FUNDAMENTAL ASPECTS OF THIOSULFATE LEACHING OF SILVER
SULFIDE IN THE PRESENCE OF ADDITIVES

by

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B.Sc., University of Alberta, 2010

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

January 2012

Abstract

Thiosulfate is a promising alternative for leaching silver sulfide ores such as those at the epithermal Yanacocha deposit. These ores suffer from low silver recovery, high mercury extraction and environmental challenges when treated with conventional cyanide. In this study, cupric-ammonia, ferric-ethylenediaminetetraacetic acid (EDTA), ferric-oxalate and ferric-citrate are tested with thiosulfate in a series of rotating disk experiments with silver sulfide and with ore from Yanacocha. This thesis publishes experimental evidence that supports the use of thiosulfate with different additives as a potential alternative to conventional cyanidation for silver sulfide leaching.

The leaching of silver sulfide by cupric-ammonia thiosulfate can occur either by the substitution of cupric or cuprous for silver. The cupric catalyzed reaction is favored due to a thermodynamic barrier to the cuprous reaction. Rotating disk experiments demonstrate that cupric-ammonia leaching is under mixed chemical/diffusion control. The leaching rate is maximized by stabilizing cupric in solution with ammonia and increasing the availability of thiosulfate for silver dissolution. The addition of EDTA to this system decreased the leaching rate of the silver sulfide disk by lowering the cupric reactivity, but accelerated silver leaching of the ore, likely due to the prevention of passive oxide film formation on sulfides.

Ferric complexes used were found to be very unreactive towards thiosulfate, but are reduced by sulfides present in the ore. Ferric-EDTA was the most effective oxidant of the three for leaching silver sulfide with thiosulfate. Silver recovery of the ground ore in batch leaching tests is low due to quartz locking of silver, with cupric-ammonia and ferric-EDTA leaches
exposed to air recovering 31% and 26% after 24 hours, respectively. Cyanidation recovered 34% silver with a 95% confidence interval of 28-37%. The slightly lower recovery by thiosulfate may be due to silver minerals which are not amenable to thiosulfate leaching.
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List of Symbols and Abbreviations

Standard SI units (or multiples of) and International Union of Pure and Applied Chemistry (IUPAC) approved abbreviations were used wherever possible. In the case where the norm in scientific literature in the field is the use of alternative units (ie: cm), these are used. A list of major symbols and abbreviations used:

Acronyms and Abbreviations
AAS – atomic absorption spectroscopy (technique) or atomic absorption spectrophotometer (machine)
ATS – ammonium thiosulfate
EDTA – ethylenediaminetetraacetic acid
RPM – revolutions per minute
SHE – standard hydrogen electrode
UV-vis – ultraviolet visible spectroscopy (technique) or ultraviolet visible spectrophotometer (machine)
XRD – x-ray diffraction

Roman Letters
A – absorbance (of light) or frequency factor (for Arrhenius equation)
C_a or c – concentration, or concentration of reactant a (M)
D_a – diffusivity of a or diffusion coefficient of a (m²/s)
E⁰ – standard reaction potential (V)
E_a – activation energy (kJ/mol)
ΔG⁰ – standard Gibbs free energy change at 25°C (kJ/mol)
ΔH⁰ – standard enthalpy change at 25°C (kJ/mol)
J_a – molar flux of reactant a (mol/m²/s)
I – light intensity
l – path length that light travels (cm)
N_Re – Reynolds number
P80 – 80% quantile for a particle size distribution
R – gas constant (8.314 J/mol/K)
r – radius (m)
S⁰ – entropy (valid at 25°C) (J/mol/K)
$t$ – time (units vary) or, when used as a unit: tonne (1000 kg)

$T$ – temperature ($^\circ$C or K)

$T_m$ – melting point ($^\circ$C)

**Greek Symbols**

$\alpha$ – molar absorptivity (M/cm)

$\beta$ – stability constant of a complex in solution

$\lambda$ – wavelength (nm)

$\mu$ – viscosity (Pa s)

$\nu$ – kinematic viscosity ($m^2/s$), equal to the solution viscosity divided by solution density

$\rho$ – density ($kg/m^3$)

$\omega$ – angular velocity (rad/s), equal to $2\pi/60$ times the rotation speed in RPM
Acknowledgements

I would like to thank my advisor, Dr. David Dreisinger, for the guidance provided throughout my degree and the many helpful discussions which form the basis of this thesis. Your talent and passion for hydrometallurgy is inspiring.

Thank you to Dr. Bé Wassink for patiently assisting me with my analytical techniques and answering my numerous chemistry questions. The advice of Marc LeVier, Meg Dietrich and Dr. Matthew Jeffrey at Newmont in developing the experimental test program and providing feedback on results is greatly appreciated. The assistance of my fellow graduate students in the Hydrometallurgy Group is much appreciated, especially Joon Lee for his help with experimental work and many discussions. Suggestions by my examining committee, Dr. David Dixon, Dr. Edouard Asselin and chair Dr. Warren Poole are gratefully acknowledged.

In addition, thank you to the Natural Sciences and Engineering Research Council of Canada, Dr. Dreisinger, the Department of Materials Engineering at UBC, and Newmont Mining for providing the financial assistance necessary to undertake this thesis.

I would like to thank my parents, Clayton and Pauline Deutsch for their encouragement throughout my studies. This would not have been possible without your support.

Finally, I am incredibly grateful to my wife, Kelsey, for her support, patience and love throughout my studies. Thank you.
Chapter 1: Introduction

Concern about the environmental impact of cyanidation and the rising silver price has generated significant interest in alternative processes for the hydrometallurgical treatment of primary silver ores. These ores often contain large amounts of silver sulfide. Ores which may be amenable to gold cyanidation, such as the epithermal gold/silver deposit at the Peruvian Yanacocha mine, can suffer from limited silver extraction when process optimization is driven by gold recovery. Increasing cyanide concentration will increase silver extraction; however it also increases mercury dissolution and environmental risks (AMTEL, 2010; Dreisinger, 2010). Thiosulfate, a promising alternative to cyanide which has been historically used for silver leaching in the Patera process (Fleming, 2007c), is receiving increased attention in the literature. The application of thiosulfate to the leaching of silver sulfide with a number of oxidants is the focus of this thesis.

The cupric-ammonia catalyzed system is the most widely investigated thiosulfate system (Abbruzzese et al., 1995; Flett et al., 1983; Zipperian et al., 1988). This system can rapidly leach gold and silver (Molleman and Dreisinger, 2002); however thiosulfate quickly degrades to tetrathionate and trithionate in the presence of cupric species or oxygen (Ahern, 2005). For this reason, alternatives to the cupric-ammonia complex including ferric ethylenediaminetetraacetic acid (EDTA) (Feng and van Deventer, 2010) and ferric oxalate (Chandra and Jeffrey, 2005) are being actively researched. These studies are almost all aimed at increasing metallic gold and silver recovery. With the exception of two studies (Briones and Lapidus, 1998; Flett et al., 1983), the leaching of silver sulfide with thiosulfate solutions has not been researched extensively. The studies by Briones and Lapidus and Flett et al. did
not apply the results of their investigations to a silver sulfide bearing ore, so data on extractions from naturally occurring silver sulfide is limited. In addition, there is no published data on the use of ferric EDTA or ferric oxalate instead of cupric-ammonia for silver sulfide leaching.

In this thesis a fundamental hydrometallurgical study of cupric-ammonia catalyzed thiosulfate leaching of silver sulfide is undertaken. Using a rotating disk of synthetic silver sulfide, the effects of reagent concentrations, rotation speed, temperature and pH are each investigated separately with a high degree of reproducibility. Of these variables, thiosulfate concentration, cupric concentration and solution pH have the greatest effect on the silver sulfide leaching rate. Promising alternatives to the cupric-ammonia system are also tested including ferric EDTA, ferric oxalate and ferric citrate. Of these alternatives, ferric oxalate and ferric EDTA are the most promising alternatives although both require a higher molar concentration than the cupric complex to achieve reasonable leaching rates. The results of the pure silver sulfide leaching studies are applied to leaching a silver sulfide ore from Yanacocha. Silver recovery with the cupric-ammonia thiosulfate system was 31% and 26% with ferric-EDTA. These systems were found to be the most promising for commercial application.

The remainder of this thesis is divided into four chapters which: cover the relevant background information (Chapter 2), analyze and discuss the results of a series of rotating disk studies using thiosulfate (Chapter 3), apply these results to a silver sulfide ore (Chapter 4) and provide conclusions and recommendations for future work (Chapter 5).
Chapter 2: Background and Literature Review

2.1 Silver and Society

2.1.1 Historical Uses of Silver

Silver has been known and used by society for millennia. In ancient times, most silver was mined and cupelled from lead ores after its discovery circa 2500 BCE (Patterson, 1972). Gold and silver metallurgy further developed in the Balkan Peninsula. During this time period, silver was used for decorative works and coinage due to its scarcity, luster and ease of workability. Historical world silver production peaked during 50 BCE to 100 CE with an average silver production of 200 tons per year before falling to 25 tons per year around 300 CE (Patterson, 1972). Patterson estimates that world stocks of silver fell from 10,000 to 1,300 tons during this same time period. Much of the silver loss in this time frame, from unfound caches to ships sinking and wear of coins is thought to have been converted to silver salts where it was lost. Silver production was low during medieval years, but still saw use as coins, cutlery, jewelry and decorative works.

2.1.2 Modern Uses of Silver

More recently, the US Geologic Survey estimates that annual world silver production of 5,400 tons in 1900 has since increased to 21,800 tons in 2009 (USGS, 2010). The largest silver producing countries are Mexico, Peru, China and Australia. Primary silver (silver from precious metal ores, not byproduct silver) accounted for 30% of world production (TSI, 2010). Silver was used in the United States for coins before it was phased out with the Coinage Act in 1965. Since then, silver has been used for photography, jewelry, dentistry, mirrors, catalysts, electronic and medicinal purposes. Recent developments have seen nanocrystalline silver being used to accelerate burn treatments due to its toxicity towards bacteria.
The rise in non-traditional uses for silver has led to the development of non-traditional hydrometallurgical operations such as “urban mining” applications focused on recovering silver from consumer waste and the treatment of extremely dilute streams such as waste water.

These non-traditional operations often rely on novel separation techniques based on solvent extraction or highly selective membranes. Solvent extraction techniques using calix[n]arenes have been considered for recovering silver from waste photographic solutions (Paiva, 1993; Paiva, 2000); however the high cost of synthesizing the reagents has made it impractical for commercial use to date. Highly selective membranes impregnated with macrocyclic molecules such as Kryptofix 22 DD have been proposed to treat very dilute waste streams (Stankovic et al., 2008; Tromp et al., 1988). Issues with the high cost of reagents and development of a robustly engineered membrane still need to be addressed before these techniques are implemented commercially.

2.2 Silver Production

2.2.1 Byproduct Silver

The majority of silver (70%) is produced as a byproduct of the production of base metal ores including lead, zinc and copper (TSI, 2010). For base metal ores treated by pyrometallurgical processes, silver is recovered during smelting operations. Copper smelter products may contain some silver which can be recovered during electorefining. The silver can be extracted using a pyrometallurgical route such as the Parkes process in which silver dissolved in liquid lead is extracted into liquid zinc. The immiscible liquid zinc is poured off of the lead and volatilized leaving behind a silver residue.
2.2.2 Silver Leaching with Cyanide

The low grade of many primary silver and gold ores has made cyanide leaching a popular method for the hydrometallurgical production of primary silver. The cyanidation process was patented in the late 1880s by McArthur, Forrest and Forrest following the establishment of the widely cited Elsner equation in 1846 (Fleming, 2007a). The Elsner equation governs the stoichiometry of metallic gold and silver leaching by cyanide in the presence of oxygen. The leaching stoichiometry is in agreement with the Elsner equation; however it is generally accepted that leaching proceeds through an intermediate rate determining step with a peroxide intermediate.

\[
4 \text{Au} + 8 \text{CN}^- + \text{O}_2 + 2 \text{H}_2\text{O} = 4 \text{Au(CN)}_2^- + 4 \text{OH}^{-}
\]

\[
4 \text{Ag} + 8 \text{CN}^- + \text{O}_2 + 2 \text{H}_2\text{O} = 4 \text{Ag(CN)}_2^- + 4 \text{OH}^{-}
\]

Recovery of the gold and silver in solution is generally by the Merrill-Crowe process (cementation on metallic zinc powder) or adsorption on activated carbon. The cyanidation of gold and silver has a number of recognized issues including the slower leaching of silver compared to gold (Hiskey and Sanchez, 1990) and the high toxicity of cyanide. For the treatment of the epithermal sulfidic gold/silver ore at Newmont’s Yanacocha mine (the ore treated in the case study, Chapter 4: Application to Mercury Bearing Silver Sulfide Ore), silver recovery is extremely low. The low recovery of silver combined with the large amount of mercury extracted by increasing the amount of cyanide used makes the investigation of alternative leaching chemistries attractive for this deposit.

2.2.3 Silver Leaching with Thiosulfate

The leaching of silver sulfide with thiosulfate has historically been used as a follow up to the Patera process in which a gold and silver bearing ore was processed using a chloridizing
roast (Flett et al., 1983). Silver leaching with thiosulfate is still conducted in areas of Mexico (Dreisinger, 2011) although the majority of silver ores are now leached with cyanide. Many strategies have been taken for leaching silver sulfide with thiosulfate, each utilizing different additional reagents and conditions. The cupric-ammonia catalyzed system has been the most commonly studied system because of its ability to leach gold, silver and silver sulfide (Aylmore and Muir, 2001; Briones and Lapidus, 1998; Flett et al., 1983). Current methods for leaching silver sulfide with thiosulfate will be investigated in great detail in Section 2.4: Cupric-Ammonia Thiosulfate Leaching.

2.2.4 Alternative Silver Leaching Processes

Alternative chemistries to cyanide and thiosulfate have been considered for gold and silver leaching. Thiourea (Almeida and Amarante, 1995; Balaz et al., 1996; Eisele et al., 1988), thiocyanate (Fleming, 2007c; Yang et al., 2010) and chloridization (Almeida and Amarante, 1995; Dutrizac, 1994; Fleming, 2007c) have all been considered as alternatives.

Thiourea (CS(NH$_2$)$_2$) can be used as a silver lixiviant in an acidic environment. The reaction of silver complexation as given by Balaz et al. (1996):

$$\text{Ag}^+ + 3\text{CS(NH}_2\text{)}_2 = \text{Ag}[\text{CS(NH}_2\text{)}_3]^+$$

A rotating disk study by Pesic and Seal (1990) indicates that metallic silver leaching by thiourea will only proceed in the presence of ferric ions and is highly dependent on the concentration of ferric. Increasing the amount of ferric sulfate in solution too high will cause passivation of the silver surface by the formation of a solid silver thiourea complex. When applied to leaching ores by Almeida and Amarante (1995), thiourea was found to not be an economical lixiviant.
Thiocyanate (SCN\textsuperscript{−}) is another potential lixiviant for silver extraction (Fleming, 2007c; Yang et al., 2010). Thiocyanate complexes silver ions as a number of complexes depending on the solution conditions:

\[
\text{Ag}^+ + n\text{SCN}^- = \text{AgSCN}_n^{1-}
\]

Silver leaching was accomplished in an autoclave under a large pressure of oxygen with the addition of ferric sulfate and a large amount of ammonium thiocyanate at temperatures greater than 80°C and a pH of ~1.6 by Yang et al. (2010). Like the thiourea system, more fundamental work needs to be conducted on the thiocyanate system before it can be considered a candidate for commercial silver leaching operations.

The chloride system has been demonstrated to effectively leach silver in an acidic environment with ferric and chloride in solution (Dutrizac, 1994) and even without ferric in the presence of a large amount of chloride at elevated temperatures (Almeida and Amarante, 1995). Although AgCl is extremely insoluble (only a few g/L even at 100°C), it can be dissolved by excess chloride as (Dutrizac, 1994):

\[
\text{AgCl} + 3\text{Cl}^- = \text{AgCl}_4^{3-}
\]

When leaching silver sulfide, ferric chloride leaching left behind a permeable sulfur layer on the surface that grew in thickness as leaching of the rotating disk used progressed (Dutrizac, 1994). The chloride system has potential to effectively leach gold and silver (Jeffrey et al., 2001), however the large amount of reagents necessary and high temperatures required restrict the economic viability of the system for low grade silver ores.
There are many potential silver leaching systems. Out of necessity, this thesis focuses solely on the application of the thiosulfate system to pure silver sulfide (acanthite) and the silver sulfide bearing ore at Yanacocha.

2.3 Silver Sulfide: Mineralogy and Occurrence at Yanacocha

2.3.1 Mineralogy

Silver sulfide (Ag₂S) is a covalently bonded material that exists in one of three solid crystal structures depending on the temperature (Tₘ = 825°C). The low temperature mineral, acanthite, has a monoclinic crystal structure (Anthony et al., 1994-2010; Ramsdell, 1943) while the high temperature form, argentite, has a cubic structure. Another high temperature face centered cubic structure may form at very high temperatures (above 586°C). The transformation between the argentite and acanthite is immediate upon cooling below 173°C (Anthony et al., 1994-2010). As acanthite is the only stable form of silver sulfide at most temperatures of interest in hydrometallurgy, silver sulfide and acanthite are used interchangeably in the literature (and for the duration of this thesis). Historically, argentite has also been used interchangeably with these terms although it has been conclusively demonstrated that argentite does not exist at low temperatures (Anthony et al., 2005; Ramsdell, 1943).

Mineral acanthite contains between 86.4 and 87.2% silver and between 12.0 and 12.94% sulfur when measured by electron microprobe. Acanthite is a dark black mineral with a metallic luster which exhibits no distinct cleavage planes (Anthony et al., 1994-2010). This mineral occurs in low temperature hydrothermal intrusive sulfide deposits and readily associates with other hydrothermal sulfide minerals and silver minerals. Common
associations include iron oxides (Fe\(_x\)O\(_y\)), barite (BaSO\(_4\)), chalcopyrite (CuFeS\(_2\)), pyrite (FeS\(_2\)), galena (PbS) and quartz (SiO\(_2\)). In the case of Yanacocha, acanthite has also been found with enargite (Cu\(_3\)AsS\(_4\)), covellite (CuS), digenite (Cu\(_9\)S\(_5\)), tennantite (Cu\(_{12}\)As\(_4\)S\(_{13}\)), sphalerite ((Zn,Fe)S) and a small amount of imiterite (Ag\(_2\)HgS\(_2\)) (AMTEL, 2010; Briggs, 2005). The large number of minerals with which acanthite will associate can cause problems for leaching operations. Fine grained dispersed acanthite may be entirely encapsulated by iron oxides, barite, quartz or other minerals. Other sulfide minerals can react with cyanide and alternative lixiviant (Fleming, 2007b; Xie, 2006) by pre-robbery or consuming reagents. Imiterite may be leached for both silver and mercury causing downstream issues with mercury waste management and poisoning of activated carbon in cyanidation processes.

### 2.3.2 Geology of Yanacocha

The ore used in the case study of this thesis (Chapter 4: Application to Mercury Bearing Silver Sulfide Ore) was provided by Newmont Mining Corporation from their Yanacocha mine. Yanacocha is a large open pit mining operation jointly owned by Newmont and Buenaventura located in Cajamarca, Peru. Yanacocha is a primary gold mine that also produces silver and mercury. Gold production is by conventional cyanide heap leaching which also recovers limited amounts of silver and mercury (Dreisinger, 2011). Increasing the cyanide concentration used has been shown to recover more silver while also increasing mercury extraction which is costly to treat (AMTEL, 2010). Low silver recoveries have been linked to finely dispersed silver encapsulated in iron oxides, barite and quartz (McComb and
This problem is aggravated by the slower cyanide leaching rate of silver sulfide compared to silver (Xie, 2006).

The Yanacocha mine site exploits a high sulfidation epithermal gold deposit stemming from the Yanacocha Volcanic Complex (Briggs, 2005). The host rock was significantly altered by the intrusive acidic sulfate fluids resulting in a fine grained, disseminated gold/silver deposit. The hydrothermal fluids deposited gold and silver which is hosted by the leached quartz. Hydrothermal brecciation, in which the intrusive areas fused together, can be observed although mineral association analysis indicates that the silver is still very fine grained on the order of several microns (McComb and Thogerson, 2011). Glacial erosion in the area has also resulted in the redeposition of some gold in nearby deposits (La Quinua) which are also mined at Yanacocha (Briggs, 2005).

The current exploitation strategy is cyanide heap leaching on roughly crushed or run-of-mine ore. This strategy has been very effective at leaching gold with high recoveries; however the current process is ineffective at leaching silver. For this reason, alternatives such as cupric-ammonia thiosulfate leaching are being investigated.

2.4 Cupric-Ammonia Thiosulfate Leaching

The cupric-ammonia catalyzed thiosulfate leaching system is a promising alternative to cyanidation. Historically, thiosulfate leaching was used in the Patera process to leach precious metal ores that had been treated with a chloridizing roast (Fleming, 2007c). With the advent of cyanidation, this process was widely discontinued. Recently, high silver prices, difficult to leach ores and the advantage of using relatively non-toxic reagents has renewed
interest in the atmospheric leaching of gold and silver with thiosulfate. For preg-robbing ores, silver thiosulfate has the advantage of not adsorbing on the carbonaceous ore (Aylmore and Muir, 2001) although gold losses may still be observed due to its affinity for activated carbon (Abbruzzese et al., 1995). In addition, there is potential for thiosulfate leaching to be applied to underground in-situ mining (Heath et al., 2008). In this section, the chemistry of the cupric-ammonia-thiosulfate system, the loss of cupric complexes and thiosulfate and the application to silver sulfide will be discussed.

2.4.1 Chemistry of the Cupric-Ammonia-Thiosulfate System

The majority of studies on the thiosulfate system focus on the leaching of metallic gold, and in some instances, silver. For this reason, leaching reactions found in the literature will involve these species. In the presence of dissolved oxygen, thiosulfate (S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}) could theoretically leach metallic gold and silver. Although these reactions are thermodynamically favorable, leaching does not proceed due to very slow oxygen reduction kinetics (Aylmore and Muir, 2001; Zipperian et al., 1988). Sample calculations for the standard free energy changes provided are included in the Appendix.

\[
2\text{Au}^+ + 4\text{S}_2\text{O}_3^{2-} + 1/2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Au(S}_2\text{O}_3)_2^{3-} + \text{H}_2\text{O} \quad \Delta G^0 = -208.8 \text{ kJ/mol}
\]
\[
2\text{Ag}^+ + 6\text{S}_2\text{O}_3^{2-} + 1/2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Ag(S}_2\text{O}_3)_3^{5-} + \text{H}_2\text{O} \quad \Delta G^0 = -240.6 \text{ kJ/mol}
\]

For this reason, additions of both cupric (Cu\textsuperscript{2+}) and ammonium (NH\textsubscript{4}\textsuperscript{+}) are made. In this case, the cupric-tetrammine complex (Cu(NH\textsubscript{3})\textsubscript{4}\textsuperscript{2+}) acts as the primary oxidant (Aylmore and Muir, 2001). One potential stoichiometry for this reaction is (Zipperian et al., 1988):

\[
\text{Au} + 5\text{S}_2\text{O}_3^{2-} + \text{Cu(NH}_3)_4^{2+} \rightarrow \text{Au(S}_2\text{O}_3)_2^{3-} + 4\text{NH}_3 + \text{Cu(S}_2\text{O}_3)_3^{5-} \quad \Delta G^0 = -7.7 \text{ kJ/mol}
\]

The mechanism is complicated by the potential oxidation of thiosulfate to trithionate (S\textsubscript{3}O\textsubscript{6}\textsuperscript{2-}) and tetrathionate (S\textsubscript{4}O\textsubscript{6}\textsuperscript{2-}) which occurs readily below pH 10 (Ahern, 2005; Aylmore and
Muir, 2001). This issue is discussed further in Section 2.4.2 Loss of Cupric Complexes and Thiosulfate. In the remainder of this section, the thermodynamics and solution speciation in the copper-ammonia-thiosulfate system will be discussed.

Eh-pH diagrams were generated using Outokumpo HSC Chemistry with the internal free energy database and additional thermodynamic data from Aylmore and Muir (2001). The metastable sulfur-water diagram is shown below in Figure 2.1 (after (Zhang, 2004)). In this diagram, stable species such as sulfate have been excluded due to the slow oxidation of thiosulfate to sulfate. Thermodynamic data used is included in the Appendix. Decreasing the pH too low will result in the formation of sulfur or tetrathionate, hence the use of alkaline solutions.

![Eh-pH diagram for metastable sulfur complexes](image)

**Figure 2.1** Eh-pH diagram for metastable (excludes sulfate) sulfur complexes including thiosulfate, polythionates and sulfite with 0.2 m sulfur.

The Eh-pH diagram for the ammonia-water system is shown below (Figure 2.2), excluding dissolved nitrogen gas. This diagram serves to show the stability of ammonia/ammonium in solution due to the unlikely formation of nitrates, nitrites and hydroxylamine derivatives.
Figure 2.2  Eh-pH diagram for ammonia-water system with 0.7 m nitrogen, excluding nitrates/nitrites and hydroxylamine derivatives which generally only form in the presence of nitrates.

Figure 2.3 is an Eh-pH diagram for 1x10^{-4} m silver, 0.1 m thiosulfate and 0.7 m ammonia.

The two upper bounds on the silver thiosulfate stability region are due to conversion of thiosulfate to dithionate (low pH line) or sulfite (high pH line).

Figure 2.3  Eh-pH diagram for 1x10^{-4} m silver, 0.1 m thiosulfate and 0.7 m ammonia with the species used in previous Eh-pH diagrams.
Although there are errors when measuring the potential of solution, the potential measured during leaching experiments never exceeded 300 mV vs SHE. Therefore, it is reasonable to assume that the dominant silver thiosulfate complex in solution is \( \text{Ag(S}_2\text{O}_3\text{)}_3^{5-} \) for the range of conditions relevant to a low temperature cupric-ammonia catalyzed thiosulfate leach.

The Eh-pH diagram for \( 1\times10^{-3} \) m copper, 0.1 m thiosulfate and 0.7 m ammonia is shown below in Figure 2.3. In the leaching range of interest, the cupric-tetrammine complex may dominate or cuprous-thiosulfate complexes depending strongly on the reagent concentrations, pH and potential. A drop in solution potential will result in the formation of various cuprous-thiosulfate complexes or precipitation of copper from solution.

**Figure 2.4** Eh-pH diagram for \( 1\times10^{-3} \) m copper, 0.1 m thiosulfate and 0.7 m ammonia.

Although the Eh-pH diagrams illustrate the dominant species in solution for the copper-ammonia thiosulfate system, it is useful to consider the speciation of the copper-ammonia-thiosulfate complexes at a variety of conditions. For these diagrams, ChemEQL v3.1 (Müller, 1994) was used. Thermodynamic data was drawn from the internal program library, the table
Speciation in the copper-ammonia thiosulfate system is very complicated, so there is considerable debate about the presence of mixed species in solution (Black, 2006). Recent work done by Black indicates that mixed cuprous complexes such as \( \text{Cu(NH}_3\text{)(S}_2\text{O}_3\text{)}_2^{3-} \) are more stable than the commonly specified \( \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} \) at high reagent concentrations. The precise speciation of these mixed complexes will depend on the ammonia to thiosulfate concentration ratio. As thermodynamic data is limited on these mixed species, uniform ligand complexes were used in the generation of the following speciation diagrams. The Eh-pH diagrams plotted are based on solution thermodynamics while the speciation diagrams are generated to consider copper ions present in solution as either cupric or cuprous, depending on the diagram. The speciation diagrams are useful in demonstrating how cupric and cuprous species are complexed in solution while Eh-pH diagrams are useful in determining the dominant species.

Speciation diagrams were generated from a baseline condition of 0.1 M thiosulfate, 0.7 M total ammonia, 1 mM copper (present as either cupric or cuprous), 200 mV vs SHE and a pH of 9.5 at 25°C. The distribution of dominant cupric-ammonia-thiosulfate complexes for a range of pH values is shown in Figure 2.5. Note that at pH values greater than 11, \( \text{CuO (tenorite)} \) precipitation will occur. Any complexes of cupric formed with thiosulfate will result in the reduction of the cupric to cuprous and oxidation of thiosulfate to tetrathionate will occur (Zhang, 2004). For this reason, alkaline leaching conditions are used with this system.
The speciation of cuprous-ammonia-thiosulfate complexes is not affected as greatly by pH as the cupric complexes (Figure 2.6). Increasing the pH above 9 will result in a small amount of Cu(NH$_3$)$_2^+$ formation.
Cupric speciation for a range of thiosulfate concentrations is shown below in Figure 2.7. Increasing the thiosulfate concentration decreases the stability of the cupric-tetrammine complex in solution. Although increasing the thiosulfate concentration simultaneously increases the driving force for thiosulfate oxidation and cupric reduction, it also increases the availability of thiosulfate for silver dissolution. This implies that any leaching system must carefully balance the concentrations of ammonia, thiosulfate and cupric in solution in addition to the pH.

![Figure 2.7 Speciation of cupric-ammonia-thiosulfate complexes at 0.7 M total ammonia, 1 mM cupric, 200 mV vs SHE at 25°C and pH 9.5 for a range of thiosulfate concentrations.](image)

The cuprous-ammonia-thiosulfate complexes for a range of thiosulfate concentrations are plotted below (Figure 2.8). Cuprous-thiosulfate species begin to dominate at thiosulfate concentrations greater than 0.025 M thiosulfate. Increasing the thiosulfate concentration to very high values will result in the formation of the mixed ammonia-thiosulfate complexes discussed by Black (2006).
Figure 2.8  Speciation of cuprous-ammonia-thiosulfate complexes at 0.7 M total ammonia, 1 mM cuprous, 200 mV vs SHE at 25°C and pH 9.5 for a range of thiosulfate concentrations.

Cupric complex speciation for a range of ammonia concentrations is shown below in Figure 2.9. In this case, increasing the ammonia concentration drastically increases the concentration of the cupric-tetrammine complex in solution. Due to increased coordination of cupric, the solution potential will also simultaneously decrease as ammonia is added to the system.
Figure 2.9   Speciation of cupric-ammonia-thiosulfate complexes at 0.1 M thiosulfate, 1 mM cupric, 200 mV vs SHE at 25°C and pH 9.5 for a range of ammonia concentrations.

The speciation for cuprous-ammonia-thiosulfate complexes is plotted below in Figure 2.10 for a range of ammonia concentrations. The effect of increasing ammonia on cuprous complexation is minimal. Only at very high ammonia concentrations do cuprous-ammonia species form.
Figure 2.10  Speciation of cuprous-ammonia-thiosulfate complexes at 0.1 M thiosulfate, 1 mM cuprous, 200 mV vs SHE at 25°C and pH 9.5 for a range of ammonia concentrations.

For heap leaching, where very low reagent concentrations may be desirable, a speciation diagram was generated from a baseline condition of 10 mM thiosulfate, 20 mM total ammonia, 1 mM cupric and 200 mV vs SHE at 25°C (Figure 2.11). With this low concentration of ammonia, the cupric-ammonia complexes are highly unstable in solution. Speciation at this low ammonia concentration is largely unaffected by pH.
Complexation of cuprous at these low reagent conditions by thiosulfate and ammonia is plotted in Figure 2.12. For these low thiosulfate conditions, the cuprous is mainly coordinated by only one or two thiosulfate ions.

Figure 2.11 Speciation of cupric-ammonia-thiosulfate complexes at 10 mM thiosulfate, 20 mM ammonia, 1 mM cupric, 200 mV vs SHE at 25°C for a range of pH values.

Figure 2.12 Speciation of cuprous-ammonia-thiosulfate complexes at 10 mM thiosulfate, 20 mM ammonia, 1 mM cuprous, 200 mV vs SHE at 25°C for a range of pH values.
Other Eh-pH and speciation diagrams at various conditions have been generated by other researchers including Aylmore and Muir (2001) and Black (2006) among others.

### 2.4.2 Loss of Cupric Complexes and Thiosulfate

A significant challenge to using a cupric-ammonia catalyzed thiosulfate leaching system is the inherent instability. A neutral to alkaline pH must be used to prevent disproportionation of thiosulfate to sulfite and sulfur as shown in the Eh-pH diagram (Figure 2.1). In an alkaline cupric-ammonia containing leach solution, thiosulfate oxidation will occur by either oxygen in solution or cupric:

\[
2 \text{S}_2\text{O}_3^{2-} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{OH}^- \quad \Delta G^0 = -53.2 \text{kJ/mol}
\]

\[
8 \text{S}_2\text{O}_3^{2-} + 2\text{Cu(NH}_3)_4^{2+} \rightarrow 2\text{Cu(S}_2\text{O}_3)_3^{5+} + \text{S}_4\text{O}_6^{2-} + 8\text{NH}_3 \quad \Delta G^0 = -19.8 \text{kJ/mol}
\]

Oxidation of thiosulfate in alkaline solutions by dissolved oxygen in solution is slow (Breuer, 2002); significant oxidation of thiosulfate is only observed in the presence of sulfur oxidizing bacteria or an oxidizing agent such as cupric. In the absence of any ammonia, the reduction of cupric in solution and oxidation of thiosulfate is nearly quantitative and complete in seconds (Breuer and Jeffrey, 2003b). In the presence of dissolved oxygen, cuprous species will be re-oxidized to cupric. Due to this reaction, a constant decrease in thiosulfate concentration will be observed. Kinetically, the reduction of cupric species to cuprous species at pH 9.8 is first order (\(\log([\text{Cu(II)}])\) versus time is linear) (Breuer and Jeffrey, 2003b). At pH 11.4, the reduction was second order (1/[Cu(II)] versus time is linear).

The primary oxidation product is tetrathionate (\(\text{S}_4\text{O}_6^{2-}\)), although other degradation products can be generated such as trithionate (\(\text{S}_3\text{O}_6^{2-}\)) and sulfite (\(\text{SO}_3^{2-}\)) (Ahern, 2005). These polythionates will eventually be oxidized to sulfate (Breuer and Jeffrey, 2003b). One
proposed mechanism for the cupric-tetrammine catalyzed oxidation of thiosulfate is by the coordination of thiosulfate on the axial site of the cupric-tetrammine complex (Breuer and Jeffrey, 2003b; Byerley et al., 1973; Jeffrey et al., 2003). This is because the cupric-tetrammine complex exists as a square planar complex and may be coordinated by other anions (Byerley et al., 1975). A schematic of this mechanism (after Jeffrey et al.) is shown below in Figure 2.13:

![Figure 2.13 Schematic of thiosulfate oxidation to tetrathionate by coordination with axial site of cupric-tetrammine complex.](image)

This reaction is catalyzed in solutions containing dissolved oxygen, so the amount of oxygen in solution should be carefully controlled (Breuer and Jeffrey, 2003a). Increasing the amount of dissolved oxygen in solutions significantly increases the rate of thiosulfate consumption. Breuer and Jeffrey achieved good leaching kinetics for metallic gold and low thiosulfate consumption when 2% oxygen was sparged into the solution compared to the sparging of air or pure oxygen. In addition, increasing the total amount of copper ions in solution increased the cupric:cuprous ratio and subsequent thiosulfate oxidation.

Sulfite has been considered as an addition to the cupric-ammonia system to delay the oxidation of thiosulfate (Breuer and Jeffrey, 2003b). Although initially sulfite delays loss of
thiosulfate, it simply serves as a substitute for thiosulfate oxidation. After reacting with sulfite in solution, thiosulfate is then oxidized by cupric (Breuer, 2002). There are numerous other possible oxidizing agents that will attack thiosulfate including ferric, copper metal and iodine (used for the quantitative analysis of thiosulfate in solution) (Wassink, 2011).

Tetrathionate may disproportionate to form thiosulfate and trithionate (Zhang et al., 2005). This process can result in the eventual regeneration of a small portion of oxidized thiosulfate and is catalyzed by bacteria such as *Thiomonas intermedia* K12 (Wentzien and Sand, 2004).

$$4S_2O_6^{2-} + 4H_2O \rightarrow 6S_2O_3^{2-} + S_4O_6^{2-} + SO_4^{2-} + 8H^+ \quad \Delta G^0 = -64.5 \text{ kJ/mol}$$

Further research on thiosulfate degradation in cupric ammonia leach solutions has been undertaken by numerous researchers (Ahern, 2005; Aylmore and Muir, 2001; Breuer and Jeffrey, 2003a; Breuer and Jeffrey, 2003b; Jeffrey et al., 2003).

### 2.4.3 Application to Silver Sulfide Leaching

Leaching of silver sulfide with the thiosulfate-ammonia-copper system has been previously studied by Flett et al. (1983) and Briones and Lapidus (1998). Table 2.1 provides the results of a selection of the conditions studied by these researchers. Flett et al. leached 0.002 M silver sulfide with the reagents listed below without adjusting the pH in a stirred tank open to the air. This molar quantity of silver sulfide was chosen so it could be directly compared to the amount of copper added to the solution as a stoichiometric multiple. Briones and Lapidus leached silver sulfide particles at ambient temperature under a nitrogen atmosphere and controlled the pH.
Table 2.1  Previously studied conditions for the leaching of silver sulfide with the thiosulfate-ammonia-copper system by (Flett et al., 1983) and (Briones and Lapidus, 1998)

<table>
<thead>
<tr>
<th>Thiosulfate (M)</th>
<th>Total Ammonia (M)</th>
<th>Copper (M)</th>
<th>Atmosphere</th>
<th>Temp. °C</th>
<th>pH</th>
<th>Silver Dissolution %</th>
<th>Leaching Time hrs</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0038</td>
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<td>0.002</td>
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<td>-</td>
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<td>-</td>
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<td>6.0</td>
<td>Flett</td>
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<td>0.015</td>
<td>N2</td>
<td>-</td>
<td>9.0</td>
<td>28.0</td>
<td>6.3</td>
<td>Briones</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.200</td>
<td>0.003</td>
<td>N2</td>
<td>-</td>
<td>9.0</td>
<td>40.0</td>
<td>5.5</td>
<td>Briones</td>
</tr>
<tr>
<td>0.1000</td>
<td>1.000</td>
<td>0.003</td>
<td>N2</td>
<td>-</td>
<td>9.0</td>
<td>21.0</td>
<td>4.7</td>
<td>Briones</td>
</tr>
</tbody>
</table>

There are a number of trends visible in this table. Silver sulfide dissolution increases with increasing thiosulfate concentration and increasing copper concentration. Flett et al. (1983) found that the addition of ammonium hydroxide increased silver dissolution slightly while Briones and Lapidus (1998) found that increasing the total ammonium in the system decreased silver dissolution. This may be because silver dissolution was aided by the increased basicity from the addition of ammonium hydroxide in the research of Flett et al. while Briones and Lapidus maintained a constant pH by adjusting the amount of sodium hydroxide they added.

Flett et al. also found that silver sulfide leaching with cuprous-thiosulfate (no ammonia) was possible, although the silver leached after 24 hours was lower than it was with the addition of small amounts of ammonia. The effects of thiosulfate, ammonia, copper, temperature and pH will be explored further in this thesis.
Flett et al. (1983) proposed two reactions for silver sulfide leaching with cupric or cuprous.

They claim that a cuprous substitution reaction will proceed in the absence of air forming chalcocite (Cu$_2$S):

$$\text{Cu}_2\text{S}_2\text{O}_3 + \text{Ag}_2\text{S} \rightarrow \text{Cu}_2\text{S} + \text{Ag}_2\text{S}_2\text{O}_3$$

In the presence of air, a cupric substitution reaction is proposed which forms covellite (CuS):

$$3(\text{NH}_4)_2\text{S}_2\text{O}_3 + \text{CuSO}_4 + \text{Ag}_2\text{S} + 1/2\text{O}_2 \rightarrow$$

$$\text{CuS} + \text{Ag}_2\text{S}_2\text{O}_3 + (\text{NH}_4)_2\text{S}_4\text{O}_6 + (\text{NH}_4)_2\text{SO}_4 + 2\text{NH}_3 + \text{H}_2\text{O}$$

Using the most prevalent species in the cupric ammonia thiosulfate system based on the speciation calculations in Section 2.4.1, the reactions can be rewritten as:

$$\text{Ag}_2\text{S} + 2\text{Cu(S}_2\text{O}_3)_{5^c} \rightarrow \text{Cu}_2\text{S} + 2\text{Ag(S}_2\text{O}_3)_{5^c} \quad \Delta G^0 = 7.1 \text{ kJ/mol}$$

$$\text{Ag}_2\text{S} + \text{Cu(NH}_3)_4^{2^+} + 8\text{S}_2\text{O}_3^{5^c} + 2\text{NH}_4^+ + 1/2\text{O}_2 \rightarrow$$

$$2\text{Ag(S}_2\text{O}_3)_{5^c} + \text{CuS} + \text{S}_4\text{O}_6^{2^c} + 6\text{NH}_3 + \text{H}_2\text{O} \quad \Delta G^0 = -113.3 \text{ kJ/mol}$$

If cuprous reacts with the silver sulfide, then a molar ratio of 1 Cu$^{+}$ to 1 Ag$^{+}$ is required while if the cupric reaction proceeds a molar ratio of 1 Cu$^{2+}$ to 2 Ag$^{+}$ is required. When the leach residues were analyzed with x-ray diffraction (XRD) (Briones and Lapidus, 1998; Cui et al., 2011; Flett et al., 1983), chalcocite and covellite were observed. However, in most of their experiments a mixed mode is observed where the molar ratio of silver dissolved to copper precipitated varies from 1.1 to 1.4 (for reactions under a nitrogen atmosphere) to 1.9 (for reactions under an oxygen atmosphere).

This copper precipitation phenomenon has also been observed by Briones and Lapidus (1998) and Cui et al. (2011). When leaching silver sulfide with a cupric thiosulfate solution
(no ammonia), Cui et al. observed chalcocite (Cu₂S) formation with XRD due to the immediate reduction of cupric to cuprous in the absence of ammonia. Briones and Lapidus suggested that a mixed copper-sulfur phase such as digenite (Cu₂₋ₓS) may have formed as leaching a stoichiometric amount of silver sulfide in a cupric-ammonia thiosulfate solution resulted in some leftover copper in solution. It has been suggested by multiple researchers that the leaching reaction may favor the formation of chalcocite (Cu₂S) due to the structural similarities between chalcocite and acanthite; however they are quick to point out that different diffusivities, reaction rates and ammonia complexes may exert a greater influence. In addition, the thermodynamic driving force for the cuprous reaction is unfavorable compared to the favorable cupric reaction (see Section 3.5.1).

2.5 Alternative Thiosulfate Leaching Chemistries

Alternatives to the cupric-ammonia thiosulfate system have been investigated including the addition of EDTA, the use of ferric complexes and low pH acetic acid-ammonium acetate leaching.

2.5.1 Chemistry of Additives and Complexing Agents

Multiple additives and complexing agents were considered for use with the thiosulfate leaching of silver sulfide. Before discussing the application of these chemicals to silver leaching, the background chemistry of these reagents will be introduced.

Ethylenediaminetetraacetic acid (EDTA, IUPAC: 2,2’,2”’,2’’’-(Ethane-1,2-diyldinitrilo)tetraacetic acid, C₁₀H₁₆N₂O₈ or C₁₀H₁₂N₂O₈⁴⁻) has been suggested both as an additive to the cupric-ammonia thiosulfate system (Feng and van Deventer, 2010) and as a complexing agent for ferric (Heath et al., 2008; Zhang et al., 2005). EDTA can complex most
multivalent heavy metal ions as a hexadentate ligand (Feng and van Deventer, 2010). Ferric EDTA and cupric EDTA are both stable complexes. A schematic of the hexadentate ferric EDTA complex is shown below Figure 2.14.

![Schematic of ferric EDTA complex](image)

Figure 2.14  Schematic of ferric EDTA complex $\text{FeC}_{10}\text{H}_{12}\text{N}_{2}\text{O}_{8}\text{.}$

Depending on the pH, the dominant ferric EDTA complex may be FeEDTA$^-$, Fe(OH)EDTA$^{2-}$ or Fe(OH)$_2$EDTA$^{3-}$ (Hutcheson and Cheng, 2004). Near pH values of 7.5-9.5, Fe(OH)EDTA$^{2-}$ will dominate while increasing the pH past 9.5 will increase the prevalence of Fe(OH)$_2$EDTA$^{3-}$. The reactions for the complexation of iron by EDTA are (stability constants from (Martell and Smith, 1989)):

\[
\text{Fe}^{3+} + \text{EDTA}^4- \rightleftharpoons \text{FeEDTA}^- \\
\log \beta = 25.1
\]

\[
\text{FeEDTA}^- + \text{OH}^- \rightleftharpoons \text{Fe(OH)EDTA}^{2-} \\
\log \beta = 7.49
\]

\[
\text{Fe(OH)EDTA}^{2-} + \text{OH}^- \rightleftharpoons \text{Fe(OH)}_2\text{EDTA}^{3-} \\
\log \beta = 9.41
\]

The mixed potential of solution will decrease as the pH increases and hydroxides are added to the ferric EDTA complex. Increasing the pH too much will result in the precipitation of iron hydroxides. Other relevant complexation reactions for silver and copper with EDTA are (stability constants from (Martell and Smith, 1989)): 
\[ \text{Ag}^{+} + \text{EDTA}^{4-} \rightleftharpoons \text{AgEDTA}^{3-} \quad \log \beta = 7.32 \]

\[ \text{Cu}^{2+} + \text{EDTA}^{4-} \rightleftharpoons \text{CuEDTA}^{2-} \quad \log \beta = 18.7 \]

Oxalate (IUPAC: ethanedioate, \( \text{C}_2\text{O}_4^{2-} \)) is another ligand that has been proposed for the complexation of ferric in solution (Chandra and Jeffrey, 2005). The oxalate complex acts as a bidentate ligand complexing ferric in one of three forms: \( \text{Fe(C}_2\text{O}_4)^{+} \), \( \text{Fe(C}_2\text{O}_4)_2^{-} \) or \( \text{Fe(C}_2\text{O}_4)_3^{3-} \). Based on the work of Chandra and Jeffrey, the \( \text{Fe(C}_2\text{O}_4)_3^{3-} \) complex is stable in the thiosulfate solution and minimizes the concentration of ferrous in solution. This complex is the dominant complex at a molar ratio of 3 oxalate molecules to 1 ferric in solution. A simple schematic of the five membered ring formation of this complex is shown below in Figure 2.15.

![Schematic of ferric oxalate complex Fe(C₂O₄)₃³⁻](image)

**Figure 2.15  Schematic of ferric oxalate complex Fe(C₂O₄)₃³⁻. Adapted from (Wood, 2002).**

The complexation of oxalate with ferric reduces the activity of ferric and its tendency to oxidize thiosulfate in solution (Chandra and Jeffrey, 2005). The reactions for the complexation of iron by oxalate are (stability constants from (Chandra and Jeffrey, 2005)):

\[ \text{Fe}^{3+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{FeC}_2\text{O}_4^{+} \quad \log \beta = 7.58 \]

\[ \text{Fe}^{3+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{Fe(C}_2\text{O}_4)_2^{-} \quad \log \beta = 13.81 \]

\[ \text{Fe}^{3+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{Fe(C}_2\text{O}_4)_3^{3-} \quad \log \beta = 18.6 \]
Other relevant reactions for the complexation of silver and copper by oxalate are (stability constants from (Martell and Smith, 1989)):

\[
\begin{align*}
\text{Ag}^{+} + C_2O_4^{2-} & \rightleftharpoons \text{AgC}_2\text{O}_4^{-} \quad \log \beta = 2.41 \\
\text{Cu}^{2+} + C_2O_4^{2-} & \rightleftharpoons \text{CuC}_2\text{O}_4 \quad \log \beta = 4.84 \\
\text{Cu}^{2+} + 2C_2O_4^{2-} & \rightleftharpoons \text{Cu(}_2\text{C}_2\text{O}_4)^{2-} \quad \log \beta = 9.21
\end{align*}
\]

Citrate (IUPAC: 2-hydroxypropane-1,2,3-tricarboxylic acid, C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}\textsuperscript{3-}) is another iron complexing agent that can stabilize ferric in solution (Silva et al., 2009). Although published information on the use of EDTA and oxalate for the stabilization of ferric in gold/silver leaching solutions was found, no information on the use of citrate was available. The ferric citrate complexes can take many forms depending on the ratio of ferric to citrate and solution pH; however the most common species exist in a stoichiometric ratio of 1:1 (Silva et al., 2009). For ferric to citrate ratios in the range of 1:1 to 1:2, Silva et al. determined the dominant ferric citrate complex using electrospray ionization mass spectrometry. In this case, the dominant complex was the trinuclear \([\text{Fe}_3\text{O(C}_6\text{H}_4\text{O}_7)_3\text{H}_3]^{2-}\) complex; however other researchers have found the mononuclear ferric complex predominant (Martell and Smith, 1989). A schematic of a potential trinuclear ferric citrate complex, adapted from Silva et al. is shown below in Figure 2.16.
Relevant complexation reactions for iron, copper and silver with citrate are complicated by the potential for citric acid to act as up to a tetrabasic complex (Silva et al., 2009). In acidic solutions (used in this thesis) with comparable amounts of citrate to ferric, it is reasonable to treat citrate as a tribasic ligand. Complexation reactions and stability constants are included for mononuclear complexes assuming that the citrate ligand is a tribasic complex (Martell and Smith, 1989). Silver citrate is only soluble in concentrated citric acid solutions (and can precipitate out over time), so is not included in the list (Djokić, 2008).

\[
\begin{align*}
\text{Fe}^{3+} + \text{C}_6\text{H}_5\text{O}_7^{3-} & \rightleftharpoons \text{FeC}_6\text{H}_5\text{O}_7^{3-} & \log \beta = 11.5 \\
\text{Cu}^{2+} + \text{C}_6\text{H}_5\text{O}_7^{3-} & \rightleftharpoons \text{CuC}_6\text{H}_5\text{O}_7^{3-} & \log \beta = 5.9
\end{align*}
\]

Pyrophosphate (P$_2$O$_7^{4-}$) was another complexing agent considered for the stabilization of ferric in solution as it is often grouped with citrate, oxalate and EDTA. However, initial tests demonstrated that ferric pyrophosphate is not soluble at a pH where thiosulfate is stable so this ligand was not used in further tests.

### 2.5.2 Cupric-Ammonia Thiosulfate Leaching with the Addition of EDTA

EDTA has been proposed as an additive to traditional cupric-ammonia thiosulfate solutions (Feng and van Deventer, 2010). EDTA strongly complexes a portion of the cupric in solution.
and reduces the amount of thiosulfate consumed during leaching by the reduction of cuprous to cuprous. When leaching pure gold with a 0.1 M thiosulfate, 0.7 M total ammonia, 50 mg/L (0.8 mM) cupric solution, Feng and van Deventer found that adding 0.125 mM EDTA increased the amount of gold dissolved by approximately 25%. Adding more EDTA (up to 1.0 mM) greatly decreased gold dissolution rates. Although increasing EDTA additions decreased gold dissolution for the pure metal, when leaching a real sulfide ore for 48 hours under the same conditions, the addition of EDTA increased gold extraction. The improvement in total gold extraction showed an almost linear improvement with increasing EDTA additions of up to 2.0 mM. This same improvement was also observed for silver extraction from the sulfide ore during leaching.

The increase in gold dissolution when leaching the real ore was attributed to a decrease in thiosulfate consumption. With 2.0 mM EDTA added, thiosulfate consumption over the course of 48 hours decreased from 9.63 kg/t to 3.85 kg/t (Feng and van Deventer, 2010). They suggest that EDTA addition also prevented passivation of the leaching surface and decreased interference by heavy metal ions present in the sulfide ore. Gold passivation was observed in the absence of EDTA using Raman spectroscopy which indicated a copper sulfide on the surface of the metal. With EDTA added, this species was not observed.

### 2.5.3 Ferric EDTA Thiosulfate Leaching

The use of ferric EDTA to treat gold/silver ores has been proposed by a number of researchers with the primary advantage being slower thiosulfate degradation compared to the cupric-ammonia system (Heath et al., 2008; Zhang et al., 2005). In the study by Heath et al., ferric EDTA leaching was carried out at pH 7 with 50 mM ammonium thiosulfate and
between 1 and 10 mM ferric EDTA. Zhang et al. used 0.3 M sodium thiosulfate with 10 mM thiourea and 2-3 mM ferric EDTA at a pH between 6 and 7. Gold recoveries using ferric EDTA exceeded 90% after 8 hours or less.

In both of the studies by Heath et al. (2008) and Zhang et al. (2005), thiourea was added to the thiosulfate leach solution because of the catalytic effect it has on metallic gold leaching. Formamidine disulfide (an oxidation product of thiourea) also had a beneficial effect when leaching metallic gold. This significantly improved leaching rates for all oxidants considered in the study. Temperature was not found to have a significant effect on the leaching rate. In the study by Heath et al., the addition of sulfide minerals (pyrite and pyrrhotite) decreased gold leaching rate for both ferric EDTA and ferric oxalate.

### 2.5.4 Ferric Oxalate Thiosulfate Leaching

Ferric oxalate is another potential oxidant that has been suggested to replace the cupric-ammonia system due to decreased reactivity with thiosulfate (Chandra and Jeffrey, 2005; Heath et al., 2008). Using ferric oxalate with a molar ratio of 1 ferric to 2.5-3 oxalate, gold was leached effectively with only limited thiosulfate consumption (less than 2% after 5 hours).

The possibility of ferrous oxalate dihydrate precipitation was pointed out by Chandra and Jeffrey (2005). Increasing the amount of oxalate to a molar ratio of 1:10 was enough to prevent this occurrence. In this case, the ferrous oxalate complex was re-oxidized by air to form the ferric oxalate complex, although this reaction was slow. As ferric oxalate was
shown to be relatively unreactive towards thiosulfate, using this excessive amount of oxalate would likely only be necessary for highly reductive ores (Chandra and Jeffrey, 2005).

When equivalent molarities of ferric EDTA and ferric oxalate were used to leach metallic gold by Heath et al. (2008), ferric oxalate initially leached gold faster than ferric EDTA. This was observed even under comparable solution potentials. At very long run times in excess of 48 hours, ferric EDTA was sometimes more effective than ferric oxalate. Optimizing the amount of ferric species, ammonium thiosulfate, thiourea additions and pH seem critical to the effective leaching gold using both ferric EDTA and ferric oxalate.

2.5.5 Acetic Acid-Ammonium Acetate Buffered Thiosulfate Leaching

Although basic or near-neutral thiosulfate leaching chemistries are the most commonly considered, alternatives have been investigated including a low pH ammonia-thiosulfate leach (Ayata and Yildiran, 2001). Silver sulfide was successfully leached at a pH of 4.15 in an acetic acid-ammonium acetate buffer solution with 1.0 M thiosulfate at 50-60°C. The silver sulfide reacts with thiosulfate and acid forming elemental sulfur and water as leaching byproducts.

\[
2 \text{Ag}_2\text{S} + 9\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ \rightarrow 4\text{Ag(S}_2\text{O}_3)^{\frac{1}{2}} + 4\text{S} + 3\text{H}_2\text{O}
\]

Increasing the pH to 7.15 or using only 0.1 M thiosulfate resulted in only a minimal amount of silver dissolution. At this low pH and high temperature, increased thiosulfate degradation is an issue, so further work needs to be done to investigate this system.

2.5.6 Cupric Thiosulfate Leaching in the Absence of Ammonia

Recently, an investigation into cupric-thiosulfate leaching in the absence of ammonia (Cui et al., 2011) was performed which yielded very high silver extractions from a synthetic silver
sulfide powder (up to 95.1%) in a 0.12 M thiosulfate solution with 0.05 mol/L cupric. The ratio of cupric to thiosulfate was the most important variable in the system. No information was provided on the loss of thiosulfate although ammonia is typically added to slow degradation of the thiosulfate complex to tetrathionate, trithionate and other sulfur species.

2.5.7 Recovery of Silver from Thiosulfate Leach Solutions

There are three primary methods for silver recovery from thiosulfate leach solutions: electrowinning, cementation and ion exchange. The application of ion exchange resins for silver recovery has been extensively researched from the point of view of photographic developing and fixing where silver thiosulfate is extensively used. Silver can be removed using a weak or strong base resin, often in a styrene gel matrix (Grosse et al., 2003; Paiva, 2000). Many commercial resins have been examined; Grosse et al. have reviewed published data on silver recovery from thiosulfate solutions (Grosse et al., 2003). Many resins can achieve very good recoveries (>96%) including the weak base IRA-68 and strong base IRA-67, IRA-458 and GT-73 resins. The weak base resins can be eluted with 1 M sodium thiosulfate and the strong base resins with sulfuric acid.

Electrowinning is another possible method for the recovery of gold and silver from thiosulfate (Abbruzzese et al., 1995). The proposed cathode reactions for gold and silver are:

\[
\begin{align*}
\text{Au(S}_2\text{O}_3\text{)}_2^{3-} + e^- & \rightarrow \text{Au} + 2\text{S}_2\text{O}_3^{2-} & E^0 = 0.15 \text{ V} \\
\text{Ag(S}_2\text{O}_3\text{)}_2^{3-} + e^- & \rightarrow \text{Ag} + 2\text{S}_2\text{O}_3^{2-} & E^0 = 0.01 \text{ V}
\end{align*}
\]

Parasitic cathodic reactions may include the reduction of water:

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- & E^0 = -0.828 \text{ V}
\]
As electrowinning is carried out in a basic solution for complex stability, the anodic reaction is evolution of oxygen:

\[ 4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \quad E^0 = 0.40 \text{ V} \]

Cementation using metallic copper, zinc or iron has also been considered for gold and silver recovery from thiosulfate solutions (Aylmore and Muir, 2001). These systems are analogous to the Merrill-Crowe process for gold recovery from cyanide leach solutions using zinc powder. In this case, recovery (shown below for gold) is by a simple charge transfer reaction.

\[ 2 \text{Au(S}_2\text{O}_3)_2^+ + 2 \text{Zn}^0 + 4 \text{NH}_3 \rightarrow 2 \text{Au}^0 + 2 \text{S}_2\text{O}_3^{2-} + \text{Zn(S}_2\text{O}_3)_2^{2-} + \text{Zn(NH}_3)_4^{2+} \]

This process does not yield as pure of a product as the Merrill-Crowe process due to consumption of the zinc metal by cupric in solution. Electrowinning, cementation and ion exchange have potential for the recovery of gold and silver from thiosulfate solutions. Developments in the thiosulfate leaching process will drive further investigation of these recovery processes in coming years.
Chapter 3: Leaching of Silver Sulfide

3.1 Introduction

To investigate the kinetics of silver sulfide leaching with thiosulfate, a series of rotating disk experiments were conducted. Rotating disk experiments using silver sulfide have previously been undertaken by Xie (2006) and Dutrizac (1994) to investigate ferricyanide and chloride leaching of silver sulfide, respectively. Both have shown that it is possible to compress silver sulfide powder into a dense disk with minimal porosity without heating. Simply pressing the powder maintains the integrity of the synthetic silver sulfide. Using this disk, the effect of changing variables in the cupric-ammonia catalyzed thiosulfate system was investigated (Section 3.3). In addition, the use of ferric complexes as alternative oxidants was tested (Section 3.4). The resulting silver sulfide leaching rates are then analyzed and discussed (Section 3.5). Finally, some conclusions on the use of these systems are made (Section 3.6).

3.2 Experimental Methods

Rotating disk experiments are widely used for investigating the kinetics of leaching systems, particularly for metallic gold, silver and gold-silver alloys. Although traditionally used for electrochemical experiments for the measurement of current and correlation to a leaching rate (Hiskey and Sanchez, 1990), these experiments have also been applied where the concentration of dissolved metal was measured with time (Dutrizac, 1994; Xie, 2006). By removing small volumes of solution at specified time intervals and measuring dissolved metal content, average leaching rates can be determined. This section will describe the experimental apparatus, analytical methods and validate the use of these methods for silver sulfide leaching experiments.
3.2.1 Rotating Disk Experiments

The primary advantage of rotating disk experiments compared to alternative batch powder leaching experiments is that the mass transport conditions are known precisely if the disk is operating in the laminar regime (Levich, 1962). By adjusting the rotation speed, system variables can be studied in a systematic way that is more difficult in batch leaching experiments where particle size distribution and pulp density can significantly affect extractions.

Provided that fluid flow at the surface of the disk is in the laminar regime, the flux of reagent $a$, $J_a$ (mol/m$^2$/s), is given by the Levich equation in terms of the diffusivity of $a$, $D_a$ (m$^2$/s), the solution kinematic viscosity, $v$ (m$^2$/s), the angular velocity of the disk, $\omega$ (rad/s) and the bulk concentration of $a$, $C_a$ (mol/m$^3$). The system is in the laminar flow regime for a Reynolds number ($N_{Re}$) less than approximately 1.8-3.1x10$^5$ calculated based on the disk radius $r$, angular velocity and solution kinematic viscosity.

$$J_a = 0.620D_a^{2/3}v^{-1/6}\omega^{1/2}C_a$$

$$N_{Re} = \frac{r^2\omega}{v}$$

Using the kinematic viscosity of water at 25°C (8.9x10$^{-7}$ m$^2$/s) and the holder radius (15 mm), the rotator used in this work can be used up to very high speeds in excess of 6000 RPM before laminar flow and the Levich equation no longer applies to this system. Early tests at speeds in excess of 500 RPM showed a slight deviation from linearity. The reason for this deviation is due to practical limitations on the use of the large rotating disk such as vibrations at higher speeds. For this reason, rotating speeds of 400 RPM or less were used in this series of tests.
A picture of the experimental setup used for rotating disk experiments is shown below (Figure 3.1). A water bath was used to maintain a constant temperature during leaching. This water bath included a stainless steel container, heater and temperature controller accurate to 0.1°C. A stirrer circulated water throughout the tank to maintain a uniform temperature distribution. This setup was capable of controlling water temperature to within 0.5°C of set temperature for the duration of the experiments. A Pine Instrument Company AFCPRB Single Element Rotator was used to rotate the fabricated silver sulfide disk. This rotator is accurate to within 3% of set rotation speed. The rotation speed was validated using a laser tachometer. An 800 mL glass reaction vessel with 4 ports on the top was used with the rotating disk inserted in the central port. The three peripheral ports were used for the nitrogen tube, ORP probe and removing samples during leaching.

Figure 3.1  Rotating disk experimental setup

The rotating disk used was fabricated using synthetic silver sulfide powder (AD Mackay Chemicals) which was pressed using a hydraulic ram into a disk 19 mm across (exposed area of $2.835 \times 10^{-4}$ m$^2$) contained in the 30 mm epoxy holder. This silver sulfide powder has been
examined by EDX and x-ray diffraction before (Xie, 2006) and confirmed to have the structure and composition of acanthite. This disk was mounted in cold mounting epoxy before being ground, polished and glued to an adaptor to fit the rotator. Cold mounting epoxy was used to prevent decomposition of the sulfide during curing. The exposed surface of the disk and surrounding epoxy was ground and polished using standard metallurgical sample preparation procedures. Prior to each leaching experiment, the disk was ground using 1200 grit silicon carbide paper and polished with 6 micron diamond paste to remove any residue on the surface and expose a new silver sulfide surface. Diamond paste residue was washed away with deionized water. Extremely fine polishing has been linked to crystal deformation and a large increase in surface activity, so polishing finer than 6 microns was not used (Heath et al., 2008). The resulting disk was smooth with only a minor amount of porosity (Figure 3.2). Porosity visible in the resin was at the upper surface and was not exposed to solution. Due to shrinking of the resin around the disk, a second small amount of epoxy was applied to seal this shrinkage gap (visible around the outside of the disk). This prevented the intrusion fluids into the side of the disk and made for a smooth surface. An alternative method would be to paint the outside edge of the disk with nail polish which would prevent fluid contact with the disk edge.

Figure 3.2  Synthetic silver sulfide rotating disk, shown here after grinding prior to polishing.
Rotating disk experiments of this nature generally use a large leaching volume to minimize the impact of reagent depletion as the test progresses. Preliminary experiments demonstrated that only a very small amount of silver is leached during testing (less than 1 mg per test), so only a small volume of solution was necessary. However, to minimize solution volume changes from removing the 5 mL of leach solution at each sampling interval required for atomic absorption, leach solution volumes of 500 mL were used for the tests conducted. Over the 40 minute test duration, samples were taken at 5, 10, 20, 30 and 40 minutes.

The experimental conditions tested using the rotating disk can be classified into experiments investigating the cupric-ammonia thiosulfate system and experiments where ferric complexes were used as the oxidant. A systematic look at variables affecting the thiosulfate leaching of silver sulfide with the cupric-ammonia system was taken. The variables examined were thiosulfate, ammonia, and cupric concentrations in addition to pH, temperature and disk rotation speed. Based on the work of Feng and van Deventer (2010), ethylenediaminetetraacetic acid (EDTA) was also considered as an additive which might aid silver leaching.

Based on the literature review of previously studied conditions for leaching silver sulfide using the cupric-ammonia-thiosulfate system (Table 2.1) and typically investigated leaching conditions (Breuer, 2002), test conditions are given in Table 3.1. A baseline condition is given for each of the variables studied followed by the other conditions studied to determine the effect of each variable on silver sulfide leaching. For the majority of tests, one variable was varied at a time while the others were held constant at the baseline condition. A number
of very low reagent tests were also undertaken; these are discussed separately in Section 3.3.4. Total ammonia refers to the molar sum of ammonia in solution contributed by ammonium thiosulfate and ammonium sulfate.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Baseline</th>
<th>Other Test Conditions Studied</th>
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</thead>
<tbody>
<tr>
<td>Thiosulfate (M)</td>
<td>0.10</td>
<td>0.025 0.05 0.075 0.125 0.15 0.20</td>
</tr>
<tr>
<td>Total Ammonia (M)</td>
<td>0.7</td>
<td>0.20 0.35 1.05</td>
</tr>
<tr>
<td>Cupric (mM)</td>
<td>1</td>
<td>5 10</td>
</tr>
<tr>
<td>EDTA (mM)</td>
<td>0</td>
<td>0.05 1</td>
</tr>
<tr>
<td>pH</td>
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<td>9.25 9.62 9.75 10.0</td>
</tr>
<tr>
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<td>Nitrogen</td>
<td>Air</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>15 35</td>
</tr>
<tr>
<td>Disk Rotation Speed (RPM)</td>
<td>400</td>
<td>0 100 200 200 350</td>
</tr>
</tbody>
</table>

The approach taken of investigating one variable at a time while holding the other variables constant neglects higher order effects (e.g., the impact of changing ammonia and cupric concentrations simultaneously). Although experimental design techniques such as a fractional factorial design could have been employed, the approach taken here provides a solid framework for gaining a fundamental understanding of the physical and chemical processes which control the thiosulfate leaching of silver in the cupric-ammonia thiosulfate system.

For these experiments, thiosulfate was added as ammonium thiosulfate, ammonia as ammonium sulfate and cupric as cupric sulfate pentahydrate. The pH was adjusted to the experimental value using sodium hydroxide. ACS grade chemicals were used for all experiments with deionized water. Reagent specifications and suppliers are included in the Appendix (A.4).
The second set of experiments conducted investigated the use of ferric complexes for the thiosulfate leaching of the silver sulfide rotating disk. Based on the work of Heath et al. (2008), ferric EDTA and ferric oxalate were considered as potential alternatives to the cupric-ammonium system. When discussing EDTA and oxalate complexes, citrate and pyrophosphate are often considered as alternatives. Initial tests demonstrated that ferric pyrophosphate was insoluble at a pH suitable for thiosulfate leaching; however ferric citrate was readily soluble in solution with mild heating while stirring. The conditions studied are shown in Table 3.2. For this preliminary set of experiments, the leaching rate of the oxidants was compared at different concentrations (5 and 10 mM) at a pH suitable for the complex (see Section 3.4.1). In addition to these experiments, tests with very low reagent concentrations were undertaken in Section 3.4.4.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Baseline</th>
<th>Test Conditions Studied</th>
</tr>
</thead>
<tbody>
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<td>Thiosulfate (M)</td>
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<td>5</td>
</tr>
<tr>
<td>Total Ammonia (M)</td>
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<td>5</td>
</tr>
<tr>
<td>Ferric EDTA (mM)</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Ferric Oxalate (mM)</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Ferric Citrate (mM)</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>pH</td>
<td>Dependent on ferric complex used</td>
<td></td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Nitrogen</td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Disk Rotation Speed (RPM)</td>
<td>400</td>
<td></td>
</tr>
</tbody>
</table>

### 3.2.2 Analytical Methods

Solution samples were assayed for silver using a Varian 240 Atomic Absorption Spectrophotometer (AAS) instrument with an air-acetylene flame. Other metals including copper and iron were also assayed using this instrument. AAS is a widely used method for the accurate determination of metal concentrations in solution. The absorbance of light at a characteristic wavelength (328.1 nm for silver) can be related to the concentration of the
element using the Beer-Lambert law and a series of standards with known metal contents.

The Beer-Lambert law is a linear relationship between the molar absorptivity $\alpha$, molar concentration $c$, path length $l$ and absorbance $A$. The absorbance of a sample is defined as the negative logarithm of the ratio of the intensities of the transmitted ($I$) and incident ($I_0$) light.

$$A = -\ln \left( \frac{I}{I_0} \right) = \alpha cl$$

For a constant path length (as used in AAS) and constant absorptivity $\alpha$, the concentration of the absorbing species is a linear function of absorbance. Many elements, such as iron, will absorb light of one or more characteristic wavelengths. When analyzing for iron, the wavelength used was based on the concentration of iron in the diluted sample. The Beer-Lambert law is also used for ultraviolet visible spectroscopy (UV-vis), described later.

For the flame type of atomizer used by this spectrophotometer, sample solution is atomized by an air-acetylene flame as it is sprayed into the air. The amount of sample that is atomized and droplet size is a function of the physical solution properties, so standards with properties similar to the samples were used. These standards were prepared by alkalizing a small amount of 1000 mg/L silver AAS standard (provided in nitric acid solution) and diluting to a series of standards. Thiosulfate, ammonium and cupric were added in amounts comparable to the baseline leach solution conditions (see Appendix for complete details). The preparation of atomic absorption standards for copper and iron followed a similar procedure.

The concentration of thiosulfate in solution was determined using an iodometric titration. This titration can be used to quickly and accurately determine the thiosulfate concentration. In this titration, a known concentration of iodine is titrated with the thiosulfate bearing
solution in the presence of a starch indicator. The principal reaction is the oxidation of thiosulfate to tetrathionate by iodine.

\[ 2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \]

This reaction proceeds quantitatively. In the presence of iodine, the soluble starch stains the solution a deep blue-black colour. This titration is robust; however there are a number of interferences including the cupric-tetrammine complex. To minimize errors due to the presence of this complex, a 5% pH 5.5 acetic acid-acetate buffer was added to the solution (after Feng and van Deventer (2010)). Based on a series of calibration tests, it is possible to determine the thiosulfate concentration in leach solutions to within 1.5%, even in the presence of the cupric-tetrammine complex. Titrations conducted without the addition of the buffer solution had errors in excess of 4%. The complete details of the calibration tests and procedures followed are included in the Appendix (A.1 Iodometric Titration for Thiosulfate).

The concentration of the cupric-tetrammine complex was measured using ultraviolet visible spectroscopy (UV-vis). The instrument used was a Shimadzu Mandel Scientific UV-2401 PC with 100 mm path length quartz cuvettes. The cupric-tetrammine complex absorbs at a wavelength of approximately 598.0 nm (Lam and Dreisinger, 2003). This peak is extremely broad, so analytical work was limited to measuring the concentration of the complex in solution. Based on the work of Lam and Dreisinger, standards containing different amounts of the cupric tetrammine complex were prepared at pH 10 to calibrate the absorbance values to concentration of the complex. Care was taken to prepare standards which contained the same amount of thiosulfate as the samples since increasing thiosulfate concentrations will
increase absorbance due to coordination of the cupric-tetrammine complex (Byerley et al., 1973).

Other variables measured include the solution potential and pH. The oxidation-reduction potential (ORP) was measured using a sealed, double junction saturated Ag/AgCl reference electrode with a platinum pin (Cole Parmer, approximately 231 mV reading in Zobell solution). pH measurements were taken using a single junction Ag/AgCl pH combination electrode (Fisher) in conjunction with an automatic temperature compensation probe. Readings from the pH probe and ORP probe were collected using a Fisher accumet AB15+ reader. The solution pH was measured at the beginning and end of every test while the ORP was measured continuously during testing and recorded at the sampling intervals. All experimental work was conducted using ACS grade reagents; a detailed list of reagents used is included in the Appendix (A.4 Reagent Specifications).

### 3.2.3 Validation of Methodology

The rotating disk method was chosen as the principal method of studying mineral leaching kinetics for a number of reasons. When properly operated in the laminar regime, leaching results from rotating disk experiments are highly reproducible because a) the surface of the disk is uniformly accessible by the leach solution and b) the rate of reagent transport to the surface is uniform and governed by the solution properties, disk rotation speed and size.

Although a large leach solution volume was used and the rotation speed was within the laminar region, deviation from linear leaching was observed (Figure 3.3). Three separate tests were conducted at the baseline cupric-ammonia thiosulfate conditions yielding very
similar leaching curves, all of which exhibited significant nonlinearity. Similar deviations from linear leaching using silver sulfide rotating disks have previously been observed by Dutrizac (1994). In Dutrizac’s analysis, a parabolic rate constant was used to account for this behavior when silver sulfide was leached with a chloride system.

The suspected reason for this deviation from linearity is rapid reduction of the cupric-tetrammine complex. This loss of copper(II) has been observed previously in experiments with the cupric-ammonia thiosulfate system (Lam and Dreisinger, 2003). This theory was investigated using UV-vis in Section 3.3.1.

To account for the non-linearity, the first derivative at 0 minutes of a least squares quadratic regression of the data was used. In a series of three rotating disk experiments conducted (Figure 3.3), the average initial slope (leaching rate) was 0.018 mg/min with a coefficient of variation of 4% between tests. The error for atomic absorption spectroscopy is approximately
5%, so the root sum squared error for these tests is ±6% of the leaching rate. For comparison of the leaching rate between tests, the leaching rate at a given set of conditions will be taken to be this initial rate and given in \( \mu m \text{Ag}_2\text{S dissolved/hr} \) (\( \mu m/\text{hr} \)) or \( \mu \text{mol Ag dissolved/m}^2/\text{s} \) (\( \mu \text{mol/m}^2/\text{s} \)). The baseline conditions give an average leaching rate of 9.8 \( \mu \text{mol/m}^2/\text{s} \) (0.60 \( \mu m/\text{hr} \)). Complete details on the unit conversions are included in the Appendix (B.1 Conversion of Leaching Rates).

The atmosphere above the solution was controlled for two reasons: to minimize re-oxidation of cuprous to cupric and to reduce the amount of ammonia loss due to volatilization at higher temperatures and pH values. Re-oxidation is an issue because increasing the disk rotation speed increases the amount of air pulled into solution re-oxidizing cuprous to cupric. This causes deviations from the assumption of a constant bulk cupric concentration which is used in the Levich equation. To minimize these effects, nitrogen was purged through the solution (before adding the oxidant) for at least 15-20 minutes prior to leaching to minimize the amount of dissolved oxygen. During leaching the nitrogen tube was positioned approximately 5 mm above the surface of the solution to maintain a nitrogen blanket on top.

The short leaching time (40 minutes) used means that changes to the solution pH were minimal. For the baseline conditions, the solution pH increased by 0.02-0.03. This slight increase in solution pH was observed for all cupric-ammonia-thiosulfate leaching tests.
The results of the leaching of the synthetic silver sulfide disk are divided into two areas based on the solution type: cupric ammonia or ferric complex based. After describing the results of the leaching experiments, the results are analyzed and discussed.

### 3.3 Results: Cupric-Ammonia Thiosulfate System

#### 3.3.1 Loss of the Cupric-tetrammine Complex

The reduction of the cupric-tetrammine complex with time is believed to be the primary reason for the deviation of the leaching rate from linear leaching. As the amount of silver dissolved over the 40 minutes is small (3 orders of magnitude less than the concentration of copper in solution), this effect is not due to loss of copper ions from solution. The simplest experiment to demonstrate that copper(II) reduction results in a decrease in leaching rate is to prepare a leach solution and leave the solution overnight before running the leaching test in the morning. In addition to this test, a fresh solution was run open to the air rather than under a nitrogen blanket. Operating the solution open to the air resulted in a slightly increased leaching rate which is attributed to re-oxidation of cuprous to cupric. Initially, the silver dissolution rate was the same for air and nitrogen atmospheres. As time passed the difference between the nitrogen and air atmosphere leaching rates increased (Figure 3.4).
Figure 3.4  Silver dissolution in a solution left overnight and in a solution left open to the air compared to baseline leaching (0.1 M thiosulfate, 0.7 M total ammonia, 1 mM cupric, pH = 9.5, nitrogen atmosphere, 25°C and 400 RPM)

The aged leach solution leached silver slower than a freshly prepared leach solution. The solution left open to the air leached silver more quickly than a solution under a nitrogen atmosphere. In addition, the slight increase in the pH of leaching solutions over the 40 minute leaching time (0.02-0.03 pH) may be due to the cupric-thiosulfate redox reactions which generate hydroxide. The reduction of the cupric-tetrammine complex was further investigated using UV-vis operating at a wavelength of 598 nm (Lam and Dreisinger, 2003).

To determine the rate of reduction of the cupric-tetrammine complex, ultraviolet visible spectroscopy (UV-vis) was used. Two solutions were prepared: a solution containing 0.12 M thiosulfate and 0.84 M total ammonia at a pH of 9.50 and a 6 mM cupric sulfate solution. These solutions were mixed in a 100 mM path length cuvette. 25 mL of the ammonia thiosulfate solution was mixed with 5 mL of the cupric sulfate solution to produce a solution at the baseline conditions (0.1 M thiosulfate, 0.7 M total ammonia and 1 mM cupric) in the
cuvette. The absorbance at 598.0 nm with a slit width of 0.5 nm was monitored with time (Lam and Dreisinger, 2003). The absorbance values measured were then transformed to concentrations by measuring the absorbance of a series of standards. Further details on the use of UV-vis in this experiment are included in the Appendix (A.3).

In this experiment, rapid decay of the cupric-tetrammine complex was observed (Figure 3.5). Based on the speciation diagrams presented earlier (2.4.1), decay of the cupric-tetrammine complex to cupric-thiosulfate species and rapid redox to cuprous-thiosulfate is expected. After 40 minutes, approximately 50% of the cupric-tetrammine complex remained in solution. As the cuvette was sealed, no re-oxidation of cuprous to cupric was expected or observed.

The observed decrease in solution potential is comparable to the loss of cupric-tetrammine complex with time (the graphs are plotted on the same timescale) (Figure 3.6).
Based on the results of these tests, leaching experiments were conducted immediately after preparing the solutions under a nitrogen atmosphere.

### 3.3.2 Effect of Variables

The effect of different variables including rotation speed, reagent concentrations, solution pH and temperature were investigated in a battery of tests. A comparable series of tests is standard for hydrometallurgical processes to increase fundamental knowledge of the leaching system. The effects of operating under an air atmosphere and using an aged solution were previously examined, so the impact of changing rotation speed was tested first.

The primary advantage of using rotating disk experiments is the uniform transport of reagents to the surface. Rotation speeds varying from 0 to 400 RPM were used for this series of experiments. The amount of silver dissolved as a function of time at the baseline conditions (0.1 M thiosulfate, 0.7 M total ammonia, 1 mM cupric, pH 9.50 and 25°C) with a

![Figure 3.6 Solution potential as a function of time at the baseline conditions (0.1 M thiosulfate, 0.7 M total ammonia, 1 mM cupric, pH 9.5, nitrogen atmosphere, 25°C and 400 RPM)]
varied rotation speed is plotted in Figure 3.7. The 0 RPM test is not shown on this figure because the test was run for 2 hours to dissolve a detectable amount of silver. The baseline rotation speed used across leaching experiments was 400 RPM.

One of the variables with the greatest range of conditions considered in literature for the cupric-ammonia thiosulfate system is the cupric concentration (Breuer, 2002). Concentrations from 1 to 100 mM are commonly cited. The effect of varying cupric from 1 mM (baseline condition) to 10 mM was tested in a series of experiments (Figure 3.8). In this plot, an increasing tendency towards linear leaching can be observed as cupric concentration is increased. Statistically, the quadratic term for fitting the 10 mM cupric leaching curve was insignificant, so linear leaching was observed.
The total ammonia concentration was varied from 0.20 M to 1.05 M from the baseline condition of 0.70 M in a series of tests (Figure 3.9). A decrease in silver dissolution is observed for increasing amounts of total ammonia, with the exception of the lowest concentration (0.20 M).
The thiosulfate concentration was varied from the low concentration of 0.025 M to a high concentration of 0.20 M from the baseline of 0.10 M (Figure 3.10). For all of these tests the total ammonia concentration was held constant at 0.70 M by adjusting the amount of ammonium sulfate added. An increase up to 0.125 M thiosulfate is observed followed by a decrease in silver dissolution as thiosulfate is increased to 0.20 M.
Figure 3.10  Silver dissolution with time for different thiosulfate concentrations (0.7 M total ammonia, 1 mM cupric, pH = 9.5, nitrogen atmosphere, 25°C and 400 RPM)

Solution pH was varied from 9.0 to 10.0 from the baseline conditions of pH 9.5 (Figure 3.11). Silver dissolution increased with pH up to a pH of 9.5 before decreasing dramatically with any further increase in pH. For low pH tests, a larger pH increase of around 0.05 was observed over the 40 minute leaching time (at baseline conditions the change was an increase of 0.02-0.03 pH).
The leaching temperature was varied from 15°C to 35°C from the baseline condition of 25°C (Figure 3.12). Increasing the solution temperature moderately increased silver dissolution, at least initially.
3.3.3 24 Hour Leaching Test

A 24 hour leaching experiment at the baseline conditions was conducted to measure copper and silver concentrations with time (Figure 3.13). Solution samples taken at 1, 2, 4, 8 and 24 hours were analyzed for silver, copper and thiosulfate. Copper loss from solution was observed over the course of leaching. No steady state leaching rate for silver was observed; the leaching rate continued to decrease over the 24 hour period.

![Graph showing silver dissolution and copper precipitation](image)

**Figure 3.13** Silver dissolution and copper precipitation for a 24 hour leaching test at baseline conditions (0.1 M thiosulfate, 0.7 M total ammonia, 1 mM cupric, pH = 9.5, nitrogen atmosphere, 25°C and 400 RPM)

The change in solution potential and thiosulfate concentration were measured over the 24 hours (Figure 3.14). A rapid decay in solution potential was observed followed by a slow decrease. Over the course of leaching, approximately 14% of thiosulfate in solution was consumed.
Figure 3.14 Thiosulfate concentration and solution potential for a 24 hour leaching test at baseline conditions (0.1 M thiosulfate, 0.7 M total ammonia, 1 mM cupric, pH = 9.5, nitrogen atmosphere, 25°C and 400 RPM)

3.3.4 Very Low Reagent Conditions

Very low reagent conditions were tested to determine the leaching rate if low reagent concentrations were to be used for an extended period of time, such as in heap leaching. Leaching experiments were conducted with 1 mM cupric, 10 mM ammonium thiosulfate at pH 9.5 and 1 mM cupric, 10 mM sodium thiosulfate at pH 7. There was a significant difference between the ammonium thiosulfate and sodium thiosulfate leaching experiments (Figure 3.15). In the presence of even 20 mM ammonia from the use of ammonium thiosulfate, leaching was significantly faster than in the absence of any ammonia. This same effect was observed by Flett et al. (1983); leaching of silver sulfide by cuprous-thiosulfate in the absence of ammonia is thermodynamically unfavorable.
3.3.5 Addition of EDTA

In the recent work of Feng and van Deventer (2010), the addition of EDTA in comparable amounts to the concentration of cupric was found to increase gold and silver recovery. EDTA was added to the baseline leaching conditions in two amounts: 0.5 mM and 1.0 mM (50% and 100% of the cupric concentration, respectively). The amount of silver leached sharply decreased with increased additions of EDTA (Figure 3.16). This decrease in leaching rate was accompanied by a large drop in solution potential.
Figure 3.16 Silver dissolved for different additions of EDTA to the baseline leaching conditions (0.1 M thiosulfate, 0.7 M total ammonia, 1 mM cupric, pH = 9.5, nitrogen atmosphere, 25°C and 400 RPM)

3.4 Results: Ferric Complex Thiosulfate System

Three ferric complexes were considered: ferric-EDTA, ferric-oxalate and ferric-citrate. Ferric complexes were prepared as 0.25 M stock solutions in acidified deionized water. The ratio of ferric to the ligand used was chosen based on the literature review: 1:1 for ferric-EDTA ($\text{Fe(C}_{10}\text{H}_{12}\text{N}_{2}\text{O}_{8})$), 1:3 for ferric-oxalate ($\text{Fe(C}_{2}\text{O}_{4})_3^{3-}$) and 1:1 for ferric-citrate ($\text{FeC}_{6}\text{H}_{5}\text{O}_7$). 2% more ligand than stoichiometrically necessary was added to ensure that all iron in solution was complexed. Before leaching silver sulfide with the ferric complexes, potential-pH curves were generated for each complex (3.4.1). The silver sulfide disk was then leaching for each ferric complex at 25°C, 400 RPM and 0.1 M ammonium thiosulfate at the chosen pH (3.4.2). A nitrogen atmosphere was used for all experiments to prevent re-oxidation of ferrous and so that conditions would be comparable to those used for the baseline cupric-ammonia thiosulfate system. A 24 hour leaching experiment with ferric-EDTA was conducted to measure iron concentration with time and the effectiveness of the reagent over
long leaching periods (3.4.3). Low reagent leaching tests were also conducted for these systems (3.4.4).

3.4.1 Optimal pH for Ferric Complexes in Thiosulfate Solutions

Plots of solution potential as a function of pH for 5 mM ferric complexes in 0.10 M ammonium thiosulfate solution were generated by varying the pH of the solution and measuring the potential with the combination saturated Ag/AgCl electrode. These rudimentary plots were then used to determine the solution pH that would be used for silver sulfide leaching experiments. The leaching pH chosen was the highest pH for which no iron precipitation was observed with a leaching potential of around 50 mV versus the saturated Ag/AgCl reference electrode.

The potential-pH plot for ferric-EDTA is shown below in Figure 3.17. As discussed in the literature review, increasing the pH of a ferric-EDTA containing solution will hydrolize the ferric-EDTA complex. This change was observed as the solution color changed with increasing pH. The start of ferric precipitation was observed at pH values above approximately 9.5.
Based on the potential-pH plot for ferric-EDTA, the leaching pH used was a pH of 7. A similar plot was generated for ferric-oxalate (Figure 3.18). Precipitation of iron was observed at much lower pH values compared to ferric-EDTA and started at a pH near 7. A leaching pH of 5.5 was used for ferric-oxalate.
Figure 3.18  Solution potential as a function of pH for 5 mM ferric-oxalate in 0.10 M ammonium thiosulfate solution

The potential-pH plot for ferric-citrate is shown below (Figure 3.19). Precipitation of iron hydroxides was observed for pH values near 6 for this system. A pH of 4.5 was used for ferric-citrate leaching.

Figure 3.19  Solution potential as a function of pH for 5 mM ferric-citrate in 0.10 M ammonium thiosulfate solution
A plot of all potential-pH curves together shows the different stability regions for the complexes. Ferric-EDTA is the most stable complex over a range of pH values in the ammonium thiosulfate solution while ferric-citrate is the least. Decreasing the pH too low for any system (below approximately 3.5) resulted in the disproportionation of thiosulfate to form elemental sulfur and tetrathionate.

![Comparison of solution potential-pH curves for ferric complexes](image)

**Figure 3.20**  Comparison of solution potential-pH curves for ferric complexes

### 3.4.2 Comparison of EDTA, Oxalate and Citrate

Leaching experiments of the silver sulfide rotating disk were conducted for 5 and 10 mM ferric-EDTA at pH 7 (Figure 3.21). The silver dissolution curve for the baseline cupric-ammonia thiosulfate conditions is plotted in addition to the leaching curves for ferric-EDTA. A significant improvement in silver leaching is observed when the amount of ferric-EDTA is increased for this system. At 10 mM ferric-EDTA, silver dissolution is comparable to the baseline cupric-ammonia thiosulfate conditions.
Figure 3.21  Silver dissolved for different concentrations of ferric-EDTA (0.1 M thiosulfate, 0.2 M total ammonia, pH = 7, nitrogen atmosphere, 25°C and 400 RPM)

Silver dissolution for the ferric-oxalate system is plotted for 5 and 10 mM at pH 5.5 (Figure 3.22). For this system, no improvement in silver dissolution was observed when the amount of ferric-oxalate was increased.

Figure 3.22  Silver dissolved for different concentrations of ferric-oxalate (0.1 M thiosulfate, 0.2 M total ammonia, pH = 5.5, nitrogen atmosphere, 25°C and 400 RPM)
Leaching curves for 5 and 10 mM ferric-citrate at pH 4.5 are plotted below (Figure 3.23). Only a marginal improvement is observed for increasing ferric-citrate concentration. Silver dissolution is significantly slower compared to the baseline cupric-ammonia thiosulfate conditions.

![Graph showing leaching curves for 5 and 10 mM ferric-citrate at pH 4.5](image)

**Figure 3.23** Silver dissolved for different concentrations of ferric-citrate (0.1 M thiosulfate, 0.2 M total ammonia, pH = 4.5, nitrogen atmosphere, 25°C and 400 RPM)

### 3.4.3 24 Hour Leaching Test

A 24 hour leaching experiment with 5 mM ferric-EDTA was conducted under a nitrogen atmosphere. Silver dissolution over the 24 hours for ferric-EDTA was lower compared to the cupric-ammonia thiosulfate system (Figure 3.24). This was expected based on the 40 minute leaching curves. Approximately 70% of the silver leached by the cupric-ammonia system was leached by ferric-EDTA. No steady state leaching rate was observed for ferric-EDTA leaching under a nitrogen atmosphere over the 24 hour leach.
Figure 3.24  Silver dissolved with 5 mM ferric-EDTA, 0.1 M ammonium thiosulfate, 25°C, nitrogen atmosphere, pH = 7 and 400 RPM (24 hour cupric-ATS results plotted for reference)

Although silver dissolution was lower; thiosulfate degradation was very low for this system (Figure 3.25). After 24 hours, only 2.5% of the thiosulfate had reacted with the ferric-EDTA. The solution potential decreased by approximately 60 mV over the course of the 24 hour leach due to reduction of ferric.
Iron concentration was measured using atomic absorption for samples taken during the leaching period. No change in iron concentration was observed during the 24 hour leach indicating that no iron precipitation had occurred.

### 3.4.4 Very Low Reagent Conditions

To compare with the low reagent cupric-ammonia thiosulfate leaching rates, low reagent ferric complex leaches were also conducted. 1 mM ferric complex was used with 10 mM sodium thiosulfate. The pH used for each system was the same as the pH used for higher reagent leaches. The resulting plot of silver dissolution with time indicates that ferric complexes, which leach silver sulfide comparatively quickly at 5 and 10 mM, is extremely slow when low reagent conditions are used (Figure 3.26).
Figure 3.26  Silver dissolution with 10 mM thiosulfate, 25°C, nitrogen atmosphere, 400 RPM for 1 mM ferric-EDTA (pH=7), 1 mM ferric-oxalate (pH=5.5) and 1 mM ferric-citrate (pH=4.5)

3.5  Analysis and Discussion

Analysis and discussion of the leaching results from the cupric-ammonia thiosulfate system and ferric complexes will be discussed separately before comparing these rates in Section 3.6.

3.5.1  Leaching Silver Sulfide with the Cupric-Ammonia Thiosulfate System

To use the cupric-ammonia thiosulfate system for leaching silver sulfide, knowledge of the rate controlling mechanism is critical. Briones and Lapidus (1998) conclude in their study that for their range of conditions studied, the process is diffusion controlled. The mathematical model developed in their article assumes an instantaneous substitution reaction of copper ions (as cupric or cuprous) for silver. This assumption and the conclusion of a diffusion controlled process, was investigated in this work.
For diffusion controlled leaching, a plot of the square root of angular velocity of the disk against the leaching rate should yield a linear plot that passes nearly through the origin. A Levich plot of the initial leaching rate (slope of the quadratic fit of silver dissolution at time zero) against the square root of angular velocity yields a linear fit (Figure 3.27).

This suggests that the leaching rate may be under diffusion control. If the reaction were under pure chemical control, varying the disk rotation speed would have a negligible effect on the leaching rate. In the leaching experiments, cupric was added as cupric sulfate immediately before leaching. This procedure, also followed for the loss of copper(II) experiments, results in the immediate formation of the cupric-tetrammine complex which then decomposes with time. It is then reasonable to assume that the dominant leaching agent will initially be the cupric-tetrammine complex. For silver dissolution, thiosulfate is also necessary at the surface. A molar ratio of 100:1 thiosulfate:cupric implies that transport of cupric to the surface will be significantly slower than transport of thiosulfate. From this molar ratio and
the requirement for copper ions at the surface, it is unlikely that thiosulfate would be the limiting reagent at the surface for a diffusion controlled process.

The diffusion constant of the cupric-tetrammine complex has been estimated by measuring the diffusion limiting current for reduction of the complex on metallic gold to be $0.46 \times 10^{-9}$ m$^2$/s at 20°C by Jeffrey (2001). Using this diffusion constant, the viscosity of water ($8.9 \times 10^{-7}$ m$^2$/s) and an initial cupric-tetrammine concentration of 1 mM (equal to 1 mol/m$^3$) the flux of the cupric-tetrammine complex to the surface is calculated to be $24.4 \ \mu$mol/m$^2$/s. Since the leaching temperature of interest was 25°C and some of the cupric-tetrammine complex would have degraded, there will be slight errors in this calculation. These slight errors cannot account for the difference between the observed rate of $9.8 \ \mu$mol/m$^2$/s and the calculated flux of cupric-tetrammine complex ($24.4 \ \mu$mol/m$^2$/s).

This deviation is observed for all cupric concentrations considered. The initial silver dissolution rate as a function of cupric concentration is plotted in Figure 3.28. Increasing the concentration of cupric ions increased the silver sulfide leaching rate. This increase was not linear with cupric concentration, as would be expected using the Levich equation if leaching was under pure diffusion control.
Figure 3.28  Effect of cupric concentration on silver sulfide leaching rate (0.1 M thiosulfate, 0.7 M total ammonia, pH = 9.5, 25°C, nitrogen atmosphere and 400 RPM)

This parabolic behavior is very similar to the observations of Jeffrey (2001) when gold was leached with the cupric-ammonia thiosulfate system. Jeffrey observed significantly slower leaching than predicted by the Levich equation, deviation from the expected behavior of increasing cupric concentrations and a linear dependence of the leaching rate on thiosulfate concentration. Based on these results, it was concluded that for the conditions studied gold is under a mixed diffusion/chemical control. The linear dependence on thiosulfate concentration suggested that a slow chemical step at the gold surface depends on the thiosulfate concentration.

In the current study, a linear dependence on thiosulfate concentration on the leaching rate is observed up to 0.125 M thiosulfate (Figure 3.29). Further increases in thiosulfate concentration cause a decrease in the initial rate, as shown by the data points at 0.15 and 0.20 M thiosulfate.
The initial linear relationship supports the hypothesis of mixed chemical/diffusion control with a slow thiosulfate chemical step on the silver sulfide surface. It is very unlikely that thiosulfate which is present in abundance in solution would limit a diffusion controlled process. A similar conclusion was reached by Jeffrey when studying the cupric-ammonia thiosulfate leaching of gold (2001). The speciation diagram of the cupric-ammonia-thiosulfate system for varying thiosulfate concentrations (Figure 2.7) shows a large decrease in stability of the cupric-tetrammine concentration as the thiosulfate concentration is further increased. This sets an upper limit on the thiosulfate concentration that can be used to increase the rate as further increases will cause excessive reduction of the cupric-tetrammine complex to cuprous-thiosulfate. This also suggests that a kinetic difference between the cupric and cuprous leaching reactions exists.
The substitution leaching mechanism for silver sulfide by copper ions means that silver sulfide can be leached by either cupric or cuprous. Using the most common species at the baseline conditions (based on the speciation diagrams, Section 2.4.3) and thermodynamic data from Aylmore and Muir (2001), the two reactions from Flett et al. (1983) for cuprous and cupric, respectively are:

\[
\begin{align*}
\text{Ag}_2\text{S} + 2 \text{Cu(S}_2\text{O}_3\text{)}_5^{\cdot\cdot\cdot} & \rightarrow \text{Cu}_2\text{S} + 2 \text{Ag(S}_2\text{O}_3\text{)}_5^{\cdot\cdot\cdot} & \Delta G^0 = 7.1 \text{ kJ/mol} \\
\text{Ag}_2\text{S} + \text{Cu(NH}_3\text{)}_4^{2+} + 8\text{S}_2\text{O}_3^{2-} + 2 \text{NH}_4^+ + 1/2 \text{O}_2 & \rightarrow \\
2 \text{Ag(S}_2\text{O}_3\text{)}_5^{\cdot\cdot\cdot} + \text{CuS} + \text{S}_4\text{O}_6^{6-} + 6 \text{NH}_3 + \text{H}_2\text{O} & \Delta G^0 = -113.3 \text{ kJ/mol}
\end{align*}
\]

The cupric reaction as presented in the literature (Flett et al., 1983) includes the oxidation of thiosulfate to tetrathionate by dissolved oxygen. It is probably unrealistic to include oxygen and oxidation of thiosulfate to tetrathionate in the cupric reaction. An alternative reaction for the leaching of silver sulfide with cupric in the absence of oxygen would be:

\[
\begin{align*}
\text{Ag}_2\text{S} + \text{Cu(NH}_3\text{)}_4^{2+} + 6\text{S}_2\text{O}_3^{2-} & \rightarrow 2 \text{Ag(S}_2\text{O}_3\text{)}_5^{\cdot\cdot\cdot} + \text{CuS} + 4 \text{NH}_3 & \Delta G^0 = -5.7 \text{ kJ/mol}
\end{align*}
\]

In the absence of ammonia in solution, the cuprous leaching reaction is unfavorable. The formation of mixed ammonium thiosulfate complexes of copper and silver may make this reaction slightly more favorable (Black, 2006; Flett et al., 1983). This is supported by the work of Flett which showed low silver leaching in the absence of ammonia. This conclusion is further supported by the results of the low reagent tests conducted in this work in the presence and absence of ammonia. Leaching in the absence of ammonia, where all copper in solution would be present as cuprous-thiosulfate, was very slow.

Furthermore, the decrease in leaching rate with excessive increases in thiosulfate concentration which result in cupric reduction suggests that the cuprous leaching reaction is
slower than the cupric reaction. This is further supported by the decrease in leaching rate with time observed for all low-cupric (below 10 mM) leaching curves. This decrease in the leaching rate with time is correlated with a decrease in the concentration of the cupric-tetrammine complex and solution potential. The plots of cupric-tetrammine concentration (Figure 3.5), decrease in solution potential (Figure 3.6) and silver dissolution with time under different atmospheres and with an aged solution (Figure 3.4) at the baseline conditions are composited together in Figure 3.30.

The concentration of cupric-tetrammine and redox potential for the nitrogen purged, fresh solution both show large decreases. Under an air atmosphere, where cuprous could be re-oxidized to the cupric-tetrammine complex, the leaching rate does not decrease as much over the 40 minute leaching time as it does under the nitrogen atmosphere. In addition, the solution that was aged overnight leached silver much more slowly.

The solution potential and concentration of the cupric-tetrammine complex are correlated, so a plot of the initial silver dissolution rate against the initial solution potential should show a moderate correlation if the cupric reaction is faster. This scatterplot (Figure 3.31) has a Pearson correlation coefficient of 0.67 indicating that these variables are positively
correlated. This scatter plot is useful for demonstrating that there is a correlation; however it is important to note that other effects, such as solution speciation and reagent concentrations will play a large role. For example, under mixed diffusion/chemical control, increasing the quantity of the limiting reagent will increase the leaching rate even if no change is observed in the solution potential.

![Scatter plot of initial silver dissolution rate as a function of initial solution potential (ORP)](image)

Figure 3.31  Scatter plot of initial silver dissolution rate as a function of initial solution potential (ORP) with a correlation coefficient of 0.67.

In addition, the decrease in the baseline (nitrogen purged, fresh solution) leaching rate cannot be explained purely by a decrease in thiosulfate concentration. When the final 40 minute leach solutions were titrated for thiosulfate, there was no detectable difference outside of the titration error of 1.5%.

In the study by Breuer on the thiosulfate leaching of gold with the cupric-ammonia system (Breuer and Jeffrey, 2003b), increasing the total amount of copper ions increased the ratio of cupric to cuprous increased as well as the thiosulfate oxidation rate. The increase in the ratio
of cupric to cuprous is supported in the current work by the observed increase in solution potential when increasing amounts of cupric were added. Increasing the amount of cupric added to solution to 10 mM was sufficient to maintain a constant leaching rate over the 40 minute leaching time as shown in Figure 3.8. The increase in the cupric to cuprous ratio has an effect on the initial leaching rate beyond the increase in reactant availability. The observation of a higher, maintained dissolution rate for increased cupric concentrations supports the hypothesis that the cupric reaction is faster than the cuprous reaction.

The effects of varying the rotation speed, cupric and thiosulfate concentrations suggest that the leaching of silver sulfide with the cupric-ammonia thiosulfate system is under mixed control for the conditions studied. Using the leaching rates at different temperatures, an Arrhenius plot was generated (Figure 3.32).

![Arrhenius plot](image.png)

**Figure 3.32** Effect of temperature on silver sulfide leaching rate (Arrhenius plot) (0.1 M thiosulfate, 0.7 M total ammonia, 1 mM cupric, pH = 9.5, nitrogen atmosphere and 400 RPM)
The Arrhenius equation gives the rate as a function of a frequency factor $A$, the activation energy $E_a$, the universal gas constant $R$ (8.314 J/mol K), and absolute temperature $T$.

$$rate = A \exp\left(-\frac{E_a}{RT}\right)$$

The activation energy is often used as a guide to the controlling mechanism. The cutoff between diffusion controlled processes and chemically controlled processes is often observed for an activation energy of 25 kJ/mol (Breuer, 2002). From the linear fit of Figure 3.32, the activation energy for this process is 7.4 kJ/mol. This low activation energy points to a diffusion controlled mechanism although Levich calculations have demonstrated that the mechanism is not pure diffusion control. This means that the slow chemical step at the surface is not significantly affected by temperature changes for the conditions studied.

Increasing the temperature will result in higher volatilization of ammonia and serve to increase the rate of thiosulfate degradation, so the slightly increased rate of silver sulfide leaching at high temperatures may not be worth the reagent cost.

Increasing the ammonia above 0.35 M in solution decreased the solution potential and leaching rate (Figure 3.33). This is because too much ammonia in solution decreases the activity of the cupric-tetrammine complex resulting in a lower silver dissolution rate. This effect has been observed before (Briones and Lapidus, 1998; Flett et al., 1983). Decreasing the ammonia concentration below 0.35 M resulted in a lower leaching rate. This is attributed to the requirement for large amounts of ammonia in solution to stabilize cupric as the cupric-tetrammine complex and prevent excessive reduction to cuprous. The highest leaching rate is achieved when cupric is stabilized in solution, but not so excessively as to decrease the potential of the cupric complex too much. A very similar plot for the effect of ammonia
concentrations on gold leaching was observed by Jeffrey (2001) for gold leaching with the cupric-ammonia thiosulfate system.

Figure 3.33  Effect of total ammonia concentration on silver sulfide leaching rate (0.1 M thiosulfate, 1 mM cupric, pH = 9.5, 25°C, nitrogen atmosphere and 400 RPM)

Changes to the solution pH had a dramatic effect on the leaching rate of silver sulfide (Figure 3.34). For solution pH values between approximately 9.25 and 9.50, the leaching rate was relatively constant. When more alkaline solutions were used, the leaching rate significantly decreased up to a pH of 9.75. Increasing the pH to 10 did not cause a change in the leaching rate from a pH of 9.75.
Increasing the solution pH above 9.50 caused a rapid drop in solution potential. When the amount of ammonia in solution was increased, a similar drop off in solution potential and leaching rate was observed. This has been attributed in the literature to reduced activity of the cupric-tetrammine complex (Jeffrey, 2001). The buffer point of the ammonium-ammonia system is at a pH of 9.25, so increasing the pH will result in more ammonia in solution. This increased concentration of ammonia in solution is the likely culprit for the reduced solution potential and correspondingly lower leaching rate when the solution pH is increased past 9.5.

The addition of EDTA to the baseline leaching system resulted in a large decrease in leaching rate (Figure 3.35). Feng and van Deventer (2010) observed the same precipitous drop when they leached metallic gold in a comparable solution. This was attributed to a decrease in the leaching potential of the cupric/cuprous couple. From this test it is clear that EDTA additions negatively impact dissolution of the silver sulfide mineral. In the study by
Feng and van Deventer, increased dissolution of other sulfides in the ore such as chalcocite was observed when EDTA was added. This enhanced leaching of the sulfide ore studied. The use of EDTA as an additive for leaching ore will be explored further in Chapter 4.

![Graph showing the effect of EDTA additions on silver sulfide leaching rate](image)

**Figure 3.35** Effect of EDTA additions on silver sulfide leaching rate (0.1 M thiosulfate, 0.7 M total ammonia, 1 mM cupric, pH = 9.5, 25°C, nitrogen atmosphere and 400 RPM)

Precipitation of copper was observed during the 24 hour leaching experiment, although not at a stoichiometric ratio matching pure cupric or pure cuprous substitution leaching. A plot showing the theoretical copper precipitation that should be observed for pure cupric (2:1) or pure cuprous (1:1) leaching of silver sulfide shows a mixed ratio (Figure 3.36). 69% of the silver leached over the 24 hour period was from the cupric substitution reaction and 31% from the cuprous reaction. Mixed reaction modes have previously been observed in the literature for this system. Leaching of silver sulfide being 69% by the cupric reaction aligns with the hypothesis that the cupric reaction is faster.
Figure 3.36  Loss of copper from solution expected for cupric and cuprous reactions compared to observed loss at baseline conditions (0.1 M thiosulfate, 0.7 M total ammonia, 1 mM cupric, pH = 9.5, 25°C, nitrogen atmosphere and 400 RPM)

The low reagent tests with 1 mM cupric and either 10 mM ammonium thiosulfate or 10 mM thiosulfate show the importance of having some ammonia present in solution to stabilize cupric and increase the silver sulfide leaching rate. In the absence of any ammonia, leaching was slow (0.9 µmol/m²/s). The rapid reduction of uncomplexed cupric by thiosulfate in solution means that this leaching rate was only from the cuprous substitution for silver. In the presence of ammonia, the leaching rate was quick (8.8 µmol/m²/s) and would have been enhanced by the low concentration of ammonium in solution. Using very high cupric to ammonia-thiosulfate ratios resulted in fast leaching kinetics, but rapid thiosulfate degradation would limit the use of this system for long leaching leaching periods. For this reason, higher thiosulfate concentrations are often cited in the literature.
A large amount of information has been presented on the cupric-ammonia thiosulfate leaching system. This information will be summarized and reviewed together with results from the ferric complex leach experiments in Section 3.6.

3.5.2 Leaching Silver Sulfide with Ferric Complexes and Thiosulfate

All three ferric complexes show low reactivity with thiosulfate over the 40 minute leaching times. Iodometric titrations for thiosulfate were within error of the starting concentration for all three ligands. Changes to the concentration of the ferric complex resulted in very different behavior for each of the three ligands (Figure 3.37). The low 1 mM ferric complex concentrations were conducted with 0.01 M thiosulfate compared to the 0.1 M thiosulfate used for other tests.

Ferric-EDTA exhibits an almost linear increase in silver dissolution rate with increasing concentration. This contrasts with the ferric-oxalate and ferric-citrate tests where increasing the ferric concentration had only a very small effect past 5 mM. The different behavior for
these ferric complexes may be due to differing diffusivities since all three complexes differ in size and affinity towards water. In addition, the reactivity of the ferric complexes towards silver sulfide may also differ as all complexes are highly coordinated, even more so than the cupric-tetrammine complex.

Based on these results, ferric-EDTA and ferric-oxalate are the most suited to silver sulfide leaching from an engineering point of view. Ferric-citrate leached silver sulfide at the same rate as ferric-EDTA in the best case, and would likely suffer from increased thiosulfate degradation over long leach times due to the low pH used. Ferric-EDTA and ferric-oxalate look very promising for use with silver sulfide ores due to their reduced reactivity with thiosulfate and reasonable leaching rates. The 24 hour tests demonstrated significantly lower consumption of thiosulfate for the ferric-EDTA test compared to the cupric-ammonia leach (2.5% vs 14%). This was observed even though a larger molar amount of oxidant was used.

The silver sulfide leaching rate of these complexes, even at 10 mM ferric complex concentrations, was significantly lower than the baseline cupric-ammonia thiosulfate results. Any use of ferric complexes as alternatives to the cupric-ammonia system would need to be driven by the low reactivity towards thiosulfate. This may make this system attractive for a heap leaching situation where slow leaching rates are not a barrier to implementation if reagent cost is low.
The initial leaching potential of the systems had no discernible effect on the initial rate of silver sulfide leaching; all systems had an initial potential of approximately 50 mV against a Sat. Ag/AgCl electrode.

The work by Heath et al. (2008) suggests that the primary roadblock to the use of ferric complexes for commercial thiosulfate leaching of gold is their reactivity towards sulfide mineral components in the ore. Sulfides in the ore will reduce ferric to ferrous reducing the availability in solution for leaching. The utility of ferric complexes such as ferric-EDTA and ferric-oxalate for leaching silver sulfide has been confirmed in this work. Future work would need to focus on determining their reactivity towards mineral components in orebodies and methods of mitigating this reactivity. This will be discussed further in Chapter 4.

3.6 Summary and Conclusions

A systematic approach to examining the effect of variables on the leaching rate of silver sulfide with the cupric-ammonia thiosulfate system was taken. In addition, the use of ferric-EDTA, ferric-oxalate and ferric-citrate was investigated.

The leaching of silver sulfide by the cupric-ammonia thiosulfate system is complex. In a cupric-ammonia thiosulfate solution, silver sulfide will be leached by a cupric or cuprous substitution mechanism. Thermodynamic calculations demonstrate that the cuprous reaction is thermodynamically unfavorable; however numerous experiments in the literature, and this work, demonstrate that this reaction will proceed, although slowly. The presence of ammonia may accelerate this reaction from the formation of mixed ammonium-thiosulfate complexes which could lower the thermodynamic barrier to leaching. The cupric-tetrammine reaction
has been demonstrated to occur more rapidly in solution. The maximum silver sulfide leaching rate was observed for conditions where the cupric-tetrammine complex is stable in solution.

Diffusion of the cupric-tetrammine complex to the surface is not the limiting step for silver sulfide leaching as would be expected from the very low concentration in solution. Instead, the thiosulfate concentration (which is 2 orders of magnitude larger than the copper concentration) has a linear effect on the leaching rate indicating partial chemical control. Therefore, for the range of conditions studied, a mixed chemical/diffusion controlled mechanism is proposed with thiosulfate concentration limiting the slow chemical step.

The optimization of system variables is important to maximize silver dissolution rate while simultaneously minimizing oxidative loss of thiosulfate. A composite figure which compares the effects of variables in this system on silver sulfide leaching is plotted below (Figure 3.38). The maximum silver dissolution rate will occur when cupric in solution is fully complexed by ammonia with large amounts of thiosulfate present to accelerate the chemical step at the surface. Adding too much ammonia, or alternatively increasing the pH too high, will decrease the activity of the cupric complex and the silver sulfide leaching rate. Although the reaction is under mixed control, increasing the temperature has only a mild effect on leaching rate and will result in increased ammonia loss.
The optimal conditions for silver sulfide leaching with this system may not be the same as the optimal conditions for gold or silver leaching. Further research would need to be done in this area. The addition of EDTA in amounts comparable to the concentration of the cupric-tetrammine complex severely decreased the silver sulfide dissolution rate, so is not plotted in Figure 3.38.

Silver sulfide dissolution rates with the ferric complexes ranged from 0.8 \( \mu \text{mol/m}^2/\text{s} \) for low concentrations (1 mM) to 7 \( \mu \text{mol/m}^2/\text{s} \) for high concentrations (5-10 mM). Ferric-EDTA and ferric-oxalate show the most promise for commercial implementation of the three complexes. Ferric-citrate was the least reactive towards the silver sulfide and used the lowest pH which is not desirable for long term thiosulfate stability.
Table 3.3 compares the silver dissolution rates for silver sulfide (obtained from this work), metallic silver and metallic gold. The error for initial leaching rates obtained from this work is ±6%. For the cupric-ammonia thiosulfate system, the leaching rates of silver sulfide is an order of magnitude less than leaching metallic silver, and more comparable to gold leaching. This is likely due to the mixed diffusion/chemical control mechanism observed for both silver sulfide and gold leaching. Leaching rates obtained for ferric-EDTA and ferric-oxalate leaching of silver sulfide are comparable to those reported by Heath et al. (2008) for gold leaching with these complexes. Thiourea, used to prevent passivation of the metallic gold surface, was not used for silver sulfide leaching.

Over the 24 hour leaching tests, ferric-EDTA was much less reactive towards thiosulfate compared to the cupric-ammonia thiosulfate system. In 24 hours, ferric-EDTA leached 70% of the silver that the cupric-ATS system leached. Only 2.5% thiosulfate loss was measured when ferric-EDTA was used compared to a 14% loss for the cupric-ATS system. The applicability of these reagents will be compared further in Chapter 4 with the application to ore from Yanacocha.
Table 3.3  Comparison of initial silver sulfide leaching rates obtained in this work with literature values for metallic silver and gold (Note: ATS=ammonium thiosulfate, TS=thiosulfate)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Metal Leaching Rate (µmol/m²/s)</th>
<th>Leaching System</th>
<th>Leaching Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂S</td>
<td>9.8</td>
<td>Cu-ATS</td>
<td>1 mM cupric, 0.10 M thiosulfate, 0.70 M total ammonia, pH 9.5, 25°C, 400 RPM (baseline)</td>
<td>Current Work</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>19.9</td>
<td>Cu-ATS</td>
<td>10 mM cupric, 0.10 M thiosulfate, 0.70 M total ammonia, pH 9.5, 25°C, 400 RPM</td>
<td>Current Work</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>8.8</td>
<td>Cu-ATS</td>
<td>1 mM cupric, 0.01 M thiosulfate, 20 mM total ammonia, pH 9.5, 25°C, 400 RPM</td>
<td>Current Work</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>0.9</td>
<td>Cu-TS</td>
<td>1 mM cupric, 0.01 M thiosulfate, pH 7, 25°C, 400 RPM</td>
<td>Current Work</td>
</tr>
<tr>
<td>Ag</td>
<td>266</td>
<td>Cu-ATS</td>
<td>25 mM cupric, 0.40 M thiosulfate, 0.84 M total ammonia, pH 10, 20°C, 300 RPM</td>
<td>(Jeffrey, 2001)</td>
</tr>
<tr>
<td>Au</td>
<td>39</td>
<td>Cu-ATS</td>
<td>25 mM cupric, 0.40 M thiosulfate, 0.84 M total ammonia, pH 10, 20°C, 300 RPM</td>
<td>(Jeffrey, 2001)</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>6.9</td>
<td>Fe-EDTA-ATS</td>
<td>10 mM ferric-EDTA, 0.10 M ammonium thiosulfate, pH 7, 25°C, 400 RPM</td>
<td>Current Work</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>0.6</td>
<td>Fe-EDTA-TS</td>
<td>1 mM ferric-EDTA, 0.01 M thiosulfate, pH 7, 25°C, 400 RPM</td>
<td>Current Work</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>7.1</td>
<td>Fe-oxalate-ATS</td>
<td>10 mM ferric-oxalate, 0.10 M ammonium thiosulfate, pH 5.5, 25°C, 400 RPM</td>
<td>Current Work</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>1.1</td>
<td>Fe-oxalate-TS</td>
<td>1 mM ferric-oxalate, 0.01 M thiosulfate, pH 5.5, 25°C, 400 RPM</td>
<td>Current Work</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>3.4</td>
<td>Fe-citrate-ATS</td>
<td>10 mM ferric-citrate, 0.10 M ammonium thiosulfate, pH 4.5, 25°C, 400 RPM</td>
<td>Current Work</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>0.7</td>
<td>Fe-citrate-TS</td>
<td>1 mM ferric-citrate, 0.01 M thiosulfate, pH 4.5, 25°C, 400 RPM</td>
<td>Current Work</td>
</tr>
<tr>
<td>Au</td>
<td>3.2</td>
<td>Fe-EDTA-ATS</td>
<td>5 mM ferric-EDTA, 0.05 M ammonium thiosulfate, pH 7, 22°C, 300 RPM, 5 mM thiourea</td>
<td>(Heath et al., 2008)</td>
</tr>
<tr>
<td>Au</td>
<td>17</td>
<td>Fe-oxalate-ATS</td>
<td>5 mM ferric-oxalate, 0.05 M ammonium thiosulfate, pH 5.5, 22°C, 300 RPM, 5 mM thiourea</td>
<td>(Heath et al., 2008)</td>
</tr>
</tbody>
</table>
Chapter 4: Application to Mercury Bearing Silver Sulfide Ore

4.1 Introduction

Mercury bearing silver sulfide ore was provided by Newmont from their Yanacocha operation for this study (see Section 2.3 for mineralogy and occurrence). This roughly crushed ore was removed from a heap leach pad that had already been treated with cyanide to recover gold and silver. Only gold was recovered efficiently when treated by cyanide at the mine. As silver recovery is very low in the cyanide process used at Yanacocha, the ore was ground and treated with thiosulfate in a series of batch tests to quantify recovery of the remaining silver, gold and mercury in the ore. The thiosulfate conditions chosen were taken from the tests conducted with the cupric-ammonia and ferric complex thiosulfate systems in Chapter 3.

The ore has been previously treated by cyanide, so the majority of gold (>85%) in the ore has already been recovered. The silver, gold and mercury content and standard deviation for the samples treated is provided in Table 4.1. The total sulfur content of the ore is 0.6±0.2% when samples were analyzed by ICP-MS.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Assay (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>20.1±3.4</td>
</tr>
<tr>
<td>Gold</td>
<td>0.18±0.04</td>
</tr>
<tr>
<td>Mercury</td>
<td>7.3±1.0</td>
</tr>
</tbody>
</table>

4.2 Experimental Methods

As received, the ore size varied from fine (~50 micron) to coarse pebbles (~3 cm). Before conducting batch leaching experiments, grinding was required (4.2.1). The test conditions
used and batch leaching setup are then described (4.2.2) and the additional analytical methods used (4.2.3).

4.2.1 Ore Preparation

A total of 2 kg of ore was received for testing with thiosulfate and cyanide. Thiosulfate testing was conducted in this work. Future testing of this ore with cyanide is being conducted by a fellow graduate student. Short time batch leaching experiments were chosen as a method for comparing the relative extractions of the different thiosulfate and cyanide systems. These experiments use ore ground to a relatively fine particle size with an 80% passing size (P80) in the range of 75-100 μm.

Ore comminution was accomplished using a laboratory rod mill with a 60% pulp density. The ore was wet ground in two 1 kg charges using a rubber lined laboratory rod mill with steel rods. Prior to grinding, the rods were cleaned using a quartz charge to remove rust. Ground ore was dewatered and dried at low temperature (~50°C) overnight. The ore was split into ~100 g portions using a laboratory splitter. A split portion was size analyzed using a series of dry sieves. The comminuted ore samples had a P80 of 80.6 μm which is within the desired range (Figure 4.1).
4.2.2 Test Conditions and Setup

The use of thiosulfate for leaching the Yanacocha ore was tested using a series of batch tests performed on \(~100\) g portions. The ore was leached at 35\% pulp density (solids by weight) in a baffled beaker. A pitched blade overhead stirrer rotating to push the slurry downwards was operated at 400 RPM. This speed was sufficient to keep the solids entirely suspended. The rotation speed was validated using a laser tachometer to keep it consistent for all tests. For experiments under a nitrogen atmosphere, the nitrogen sparging tube was maintained 3-5 mm above the surface of the slurry. A photograph of this setup is shown below (Figure 4.2). The same water bath used for rotating disk experiments was also used here to maintain a temperature of 25\(^\circ\)C for all experiments.
Leaching experiments were conducted for 24 hours with samples removed at 1, 2, 4, 8 and 24 hours. Slurry samples were removed at the specified intervals using a syringe. This caused a decrease in the total slurry mass with time, but did not change the pulp density. Intermediate slurry samples were vacuum filtered, measured, and split into samples for analysis. Small samples (~10 mL slurry) were removed to minimize total slurry volume change, so atomic absorption samples were the priority. The final 24 hour solution was also assayed for silver, gold, copper, iron, sulfur, mercury and a host of other elements by ACME Labs using ICP-MS. Solid residues were fire assayed for gold, silver and mercury to determine metal extraction from the solution assays. Acid dissolution and subsequent analysis for other metals and total sulfur content were also conducted on the solid residues.

Tests on the Yanacocha ore focused on the baseline conditions tested with the cupric-ammonia and ferric complex thiosulfate systems. The addition of EDTA to the cupric-ammonia thiosulfate leach system decreased the silver sulfide leaching rate in the synthetic...
experiments, but this system was still tested to determine the effect in the presence of ore and accompanying impurities. The experimental conditions tested are given in Table 4.2.

<table>
<thead>
<tr>
<th>Conditions studied ore leaching experiments</th>
<th>Test</th>
<th>Atmosphere</th>
<th>Thiosulfate (M)</th>
<th>Total Ammonia (M)</th>
<th>Oxidant</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu-ATS (N₂)</td>
<td>Nitrogen</td>
<td>0.10</td>
<td>0.70</td>
<td>1 mM cupric</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>Cu-ATS</td>
<td>Air</td>
<td>0.10</td>
<td>0.70</td>
<td>1 mM cupric</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>Cu-ATS (EDTA)</td>
<td>Air</td>
<td>0.10</td>
<td>0.70</td>
<td>1 mM cupric + 0.5 mM EDTA</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>Fe-Oxalate</td>
<td>Air</td>
<td>0.10</td>
<td>0.20</td>
<td>5 mM ferric-oxalate</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Fe-Citrate</td>
<td>Air</td>
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<td>0.20</td>
<td>5 mM ferric-citrate</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Fe-EDTA</td>
<td>Air</td>
<td>0.10</td>
<td>0.20</td>
<td>5 mM ferric-EDTA</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>Fe-EDTA (N₂)</td>
<td>Nitrogen</td>
<td>0.10</td>
<td>0.20</td>
<td>5 mM ferric-EDTA</td>
<td>7.0</td>
</tr>
</tbody>
</table>

4.2.3 Analytical Methods

Similar analytical methods were used for analyzing the solution for metal contents and thiosulfate as for the synthetic silver sulfide tests (see Section 3.2.2). Slurry samples were filtered using fine-slow filter paper (Fisher P4) to remove solid particles which would have interfered with the atomic absorption and titration results. No known interferences were found for silver and copper analysis in solution by atomic absorption. The ICP-MS metal assays of 24 hour solution samples were within error of the atomic absorption results. A large number of interferences were found for the iodometric titration for thiosulfate concentration.

One potential method to reduce interferences for thiosulfate analysis is to remove potentially interfering cations by using a technique such as ion chromatography. In this case, an anion exchange column is used to retain large anions which are then eluted at different rates by a high ionic strength eluent. An alternative method is to use a strong base anion exchange resin and analyze the eluate with an iodometric titration which will be free of most interferences that could be present in solution (Wassink, 2011). The procedure of loading the anion

95
exchange resin and analyzing the stripped solution for thiosulfate is described in detail in the Appendix. Stripping thiosulfate from the resin is complete with no detectable losses. Samples were analyzed as soon as possible after sampling to prevent further thiosulfate oxidation. This titration was found to have the same error as the standard iodometric titration (1.5%).

4.3 Results: Cupric-Ammonia Thiosulfate System

Three leaching tests were conducted with the cupric-ammonia thiosulfate system at 1 mM cupric, 0.10 M thiosulfate, 0.70 M total ammonia, 25°C, pH 9.5: leaching open to air, leaching under a nitrogen atmosphere and leaching open to air with the addition of 0.5 mM EDTA. In addition to these tests, a very high dose cyanide leach test was conducted (10 g/L NaCN) for 24 hours at a pH of 10.5. Solid assays are still forthcoming; however given the mean silver head assay from other tests, cyanidation extracted 34% with a 95% confidence interval of 28-37% silver extraction.

The thiosulfate loss over the course of leaching varied significantly between tests (Figure 4.3). Due to the rapid loss of thiosulfate in the cupric-ammonia test open to the air, the test was stopped after 10 hours. This was done to prevent loss of all thiosulfate and subsequent precipitation of leached silver.
Figure 4.3  Thiosulfate loss during ore leaching for cupric-ammonia thiosulfate tests.

Compared to tests conducted open to air, leaching under a nitrogen atmosphere prevented excessive oxidative destruction of thiosulfate. The addition of EDTA slightly decreased thiosulfate consumption allowing leaching to continue for 24 hours.

The silver extraction from ore samples using the cupric-ammonia systems is plotted in Figure 4.4. Ultimate silver recovery was comparable for all three systems, although the leaching rates differed. The tests open to air leached silver quicker than the test conducted under a nitrogen atmosphere. Although the addition of EDTA had a negative effect on the silver sulfide extraction rate in the rotating disk tests, EDTA enhanced the silver leaching rate when added to the ore pulp.
4.4 Results: Ferric Complex Thiosulfate System

Four leaching tests were conducted with 5 mM ferric complexes and 0.10 M ammonium thiosulfate, 25°C: ferric-EDTA at pH 7.0, ferric-EDTA at pH 7.0 under a nitrogen atmosphere, ferric-oxalate at pH 5.5 and ferric-citrate at pH 4.5.

The thiosulfate consumption for tests open to air was comparable (Figure 4.5). Each of the ferric complexes studied was less reactive towards thiosulfate than the cupric-ammonia conditions studied. Ferric precipitation was only observed for the ferric-oxalate tests. By the end of the test, only 0.6 mM ferric remained in solution.
Overall silver recovery varied widely for ferric complex leaching (Figure 4.6). Under a nitrogen atmosphere, silver leached by ferric-EDTA precipitated out after 2 hours resulting in a very low overall silver extraction. The measured solution potential versus a saturated Ag/AgCl reference electrode was -260 mV at the end of the leaching test, which would have significantly reduced the stability of the silver thiosulfate complex. For comparison, the average leaching potential when the ferric complexes were used open to air was 50 mV and the potential of the cupric-ammonia system under nitrogen was -80 mV at the end of the 24 hours. Of the three ferric complexes, ferric-EDTA was the most effective at leaching silver sulfide when used in an air atmosphere.
4.5 Results: Copper, Gold and Mercury

The copper concentration was measured with time to determine if copper was lost from solution as leaching proceeded due to the substitutional leaching mechanism (in the cupric-ammonia tests). Final solution assays for cupric-ammonia and ferric complex tests all indicated significant copper dissolution from the ore. In the ferric complex leaching tests, the final copper concentration in the solution was up to 20 mg/L (no copper was added to the solution at the beginning of the test). The ore initially contained approximately 320 ppm copper. By the end of the leaching tests the copper content of the ore was 260±20 ppm indicating that copper was leached into solution. The mineralogical report for Yanacocha indicates that the primary copper carrier is covellite (AMTEL, 2010).

Very little mercury and gold dissolution was observed across all tests. In the final solution assays conducted with ICP-MS, the final mercury concentration was 0.3±0.2 ppb or less. The final gold concentration was similarly low and varied between <0.5 to 2±0.5 ppb. Up to 5 g/L
calcium dissolution was observed across the tests. This is likely due to residual calcium contamination of the ore from the treatment with lime to maintain an alkaline pH for cyanide heap leaching.

4.6 Analysis and Discussion

4.6.1 Metal Recovery

The use of thiosulfate with cupric-ammonia or ferric complexes did not leach gold or mercury from the ground Yanacocha ore. Based on the mineralogical report of Yanacocha, gold remaining in the ore was likely very fine and trapped in quartz or other minerals (AMTEL, 2010). The P80 size of 80.4 µm that this ore was ground to was not fine enough to recover residual gold in the samples.

Significant mercury dissolution was not observed for any of the leach tests conducted. Thiosulfate has been shown to have a similar reactivity towards metallic mercury and mercury chloride as cyanide, so if exposed mercury or mercury chloride was present in the ore then it would have been leached (Oraby et al., 2010). Oraby et al. report that thiosulfate leaches cinnabar (mercury sulfide) much slower than cyanide. Mercury at a comparable Yanacocha composite is in the form of 69% cinnabar and 31% velkite (Cu₂HgSnS₄) (McComb and Thogerson, 2011) which explains the low mercury dissolution by thiosulfate.

The overall silver recovery into solution ranged from 0.3% with the ferric-EDTA system under a nitrogen atmosphere to 32% with the cupric-ammonia thiosulfate system with the addition of 0.5 mM EDTA. For all tests, the cupric-ammonia thiosulfate systems recovered
more silver compared to the use of ferric complexes. The effect of nitrogen, addition of EDTA and use of different ferric complexes on silver recovery will be discussed.

Purging the solution with nitrogen had a dramatically different effect when the cupric-ammonia system was used compared to the use of ferric-EDTA. When cupric-ammonia thiosulfate leaching was carried out in an anaerobic environment, silver leached slower compared to the aerobic conditions. Aerobic conditions would have maintained a consistently higher amount of cupric in solution. This agrees with the conclusion in Chapter 3 that silver sulfide leaching by the cuprous reaction must overcome a significant thermodynamic barrier. Silver recovery was slower when nitrogen was purged although this prevented excessive oxidative loss of thiosulfate allowing the leaching process to continue for 24 hours.

When ferric-EDTA was used under a nitrogen atmosphere, the reduction of all ferric to ferrous and subsequent drop in solution potential reduced the stability of silver thiosulfate to the point where it precipitated out of solution. If ferric-EDTA were to be used in an anaerobic leaching environment, sufficient ferric-EDTA would need to be added to maintain an oxidizing environment. In the presence of sulfide minerals, such as in the Yanacocha ore which contains small amounts of pyrite and arsenopyrite, ferric-EDTA would be reduced in solution.

The addition of EDTA to the cupric-ammonia thiosulfate system increased the initial silver leaching rate compared to the other cupric-ammonia tests. Data collected on the silver sulfide leaching rate in Chapter 3 demonstrates that mineral acanthite leaches slower with the
addition of EDTA. However, accelerated silver leaching in the presence of EDTA when leaching a sulfide ore has been previously observed by Feng and van Deventer (2010). This was attributed to increased sulfide dissolution rate by preventing the buildup of passive oxide layers on sulfide surfaces. For acanthite particles partially surrounded by other sulfide minerals, the addition of EDTA would have a positive effect.

Increased copper dissolution from the ore was also observed in the presence of EDTA by Feng and van Deventer. Copper was recovered from the ore into the leach solution by thiosulfate with all systems tested in this study. The amount of copper recovered between tests was comparable; numerous experiments would need to be conducted to discern a statistically significant difference. If EDTA increases copper dissolution from the ore as reported by Feng and van Deventer, then this should have a positive effect on leaching with this system as it would increase the availability of copper ions for the substitution reaction.

Of the ferric complexes, ferric-EDTA in an aerobic environment was the most effective at recovering silver. By the end of the 24 hour leaching test, 26% of the silver was recovered which is comparable to the 31% recovered in the cupric-ammonia tests. Ferric-citrate and ferric-oxalate were not as effective at recovering silver, leaching 19% and 7%, respectively. When used to leach synthetic silver sulfide, ferric-oxalate and ferric-EDTA were much more effective than ferric-citrate. This discrepancy is explained by the large amount of iron precipitation observed when ferric-oxalate was used. The final concentration of iron in solution when ferric-oxalate was used was 0.6 mM. No iron loss from solution (within error) was measured when ferric-EDTA and ferric-citrate were used. For this ore, ferric-oxalate was
much less stable compared to ferric-citrate or ferric-EDTA, so would be unsuitable for silver leaching.

4.6.2 Thiosulfate Loss

For leaching tests conducted open to air, thiosulfate consumption in the cupric-ammonia systems was much higher than it was for ferric complexes. Under a nitrogen atmosphere, thiosulfate consumption was comparable for the two systems.

When open to air, the cupric-ammonia thiosulfate system consumed the most thiosulfate. This was expected due to the inherent instability of the cupric-tetrammine complex in the presence of thiosulfate. For this reason, the cupric-ammonia thiosulfate system was stopped after 10 hours to prevent loss of all thiosulfate from the system. Other researchers have noted the importance of controlling oxygen in the cupric-ammonia system to prevent excessive loss of thiosulfate (Jeffrey et al., 2003; Senanayake, 2005). The addition of EDTA decreased thiosulfate consumption from 14.8 to 11.8 kg/t. Although EDTA was found to depress silver leaching for the synthetic silver sulfide leaching tests, it had a positive effect on both silver extraction and thiosulfate consumption when leaching Yanacocha ore.

The thiosulfate consumption for ferric complexes open to air was comparable, ranging from 6.2 to 9.0 kg/t. Ferric-EDTA consumed the lowest amount of thiosulfate at 6.2 kg/t and leached the most silver. Ferric-citrate consumed the most thiosulfate of the ferric complexes, probably due to the lower stability of the thiosulfate complex at the acidic pH of 4.5 used with ferric-citrate. The lower consumption of thiosulfate by ferric-EDTA in an anaerobic environment is irrelevant given the negligible amount of silver leached.
4.7 Summary and Conclusions

None of the systems tested leached significant amounts of gold or mercury. The silver recovery and thiosulfate consumption (kg S$_2$O$_3^{2-}$ consumed/t ore) for each of the leaching tests is given below in Table 4.3. Overall silver recovery for all systems was low, likely due to silver locking in quartz (AMTEL, 2010). This has been previously observed for cyanide heap leaching tests of this ore. In the cyanidation test conducted, 34% silver extraction was achieved with a 95% confidence interval of 28-37%. This indicates that thiosulfate tests with the cupric-ammonia and ferric-EDTA complexes are capable of leaching almost all silver accessible to cyanide. Silver unleached by thiosulfate could be in a mineralogical form that is not leached by thiosulfate at the conditions tested.

Table 4.3 Comparison of silver recovery and reagent consumption across all ore leaching tests for 24 hour leaching tests (10 hours for Cu-ATS).

<table>
<thead>
<tr>
<th>Test</th>
<th>Overall Silver Extraction (%)</th>
<th>Thiosulfate Consumption (kg/t)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-ATS (N$_2$)</td>
<td>31%</td>
<td>3.1</td>
</tr>
<tr>
<td>Cu-ATS</td>
<td>31%</td>
<td>14.2</td>
</tr>
<tr>
<td>Cu-ATS (EDTA)</td>
<td>32%</td>
<td>11.8</td>
</tr>
<tr>
<td>Fe-Oxalate</td>
<td>7%</td>
<td>6.4</td>
</tr>
<tr>
<td>Fe-Citrate</td>
<td>19%</td>
<td>9.0</td>
</tr>
<tr>
<td>Fe-EDTA</td>
<td>26%</td>
<td>6.2</td>
</tr>
<tr>
<td>Fe-EDTA (N$_2$)</td>
<td>0.3%</td>
<td>2.5</td>
</tr>
<tr>
<td>10 g/L NaCN</td>
<td>34% (95% CI of 28-37%)</td>
<td></td>
</tr>
</tbody>
</table>

*Thiosulfate consumption given in kg S$_2$O$_3^{2-}$/t ore. The equivalent amount of thiosulfate from the sodium and ammonium salts: 1 kg S$_2$O$_3^{2-}$ = 1.41 kg Na$_2$S$_2$O$_3$ = 1.32 kg (NH$_4$)$_2$S$_2$O$_3$. See Appendix for sample calculations.

The cupric-ammonia thiosulfate system is capable of recovering silver in an aerobic or anaerobic environment with or without the addition of EDTA. Adding EDTA accelerates leaching in an aerobic environment and decreases thiosulfate consumption. In an anaerobic environment, silver sulfide is leached slower; however thiosulfate consumption is very low making this an attractive option for heap leaching. The ability to leach small amounts of
copper in the ore is a bonus for this system since it increases the availability of copper in solution for silver leaching.

The most suitable ferric complex for silver leaching from the Yanacocha ore was ferric-EDTA which recovered the most silver and used the lowest amount of thiosulfate. The use of ferric complexes is limited to aerobic environments or the use of excess ferric to maintain an oxidizing environment and prevent silver precipitation. Ferric-oxalate precipitated out of solution during leaching, so was ineffective. Ferric-citrate effectively leached silver sulfide, but consumed more thiosulfate than ferric-EDTA due to the lower pH used.
Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The application of thiosulfate to leach a synthetic silver sulfide rotating disk and a silver sulfide bearing ore using cupric-ammonia, cupric-ammonia with EDTA, ferric-EDTA, ferric-oxalate and ferric-citrate has been studied.

In a cupric-ammonia thiosulfate leach, silver sulfide can be leached either by a cupric-tetrammine or cuprous-thiosulfate substitution reaction. The cuprous substitution reaction must overcome a large thermodynamic barrier to occur. The rate of leaching by the cupric-tetrammine complex depends on maximizing both the stability of cupric in solution and thiosulfate availability to dissolve silver. For the conditions tested, leaching with the cupric-ammonia thiosulfate system is under mixed chemical/diffusion control with thiosulfate concentration limiting the slow chemical step. The addition of EDTA in amounts comparable to the concentration of cupric in solution decreased the leaching rate of synthetic silver sulfide.

When leaching the Yanacocha ore with the cupric-ammonia thiosulfate system, the silver sulfide leaching rate was maximized when leaching was conducted in an air atmosphere with the addition of EDTA. Thiosulfate consumption for cupric-ammonia tests conducted open to air was high; even with the addition of EDTA, thiosulfate consumption was 11.8 kg/t. Under a nitrogen atmosphere thiosulfate consumption decreased to 3.1 kg/t. Silver recoveries were comparable after 24 hours, although anaerobic conditions slowed down the leaching process. This would not be an obstacle for heap leaching operations where reagent consumption is
more important than shortening leach times. In addition, the ability of the thiosulfate solution to leach some copper present in the ore is advantageous for silver recovery.

Three ferric complexes were considered as potential oxidants for silver sulfide leaching with thiosulfate: ferric-EDTA at pH 7, ferric-oxalate at pH 5.5 and ferric-citrate at pH 4.5. Leaching of synthetic silver sulfide was fastest for ferric-EDTA and ferric-oxalate. When applied to the Yanacocha ore, ferric-oxalate precipitated out of solution resulting in very low silver recoveries. Ferric-EDTA recovered more silver and consumed less thiosulfate than ferric-citrate making it the most suitable ferric complex oxidant. Thiosulfate consumption was low when ferric complexes were used open to air (6.2 kg/t for ferric-EDTA). Under a nitrogen atmosphere, reduction of all ferric in solution from reaction with sulfides in the ore and the accompanying decrease in potential caused silver to precipitate out of solution. In a heap leach situation, the low reactivity of ferric-EDTA towards thiosulfate makes it an attractive alternative to the cupric-ammonia system; however sufficient ferric-EDTA or oxygen needs to be present to maintain an oxidizing environment in the presence of sulfides.

Silver recovery from the Yanacocha ore was low in all cases (<32%), likely due to silver locking in quartz. Cyanidation with very high concentrations of cyanide (10 g/L NaCN) was unable to recover significantly more silver at 34% with a 95% confidence interval of 28-37%. This is due to silica locking of silver and has been previously observed for cyanide leaching tests of this ore. Thiosulfate was able to recover more silver from this already leached ore, but unfortunately there is considerable metal value that remains trapped in the ore after leaching.
5.2 Recommendations and Future Work

The behavior of thiosulfate leach solutions has been explored for relatively short time periods; this is useful in understanding kinetics but more work would be necessary to understand long term stability. Long term column leaching tests on Yanacocha heap ore in its original form should be undertaken with both ferric-EDTA and the cupric-ammonium thiosulfate systems. This would provide a better understanding of thiosulfate consumption in both systems and the required amount of ferric-EDTA required in solution to prevent precipitation of silver in an environment with very little dissolved oxygen. Current understanding of the effect of sulfides on ferric is limited; more work in this area is necessary to gain a fundamental understanding of ferric leaching processes and the effect of sulfides.

The addition of EDTA to the cupric-ammonium thiosulfate system when leaching synthetic silver sulfide depressed leaching, but when added to the ore pulps enhanced silver leaching. Further work to understand the reason for this change should be undertaken to determine if EDTA would be a valuable addition to a real ore leaching operation.

Further comparison of silver recovery by thiosulfate and cyanide should be accomplished by performing a comparable series of batch leaching tests and measuring silver recovery.

Finally, a series of batch leaching tests using different particle size distributions of the Yanacocha should be conducted to understand the limitations on silver extraction from all systems studied due to silver locking in quartz and associated minerals.
References


AMTEL, 2010. Silver Deportation of Two (2) Minera Yanacocha Silver Study Samples.


Appendices

Appendix A  Analytical Methods

The main analytical methods used are documented here. For chemical analysis, atomic absorption spectroscopy (AAS), ultraviolet visible spectroscopy (UV-vis) and titrations were used. All water used was deionized and chemicals were at least ACS grade. ACME Labs in Vancouver (a certified assayer) performed fire assaying for gold on solid ore samples and ICP-MS on some solution samples from the Yanacocha ore leaching experiments.

A.1  Iodometric Titration for Thiosulfate

Theory

Thiosulfate concentration in solution was determined using an iodometric titration. The principal reaction is the oxidation of thiosulfate to tetrathionate and the reduction of iodine to iodide.

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Iodine is both volatile and insoluble in water. It can be kept in solution by the addition of excess iodide. Iodine reacts reversibly with iodide to form the highly soluble triiodide ion.

$$I_2 + I^- \rightleftharpoons I_3^-$$

As iodine is notoriously difficult to weigh due to its hydroscopic behavior, it was generated in solution by reacting a known amount of iodate with excess iodide in dilute sulfuric acid according to the following reaction. The addition of excessive sulfuric acid will result in rapid disproportionation of thiosulfate when the iodine is introduced, so care must be taken.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
This iodine is then stabilized as triiodide with the excess iodide in solution. In the presence of the triiodide ion, starch indicator in solution will stain the solution a deep blue/black colour from the formation of polyiodide chains.

**Procedure**

Much of the procedure was developed through discussions with Bé Wassink and referencing Quantitative Chemical Analysis (Harris, 1991). The starch indicator was prepared frequently (once per week) as it decomposes rapidly from light and bacterial attack. Indicator solutions were approximately 1% by mass starch and 0.001% mercuric iodide to slow indicator degradation. The indicator was prepared by adding 1 g of starch and 1 mg of mercuric iodide (HgI₂) to 10 mL of boiled and cooled deionized water to form a paste. This paste was then added to 100 mL of boiling water and boiled which was boiled until the solution was clear.

The iodine titrant was prepared by dissolving 0.143 g of potassium iodate, 4.0 g of potassium iodide and ~1.5 mL of concentrated sulfuric acid (added until all solids had dissolved) in 200.0 mL of deionized water. The resulting solution was a 0.010 M iodine solution. This titrant was frequently made to prevent errors from solution degradation.

The titration was conducted by pipetting a known amount of thiosulfate containing solution into a flask, adding 2 mL of starch indicator, making up the volume to 25 mL and titrating until the solution turned a permanent deep blue/black colour.

The cupric ion is known to interfere with iodometric titrations, so steps must be taken to minimize this effect for accurate titration results. One method of minimizing this effect is to
pass the solution over a strong base anion exchange resin prior to titrating, however this method is slow and labor intensive. For solutions from synthetic silver sulfide leaching experiments, the effect of the cupric tetrammine complex was minimized by the addition of 2 mL of pH 5.5 acetic acid-sodium acetate (5%) buffered solution to suppress this interference. The pH of the solution was kept above 5.5 to prevent thiosulfate disproportionation excessively acidic conditions.

To deal with the large number of interferences in leach solutions from real ore leaching experiments, the thiosulfate containing solution was passed over a strong base anion exchange resin. The resin used in this study was Amberlite IRA 400 Cl. A column of 7.5 g of resin in a 25 mL buret was prepared. The procedure developed by Wassink (2011) for thiosulfate analysis in the presence of interferences was used. It will be briefly described here.

30 mL of 1 M solution of sodium nitrate at pH 8 is first passed over the resin and the resin rinsed with 30 mL of deionized water. The thiosulfate bearing solution is passed over the resin and rinsed with 30 mL deionized water. Elution of the resin is accomplished by passing the 30 mL of the sodium nitrate solution over the resin. This eluate is then immediately titrated for thiosulfate using the iodometric titration. All solutions are slowly passed over the resin, at a rate of approximately 2 mL/min. The error of this method for the titrations is less than 1.5%.
Standardization

This iodometric titration procedure and addition of acetic acid-acetate buffer solution to minimize copper interference was validated in a number of tests. Solutions of known compositions were titrated to determine the relative error in this titration under a variety of conditions. The resin method was only briefly validated and found to have the same error as the regular titration. Further details on the errors associated with this method have been documented by Wassink. Thiosulfate standards were made up by dissolving ammonium thiosulfate, ammonium sulfate and sodium hydroxide in freshly boiled and cooled water (to kill bacteria prior to adding the thiosulfate). This solution was stored in a tightly capped amber bottle to slow solution degradation. The results of the standardization tests are given below in Tables A.1-A.4.

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<tr>
<th>Table A.1 Starch solution composition.</th>
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<tr>
<td>Starch (g)</td>
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<td>Mercuric Iodide (mg)</td>
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<td>Volume (mL)</td>
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<table>
<thead>
<tr>
<th>Table A.2 Iodine titrant composition.</th>
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<tbody>
<tr>
<td>Potassium Iodate (g)</td>
</tr>
<tr>
<td>Potassium Iodide (g)</td>
</tr>
<tr>
<td>Volume (mL)</td>
</tr>
<tr>
<td>Iodine (M)</td>
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</table>

<table>
<thead>
<tr>
<th>Table A.3 Thiosulfate standard solutions compositions.</th>
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<tr>
<td>Solution ID</td>
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<tr>
<td>Ammonium Thiosulfate (g)</td>
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<tr>
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</tr>
<tr>
<td>Cupric Sulfate (g)</td>
</tr>
<tr>
<td>Ammonium Sulfate (g)</td>
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<td>Cupric (M)</td>
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<td>Total Ammonia (M)</td>
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Table A.4 Titration standardization test results.

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Titrant Added (mL)</th>
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<th>Theo. Iodine (mmol)</th>
<th>S₂O₃ Vol (mL)</th>
<th>Thiosulfate (mmol)</th>
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<td>Cal D5</td>
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<td>0.152</td>
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<tr>
<td>Cu</td>
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<td>E</td>
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<tr>
<td>Cu</td>
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<td>0.0364</td>
<td>E</td>
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</tr>
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<td>Cu Cal</td>
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<td>0.0758</td>
<td>F</td>
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<td>0.0758</td>
<td>F</td>
<td>3.00</td>
<td>0.152</td>
</tr>
<tr>
<td>Cu + 2mL AA-Ac</td>
<td>7.36</td>
<td>0.0730</td>
<td>0.0752</td>
<td>G</td>
<td>3.00</td>
<td>0.150</td>
</tr>
<tr>
<td>Cu + 2mL AA-Ac</td>
<td>7.49</td>
<td>0.0743</td>
<td>0.0752</td>
<td>G</td>
<td>3.00</td>
<td>0.150</td>
</tr>
<tr>
<td>Cu + 2mL AA-Ac</td>
<td>7.44</td>
<td>0.0738</td>
<td>0.0752</td>
<td>G</td>
<td>3.00</td>
<td>0.150</td>
</tr>
<tr>
<td>Cu + 2mL AA-Ac</td>
<td>7.51</td>
<td>0.0745</td>
<td>0.0752</td>
<td>G</td>
<td>3.00</td>
<td>0.150</td>
</tr>
</tbody>
</table>

When cupric sulfate was added to the thiosulfate solution, the titration results were not reliable with errors ranging from 2.6-10.5%. The addition of 2 mL of pH 5.5 acetic acid-sodium acetate buffer reduced this error to the more manageable level of 1.5%.

A.2 Atomic Absorption Spectrophotometry (AAS)

Theory and Procedure

The theory of atomic absorption spectrophotometry was introduced in Section 3.2.2. This method relies on the atomization of a small amount of sample. The absorption of light at a characteristic wavelength is related to the concentration of an element with the Beer-Lambert law. Standard operating procedures were followed for the use of an air-acetylene flame.

Preparation of Standards

Atomic absorption standards were acquired from Fisher at a concentration of 1000 ppm. Standards were originally in a nitric acid matric which would not be suitable for comparing solution results from thiosulfate leach tests. Solution properties can have a significant effect
on absorbance values as physical properties will change the amount of solution that is volatilized by the nebulizer as well as droplet size and dispersion. Therefore, volumetric amounts of standard solutions were neutralized using sodium hydroxide followed by the addition of ammonia/ammonium sulfate buffer and thiosulfate to approximate the concentrations of these species in the samples. All standards were stored in the dark and kept for no longer than 1 week.

Copper
The detection range for copper is between 0 and 5 mg/L at a wavelength of 327.4 nm. The absorbance curve was linear over the range of interest.

Silver
The ideal detection range for silver is between 0 and 4 mg/L at a wavelength of 328.1 nm. The absorbance curve deviated slightly from linear behavior at high concentrations.

Iron
The detection range for iron is 1-100 mg/L at a wavelength of 372.0 nm. The absorbance curve deviates significantly from linear behavior at high concentrations. In addition, high sulfate concentrations will interfere with iron absorbance. High sample dilution meant that this was not an issue.

A.3 Ultraviolet Visible Spectroscopy (UV-vis)

Theory and Procedure
The theory of ultraviolet visible spectroscopy (UV-vis) is very similar to the theory for atomic absorption, although it is applied to complexes. The Beer-Lambert law can be used to relate the absorbance of ultraviolet light at a specific wavelength, corresponding to the cupric-tetrammine peak, to a concentration. This is done through the preparation of standards
with known concentrations. All solutions were mixed in the cuvette to minimize the time for copper(II) loss due to transferring solutions.

**Preparation of Standards**

Standards were prepared at pH 10 in the cuvette. Preparing the standards in the cuvette minimized the time for reduction of cupric-tetrammine complex. A detailed procedure for standard preparation is discussed in the work of Ahern (2005).

### A.4 Reagent Specifications

The sources and grades of primary reagents used in this study are specified in the table below.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molecular Weight</th>
<th>Grade/Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH</td>
<td>60.05</td>
<td>99.0+% ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>(NH₄)₂SO₄</td>
<td>132.14</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Ammonium thiosulfate</td>
<td>(NH₄)₂S₂O₃</td>
<td>148.19</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>Ca(OH)₂</td>
<td>74.093</td>
<td>ACS</td>
<td>BDH Chemicals</td>
</tr>
<tr>
<td>Cupric sulfate pentahydrate</td>
<td>CuSO₄·5H₂O</td>
<td>249.70</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Ferric ammonium sulfate</td>
<td>NH₄Fe(SO₄)₂·12H₂O</td>
<td>482.25</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Lead nitrate</td>
<td>Pb(NO₃)₂</td>
<td>331.20</td>
<td>ACS</td>
<td>MCB Chemicals</td>
</tr>
<tr>
<td>Mercuric iodide</td>
<td>HgI₂</td>
<td>454.40</td>
<td>99.0+% ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Potassium iodate</td>
<td>KIO₃</td>
<td>214.00</td>
<td>99.5+%</td>
<td>BDH Chemicals</td>
</tr>
<tr>
<td>Potassium iodide</td>
<td>KI</td>
<td>166.00</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Silver sulfide (acanthite)</td>
<td>Ag₂S</td>
<td>247.80</td>
<td>-</td>
<td>AD Mackay Inc</td>
</tr>
<tr>
<td>Sodium acetate trihydrate</td>
<td>Na₃C₆H₅O₂</td>
<td>136.03</td>
<td>99.5+%</td>
<td>BDH Chemicals</td>
</tr>
<tr>
<td>Sodium citrate dihydrate</td>
<td>Na₃C₆H₇O₇·2H₂O</td>
<td>294.10</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Sodium pyrophosphate</td>
<td>Na₃P₂O₇</td>
<td>265.90</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Sodium oxalate</td>
<td>Na₂C₂O₄</td>
<td>134.00</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Sodium thiosulfate</td>
<td>Na₂S₂O₃</td>
<td>158.11</td>
<td>ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Starch (for iodometry)</td>
<td>-</td>
<td>-</td>
<td>ACS</td>
<td>Nichols Chemical Co</td>
</tr>
</tbody>
</table>
A.5  Synthesis of Ferric Complexes

Ferric complexes were synthesized in the lab using ferric ammonium sulfate (FAS) and the sodium salts of the complexing agents so that the stoichiometry could be controlled. 2% more of each complexing agent than necessary by the stoichiometry was added to ensure that sufficient reagent was present to account for any impurities in the reagents. The deionized water was slightly acidified using dilute sulfuric acid to stabilize the complex in solution. Dissolution was accomplished by heating on a stirred hotplate. The concentration of 0.25 M was achieved by dilution in a volumetric flask. Ferric-oxalate and ferric-citrate were readily prepared. Ferric-EDTA required heating above 50°C and stirring overnight to fully dissolve in solution. Once dissolved, the solution was stable at room temperature.
Appendix B  Sample Calculations

In this Appendix sample calculations for the main calculations used in this thesis are detailed.

B.1  Conversion of Leaching Rates

Multiple leaching rate conversions were used to express the measured leaching rates in useful units such as mmol$_{\text{Ag leached}}$/m$^2$/s or µm Ag$_2$S$_{\text{dissolved}}$/hr.

Conversion of original leaching data (in mg$_{\text{Ag}}$/min for the 2.835 x 10$^{-4}$ m$^2$ disk in use) to µm/hr:

\[
\frac{1 \text{ mg} \text{ Ag}}{\text{min}} \cdot \frac{\text{g}}{1000 \text{ mg}} \cdot \frac{\text{mol Ag}}{107.868 \text{ g Ag}} \cdot \frac{\text{mol Ag}_2\text{S}}{2 \text{ mol Ag}} \cdot \frac{247.80 \text{ g Ag}_2\text{S}}{\text{mol Ag}_2\text{S}} \cdot \frac{60 \text{ min}}{1 \text{ hr}} \cdot \frac{\text{cm}^3}{7.23 \text{ g Ag}_2\text{S}} \cdot \frac{\text{m}^2 \mu\text{m}}{\text{cm}^3} = 33.624 \frac{\mu\text{m Ag}_2\text{S}_{\text{dissolved}}}{\text{hr}}
\]

Conversion of original leaching data (in mg$_{\text{Ag}}$/min for the 2.835 x 10$^{-4}$ m$^2$ disk in use) to mmol$_{\text{Ag leached}}$/m$^2$/s:

\[
\frac{1 \text{ mg} \text{ Ag}}{\text{min}} \cdot \frac{\text{mol Ag}}{107.868 \text{ g Ag}} \cdot \frac{1}{2.835 \cdot 10^{-4} \text{ m}^2} \cdot \frac{1}{60 \text{ s}} = 0.5450 \frac{\text{mmol Ag}_{\text{dissolved}}}{\text{m}^2 \text{s}}
\]

Conversion between mmol$_{\text{Ag leached}}$/m$^2$/s and µm/hr:

\[
\frac{1 \text{ mmol Ag}}{\text{m}^2 \text{s}} \cdot \frac{\text{mol Ag}}{1000 \text{ mmol}} \cdot \frac{3600 \text{ s}}{\text{hr}} \cdot \frac{\text{mol Ag}_2\text{S}}{2 \text{ mol Ag}} \cdot \frac{247.80 \text{ g Ag}_2\text{S}}{\text{mol Ag}_2\text{S}} \cdot \frac{7.23 \text{ g Ag}_2\text{S}}{\text{cm}^3} = 61.695 \frac{\mu\text{m Ag}_2\text{S}_{\text{dissolved}}}{\text{hr}}
\]

B.2  Calculation of Silver Extraction

To calculate silver extraction, the total silver dissolved was first calculated. Calculations for other parameters such as copper loss or thiosulfate consumption are almost identical. The calculation of total silver dissolved at the time when sample $j$ was taken is a function of the
initial solution volume $V_{initial}$, the sample silver assays $C_i$ for $i=1,2,\ldots,j$ and the sample solution volumes $V_i$ for $i=1,2,\ldots,j-1$ (where the current sample is sample $j$):

$$\text{Ag}_{\text{dis}}(j)=\sum_{i=1}^{j-1} V_i C_i + \left( V_{initial} - \sum_{i=1}^{j-1} V_i \right) C_j$$

The silver dissolved was calculated for all samples $i=1,2,\ldots,n$. The total silver dissolved for the leaching period equal to the total silver dissolved when the last sample was taken: $\text{Ag}_{\text{dis}}(n)$. The unleached solids residue (from filtering slurry samples taken over the course of leaching) and final solids residue were fire assayed for silver content. The total silver present in the head sample is then:

$$\text{Ag}_{\text{head}} = \text{Ag}_{\text{dis}}(n) + \text{Ag}_{\text{solids}}(\text{unleached}) + \text{Ag}_{\text{solids}}(\text{final residue})$$

The silver extraction is calculated as the ratio of dissolved silver at sample $i$ to total silver initially present in the sample.

$$\text{Ag}_{\text{head}} = \text{Ag}_{\text{extr}}(i) = \frac{\text{Ag}_{\text{dis}}(n)}{\text{Ag}_{\text{head}}}$$

### B.3 Calculation of Thiosulfate Consumption

Thiosulfate consumption as kg $\text{S}_2\text{O}_3^{2-}$ was calculated for each ore based on the leaching parameters (mass of ore leached, initial solution volume) and change in thiosulfate concentration. A sample calculation for the Cu-ATS (Nitrogen) test is provided below given these parameters.

$V_{initial} = 0.2334$ L

$\text{Mass}_{\text{ore}} = 0.1257$ kg

$\text{TS}_{initial} = 0.100$ M

$\text{TS}_{final} = 0.085$ M

$\text{TS}_{consumption} = ??$ kg $\text{S}_2\text{O}_3^{2-}/t$ ore
The thiosulfate consumption is given in kg $S_2O_3^{2-}$/t ore. To convert this to the equivalent mass of sodium or ammonium thiosulfate:

\[
\frac{112.13 \text{ g } S_2O_3^{2-}}{\text{mol } S_2O_3^{2-}} \cdot \frac{1 \text{ kg } S_2O_3^{2-}}{1000 \text{ g } S_2O_3^{2-}} = 3.1 \text{ kg } S_2O_3^{2-}/t \text{ ore}
\]

Therefore, 1 kg $S_2O_3^{2-} = 1.41$ kg $Na_2S_2O_3 = 1.32$ kg $(NH_4)_2S_2O_3$.

**B.4 Thermodynamic Calculations**

Thermodynamic data used was from Aylmore and Muir (2001), Martell and Smith (1989) and the HSC and ChemEql Chemical Databases. The data used is compiled in Table A.6. The sample calculations shown below are for the calculation of the standard reaction free energy change ($\Delta G^\circ$) for the leaching of silver sulfide with cuprous and thiosulfate as given in Section 2.4.3 Application to Silver Sulfide Leaching.
Table A.6  Thermodynamic data used

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>Formula</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>Formula</th>
<th>$\Delta G^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0</td>
<td>Cu</td>
<td>0</td>
<td>S</td>
<td>0</td>
</tr>
<tr>
<td>Ag^+</td>
<td>77.2</td>
<td>Cu^+</td>
<td>50.208</td>
<td>S^3</td>
<td>91.9</td>
</tr>
<tr>
<td>AgO</td>
<td>10.9</td>
<td>Cu^{2+}</td>
<td>64.978</td>
<td>S^{2-}</td>
<td>79.7</td>
</tr>
<tr>
<td>Ag_2O</td>
<td>-10.8</td>
<td>CuO</td>
<td>-127.194</td>
<td>S_3^{2-}</td>
<td>73.8</td>
</tr>
<tr>
<td>Ag_2O_3</td>
<td>87.0</td>
<td>Cu_2O</td>
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<td>S_4^{2-}</td>
<td>69.4</td>
</tr>
<tr>
<td>AgOH</td>
<td>-92.0</td>
<td>Cu(OH)_2</td>
<td>-356.895</td>
<td>S_8^{2-}</td>
<td>66.1</td>
</tr>
<tr>
<td>Ag_2S</td>
<td>-40.5</td>
<td>CuS</td>
<td>-48.953</td>
<td>H_2S</td>
<td>-27.3</td>
</tr>
<tr>
<td>Ag(S_2O_3)_3^-</td>
<td>-506.3</td>
<td>CuS_2</td>
<td>-86.190</td>
<td>HS^-</td>
<td>12.6</td>
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<tr>
<td>Ag(S_2O_3)_2^{2-}</td>
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<td>Cu(S_2O_3)_3</td>
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<td>S_2O_4^{2-}</td>
<td>-532.2</td>
</tr>
<tr>
<td>Ag(S_2O_3)_3^{2-}</td>
<td>-1598.3</td>
<td>Cu(S_2O_3)_2^-</td>
<td>-1084.07</td>
<td>HS_2O_3^-</td>
<td>-541.8</td>
</tr>
<tr>
<td>Ag(NH_3^+)</td>
<td>31.8</td>
<td>Cu(S_2O_3)_3^-</td>
<td>-1624.65</td>
<td>S_2O_5^-</td>
<td>-600.6</td>
</tr>
<tr>
<td>Ag(NH_3)_2^{+}</td>
<td>-17.5</td>
<td>Cu(S_2O_3)</td>
<td>-59.05</td>
<td>S_2O_5^-</td>
<td>-1115.0</td>
</tr>
<tr>
<td>NH_3 (a)</td>
<td>-26.7</td>
<td>Cu(S_2O_3)_3^4^-</td>
<td>-78.23</td>
<td>S_2O_6^-</td>
<td>-958.0</td>
</tr>
<tr>
<td>NH_4^+ (a)</td>
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<td>S_2O_6^-</td>
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<tr>
<td>H_2O</td>
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<td>SO_3^-</td>
<td>-486.5</td>
</tr>
<tr>
<td>O_2</td>
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<td>-32.259</td>
<td>HSO_3^-</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>-73.212</td>
<td>H_2SO_3</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Cu(NH_3)_4^2+</td>
<td>-112.968</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note: Cu(NH_3)_5^{2+} only forms for >3M ammonia (Breuer, 2002)

Reaction:

$$\text{Ag}_2\text{S} + 2\text{Cu(S}_2\text{O}_3)_3^{2-} \rightarrow \text{Cu}_2\text{S} + 2\text{Ag(S}_2\text{O}_3)_3^{2-} \quad \Delta G_{\text{Cu+Rxn}}^0 = ??? \text{kJ/mol}$$

Calculation:

$$\Delta G_{\text{Cu+Rxn}}^0 = 2 \cdot \Delta G^0 (\text{Ag(S}_2\text{O}_3)_3^{2-}) + \Delta G^0 (\text{Cu}_2\text{S}) - \Delta G^0 (\text{Ag}_2\text{S}) - 2 \cdot \Delta G^0 (\text{Cu(S}_2\text{O}_3)_3^{2-})$$

$$= 2 \cdot (-1598.3) + (-86.19) - (-40.5) - 2 \cdot (-1624.7)$$

$$= 7.11 \text{kJ/mol}$$