>248.7</td>
<td>$[\text{Fe}(\text{SO}_4)_2\text{H}]^-$</td>
</tr>
<tr>
<td>255.8</td>
<td>$[\text{Cu}(\text{SO}_4)_2\text{H}]^-$</td>
</tr>
<tr>
<td>320.7</td>
<td>$[\text{Fe(AsO}_3)(\text{AsO}_4)\text{H}_3]^-$</td>
</tr>
<tr>
<td>327.7</td>
<td>$[\text{Cu(AsO}_3)(\text{AsO}_4)\text{H}_3]^-$</td>
</tr>
<tr>
<td>337.7</td>
<td>$[\text{Fe}(\text{SO}_4)\text{Cu(AsO}_3)]^-$</td>
</tr>
</tbody>
</table>

The most abundant compound was found at m/z=247.9 and corresponded to $[\text{Fe}(\text{SO}_4)_2]^-$ . The peak at 80.2 m/z could not be identified but all other peaks shown in Figure 5.23 were associated with specific complexes. The presence of As(III) was observed at 168.9 m/z and combinations of As(III) and As(V) were observed at 320.7 m/z and beyond. The abundance of $\text{AsO}_3^{3-}$ and $\text{AsO}_4^{3-}$ in solution was determined by multiplying the intensity of the peaks where these compounds appear, and the number of molecules of the corresponding oxyanion in each complex. Based on this calculation, 66% of the total dissolved $\text{As}$ was $\text{As(III)}$ and 34% was $\text{As(V)}$. Thus, the dissolution of enargite based on the ratio 2:1 $\text{As(III)}$ to $\text{As(V)}$ occurs as follows:

Eq. 5.8  

$6 \text{Cu}_3\text{AsS}_4 + 29 \text{Fe}_2(\text{SO}_4)_3 + 20 \text{H}_2\text{O} \rightarrow 18 \text{CuSO}_4 + 58 \text{FeSO}_4 + 24 \text{S} + 4 \text{H}_3\text{AsO}_3 + 2 \text{H}_3\text{AsO}_4 + 11 \text{H}_2\text{SO}_4$
This result agrees with the work of Escobar et al. (1997), who detected the presence of As(III) by titration. However, other studies did not determine the ratio of As(III) and As(V) in solution, but only assumed the formation of As(V) as product of dissolution based on the ratio of dissolved Fe(II) and Cu(II).

Figure 5.21 Copper and arsenic dissolution from enargite leaching at 80°C, 480 mV vs. Ag/AgCl, 60 g H₂SO₄, 20 g total Fe, and a Py:En ratio of 3:1.
Figure 5.22  Steady ratio of dissolution between copper and arsenic during the leaching of enargite.
Figure 5.23  Mass spectrum of an enargite leaching solution. The larger peak at 247.9 m/z corresponds to the compound $[\text{Fe(SO}_4\text{)}_2]^-$.
5.4. CONCLUSIONS

This study has successfully demonstrated that complete leaching of enargite in acidic ferric sulfate media is possible. Using ground pyrite in solution as a catalyst, virtually complete extraction of copper from enargite was achieved within 24 hours.

Temperature had the largest influence on dissolution, followed by enargite particle size. Solution potential had a moderate effect, giving the best results at 460 to 470 mV vs. Ag/AgCl. Iron concentration and pulp density did not affect the extraction of copper from enargite over the ranges studied. On the other hand, the concentration of sulfuric acid had a negligible effect.

Oxidation kinetics of enargite seem to be controlled by surface reaction with an activation energy of 48 kJ/mol. A porous layer of elemental sulfur was formed which did not present a barrier for the transport of solutes to the enargite surface. Arsenic in solution followed the same dissolution pattern as copper, with no evidence of precipitation. As(III) was the predominant form of arsenic in solution.

This new route of enargite treatment is capable of treating copper-arsenic concentrates in conventional tanks at atmospheric pressure, without the need for roasting, ultrafine grinding, high pressure reactors, corrosive chemical additives or bacteria.

5.5. ACKNOWLEDGEMENTS

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CHAPTER 6.
GENERAL CONCLUSIONS

6.1. CONCLUSIONS AND OVERALL SIGNIFICANCE OF THE RESEARCH

As described in the introductory chapter, the high consumption and steadily increasing demand of copper will become an important problem to be faced by the base metals extraction industry. A major contributing factor to the problem is the difficulty presented during the extraction of copper from chalcopyrite and enargite using hydrometallurgical processes. Passivation of chalcopyrite and enargite is the problem to solve, and there are many ways to study the problem, including electrochemical procedures, leaching tests and surface characterization aspects.

The research work presented in this thesis addresses the problem of passivation of chalcopyrite and enargite during leaching in ferric sulfide media. Some of the associated challenges were explored and a few creative solutions provided.

First, an electrochemical study was conducted on massive samples of chalcopyrite, and leaching studies were conducted on chalcopyrite concentrates (Chapter 2). The purpose was to evaluate the oxidative behavior of chalcopyrite in solutions containing sulfuric acid (H₂SO₄), ferric sulfate (Fe₂(SO₄)₃) and ferrous sulfate (FeSO₄). The results of these studies demonstrate that chalcopyrite oxidation displays the classical active-passive behavior observed in passivating metals; values predicted electrochemically for the passivation potential $E_{pp}$ are in excellent agreement with leaching experiments. This result substantially improves the knowledge of the anodic behavior of chalcopyrite, which has been reported so far mostly as pseudo-passive. Imposing a continuous series of potentiostatic pulses (increasing by 10 mV every hour), 3D current density-time-potential surfaces were generated in order to establish the effects of acidity and temperature on the passivation potential, the passive current and the critical current of chalcopyrite leaching.
The concentration of sulfuric acid was systematically varied from 2 to 100 g/L and the temperature from 25 to 80°C. $E_{pp}$ increased with increasing temperature from 440 mV at 25°C to 515 mV at 80°C; it was practically insensitive to acidity at low (25–40°C) and high (60–80°C) temperatures. At 50°C an acid-dependent transition of $E_{pp}$ was observed from 440 mV to 515 mV. The passive currents were at most one order of magnitude lower than the maximum critical current. The origin of the sample had a major influence on whether a passivation potential was observed or not. The active-passive transition was not observed in certain samples of chalcopyrite when the technique was applied under the same conditions for comparative purposes.

The application of long-duration anodic potentiostatic steps illustrated that massive chalcopyrite electrodes require long polarization times to exhibit active-passive behavior. This indicates that the layer causing passivation of the electrodes is generated very slowly. This protective layer was formed in solutions of H$_2$SO$_4$ only and also when cupric and ferrous ions were added. This indicates that these ions are not necessarily a trigger for the passivation of chalcopyrite.

The absence of distinct active-passive behavior in previous electrochemical studies on massive samples of chalcopyrite could be due to time restrictions. Cyclic voltammetry studies and anodic polarization techniques only capture the initial times of a reaction, and cannot sense the effect that a passivating layer could cause if generated slowly. In addition, it is also possible that only some grains at the surface of the massive working electrode are being affected by the applied potential at any given time.

Figure 6.1A shows a massive particle of chalcopyrite with a surface comprised by various grains after the particle was polarized at 1.2 V vs. SCE. Two different color shades can be observed on its surface. As analyzed by EDX mapping (Figure 6.1B), the blue region corresponds to sulfur and the green regions to chalcopyrite. This demonstrates the different level of reactivity that certain grains of the same
mineral present to an external stimulus. This could be because of impurities isolating certain grains, preferential planar attack, or most probably the effect of surface mechanical stresses in polished surfaces.

Figure 6.1 Massive sample of chalcopyrite polarized to 1.2 V for 2 minutes at 20°C. A) SEM image, and B) EDX mapping for sulfur (blue areas) and chalcopyrite (green areas).

One way to address this problem was evaluated in Chapter 3. An electrochemical microcell was constructed which is capable of working with ore particles smaller than 100 μm. Open circuit potential measurements, constant-potential polarization, and anodic dissolution of both chalcopyrite and enargite particles were conducted using this tool. This new tool, together with surface characterization techniques such as SEM and XRD, allowed the study of sulfur formation and morphologies during leaching (Chapter 4).

The active-passive behavior was observed in single particle microelectrodes as expected. This behavior was more significant at higher temperatures. Using the same chalcopyrite sample from Chihuahua for both massive and microelectrode
techniques, the active-to-passive transition was found to occur at 500 mV and 490 mV vs. SCE at 60°C and 90 g/L H₂SO₄, respectively. As observed with massive electrodes, acid concentration seems to have no effect on the active-passive transition of chalcopyrite microelectrodes.

The formation of areas of non-stoichiometric chalcopyrite and elemental sulfur was observed on the surface of particles during cyclic voltammograms. These formations appeared at potentials corresponding to the active-passive region, and passivated chalcopyrite without the formation of a dense layer of elemental sulfur. This formation continued unabated until transpassive potentials were reached. At high potentials, dense layers of elemental sulfur formed which encapsulated the particles completely. This sulfur was found to be a non-conductive layer when cyclic voltammograms were applied and the working electrode was only in contact with the sulfur layer. When pressure was applied to the particle and firm contact between the carbon wire electrode and the unleached particle core was made, very rapid dissolution of chalcopyrite particles was observed. Total dissolution of chalcopyrite particles was achieved in only 4 minutes. When no attempt to remove this dense sulfur layer was made, the particles presented a passivating behavior.

Sulfur generated at high potentials in solutions with H₂SO₄ was easily removed from particle surfaces. This sulfur had the appearance of a transparent plastic film and it could not be dissolved with CS₂. At high potentials in a solution of H₂SO₄ + NaCl the sulfur layer changed noticeably. This sulfur layer was very porous and had the texture of rubber sponge. When the formation of sulfur on particles was studied, it was observed that the sulfur formed in solutions with H₂SO₄ only appeared first at dislocations, inclusions and grains boundaries with no clear signs of corrosion on the surface of the particles. Different was the case for sulfur formed in solutions where NaCl was added. Corrosion pits were distributed evenly throughout the particle surface. Interestingly, these corrosion pits had a triangular shape, and were all roughly the same size. They appear to be equilateral triangles 8 µm on a side and 2 µm in depth, as shown in Figure 6.2. Initial formation of
elemental sulfur was observed in the bottom center of these pits, and with time the sulfur grew out of the pit in a dendritic formation. It would be interesting to observe the influence of NaCl concentration, applied potential and temperature on the shape and size of these corrosion pits, as the resulting porous sulfur may influence the dissolution of chalcopyrite.

Sulfur and sulfate yields were calculated based on the total charged transferred during the complete dissolution of chalcopyrite particles in H₂SO₄ and H₂SO₄ + NaCl solutions. Elemental sulfur formation accounted for 88.8% and 76.8% of total sulfur oxidation for solutions with H₂SO₄ only and solutions where NaCl was added, respectively.

In tank leaching tests of chalcopyrite, the presence of pyrite prevented the passivation effect of chalcopyrite at low potentials. The pyrite effect was observed even when it was added after chalcopyrite was passivated (after 24 hours of leaching). SEM studies of solids harvested during the test showed that pyrite had this effect on passivated particles that did not show sulfur layers on their surfaces. This kind of passivation was the most commonly observed in this study. Final residues for particles completely leached showed that the sulfur did not form a dense layer, but instead a very porous sponge-like morphology.
Electrochemical studies of enargite were initiated by measuring the open circuit potential (OCP) under various conditions. The measurement of OCP in single particles had a particular characteristic, a quasi-steady-state was attained within seconds. Visible impurities and gas bubbles attached to the particles caused instability in OCP readings. A notable difference between pyrite and enargite OCP readings suggested that pyrite could catalyze the dissolution of enargite by the galvanic effect.

Enargite presented a wide window of active potentials. Based on cyclic voltammetric tests, enargite becomes anodically active at around 300 mV vs. SCE and its active-passive transition occurs at 700 mV. Acid concentration did not have a notable effect on the active-passive behavior of enargite and the anodic dissolution current increased with increasing temperature.

Surface characterization by EDX and SEM of enargite was also conducted. At
potentials where the passive regime began there was a preferential dissolution of arsenic over copper into solution from certain areas on the surface. On the other hand, a sulfur layer covering almost the entire particle was found to form at high potentials of around 1.4 V vs. SCE. This sulfur layer was strongly attached to the particle and could be removed easily by mechanical means. Thus, contrary to chalcopyrite, rapid dissolution of enargite was not possible at high potentials.

From the results of OCP and active dissolution potential measurements for enargite, the idea of using pyrite to enhance the dissolution of enargite was considered (Chapter 5). Leaching tests at controlled potentials in a ferric acidic media were employed. Effectively, it was proven that pyrite enhances the dissolution of enargite dramatically, giving essentially complete Cu recovery in 24 h at a pyrite-to-enargite ratio of 4 to 1. Additional pyrite added to the system did not enhance the leach rate further. Temperature had a significant effect with Cu extractions of 35 and 86% at 50 and 80°C respectively at a Py/En ratio of 3 to 1. Chemical reaction was determined to be the rate controlling step based on an apparent activation energy of 48 kJ/mol. Electrochemical studies showed that enargite will leach faster as the solution potential is increased up to 700 mV vs. SCE. However, during leaching experiments, the best results were obtained at potentials in the range of 460 to 470 mV vs. Ag/AgCl (415 to 425 mV vs. SCE). This limiting potential can be attributed to pyrite, which begins to dissolve at higher potentials. Finally, the total iron concentration and the acidity of the solution had no effect on the dissolution rate of enargite.

Solution analysis determined that arsenic was dissolved from enargite at the same rate as copper. Surface analysis by EDX and SEM showed that final enargite residues were comprised solely of elemental sulfur, which confirms that all of the arsenic reported to solution. The oxidation state of arsenic in solution was calculated to be 1/3 As(V), and 2/3 As(III).

The elemental sulfur residues had a very porous morphology. The same sulfur
morphology was also seen when chalcopyrite particles were leached galvanically with pyrite. The galvanic effect between enargite and pyrite was assumed to be the cause of the rapid leaching of enargite. For this to occur, pyrite and enargite must be in intimate contact. There is a strong possibility that this contact will be broken after an appreciable sulfur layer grows on the surface of enargite. This would not be an issue if the sulfur layer were conductive, but based on our results this layer has a very high electrical resistivity. Based on this, it could be concluded that the galvanic effect is only relevant at the beginning of the leaching process.

Based on a study by Nicol and Lazaro (2003), chalcopyrite can be dissolved to a certain extent by a non-oxidative reaction (Eq. 6.1). During dissolution, the copper ions can precipitate as CuS on the surface of the particles being leached as indicated by Eq. 6.2. In order to avoid this mechanism and ensure the continuity of chalcopyrite dissolution, a suitable oxidation agent such as Fe$^{3+}$ must be present to oxidize H$_2$S to S as shown in Eq. 6.3.

\begin{align*}
\text{Eq. 6.1} & \quad \text{CuFeS}_2 + 4 \text{H}^+ \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2 \text{H}_2\text{S} \\
\text{Eq. 6.2} & \quad \text{Cu}^{2+} + \text{H}_2\text{S} \rightarrow \text{CuS} + 2 \text{H}^+ \\
\text{Eq. 6.3} & \quad 2 \text{H}_2\text{S} + 4 \text{Fe}^{3+} \rightarrow 2 \text{S} + 4 \text{Fe}^{2+} + 4 \text{H}^+
\end{align*}

If Eq. 6.3 is a faster reaction that Eq. 6.1, the non-oxidative dissolution will continue. Based on this model, there is another probability of passivation: the incomplete oxidation of H$_2$S and the formation of polysulfides according to the following reactions:

\begin{align*}
\text{Eq. 6.4} & \quad \text{H}_2\text{S} + \text{S}_n \rightarrow \text{H}_2\text{S}_n \\
\text{Eq. 6.5} & \quad \text{Cu}^{2+} + \text{H}_2\text{S}_n \rightarrow \text{CuS}_n + 2 \text{H}^+
\end{align*}
where S is formed from two possible reactions that include the complete oxidation of H₂S by oxygen as per Eq. 6.6 (which requires high temperatures) or by the oxidative dissolution of chalcopyrite as per Eq. 6.7.

Eq. 6.6 \[ \text{H}_2\text{S} + \frac{1}{2} \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O} \]

Eq. 6.7 \[ \text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2 \text{S} + 4 \text{e}^- \]

When polysulfides are formed, we have the second condition for passivation to occur as detected in the work of Hackl et al. (1995). Thus, the ideal scenario would be to oxidize the H₂S to elemental sulfur before these two mechanisms of passivation can occur.

This hypothesis can be shown to be valid based on the fact that chalcopyrite shows enhanced dissolution with activated carbon and hematite (Sanchez et al., 1996) and those two reactions are well known to occur during hydrogen sulfide removal in water treatment and in fuel gas cleaning plants respectively, as follows:

Eq. 6.8 \[ 2 \text{H}_2\text{S} + \text{O}_2 \rightarrow \frac{1}{4} \text{S}_8 + 2 \text{H}_2\text{O} \quad \text{(Carbon Catalyzed)} \]

Eq. 6.9 \[ \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{S} \rightarrow \text{Fe}_2\text{S}_3 + 3 \text{H}_2\text{O} \]

When a sample activated carbon specially formulated to oxidize H₂S (Darco H₂S) was used in a leaching test, the results were more encouraging, as demonstrated in parallel studies in our laboratory testing various activated carbons. More investigation is necessary to prove or disapprove this hypothesis. A special emphasis should be put on measuring the oxidation rate of H₂S on pyrite surfaces and on various activated carbons. This could become a protocol to measure the catalyst performance of certain materials to efficiently leach chalcopyrite and enargite. With a better understanding of this phenomenon, specialized materials
could be created to achieve this goal and these copper sulfides could be more easily dissolved.

6.2. ORIGINAL CONTRIBUTION AND FIELD APPLICATION

*Single particle microelectrode technique*

The single particle microelectrode technique was successfully applied for the first time to dissolution studies of chalcopyrite and enargite. Several standard electrochemical transient techniques were applied. For example cyclic voltammetry is particularly useful for surveying electrochemical processes of both non-faradic and faradic character. This technique resulted in a highly sensitive method for monitoring reactions on the particle surfaces. This technique could also be useful on other fronts of the hydrometallurgical and mineral processing field, including:

- measuring biological-mineral interactions,

- calculating potential ranges to float specific species from complex ore assemblages,

- conducting electrochemical studies on mineral species than are not found in nature as large samples, or are only produced as fine particles as sedimentary pyrites, pentlandite, mineral concentrates, etc,

- coupled with a Raman microscope, measuring in-situ surface changes and layer formations at various applied potentials.

Although this technique has proven to be useful for our purposes, it is important to mention a few constraints related to the size and morphology of the sample. The surface area of the sample can only be estimated since these particles generally are not geometrically or morphologically well defined. Hence, determination of a
reaction rate at a given applied potential, based on the amount of reaction products put into solution, represents a challenge since such tiny quantities lead to unreliable stoichiometric calculations.

**Transpassive leaching of chalcopyrite**

This study demonstrated for the first time that the dissolution of chalcopyrite is possible at elevated potentials >1 V vs. SCE in just a few minutes. The very rapid dissolution of chalcopyrite would never have been noticed without the single particle microelectrode technique. The size of the sample being evaluated and the arrangement under a microscope were key factors in this observation. Since chalcopyrite concentrates are generally in the order of 80% passing ~74 μm, this discovery could have an industrial application.

Due to the rapid dissolution of the mineral, the residual elemental sulfur that surrounds the unleached core of the particle is far from thermodynamic equilibrium and changes its mechanical properties with time. Advantage could possibly be taken of the unique mechanical and morphological properties of the remaining sulfur to develop a novel technology for the nearly instantaneous leaching of passivating sulfide minerals.

The design of a reactor capable of treating concentrates using transpassive leaching represents a real engineering challenge. This reactor has to provide constant contact between the unleached particle cores and an external source of applied potential. Additionally, the sulfur layer being generated on the surface of the particles must be broken and removed to guarantee the continuity of the electrochemical dissolution. Materials selection and electricity consumption will be other issues to deal with. If a suitable reactor can be designed to provide all of the necessary conditions for transpassive leaching, this finding will lead to a process that would be difficult to ignore and a serious threat to established chalcopyrite treatment processes.
Atmospheric leaching of high arsenic copper concentrates

This study demonstrated for the first time that enargite (Cu₃AsS₄) can be leached in a sulfate medium with the addition of pyrite at controlled potentials and at atmospheric pressure. The scale up of this process to an industrial level will be highly expected since it will be a process that can leach high arsenic copper concentrates (dirty concentrates) without additional cleaning stages at the concentration stage (selective or oxidative flotation). Additionally, this process does not require equipment for autoclaving, ultra-fine grinding, or special construction materials for corrosive reagents. This will represent savings in capital cost for new plants, and it could also be adapted to existing leaching/SX/EW facilities, and also could represent an extra revenue by increasing copper recovery during concentration by only applying a rougher flotation stage to recover chalcopyrite/enargite/pyrite bulk concentrates. This kind of concentrate is totally amenable to the process since chalcopyrite also has been proven to leach under the same conditions as enargite leaching in the presence of pyrite (Dixon et al., 2008). The following diagrams represent conceptual flow sheets for: the treatment of highly arsenic content copper concentrates by flotation, oxidative flotation (Byrne et al., 1995; Kantar, 2002), and pyrometallurgical treatment (Figure 6.3); and the pyrite-catalyzed leaching process proposed in this study (Figure 6.4).
Figure 6.3 Conceptual representation for the production of copper from high grade As copper ores by oxidative flotation and pyrometallurgical processes.
6.3. RECOMMENDATIONS FOR FUTURE WORK

Based on the research presented in this dissertation, some ideas are suggested for further investigation:

- The use of metal ions such as ferric, ferrous, and cupric is suggested in electrochemical studies of single particles. The effects on passivation...
potentials, transpassive leaching and sulfur morphology could be addressed.

- The effect of different light frequencies on possible photo-induced dissolution of primary copper sulfides by electrochemical microelectrode techniques. Using this technique, the effect of light could be evaluated more realistically since the light beams will be projected into a single unpolished semiconducting particle.

- Raman microscopy would be as an complement to future electrochemical studies of single particles. This technique will provide a better understanding of the nature, morphology, and kinetics of compounds formation and the effects of passivating agents on the surface of the particles when tested under different conditions in-situ and in real-time.

- The design of a reactor capable of supporting the conditions for transpassive leaching of chalcopyrite, as explained in the previous section, should be investigated further.

- A tool to evaluate the oxidation of H₂S in the presence of diverse catalyst materials that have been proven to catalyze the dissolution of chalcopyrite and/or enargite could have bearing on the performance of such materials during leaching. Thus, this possibility should be investigated. If shown to be relevant, then

- The creation and evaluation of materials capable of enhancing the oxidation of H₂S should be studied. The use of biological entities specific for this task also deserves further research.
6.4. REFERENCES


APPENDIX A
REPRODUCIBILITY OF OCP MEASUREMENTS IN PARTICLES

All of the open circuit potentials (OCP) presented in this work for chalcopyrite, enargite and pyrite are real values from representative electrodes which fall within the range of values measured on five different electrodes under the same conditions. The OCP were measured after the sulfide particles had been immersed in the electrolyte for approximately five minutes. Inefficient particle-electrode contact caused noise in the measurements at the beginning of the test, but was remedied by applying gentle pressure to the carbon wire (working electrode). Following that, a virtually constant value was attained after just a few seconds. When OCP measurements were performed with different particles, the measurements were stable after appropriate contact was achieved, and were reproducible among various particles.

Figure A1 shows the OCP measurements of five different chalcopyrite particles in a 10 g/L H₂SO₄ solution at 20°C. Some of these measurements presented noise at the beginning of the measurement but were stabilized as indicated above. The nature of the difference in OCP among different particles is not clear. Although a significant effort was made to select the most pure sulfide particles for these measurements using SEM, EDX and optical microscopy, lattice impurities impossible to detect by these techniques may be the reason for this OCP variation among particles. Additionally, in some cases, variations of OCP were found when a single particle was measured at different locations on its surface. There is no clear and proven reason for this variability, but probable causes may include non-uniform distribution of impurities and/or preferential plane dissolution of the particles creating layers which alter OCP values. A more detailed study will be needed to elucidate the reasons behind these observed differences.
Figure A.1  OCP measurements of different single particle electrodes of chalcopyrite in a 10 g/L H₂SO₄ solution at 20°C.
APPENDIX B
SULFUR OXIDATION CALCULATION AT HIGH POTENTIALS

The oxidation of sulfide sulfur during the dissolution of chalcopyrite at high potentials was assumed to form only elemental sulfur \((S^0)\) and sulfate \((SO_4^{2-})\) according to Equations 4.4 and 4.5. The degree of sulfur oxidation may be indicated by the following equation:

\[
\text{Eq. B.1 } \text{CuFeS}_2 + 8y \text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2y \text{SO}_4^{2-} + 2(1-y) \text{S} + 16y \text{H}^+ + (12y + 5) \text{e}^- 
\]

If the number of electrons produced during the reaction of chalcopyrite is known, by a simple calculation with the above equation, the amount of sulfate generated \((y)\) could be estimated as follows:

\[
n = e^- = 12y + 5 \quad \text{and} \quad y = \frac{n - 5}{12}
\]

Then by Faraday’s law the number of electrons is calculated:

\[
m = \frac{QM}{nF}
\]

therefore:

\[
y = SO_4^{2-} = \left(\frac{QM}{Fm}\right) - 5 \quad \text{and} \quad S^0 = 1 - y
\]

where:

\[m\] is the mass of dissolved copper in solution (g)
**Q** is the total electric charge passed through the solution (C)

**n** number of transferred electrons (e⁻)

**M** is the molar mass of copper (63.55 g mol⁻¹)

**F** is the Faraday constant (96485 C mol⁻¹)

**SO₄²⁻** yield of sulfate produced

**S⁰** yield of elemental sulfur produced

Thus, the values of **m** and **Q** were acquired experimentally, and the amounts of sulfur and sulfate were calculated as given in Table 4.1.