

**ASSISTED DISSOLUTION OF COPPER SULFIDES IN FERRIC SULFATE
SOLUTIONS: THIOUREA AND ITS DERIVATIVES**

by

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Assisted dissolution of copper sulfides in ferric sulfate solutions: thiourea and its derivatives

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Abstract

A study of the effects of thiourea and various thiourea-related chemicals as additives to acidic ferric sulfate leaching of copper sulfides (chalcopyrite, covellite, and chalcocite) has been performed, considering high-purity copper sulfide species and low-grade chalcopyrite ores from different sites in stirred tank, bottle roll, and small-scale column leaching configurations.

The use of low concentrations of thiourea yields a significant increase in the extraction of copper from the considered copper sulfide species; thioacetamide and formamidine disulfide also display an increase in copper extraction.

The increase in copper extraction using thiourea as an additive in ferric sulfate can decrease as the depth of the ore bed is increased. The extraction rates for cases with and without the use of additives also decrease with respect to time in column leaching. The difference in copper extraction between the cases with and without thiourea is gradually decreased in long-term column leaching experiments.

Lay Summary

Thiourea and several derivatives of thiourea can be used as additives to enhance the dissolution of copper from copper-bearing sulfides to produce copper metal.

This was studied using different configurations of copper dissolution. These configurations included stirred tanks and powdered pure copper sulfides, agitated bottles containing copper sulfides and solution, and 30 cm columns packed with copper sulfide ore. All cases used ferric sulfate and sulfuric acid with one additive per experiment.

The three compounds that enhanced copper dissolution consistently were thiourea, formamidine disulfide, and thioacetamide. The way in which thiourea affects the speed of copper leaching from pure sulfides and sulfide ores, compared to conventional leaching, mainly depends on how much thiourea is added to the solution. The enhancement of dissolution caused by thiourea changes with time compared to conventional leaching. It can also be affected by the depth of the ore bed in column leaching.

Preface

The present work contains research conducted, performed, and analyzed by Luis Sergio Quiroz Castillo. This document was written by Luis Sergio Quiroz Castillo under the guidance of Dr. David G. Dixon. Experimental work was conducted by Luis Sergio Quiroz Castillo under the guidance of Dr. Laurence Dyer, Dr. Oscar Olvera, and Dr. Ryan Ren.

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List of Abbreviations

2-PYTA: 2-pyridine thioamide

Cys: Cysteine

DTO: Dithiooxamide

ETC: Ethylene trithiocarbamate

FDS: Formamidine disulfide

K-TA: Potassium thioacetate

SDMDTC: Sodium dimethyldithiocarbamate

TA: Thioacetamide

TSC: Thiosemicarbazide

TU: Thiourea

TUO₂: Thiourea dioxide

UR: Urea

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Chapter 1: Introduction

In the metallurgical industry, chalcopyrite (CuFeS_2) is considered the most important copper mineral: approximately 70% of global copper reserves consist of chalcopyrite ores (Wang, 2005). Other copper sulfides are also considered relevant, such as chalcocite (Cu_2S) and covellite (CuS).

Approximately 80% of global copper production consists of pyrometallurgy. The remaining 20% consists of hydrometallurgy (Index Mundi, 2015). Pyrometallurgy consists in high grade copper sulfide concentrate smelting and copper cathode electro-refining. Hydrometallurgy consists in processing low-grade copper oxide and secondary sulfide ores using aqueous leaching, solution purification through solvent extraction, and copper metal production using electrowinning (Davenport, 2002).

The production of copper cathodes via pyrometallurgical processing becomes economically non-viable as chalcopyrite ore grades decrease (Watling, 2013). Because of this, the copper industry recurs to alternative processes and hydrometallurgical routes, to extract the copper from low-grade sulfide ores.

An extensive amount of research in hydrometallurgy has been performed to develop a high-efficiency process to recover copper from chalcopyrite. So far, chalcopyrite has been refractory to many conventional hydrometallurgical treatments. This has been attributed to a host of reasons related to the nature of the mineral and the solutions used for its processing.

Many hydrometallurgical alternatives to process copper sulfides have been studied. These processes can be classified by the type of lixiviant used, including sulfate, chloride, nitrate, and ammonia solutions. Ferric sulfate leaching has been considered to have several key advantages such as low operational and capital costs, simplicity of the leaching reaction, and compatibility with solvent extraction and electrowinning technologies (Córdoba et al., 2008a).

One of the most recurrently reported reasons why chalcopyrite is recalcitrant to these methods is that a passivation layer is formed on the surface of chalcopyrite, affecting the kinetics of copper dissolution and drastically reduces the leaching rates (Hackl et al., 1995). Few of the hydrometallurgical processes and process concepts to treat chalcopyrite ores and concentrates have been further developed into pilot plant, industrial, and commercial stages (Dreisinger, 2006).

Thiourea (TU) has been used in hydrometallurgy as a levelling agent for copper cathodes in electrowinning. Thiourea is added to lower the roughness of copper cathodes produced through electrodeposition, where the role of thiourea is related to the distribution and the formation of grains and their sizes in the cathodes (Gómez et al., 2009). Thiourea has also been studied extensively as a substitute for sodium cyanide as a leaching reagent for gold (Li et al., 2006). Various thiourea derivatives have also been used as corrosion inhibitors in the steel industry (Awad, 2004).

A series of electrochemical experiments with chalcopyrite in ferric sulfate displayed an increase in dissolved copper with increasing thiourea concentration. These results, obtained by Drs. Dixon and Asselin's groups in UBC Vancouver, indicated the possibility of an assisted leaching process using thiourea as an additive. Based on the aforementioned, the present study was performed.

1.1 Objectives

An objective of this study was to further elucidate this case of chalcopyrite dissolution by using thiourea in leaching three different copper sulfides and various leaching configurations, e.g. bottle roll leaching, column leaching, and stirred tank leaching. Subsequently, the following objective consisted in investigating the effect of this chemical in the established leaching mechanisms of

copper sulfides in ferric sulfate. This was approached by using other chemicals with a molecular structure similar to thiourea, in order to determine if the presence of a radical or functional group is responsible for the enhancing effect, and by understanding the specific way the compounds interact.

The objectives of the present study were the following:

- To assess the effect of the addition of thiourea in ferric sulfate leaching of high-purity copper sulfide species in agitated reactors.
- To assess the effect of the addition of thiourea in ferric sulfate leaching of low-grade copper sulfide ores, in bench-scale columns.
- To assess the effect of other chemicals that possess a similar structure to thiourea, such as oxidation products and different chemicals which share certain functional groups with thiourea.

Chapter 2: Literature Review

The following literature survey focuses on the different technologies for copper extraction from chalcopyrite, covellite, and chalcocite. Additionally, this includes information on several chemicals such as thiourea, formamidine disulfide, and various other chemicals with similar structures to thiourea and its derivatives, which were used in this study's experiments.

2.1 Copper Sulfide Leaching

Copper hydrometallurgy has been widely used for copper oxide ores in processes such as heap leaching. Hydrometallurgical processes for copper sulfide ores have been studied and developed for many years.

Certain copper sulfides such as chalcopyrite and covellite display slower leaching kinetics in sulfuric acid solutions compared to copper oxides (Dreisinger, 2006). These processes are classified according to their operating conditions and type of leaching solutions, principally, sulfates and chlorides.

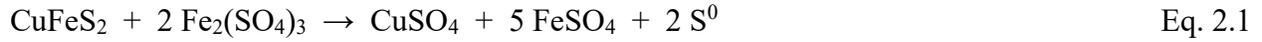
Ferric sulfate leaching is considered as the most desirable technique due to its compatibility with purifying technologies for copper production, i.e., solvent extraction and electrowinning. The following sections focus on ferric sulfate of each copper sulfide species considered for the study.

2.2 Chalcopyrite Leaching in Ferric Sulfate

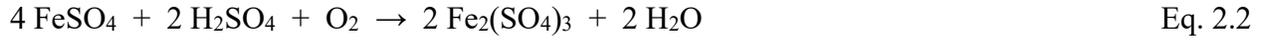
2.2.1 General Aspects

Chalcopyrite oxidation and extraction of copper is most commonly performed using the sulfuric acid-ferric sulfate system. This system is used for heap leaching and dump leaching of low-grade ores (Watling, 2006) as well as stirred tanks for concentrates (Batty et al., 2006).

Eq. 2.1 represents the generally accepted equation for chalcopyrite leaching in ferric sulfate solution (Watling, 2013).



Ferrous sulfate is re-oxidized to ferric sulfate in the presence of sulfuric acid and oxygen according to Eq. 2.2 (Watling, 2013).



The thermodynamic potential-pH (Pourbaix) diagram for the $\text{CuFeS}_2\text{-H}_2\text{O}$ system at 25°C (Garrels et al., 1965, as cited by Córdoba et al., 2008a) is displayed in Figure 1.

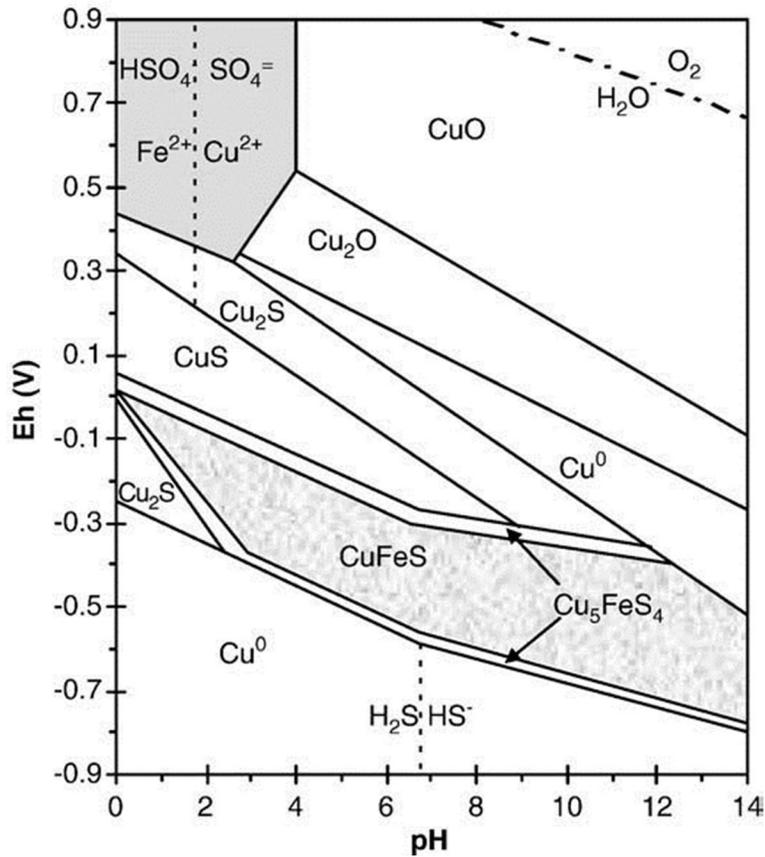


Figure 1. Potential-pH diagram for the $\text{CuFeS}_2\text{-H}_2\text{O}$ system at 25°C (Garrels et al., 1965, as cited by Córdoba et al., 2008a)

According to the diagram, in order to achieve chalcopyrite dissolution, a pH below 4.0 and an oxidation-reduction potential of + 400 mV or higher is required. These conditions can be met using ferric ion and sufficient acid, and such is the case for the sulfuric acid-ferric sulfate system.

The kinetics of oxidation of chalcopyrite in this system are considered slow, therefore, the leaching of this mineral is often incomplete. Several authors (Hackl et al., 1995., Warren et al., 1982, Parker et al., 1981) attribute this to the production of product layers (e.g. elemental sulfur) on chalcopyrite surfaces, as indicated by Eq. 2.1. Modern studies on chalcopyrite leaching has been focused on researching the reaction mechanisms of this process in order to improve the kinetics in ferric sulfate systems.

With respect to the parameters that affect leaching in this system, various researchers consider the effects of ferric ion concentration, pH, and temperature, as the most significant parameters in the process. Various authors indicate that increasing ferric ion concentration, within the range of 0.001 – 0.1 M can increase the dissolution of chalcopyrite (Hirato et al., 1991; Linge, 1976; Muñoz et al., 1979).

According to Dutrizac (1981), chalcopyrite leaching can be considered independent of acid once the solution reaches a concentration sufficient to keep ferric iron in solution, however, Córdoba et al. (2008a) indicates dissolution of chalcopyrite diminishes with decreasing pH, considering speciation data for iron (III) in sulphate solution.

Finally, various authors report high values of activation energy (greater than 40 kJ/mol) for chalcopyrite leaching at high temperatures and atmospheric pressure (Muñoz et al., 1979; Hirato et al., 1987). These activation energies can be associated with leaching under chemical reaction-controlled kinetics. The rates of leaching of this type of process can be enhanced by increasing temperature, as indicated by Dreisinger et al. (2002) and Sokic et al. (2009).

2.2.2 Passivation of Chalcopyrite in Ferric Sulfate Leaching

As aforementioned, chalcopyrite presents slow leaching kinetics in the sulfuric acid-ferric sulfate system. Regarding these slow kinetics, most researchers are in consensus with respect to the formation of a passivating layer on the surface of chalcopyrite, which slows down the oxidation. Nevertheless, the nature of the passivation layer has not been fully confirmed (Córdoba et al., 2008).

According to several studies, the reaction products which are thought to be implicated in the passivation of chalcopyrite include the following:

1. An unreactive, copper-rich layer on chalcopyrite surfaces that are partially oxidized (Hackl et al., 1995; Linge, 1976; Warrant et al., 1982.), or complex films of sulfides, polysulfides, and/or elemental sulfur (as displayed in Eq. 2.1)
2. Iron oxides, iron hydroxides, iron hydroxysulfates, and/or jarosite (Córdoba et al., 2008a, 2008b; Parker et al., 2003)

Klauber (2008) proposed a conceptual four-stage model for dissolution of chalcopyrite, consisting of the following stages:

Stage 1 consists of an initial reaction of “fresh” chalcopyrite, which is dependent upon surface preparation history. This reaction has a high rate and a low activation energy. In Stage 2, a thick elemental sulfur layer hinders dissolution, and electron transport causes reaction to have a low rate and high activation energy. If during this stage, the leaching conditions do not favor the removal of this sulfur layer, the leaching continues to show a parabolic rate curve. During Stage 3, the leaching conditions favor peeling of the sulfur layer and the reaction rate increases to display a linear rate curve. This linear rate continues if the pH and the concentration of ferric prevent jarosite formation. In the case of jarosite formation and coating of the remaining chalcopyrite,

Stage 4 consists of the parabolic rate curve reappearing due to reduced surface area/mass transport control. Alternatively, jarosite may precipitate independent of the remaining chalcopyrite and the linear rate curve continues.

With respect to the surface layers possibly considered as “passivation candidates” Klauber (2008) concluded that polysulfides are oxidised rapidly to elemental sulfur once exposed to air, and the presence of metal-deficient sulfides is questionable, therefore, these can be rejected as causes for passivation. Elemental sulfur overlayers might be peeled off during the leaching process, Klauber (2008) continues, and overlayers of jarosite and other iron (III)-insoluble compounds are inevitable during long leaching times.

2.2.3 Electrochemical Aspects of Chalcopyrite Leaching in Ferric Sulfate

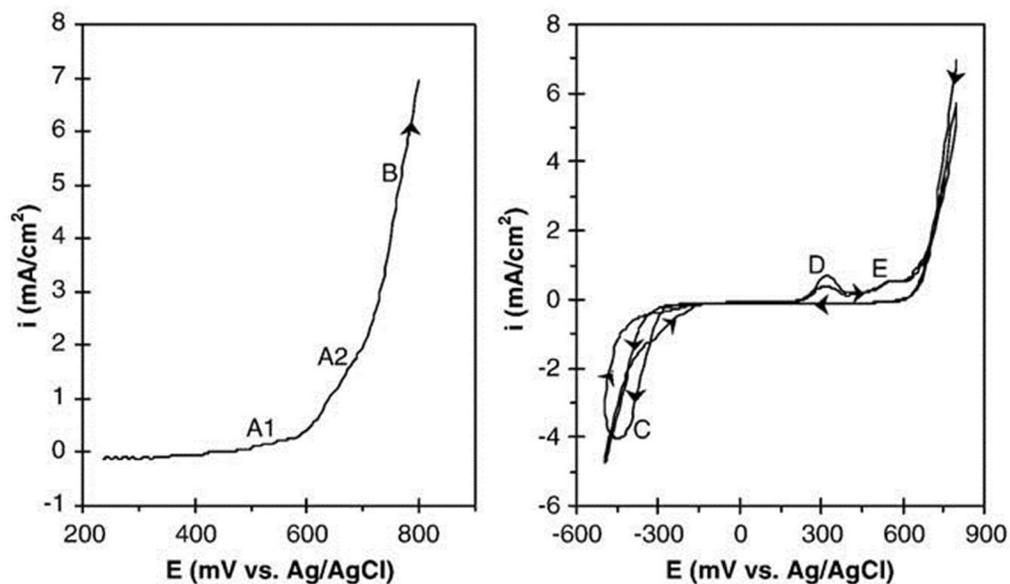
The electrochemical analysis of chalcopyrite leaching in ferric sulfate can provide highly useful insights into the nature of mechanisms on mineral dissolution. During corrosion of sulfide electrodes, there is the possibility of three electrochemical processes that can occur in iron or copper solutions: sulfide oxidation, ferric or cupric ion reduction, and ferrous or cuprous ion oxidation on the surface of the electrode (Debernardi et al., 2012; Parker et al., 1981).

Nicol and Lázaro (2002) studied the relationship between redox potential in solution and the rest potential of a chalcopyrite electrode. A mineral electrode in a sulfates solution could achieve maximum potentials up to approx. +900 mV vs. SHE (standard hydrogen electrode), and the differences in potential of the bulk solution can be considered negligible in Fe(III)/Fe(II) ratios close to one, and can be considerable in ratios close to 100.

The dissolution of semiconductor materials such as chalcopyrite can be influenced by the aqueous phase as well as the solid phase of the process (Debernardi et al., 2012). Electron transfer

rate will be proportional to the charge carriers in the semiconductor. If the dissolution rate exceeds a certain critical value, the concentration of metal ions near the electrode surface could exceed the solubility of the metal oxide or hydroxide. This causes the formation a precipitate layer, with increasing thickness, over the electrode surface. The layer reduces the anodic current and ultimately stops dissolution, which is known as passivation.

Anodic current curves are determined by applying a sweep of potential at a determined scan rate and recording the corresponding current responses. Passivation curves obtained through this method will depend on the scan rate utilized, since the formation of the layer is a kinetic process. Figure 2 displays the anodic polarization and cyclic voltammetry analyses of a massive chalcopyrite electrode at 35°C (Córdoba et al., 2008a).

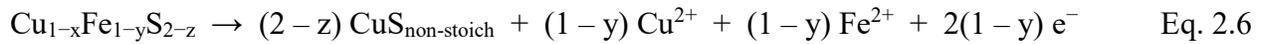
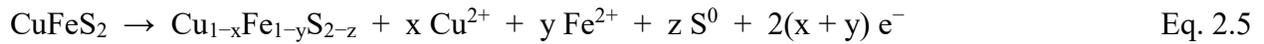
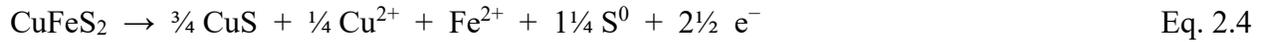
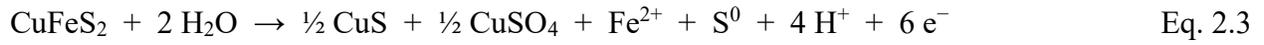


**Figure 2. Electrochemical characterization of a massive chalcopyrite electrode at 35°C.
Left: anodic polarization. Right: Cyclic voltammetry (Córdoba et al., 2008a)**

It is generally accepted that there are two different electrochemical responses during anodic polarization of chalcopyrite from its rest potential. The first peak located between the rest potential (+230 mV vs. Ag/AgCl) and approx. + 740 mV vs. Ag/AgCl, corresponds to the “passive zone”,

or “prewave”, and at higher potentials, a second peak corresponds to the denominated “transpassive zone”, as shown in Figure 2 (Left).

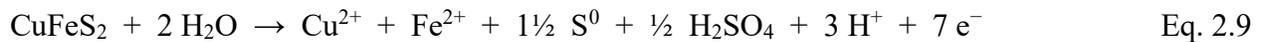
Several authors (Jones et al, 1976; Biegler et al., 1979; Biegler et al, 1985; Warren et al., 1985) indicate the behavior of chalcopyrite in the passive zone using the following reactions:



where $y > x$.

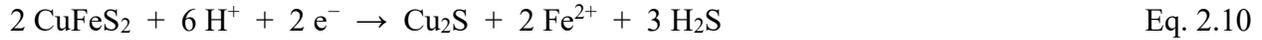
These different authors indicate that the chalcopyrite surface transforms into a copper-rich sulfide similar to CuS, and elemental sulfur, due to preferential dissolution of iron from chalcopyrite, as shown in Eqs. 2.3 and 2.4. It may also transform into an intermediate phase similar to bornite, which is subsequently oxidized into a non-stoichiometric form of covellite, as shown in Eqs. 2.5 and 2.6. The authors also agree that the formation of this copper sulfide is responsible for passivation of chalcopyrite under these conditions.

In the transpassive zone, the passive layer breaks down and chalcopyrite dissolution takes place (Yin et al., 1995, Gómez et al., 1996) according through the following equations:



The passivation zone comprises electrochemical responses A1 and A2 in Figure 2 (Left) corresponding to the reactions in Eqs. 2.5 and 2.6.

Considering the cyclic voltammetry in Figure 2 (Right), for the cathodic branch, when scan direction shifts at +800 mV, current density displays a sharp drop to zero and remains at said value over a wide range of potentials. From -150 mV to -500 mV, a large cathodic response (peak C) is displayed, corresponding to reduction of chalcopyrite and covellite as indicated by the following equations:



Once the shift to anodic values occurs, the current density increases showing two new anodic peaks at approx. +310 mV (peak D) and +570 mV (peak E) in Figure 2 (Right). Peak D corresponds to the oxidation of non-stoichiometric sulfides (Cu_8S_5 , Cu_7S_4 , etc.), Cu_2S , formed during cathodic scan of the electrode, as indicated by the following equation.



The anodic peak E can be associated with the passive zone at low potential, indicated by peak A in Figure 2 (Left) and the chalcopyrite oxidation to CuS and elemental sulfur (Eqs. 2. 3 to 2. 6), and it also could be further related to the oxidation of ferrous iron and later precipitation of ferric iron. Tshilombo and Dixon (2003) observed the formation of ferric hydroxides during electrochemical oxidation of chalcopyrite at high potentials and temperature. The authors conclude that these precipitates formed by chemical precipitation of ferric iron generated by oxidation of ferrous iron.

A characterization study focused on the anodic dissolution of n-type and p-type chalcopyrite, in sulfate and chloride media, was conducted by McMillan et al. (1982). One of the relevant conclusions from this study points to the formation of a solid electrolyte interphase (SEI) which slows the rate of electron transfer for various redox couples, and different SEI's are

produced using different electrolytes. The reversibility of these redox couples was also compared, and this study included ferric/ferrous, cupric/cuprous, and iodide/triiodide, for both n-type and p-type chalcopyrite electrodes. This study indicates that the ferric/ferrous couple is less reversible on p-type chalcopyrite electrodes in the potential region where electron transfer occurs readily to the other two couples.

2.2.4 Assisted Leaching Technologies for Chalcopyrite Concentrates

Numerous researchers have considered the acidic ferric sulfate system, key process parameters, as well as electrochemical analysis results to develop alternative leaching technologies for chalcopyrite. This has been achieved by modifying the processing conditions of the leach, such as temperature, pressure, and particle size, and incorporating additives that can assist and enhance copper extraction.

Table 1 presents four examples of assisted leaching processes for chalcopyrite, including their operating temperature, operating pressure condition, as well as the assisted leaching condition for each case.

Table 1. Examples of assisted leaching processes for chalcopyrite in sulfuric acid-ferric sulfate systems.

Process	Temperature	Pressure	Assisted leaching conditions
Galvanox (Dixon et al., 2008)	80°C	Atmospheric	Pyrite addition
Albion (Hourn et al., 1999)	85 – 90°C	Atmospheric	Fine grinding/O ₂
CESL (Defreyne et al., 2004)	--	High/Atmospheric	Chloride ions
Dynatec (Collins et al., 1998)	150°C	High	Anti-agglomerant (Coal)

Galvanox technology for chalcopyrite concentrates consists of the use of ground pyrite added to chalcopyrite concentrate, in a ratio of 2 to 4 times the mass of chalcopyrite, in stirred tank

leaching. This technology takes advantage of the galvanic couple formed by pyrite and chalcopyrite to ensure rapid oxidation of chalcopyrite concentrates. The leach is conducted at atmospheric pressure, redox potential of 470 mV vs. Ag/AgCl, and temperature of 80°C (Dixon et al., 2008).

The Albion process consists of a combined process using ultrafine grinding and oxidative leaching using reactors with high oxygen mass transfer efficiency (Hourn et al., 1999). The process feed is sulfide concentrates which contain base or precious metals, with the objective of oxidizing the sulfides in said concentrate to liberate metals for their subsequent recovery.

The CESL process is also a combination process, using a first stage of pressure oxidation of finely ground copper sulfide concentrates, using chloride ions as an enhancing additive. During this stage, copper is converted to basic copper sulfate, iron is converted to hematite, and sulfur to elemental sulfur. The following stage is an atmospheric leaching of the residues obtained in the first stage, where the pregnant leach solution (PLS) is subsequently refined and purified for solvent extraction and electrowinning (Defreyne et al., 2004).

The Dynatec process consists of a stirred autoclave leaching of copper sulfide concentrates using sulfuric acid solutions as well as carbonaceous material, such as coal, used as an anti-agglomerant. The process is performed at temperatures of 135° - 175°C, and coal is added in a concentration of 50 kg/t of slurry. (Collins et al., 1998).

2.3 Covellite Leaching in Ferric Sulfate

Covellite is not considered as abundant as chalcopyrite or chalcocite, nevertheless, it is widely distributed and occurs naturally with chalcocite and bornite in various ore sites. Sullivan (1930) studied the chemistry of covellite leaching using bottle roll experiments, in a proportion of

10-grams of pulverized covellite (-74 μm) to 2.5 L of leaching solution. The most relevant parameters for this process as reported by this study were particle size and temperature, and faster kinetics were achieved using ferric sulfate compare to ferric chloride as a lixiviant.

The leaching process can be described using the shrinking core model, controlled by surface chemical processes in the initial stages of the leach and by chemical and diffusion processes for the remainder (Cheng et al., 1991b). Eq. 2.3 represents covellite leaching in ferric sulfate solution.



Leaching of synthetic covellite has been studied using rotating disk electrodes in acidic ferric sulfate solution (Thomas et al., 1967), where the rate of process at room temperature is apparently controlled by the rate of a chemical process at the interface of the particle. At higher temperatures (close to 80°C) the control shifts from chemical to transport control, accompanied by a reduction of the activation energy, from 22 kcal/mol at room temperature to 8 kcal/mol.

2.4 Chalcocite Leaching in Ferric Sulfate

Chalcocite leaching in acidic solutions, using sulfate and chloride, undergoes two stages. The first stage is a rapid leaching stage where cuprous ions diffuse through the solid to the surface of the particle and subsequently oxidized, and the second stage follows a shrinking core model behavior where a core of unreacted covellite is surrounded by a shell of sulfur that thickens gradually (Cheng et al., 1991a).

Eq. 2.4 represents the first stage of chalcocite leaching in ferric sulfate solution.



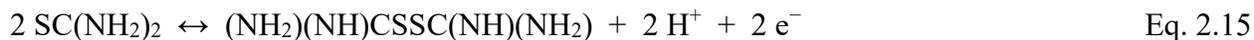
The leaching of second-stage covellite in ferric sulfate solution can also be represented by Eq. 2. 13. A recent study conducted by Niu et al. (2015) focused on leaching of chalcocite in column with redox potential control, dividing the second stage into two sub-stages based on an inflection point in the copper dissolution data. The first sub-stage consists in chemical reaction control at the sulfide-sulfur interface, and the second sub-stage has the slowest kinetics because of an elemental sulfur barrier affecting diffusion.

2.5 Thiourea, its Derivatives, and Similar Relevant Compounds

Thiourea has been widely used in the textiles industry, as well as in copper hydrometallurgy as a levelling agent for copper electrowinning. Thiourea acts as an additive to lower roughness in copper cathodes produced through electrodeposition, and it is generally accepted that the role of thiourea is related to the distribution of grain sizes and their formation (Gómez et al., 2009).

Thiourea is also used as a corrosion inhibitor, working through the formation of a polymeric film covering the given metal. Thiourea has also been used recently in organo-catalysis, to accelerate certain organic chemistry transformations through hydrogen bonding mechanisms (Takemoto, 2005; Taylor et al., 2006).

In oxidative conditions, two moles of thiourea in solution combine to produce one mole of formamidine disulfide (FDS), as described in Equation 2.5 below.

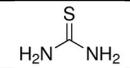
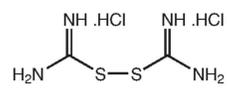
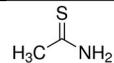
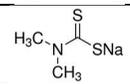
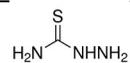
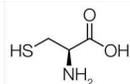
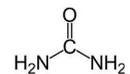
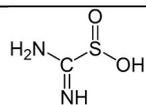
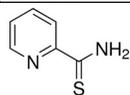
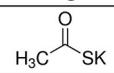
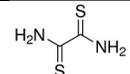


Formamidine disulfide is considered as an active oxidant for gold leaching in thiourea, and it also can be further oxidized to produce sulfinic compounds, cyanamide, hydrogen sulfide, and elemental sulfur (Örgül et al., 2002).

Relevant details regarding the additional chemicals used in the experimental sections of this study have been included in the present section. The selection of the chemicals consisted in the presence or absence of one or more carbon-sulfur double bond (thiocarbonyl) groups, as well as several compounds containing a carbon-oxygen double bond (carbonyl) group.

Table 2 displays the complete list of the chemicals used as additives in ferric sulfate leaching, including name, abbreviation, molecular, and structural formulae for each compound.

Table 2. Names and formulae of additives used in ferric sulfate leaching of copper sulfides.

Name (Abbr.)	Molecular formula	Structural formula
Thiourea (TU)	$\text{CH}_4\text{N}_2\text{S}$	
Formamidine disulfide (FDS)	$\text{C}_2\text{H}_6\text{N}_4\text{S}_2$	
Thioacetamide (TA)	$\text{C}_2\text{H}_5\text{NS}$	
Sodium dimethyl-dithiocarbamate (SDMDTC)	$\text{C}_5\text{H}_{10}\text{NS}_2\text{Na}$	
Thiosemicarbazide (TSC)	$\text{CH}_5\text{N}_3\text{S}$	
Ethylene trithiocarbonate (ETC)	$\text{C}_3\text{H}_4\text{S}_3$	
Cysteine (Cys)	$\text{C}_3\text{H}_7\text{NO}_2\text{S}$	
Urea (UR)	$\text{CH}_4\text{N}_2\text{O}$	
Thiourea dioxide (TUO2)	$\text{CH}_4\text{N}_2\text{O}_2\text{S}$	
2-pyridinethioamide (2-PyTA)	$\text{C}_6\text{H}_6\text{N}_2\text{S}$	
Potassium thioacetate (K-TA)	$\text{C}_2\text{H}_3\text{OSK}$	
Dithioamide (DTO)	$\text{C}_2\text{H}_4\text{N}_2\text{S}_2$	

Thioacetamide (TA) is a water-soluble organosulfur compound typically used as a source of sulfide ions in organic compound synthesis. It is also used to treat solutions of metal cations to produce their correspondent metal sulfides (Gharabaghi et al., 2012).

Sodium dimethyldithiocarbamate (SDMDTC) is an organosulfur compound typically found in certain rubber chemicals and pesticides, and its main oxidation product is thiuram, used as a fungicide in seed and crops (Schubart, 2000).

Potassium thioacetate (K-TA) is primarily used in the preparation of thiols and also used in the preparation of colorimetric sensors to detect palladium (II) ions in water samples (Anwar et al., 2017). Dithiooxamide (DTO), also known as rubeanic acid, is an organosulfur compound used as a chelating agent to detect cobalt, nickel, and copper, as well as a removal agent for heavy metal ions in solution (Pooré et al., 1996).

Cysteine (Cys) is a sulfur-containing amino acid which has important roles in the synthesis of proteins. It has also been used as an effective stabilizer in thiourea solutions utilized for gold recovery from leach liquors, by preventing the reaction of thiourea to formamidine disulfide (Ardiwilaga, 1999).

Urea (Ur), also known as carbamide, is an organic chemical widely used as a nitrogen-release fertilizer, and also utilized to synthesize heterogeneous catalysts by building metal-organic frameworks, with applications for gas storage, gas separation, and drug delivery (Roberts et al., 2012).

Thiosemicarbazide (TSC) is an organosulfur compound utilized for antimicrobial, anticonvulsant, and analgesic activities, and is also able to form stable chelates with essential metal ions (Nishat et al., 2008).

Ethylene trithiocarbonate (ETC) and the family of trithiocarbonate compounds have been utilized primarily as intermediates in numerous industrial processes to synthesize lubricants and pesticides (Fenoli et al., 2014). The compound 2-pyridine thioamide (2-PyTA) is part of the thioamide compound and is utilized for synthesis of heterocyclic compounds in organic chemistry (Jagodzinski, 2003).

2.6 Research using Thiourea in Hydrometallurgy

Concerning the applications of thiourea in precious metals hydrometallurgy, Li and Miller (2006) reviewed the leaching of gold in acid thiourea solutions, as an alternative to cyanide, including fundamental research for this system as well. This study considers ferric sulfate and formamidine disulfide as the most effective oxidants for gold leaching, and no passivation is observed during the process.

Li and Miller (2006) also report results of thiourea with copper in solution. Cupric ions oxidize thiourea and increase the speed of the decomposition of thiourea into elemental sulfur. Other factors for thiourea consumption included in this study are adsorption by mineral particles, thermal degradation, complexation with base metals, and oxidation by ferric and dissolved oxygen.

Zhu (1992) studied the oxidation kinetics of thiourea and ferric iron in solution. The results showed first order kinetics with respect to ferric and thiourea concentrations, second order overall, and one of the most important oxidation products of thiourea in this system is formamidine disulfide. Ferric sulfate solution allows TU to be readily oxidized to FDS, and further oxidized into sulfur within a relatively short period.

The stoichiometric ratio between ferric and thiourea was confirmed experimentally to be 1:1, and the rate of the redox reaction between these two was found to be increased by the presence

of a sulfide ore. The low value of the calculated activation energy (~ 32 kJ/mol) suggests the two reactants are adsorbed on the sulfide ore (Zhu, 1992).

Alodan et al. (1998) studied the effect of thiourea on copper dissolution and deposition in sulfuric acid solutions, where at concentrations greater than 1 mM thiourea, thiourea forms complexes with cuprous ions, which shift the open circuit potential of the copper electrode in a negative direction, causing copper to dissolve cuprous species even in sulfate media.

Another relevant aspect reported by Alodan et al. (1998) is the following: at more positive potentials, thiourea reacts with cupric ions forming a complex, and when a sufficient concentration of this complex is reached, a sulfate complex film is formed; this film is composed of a thiourea-cupric ion salt, and the solution systems in this study do not include any influence of ferric sulfate or any other iron complexes.

Bolzán et al. (2001) and Haseeb et al. (2001) studied the anodization of copper in TU- and FDS-containing acid solutions. These researchers investigated the anodic behavior of copper in aqueous 0.5 M sulfuric acid containing different amount of dissolved TU or FDS at 298 K. The data obtained from electrochemical polarization, chemical analysis, UV-Vis spectroscopy, X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDAX), as well as structural information on Cu-Tu complexes, was considered.

Some of the relevant results from this study are the following: in the measured potentials from -0.30 to $+0.075$ V (vs. SCE), there are three relevant processes occurring in the system: the formation of soluble copper(I)-thiourea complexes, the electro-oxidation of thiourea to formamidine disulfide, and the formation of copper(I)-thiourea complex polymer-like films, the formation of which depends on certain critical molar concentration ratios of thiourea to copper at the reaction interface.

Regarding the kinetics of this process, at low positive potentials, the formation of the film (denominated Film I) is under intermediate kinetic control, with diffusion of thiourea from the solution. At applied potentials greater than +0.075 V, soluble copper (II) ions are formed and a new film is formed gradually, changing from the copper(I)-TU to copper sulfide and residual copper (denominated Film II), which assists localized electro-dissolution of copper.

Bolzán et al. (2002) performed a series of electrochemical experiments on platinum electrodes using thiourea in sulfuric acid, also focusing on substituted thiourea adsorbates. According to this study, the interactions of thiourea and its derivatives with metal surfaces involves molecular electrooxidation of adsorbates and thioureas in solution through complex redox processes at intermediate potential values.

The rupture of the carbon-sulfur double bond with the formation of carbon and sulfur-containing species at high potentials. Accordingly, the balance between the strength of the metal-sulfur-carbon bond and that of the electric field at the reaction interface would determine the degree of influence of the additive on the kinetics and mechanism of the global process (Bolzán et al., 2002).

Loto et al. (2012) reviewed the effects of thiourea and thiazole derivatives as corrosion inhibitors, evaluating their effects on the corrosion of metallic alloys with a focus on the functional groups of the molecular structures of the inhibitor compounds. Kuznetsov (1996) states that most corrosion inhibition mechanisms can be treated as acid-base interactions and based on this concept, thiourea would act as a base because of its sulfur, and on iron it would behave as an acid, i.e. electron acceptors.

The inhibition efficiency of thiourea and its N-substituted derivatives is controlled by the adsorption of molecular species, which increases the inhibition, and the protonated species,

accelerating the rate of corrosion. Loto (2012) also explains that the process of protonation of thiourea derivatives appeared to be the effective parameter at high concentration with lowering of the inhibition efficiency of thiourea.

This protonation is controlled by the charge density of the sulfur atom, lengthening, and weakening of the carbon-sulfur bond, and the reactivity of the molecule, and the effect of protonation increases with increasing concentration of thiourea.

2.7 Literature Review Summary

In summary, this literature review has covered the three copper sulfide species considered in the present study, as well as certain relevant studies describing the leaching behavior of each of them in similar conditions as the experimental series performed for this work.

Chalcopyrite, covellite, and chalcocite present stages of slow kinetics during ferric sulfate leaching of copper, motivating numerous studies with the objective of overcoming these periods and properly establish an effective way of extracting copper using hydrometallurgy with low-cost alternatives.

Various results from electrochemical studies were also included to elucidate the behavior of thiourea and similar organosulfur compounds in oxidative conditions, as found in acidic ferric sulfate solutions. The present study, as aforementioned, consists in using thiourea and various organosulfur compounds as additives in acidic ferric sulfate leaching of copper from sulfide minerals, focusing on the effect these chemicals have on copper dissolution and overall behavior of the leaching process.

Chapter 3: Experimental Methodology

The leaching experiments conducted for the present study includes three different configurations: stirred tank leaching using powdered high-purity copper sulfide, small-scale column leaching of low-grade copper sulfide ore, and bottle roll leaching of low-grade copper sulfide ore.

The sulfuric acid-ferric sulfate solution utilized for all leaching experiments was prepared using reagent-grade ferric sulfate pentahydrate (Sigma Aldrich, 98% purity), concentrated sulfuric acid (Sigma Aldrich, 95 - 98% purity) and deionized water.

The leaching solution pH was approx. 1.8 – 1.9 using sulfuric acid to maintain ferric iron in solution. The concentration of ferric was 40 mM in the leaching solution. This solution was used as the principal leaching solution for every experiment included, and the solution in which all additives were dissolved. All the additives (e.g. thiourea, formamidine disulfide, etc.) were also reagent-grade chemicals procured from Sigma Aldrich, with a range of purity of 95 – 98%.

3.1 Stirred Tank Leaching Experiments

Stirred tank leaching experiments were performed using glass-jacketed reactors manufactured by CANSCI, with a capacity of 2 L. These reactors were equipped with two 6-blade impellers and three baffles made of 316 stainless steel, manufactured by Applikon Dependable Instruments (ADI).

Agitation was controlled with an external motor attached to the stirring shaft, the motor was also manufactured by ADI. A glass pH probe (AppliSens) and a redox potential probe (Analytical Sensors) were inserted into each reactor. The probes were connected to a digital controller (Honeywell UDA 2182) to display and record pH and ORP values.

The leaching solution consisted of acidic ferric sulfate prepared using de-ionized water, concentrated sulfuric acid to maintain the solution at pH 2 or lower, and ferric sulfate hydrate to achieve a concentration of 40 mM ferric for leaching copper sulfides. The stirred tank leaching equipment is depicted in Figure 3.



Figure 3. Agitated glass-jacketed reactors for stirred tank leaching experiments.

In these stirred tank experiments, 1 gram of the copper sulfide was put in contact with 1.9 liters of ferric sulfate solution to achieve a considerably large ratio of solution to solids. This was to ensure the leaching reaction would be maintained with enough lixiviant throughout the entirety of the leaching period. For the cases where additives were used, the specific amount of additive necessary for each experimental condition was added prior

3.2 High-Purity Copper Sulfide Preparation

High-purity copper sulfide species were prepared through hydrothermal precipitation, using reagent-grade salts of copper and iron and thiourea in a Teflon-lined pressure vessel. The vessel as supplied by the manufacturer is depicted in Figure 6.



Figure 4. Pressure autoclave used for hydrothermal precipitation of copper sulfides.
(Retrieved from <https://www.techinstro.com/hydrothermal-autoclave-reactor/>)

The preparation procedure of chalcopyrite, chalcocite and covellite powder consisted in the combination of iron and copper salts with a sulfur source (thiourea) in specific molar ratios. These molar ratios corresponded to the molecular formulae of chalcopyrite, chalcocite, and covellite. The calculated amounts of the salts and thiourea were dissolved in de-ionized water and the vessel was tightly sealed to avoid evaporation or escape of any gasses or vapors.

The pressure vessel was placed in a temperature-controlled lab-scale furnace set at 200°C for approximately 24 hours. After 24 hours of heating, the vessel was removed from the oven and let to cool down at room temperature. After cooling, the vessel was opened, and the precipitates were filtered using vacuum filtration and qualitative filter paper.

To ensure the elimination of any amounts of oxidized material in the copper sulfides, the solids were washed in a concentrated sulfuric acid solution for 24 hours prior to their utilization in any leaching experiment. After the acid wash stage, the solids were filtered, dried at room temperature, collected, sampled for analysis, and stored for their utilization in leaching experiments.

3.3 Small-Scale Column Leaching Experiments

Small-scale column leaching experiments were conducted using cylindrical columns with 30 cm length, 12 cm internal radius, 12.5 cm external radius. These leaching experiments used two different low-grade chalcopyrite ores, which were put in contact with an acidic ferric sulfate solution to leach copper from the copper sulfide. Figure 5 displays one of the columns used for the study as well as the low-grade ore sample as received from its mine site of origin.



Figure 5. Small-scale leaching column and low-grade copper sulfide ore sample.

Prior to leaching, the ores were cured for 72 hours using a concentrated sulfuric acid solution to neutralize acid-consuming material such as calcite, so the ore would not alter the pH of the leaching solution and precipitate the ferric sulfate.

The solution was irrigated using peristaltic pumps set to a specific irrigation flow rate per leaching area (i.e. lixiviant flux); the rates used for these experiments were maintained within the ranges commonly used for industrial heap leaching.

Each of the column has two vessels for the input and output leaching solutions; when in open-loop configuration, the input solution vessels are periodically filled with fresh leaching solution, which consisted in acidic ferric sulfate solution at pH 2; this solution was used with or without additives (such as thiourea) depending on each experiment.

10 mL samples were collected from the columns' output solution, and the solution pH and ORP were measured from this output solution as well. The ore used for the columns was used as received from the mine site. The material for the ore bed was kept at a particle size below 11.2 mm, an approximate amount of 1.7 – 2.0 kg of ore per column was used, with a flow rate per unit of leach of approximately 0.7 L/h/m².

3.4 Bottle Roll Leaching Experiments

Bottle roll leaching experiments were performed using 2 L plastic bottles, using acid-cured chalcopyrite ore and acidic ferric sulfate solution, both prepared as aforementioned; the experiments were performed using a 1% w/w solid to solution ratio, to simulate the conditions of excess leaching solution found in open loop column leaching experiments.



Figure 6. Laboratory scale bottle roller and plastic bottles used for bottle roll leaching experiments.

The leaching bottles were placed in a single speed lab-scale bottle roller for a determined period. Samples of 2.5 mL of the leaching solution were taken at 1, 4, 6, 8, and 24 hours from the start of the leach, and every 24 hours after that point. 2.5 mL of leaching solution were returned to the vessel to replenish the volume that was taken due to sampling.

3.5 Elemental Analysis of Leaching Solutions and Solids

All leaching solutions were analyzed using atomic absorption spectroscopy (AAS) using 5 standard solutions as well as inductively coupled plasma atomic emission spectroscopy (ICP-AES) using 9 standard solutions to calculate the values of copper dissolution and extraction from the ore.

The leaching experiments were performed to leaching completion, or in other cases, until the extraction values for copper from the sulfides had reached a plateau. Using the copper concentration analyses from the leaching solution in each experiment, the copper leaching experiments were constantly evaluated, balanced, and performed until reaching completion for each configuration and experiment.

The leached copper sulfide ore residues from finished experiments were also analyzed through ICP-OES to close the copper mass balance for the experiment. This was performed to determine the actual extraction values and curves for leached copper. For the case of stirred tank leaching, the amount of residue was insufficient, therefore, the results are based from the analyses of the leaching solutions.

Solids were analyzed using X-ray diffraction and Rietveld refinement to confirm the production of the prepared copper sulfide, in case of sulfides produced through hydrothermal precipitation, as well as the content of copper sulfides present in each of the sulfide ores.

A diffraction pattern typically obtained from the analysis of a batch of chalcopyrite, produced using hydrothermal precipitation and treated prior to leaching as aforementioned, is included in Figure 7.

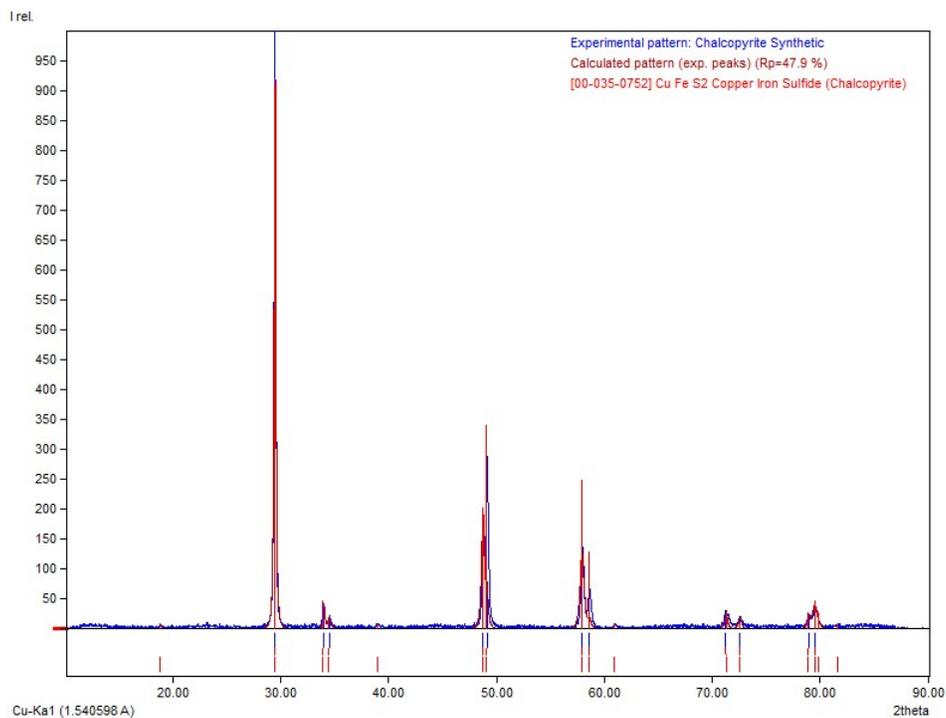


Figure 7. X-ray diffraction pattern for chalcopyrite using hydrothermal precipitation.

The X-ray diffraction and Rietveld refinement analysis of the hydrothermally-produced copper sulfides was performed using Match! Phase Identification software developed by Crystal Impact. The software used “COD-Inorg REV208743” and “PDF-2 Release 2004” databases for crystallographic data.

Chapter 4: Results and Discussion

4.1 Effects of Thiourea in Stirred Tank Leaching of High-Purity Copper Sulfides.

This section focuses on the results of the series of leaching experiments involving small quantities of high-purity copper sulfide in larger volumes of leaching solutions, with and without the use of thiourea as an additive in acidic ferric sulfate solution.

Figure 1 displays the effect of thiourea in ferric sulfate leaching solution, at a concentration of 2 mM, on the extraction of copper from high-purity chalcopyrite.

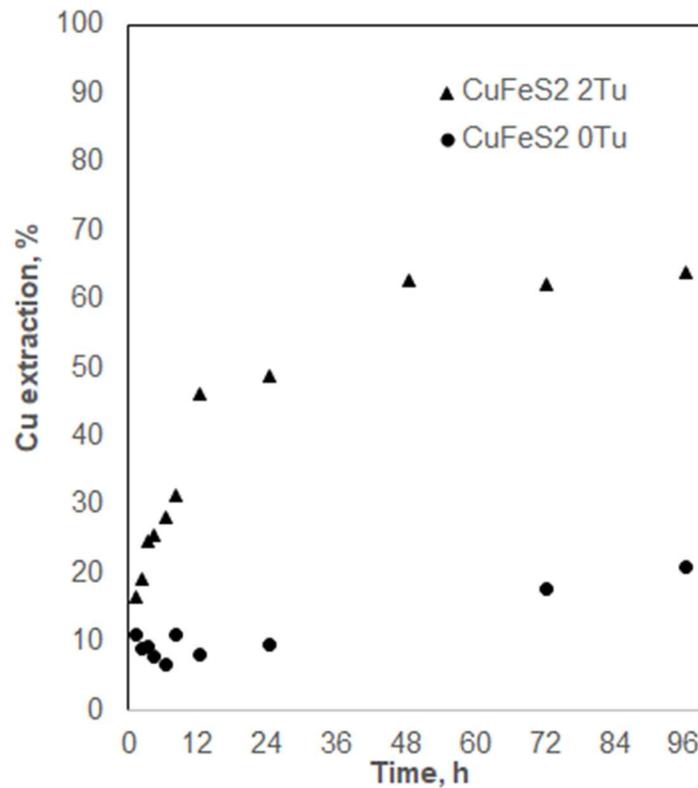


Figure 8. Effect of the addition of thiourea in ferric sulfate on copper leaching from high-purity chalcopyrite.

Figure 1 displays two extraction curves for the experiments with and without the use of thiourea as an additive to the leaching solution. The curve denominated “0 mM CPy” represents the case without additives, and the curve named “TU 2 mM CPy” represents the case where a

sufficient amount of thiourea was added to 1.9 L of leaching solution, to reach a concentration of 2 mM. All following Figures comparing ferric sulfate leaching with and without the use of additives will use a similar nomenclature, indicating the additive and concentration utilized for each case.

For ferric sulfate leaching without the use of additives, the extraction of copper from chalcopyrite reaches values of approx. 20% in 96 hours of leaching. The 2 mM Tu leaching curve displays copper extraction values of approx. 50% within the first 24 hours of the leaching period, finally reaching an approx. 63% extraction at 96 hours.

These experimental results indicate that the use of low concentrations of thiourea in ferric sulfate leaching yield a significant enhancement of copper extraction from high-purity chalcopyrite in a relatively short period of time. Considering that chalcopyrite shows slow leaching kinetics in ferric sulfate at room temperature, and the enhancement displayed through these experiments, the use of thiourea as an additive exhibits potential for use in copper extraction from other refractory sulfides.

For the case of 2 mM thiourea leaching, after 48 hours, the values of copper extraction reach approx. 63% and the curve remains around this percentage for the rest of the experiment, without displaying any further enhancement of copper dissolution compared to the 0 mM additive case, where the extraction values continue to slightly increase as the leach progresses.

Figure 2 displays the effect of the addition of different concentrations of thiourea, in a range of concentrations of 1 mM – 10 mM, on the extraction of copper from high purity chalcopyrite solids in acidic ferric sulfate solution.

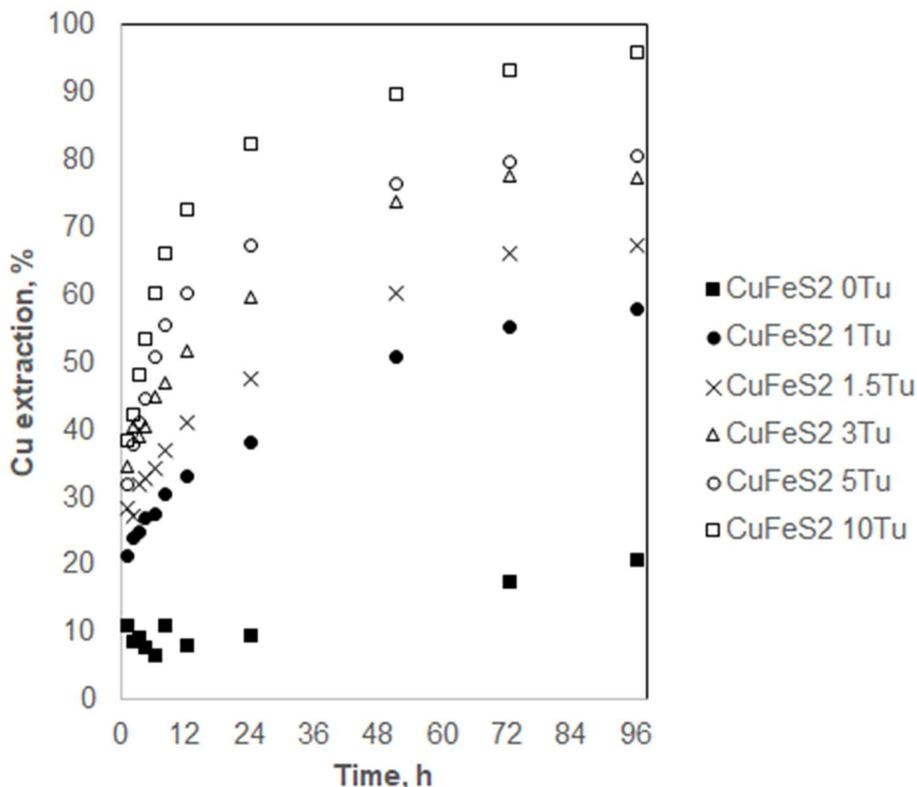


Figure 9. Effect of the concentration of thiourea (0 – 10 mM) in ferric sulfate on copper leaching from high-purity chalcopyrite

As previously displayed in Figure 1, there is a significant difference in the values of copper extraction from high-purity chalcopyrite in the cases where thiourea was added to the solution. For this experimental series, the final values of copper extraction were the following: 18% for 0 mM, 54% for 1 mM, 61% for 1.5 mM, 72% for 3 mM, 75% for 5 mM, and 95% for 10 mM. From these results it is evident that increasing the concentration of thiourea, within this range, can yield higher values of copper extraction from chalcopyrite, within 96 hours of leaching.

The increase in copper extraction values in this experimental series is displayed starting from a concentration of 1 mM thiourea in ferric sulfate leaching, with an approximate increase of 3 times the extraction of copper compared to the case without additives.

Further increasing the concentration to 1.5, 3, and 5 mM yields an enhancement of respectively 1.12, 1.33, and 1.38 times the extraction of copper compared to 1 mM thiourea, and 3.38, 4, 4.16 times respectively when the values are compared to 0 mM. Finally, the case where thiourea concentration was 10 mM displayed an approximate increase of 5.27 times the extraction of copper compared to the case without additives, and 1.26 times when compared to using 5 mM thiourea in solution.

Figure 3 displays the effect of a broader range of concentrations of thiourea, through an extended period of leaching compared to previous experiments. This series includes values from 0.002 to 200 mM of thiourea in acidic ferric sulfate solution, through 192 hours of leaching.

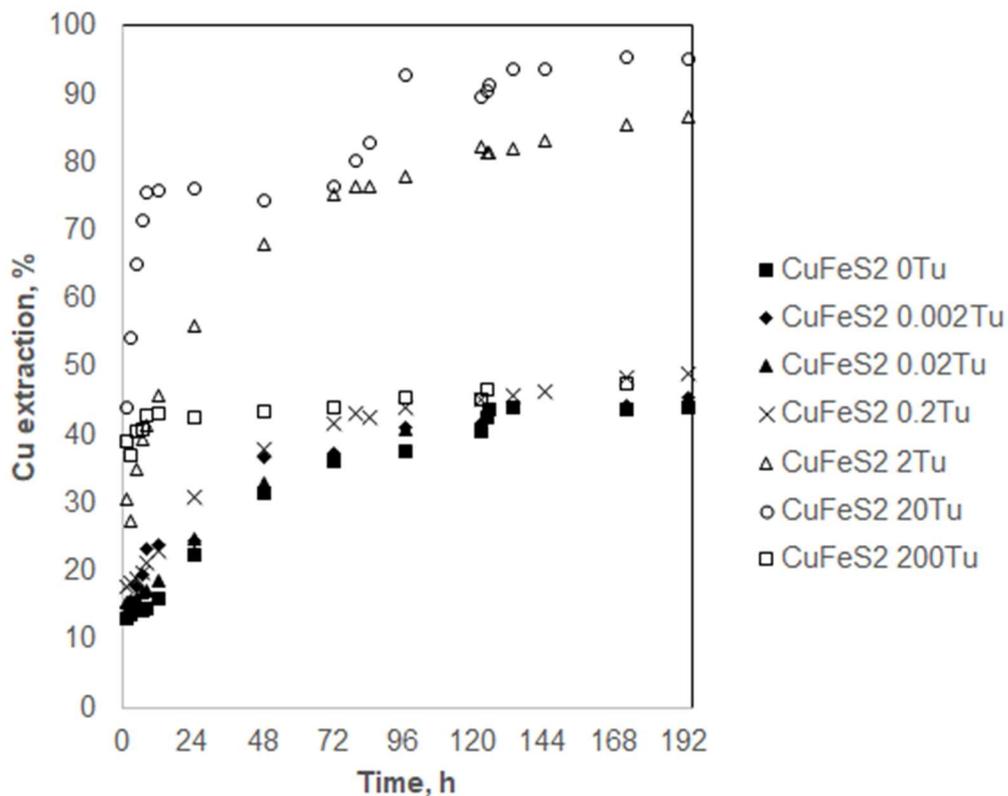


Figure 10. Effect of the concentration of thiourea (0 – 200 mM) in ferric sulfate copper leaching from high-purity chalcopyrite over extended periods.

Based on the leaching curves displayed in Figure 3, the use of 0.002 mM – 0.2 mM of thiourea in acidic ferric sulfate leaching does not appear to enhance the copper extraction as much as other cases previously shown in Figures 1 and 2, compared to the 0 mM case.

The extraction values increase approx. 4 – 5% in average through the entire leach for the 0.2 mM case, compared to 0 mM, reaching approx. 44% and approx. 40% respectively at the end of the leach.

This indicates that within the studied range, the lower limit of thiourea concentration yielding a consistent enhancement of copper extraction can be considered as 0.2 mM in ferric sulfate solution, and the studied concentrations below this level do not appear to yield significant and consistent enhancement of dissolved copper, compared to the case without additives.

The results obtained for 2 mM thiourea in leach for this series indicate a consistent and significant increase of copper extraction values, compared to the case without additives. The 2 mM curve reaches approx. 55% extraction of copper within 24 hours of leach, compared to approx. 22% for the 0 mM curve.

Considering these two curves after 72 hours of leaching, the increase in copper extraction values as time progresses is lower compared to the values observed within the first 72 hours, and both curves reach a slight extraction plateau with slow apparent kinetics by the end of the leaching period.

For the case where a concentration of 20 mM thiourea was used, additional amounts of ferric sulfate were added to the stirred leaching tank at 72 hours after the beginning of the experiment. Sufficient ferric sulfate was added to increase the concentration of ferric to an additional 20 mM over the initial 40 mM ferric in solution. The 20 mM leaching experiment starts

to display an extraction plateau after 120 hours of leach and yields a final extraction value of approx. 94% after 192 hours.

Finally, for 200 mM thiourea, the values of copper extraction increase to approx. 42% within the first 12 hours of leach, and the curve remains in a plateau for the remainder of the leaching period, yielding extraction values comparable to the cases without additives and with concentrations of thiourea below 0.2 mM. This behavior can be attributed to the effect of thiourea on the oxidation-reduction potential of the solution, since sufficiently high concentrations of thiourea in ferric sulfate can modify the ORP values measured during the leach.

Figure 4 displays the oxidation-reduction potential data measured for the experimental series displayed in Figure 3, covering the range of 0.002 – 200 mM thiourea as well as ferric solution without additives.

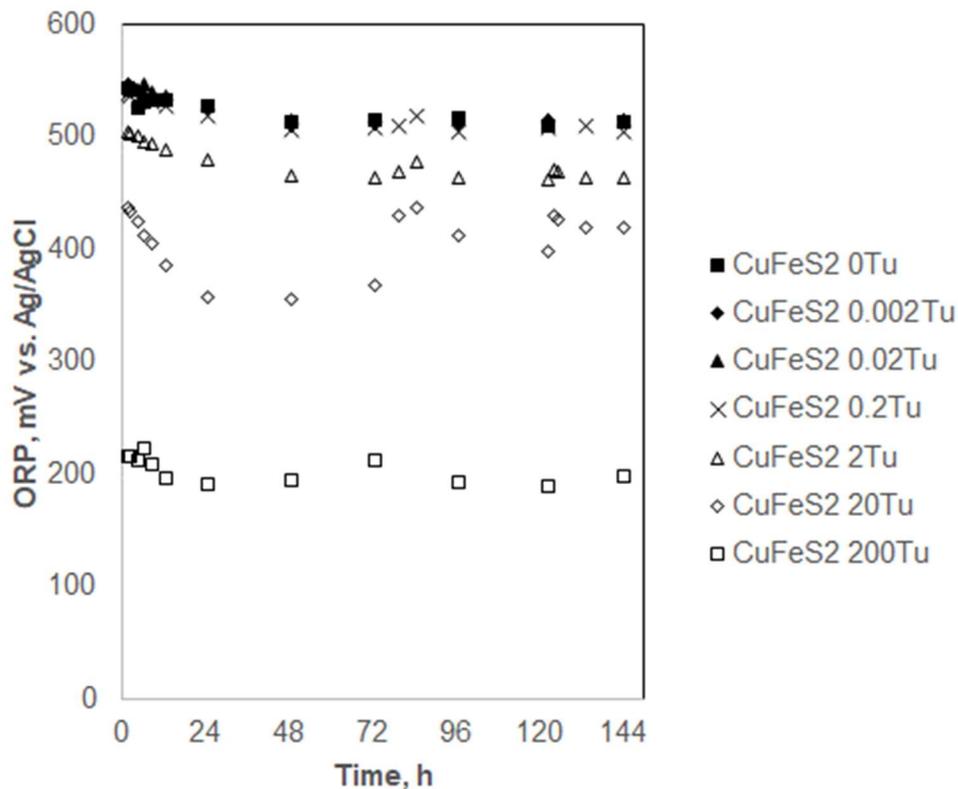


Figure 11. Effect of the concentration of thiourea (0 – 200 mM) in ferric sulfate on oxidation-reduction potential in high-purity chalcopyrite leaching.

As displayed in Figure 4, the values of ORP vs. Ag/AgCl for ferric sulfate solution decrease with increasing thiourea concentration, starting from 2 mM. The values observed for the cases of 0.002 – 0.2 do not have a significant effect on the ORP when compared to ferric sulfate solution without additives. The effect of thiourea in the redox potential of the solution becomes noticeable and a significant change in the ORP is measured when concentrations of 2 mM and higher are used, and additionally, ORP decreases as the concentration of thiourea is further increased from this value.

Chalcopyrite leaching in ferric sulfate solution is typically affected by the oxidation reduction potential, where potential values outside of a certain range can lead to slow leaching kinetics and passivation behaviour observed in the particle surface.

The ORP values corresponding to the various concentrations of thiourea from the experiments fall into four different ranges: 510 – 548 mV for 0 – 0.2 mM thiourea, where all curves are considered almost identical; 466 – 507 mV for 2 mM thiourea, 360 – 439 mV for 20 mM thiourea, where additional ferric sulfate was added to the leaching solution, and 193 – 217 mV for 200 mM. Considering this, the concentrations of thiourea yielding more favorable extraction of copper maintained the ORP values within a favorable range for chalcopyrite leaching.

As a summary of the results displayed in Figures 1 – 3, the addition of thiourea to acidic ferric sulfate solution yields an increase in the dissolution of copper from high-purity chalcopyrite. From a broad range of concentrations of thiourea tested, the interval of thiourea concentrations that yields consistent and significant enhancement on the values of copper extraction from chalcopyrite is 0.2 – 10 mM in 40 mM ferric solution.

The studied cases where higher concentrations of thiourea were used required additional oxidants to be added to the leaching solution to avoid extraction plateaus, as observed in the 20 mM case, or yielded final extraction values that did not represent an overall enhancement in the extraction of copper, as observed in the 200 mM case.

Considering the results obtained for chalcopyrite, two additional copper sulfides were utilized in various leaching experiments using thiourea as an additive in ferric sulfate solution, these sulfides were covellite and chalcocite. Covellite is also considered refractory to ferric sulfate leaching at room temperature. The effect of the addition of thiourea in ferric sulfate for high-purity covellite in extended periods of leaching are displayed on Figure 5.

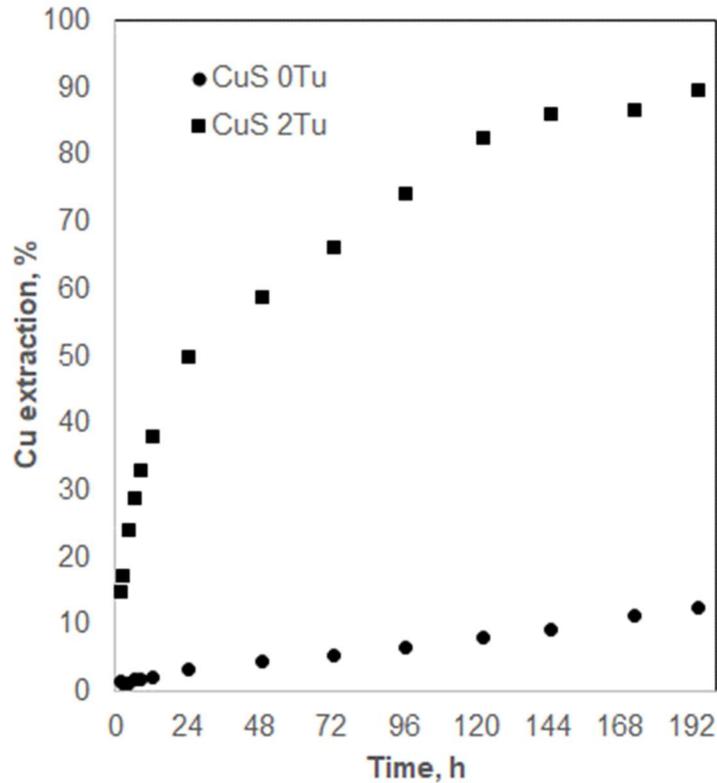


Figure 12. Effect of the addition of thiourea in ferric sulfate on copper leaching from high-purity covellite.

The leaching curve corresponding to ferric sulfate leaching without the use of thiourea displays copper extraction values of approx. 3 – 4% at 48 hours, following an almost linear increase during the remainder of the experiment until reaching approx. 11% copper extraction after 192 hours. In a similar manner to the case of chalcopyrite, higher extractions of copper are obtained using a concentration of 2 mM thiourea in ferric sulfate solution for covellite, the extraction of copper reaches approx. 60% in 48 hours.

The final extraction values for the case of 2 mM thiourea after the entire leaching period were approx. 87%. Comparing this case with what was observed in chalcopyrite, the enhancement in copper extraction from covellite in the case where thiourea is used corresponds to approx. 8

times the values obtained from ferric leaching without the use of additives, whereas with chalcopyrite, this was approx. 3 times.

For the 2 mM thiourea case, the leaching curve exhibits an evolution of the leaching behavior as the experiment progresses. Approx. 50% copper extraction is achieved during the first 24 hours of leaching, an average of 2.08% copper extraction per hour.

The values obtained between 48 hours and 120 hours of leaching correspond to an average of approx. 0.41% copper extraction per hour of experiment, and from 144 hours onward, the extraction curve reaches an apparent plateau where the values obtained are approx. 85%, reaching a final extraction of 87% at 192 hours.

Covellite leaching in ferric sulfate solution is typically most affected by leaching temperature, where the kinetics of copper dissolution increase when temperature increases. For the case of covellite in chloride solutions, Nicol et al. (2017) suggest that there is also a potential range in which covellite undergoes a type of passivation.

All experimental series included in this study were performed at room temperature, which further displays the possibility of the use of thiourea as an enhancing additive for copper leaching from sulfides. With respect to the effect of potential in this case, Figure 6 displays the data of the oxidation-reduction potential measure during the covellite leaching experiments, with and without the use of thiourea.

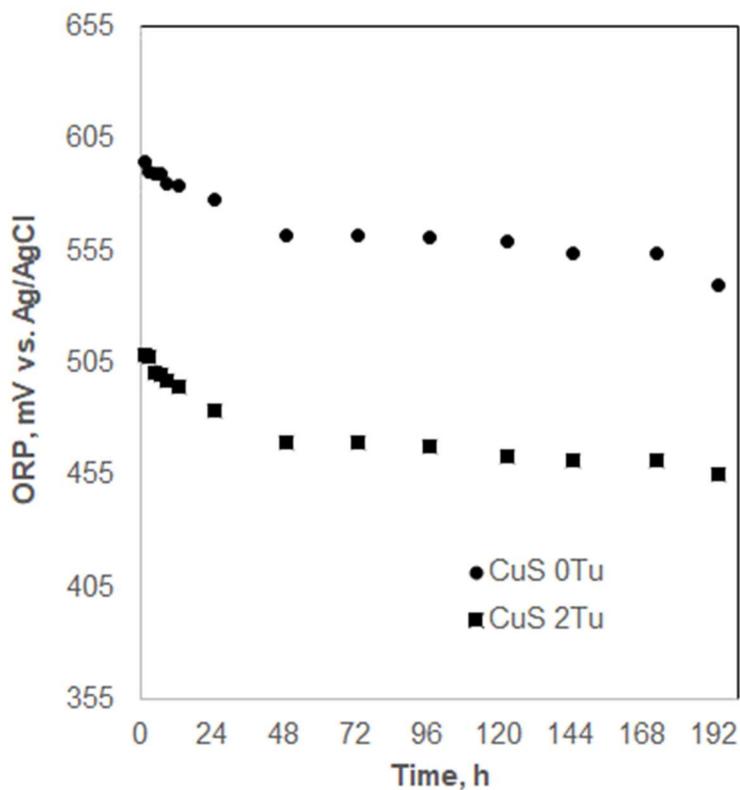


Figure 13. Effect of the addition of thiourea in ferric sulfate on oxidation-reduction potential in high-purity covellite leaching.

The values of ORP for the ferric sulfate solution without additives range between 541 – 596 mV vs. Ag/AgCl, whereas the values for the 2 mM Ty case, the values range between 464 – 510 mV. The curves for both cases follow a remarkably similar behavior, showing a gradual decrease in ORP during the first 48 hours of leaching, dropping approx. 33 and 39 mV for the 0 and 2 mM cases, respectively.

For the remainder of the experiment, the potential for both cases continues to drop gradually, albeit at a lower rate, decreasing approx. 22 and 15 mV for 0 and 2 mM respectively in a total of 144 hours. The difference between the two curves consists in an offset of 86 mV, caused by the addition of thiourea to the leaching solution from the beginning of the experiments.

The third copper sulfide included in this study was chalcocite, which in acidic ferric sulfate solution, undergoes two well-known, significant stages of leaching (Bolorunduro, 1999). The first stage consists of copper extraction from chalcocite and subsequent conversion to covellite, denominated “second stage covellite”.

First stage leaching is considered as a relatively rapid leaching, the rates remain the same at most leaching temperatures, and is not affected by oxidation reduction potential. During the second stage, the covellite sub-product formed previously starts to dissolve and form a product layer of elemental sulfur around the particle. The second stage process is considered to have slow kinetics of leaching, which is why this sulfide is also considered refractory.

Figure 7 displays the effect of the addition of thiourea to ferric sulfate solution for chalcocite leaching.

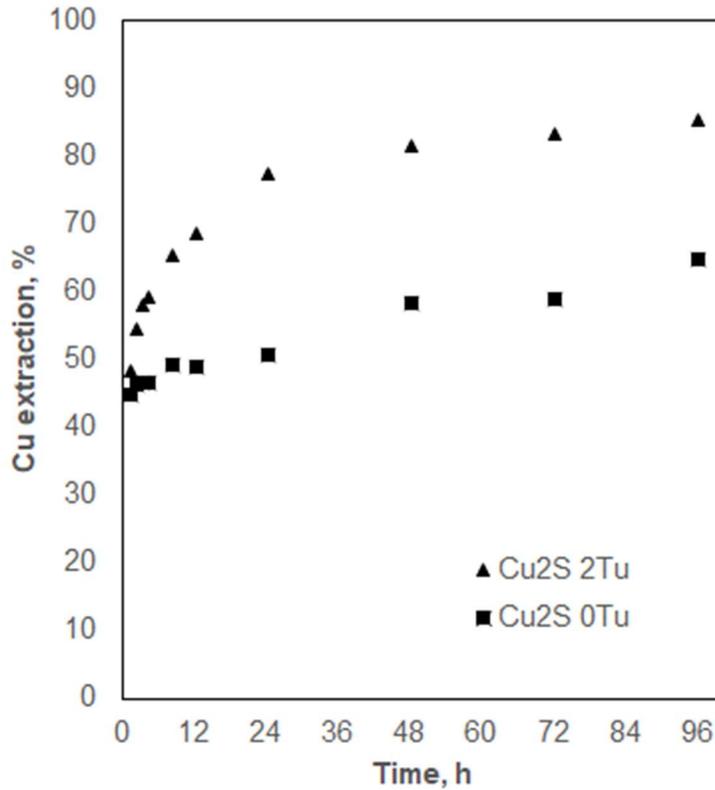


Figure 14. Effect of the addition of thiourea in ferric sulfate on copper leaching from high-purity chalcocite.

The copper extraction values for the case without additives reach approx. 45% within the first two hours of leaching, in contrast to chalcopyrite and covellite. In the same period, copper extraction reached approx. 14% and approx. 3% respectively, confirming that chalcocite can be dissolved in ferric sulfate solution more readily than chalcopyrite or covellite within the first two hours of leaching, without the use of additives. For the case where thiourea was added to the leaching solution, the extraction of copper reached approx. 65% for the first 8 hours, and after 96 hours of leaching it was approx. 82%.

During the first 24 hours of leaching for this case, the leaching curve presents a different behavior compared to the remainder of the 2 mM thiourea and the 0 mM thiourea curve, with rapid apparent leaching kinetics and average values of approx. 0.92% copper extraction per hour. Copper

dissolution has relatively rapid leaching kinetics in the 2 mM thiourea case until it reaches an apparent extraction plateau after 48 hours, where the average values reach 0.083% copper extraction per hour. For the case without additives, the extraction curve maintains an apparently steady, almost linear behavior, with average values of 0.15% copper extraction per hour, reaching approx. 65% at the end of the experimental period.

In summary, based on the results obtained for these three different high-purity sulfides, the addition of low concentrations of thiourea to ferric sulfate solutions, in the range of 0.2 – 10 mM, yields an increase for the values of copper extraction during leaching in stirred tank configuration, compared to the case without additives.

4.2 Effects of Other Additives in Stirred Tank Leaching of High-Purity Copper Sulfides.

The present section contains various series of experiments where the three high-purity copper sulfide species were submitted to stirred tank leaching in acidic ferric sulfate, with the difference that for these series, various organosulfur compounds and some of their derivatives were used as additives instead of focusing solely on thiourea.

The chemicals selected for this section were considered based on the presence or absence of certain functional groups, such as a carbon-sulfur double bond group (thiocarbonyl group). Additionally, several oxidation products of thiourea, such as formamidine disulfide and urea, were used as additives for copper sulfide leaching.

Each of the compounds used as additives for leaching were added to acidic ferric sulfate solution as reagent-grade chemicals and, as performed in the previous section, the high-purity copper sulfides utilized were covellite, chalcocite, and chalcopyrite.

Figure 8 displays the results of copper extraction from high-purity covellite and the comparison of effects of three different reagents: formamidine disulfide (FDS, oxidation product of thiourea); thioacetamide (TA), and sodium dimethyl-dithiocarbamate (SDMDTC), both of which possess a carbon-sulfur double bond such as the one found in the molecular structure of thiourea. This Figure also contains the extraction curves for the cases where 2 mM thiourea was used, as well as the case without additives, for comparison purposes.

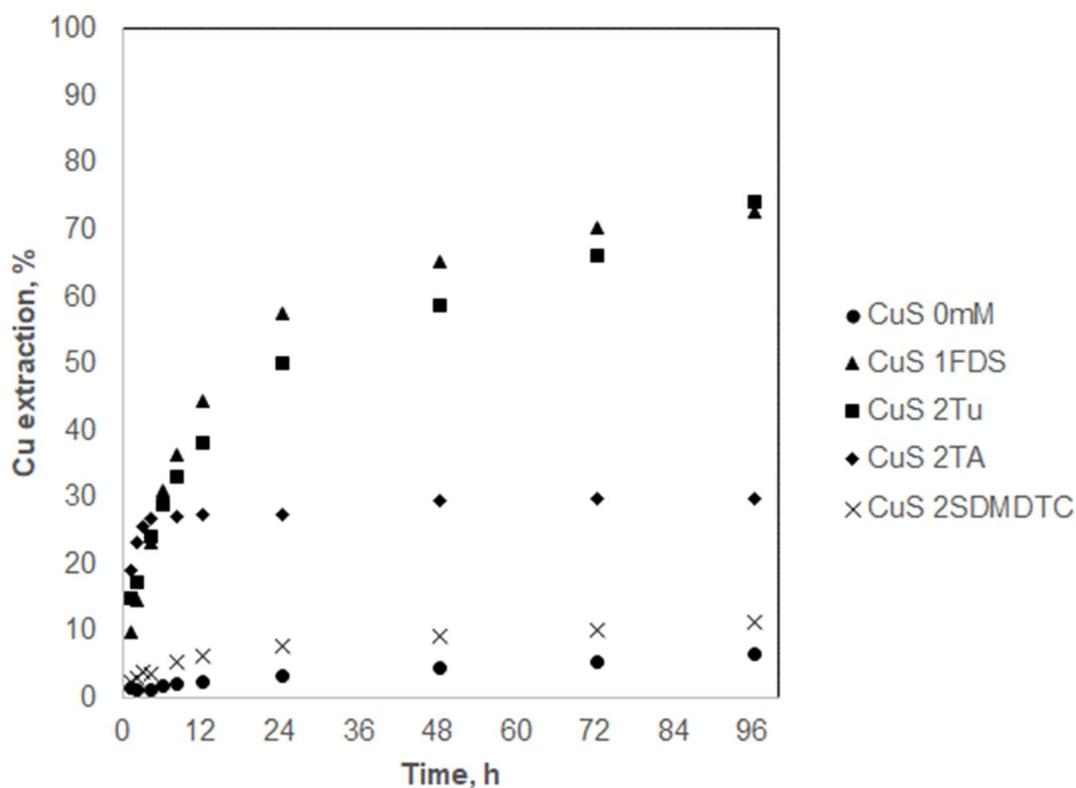


Figure 15. Effect of the addition of formamidine disulfide and thiourea-related chemicals in ferric sulfate on copper extraction from high-purity covellite.

As aforementioned, in oxidative conditions, two moles of thiourea are converted into 1 mol of formamidine disulfide, therefore, a concentration of 1 mM of FDS was used for a closer

comparison between the two compounds. Considering this, the curves from Figure 8 show that in leaching of high-purity covellite, both thiourea and formamidine disulfide reach approx. 73% copper extraction at 96 hours of leaching, and the extraction curves for both chemicals show a remarkably similar behavior throughout the experimental period, with FDS displaying a difference of 4 – 5% higher extractions of copper in comparison to thiourea between 12 and 72 hours of leach.

For the case of thioacetamide, when a concentration of 2 mM of this compound was used as an additive in the leach, copper extraction reaches values of approx. 27% within the first 8 hours, following a virtually identical behavior to the thiourea and formamidine disulfide curves. From 8 hours of leaching until the end of the experiment, the thioacetamide case remains in an extraction plateau, reaching extraction values of approx. 28% by 96 hours.

Comparing the case of 2 mM thioacetamide to the case without additives, thioacetamide can be considered as an enhancing additive because of the copper extraction increase displayed in the first 8 hours, nevertheless, this increase is not continuous through the rest of the leaching period as the cases of both thiourea and formamidine disulfide.

Compared to covellite leaching without the use of additives, the 2 mM SDMDTC case displays a reduced enhancement of the extraction values in comparison to the other additives tested, reaching approx. 8% in 96 hours compared to 5% extraction from leaching without additives.

Both 0 mM and 2 mM SDMDTC leaching curves display relatively slow kinetics and leaching behavior after 12 hours of leach, and for the first 12 hours, the presence of the additive increases the values of copper extraction to approx. 6% compared to approx. 3% obtained for the case without additives.

In summary, for the case of covellite, the compounds that yielded the highest increase in the extraction of copper from this sulfide were thiourea and formamidine disulfide, reaching final extraction values of approx. 73% and displaying leaching curves with rapid apparent leaching kinetics compared to the case without additives.

The use of thioacetamide in leaching also displayed increased extraction values compared to the case without additives, albeit the leaching curve displays an extraction plateau for the majority of the leaching period, with rapid apparent kinetics within the first 12 hours of the experiment.

Finally, SDMDTC displays extraction values of approx. 6 – 8% copper extraction, which compared to 3 – 4% extraction obtained without additives, is not considered as significant as the rest of the compounds included in the series, with respect to extraction values and leaching curve behavior.

Considering the results obtained for covellite using the aforementioned compounds, the following copper sulfide included in this section is chalcocite with formamidine disulfide and thioacetamide as additives in ferric sulfate solution. The copper extraction data for three different additives in total (formamidine disulfide, thioacetamide, and thiourea) is displayed in Figure 9.

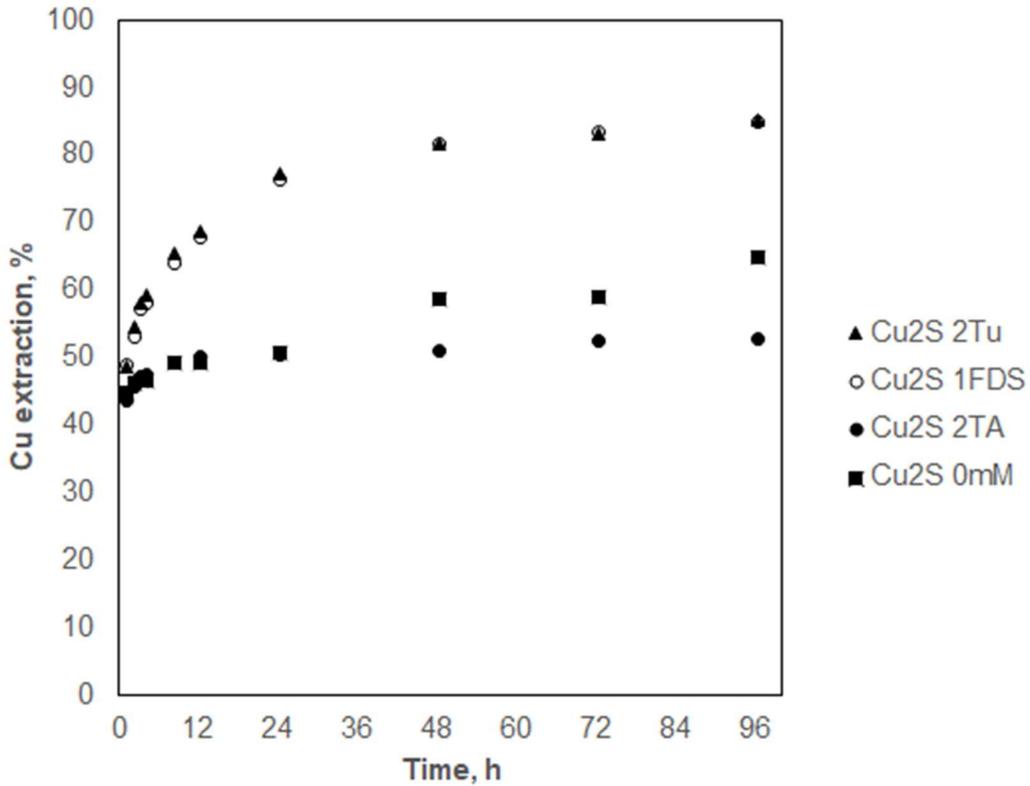


Figure 16. Effect of the addition of formamidine disulfide in ferric sulfate on copper extraction from high-purity chalcocite.

As displayed in the previous section, high-purity chalcocite is more readily dissolved in ferric sulfate solution than chalcopyrite and covellite for the first hours of leaching without the use of additives, with final extractions of approx. 60% in 96 hours of stirred tank leaching, as indicated by the 0 mM leaching curve.

The curves for thiourea and formamidine disulfide are almost identical, with a difference of approx. 1 – 2% in extraction values within the first 12 hours. This difference further decreases as the experiment continues, with both leaching curves approaching apparent extraction plateaus at 48 hours, with final extraction values of approx. 84% in 96 hours.

The addition of thioacetamide to ferric sulfate leaching of chalcocite does not yield a considerable enhancement in copper extraction compared to ferric sulfate without additives. During the first 24 hours of leaching, both curves for thioacetamide and no additives are almost identical, reaching approx. 50% extraction of copper at approx. 0.20% copper extracted per hour of leach.

In the period from 24 hours to 96 hours of leaching, the curve representing no additives reaches higher extractions than the thioacetamide leaching curve, with values of approx. 60% and 50% respectively at 96 hours of the leaching period. The behavior of the thioacetamide curve in chalcocite leaching is comparable to its analogous curve in the case of covellite leaching, where through the majority of the leaching period, an extraction plateau is displayed after reaching 12 hours of extraction, which indicates a possible reaction of thioacetamide with the ferric sulfate solution that affects the compound and the effects it presents for the copper sulfide leach.

Summarizing the results from other additives besides thiourea, the compound that yields the highest increase in extraction values compared to ferric sulfate leaching without additives was formamidine disulfide, which displays a remarkably similar leaching behavior to thiourea. The curves for both compounds differ in approx. 1 – 2% extraction of copper throughout the leaching period, showing rapid apparent leaching kinetics for the first 24 hours, followed by an extraction plateau for the remainder of the leaching period, and obtaining values of approx. 84%.

Thioacetamide presents slow leaching kinetics that appear almost identical to the leaching curve without additives within the first 12 hours of the experiment. After 12 hours of leaching, the thioacetamide case presents an extraction plateau at approx. 50% extraction for the remainder of the experiment, whereas the case without additives yields a final extraction of approx. 60% at 96

hours. This indicates that thioacetamide as an additive in ferric sulfate leaching of chalcocite does not yield an enhancement in the extraction of copper from this sulfide.

Given that chalcopyrite is considered as an important sulfide species in extractive metallurgy of copper, the number of compounds used as additives for copper leaching for this case was higher, including oxidation products of thiourea and various derivatives of this chemical. Additionally, the molecular structure of various of these compounds present several differences from that of thiourea, for example, the presence of several thiocarbonyl groups instead of a single group, and the presence of carbonyl (carbon-oxygen double bond) groups instead of thiocarbonyl groups.

Figure 10 displays the effects of five different chemical reagents as additives to ferric sulfate leaching of high-purity chalcopyrite. The chemicals considered for this experimental series were thiourea, thioacetamide (TA), thiosemicarbazide (TSC), ethylene trithiocarbamate (ETC), and sodium dimethyldithiocarbamate (SDMDTC), all of which possess a single thiocarbonyl group in their molecular structure and include other radicals and functional groups which vary from the ones in the structure of thiourea. The results for 0 mM additives and 2 mM thiourea are also included in Figure 10 for comparison purposes.

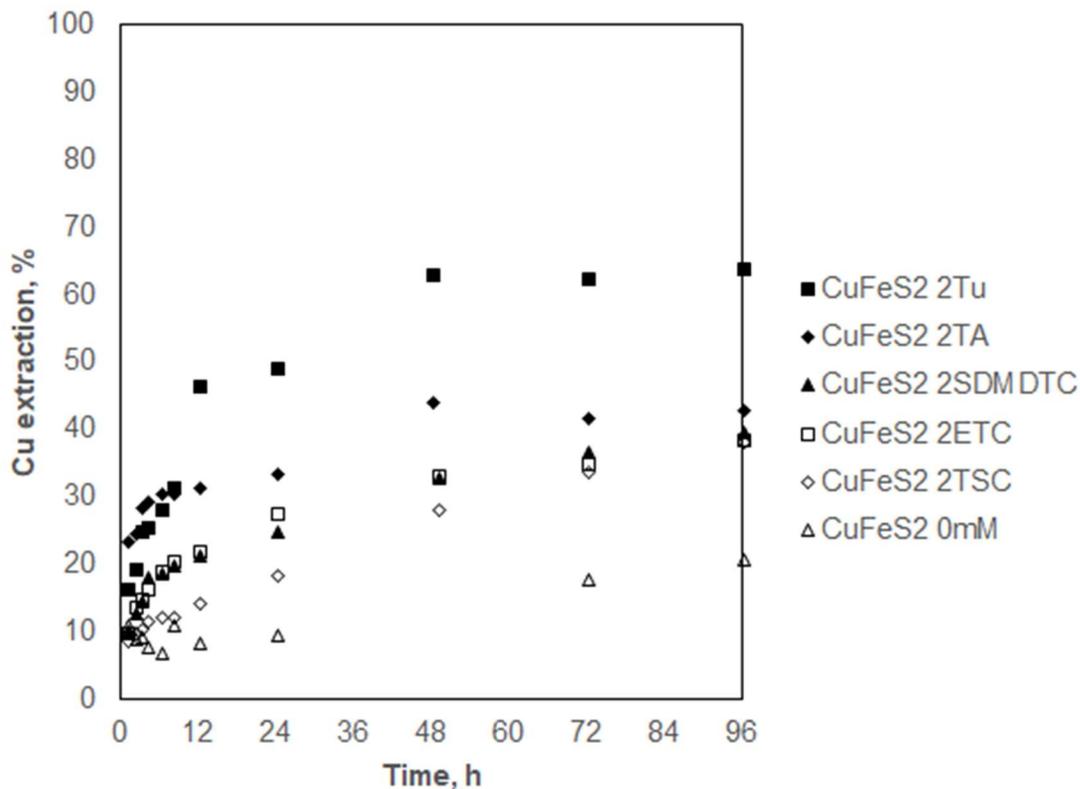


Figure 17. Effect of the addition of formamidine disulfide and thiourea-related chemicals in ferric sulfate on copper extraction from high-purity chalcopyrite.

Based on the leaching results for this group of additives, thiourea yields significantly higher extraction values compared to the rest of the compounds included, and to ferric sulfate without additives, reaching approx. 64% extraction of copper in 96 hours, as mentioned previously. Considering the final extraction values for the cases of the remaining four additives, all the chemicals considered displayed an increase in the values of copper extraction compared to the case without additives. Thioacetamide in ferric sulfate yielded approx. 40% copper extraction after 96 hours of leaching, and the remaining three reagents reach approx. 37% at the end of the leaching period. Finally, for the case without additives, the final extraction reached in the leaching curve is approx. 20% at 96 hours.

The curve for the case where thioacetamide was used as an additive presents rapid apparent kinetics and extractions of approx. 30% for the first 8 hours of leaching. These values obtained for thioacetamide are similar to those for the case of thiourea within the same period, however, at 12 hours both curves diverge drastically, where the thiourea curve reaches approx. 45% copper extraction and thioacetamide remains at approx. 30%.

Both curves display an increase in the extraction values between 12 and 48 hours of leach, approx. 10% and 13% for TA and TU respectively, and as time progresses, both remain in an apparent plateau for the remainder of the leach, at 40% extraction of copper for TA, and 64% for TU.

The three remaining chemicals used as additives to leach chalcopyrite show similar behaviors with respect to the final extraction values for copper, and present noticeable differences with respect to apparent kinetics and leaching behavior during the experiment. During the first 48 hours of leaching, the curve for thiosemicarbazide presents a distinct behavior compared to the cases where ETC and SDMDTC were used.

The curves for these two reagents display an almost identical behavior and reach approx. 20% extraction within the first 8 hours, whereas the curve for TSC reaches approx. 12% within the same period. From 8 hours onward, the copper extraction curves for the three compounds behave almost linearly, where the extraction of copper increases throughout the rest of the period, until the three curves reach a final value of 37% extraction of copper at 96 hours.

Summarizing the results from this group of compounds as additives to enhance copper leaching from chalcopyrite, thiourea yields the highest extraction values compared to ferric sulfate without additives, followed by thioacetamide, SDMDTC, ETC, and TSC. The leaching curves for thioacetamide and thiourea follow a similar behavior through the experimental period,

nevertheless, both curves diverge at 12 hours of leaching and thiourea displays higher extraction values after 96 hours. SDMDTC and ETC also present a nearly identical leaching behavior with extractions of copper of approx. 37%.

Figure 11 displays the copper extraction curves for ferric sulfate leaching of chalcopyrite using six additional chemicals, which include certain thiourea derivatives, thiourea oxidation products, and other reagents with a slightly varied structure compared to thiourea, i.e., one chemical with two carbon-sulfur double bond groups, two thiourea oxidation products, and reagents which possess a carbon-oxygen double bond group (carbonyl group) instead of carbon-sulfur double bond groups (thiocarbonyl group). Figure 11 also includes the case without the use of additives for comparison purposes.

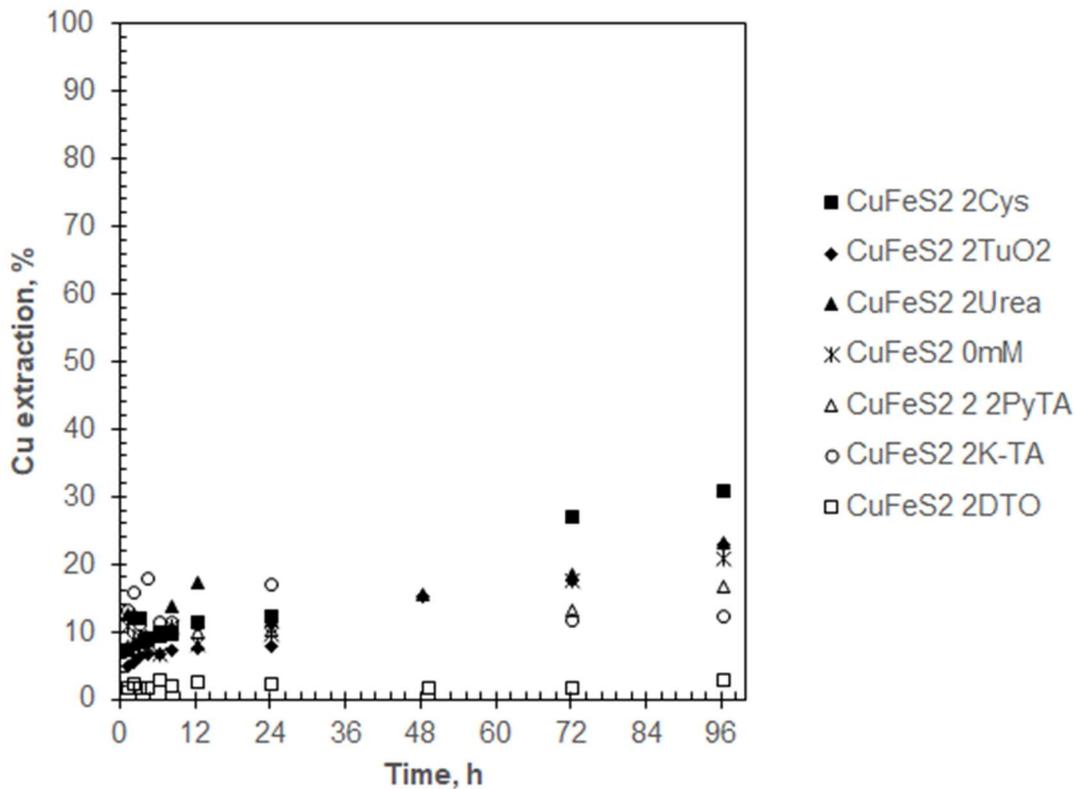


Figure 18. Effect of thiourea dioxide and “carbon-oxygen group” additives in ferric sulfate on copper extraction from high-purity chalcopyrite.

Ferric sulfate leaching of chalcopyrite without the use of additives reached approx. 20% copper extraction for a period of 96 hours, and in contrast to the previously studied group of chemicals, most of the compounds utilized in this series did not yield a significant and consistent enhancement or increase in copper extraction compared to the aforementioned case.

The two oxidation products of thiourea, urea and thiourea dioxide, which were used as additives to ferric sulfate leaching of chalcopyrite, do not appear to have a significant effect with respect to copper extraction, since the leaching curves and extraction values displayed in the experimental results are practically identical between these two chemicals and ferric sulfate without the use of additives.

For the case where potassium thioacetate was used as an additive, the leaching values displayed in the results are approx. 18% extraction of copper within the first 8 hours of leaching. These extractions were higher than the values obtained through ferric sulfate leaching without additives within the same period, however, as the experiment progressed and by the end of the leaching period, copper extraction did not increase further. The extraction reached at the end of the experiment for the potassium thioacetate case was approx. 16%, which is below the values obtained for urea, thiourea dioxide, and ferric sulfate without additives at the end of the leaching period.

The additives mentioned so far include a carbon-oxygen double bond group instead of a carbon-sulfur double-bond group in its structure, as is the case with thiourea. For the case of 2-pyridinethioamide, which does have a thiocarbonyl group, the values of copper extraction at the end of the leaching period were lower than the case where no additives were used in ferric sulfate, reaching approx. 14% and 20% respectively at 96 hours.

The reagent dithiooxamide was also used as an additive in ferric sulfate leaching, however, the values of copper in solution were lower than those obtained using ferric sulfate without additives. This can be attributed to the properties of dithiooxamide and a possible chelating effect with copper in solution.

From the results obtained from this experimental series, the additive that displayed a slight increase in copper extraction values by the end of the leaching period was cysteine, showing approx. 30% extraction of copper in 96 hours. The extraction curve for this reagent displayed a similar leaching behavior to the case without additives, with values of approx. 10% and 8% copper extraction respectively and diverging drastically from the 0 mM curve after 48 hours of leaching.

Considering the results obtained from the use of these various compounds as additives in ferric sulfate leaching of copper sulfides, most of the reagents that displayed a significant and consistent increase in copper extraction contained a single carbon-sulfur double bond group in their structure.

The majority of the reagents containing a carbonyl group did not present significant increases in copper extraction, with the exception of cysteine showing an additional 10% extraction after 48 hours of leaching. The compounds that showed the highest increase of copper extraction overall, compared to ferric sulfate leaching without additives, were thiourea and formamidine disulfide for all three high-purity copper sulfides, and by thioacetamide, for chalcopyrite and covellite.

The experimental results included in this section of the present study display that the enhancing effect of the additive compounds can be partially attributed the presence of a single thiocarbonyl group in the molecular structure of the chemical. Additionally, the stability of said chemical in acidic ferric sulfate solution is another necessary factor to consider, since any

enhancing effects in copper leaching can be hindered by a rapid degradation of the additive into other oxidation sub-products.

Considering the potential of the results obtained so far, in terms of the possibility of increasing the extraction of copper from three high-purity sulfide species considered refractory to ferric sulfate leaching, the following section of this study is focused on the use of thiourea in leaching low-grade copper sulfide ores in bottle roll leaching and small-scale leaching columns.

4.2.1 Effect of Thiourea in Low-Grade Copper Sulfide Ore Leaching.

The present section focuses on various experimental series in two different leaching configurations, bottle roll leaching and small-scale column leaching, using thiourea as an additive in ferric sulfate leaching of copper from low-grade copper sulfide ores. Table 1 includes the results of a quantitative phase analysis by X-ray diffraction (XRD) and Rietveld refinement of a low-grade ore denominated “Ore A”.

Table 3. Results of quantitative phase analysis by XPS-Rietveld for low-grade chalcopyrite ore "A"

Mineral	Ideal Formula	wt. %
Chalcopyrite	CuFeS_2	1.5
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	2.3
K-Feldspar	KAlSi_3O_8	17.9
Molybdenite	MoS_2	< 0.1
Muscovite	$\text{KA}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	21.9
Plagioclase	$\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$	13.6
Pyrite	FeS_2	2.3
Quartz	SiO_2	40.0
Rutile	TiO_2	0.4
Total		100

The results displayed in Table 3 indicate that the copper sulfide contained in this low-grade ore is chalcopyrite, with a significant amount of quartz and acid-consuming species. Because of this, prior to the leaching experiments, the ore was cured using concentrated sulfuric acid solution to dissolve any acid consuming material that would modify the pH of the leaching solution and precipitate the ferric sulfate; this step was also mentioned in the Experimental Methodology section.

Figure 12 displays the leaching results obtained from a series of bottle roll experiments using the acid cured ore “A” and a range of concentrations of thiourea from 2 to 10 mM in ferric sulfate solution, for a period of approx. 10 days (240 hours). The case of ferric sulfate leaching without additives was also included for comparison purposes.

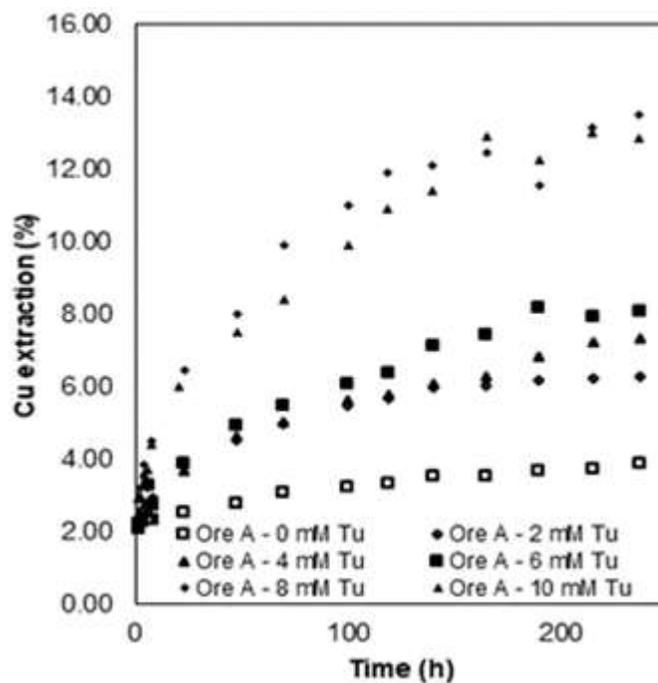


Figure 19. Effect of the addition of thiourea in ferric sulfate on copper extraction of low-grade chalcopyrite ore “A” in bottle roll leaching.

In a similar way as the previous results obtained from high-purity chalcopyrite, these leaching curves indicate that as the concentration of thiourea in ferric sulfate increases, the extractions of copper from the-low grade chalcopyrite ore increase as well. The higher copper extraction values in this bottle roll leaching series were obtained for the cases of 8 and 10 mM thiourea in ferric sulfate solution, reaching approx. 13% extraction by the end of the experimental period.

Both 8 and 10 mM curves display a similar leaching behavior throughout the entire leaching period, with a difference of approx. 0.5 – 1% extraction of copper between the two cases, with the case of 10 mM showing the slightly higher values of extraction. The curves for thiourea concentrations in the range of 2 – 6 mM also follow a similar extraction behavior between them, where the values for the case of 6 mM thiourea reach slightly higher values at approx. 8% extraction, compared to approx. 6.5 and 5.5% for 4 mM and 2 mM thiourea respectively.

Finally, the case of ferric sulfate leaching without the use of additives displays values of approx. 3% copper extraction by the end of the experimental period. The overall extraction values for all the cases of bottle roll leaching range between 3 – 13% extraction of copper, which are lower in comparison to the values obtained from the high-purity chalcopyrite experiments. This can be attributed to an effect of the ore interactions with thiourea and to a possibly less direct access to the chalcopyrite located within the ore.

Considering the results from the use of a broad range of chemicals, thiourea yields the highest and most consistent increase in the extraction of copper from all high-purity sulfides included in this study. From the broad range of concentrations of thiourea utilized so far, an addition of thiourea for 10 mM concentration in chalcopyrite leaching can be considered as the case yielding the greatest increase and most consistent leaching behavior in the case of copper

dissolution from chalcopyrite, with relatively good apparent leaching kinetics compared to ferric sulfate without additives.

The following small-scale column experiments utilize a concentration of 10 mM thiourea in ferric sulfate to assess its effect on low-grade ore leaching through extended periods of leaching. Figure 13 displays the leaching results for the low-grade chalcopyrite ore “A” in small scale column configuration, with and without the use of thiourea as an additive in acidic ferric sulfate.

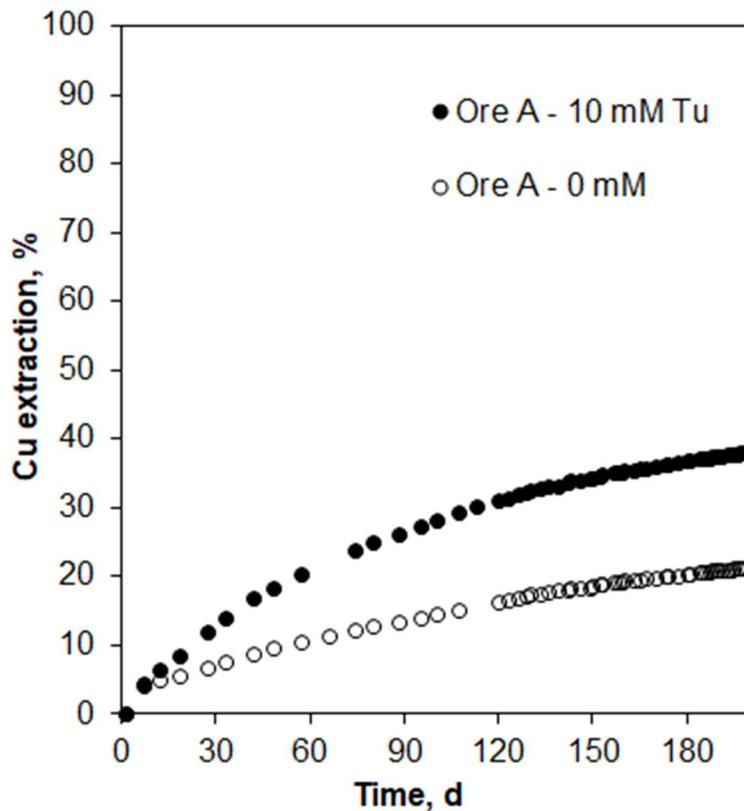


Figure 20. Effect of the addition of thiourea in ferric sulfate on copper extraction from low-grade chalcopyrite ore “A” in small-scale column leaching.

During the entirety of the leaching period, the chalcopyrite ore continuously received freshly prepared ferric sulfate solutions, with and without additives for each particular case, without recycling of the output solution. During an approx. 200-day period under the

aforementioned conditions, the addition of thiourea to the ferric sulfate solution displays an increase in the values of extraction of copper from the ore, compared to the case of ferric sulfate without additives.

By the end of the leaching period, the extraction curve for the ferric sulfate leach without the use of additives shows values of approx. 20% copper extraction from the chalcopyrite ore. The leaching curve for the case which had 10 mM thiourea concentration in the input leaching solution displays copper extraction values of approx. 38% within the same period as the case without additives.

These results represent an overall increase in the extraction of copper of approx. 1.9 times when a concentration of 10 mM is added to the ferric sulfate solution, compared to ferric sulfate leaching without additives. These results are considered to be in general agreement with what was previously observed for the cases of high-purity chalcopyrite in stirred tank leaching, with respect to the increase in the extraction of copper when thiourea is present in the solution.

The differences between the two cases can be attributed to the differences in the copper sulfide material and the leaching configuration utilized for both cases, as well as the interactions of thiourea with the low-grade ore during the leach.

With respect to the leaching behavior observed in the curves, Figure 14 displays the calculated daily leaching rates, expressed in mg of leached copper per day, for both small-scale column leaching experiments using “Ore A”, with and without the use of additives in the ferric sulfate leaching solution.

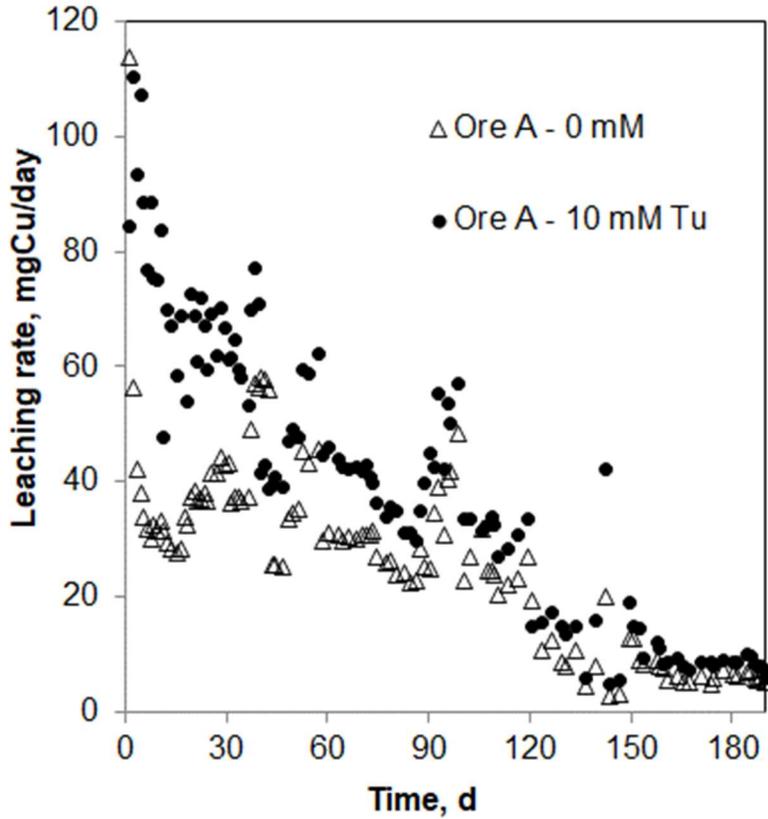


Figure 21. Effect of the addition of thiourea in ferric sulfate on daily leaching rate of copper from low-grade chalcopyrite ore “A” in small-scale column leaching.

These values displayed in Figure 14 were calculated using the copper concentration analysis from the extraction curves in Figure 13. During the first 100 days of the leaching period, the daily leaching rates for the 10 mM thiourea case reach higher values of extracted mg Cu/day compared to the case without the use of additives. The difference between the values obtained for the 10 mM case and the values for ferric sulfate leaching without additives range from 15 – 40 extracted mg Cu/day.

The leaching behavior for both cases, as shown on Figure 13 and Figure 14, displays a gradual decrease in the daily rates of copper extraction, reaching similar values by the end of the

experimental period. The increase in the values of copper dissolution and the overall behavior of the leach using 10 mM thiourea, is present through the entire leaching period, nevertheless, the leaching behaviors of both cases become increasingly similar during the latter half of the experiment, from approx. day 100 onward, and closer to the end of the leaching period, the differences between daily rates of copper extraction also decrease, reaching approx. 2 – 3 mg Cu/day in contrast to 15 – 40 mg Cu/day as previously obtained.

The increasing similarity in the leaching behavior for the cases with and without additives is also considered in general agreement with the results observed in stirred tank leaching of high-purity chalcopyrite, indicating that this enhancement in copper extraction in presence of thiourea in solution can yield larger differences in the apparent leaching kinetics during the initial stages of copper sulfide leaching. Potentially, the dosage of thiourea to the leaching solution could be adjusted to modify the degree of enhancement of copper leaching during long-term operations.

Considering the results obtained with ore “A”, a second low-grade chalcopyrite ore procured from a different mine site was also submitted to small-scale column leaching, in the same configuration as the previous experiments. Table 2 displays the results of a quantitative phase analysis by X-ray diffraction (XRD) and Rietveld refinement of a low-grade ore denominated ore “B”.

Table 4. Results of quantitative phase analysis by XRD-Rietveld for low-grade chalcopyrite ore "B".

Mineral	Ideal Formula	wt. %
Actinolite	$\text{Ca}_2(\text{Mg},\text{Fe}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	1.8
Biotite	$\text{K}(\text{Mg},\text{Fe}^{2+})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	4.2
Calcite	CaCO_3	19.3
Chalcopyrite	CuFeS_2	3.5
Clinocllore	$(\text{Mg},\text{Fe}^{2+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$	15
Diopside	$\text{CaMgSi}_2\text{O}_6$	3.5
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1.2
Hematite	$\alpha\text{-Fe}_2\text{O}_3$	0.2
K-feldspar	KAlSi_3O_8	10.8
Magnetite	Fe_3O_4	0.8
Muscovite	$\text{KAl}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	6
Plagioclase	$\text{NaAlSi}_3\text{O}_8 - \text{CaAlSi}_2\text{O}_8$	25.4
Quartz	SiO_2	8.3
Siderite	$\text{Fe}^{2+}\text{CO}_3$	0.1
Total		100

As it was the case with ore "A", the low-grade copper sulfide ore "B" contains several acid-consuming species such as actinolite and muscovite, and the only copper sulfide contained in this is chalcopyrite. Figure 15 displays the curves for copper extraction from the low-grade chalcopyrite ore denominated "B" in the exact configuration as performed with ore "A", including cases with 0 and 10 mM thiourea in ferric sulfate solution. This column leaching experiment was performed for approx. 300 days.

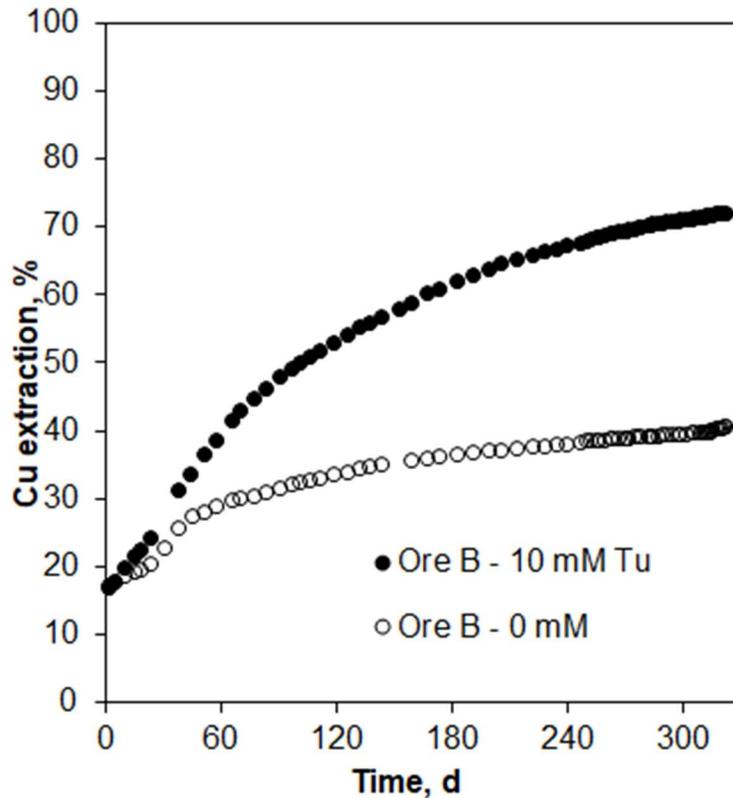


Figure 22. Effect of the addition of thiourea in ferric sulfate on copper extraction from low-grade chalcopyrite ore “B” in small-scale column leaching.

The leaching curves for the columns using ferric sulfate solution with and without the use of thiourea are displayed in Figure 15, where the case without the use of additives in ferric sulfate solution yielded approx. 35% extraction of copper after a 320-day leaching period.

The curve corresponding to the case where 10 mM thiourea concentration was used, the values obtained for copper extraction reached approx. 73% at the end of the 320-day leaching period. These values represent an increase in copper extraction of approx. 2.08 times for the 10 mM thiourea case compared to ferric sulfate leaching without additives, which is similar to the increase obtained for ore “A”.

These results indicate that the overall enhancing effect caused by the presence of thiourea in the leach is apparently not affected in a major way by the characteristics of the low-grade ore,

for the cases included in this study. With respect to the leaching behavior for both cases, with and without thiourea, Figure 16 displays the effect of thiourea on the daily leaching rate, expressed in mg of copper extracted per day, for the column leaching experiments for ore “B”, in a similar way as previously displayed for ore “A”.

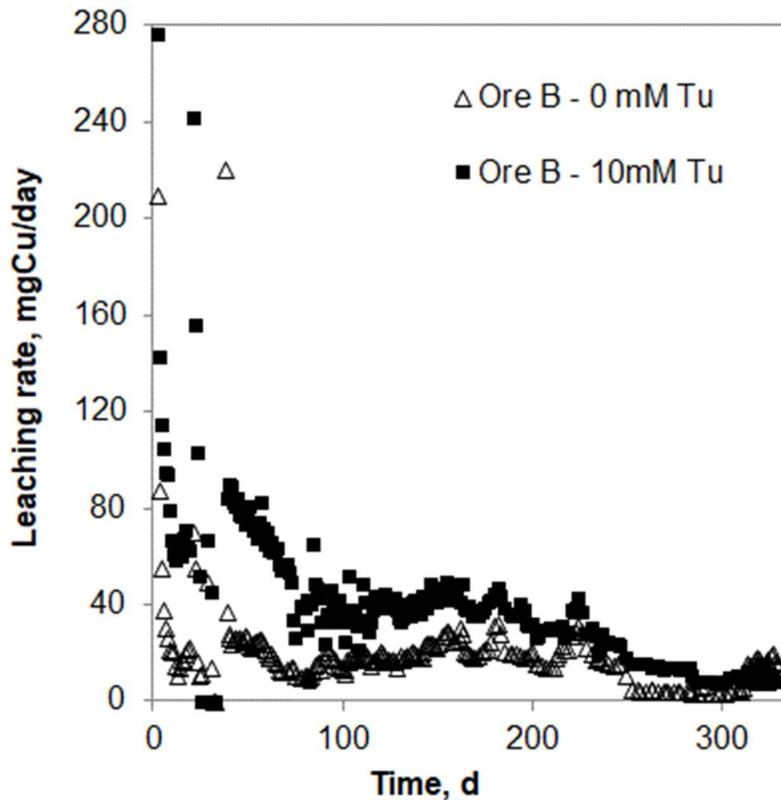


Figure 23. Effect of the addition of thiourea in ferric sulfate on daily leaching rate of copper from low-grade chalcopyrite ore “B” in small-scale column leaching.

The daily leaching rates for this experimental series also display the effect of a concentration of 10 mM thiourea in the ferric sulfate solution, yielding higher values of extracted copper per day compared to ferric sulfate solution without the use of additives. Figure 16 also displays distinct periods of leaching throughout the entirety of the experiment, with the highest

leaching rates for both experiments within the first 14 days; these can be attributed to the extraction of any copper that was partially dissolved during the acid curing of the ore.

Following this initial high extraction period, from day 14 to approx. day 85, the daily leaching rates for both experiments appear to decline at with a similar trend, although the values for the 10 mM thiourea case are constantly higher than the ones presented for ferric sulfate leaching without additives. The difference of the daily extraction rates between the two leaching experiments falls between the range of approx. 20 – 60 mg Cu extracted/day, in the period between 0 and approx. 85 days.

From approx. day 85 to day 220 the difference of daily leaching rates between 0 mM and 10 mM thiourea is lower in comparison to previous days, ranging between approx. 10 – 30 mg Cu extracted/day, and from day 220 towards the end of the leaching period, this difference gradually decreases until reaching values of approx. 5 – 10 mg Cu extracted/day. Even considering the increasingly similar leaching behavior between the two cases, the overall extraction values from the 10 mm thiourea column remain higher than the case without additives.

These results are also considered in agreement with previous observations obtained from low-grade ore “A” as well as the high-purity chalcopyrite leaching experiments in stirred tanks. The results from low-grade ore “B” confirm that the use of thiourea in ferric sulfate leaching can potentially increase the extraction of copper from sulfide ores.

A leaching experiment of low-grade chalcopyrite ore “A” was performed where four 30-cm leaching columns (S1, S2, S3, and S4) were arranged vertically and connected in series. The column located on the top (S1) received leaching solution directly from an input solution reservoir. the next column (S2) received the output solution from S1 by gravity and is fed into the ore inside the column. The output solution from column S2 feeds columns S3, and the process is repeated

from S3 to S4, and the output solution from column S4 is collected in a separate reservoir. This experiment was also conducted as an open-loop leaching experiment, where no recycling of the output solution was performed.

The solution in the input reservoir was freshly prepared ferric sulfate solution without additives for the initial weeks of leaching, and after this initial period, thiourea was added to achieve a concentration of 10 mM to feed the column system. This experiment was performed to assess if the enhancing effect of thiourea in the extraction of copper from the ore is affected by an increase in the depth of the ore bed, which is simulated by these four small-scale columns. The results obtained from this columns-in-series experiment are displayed in Figure 17.

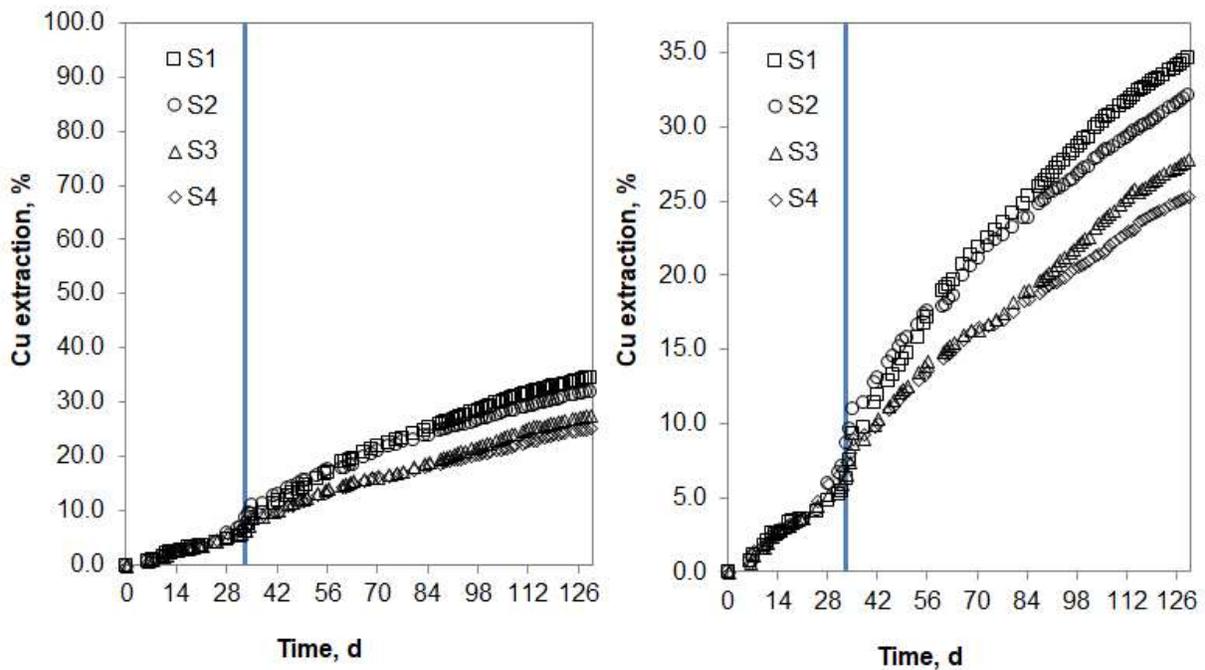


Figure 24. Leaching-in-series of four small scale columns using thiourea-ferric sulfate solution for copper extraction from chalcopyrite ore "A"; left: full-scale plot, right: magnified plot.

The plot on the left-hand side of Figure 17 uses a scale of 0 – 100% copper extraction to better comparison with previously obtained leaching results, and the plot on the right-hand side of the Figure has a scale of 0 – 38% to better represent the behavior of the leaching curves throughout the experiment. Figure 17 presents an individual leaching curve for each individual small-scale column segment, to better assess the behavior of the leach.

As aforementioned, the leaching-in-series of these four columns was initially conducted using ferric sulfate solution without additives. During this period, from day 1 to approx. day 32, the four curves displayed nearly identical leaching behavior, reaching approx. 5% copper extraction within this period. Thiourea was added to the input leaching solution at approx. day 32 of the experiment, which is indicated by a vertical line in Figure 17.

In the following week after the addition of thiourea, the values of copper extraction gradually increased from approx. 5% to approx. 9% copper extraction in the four leaching columns, and from approx. day 32 to day 84, the overall leaching values of the four columns presents an increase in comparison to previous extractions without additives.

During the period from approx. day 32 to day 84, the leaching curves for the top two columns (S1 and S2) diverge from the bottom two columns (S3 and S4), where S1 and S2 reach approx. 23 – 24% copper extraction respectively, and the bottom two columns display values of 17 – 18% extraction. Additionally, the leaching behavior of the curves for columns S1 and S2 are almost identical, as is the case between the behavior of the curves for the bottom two sections.

Finally, from approx. day 84 to the end of the experiment, the leaching curve corresponding to column S1 separates itself from the S2 leaching curve, reaching slightly higher values at approx. 34% extraction of copper by the end of the experimental period, compared to 31% obtained from S2 at the same period. Considering the bottom two sections of the experiment, the leaching

behavior of S3 also separates slightly from the curve of S4, reaching approx. 26% and 23% extraction of copper respectively by the end of the leaching period.

Considering the results displayed on the leaching curves on Figure 17, after the addition of thiourea to the ferric sulfate solution to achieve 10 mM, the leaching behavior of the four segments shows an increase in copper extraction compared to those obtained using ferric sulfate without additives. As the leach progresses, this enhancing effect is gradually affected as the solution travels through each of the four columns.

The top column S1 receives freshly prepared thiourea-ferric sulfate solution from the input reservoir and presents the highest copper extraction values of the four segments, and the values of copper extraction decrease slightly for each subsequent column segment. This can be attributed to a certain degree of adsorption of the thiourea in the input solution to the low-grade ore within the top column segments, where the remaining segments do not display a similar degree of copper extraction enhancement as the segments receiving fresh solution.

Considering the results from Figure 17, the daily leaching rates of copper extraction for each individual segment of the leaching experiment are displayed in Figure 18, shown in a similar way as previously done with the single small-scale column experiments. The effects of the addition of thiourea are displayed to the right of the vertical line, as displayed before in Figure 17.

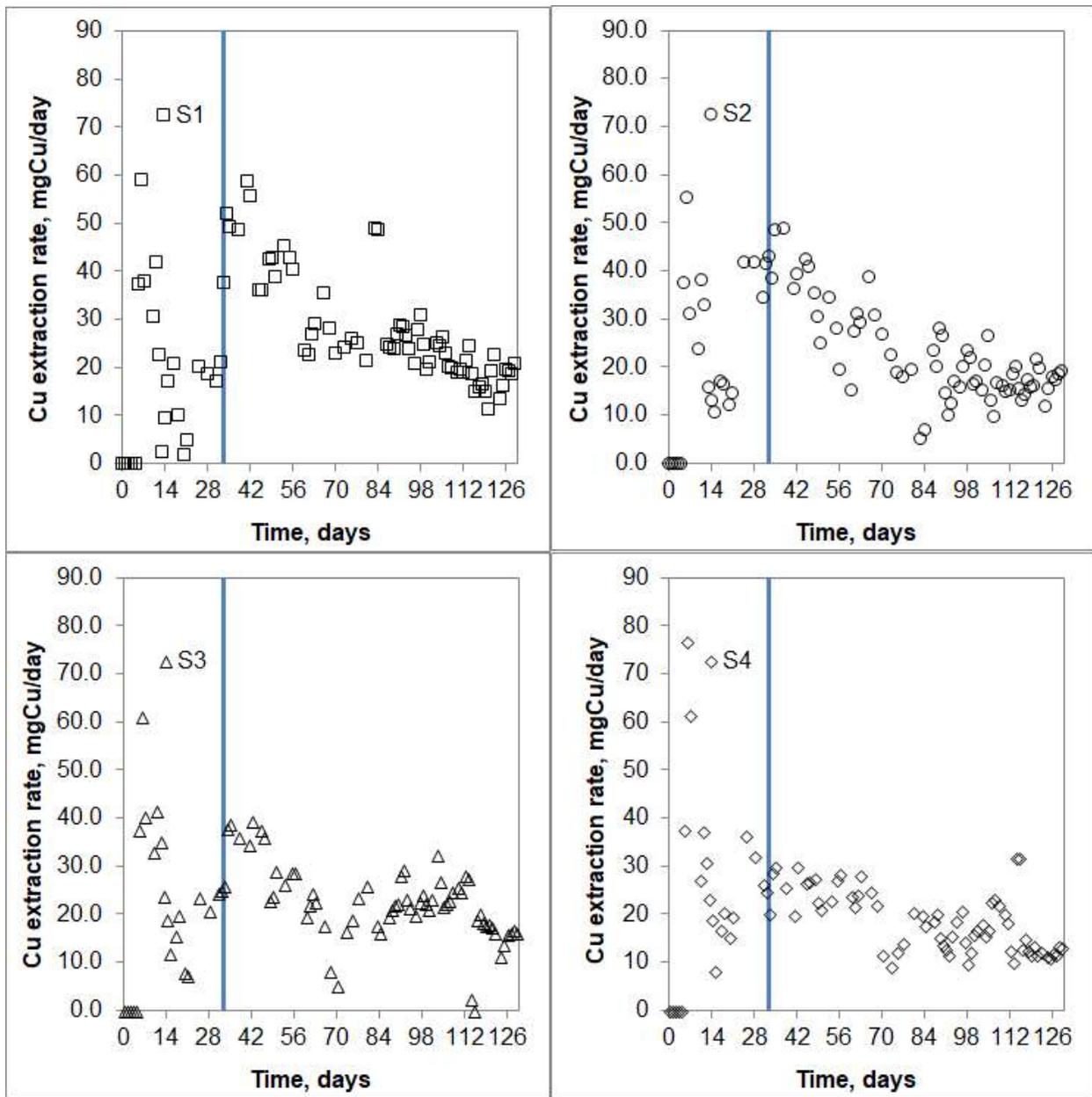


Figure 25. Daily leaching rates of copper from chalcopyrite ore “A” in the individual segments of the leaching-in-series experiment.

From the start of the experiment until approx. day 32, the daily leaching rates for the four columns follow a similar behavior, where a significant amount of copper is dissolved from the ore during the first few days of leaching, due to copper previously dissolved during acid curing.

As the leaching progresses and prior to the addition of thiourea to the leaching solution, the daily leaching rates for the four column segments follow a similar trend, displaying a gradual decrease in copper extraction in comparison to the first few days of leach. The four segments start to present key differences following the addition of thiourea to the feed solution.

For segment S1, the daily leaching rates reach a maximum value of 59 mg Cu/day after thiourea addition, followed by a steep decrease to approx. 30 mg Cu extracted/day, within the period from approx. day 42 to day 60 of leaching. Segment S2 presents a maximum daily leaching rate of 50 mg Cu/day after the addition of thiourea and within the aforementioned period, the rate also decreases, reaching values closer to approx. 26 mg Cu/day.

Considering the remaining to sections, column S3 presents 40 mg Cu/day maximum and also show a decrease reaching approx. 20 mg Cu extracted /day; the decrease for column S3 is considered gradual in comparison to the steep decreases in the top sections. Finally, for segment S4, the curve displays maximum extractions of approx. 30 mg Cu/day, and the apparent trend of these leaching rate values does not show a decrease as notorious as the previous cases, ranging at approx. 24 mg Cu/day.

The four segments received the same feed solution and were connected in series as aforementioned and based on the results on Figures 17 and 18, the enhancing effect of thiourea becomes diminished as the solution travels from one segment to another. This behaviour can be attributed to a partial degradation of the thiourea in the input solution as it contacts the low-grade ore, travelling through a simulated larger ore bed size.

A possible adsorption of the input thiourea onto the ore could also occur within the first two segments, causing lower concentrations of the chemical to reach the bottom two segments of the column-in-series experiment. Taking these results into consideration, the option of increasing

the concentration of thiourea in the input ferric sulfate solution can be considered as a possible process route to maintain significant enhancements in the extraction of copper for all the low-grade ore, without reaching excessive thiourea concentrations that lead to hindering this effect, as previously displayed in the high-purity chalcopyrite results.

Summarizing the results obtained from this section, the use of thiourea in ferric sulfate can increase the values of copper extraction in small-scale column leaching of low-grade ores. The cases where thiourea was used in solution display an increase in copper extraction by a factor of approx. 1.9 – 2.08 compared to ferric sulfate leaching without additives, which is considered in general agreement to the results obtained for the case of high-purity chalcopyrite, covellite, and chalcocite species in stirred tank leaching.

Two low-grade ores from different mine sites were submitted to leaching experiments to assess the effect of thiourea on copper extraction, and the extraction values from both ores were increased in the cases where thiourea was used. Nevertheless, the enhancing effect of thiourea can be affected by the depth of the leaching ore bed as displayed by the column-in-series experiment previously shown.

The thiourea in the ferric sulfate leaching solution can possibly undergo a degree of degradation as the solution travels through the ore bed, causing that the extraction from the ore particles located within deeper levels of the bed displays a reduced level of extraction enhancement compared to the particles receiving the solution at the surface of the bed. Additionally, a portion of the thiourea can possibly adsorb to the ore particles located at shallow levels of the bed, also affecting the extraction enhancement of the particles within the bed.

As a general summary of the results obtained for all cases included in this study, thiourea and other organosulfur compounds with similar structures can assist and enhance the values of copper extraction when used as additives in the ferric sulfate leaching of three copper sulfides.

The copper sulfide species chalcopyrite, covellite, and chalcocite are considered refractory to ferric sulfate leaching to a varying degree, and the use of organosulfur compounds such as thiourea, formamidine disulfide, and thioacetamide, can increase the values copper dissolution from these sulfides to a varying degree as well, as shown through stirred tank leaching experiments of high-purity copper sulfide species.

From the range of additives presently studied, the compounds which yield consistent and significant enhancement of copper extraction contain a single thiocarbonyl group in their structure and are considered relatively stable in acidic ferric sulfate solution.

The enhancing effect of thiourea displayed in stirred tank leaching of high-purity copper sulfides is also displayed in the results obtained from bottle roll leaching and small-scale column leaching of low-grade chalcopyrite ores.

The low-grade ore leaching results over extended periods are considered in general agreement with the results obtained from stirred tank leaching of high-purity chalcopyrite, with a few differences that can be attributed to the use of different materials in the leach, i.e. coarse sulfide ore and high-purity powdered sulfide, and the interactions of thiourea with the ore particles as the solution travels through the ore column.

Considering results from the experiment simulating larger ore depths, the enhancing effect of thiourea in copper extraction is indeed affected in a certain degree by the depth of the ore bed, where the enhanced extraction gradually decreases as the solution travels deeper through the ore,

which can be possibly attributed to partial degradation of thiourea in the solution, as well as thiourea adsorption to the ore particles.

Finally, this assisted dissolution of copper from refractory sulfides in ferric sulfate leaching solution using organosulfur compounds such as thiourea is considered as a technique with the potential to be further researched and implemented in copper extraction operations in the future, due to its relative simplicity and use of slight modification to a well-established technology such as ferric sulfate leaching.

An increase in the extraction of copper as displayed in the results included in this study can be considered as highly beneficial for current copper hydrometallurgical operations, which can justify the aforementioned research and further development of this technology.

Chapter 5: Conclusions

The use of low concentrations (0.02 – 20 mM) of thiourea in acidic ferric sulfate leaching solutions produce significant increases in the extraction of copper from chalcopyrite, covellite, and chalcocite. This increase in copper extraction is displayed in various cases using high-purity copper sulfide species and low-grade copper sulfide ores, in stirred tank, bottle roll, and small-scale column configurations.

From the copper sulfide species included in the present study, the sulfide that showed the highest increase in extraction of copper in ferric sulfate leaching with thiourea was covellite, followed by chalcopyrite, and finally chalcocite.

Stirred tank leaching of high-purity covellite using a concentration of 2 mM of added thiourea displayed an increase of approx. 9 times the extraction of copper compared to ferric sulfate leaching without the use of additives.

Thiourea as an additive for high-purity chalcopyrite leaching under the same conditions as covellite yielded 3.25 times higher copper extraction than ferric sulfate leaching. The corresponding values for the case of chalcocite were 1.33 times higher extractions of copper compared to the case without additives.

The addition of certain compounds with structures similar to thiourea also yielded an increase in the extraction of copper from copper sulfides. The compounds that show a significant increase contain a single carbon-sulfur double bond functional group, such as thioacetamide, and formamidine disulfide, an oxidation product of thiourea.

From the series of reagents considered in this study, most of the compounds with a carbon-oxygen double bond group, such as thiourea dioxide and urea, did not present significantly higher copper extractions. One exception for this functional group was the case of cysteine in the leaching

of high-purity chalcopyrite, displaying an approx. 10% additional copper extraction compared to ferric sulfate leaching without additives.

With respect to long-term open-loop column leaching experiments of copper sulfide ores, considering the results from the start of the experiments until an extraction plateau was reached, various leaching behaviors were observed.

During the initial period of open-loop leaching, corresponding to approx. 25% – 30% of the total experimental period, the average of the differences of the daily leaching rates between using ferric sulfate solution with and without additives was approx. 20 – 35 extracted mgCu/day for chalcopyrite ores “A” and “B”.

A second leaching period is observed following the aforementioned behavior, corresponding to approx. 30% – 45% of the total experimental period, where the difference of leaching rates between 0 and 10 mM thiourea concentration decreases to approx. 5 – 15 extracted mgCu/day.

Finally, within the remaining 30% – 40% of the leaching period, the difference between the daily leaching rates further decreases until reaching approx. 0.9 – 4.8 mgCu/day, indicating that the increase in the extraction of copper using thiourea in column leaching varies with respect to time in the cases presented in this study.

Considering the four-column leaching-in-series experiment simulating larger ore bed height/depth, the effects of the use of 10 mM thiourea concentration present certain variations throughout the four column segments.

Considering the behavior of chalcopyrite ore “A” in the single-column case with and without additives (33% and 15% copper extraction respectively), all segments in the leaching-in-series experiment present a degree of increase when a 10 mM thiourea concentration is used in the

input solution, however, as this solution travels through each segment, the increase in copper extraction compared to the case without additives decreases by around 3 – 5% per segment, reaching approx. 34% in the top segment S1, 31% in the following S2, 26% in S3, and 23% in S4.

This behavior is also noticed in the daily leaching rate values for each individual segment, indicating that even when an increase in copper extraction is still observed when using thiourea as an additive (compared to the case without additives), the effects of the additive are apparently influenced by the passing of the leaching solution through several columns of low-grade ore.

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