THE MODES OF GOLD LOSS IN THE CALCIUM THIOSULFATE LEACHING SYSTEM

by

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Abstract

The processing of gold is becoming more complicated due to the increasingly complex nature of the remaining gold-bearing ore bodies. This worldwide phenomenon is the driving force for the development of alternative technologies for the leaching and recovery of gold from so-called double refractory ores. Barrick Gold recently commercialized a unique calcium thiosulfate leaching plant to treat these problematic ores after an autoclave pre-treatment with simultaneous recovery of the dissolved gold-thiosulfate complex onto anion exchange resins. Nonetheless, this new process can experience unexpected losses in gold from solution. It is hypothesized that the reagent’s degradation products known as polythionates and various mineral additions could adversely affect soluble gold stability along with their known detrimental effect on gold recovery. This dissertation aims to understand the possible causes of gold losses by means of a thorough investigation of the effects of polythionate and mineral additions into synthetic calcium thiosulfate leaching solutions. A series of batch leaching experiments were subsequently conducted on actual preg-robbing ores to further elucidate the effects of polythionates on the stability soluble gold complexes in the calcium thiosulfate system. A subsequent study on the rates of polythionate species loading on the resin and their competitive loading behaviour was made and extended to include their effects on the displacement of gold from the resin. This was demonstrated in the form of gold loading isotherms tailored to the calcium thiosulfate leaching system. Ultimately, the processes of gold leaching from refractory ores and gold recovery by resin loading in the presence of polythionates were tied together in a last study to quantify their harmful outcomes on overall gold extraction.
Lay Summary

This dissertation seeks to investigate unwanted gold losses during the gold extraction of difficult to treat ores using calcium thiosulfate as the leaching reagent. Observed losses in soluble gold were hypothesized to be related to the reagent’s degradation products and through interactions with various mineral phases. To this end, synthetic leaching solutions were prepared and experimented on with various conditions, reagent and mineral additions. Subsequently, artificial degradation product additions were made during the leaching of real ores to confirm the gold losses observed in the synthetic leaching systems. In order to alleviate gold losses during extraction, a resin material with gold adsorption properties was introduced simultaneously into the leach reactor. The thiosulfate degradation products were shown to have varying loading rates and degrees of affinities on the resin with the capability of displacing gold from the resin back into solution. The detrimental effects of the degradation products was subsequently quantified.
Preface

The foundation of this project stems from consultations with Barrick Gold Corporation, a UBC Hydrometallurgy Chair Sponsor, together with myself and my thesis supervisor as well as principal investigator and chair holder, Prof. David Dreisinger. The strategy for investigating the effects of polythionates on gold stability as well as the experimental design and the development of analytical methods were formulated and carried out by myself. General inputs, direction and safety strategies were given by Dr. Bé Wassink. Analysis and data collection was completed either by myself or by undergraduate research assistants under my direct supervision. Gold analyses by the fire assay method for feed materials, residues, resins and standard solution samples were conducted at AuTec by Mr. Jack Biln. X-ray characterization of the pyrite mineral was conducted by Mr. Jacob Kabel at the Materials Electron Microscopy Lab, UBC.

Partial results from Chapters 4, 5 and 6 were published in the ALTA 2016 conference proceedings [Daenzer R, Dreisinger D, Choi Y. Role of polythionates on the stability of gold in the leaching of double refractory ores in the calcium thiosulfate-air leaching system. Perth, Australia, ALTA Metallurgical Services Publications].

The dissertation was composed by myself with manuscript edits by my thesis advisor Dr. David Dreisinger.
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<td>3T</td>
<td>Trithionate Acronym</td>
</tr>
<tr>
<td>4T</td>
<td>Tetrathionate Acronym</td>
</tr>
<tr>
<td>5T</td>
<td>Pentathionate Acronym</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy, an analytical method to determine the concentration of elements in solution</td>
</tr>
<tr>
<td>AC</td>
<td>Activated Carbon, material used to recovery gold cyanide in the CIL/CIP process</td>
</tr>
<tr>
<td>AGI</td>
<td>Mixing method by overhead agitator</td>
</tr>
<tr>
<td>ATS</td>
<td>Ammonium Thiosulfate</td>
</tr>
<tr>
<td>AuTS</td>
<td>Gold-thiosulfate or Aurothiosulfate</td>
</tr>
<tr>
<td>BGC</td>
<td>Barrick Gold Corporation, the world’s biggest gold mining company</td>
</tr>
<tr>
<td>BLK</td>
<td>Blank Acronym</td>
</tr>
<tr>
<td>BV</td>
<td>Bed Volume, typical unit of measure in mL of resin materials in a column</td>
</tr>
<tr>
<td>CaTS</td>
<td>Calcium Thiosulfate</td>
</tr>
<tr>
<td>CIL</td>
<td>Carbon-in-leach, a gold recovery process whereby the leaching of aurocyanide species and their loading on activated carbon occurs simultaneously</td>
</tr>
<tr>
<td>CIP</td>
<td>Carbon-in-pulp, a gold recovery process whereby aurocyanide species are loaded onto activated carbon in a separate reactor after leaching</td>
</tr>
<tr>
<td>CSIRO</td>
<td>Commonwealth Scientific and Industrial Research Organisation</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized Water</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid, a complexing agent</td>
</tr>
<tr>
<td>GS</td>
<td>Goldstrike, A mine site operated by Barrick Gold Corporation</td>
</tr>
<tr>
<td>GSBR</td>
<td>Goldstrike Barren Resin</td>
</tr>
<tr>
<td>GSLR</td>
<td>Goldstrike Loaded Resin</td>
</tr>
<tr>
<td>HSC</td>
<td>Acronym for enthalpy (H), entropy (S) and heat capacity (C). HSC is an Outotec software capable of conducting thermodynamic calculations for chemical processes</td>
</tr>
<tr>
<td>IC</td>
<td>Ion Chromatography, an analytical method used to determine the concentration of anions such as thiosulfate and polythionates</td>
</tr>
<tr>
<td>ISL</td>
<td>In-situ Leaching, a mining process used to recover metals with reagents passing through boreholes without the need for ore extraction</td>
</tr>
<tr>
<td>IX</td>
<td>Ion Exchange</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
</tr>
<tr>
<td>LPM</td>
<td>Liter per minute</td>
</tr>
<tr>
<td>MAG</td>
<td>Mixing method by magnetic stirring</td>
</tr>
<tr>
<td>MIBK</td>
<td>Methyl Isobutyl Ketone, organic phase used for gold solvent extraction</td>
</tr>
<tr>
<td>NA</td>
<td>Not Applicable or Not Available</td>
</tr>
<tr>
<td>NIST</td>
<td>The National Institute of Standards and Technology is a measurement standards laboratory</td>
</tr>
<tr>
<td>PD</td>
<td>Particle Density, solids content in a slurry given in weight percent</td>
</tr>
<tr>
<td>PolyTS</td>
<td>Polythionates</td>
</tr>
<tr>
<td>POX</td>
<td>Pressure Oxidation, an autoclave process</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene, an inert thermoplastic polymer</td>
</tr>
<tr>
<td>QC</td>
<td>Quality Control</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating Disc Electrode</td>
</tr>
<tr>
<td>REQCM</td>
<td>Rotating Electrochemical Quartz Crystal Microbalance</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
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<tr>
<td>RIL</td>
<td>Resin-in-leach, a gold recovery process whereby the leaching of AuTS species and their loading onto a resin material occurs simultaneously</td>
</tr>
<tr>
<td>RIP</td>
<td>Resin-in-pulp, a gold recovery process whereby AuTS species are loaded onto an IX resin material in a separate reactor after leaching</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square error, a measure of the difference between modeled and observed values</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>SWB</td>
<td>Mixing method by a shaking water bath</td>
</tr>
<tr>
<td>SX</td>
<td>Solvent Extraction</td>
</tr>
<tr>
<td>TCM</td>
<td>Total Carbonaceous Matter</td>
</tr>
<tr>
<td>TS</td>
<td>Thiosulfate Acronym</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy, a quantitative analytical technique to measure elemental composition</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction, an analytical method to characterize and identify the crystal structure of a material</td>
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Dedication

Für Lina Schmid-Dänzer
1 Introduction

1.1 A Brief History of Gold

Gold is one of the world’s most prestigious metals highly sought after by humans due to its luster, malleability and easy workability, virtual indestructibility and rarity (Thomas 1994). Gold has been collected, worked and treasured since the chalcolithic times (4th Millennium BC) in regions such as the Levant (Gopher et al. 1990), Anatolia (Swann et al. 1997) and Mesopotamia (Moorey 1982). Since the beginning of civilization gold has been considered a symbol of status and wealth. Today, although roughly fifty percent of the world’s gold production is still used in the jewelry industry, the demand for gold has grown in other industries and disciplines such as modern medicine, dentistry, electronics, financial applications, space and aeronautics just to name a few.

The increased demand for gold production and the diminishing sources of easily processed gold ores are responsible for a shift towards the adoption of new extraction technologies for the processing of lower grade and increasingly more complex and refractory ores. This statement holds true for two distinct eras of gold mining. The earlier one, between the mid-19th century and the turn of the 20th century, occurred when traditional gravity concentration and amalgamation processing routes were becoming unsuitable for the recovery of fine gold or gold associated with sulfide minerals. These traditional routes were replaced and/or modified by early hydrometallurgical processes such as chlorination (Plattner process). At the same time, new roasting pre-treatments were developed to oxidize concentrates and ores prior to leaching. Moreover, other chemicals capable of dissolving gold and silver were discovered including bromine/bromide, cyanide, thiosulfate and thiourea solutions (Marsden et al. 2006). The need for new gold leaching techniques paved the way for the development of the commercial cyanidation leaching process patented by MacArthur and the Forrest brothers in 1887. By 1889, when the first cyanidation plant was operating, gold dissolution by cyanide had become the industry standard for the next century and beyond. The second era of major technological development occurred more recently, in the 1970’s, when economic factors prompted the renewed interest in precious metals exploration and mining. New technologies such as heap leaching (1970) and carbon-in-pulp adsorption of gold (1973) were established to increase recoveries after gold dissolution by cyanidation.
To address the problem of even further refractory ores and concentrates (e.g. carbonaceous “preg-robbing”, telluride and sulfidic ores) by means other than roasting, new processes were developed such as bacterial oxidation and pressure oxidation. The latter one, amongst others, capable of tackling the problem of arsenical ores, gained considerable attention for environmental reasons. As a result, hydrometallurgical pressure oxidation processes became increasingly popular to deal with both environmental regulations and refractory type ores. Although cyanide is still considered the predominant gold leaching reagent in the industry for its typically high gold recoveries for a variety of ores and its low cost, research into alternative reagents is ongoing driven mainly by toxicity and environmental concerns (Li et al. 2012). Indigenous groups and NGO’s have lobbied for the mining industry to develop less toxic leaching processes (Hilson et al. 2006) and to comply with local environmental regulations and restrictions (Choi et al. 2007). Moreover, cyanidation of high copper ores is known to be uneconomical due to high cyanide consumption and loss of gold to tailings due to naturally occurring carbon in carbonaceous “preg-robbing” ores (Schmitz et al. 2001) are additional reasons for the development of new alternative leaching systems. Suitable alternative gold lixiviants are to be selected based on several criteria: Leaching rates, economic considerations (cost, availability), non-toxicity and process applicability (recyclability, selectivity, detoxification) (Hilson et al. 2006).

One such alternative reagent, whose gold leaching properties were initially discovered in the 1900’s, is thiosulfate and it has received renewed interest and considerable attention in the last thirty years due to the aforementioned reasons (Aylmore et al. 2001, Muir et al. 2005, Senanayake 2012). Current research is focused on understanding the complex chemistry of gold dissolution by thiosulfate and its subsequent side reactions and degradation products, the thiosulfate leaching behaviour of different types of ores and concentrates, methods of separation, chemical speciation, equilibria and reactions mechanisms (Senanayake 2005b). Despite these efforts, there are still many research questions that need to be addressed.

Presently, one of the main industrial drawbacks of using thiosulfate as a leachant is the subsequent recovery process for the dissolved gold thiosulfate complex. It is unfortunately not adaptable to carbon adsorption via CIL or CIP due to its low affinity for activated carbon (Gallagher et al. 1990). Therefore, the application of thiosulfate leaching represents a challenge for its recovery using suitable alternative methods requiring capital investments for new installations or modification to
current ones. The most promising gold thiosulfate recovery process to date is by anion exchange onto resins. Gold complexes have high affinities for adsorption sites on strong base resins but unfortunately, so do the thiosulfate degradation products. Thiosulfate oxidizes to produce higher oxidation state sulfur species such as trithionate, tetrathionate and pentathionate. This competition for adsorption sites on anion exchange resins is another important drawback of the recovery process. Moreover, the stability of gold thiosulfate complexes is another concern where gold losses over time are observed during the leaching stages. Adsorption limitations and gold losses can be prevented to a certain extent by applying engineering solutions such as the use of a resin-in-leach (RIL) process instead of resin-in-pulp (RIP) and enhancing the recovery by modifications to the flowsheets (e.g.: co- and counter-current vs. traditional counter-current leaching) resulting in reduced effects of degradations products on gold adsorption.

1.2 Goldstrike Thiosulfate Leaching Process

The commercialization of a thiosulfate gold leaching process has recently become a reality at the Barrick Goldstrike mine in Nevada. In November 2014, Goldstrike poured its first gold bar produced using their patented thiosulfate leaching technology (Weinberg 2015). This milestone marked the industrial beginning of a new process developed to extract gold from double refractory ores that could not be treated via traditional cyanidation/carbon-in-leach (CIL). Previously, single refractory sulfide ores were pretreated by pressure oxidation using autoclaves to liberate and expose the surface of the trapped gold particles followed by a cyanide leach and gold recovery by CIL. In parallel, the continuing mining efforts and characterization of future mining zones of the deposit predicted an increase in levels of carbonate content and of total carbonaceous matter (TCM) in the forthcoming ore. The former mineral negatively impacts the acidic pressure oxidation pre-treatment to breakdown sulfides by consuming acid. The latter, similar to commercial activated carbon (Schmitz et al. 2001), contributed to the preg-robbing phenomenon observed during the cyanidation of these so-called double-refractory ores by adsorbing the aurocyanide complexes onto the fine carbon matter. These gold losses to the tailings made the autoclave-cyanidation process uneconomical. A partial solution to the impeding TCM problem was the commissioning in 2000 of a roaster to oxidize the carbon and the sulfides allowing for economical operation of a gold cyanidation/CIL recovery circuit (Fleming et al. 2003, Thomas et al. 2005). However, even with the roasters running at capacity, the Goldstrike mine continued to stockpile upwards of 4 million ounces of gold which would have to be processed after the end of the mine’s life. As a result, the calcium thiosulfate
leaching process was developed to increase gold production from TCM ores (Choi 2013b). This process’ foundation was built on previously existing capital assets, namely six autoclaves, the retrofitting of two former seven tank CIL circuits into new RIL circuits for gold recovery and the building of a thiosulfate reagent plant. The ramp up to full capacity was expected to be reached by Q3 2016 at rate of 13,400 tons of ore processed daily ("Goldstrike Operation" 2016).

Although calcium thiosulfate gold leaching is currently an industrial reality, there remain some unanswered fundamental questions regarding the effects and role of polythionates on the gold thiosulfate complex stability in leaching solutions and the loading behaviour of these species onto anion exchange resin materials. The work herein attempts to unravel some of these fundamental questions.
2 Literature Review

The following literature review is divided into several sections with the intent on providing adequate background information on the research area of interest and to set up the framework for the eventual thesis work presented herein. Firstly, the state of the industrial thiosulfate leaching process will be introduced leading to the current process limitations and areas in need of development. Secondly, a general overview of previous research and technologies is given with emphasis on the calcium thiosulfate leaching (CaTS) leaching system. Thirdly, a section is dedicated to summarizing the alkaline degradation mechanisms of thiosulfate and polythionates, which are important species to consider when discussing the adsorption of gold thiosulfate onto ion exchange resins. Finally, a relationship is drawn between gold-thiosulfate stability, host minerals and the presence of polythionates.

2.1 Current Industrial Status

Due to problems associated with the cyanidation of preg-robbing ores, as briefly mentioned in the introduction, a common goal for gold producers is to develop a robust overall thiosulfate process flowsheet that can be realistically used and costed for a range of actual ores - including gold recovery, reagent re-cycling or destruction and impurity control (Muir et al. 2004).

There has been substantial research conducted on the thiosulfate leaching system but primarily limited to the lab-scale. There are few known attempts of using thiosulfate technology at the pilot plant scale, most notably in a heap leach process using ammonium thiosulfate for recovery from low-grade carbonaceous sulfidic gold ores (Wan et al. 2003) and the piloting of a pressure oxidation-ammoniacal thiosulfate leaching process followed by resin-in-pulp gold recovery for the treatment of preg-robbing Goldstrike ores (Thomas et al. 1998, Fleming et al. 2003).

Barrick Gold Corporation (BGC) is at the forefront of research involving thiosulfate as made evident by their involvement in research as sponsors and numerous issued patents and patent applications (Marchbank et al. 1996, Thomas et al. 1998, Choi et al. 2009, Choi et al. 2012a, Choi et al. 2012b, Langhans et al. 2012, Choi et al. 2013). More so, Barrick is the only gold producer to date to have successfully developed and achieved commercial production (Q3 2015) using a thiosulfate leaching technology (Dushnisky et al. 2015). The year 2016 saw a 34 % increase in TCM ore processed by the autoclaves-TS leaching circuit to 3.5 M tons for an overall gold recovery of 63 % (up 12% from
As mentioned previously, the use of thiosulfate as a lixiviant is driven mainly by the carbonaceous preg-robbing nature of the ores. Such ores are not amenable by cyanidation due to the adsorption of aurocyanide complex by naturally occurring carbon whereas, when leached with thiosulfate, the thiosulfateaurate(I) uptake by natural carbon is highly limited (Schmitz et al. 2001). However, Figure 1 taken from a Barrick patent application (Choi et al. 2012a) shows that the leaching of a gold-bearing material containing a preg-robbing component yields slower leaching kinetics and gold recoveries than materials free of preg-robbing components. This decrease in recovery is said to be
due to the adsorption of the gold thiosulfate complex by the preg-robbing material. More importantly, Figure 1 also shows that in the presence of a preg-robbing component, the addition of resin-in-leach improves the initial leaching kinetics and overall gold recovery. This evidence is the first indication that RIL significantly contributes to the overall process efficiency.

Another problem associated with thiosulfate is its degradation into polythionates over time. These products together with other impurities are undesirable as they are competitively adsorbed onto the ion exchange resins and, over time, can reduce the overall gold recovery. For instance, tetrathionate and trithionate concentrations of 420 and 350 mg/L respectively have been found to reduce gold loading onto Purolite A500C resin from 26 to 2 kg Au/t resin from a solution containing 0.3 mg/L Au (Marsden et al. 2006). The affinities of these unwanted species onto strong base ion exchange follows the order: Gold > Mercury > Pentathionate > Tetrathionate > Copper > Trithionate (Choi et al. 2012a). The effects of tetrathionate loading on the gold loading on resin in a typical counter current RIL process is shown in Figure 2.

![Figure 1: Effect of resin concentration on gold recovery in preg-robbing and non preg-robbing ores (Choi et al. 2012a).](image-url)
Gold adsorption limitation and losses due to the effects of the polythionates can be prevented to a certain extent by applying engineering solutions such as the use of a RIL process instead of RIP (Breuer et al. 2012). The recovery of gold can also be enhanced by modifications to the flowsheet such as using a combined co-current and counter current mixed flow, which maximizes resin gold adsorption during initial contact with fresh slurry at the front end of the process and benefits from the gold scavenging effect of a counter current flow at the back end of the process. Such process modifications are designed to reduce the influence of polythionate loading on resin, specifically tetrathionate, which lowers gold recoveries (Choi et al. 2012a).

### 2.1.2 Gold-Thiosulfate Recovery Process

#### 2.1.2.1 Gold Loading on Ion Exchange Resins

Gold-thiosulfate complexes have high affinities for adsorption sites on strong base anion exchange resins. Unfortunately, so do the degradation products of the thiosulfate leaching reagent. This competition for adsorption sites on the resin beads is an important drawback of the recovery process. Moreover, the stability of gold thiosulfate complexes is another concern where gold losses over time have been observed during the leaching stages (Figure 1). To further reduce the effects of the
thiosulfate degradation products during gold adsorption, additional strategies are employed. Namely, the control of polythionate levels in the RIL circuit is performed by treating partially loaded resins from the counter-current portion of the circuit with sulfite to ultimately convert tetrathionate, pentathionate and other higher polythionates into trithionate and thiosulfate while leaving the gold on the resin as depicted by Equation 1 (Breuer et al. 2012).

\[
R_{2S_x}O_6 + SO_3^{2-} \rightarrow R_{2S_{(x-1)}}O_6 + S_2O_3^{2-}
\]

In this instance, trithionate is not as strongly adsorbed nor as detrimental to gold loading on the resin as other polythionates. The treated partially gold-loaded resin can continue adsorbing gold in the co-current portion of the leach before being eventually removed for gold elution.

2.1.2.2 Detailed Gold Elution Process

The known negative impact of trithionate on resin gold loading can be utilized as a strategy for gold recovery. The process described below is schematically shown in Figure 3.

![Diagram of the gold elution process](image)

Figure 3: Method for recovering precious metals and copper from leach solutions (Choi et al. 2013).

In a first step, the loaded resin removed from the leach tanks is pre-eluted with re-claimed thiosulfate (0.27-1.78 M) from the process to recover copper (100-1500 mg/L) that was co-adsorbed with gold albeit less strongly. This copper eluate can contain peroxide in order to promote more efficient stripping of higher quantities of copper from the resin. The added advantage of peroxide in the copper pre-elution is the in-situ generation of low trithionate concentrations (Equation 2) which
adsorb on and condition the resin for more effective subsequent gold elution. The copper-rich product containing thiosulfate is recycled back into the leach.

\[ 2Na_2S_2O_3 + 4H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O \]  

For the gold elution stage, trithionate, produced in a separate reactor through the oxidation of thiosulfate by hydrogen peroxide as given by Equation 2, is used as a gold stripping agent along with sulfite (~0.2 M each) to effectively displace the gold-thiosulfate complex from the resin (Equation 3) (Choi et al. 2013). The gold-rich strip solution (100-500 mg/L Au) is sent to an electrowinning stage where greater than 99% of gold is recovered. The barren electrowinning solution containing thiosulfate and sulfite can be optionally sent for recycle to the trithionate synthesis reactor and/or to a step after copper pre-elution where sulfite reacts with any adsorbed tetrathionate on the resin to form trithionate as an additional conditioning step for gold elution.

\[ 2R_3Au(S_2O_3)_2 + 3S_3O_6^{2-} \rightarrow 3R_2S_3O_6 + 2Au(S_2O_3)_2^{3-} \]  

The barren resin, now loaded with trithionate, is regenerated by addition of sulfide resulting in the in-situ formation of thiosulfate on the resin and in solution according to Reaction 4. The barren resin, free of polythionates, is recycled to the leaching circuit whereas the spent regeneration solution containing thiosulfate is treated in the trithionate synthesis reactor for the next elution after renewed conversion to trithionate by peroxide (Equation 2).

\[ R_2S_3O_6 + Na_2S \rightarrow R_2S_2O_3 + Na_2S_2O_3 \]  

As was highlighted above, the performance of the leaching circuit is therefore highly dependent on the management and control of the polythionates species.

### 2.1.3 Barrick CaTS Leaching and Associated Problems

Figure 4 shows typical CaTS leaching curves for a variety of pre-treated feeds from the Goldstrike mine. As can be seen, the rate of leaching is very fast due to the fine nature of the gold particles. However, there are clear differences in the leaching rates of feeds with different pre-treatments (57 to 80 % gold extraction within 1 hour). Ores are either pre-treated by an autoclave (acid or alkaline mode) or roasting process. Nonetheless, stable gold extractions between 72 and 84 % are achieved after 24 hours in the presence of resin (RIL).
Figure 4: Typical CaTS leaching test curves in the presence of resin (RIL) for various pre-treated ore feeds. Unidentified samples (BR 21, BR 24, BR 31, MP 4) were pre-treated by acid pressure oxidation (Choi 2013a).

On the other hand, without the presence of resin-in-leach, the initial gold extraction rates and gold extractions after 24 hours are reduced significantly (Figure 5). More importantly, in some cases, gold extraction completely drops after reaching a maximum as is the case for Roaster Feed B (Run 4) and BR 24 (Acid POX).

Figure 5: Typical CaTS leaching test curves without the presence of resin for various pre-treated ore feeds. Unidentified samples (BR 21, BR 24, BR 31, MP 4) were pre-treated by acid pressure oxidation (Choi 2013a).
In the case of the alkaline Pox feed, leaching without resin is initially lower compared to RIL (max. 65 vs. 80 % after 1 hour) and overall recovery is also lower (max. 74 vs. 84 % after 24 hours). This indicates that in order to yield the best possible gold extractions, the use of RIL is essential and therefore other recovery methods for gold after leaching such as cementation and solid liquid separation cannot be utilized.

It is suggested that these observations are linked to the effects of thiosulfate degradation products (Choi 2013a). Yet the reasons for the differences in gold extraction between the various pre-treatments of the ores are still unknown. In fact, all feeds are basically fully oxidized although there may be some residual sulfide due to roaster and autoclave oxidation efficiencies slightly lower than 100 percent. Nonetheless, at the very least, the surfaces of the ore particles should have been oxidized. If there were any traces of sulfides left, their surfaces should not be left exposed to promote or catalyze lixiviant degradation.

2.2 Properties of Thiosulfate and Metastable Sulfur Species

2.2.1 S-H₂O Eh-pH Diagrams and Thermodynamic Considerations

The most stable sulfur species have sulfur oxidation states of S(−2), S(0) and S(+6) represented by sulfide species, elemental sulfur and sulfate species respectively to name a few (Kelsall et al. 1993). As a result, other “metastable” sulfur species such as thiosulfate are not represented in thermodynamically correct Pourbaix diagrams as shown in Figure 6. This does not mean that their existence is precluded in hydrometallurgical processes as they are known to have significant kinetic stabilities under certain conditions. For this reason, the onus is on the user to select appropriate species for the leaching system of interest and their corresponding free energies of formation. Table 2 contains three data sets that include gold and sulfur species that were found to be repeatedly used in the literature. The first set of data is taken from the popular publication called “Standard Potentials in Aqueous Solution” by Bard et al. (1985). The second set comes from the National Institute of Standards and Technology (Martell et al. 1974, Smith et al. 1998) and the third is composed of the default free energy data (various sources) used in the HSC Chemistry 5.11 program (Roine 2002).
Figure 6: The S-H$_2$O Eh-pH diagram, 25 °C, activities of sulfur species is 0.1 M as TS, 1 atm pressure. If a $\Delta G^\circ (S^{2-}) = 120.5$ kJ/mol were used, then the $S^{2-}$ region would disappear. The Bard et al. data set was used.

Figure 6 shows a stable region for sulfide ions above pH 13. This region disappears when a free energy of formation, $\Delta G^\circ (S^{2-}) = 120.5$ kJ/mol, is used for sulfide. Several authors have commented on the validity of this free energy value over the more commonly used ones in Table 2 (Williamson et al. 1992, Kelsall et al. 1993).

Over time, metastable species will degrade into the final aforementioned stable species. To illustrate the predominance areas of the metastable species, sulfate and possibly other S(+6) and higher oxidation sulfur species need to be omitted. Several authors have already shown these kinds of Pourbaix diagrams for metastable species (Williamson et al. 1992, Kelsall et al. 1993, Molleman et al. 2002). For Figure 7, the sulfate and bisulfate species listed in Table 2 were omitted.
In the leaching system studied in this work, gold complexes exclusively as aurothiosulfate unlike in the ammonium thiosulfate leaching system, where the presence of the ammonia ligand adds a complication to the leaching system. As such, the construction of a representative species predominance diagram is greatly simplified.
Table 2: Gibbs free energy of formation (kJ/mol) data sets from various sources. Bard et al. 1985, NIST (Smith et al. 1998) and HSC 5.11 (Roine 2002).

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</table>

In addition, Senanayake (2003) used linear free energy relationships to scrutinize the free energy of formation value of AuTS. This work lead to an adjustment of the stability constant for Au(S₂O₃)²⁻ to logβ₂ = 24 and a resulting Gibbs free energy of −1038 kJ/mol. As a result, the new thermodynamic data can now corroborate previous experimental observations made by several other researchers about the stability of the AuTS complex. Figure 8 compares two Au-S₂O₃²⁻-H₂O Eh-pH diagrams using two different Gibbs free energy data sets found in Table 2. The solid black lines (NIST) shows a slightly reduced stable area for the AuTS complex (ΔG°f = −1038 kJ/mol) and the appearance of auric gold in solution at low pH values compared to the dashed lines (Bard et al. 1985). Nonetheless, both data sets show that gold can complex and remain stable as AuTS. The HSC data set lacks gold species in order to construct the wanted diagram.
A number of other known sulfur species exist having some metastable persistence are ordered in Figure 9 by average oxidation state and number of sulfur atoms. At a glance, any number of reduction half reactions can be written by simply selecting a sulfur species of higher average formal charge on the sulfur atom to accept electrons thus reducing to a species of lower average charge. Polysulfides are charged polymeric sulfur chains with an ionic charge of −2. A sulfate structure in which one of the oxygen atoms is replaced by a sulfur atom gives thiosulfate. The lengthening of the thiosulfate with additional sulfides creates a polysulfur chain with a sulfonate (SO3) group ending and a general formula $S_n$-$SO_3^{2−}$. These species are also known as polythiosulfates or sulfane monosulfonic acids. Polymeric sulfur chains terminated at both ends by sulfonates are called polythionates, polysulfane disulfonic acids or polysulfane disulfonates.
Figure 9: Sulfur oxidation state and number of atoms for aqueous sulfur species that are thermodynamically stable or have metastable persistence (adapted from Williamson et al. (1992)).

2.2.2 Molecular Structures

Table 3 describes and shows the molecular structure of thiosulfate and that of metastable polythionates species considered in this work. Similarly to sulfate, the thiosulfate group is tetrahedral with the hexavalent sulfur at the center. A charge distribution directed towards the sulfonate end groups of polythionates results in a partial negative charge the end of the chains.
Table 3: Molecular Structure of Sulfur Oxyanions.

<table>
<thead>
<tr>
<th>Species</th>
<th>Description (Druschel et al. 2003)</th>
<th>Molecular Structure</th>
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<tbody>
<tr>
<td>Thiosulfate ($S_2O_3^{2−}$)</td>
<td>Sulfur structure where an oxygen atom is replaced by a sulfur atom.</td>
<td><img src="image" alt="Thiosulfate Diagram" /></td>
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<td>Trithionate ($S_3O_6^{2−}$)</td>
<td>Single sulfur atom with two sulfonate groups on each side. The central sulfur atom is more reduced than the terminal sulfurs. The central sulfur is more reduced than the terminal sulfurs.</td>
<td><img src="image" alt="Trithionate Diagram" /></td>
</tr>
<tr>
<td>Tetrathionate ($S_4O_6^{2−}$)</td>
<td>Sulfur chain composed of two sulfur atoms terminated at both ends by sulfonate groups. The central S-S bond is shorter than the two symmetrical bonds involving the terminal sulfurs bonded to the oxygens.</td>
<td><img src="image" alt="Tetrathionate Diagram" /></td>
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<td>Pentathionate ($S_5O_6^{2−}$)</td>
<td>Sulfur chain composed of three sulfur atoms terminated at both ends by sulfonate groups. The central sulfurs are more reduced than the terminal sulfurs.</td>
<td><img src="image" alt="Pentathionate Diagram" /></td>
</tr>
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</table>
2.3 Gold-Thiosulfate Leaching Technologies

As mentioned earlier, thiosulfate is a promising alternative reagent to cyanide for its non-toxicity, comparable leaching rates and adaptability on high carbonate ores. The dissolution of gold by thiosulfate and the many possible side reactions taking place and involved in the leaching mechanism contribute to the complexity of the thiosulfate chemistry. The following section broadly reviews the most studied system, namely the ammoniacal thiosulfate leaching system, and its common gold recovery methods with an emphasis on resin adsorption and its issues with thiosulfate degradation products. This process is subsequently mirrored in terms of non-ammoniacal thiosulfate leaching systems with particular attention placed on the CaTS reagent.

2.3.1 Ammoniacal Thiosulfate Leaching System

The most studied gold thiosulfate leaching system encountered in the literature is the copper catalyzed ammoniacal thiosulfate leaching system. It makes use of the ammonium thiosulfate salt and ammonia to stabilize copper in solution which acts as a catalyst for gold oxidation. The gold dissolution can be simply described by the following Cu catalyzed reactions:
There is an ideal ratio of ammonia to copper, typically added as cupric sulfate, that will yield acceptable and therefore the most efficient leaching results (Abbruzzese et al. 1995, Wan et al. 1997, Breuer et al. 2000, Jeffrey et al. 2001, Ouyang 2001, West-Sells et al. 2005). Leaching composition and conditions for the ammonia thiosulfate (ATS) system vary between 0.1-0.71 M S$_2$O$_3^{2-}$, 0.1-6 M NH$_3$, 0.001-0.047 M Cu$^{2+}$, pH 6.9-10.5 and gold extractions between 50.7-97 % (Li 2003). In more recent literature, Xu et al. (2016) determined the optimal ATS leaching conditions to be 0.2 M S$_2$O$_3^{2-}$, 1.2 M NH$_3$, 0.012 M Cu$^{2+}$, pH 10 capable of extracting 86.1 % of the gold from a sulfidic concentrate containing high levels of C (3.61 %), As (1.7 %) and Sb (0.94 %) following an alkaline pressure oxidation pre-treatment. The thiosulfate consumption was decreased (35.3 kg/t) by eliminating the catalytic thiosulfate decomposition effect of sulfides as a result of the pressure oxidation. The higher gold extraction by ATS (86.1 %) compared to cyanidation (80.1 %) was due to the gold cyanide preg-robbing effect of the residual carbonaceous matter contained in the oxidized autoclave discharge.

2.3.1.1 Recovery Methods

The loading of the gold-thiosulfate complex on activated carbon has been shown to be very poor (Gallagher et al. 1990). As such, the use of conventional CIP and CIL technology for the recovery of gold from the thiosulfate system is not possible. An exception to this is the use of a technique that pre-treats activated carbon with copper cyanide which can then be used to recover gold from thiosulfate solutions (Young et al. 2011, Young et al. 2012). This technology would greatly reduce the overall use of cyanide but its presence would not be eliminated from the processing plant. Therefore, alternative methods need to be employed. Cementation with zinc or copper (Guerra et al. 1999, Hiskey et al. 2003, Lee et al. 2008) can be used but significant consumption of zinc and passivation by cuprous sulfide are disadvantageous. Another gold recovery technology that may be used is gold-thiosulfate adsorption onto anion-exchange resins (Nicol et al. 2002, O'Malley 2002, Zhang et al. 2002a, b, Fleming et al. 2003, Zhang et al. 2004, Jeffrey et al. 2007, Jeffrey et al. 2010).


2.3.1.1 Ion Exchange Resin Recovery

Zhang and Dreisinger (2002a) investigated the recovery of gold from batch ATS solutions using three weakly basic and eight strongly basic anion-exchange resins. It was generally shown with gold loading isotherms that strong base resins have much higher gold loadings than weak base resins. All plots of gold loading on resin (kg Au/t resin) against equilibrium gold concentration (mg/L Au) obeyed the empirical Freundlich adsorption model given by Equation (8):

\[
\frac{x}{m} = Kc^n
\]

Where \( x \) = mass of adsorbate (Au, in kg)

\( m \) = mass of adsorbent (resin, in tons)

\( c \) = equilibrium concentration of adsorbate in solution

\( K \) and \( n \) = constants

A plot of the natural logarithm of Equation (8) in the form \( y = mx + b \) giving a straight line confirms the Freundlich model and the empirical constants \( K \) and \( n \) can be solved.

Fleming et al. (2003) present an excellent review of the laboratory and pilot-plant work conducted by BGC between 1995 and 2003 for the development of an “in-pulp” gold extraction process. This research led to several patents (Marchbank et al. 1996, Thomas et al. 1998) describing an effective and efficient RIP process. Typical copper and gold loadings on Purolite A-500C strong-base resin were in the range of 10-20 kg/t and 2-3 kg/t respectively. Elution of copper was achieved with strong thiosulfate solutions and gold was eluted using thiocyanate. The latter eluent was eventually deemed uneconomical and environmentally undesirable such that research efforts were focused on developing a stripping method utilizing tetrathionate and trithionate. Although this new method was successful at stripping gold, the eluted resin required a regeneration step to remove the loaded polythionates. This was accomplished by treating the resin with sodium hydrogen sulfide and using the resulting thiosulfate for the copper pre-elution step. Gold was finally precipitated using sulfide after cementation with iron and or copper was deemed to be too difficult.

Nicol et al. (2002) revealed that gold can be removed from an ore blend in a small-scale continuous countercurrent RIP process yielding gold loadings of 3000 mg/L with a barren pulp containing less than 0.05 mg/L Au. The leach pulp however, contained 20 mg/L each of tri- and tetrathionate which limited potentially higher gold loadings as discussed later in Section 2.3.1.2.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Leaching system</th>
<th>Resin Type</th>
<th>Resin Loading</th>
<th>Stripping Reagent</th>
<th>Concentration</th>
<th>pH</th>
<th>Type of Process</th>
<th>% recovery, # BV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thomas, K.G. (1998)</td>
<td>0.04 M ATS, 10-100 ppm Cu&lt;sup&gt;2+&lt;/sup&gt;, 0.01-0.05 M SO&lt;sub&gt;3&lt;/sub&gt;²⁻, pH 7.5-7.7</td>
<td>Strong Base</td>
<td>2-5 kg Au/t resin</td>
<td>Thiocyanate</td>
<td>100-200 g/L KSCN</td>
<td>pH 6-7</td>
<td>RIP/RIL</td>
<td>90 %, 5-6 BV</td>
</tr>
<tr>
<td>Zhang and Dreisinger (2002a)</td>
<td>Synthetic 0.1 M ATS, 0.2 M NH₃, 20 ppm Au, 500 ppm Cu</td>
<td>3 Weak Base, 8 Strong Base</td>
<td>~2 kg Au/t</td>
<td>Sodium sulfite</td>
<td>2 M Na₂SO₃, 1 M NH₃</td>
<td>pH 11</td>
<td>Batch stripping</td>
<td>70 % in 24 hrs at r.t.</td>
</tr>
<tr>
<td>Nicola and O'Malley (2002)</td>
<td>Synthetic 0.05 M TS, 0.2 M NH₃, 20 mg/L metal ions, pH 9.5</td>
<td>Amberjet 4200</td>
<td>Up to 90 g Au/L wet-settled resin</td>
<td>Nitrate</td>
<td>2 M NH₄NO₃</td>
<td>N/A</td>
<td>Resin column elution</td>
<td>Over 90%, 30 BV</td>
</tr>
<tr>
<td>Fleming (2003)</td>
<td>Synthetic 0.05 M ATS, 0.2 M NH₃, 31.8 ppm Cu&lt;sup&gt;3+&lt;/sup&gt;, 20 ppm Au, 500 ppm Cu&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>SB Purolite A-500C</td>
<td>2-3 kg Au/t</td>
<td>Thiocyanate</td>
<td>50-100 g/L SCN⁻</td>
<td>pH 6-8</td>
<td>Two-stage elution</td>
<td>&gt;99.5 %, 4-6 BV</td>
</tr>
<tr>
<td>Zhang and Dreisinger (2004)</td>
<td>Synthetic 0.1 M ATS, 100-500 ppm Cu, pH 11</td>
<td>Dowex 21K</td>
<td>18.83 kg Au/t</td>
<td>Tetrathionate</td>
<td>0.25 M Na₂SO₄, 0.25 M Na₂SO₃, 0.5 M ATS</td>
<td>pH 9</td>
<td>Resin column elution</td>
<td>Au: 99.7%, 50 BV Cu: 99.3%, 50 BV</td>
</tr>
<tr>
<td>Zhang and Dreisinger (2004)</td>
<td>Synthetic 0.1 M ATS, 100-500 ppm Cu, pH 11</td>
<td>Dowex 21K</td>
<td>8.87 kg Au/t</td>
<td>Sodium sulfite with ammonia</td>
<td>2 M Na₂SO₃, 1 M NH₃</td>
<td>pH 11</td>
<td>Resin column elution</td>
<td>Au: 99.9%, 37 BV Cu: 100.0%, 37 BV</td>
</tr>
<tr>
<td>Zhang and Dreisinger (2004)</td>
<td>Synthetic 0.1 M ATS, 100-500 ppm Cu, pH 11</td>
<td>Dowex 21K</td>
<td>N/A</td>
<td>Sodium chloride with ATS</td>
<td>4 M NaCl, 0.1 M ATS</td>
<td>pH 9.2</td>
<td>Resin column elution</td>
<td>Au: 99.5 %, 42 BV Cu: 99.6%, 30 BV</td>
</tr>
<tr>
<td>Jeffrey and Brunt (2007)</td>
<td>Synthetic 50 mM ATS, 150 mM (NH₄)₂SO₄, 2 mM copper thiocyanate), polyT &amp; AuTS sol.</td>
<td>SB Purolite A500/2788</td>
<td>4452-4454 mg Au/L</td>
<td>Sodium perchlorate</td>
<td>0.5 M NaClO₄</td>
<td>N/A</td>
<td>Batch loading and stripping</td>
<td>Au: complete, 2 batch elutions of 50 mL</td>
</tr>
<tr>
<td>Jeffrey et al. (2010), (2008)</td>
<td>25 mM ATS, 0.37 mM Na₂S₂O₇, 20 mg/L Cu as CuSO₄, 1.15 mg/L Au as Au(S₂O₃)²⁻</td>
<td>SB Purolite A500/2788</td>
<td>~1500 mg Au/kg resin</td>
<td>Sodium chloride and sodium sulfite</td>
<td>2 M NaCl, 0.1 M Na₂SO₃</td>
<td>N/A</td>
<td>Continuous 7-stage mini rig</td>
<td>99.9 % Au recovered</td>
</tr>
<tr>
<td>Muslim (2010a)</td>
<td>Non ammoniacal resin-solution</td>
<td>SB Purolite A500/2788</td>
<td>N/A</td>
<td>Sodium perchlorate</td>
<td>0.5 M NaClO₄</td>
<td>N/A</td>
<td>Batch loading and stripping</td>
<td>86.4% Au loading</td>
</tr>
<tr>
<td>Breuer, Dai et al. (2012)</td>
<td>TS with Fe-EDTA oxidant and Thiourea catalyst</td>
<td>N/A</td>
<td>0.94 g Au/L resin</td>
<td>Sodium chloride and sodium sulfite</td>
<td>2 M NaCl, 0.3 Na₂SO₃</td>
<td>N/A</td>
<td>Resin column elution</td>
<td>Au: complete elution, 5 BV</td>
</tr>
</tbody>
</table>
Zhang and Dreisinger (2004) investigated the loading of gold and copper from ammoniacal thiosulfate solution onto various ion exchange resins followed by their elution. The loading solutions were made up of 20 ppm Au and/or 500 ppm Cu as CuSO$_4$ in 0.1 M ammonium thiosulfate adjusted to a pH of 11, which was selected based on the stability of thiosulfate and copper and the faster decomposition of tetrathionate in strongly alkaline solution (Zhang et al. 2002b). Their results showed that gold adsorption on resin is stronger than copper (Figure 10). Yet copper, with much higher initial concentration, loaded faster but was gradually replaced with gold. This was made evident by the consistently increasing gold loading on the resin and low effluent gold concentration compared to an initially high copper loading following by a gradual decrease in loading coupled with an increase in effluent copper concentration beyond the initial amount. The gold loading of a 1 ppm gold solution onto Dowex 21K resin was reduced considerably by the presence of 100, 200 and 500 ppm copper giving loadings of 5.5, 3.3 and 1.6 kg/t respectively.

Once loaded the resins were stripped using three different eluents. The first exploited the poisoning effects of polythionates on gold loadings reported earlier (Zhang et al. 2002a) and therefore a mixed polythionate-sulfite solution (pH 9) with an initial composition of 0.25 M Na$_2$S$_4$O$_6$, 0.25 M Na$_2$SO$_3$ and 0.5 M ATS was used. The other two eluents used were 2 M sodium sulfite with 1 M ammonia (pH 11) and 4 M sodium chloride with 0.1 M ATS (pH 9.2). These latter two eluents were found to be the most efficient and most economical respectively. The tetrathionate eluent required a resin regeneration step before returning the resin to loading as was established by Fleming et al. (2003). This was done by washing the column with 10 BV of 0.05 M NaOH at 5 BV/hr followed by DI water rinsing. It is noteworthy to mention that the procedures do not reveal the use of deaeration prior to copper additions during loading solution preparations unlike previous work (Zhang et al.}

![Figure 10: Co-loading of gold (a) and copper (b) onto Dowex 21K resin columns at different flow rates from 0.1 M ATS containing 20 ppm Au and 500 ppm Cu (pH 11) (Zhang et al. 2004).](image-url)
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It had been shown that solutions without deaeration could produce significant amounts of tetrathionate causing copper loadings to drop from an initial 11 kg/t to 2 kg/t over 24 hours. In the case of simultaneous gold and copper loading experiments, no analysis of polythionates was reported for the stripped resin solution. This could perhaps indicate if over the course of metal loading, the oxidation of thiosulfate into tetrathionate and the subsequent partial degradation of tetrathionate were in fact responsible for lowered resin metal loadings. This type of analysis was applied by Jeffrey et al. (2007) and later by Breuer et al. (2012) where the former also showed that the elution of the resin using 0.5 M sodium perchlorate completely stripped the resin (exchanged all the adsorbed species for perchlorate) and that the loadings of each species on the resin calculated from the quantification of the strip solutions were in excellent agreement with the loadings calculated from the change in solution concentration during loadings. In other words, in this case using perchlorate as the eluent, no changes in solution composition occurred during the loading and subsequent elution. Yet, if changes in species concentrations were to occur on the resin during loading, then this method could be used to determine them. Table 4 summarizes the current methods for the elution of gold from loaded resin beads.

2.3.1.2 Effects of Polythionates on Resin Gold Loading

2.3.1.2.1 Affinity of Polythionates for Anion-Exchange Resins

Early work by Iguchi (1958) reported that the separation of polythionates with anion-exchange resins is possible via anion-exchange chromatography. Distribution coefficients ($K_d$) were measured as the volume of eluent (HCl) passed through the column until the solute concentration (investigated species) became maximum minus the interstitial volume of the column divided by the mass of resin. The relationship between $K_d$ and the concentration of HCl for various polythionates was established and utilized to successively separate the polythionates by increasing the eluent concentration (See Appendix Figure A 1). This work inherently showed the increasing affinity of polythionates on the resin in the order: dithionate> trithionate> tetrathionate> pentathionate.

2.3.1.2.2 Competitive Adsorption of Polythionates

Zhang and Dreisinger (2002a) showed that 10 mM of tetrathionate severely reduced the equilibrium gold loading by nearly 90 % by strongly adsorbing on the resins and competing with the gold-thiosulfate complex for ion-exchange sites (see Figure A 3 in the Appendix). Copper equilibrium isotherms were also generated and showed initial rise in copper loading with increasing copper
concentration followed by a decline. This drop in copper loading capacity was confirmed to be due to the adsorption of tetrathionate over time. The simultaneous loading of gold and copper was also investigated for two solution compositions as specified in Figure 11. There, it can be seen that gold reached a maximum loading of 3.5 kg/t after 1-2 hours which then dropped to 3 kg/t. In the case of copper, loading was similar but the drop in concentration on the resin was more pronounced. Similar results were generated for various strong-base resins and the difference of pH from 11 to 11.5 had no effect. The drop in loading over time was suggested to arise from the incomplete decomposition of formed tetrathionate which, in the presence of oxygen, might have produced trithionate as shown below (Equation 12). The authors suspected that trithionate, formed during the loading, adsorbed strongly onto the resins and replaced the already loaded metals. However, this observation was not further investigated.

Nicol et al. (2002) showed competitive anions such as sulfate and thiosulfate have small effects on the gold adsorption on strong-based resins but that sulfite and particularly trithionate and tetrathionate are detrimental to gold adsorption via their strong affinities for resin adsorption sites (See Appendix Figure A 2). Moreover, O'Malley (2002) showed that after initial loading on strong-base resins at pH 9.5, all loaded ion metal complexes began to be displaced by either tetrathionate or trithionate in solution as shown in Figure 12. This was explained by the more rapid adsorption of metal ion complexes to the competing sulfur anions and the increasing concentration of polythionates formed from the oxidation of thiosulfate over time. It was shown that repeating the experiment to construct Figure 12 but adding 5 mM of initial trithionate resulted in an even further decrease in metal concentration on the resin and a faster displacement of metal ions from the resin.

Figure 11: Kinetics for the simultaneous loading of gold and copper onto Dowex 21 K resin from solution A (0.1 M ATS, 20 ppm Au, 500 ppm Cu) and B (Solution A + 0.2 M NH₃) at pH 11. 5g/L resin concentration (Zhang et al. 2002a).
Figure 12: The effect of metal thiosulfate complex on the loading of gold on Amberjet 4200 at 0.05 M thiosulfate, 0.2 M Ammonia, and 20 mg/L for each metal ion (O’Malley 2002).

Analysis of the solution from Figure 12 indicated only trithionate was present at a concentration of 10 mM. It was postulated that while tetrathionate is known to form according to Equation (13), it likely disproportionated to pentathionate and sulfite (O’Malley 2002). The latter reacted with additional tetrathionate to produce thiosulfate and trithionate according to Equation (9):

\[ S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-} \]  

However at the investigated pH of 9.5, the product of oxidation of thiosulfate, that is, tetrathionate, was likely rearranged into trithionate and pentathionate via Equation (10) with the latter immediately degrading to thiosulfate via Equation (11):

\[ 2S_4O_6^{2-} \rightarrow S_3O_6^{2-} + S_5O_6^{2-} \]  

\[ 2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \]

Since the reaction in Equation (11) is not rate limiting, the overall tetrathionate degradation reaction may be expressed by a single Reaction (12) whose rate constant is first order with respect to tetrathionate and hydroxide concentration (Nicol et al. 2002, Zhang et al. 2002b, Varga et al. 2007, Zhang et al. 2010).

\[ 4S_4O_6^{2-} + 6OH^- \rightarrow 2S_3O_6^{2-} + 5S_2O_3^{2-} + 3H_2O \]

Figure 13 shows the equilibrium loading isotherms of gold on resin in the presence of competing anions. All competing anions had an effect on the loading of gold with the most detrimental being tetrathionate and trithionate. It was also shown that the higher the concentration of the anion was, the less gold was adsorbed on the resin (Nicol et al. 2002, O’Malley 2002).
It is therefore highly recommended to limit the exposure of competitively adsorbing degradation products from the oxidation of thiosulfate to the resin in solution in order to limit the displacement of gold from the resin and limit lower recoveries. This can in part be achieved by optimizing the contact time of the resin in the leach solution and selecting operating conditions (e.g.: pH, reagent concentrations) that limit the generation of tri- and tetrathionate.

Jeffrey and Brunt (2007) developed a successful new method for the determination of thiosulfates and polythionate as described in Section 3.2.2. This analytical technique was used to investigate the thiosulfate degradation and polythionate formation in typical gold leaching solutions containing 50 mM ammonium thiosulfate, 150 mM ammonium sulfate, 2 mM copper(I) thiocyanate (as a stable source of Cu(I)) and sodium hydroxide concentrations of 10, 50 and 300 mM corresponding to pH’s of 8.3, 9.1, and 10.4 respectively. Results showed that thiosulfate oxidation followed a pseudo first order reaction rate with tetrathionate and pentathionate being the dominant reaction products at pH 8.3 and 9.1 in addition to a small amount of trithionate in the latter case. At pH 10.4 the main reaction product was trithionate, in agreement with the known instability of higher polythionates in alkaline solutions (Zhang et al. 2002b, Varga et al. 2007, Zhang et al. 2010). Isotherms of gold on resin vs. gold in solution in the presence of three solutions of varying polythionate concentration were also generated by plotting the results of three series of four batch experiments (Figure 14). Each series of batch experiments comprised of four 5 L solutions with different initial gold concentrations of 0.1, 0.2 0.6 and 3 mg/L containing 50 mM ammonium thiosulfate, 2 mM copper sulfate, 150 mM...
ammonium sulfate and 10 mM sodium hydroxide. The total amount of polythionates in the solutions for the three series was obtained by varying the initial sulfite, trithionate and tetrathionate concentrations.

![Figure 14: Isotherms of gold on resin vs. gold in solution, for three solutions of varying polythionate concentration (Jeffrey et al. 2007)](image)

The data shows that polythionate loadings did not vary significantly with the gold in solution. In other words, for a given series the amount of polythionates adsorbed on the resin was constant and irrespective of the gold loading. However as expected, gold loading on the resin decreased with total polythionate concentration. The reported ratios of concentration of species loaded on the resin to species in solution indicated the respective affinities of those species on the resin in decreasing order: gold thiosulfate > pentathionate > tetrathionate > trithionate > copper thiosulfate > thiosulfate.

In a study about the effects of mercury concentration on gold adsorption on resin in an initial loading solution containing 100 mM thiosulfate (as ATS) and 4 mM trithionate, the speciation of polythionates was monitored in the barren solution following 5 hours loading and in the stripping solution (Oraby 2009, Oraby et al. 2010). Unfortunately, due to limitations in the available data (exact solution volumes and mass of resin) the possible differences between polythionate compositions calculated from the barren solution and that of the stripping solution could not be determined. It is believed that being able to calculate these differences could possibly reveal how polythionates behave during resin loading and how this influences the recovery of gold.

### 2.3.2 Non-Ammoniacal Thiosulfate Leaching Systems

Even though thiosulfate is considered to be non-toxic, there are some concerns over the presence and fate of ammonia although much less important than compared to cyanide (Oraby 2009). For this
reason, completely removing ammonia would represent a cleaner process. However, removing
ammonium in the TS leaching system will decrease the stability of the cupric ions and increase their
reaction with thiosulfate (Chandra et al. 2004). The ATS system also experiences the generation of
polythionates as observed by the homogenous reduction of copper(II) by thiosulfate as shown by
the simplified overall reaction in Equation (13) (Breuer et al. 2000).

\[
2Cu(NH_3)_4^{2+} + 8S_2O_3^{2−} \rightarrow 2Cu(S_2O_3)_{5}^{5−} + 8NH_3 + S_4O_6^{2−}
\]

13

The loss of thiosulfate and resulting decrease in reagent concentration ultimately decrease gold
dissolution. Moreover, the generation of polythionates have been shown to have a negative impact
on both gold dissolution and the recovery of gold using ion exchange resins (Chandra et al. 2004).
These are the main reasons for the development of non-ammoniacal thiosulfate leaching systems.

2.3.2.1 In-situ Thiosulfate Leaching

Another reason for the development thiosulfate leaching systems using different oxidants is for the
in-situ leaching (ISL) of low gold grade oxide ores. This process, taking place in anaerobic
conditions, requires long contact times between lixiviant and ore minerals and hence the stability of
the solution, in particular the oxidant, is essential. The traditional Cu-ATS system is therefore not
suitable due to the rapid oxidation of thiosulfate by the copper(II)-ammine complex (Equation 13)
and the subsequent inability for the system to regenerate the necessary cupric under anaerobic
conditions of ISL for sustained gold leaching as shown by Equation (14):

\[
4Cu(II)(S_2O_3)_{3}^{3−} + O_2 + 2H_2O + 16NH_3 \rightarrow 4Cu(II)(NH_3)_{4}^{2+} + 8S_2O_3^{2−} + 40H^- 
\]

14

A proposed suitable lixiviant for ISL is the ferric-EDTA-thiosulfate system (Heath et al. 2008). It
uses a small amount of thiourea as a catalyst for gold oxidation. The main advantage of this system
over the conventional ATS one is the relatively low reactivity between the ferric-EDTA oxidant and
thiosulfate (Breuer et al. 2012). Similarly, ferric oxalate in the presence of thiourea as a catalyst is
another proposed alternative oxidant for a thiosulfate leaching system. With an oxalate to iron ratio
of three, the gold dissolution rate was shown to be stable over time and compared favorably to the
Cu-ATS system under similar leach conditions (Chandra et al. 2005).

2.3.2.1.1 Gold and Polythionate Loading from Synthetic Fe-EDTA Leach Solutions

Although this leaching system is of lesser interest, it is noteworthy from the point of view of
polythionates loading and elution and their effects on gold recovery. The leach solution used was
composed of 0.1 M thiosulfate, 10 mM thiourea, 3 mM FeEDTA, 2 mM trithionate, 2 mM tetrathionate and 4 mg/L gold (Breuer et al. 2012). Moreover, the column was preloaded with trithionate to half its capacity to simulate a recycled column. The loading process was described by measuring the concentration of species over time in the outlet solution of the resin column (Figure 15). It was shown that thiosulfate was quickly loaded initially due to its availability and high concentration and was subsequently displaced by trithionate, tetrathionate and gold as evidenced by the higher thiosulfate effluent concentration compared to the feed concentration. Tetrathionate had an equilibrium breakthrough concentration at the column exit that was lower than its feed concentration. This indicated that it was converted to trithionate through reaction with thiosulfate. In the case of trithionate, its concentration in the effluent eventually plateaued to a level of 3.5 mM which is higher than its feed concentration and can be attributed to its generation from tetrathionate.

![Figure 15: Concentration profiles for various species in the outlet solution of a resin column for gold loading from a synthetic FeEDTA-thiosulfate solution (Breuer et al. 2012).](image)

Afterwards, the loaded column was stripped using 2 M NaCl and 0.3 M Na₂SO₃ as presented in Figure 16 A and B. Gold was completely eluted within 5 BV and the results also showed the stronger affinity of trithionate onto resin over thiosulfate due to broader elution profiles. Based on the elution results it could be suggested that the affinities of the species for resin adsorption sites follows the order: Thiosulfate < gold thiosulfate < trithionate ≈ tetrathionate (low concentrations).
Here, the researchers followed the fate of polythionates during loading and elution and showed their instability. This type of thorough investigation could help elucidate the reasons for lowered gold loading as observed by Zhang and Dreisinger (2002a) and discussed in Section 2.3.1.1.

2.3.2.2 Thiosulfate Pressure Leaching

Ji et al. (2003) investigated the TS pressure oxidation leaching of a preg-robbing carbonaceous ore without ammonia and cupric copper. Leaching conditions ranged between 40-80 °C, 10-100 psig oxygen partial pressure, a pulp density of 40-50 % and an initially adjusted slurry pH of 11-12. Generally, within 6-8 hours residence time, gold extractions reached close to the maximum leachable by TS (82.3 %). Increasing the oxygen pressure, pH, temperature and slurry pulp density all caused an increase in thiosulfate degradation into trithionate and tetrathionate. Additions of 50 mg/L cupric ions to this leaching system did not significantly impact the gold leaching rate nor the gold recovery. In fact, it generated nearly twice the amount of degradation products.

2.3.2.3 Calcium-Thiosulfate Leaching System

The last non-ammoniacal thiosulfate leaching system, discussed in greater details due to its relevance to BGC’s Autoclave-TCM processing technology, involves the calcium-thiosulfate (CaTS) salt. Recently published results revealed the use of a simple alkaline calcium-thiosulfate-oxygen leach system (Breuer et al. 2012). Although the dissolution of gold alone in CaTS solution with dissolved oxygen as the oxidant is very slow, in the presence of pyrite ores, gold dissolved and was recovered comparably to other systems. In addition copper dissolution was eliminated and, depending on the leaching conditions, thiosulfate was even generated. The latter occurrence was believed to be a result of the in-situ generation of thiosulfate from alkaline oxidation of pyrite.
(Breuer et al. 2008) but needed to be verified (Breuer et al. 2012). Other research has since shown the feasibility of gold dissolution during the oxidation of gold-bearing pyrite through simultaneous thiosulfate generation as the gold leaching lixiviant (Melashvili et al. 2016). Nevertheless, this CaTS leaching system is capable of dissolving gold from refractory pyritic ores as shown by the results in Figure 17. The reason behind this ore matrix effect is unclear but it was believed to be linked to the galvanic interactions between gold particles and the surface of pyrite facilitating gold leaching via oxygen reduction on the pyrite surface (Breuer et al. 2012).

As expected, the TS consumption during the pyrite concentrate leaching was high (Figure 17 Right, curves B and D) due to the catalyzed oxidation of TS on the sulfide minerals (Feng et al. 2002, 2003, 2006, Zhang et al. 2008). The measured concentrations for trithionate were high and those for tetrathionate were low due to its disproportionation to TS and trithionate at high pH as shown by Equation (15) (Breuer et al. 2004).

\[
4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O
\]

Zhang et al. (2013) showed the best gold leaching rates during the dissolution of a rotating gold disc electrode (300 rpm, pH 10, pure oxygen as oxidant) were obtained with 50 °C (vs. 25 °C), 2 mM Cu (vs. none), 0.1 M CaTS (vs. NaTS) and an electrical connection (vs. none) to a pyrite crystal simulating a leaching condition where the gold was associated with sulfidic ore. In the process they confirmed increased leaching rates based on the background cations associated with TS-salts, where leaches with Ca\(^{2+}\) cations out-performed those with Na\(^{+}\) cations. This was also described in other works (Feng et al. 2010b, Sitando et al. 2015). Figure 18 (Zhang et al. 2013) shows additional results.
from the research group’s CaTS leaching system using pure oxygen sparging and 50 °C that complements Figure 17 using air sparging and 40 °C (Breuer et al. 2012).

Figure 18: Gold recovery during leaching of various ore samples (A= Oxidized ore, P<sub>W</sub>-90, 4.4 g/t Au, 0.49 % S<sup>2-</sup>; B= Cu-Au flotation conc., P<sub>W</sub>-60, 7.7 g/t, 28.4 % S<sup>2-</sup>, with small %-age of copper sulfides; D*= Pyrite conc., P<sub>W</sub>-26, 45 g/t Au, 30 % S<sup>2-</sup>, without fine grinding) using the CaTS-O<sub>2</sub> system (Left) and the resulting thiosulfate consumptions (Right) (0.3 M CaTS, 2 mM CuSO<sub>4</sub>, pH 10, 50 °C, pure oxygen sparging) (Zhang et al. 2013).

Figure 18 shows the beneficial effect on gold recovery by increasing the temperature and changing the oxidant to pure oxygen gas. On the other hand, after 48 hours of leaching, thiosulfate consumption was seen increasing especially in the case of the Cu-Au flotation concentrate, B, which contained sulfides. With fine grinding, the final gold extraction and thiosulfate concentration for the pyrite concentrate, D, at 50 °C and with oxygen sparging were 50.9 % and 0.005 mM (not shown) compared to 41.5 % and 0.094 mM with 40 °C and air sparging (Figure 17). In the case without fine grinding for the pyrite concentrate, D*, the final gold extraction and thiosulfate concentration at 50 °C and with oxygen sparging were 52.4 % and 0.147 mM (Figure 18). This shows the adverse effect of fine grinding of a sulfide ore on the consumption of thiosulfate where an increase in freshly exposed sulfide mineral surface area can strongly catalyze the thiosulfate decomposition. A last noteworthy result was the leaching performance of the CaTS-O<sub>2</sub> leaching system at 50 °C on concentrate B (71.4 %, 48 hrs) which bested that of cyanidation (62 %, 24 hrs, 50 kg/t NaCN).

Sitando et al. (2015) continued to investigate the CaTS leaching system using a rotating disc electrode (RDE) and a rotating electrochemical quartz crystal microbalance (REQCM). They confirmed an increase in temperature (up to 60 °C), thiosulfate concentration (not specified), up to 2 mM copper additions and the use of the calcium thiosulfate salt contributed positively to the leaching of gold. The galvanic interactions between various sulfide minerals (as RDE’s) electrically connected to gold (as a REQCM electrode) were also investigated. This work showed an enhanced
reduction of oxygen on the pyrite surface thereby increasing the cathodic current. This was seen as an increase in the mixed potential of the solution from 108 mV to 175 mV resulting in a threefold increase in the gold leaching rate to a level of $10^{-5}$ mol/m$^2$s, a rate equivalent in magnitude to cyanidation. Furthermore, 24 hour CaTS leaching of gold powders in the presence of pyrite (2 mM Cu, 0.2 M CaTS, 10 mL/min O$_2$, 60 mg/L Au, −100 μm pyrite powder) followed a reaction-controlled shrinking sphere model where pyrite additions of 1 and 2.5 % (wt/v) resulted in 79.6 and 86.2 % gold dissolution respectively compared to just 61 % by 10 mM NaCN-Air leaching. Finally, 48 hour CaTS leaching tests were conducted on two sulfide ore samples, A and B, having similar properties as the ores C and D* respectively tested by Zhang et al. (2013) as summarized in Table 5.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sulfide Ore</th>
<th>NaCN Leaching</th>
<th>%Au (24 hrs)</th>
<th>CaTS Leaching</th>
<th>%Au (24 hrs/48hrs)</th>
<th>Consumption mM [Cu]</th>
<th>[TS]</th>
<th>[3T]</th>
<th>[4T]</th>
<th>[Cu]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Sitando et al. 2015)</td>
<td>28.5 % pyrite, 13 g/t Au, 1.6 % Cu</td>
<td>241 kg/t, 20 mL/min O$_2$</td>
<td>98.5</td>
<td>0.3 M CaTS, 2 mM Cu, 50 °C, 4 mL/min O$_2$</td>
<td>73.3/80.5</td>
<td>185.9</td>
<td>47.9</td>
<td>13.7</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>C (Zhang et al. 2013)</td>
<td>Cu-Au flotation conc., 15 g/t Au</td>
<td>241 kg/t, O$_2$</td>
<td>98</td>
<td>0.3 M CaTS, 2 mM Cu, 50 °C, O$_2$</td>
<td>74 (24 hrs)</td>
<td>183 (24 hrs)</td>
<td>-</td>
<td>-</td>
<td>35.8</td>
<td></td>
</tr>
<tr>
<td>B (Sitando et al. 2015)</td>
<td>70.7 % pyrite, 45 g/t Au, 0.25 % Cu</td>
<td>10.8 kg/t, 4 mL/min air</td>
<td>62</td>
<td>0.3 M CaTS, 2 mM Cu, 50 °C, 4 mL/min O$_2$</td>
<td>30.3/52.3</td>
<td>196</td>
<td>45</td>
<td>10.6</td>
<td>30.3</td>
<td></td>
</tr>
<tr>
<td>D* (Zhang et al. 2013) (Figure 18)</td>
<td>Pyrite conc., 30 % pyrite, 45 g/t, P$_{80}$-26</td>
<td>“intensive cyanidation on P$_{80}$-10”</td>
<td>90 (48hrs)</td>
<td>0.3 M CaTS, 2 mM Cu, 50 °C, O$_2$</td>
<td>39.3/52.4</td>
<td>153</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
<td></td>
</tr>
</tbody>
</table>

*Digitally estimated, *Without fine grinding

Figure 19 contains the CaTS gold leaching curves over time for the samples given in Table 5. Due to the strong similarities between ore pairs A-C and B-D*, it is reasonable to assume these generated results come from the same ores.
The steady rise in the leaching curves for B and D* in Figure 19 indicate additional time would have led to higher gold extractions as long as free thiosulfate was present. In contrast, the copper containing ore, sample A, was seen arriving at a plateau possibly caused by 1) a decrease in free thiosulfate, 2) passivation of the gold surface by copper precipitates and/or 3) a gold thiosulfate stability issue where it was hypothesized that “tetrathionate, a thiosulfate degradation product, is a precursor for the precipitation of gold and silver, particularly in the presence of copper, as a mixed metal sulphide.” In fact, finally, Sitando et al. (2015) remark that thiosulfate consumptions in their tests were high and that considerable attention must be given to minimize the resulting degradation products for effective downstream gold processing.

Recently, an unknown additive “Y” added to CaTS leaching solutions (0.3 M TS, 2 mM Cu(II), pH 10, 50 °C and an oxygen flow rate of 10 mL/min) significantly improved the gold leaching efficiency of four different gold ore types compared to cyanidation (free cyanide concentration of 10 mM, ambient temperature, pH >10, 4 mL/min air) (Dai et al. 2017). Table 6 summarizes the results which compares the percent gold leached over time using CaTS with and without additive “Y” versus cyanidation.
Table 6: Percent gold leached using CaTS with and without additive "Y" compared to cyanidation. Cyanidation (1) 33.75 g/L Y; (2) 67.5 g/L Y; (3) 75 g/L Y (Dai et al. 2017).

<table>
<thead>
<tr>
<th>Feed Material</th>
<th>CaTS (%)</th>
<th>CaTS w/ additive “Y” (%)</th>
<th>Cyanidation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 hrs</td>
<td>48 hrs</td>
<td>24 hrs</td>
</tr>
<tr>
<td>Cu-Au conc.</td>
<td>73</td>
<td>80</td>
<td>NA</td>
</tr>
<tr>
<td>Pyrite conc.</td>
<td>40</td>
<td>51</td>
<td>77(2)</td>
</tr>
<tr>
<td>Calcine conc.</td>
<td>20</td>
<td>32(3)</td>
<td>52(3)</td>
</tr>
<tr>
<td>Pox discharge</td>
<td>43</td>
<td>52(5)</td>
<td>62(1)</td>
</tr>
<tr>
<td>Oxide ore</td>
<td>43</td>
<td>59(5)</td>
<td>62(1)</td>
</tr>
</tbody>
</table>

(5) Digitally estimated

It should be noted that the authors expressed concerns over “preg-robbing” behaviours exhibited by the pyrite concentrate leaches where additive concentrations of 45 g/L and above resulted in soluble gold decreases between 24 and 48 hours. The addition of 75 g/L Y resulted in a decreased gold leaching efficiency from the pyrite concentrate. Moreover, for all minerals studied, it was observed that increases in the additive concentration resulted in the enhanced degradation of thiosulfate and resulting polythionate generation. The authors postulated the catalytic oxidation of thiosulfate by the additive caused a lowered free thiosulfate concentration resulting in gold losses via preg-robbing onto sulfide minerals such as pyrite. The role of the high concentrations of polythionates measured in the leach solutions (e.g. 107.7 mM 4T & 21.5 mM 3T after 48 hrs with 75 g/L Y) on the gold loss was not ruled out by the mention of tetrathionate being a precursor for the precipitation of gold as a mixed metal sulfide.

Other research and available data involving the use of CaTS salt as a leachant are very limited. Of the few, Feng and van Deventer (2010b) compared the leaching of pure gold and two gold ores of different mineralogy using three thiosulfate salts, namely ATS, NaTS and CaTS in a solution containing 0.5 M NH₃ and 4 mM Cu²⁺. For the leaching of gold foils, CaTS provided higher dissolution rates due to the ability of the divalent Ca²⁺ cations to form stronger ion-pairs with gold thiosulfate ions compared to the other monovalent cations. The stronger association and hence higher stability constants for divalent cations/thiosulfate complexes over monovalent cations likely resulted in the increased gold dissolution rates. In the case of gold leaching from the pyrite concentrate containing a high sulfide mineral content, ATS edged CaTS over the 24 hour leach although the latter had faster initial leaching kinetics. The better ATS leaching performance was attributed to the availability of free ammonia to enhance the leaching of the sulfide mineral, which is beneficial for gold leaching, and to stabilize the resulting increase in copper concentration. The sulfide ore had a lower sulfide content than the pyrite concentrate and therefore its gold leaching was less dependent on the interactions of gold with the associated sulfide minerals (Feng et al. 2002,
The gold leaching of the sulfide ore was highest for the CaTS solution similarly to the leaching of pure gold. Moreover, the higher leaching rate of CaTS was attributed to the higher mixed solution potential and the higher solution pH which hampered the catalytic decomposition of TS (Equation 13) and increased TS stability (Equation 15). It is noteworthy to mention that in all cases the calcium cations significantly reduced TS consumption compared to the ATS salt. This was due to the increased dissolution of copper minerals in ATS solutions and ensuing increase in cupric tetra-amine concentration which can decompose TS according to Reaction (13).

### 2.3.2.3.1 CaTS Gold Recovery by Ion Exchange Resins

Trithionate is undesirable as it competitively adsorbs on resin adsorption sites, reducing the gold recovery. In the CaTS system discussed earlier by Breuer et al. (2012), this was made evident by how the decrease in solution gold closely followed the decrease in trithionate concentration during RIP recovery (Table 7). In other words, trithionate competes strongly with gold TS for the resin adsorption sites.

Table 7: Resin-in-pulp adsorption from a pyritic concentrate leach slurry (Resin:Slurry volume ratio 1:60) (Breuer et al. 2012).  

<table>
<thead>
<tr>
<th>Resin contact (2 hrs each)</th>
<th>Solution Concentration</th>
<th>Loading on Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au (mg/L)</td>
<td>S$_2$O$_7^{2-}$ (mM)</td>
</tr>
<tr>
<td>0</td>
<td>0.3</td>
<td>216.9</td>
</tr>
<tr>
<td>1st</td>
<td>0.09</td>
<td>157.7</td>
</tr>
<tr>
<td>2nd</td>
<td>0.03</td>
<td>183.6</td>
</tr>
<tr>
<td>3rd</td>
<td>0.00</td>
<td>146.9</td>
</tr>
</tbody>
</table>

In order to fully recover gold without using large quantities of resin it is necessary to remove trithionate. The authors suggested regenerating the resin between adsorption stages using sulfide as per Equation (16). The resin would maintain and continue adsorption of the gold-thiosulfate complexes between the stages until appropriate gold loadings were achieved suitable for elution.

$$ S_3O_6^{2-} + S^{2-} \rightarrow 2S_2O_3^{2-} $$  \[ 16 \]

It was also mentioned that the CaTS leaching system was rather unstable during leaching and that gold, complexed as gold-thiosulfate, could likely precipitate as metal sulfide due to the oxidation of thiosulfate and sulfide minerals. More importantly, it was revealed that using a RIP process improved precious metal recovery and that the use of RIL would likely be even more beneficial. This latter statement seems to be in accordance the observations made by the Goldstrike CaTS trials.
discussed in Section 2.1.3 and by RIP pilot-plant campaigns yielding an additional 0.3 g/t gold versus a process involving solid-liquid separation after thiosulfate leaching (Fleming et al. 2003).

A recent publication compared gold extractions between CaTS with RIL (See Table 1) and cyanidation with CIL after a novel oxidative atmospheric tank leaching (ATL) pre-treatment (Choi et al. 2017). The pre-treatment (48 hrs, 83 °C, 0.8 L/min O₂, 800 rpm) was designed to break down sulfides using as baseline conditions sulfuric acid (90 g/L) and ferric sulfate (17 g/L) as reagents and a carbon matrix resin (30.3 g/kg) acting as a catalyst for sulfide oxidation and as a sulfur collector. The results showed gold recoveries using Purolite A500 resin (20 mL/L slurry) were very similar to CIL extracting up to 68.9 % of the total gold in an ore containing 58 % pyrite and 12.8 % arsenopyrite (S1, Table 8). The general trend showed increased gold recoveries with increased sulfide dissolution as a result of improvements to the ATL pre-treatments. Other results conducted on different mineral samples using baseline pre-treatment conditions are summarized in Table 8 showing that in most instances, the CaTS-RIL leaching and recovery process outperformed cyanidation with CIL.

<table>
<thead>
<tr>
<th>Mineral Sample</th>
<th>Au recovery w/o pre-treatment</th>
<th>Au recovery after pre-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CN-CIL (%)</td>
<td>CN-CIL (%)</td>
</tr>
<tr>
<td>S1 (Arsenopyrite)</td>
<td>10.1</td>
<td>50.0</td>
</tr>
<tr>
<td>S2</td>
<td>27.3</td>
<td>71.2</td>
</tr>
<tr>
<td>S3</td>
<td>3.9</td>
<td>68.3</td>
</tr>
<tr>
<td>S4</td>
<td>10.6</td>
<td>75.1</td>
</tr>
</tbody>
</table>

2.3.2.4 Resin Loading in Non-Ammoniacal Thiosulfate Solutions

The gold loading on a sulfite treated 0.1 M TS pressure leached solution with a low polythionate slurry composition of 1.61 mM trithionate and 0.22 mM tetrathionate yielded 9.96 kg/t (Purolite A-500C) in equilibrium with a solution concentration of 4.56 mg/L Au (Ji et al. 2003). Additional batch leach testing slurries with various polythionate compositions were allowed to equilibrate overnight in contact with Purolite A-500C resin. A plot of these results is given in Figure 20 showing the presence of trithionate and tetrathionate was clearly detrimental to gold loading.
In parallel to this work, West-Sells et al. (2003) further investigated the effects of low concentrations of tri- and tetrathionate (< 1000 mg/L) on gold loading. In the absence of polythionates, gold loading reached 76 kg/t on the resin at equilibrium with 0.7 mg/L gold in solution. Tetrathionate was seen as having the most detrimental effect on gold loading in comparison to trithionate. For example, only 2200 g/t gold loaded on the resin in equilibrium with 0.3 mg/L gold for a solution containing 420 mg/L tetrathionate initially. Gold loading isotherms from initial solutions with equal parts tetrathionate and trithionate were found not to differ much from solutions containing only tetrathionate at the same concentration. Ultimately it was determined that the tetrathionate concentration overshadowed that of trithionate in terms of detrimental effects on the loading of gold.

Similarly to work by Jeffrey and Brunt (2007), Muslim (2010a) investigated the loading of synthetic non-ammoniacal leach solutions (gold thiosulfate, sodium-thiosulfate and trithionate) in contact with 0.5 g Purolite A500 resin over 5 hours. Changes between the initial solution and post loading solution compositions allowed for the determination of the gold and polythionate loading on resins at various initial gold concentrations. It was shown that gold loading isotherms, plotting the gold loading on resin (% of theoretical capacity) versus equilibrium gold concentration in solution, produced linear curves. Moreover, polythionate loadings on resin calculated from initial and final
loading solution concentrations and from the concentration of resin stripping solutions were found to be more or less equal. Thiosulfate was shown to be rather stable throughout loading and elution, and trithionate concentrations seemed constant regardless of initial gold concentration. Yet the author claimed that gold loading on resin increased with equilibrium thiosulfate concentrations even though the total polythionate concentration also increased therefore contradicting the findings from Jeffrey et al. (2007). This is shown in Figure 21 using data adapted from Muslim (2010a) and plotted with corrected results from Jeffrey et al. (2007) keeping in mind that the two leaching systems do differ. The methodology for the construction of this gold isotherm is available in the Appendix Section A.5.

As can be seen, the gold loading on resin reported by Muslim (2010a) with higher polythionate concentration (2.8 mM) is greater than that with lower polythionate concentration (0.9 mM). These conflicting views need to be verified and also applied to the CaTS-air leaching system to determine
the effects of polythionates and/or thiosulfate on the gold isotherms to ultimately improve a model for the RIP and RIL processes.

2.3.2.4.1 Modelling of Gold and Polythionate Loading on Resin

The literature shows that the former Parker Cooperative Research Center (2005-2012) in Perth, Australia was involved in the “Modelling of gold thiosulfate leaching system” (Muslim in preparation) and this is supported by several publications (Muslim 2009, Muslim et al. 2009, Muslim 2010b) which are described below.

Firstly, in the study of the adsorption of polythionates and thiosulfate on resin (Muslim et al. 2009), experimental adsorption rate data of the sulfur oxoanion adsorption on resin was used to calculate the rate constants using Equation (17) and assuming a first order mass transfer process.

\[
[S_{x}O_{y}^{2-}]_t = ([S_{x}O_{y}^{2-}]_0 - [S_{x}O_{y}^{2-}]_{eq}) \times \exp(-k_it) + [S_{x}O_{y}^{2-}]_{eq}
\]  \hspace{1cm} 17

where \( y = 6 \) if \( x \geq 3 \) (polythionates)

\( y = 3 \) if \( x = 2 \) (thiosulfate)

The variable rate constants \((k_i)\) were determined by a method of least squares to fit the experimental data and fixing the initial sulfur species concentration \(([S_{x}O_{y}^{2-}]_0)\) and equilibrium sulfur species \(([S_{x}O_{y}^{2-}]_{eq})\) to the experimental values. The results yielded rate constants of 0.058, 0.035 and 0.019 \( \text{min}^{-1} \) for thiosulfate, trithionate and tetrathionate respectively indicating the loading process is faster with increasing sulfur atoms in the species.

Secondly, the study investigated the competitive adsorption between species by conducting two component adsorption experiments. An example is given in Figure 22 showing a trithionate adsorption isotherm at various tetrathionate concentrations. As expected the loading of trithionate on the resin increased with increasing trithionate in solution but overall decreased in the presence of increasing levels of competing tetrathionate anions.
As a result, an equilibrium equation can be written in the form of Equation (18):

\[
[R_2S_xO_y][S_aO_b^{2-}]K_{a/x} = [R_2S_aO_b][S_xO_y^{2-}]
\]

where \( y & b = 6 \) if \( x \geq 3 \) (polythionates)

\( y & b = 3 \) if \( x = 2 \) (thiosulfate)

\( K_{a/x} \) represents the equilibrium constant for the reactions between an oxoanion \( (S_xO_y^{2-}) \) with “\( x \)” number of sulfur atoms on the resin and a competing oxoanion \( (S_aO_b^{2-}) \) with “\( a \)” number of sulfur atoms in solution. Manipulating Equation (18) into Equation (19) and plotting the latter with experimental resin loadings and equilibrium solution concentrations of the species \( (S_xO_y^{2-}, S_aO_b^{2-}) \) from a two component system yields a straight line with the slope giving \( K_{a/x} \).

\[
\frac{[R_2S_xO_y]}{[S_xO_y^{2-}]} K_{a/x} = \frac{[R_2S_aO_b]}{[S_aO_b^{2-}]}
\]

The results showed that \( K_{3/2} \) equal to 95.1 indicated trithionate was much more strongly adsorbed than thiosulfate. Similarly, \( K_{4/3} \) equal to 1.45 implied that tetrathionate loaded more strongly than trithionate and finally, \( K_{5/4} \) equal to 1.58 meant pentathionate was more strongly loaded onto the resin than tetrathionate.

Thirdly, the equilibrium constant between the gold thiosulfate complex and a counter-anion was also determined. Trithionate was selected as the competing ion as it is known for strongly adsorbing
on resins (see above) and even proposed as an eluent (Jeffrey et al. 2010). As such, the equilibrium
between gold thiosulfate and trithionate can be represented by Reaction (20):

\[
3R_2S_3O_6(s) + 2Au(S_2O_3)_2^{3-} \text{(aq)} \leftrightarrow 2R_3Au(S_2O_3)_{2(s)} + 3S_3O_6^{2-} \text{(aq)}
\]

The equilibrium constant for Reaction (20) can be represented by:

\[
K = \frac{[R_3Au(S_2O_3)_{2}]}{[Au(S_2O_3)^{3-}]^2} \times \left( \frac{[S_3O_6^{2-}]}{[R_2S_3O_6]} \right)^3
\]

Taking the log and manipulating Equation (21) yields Equation (22):

\[
\log \left( \frac{[R_3Au(S_2O_3)_{2}]}{[Au(S_2O_3)^{3-}]^2} \right) = \frac{3}{2} \log \left( \frac{[R_2S_3O_6]}{[S_3O_6^{2-}]} \right) + \frac{1}{2} \log(K)
\]

Should the adsorption of gold thiosulfate on the resin follow this model, a plot the log of the first
term over the log of the second term would give a straight line of slope 1.5 and an intercept of 0.5
log(K). The resulting line gave a slope of 1.5248 and an intercept of −0.1992 (see Jeffrey et al.
(2010)) giving an equilibrium constant erroneously reported as 0.53 when in fact it should be 0.4.
Nonetheless, the slope of the isotherm is close to 1.5 confirming that a trivalent gold species adsorbs
on the resin.

Finally, in order to calculate the equilibrium concentrations of sulfur species and gold thiosulfate in
solution and on the resin, 10 equations (mass balances, equilibrium equations (e.g. Equation (20))
and a resin charge balance) were assembled to be used in a model. This model for calculating the
equilibrium loading, the rate constants and equilibrium constants for adsorptions are components to
be used in a future all-encompassing resin-in-pulp model.

The latest publication by the aforementioned author described and compared a new model for the
adsorption kinetics and equilibriums of thiosulfate and polythionate on resin in a batch system
(Muslim 2010b). This model was to be used to predict the amount of species adsorbed on resins
based on both liquid and solid phases. It also gives the overall adsorption capacities (mg/g) and
adsorption intensities of species on the resin in a multicomponent system. The results showed the
isotherm adsorption profile calculated using the model compared closely to the experimental results
for a solution containing thiosulfate, trithionate and tetrathionate with a concentration range of 1.3
mM (see Table 9). The adsorption intensities indicated that trithionate was the most strongly
adsorbed species on the resin followed by tetrathionate and thiosulfate. The next step in the
development of this model is to incorporate the adsorption of gold in the presence of thiosulfate and polythionates in single and multiple component batch systems (Muslim 2010b).

<table>
<thead>
<tr>
<th>Species</th>
<th>Experiment</th>
<th>Model</th>
<th>Ads. capacity (% deviation)</th>
<th>Ads. intensity (% deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiosulfate</td>
<td>0.806</td>
<td>11.223</td>
<td>0.803</td>
<td>12.392</td>
</tr>
<tr>
<td>Trithionate</td>
<td>0.811</td>
<td>14.347</td>
<td>0.808</td>
<td>16.639</td>
</tr>
<tr>
<td>Tetrathionate</td>
<td>0.810</td>
<td>13.351</td>
<td>0.807</td>
<td>14.347</td>
</tr>
</tbody>
</table>

2.4 Polythionate Degradation

Zhang and Dreisinger (2002b) showed that the alkaline degradation of tetrathionate in the absence of oxygen, copper and ammonia exhibited pseudo first order reaction kinetics with respect to tetrathionate and hydroxide. At room temperature, the rate equation for the decomposition of tetrathionate in alkaline solution can be expressed as:

$$-\frac{d[S_4O_6^{2-}]}{dt} = 1.38 \times 10^3 \left[S_4O_6^{2-}\right][OH^-] \text{ (mol} L^{-1} h^{-1})$$

According to their measured concentration of thiosulfate as a product of tetrathionate decomposition at pH 11.5, the calculated molar ratio of $S_4O_6^{2-}/S_2O_3^{2-}$ was 1:1.3 as per the proposed reaction mechanism correctly balanced in Equation (24) (Miura et al. 1983):

$$10S_4O_6^{2-} + 34OH^- \rightarrow 13S_2O_3^{2-} + \frac{38}{3}SO_3^{2-} + \frac{4}{3}S^{2-} + 17H_2O$$

However, in a technical note later published by Breuer and Jeffrey (2004), Equation (24) was found to be unlikely as their repeated experiments for the same experimental conditions as used by Zhang and Dreisinger (2002b) showed no sulfide formation and it was argued that the presence of sulfite together with tetrathionate at the given conditions was unlikely. Instead, seeing as the decomposition of trithionate in alkaline solutions is very slow in comparison to tetrathionate, the reaction mechanism was better represented by the overall Equation (25) which has a ratio of 1.25 moles of thiosulfate formed per mole of tetrathionate reacted.

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O$$

Given the measured ratio by Breuer and Jeffrey varied between 1.2 and 1.3 and the lack of sulfide and sulfite as reactions products, it is likely that the decomposition of tetrathionate by both groups was in fact represented by Equation (25).
In addition, Breuer and Jeffrey (2004) highlighted the importance of the ionic strength of solutions in the determination of the polythionate degradation reactions kinetics. They concluded that the faster kinetics of tetrathionate decomposition observed by Zhang and Dreisinger (2002b) in solution having high ionic strength compared to the literature (Rolia et al. 1982) at low ionic strength was due to the differences in ionic strength of solutions and was not related to the presence or absence of dissolved oxygen in the reaction system as initially believed. Moreover, they showed that tetrathionate decomposition of leaching solutions containing ammonia and ammonium ions was faster than compared to carbonate- or phosphate-buffered solutions and emphasized the importance of conducting experiments where the solution composition closely matches the condition of interest.

The recent publication from Zhang and Jeffrey (2010) offers an excellent overview of the mechanisms of polythionate degradation in near neutral and alkaline conditions and the subsequent degradation reactions of the resulting products as a function of pH. As such, overall reaction equations were shown to successfully describe the process of tetrathionate degradation. Their findings are in agreement with the work of Varga and Horváth (2007) who used a spectrophotometer and a software package to record and fit the kinetics of the tetrathionate degradation reaction at seven different wavelength ranging between 265-295 nm and they subsequently derived a detailed and complex 11 step reaction mechanism to describe the tetrathionate decomposition. The reactions below summarize the process of polythionate degradation in alkaline solutions.

It was determined that the main reaction in the initial stage of the degradation of trithionate over the pH range of 5.5 to 10.5 is the hydrolysis Reaction (26)

\[ S_3O_6^{2−} + H_2O \rightarrow S_2O_3^{2−} + SO_4^{2−} + 2H^+ \]  \(26\)

This was confirmed by the 1:1 stoichiometric appearance of thiosulfate and sulfate measured during hydrolysis of trithionate at pH 6.5. The calculated pseudo first order rate constant was determined to be \((6.2 \pm 0.2) \times 10^{-7} \text{ s}^{-1}\), which was in close agreement to the literature.

The first step in the degradation of tetrathionate is considered to be the thiosulfate catalyzed rearrangement of tetrathionate (29) to tri- and pentathionate as represented by sub-Reactions (27) and (28):

\[ S_4O_6^{2−} + S_2O_3^{2−} \rightarrow S_3O_6^{2−} + SO_4^{2−} \]  \(27\)
\[ S_4O_6^{2−} + SO_4^{2−} \rightarrow S_3O_6^{2−} + S_2O_4^{2−} \]  \(28\)
\[ 2S_4O_6^{2−} \rightarrow S_3O_6^{2−} + S_5O_6^{2−} \]  \(29\)
Subsequently, tri- and pentathionate further degrade according to Reactions (26) and (30) respectively based on solution pH:

$$2S_2O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O $$  \hspace{1cm} \text{(30)}$$

For solutions between pH 6 and 7, the rates of Reactions (26) and (30) are equal as indicated by the same rate of trithionate and pentathionate degradation following the rearrangement. With increasing pH the degradation of pentathionate is accelerated unlike the hydrolysis of trithionate (Reaction 26) which is unaffected by pH. At pH values between 8-9, it was shown that the degradation of pentathionate is dominant compared to the trithionate hydrolysis. At pH values over 9, all pentathionate formed was rapidly degraded and first order changes in thiosulfate and tetrathionate were observed. The reacted tetrathionate and the formation of thiosulfate and trithionate conformed to the stoichiometry of the Reaction (31), which is the combination of the tetrathionate rearrangement Reaction (29) with the pentathionate degradation Reaction (30):

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O $$  \hspace{1cm} \text{(31)}$$

At pH values over 7, Reaction (31) was found to be first order with respect to initial tetrathionate concentrations and also first order with respect to hydroxide ions. It was previously thought that Reaction (31) was catalyzed by initial thiosulfate in alkaline solutions (Rolia et al. 1982). However, it was demonstrated by Zhang and Jeffrey (2010) that the reaction was independent of thiosulfate in the neutral pH range since the degradation of pentathionate, not catalysed by thiosulfate, following the rearrangement (thiosulfate catalyzed) is rate limiting. At higher pH values, where pentathionate degradation is fast, Reaction (31) is limited by the first step in the mechanism, namely the tetrathionate rearrangement, which is catalysed by thiosulfate.

### 2.5 Relationship between Gold Thiosulfate Stability and Polythionates

#### 2.5.1 Effect of Reagent Concentrations, Additions & Conditions on Gold Stability

Gold thiosulfate can precipitate out of solution due to the presence of reagents such as sulfite or sulfide. For example, gold can be deliberately precipitated from solution by hydrogen sulfide at pH 9-10 (West-Sells et al. 2005). Ji et al. (2003) showed experimental data where a 0.4% drop in dissolved gold occurred after sulfite addition during gold pressure TS leaching at the 4.5 hours mark aimed at reducing polythionate levels in solution. During a subsequent 1.5 hour anaerobic treatment at elevated temperature after sulfite addition, a further 7% drop in dissolved gold occurred which
was hypothesized to be due to its co-precipitation with the decomposition products of polythionates. The CSIRO Australian Minerals Research Centre previously investigated the loss of precious metals from ATS-copper leaching solutions through precipitation. This unpublished work showed that tetrathionate is a precursor for the precipitation of gold and silver, particularly in the presence of copper, as a mixed metal sulfide (Sitando et al. 2015).

Another mode for gold losses from solution involves the degeneration of the complexing agent. Senanayake (2005b) stated that gold can re-precipitate in ageing leach liquors due to the deficiency of thiosulfate. Ji et al. (2003) revealed that researchers at the formerly known Placer Dome Research Centre (now Barrick Gold Corporation subsidiary AuTec Innovative Extractive Solutions) found that a minimum thiosulfate concentration of 2-3 g/L (18-27 mmole/L) was required to keep gold in solution at 60 °C. Similarly, Zhang et al. (2013) claimed that leached gold was usually stable in solution during leaching as long as thiosulfate was available and that below a critical concentration, gold could re-precipitate along with copper. This was supported by observing a complete loss of copper and most of the gold from solution after extending a leach to 48 hours where complete oxidation of thiosulfate occurred. Before that, the leach had reached 74 % gold extraction after 24 hours with 40 % initial TS remaining in solution.

In an ammonium thiosulfate system, gold can also precipitate if air sparging is ceased (West-Sells et al. 2005). Zhang et al. (2013) also described a situation where gold precipitation occurred after leaching when slurries or filtrates were left unstirred. They suggested continued reactions of sulfur species in such solutions caused a deficiency in dissolved oxygen leading to reducing conditions and possible formation of sulfide ions. The latter species could lead to the eventual precipitation of gold as gold sulfide.

**2.5.2 Effect of Host Minerals**

There are also suggestions that the composition of the leach slurry may contribute to lowered gold extractions. For instance, additions of FeS and Fe(II) into a non-ATS leaching system caused slight decreases in gold leaching rates whereas addition of metallic iron caused a depression in the rate of gold leaching going as far as cementing gold out of solution (Ji et al. 2003). In fact, for the latter case, iron added as a reducing agent even catalyzed the degradation of thiosulfate. Gold leaching can also be hampered by the presence of 0.2 M sodium carbonate and bi-carbonate which coat gold particles with an insoluble calcium carbonate layer preventing further gold dissolution. The
formation of this layer was deduced from the soluble concentration of calcium before (80 ppm) and after leaching (0.3 ppm) (Ji et al. 2003). The detrimental effects of hematite additions on gold dissolution were investigated in the ATS leaching system. It was found that in the presence of hematite, coatings passivating gold dissolution were formed increasing the thiosulfate decomposition in presence of oxygen (Feng et al. 2007a). Furthermore, the CaTS leaching system is susceptible to the generation of gypsum which can lead to complications with equipment scaling (Choi et al. 2013). The presence of gypsum in the leaching circuit may contribute to gold stability issues and is therefore also a mineral of interest.

Often, the loss of gold from solution during thiosulfate leaching is associated with the oxidation of thiosulfate and an ensuing increase in polythionate species concentrations. There are several reports that showed that host minerals may enhance the thiosulfate degradation. Recently, Xu et al. (2017) showed that all sulfide mineral additions studied increased the consumption rate of thiosulfate and hindered gold dissolution during ATS leaching. In descending order, the thiosulfate oxidation rate was highest in the presence of pyrite > arsenopyrite > chalcopyrite > galena > sphalerite with gold dissolution rates increasing in the order of sphalerite > arsenopyrite > pyrite ≈ galena > chalcopyrite. Similarly, galena was shown to promote TS degradation and passivate gold leaching by the precipitation of a PbO or Pb(OH)\textsubscript{2} layer on the surface of the gold (Liu et al. 2017). However, the main cause for lowered gold leaching rates were attributed to a reduction of the mixed potential of the slurry by the introduction of galena. Xu et al. (1995) showed that pyrite has the potential to catalyze the degradation of thiosulfate as well as several other host minerals. Dissolved gold species may also be adsorbed and reduced on the surface of pyrite (Xia et al. 2005). Due to the strong catalytic effect on the surface of the sulfide minerals, rapid oxidation of thiosulfate can occur. A mechanism for pyrite catalyzed oxidation of thiosulfate to tetrathionate (Figure 23 and Equation 32) was proposed by Xu et al. (1995). Namely thiosulfate adsorbs onto a surface area of pyrite becoming the anodic site. Next, electrons transfer from thiosulfate to the anodic site and then over to a cathodic site on the same pyrite surface via the conduction band before ultimately being accepted by oxygen.

\begin{equation}
2S\textsubscript{2}O\textsubscript{3}^- + 0.5O\textsubscript{2} + 2H^+ \xrightarrow{pyrite} S\textsubscript{4}O\textsubscript{6}^{2-} + H\textsubscript{2}O
\end{equation}

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Xia et al. (2005) also showed that increases in pyrite and to a lesser degree pyrrhotite during the ammoniacal thiosulfate leaching of a gold silicate slurry resulted in increases in TS consumption and lowered gold extractions. In a similar investigation, Feng et al. (2005) found that addition of both pyrite and pyrrhotite also catalyzed thiosulfate oxidation in the presence of oxygen. The degradation products were initially tetrathionate (Equation 32) which quickly decomposed to trithionate in the alkaline conditions of the leaching system (pH 10.3) according to Equation 33.

\[ 2S_4O_6^{2-} + 3OH^- \rightarrow \frac{5}{2} S_2O_3^{2-} + S_3O_6^{2-} + \frac{3}{2} H_2O \]  

An XPS analysis of the sulfide surface after leaching revealed the presence of a thiosulfate-like intermediate species believed to be involved in the catalytic decomposition of thiosulfate. These researchers published several more papers looking at the effects of sulfides (Feng et al. 2002, 2003, 2006, 2007c, 2010c), manganese dioxide (2007c), iron contaminants (Feng et al. 2007a, 2010a), polythionates (2007b), and a series of additives (Feng et al. 2011b, c, a) on thiosulfate degradation and gold leaching.

Zhang et al. (2008) also studied the pyrite catalyzed oxidation of TS in three different oxidant systems. They highlighted problems encountered during the thiosulfate leaching of sulfide minerals. Yet, as described in Section 2.3.2.3, gold leaching can be improved in the presence of sulfide minerals in the CaTS-Air/O\(_2\) system especially at higher temperature and in the presence of copper (Zhang et al. 2013). This was partially attributed to the galvanic effect of pyrite which increases the mixed potential of the system. In leaching tests (0.3 M CaTS, 2 mM Cu, pH 10, 40 °C, 10 mL/min Air) comparing an oxidized ore with ones containing pyrite, higher gold recoveries but also higher losses in thiosulfate were observed in the latter. For the same set of tests, it was reported that the leach solutions of the pyrite concentrates contained 20-70 mM trithionate and 1-3 mM tetrathionate after 48 hours which is in line with the expected species at pH 10 (Breuer et al. 2012).
A relevant research paper by Aylmore et al. (2014) investigated the adsorption of 10 mg/L gold and/or silver from ATS leaching solution onto selected oxide, sulfides and activated carbon as well as the added effect of copper and polythionate additions. Goethite and kaolinite did not readily adsorb precious metals in the conditions used (baseline 0.05 M TS, 0.4 M NH$_3$, pH 9.5). Activated carbon exhibited an expected preg-robbing behaviour due to its high specific surface area and its slight affinity for AuTS. Pyrite exhibited significant gold and silver adsorption which decreased in the presence of increased copper through its competitive adsorption onto the mineral’s surface. Tetrathionate was found to be adsorbed onto mineral phases, particularly pyrite and activated carbon, unlike trithionate and thiosulfate. The addition to 5 mM 4T over the course of five hours to the baseline ATS leach solution without copper resulted in increased gold and silver removal with the appearance of a reddish pink precipitate after 30 minutes. Energy dispersive X-ray analysis of the precipitated solid under scanning electron microscope revealed it was a mixed silver/gold sulfide (30 % Ag, 30 % Au, 40 % S). The presence of copper reduced precious metal losses in the presence of tetrathionate hypothesised to be due to its competitive adsorption on mineral surface sites or due to its ability to maintain high potentials to prevent mixed sulfide precipitation. Silver was found to catalyze the formation of this precipitate in the presence of tetrathionate.

### 2.6 Objectives of Current Work

The above sample of references showed that there is an undeniable effect on the gold leaching and extraction rates based on the presence of various host minerals and their interaction with thiosulfate degradation products. The presence of polythionates also negatively affects the recovery of gold-thiosulfate from solution onto ion exchange resins. A better understanding of the behaviours of polythionates during leaching and recovery could help understand why gold extractions vary with different ores as stated by Muir et al. (2004). To this end, the work herein aims at determining whether thiosulfate degradation products can affect the soluble gold stability in the calcium thiosulfate leaching system and how they prevent the gold recovery onto ion exchange (IX) resin materials. Firstly, the question of how the accumulation of different levels of thiosalts affect the stability of the gold-thiosulfate complex in synthetic CaTS leaching solutions will be investigated by setting up a thorough experimental program. Subsequently, the additional presence of mineral phases (Chapter 4) and an actual industrial preg-robbing ore (Chapter 5) to this leaching system containing polythionates will also be studied to understand their contribution to the preg-robbing phenomenon observed. The interactions of polythionate species and their behaviours during loading
onto an ion exchange resin will be examined together with their impact on the efficiency of the gold-thiosulfate complex loading (Chapter 6). Lastly, the CaTS leaching of an industrial gold-bearing preg-robbing material and the simultaneous IX recovery process of the solubilized gold using an industrial resin sample in the presence of polythionate additions will be investigated (Chapter 7). This latter study will aim at combining the observed effects from the previous studies and help define the limitations to effective gold leaching and recovery in the CaTS leaching system.
3 Materials and Methods

This section contains standard information on the experimental work conducted throughout this thesis such as the chemicals, the procedures and characterizations methods used.

3.1 Chemicals, Reagents and Materials

Most chemicals used are commercially available from suppliers such as those listed in Table 10.

<table>
<thead>
<tr>
<th>Type</th>
<th>Chemical name</th>
<th>Formula</th>
<th>Assay/Grade</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salts</td>
<td>Cupric sulfate pentahydrate</td>
<td>CuSO₄.5H₂O</td>
<td>100.9 %</td>
<td>Fisher Chemical</td>
</tr>
<tr>
<td></td>
<td>Calcium thiosulfate</td>
<td>CaS₂O₃</td>
<td>23.5-24.2 %</td>
<td>Barrick Gold/ Tessenderlo Kerley Inc.</td>
</tr>
<tr>
<td></td>
<td>Sodium thiosulfate pentahydrate</td>
<td>Na₂S₂O₃.5H₂O</td>
<td>Certified ACS</td>
<td>Fisher Chemical</td>
</tr>
<tr>
<td></td>
<td>Sodium thiosulfate monohydrate</td>
<td>Na₂S₂O₃</td>
<td>96.6 %</td>
<td>Synthesized</td>
</tr>
<tr>
<td></td>
<td>Sodium tetrathionate dihydrate</td>
<td>Na₂S₄O₆.2H₂O</td>
<td>≥98 % (titration)</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td></td>
<td>Gold(I) sodium thiosulfate hydrate</td>
<td>Na₂Au(S₂O₃)₂.xH₂O</td>
<td>35.62 % Au(I)/ 99.99 % Purity</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td></td>
<td>Sodium cyanide</td>
<td>NaCN</td>
<td>ACS 95.0 % min</td>
<td>Anacemia</td>
</tr>
<tr>
<td></td>
<td>Sodium bi-carbonate</td>
<td>NaHCO₃</td>
<td>99.7 to 100.3 %</td>
<td>Fisher Chemical</td>
</tr>
<tr>
<td></td>
<td>Sodium carbonate anhydrous</td>
<td>Na₂CO₃</td>
<td>≥99.5 %</td>
<td>Fisher Chemical</td>
</tr>
<tr>
<td>Base</td>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>Technical</td>
<td>Fisher Chemical</td>
</tr>
<tr>
<td>Acids</td>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>70 %, ACS-Pur</td>
<td>Fisher Chemical</td>
</tr>
<tr>
<td>Oxidizer</td>
<td>Hydrogen peroxide</td>
<td>H₂O₂</td>
<td>30 %, Certified ACS</td>
<td>Fisher Chemical</td>
</tr>
<tr>
<td>Standard</td>
<td>1 mg/mL AAS gold standard</td>
<td>Au (in 20% HCl)</td>
<td>1000 mg/L</td>
<td>Acros Organic</td>
</tr>
<tr>
<td>Organics</td>
<td>Methyl isobutyl ketone</td>
<td>(CH₃)₂CHCH₂COCH₃</td>
<td>≥99.5 %, for HPLC</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td></td>
<td>Aliquat 336</td>
<td>C₂₅H₅₂ClN</td>
<td>N/A</td>
<td>Cognis Corp.</td>
</tr>
<tr>
<td>Eluents</td>
<td>0.2 M sodium perchlorate monohydrate (PolyTS analysis)</td>
<td>NaClO₃.H₂O</td>
<td>HPLC grade</td>
<td>Fisher Chemical</td>
</tr>
<tr>
<td></td>
<td>1.8 mM Carbonate + 1.7 mM bicarbonate (SO₄²⁻/SO₃²⁻ analysis)</td>
<td>Na₂CO₃/NaHCO₃</td>
<td>≥99.5 %</td>
<td>Fisher Chemical</td>
</tr>
</tbody>
</table>

However, several salts used in the literature to prepare analytical standards and experimental solutions are often synthesized by the researchers themselves. Some of those chemicals and their methods of preparation are outlined below.

3.1.1 Trithionate

The following section presents the procedures used for the synthesis and analysis of a sodium trithionate standard material for use as an additive in experiments.

3.1.1.1 Synthesis

Sodium-thiosulfate and -tetrathionate are commercially available whereas trithionate is not. As such, trithionate was synthesized using a modified procedure developed by Kelly et al. (1994). Table 11
lists the number of batches and their respective trithionate yields as well as the results from purity
determinations.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Initial (g Na(_2)S(_2)O(_3).5H(_2)O)</th>
<th>Final Product (g Na(_2)S(_3)O(_6))</th>
<th>Theoretical %</th>
<th>Error %</th>
<th>% Purity (avg. 2 meas.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T-1</td>
<td>29.9</td>
<td>0.36</td>
<td>14.35</td>
<td>-97.49</td>
<td>N/A</td>
</tr>
<tr>
<td>3T-2</td>
<td>29.98</td>
<td>N/A (~14 g)</td>
<td>14.39</td>
<td>N/A</td>
<td>83.95</td>
</tr>
<tr>
<td>3T-3</td>
<td>150</td>
<td>66.51</td>
<td>71.97</td>
<td>-7.59</td>
<td>84.14</td>
</tr>
<tr>
<td>3T-4</td>
<td>60</td>
<td>29.20</td>
<td>28.79</td>
<td>1.44</td>
<td>75.08</td>
</tr>
<tr>
<td>Bulk 3T-3</td>
<td>191.13*</td>
<td>131.7</td>
<td>143.96</td>
<td>-8.5</td>
<td>96.6</td>
</tr>
</tbody>
</table>

* Na\(_2\)S\(_2\)O\(_3\) monohydrate

### 3.1.1.2 Determination of Trithionate Purity

An old yet quantitative method by Riesenfeld et al. (1923) was modified and used to determine the
purity of trithionate for its simplicity compared to the other methods in the literature (Miura et al.
1990, Koh et al. 1994). The original method required taking a small amount of product (~0.1 g),
dissolving it in 50 mL of 0.2 M cupric sulfate (CuSO\(_4\)) solution (~10 g CuSO\(_4\).5H\(_2\)O plus 3 mL
conc. H\(_2\)SO\(_4\)) and placing it in a 70 °C bath for 24 hours to convert all trithionate into covellite
(CuS). The copper solids and cupric sulfate solution were then filtered out on a glass frit and washed.
The filtered copper containing solids were then digested using aqua regia and the dissolved copper
solution was collected in a 100 mL volumetric flask filled to the mark with DI water. The copper
concentration was measured by a Cu-EDTA titration method. Copper was then back calculated to
trithionate based on a one to one molar ratio as given in Reaction (34):

\[
S_3O_6^{2-} + Cu^{2+} + 2H_2O \rightarrow CuS + 2SO_4^{2-} + 4H^+
\]  

34

To increase the accuracy for the determination of the trithionate purity, the initial mass of trithionate
was increased fivefold to 0.5 g. Moreover, the resulting CuS in the glass frit filter was directly hot-
digested with aqua regia by first boiling the solution with a heater effectively accelerating the
process. The glass frit filter was also covered with a watch glass to prevent solution from escaping
due to the vigorous reaction. Finally, Cu-AAS was used for the determination of the copper
concentration as opposed to the time consuming Cu-EDTA titration method. The percent error
between two measurements using this method did not exceed 4 % and was therefore deemed
reproducible.
3.1.1.3 Trithionate Purification

In order to improve the purity of trithionate, samples of trithionate Batch 3T-3 (Table 11) were subjected to recrystallization-precipitation purification tests. Briefly, the contaminated trithionate product was dissolved in minimal amounts of DI water at 30 °C before placing the almost saturated solution in an ice bath. By taking advantage of the different solubilities between sodium sulfate and trithionate (assumed to have similar values as for TS, see Table 12), it was aimed at recrystallizing the former followed by its separation from the trithionate solution.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Solubility (g/100 cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>0 °C</td>
<td>4.76</td>
</tr>
<tr>
<td>30 °C</td>
<td>41.28</td>
</tr>
<tr>
<td>45 °C</td>
<td>-</td>
</tr>
</tbody>
</table>

Subsequently, trithionate was recovered through precipitation by addition of absolute alcohol (EtOH) or by recrystallization by addition of maximum EtOH before precipitation occurs at 30 °C and placing in ice bath to form crystals.

Table 13: Batch 3T-3 (84.14%) Trithionate Purification.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Test</th>
<th>3T Recovery</th>
<th>Initial Mass (g)</th>
<th>3T Yield (g)</th>
<th>% Purity (avg. 2 meas.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T-3</td>
<td>PurA</td>
<td>Recrystallization</td>
<td>4.50</td>
<td>2.59</td>
<td>77.33</td>
</tr>
<tr>
<td>3T-3</td>
<td>PurB</td>
<td>Precipitation</td>
<td>9.95</td>
<td>6.68</td>
<td>85.21</td>
</tr>
<tr>
<td>3T-3</td>
<td>PurC</td>
<td>Precipitation</td>
<td>10.03</td>
<td>4.00</td>
<td>90.37</td>
</tr>
</tbody>
</table>

Table 13 shows the results of trithionate purification through sodium sulfate dissolution, recrystallization and separation followed by trithionate precipitation. The recovered “purified” trithionate results did not greatly enhance the purity of the material. Unexpectedly, trithionate recrystallization resulted in a net decrease in the product’s purity (PurA). In theory, to achieve a final pure trithionate product, the dissolution-recrystallization process would need to be applied sequentially. A major drawback using this purification method are the significant decreases in material yields for only a modest gain in purity after each iteration.

3.1.1.4 Bulk Trithionate Synthesis

For use in the comprehensive experimental program set out for this work, the objective was to produce a large quantity of high quality trithionate. As such, attempts at producing quality bulk amounts of trithionate were made with satisfactory results finally obtained as shown in Table 11. This was achieved through a major improvement to the procedure, namely the use of a freshly
polished 2.5 L stainless steel lab pan. The polished stainless steel surface provided a much larger number of nucleation sites that effectively induced the precipitation of the by-products and increased the rate of crystal growth. It was confirmed by IC that batch “Bulk 3T-3” contained no other polythioniate species other than trithionate. This final product is to be used in the preparation of IC standards and for subsequent experiments requiring additions of initial trithionate.

### 3.1.2 Synthetic Calcium Thiosulfate Leaching Solutions

#### 3.1.2.1 Leaching Conditions

The calcium-thiosulfate-air leaching process is simply represented by Equation 35.

\[
2Au + 4S_2O_3^{2-} + \frac{1}{2}O_2 + H_2O \rightarrow 2Au(S_2O_3)_2^{2-} + 2OH^-
\]  

Typical leaching conditions encountered in the calcium thiosulfate (CaTS) leaching system studied are 0.1 M thiosulfate, 50 mg/L copper, a temperature of 25-50 °C and a pH of 8.5-10. Copper is added to the system in order to improve the leaching kinetics although its role is not as well understood as in the ammoniacal thiosulfate leaching system where it acts as a catalyst. Addition of copper as cupric sulfate into the thiosulfate leaching system quickly oxidizes thiosulfate into tetrathionate as detailed in section 3.1.2.2.

During leaching, the thiosulfate reagent oxidizes over time to produce higher oxidation state sulfur species known as polythionates (PolyTS). A range of products such as trithionate (3T), tetrathionate (4T) and pentathionate (5T) are found in thiosulfate leach solutions. The resulting decomposition products are dependent on pH. Jeffrey et al. (2007) concluded that tetrathionate and pentathionate are the dominant species in the pH range of 8.5 to 9. At pH of 10.4 trithionate and sulfate are formed.

#### 3.1.2.2 Cupric Sulfate Addition into Thiosulfate Leaching Solutions

The typical addition of 50 mg/L copper as cupric into a thiosulfate leaching solution results in a quick redox reaction where thiosulfate anions are oxidized into tetrathionate. Added together, the half reactions and their standard reduction potentials give an overall cell voltage that is positive. It follows that this reaction is favorable as \(\Delta E^o\) is positive (See Reactions 36 to 38).

\[
2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \quad (E^o_{An.} = 0.08 \text{ mV}) \tag{36}
\]
\[
2Cu^{2+} + 2e^- \rightarrow 2Cu^- \quad (E^o_{Cat.}=0.16 \text{ mV}) \tag{37}
\]
\[
2S_2O_3^{2-} + 2Cu^{2+} \rightarrow S_4O_6^{2-} + 2Cu^+ \quad (\Delta E^o=E^o_{Cat.}-E^o_{An.} = 0.08 \text{ mV}) \tag{38}
\]
In practice, during the preparation of a leaching solution, it can be observed that the introduction of cupric sulfate into a 0.1 M thiosulfate solution via a pipette immediately reduces the blue cupric ions into a green cloud of cuprous ions upon contact with the thiosulfate solution. The reaction occurs spontaneously leading to the oxidation of thiosulfate into tetrathionate. The green cloud very quickly fades as the cuprous ions are complexed with thiosulfate into \( \text{Cu}(\text{S}_2\text{O}_3)_2^{3-} \). The presence of this non-oxidizing species in the CaTS-air leaching system may help reduce or remove the passivation of gold thereby enhancing gold oxidation (Zhang et al. 2013). Copper can also be present in the pretreated ore where it can also be reacting with thiosulfate.

As a result, synthetic leaching solutions to which no initial tetrathionate was added always contained a small initial concentration of tetrathionate due to copper addition (half a mole tetrathionate for every mole cupric added).

### 3.1.3 Ion Exchange Materials

#### 3.1.3.1 Commercial Resin

For work involving the loading of polythionate species and gold as aurothiosulfate, the same resin material, namely Purolite A500 strong base anion exchange resin, as is used in the current Barrick Gold operation at the Goldstrike mine in Nevada was selected. Table 14 summarizes the resin characteristics in its shipped form.

<table>
<thead>
<tr>
<th>Physical &amp; Chemical Characteristics</th>
<th>Purolite A500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Structure</td>
<td>Macroporous polystyrene crosslinked with divinylbenzene</td>
</tr>
<tr>
<td>Appearance</td>
<td>Spherical beads</td>
</tr>
<tr>
<td>Functional Group</td>
<td>Type 1 Quaternary Ammonium</td>
</tr>
<tr>
<td>Total Capacity (min.)</td>
<td>1.15 eq/L (Cl(^-) form)</td>
</tr>
<tr>
<td>Moisture Retention</td>
<td>53-58 % (Cl(^-) form)</td>
</tr>
<tr>
<td>Particle Size Range</td>
<td>300-1200 (\mu)m (dry sieved to +600 (\mu)m)</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.08 g/mL</td>
</tr>
</tbody>
</table>

Purolite A500 is a strongly basic Type 1, macroporous exchange resin with an isoporous structure that contributes to its high capacity ("Purolite A500" 2012). Strong base anion exchangers have active sites with fixed positive charges generally made up of quaternary amine functional groups having the ability to load solutes independent of the pH of the leaching solution (Adams 2005). Such anion exchange resins are traditionally produced in two reaction steps shown in Figure 24. The first is a Friedel-Crafts reaction attaching a chloromethyl group to the benzene rings of styrene-
divinylbenzene copolymer. The exchanger is then produced by the alkylation of the chloromethylated resin with trimethylamine resulting in a quaternary ammonium functional group. These functional groups result from the reaction of tertiary amines with the copolymer (polystyrene) after chloromethylation.

![Figure 24: Strong base anion exchange resin synthesis reaction (Fritz et al. 2009)](image)

It is generally accepted that strong base anion exchange resins are superior to weak-base resins for the loading of gold from thiosulfate solutions represented by Equation (39).

$$
\text{Au(S}_2\text{O}_3\text{)}_3^{3-} + 3\text{R} - \text{NR}_3\text{X}^- \rightarrow (3\text{R} - \text{NR}_3)\text{Au(S}_2\text{O}_3\text{)}_2^{3-} + 3\text{X}^- \quad 39
$$

Where three anions $\text{X}^-$, such as chlorides, are exchanged by a gold thiosulfate complex (Adams 2016).

### 3.1.3.1.1 Pre-treatment

The resin material was pre-screened dry by twice passing it through a 600 μm sieve. Only +600 μm particles were collected and subsequently used. The particle size distribution of this resin material used for experiments was determined by a manual sieve analysis (Figure 25). The median particle diameter was determined to be 739 μm.

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Before the resin is to be used for an ion exchange process it needs to be pre-conditioned. This involves soaking the resin in a solution to allow the resin to swell and to regenerate. For thiosulfate and polythionate loading tests, an arbitrary resin volume (typically < 10 mL) was soaked overnight in 50 mL of 2 M NaCl. The next day, the resin was rinsed and soaked again in concentrated sodium chloride for an hour. Before use, the resin was rinsed several times with DI water and the remaining resin volume was stored in a beaker filled with DI water.

3.1.3.1.2 Resin Volume and Mass

Publications and procedures typically refer to a volume of resin added to a certain volume of slurry giving the units of mL resin/L slurry. The volume of resin refers to a swollen wet resin that is typically measured using a graduated cylinder which is tapped on a working surface to minimize air bubbles and compact the resin beads. After gold loading experiments, resins were separated, rinsed and dried to measure their dry weight to report gold loadings on a dry resin basis (mg Au/kg resin). Resin beads were dried in an oven at 60 °C for 24 hours after which they were allowed to equilibrate to the atmosphere at room temperature until a constant mass could be measured. Averages of preliminary tests showed 1 mL of wet, swollen and compacted Purolite A500 resin was equivalent to 0.373 mg after oven drying.
3.1.3.1.3 Stripping Procedure

The resin stripping procedure used was adapted from the work of Jeffrey et al. (2007) in which typically 1 mL of wet resin was twice contacted with ~40 mL of a 0.5 M sodium perchlorate solution for 30 minutes with magnetic agitation. After each step, the volume of the strip solution was quantitatively transferred into a 50 mL volumetric flask. Appropriate dilutions of the two resulting strip solutions were made and subsequently analyzed for polythionates using IC or/and for gold using the AAS procedure.

3.1.3.2 Industrial Resin

Some work was conducted on samples of industrial resin (also Purolite A500) originating directly from the Goldstrike (GS) leaching circuit. Two types of resin materials were received namely a loaded resin (GSLR) and a barren resin material (GSBR). The latter would have been pretreated with sulfite to reduce any higher polythionates and is meant to be recycled back into the leaching circuit as discussed in Section 2.1.2.2. The GSBR described in Chapter 7 was used for gold recovery during the leaching of industrial preg-robbing ores and also to generate gold loading isotherms (Section 6.6.2.2). Additional characterization of the GSLR can be found in the Appendix Section A.4.

3.1.4 Industrial Gold Bearing Preg-robbing Materials

Several industrial gold bearing materials were supplied to UBC from the Goldstrike mine by the Barrick Gold Corporation subsidiary AuTec Innovative Extractive Solutions. These solids were received either as dried powders or in the form of dense slurries. Each material consisted of an autoclave discharge. The specific conditions of the alkaline autoclave pre-treatment of these feed materials (preg-robbing ores) was unknown but typical conditions are 225 °C and 80 psi oxygen overpressure (Langhans et al. 2012). Slurries were filtered and dried overnight in an oven at 60 °C. A summary of all materials used with their head assays is provided in Table A 9 in the Appendix Section A.6.

3.2 Analytical Methods and Methods Development

In this dissertation, the most frequently collected data are the soluble gold concentration and the concentration of thiosulfate and polythionates. As such, in order to accurately measure these respective elements and species in solution, an appropriate analytical instrument and relevant
method must be selected and/or developed based on a number of criteria dependent on the experimental conditions.

3.2.1 Sampling Procedure

Typically, predetermined and accurate volumes of samples (for mass balancing purpose) were extracted from reactors using auto-pipettes and transferred into luer-lock syringes connected to 0.22 μm PTFE filters with the plunger out. The plunger was then inserted and pushed through the syringe thereby filtering the sample into a test tube. From here, the filtrate was used for both gold and polythionate analysis.

In the case of sampling during CaTS gold leaching at 30 wt % pulp density, two methods were used: The first, allowing the tracking of gold extraction from solids samples over time, consisted of drawing a well-mixed slurry sample into a test tube which was centrifuged at 2000 rpm for 12 minutes. The overhead solution was decanted into a syringe filter and used as described above. The remaining moist solid fraction at the bottom of the centrifuge tube was weighed and then once more after drying. The gold content of the solid fraction was calculated taking the fire assay result of the dried solid and subtracting the mass of gold from the evaporated solution fraction multiplied by the measured solution gold concentration by AAS. The second method allowed for the entire solids fraction to remain in the reactor during leaching while sampling. To this end, agitation was paused for a short time to allow for the slurry to settle, after which an aliquot of light suspension was pipetted from the surface of the reactor and filtered as described above using PTFE filters connected to syringes.

Often times, as the rate of sample collection from multiple reactors exceeded the runtime for IC analysis (~7 minutes), two 1 mL aliquots of filtrates were immediately frozen inside 10 mL test tubes by submerging them in liquid nitrogen. These frozen duplicate samples were capped and stored in a freezer until analysis. A frozen 1 mL sample was quickly thawed by pipetting 7 mL of room temperature DI water into the test tube, re-capping and lightly teeter-tottering the solution until thawed. From this solution, 1 mL was diluted into a 10 mL volumetric flask to provide an appropriate final dilution factor of 80 times for thiosulfate and polythionate measurements.
3.2.2 Ion Chromatography (IC)

3.2.2.1 Thiosulfate and Polythionate Analysis

A procedure by Jeffrey et al. (2007) was simplified and used on a Dionex DX600 ion chromatograph and an AD25 absorbance UV-Vis detector set to a wavelength of 214 nm. A 4 x 50 mm AG16 guard column was connected in series to a 4 x 250 mm IonPac AS16 anion exchange analytical column. A sample loop of 25 μL was used. The mobile phase was set to a flow rate of 1 mL/min and was composed of a 0.2 M sodium perchlorate solution prepared in 18.2 MΩ deionized water and clarified by passing through a 0.2 μm membrane filter via vacuum filtration. Sodium perchlorate has a low UV absorbance, provides rapid exchange of strongly adsorbing species and does not have a propensity to degrade polythionates unlike strong alkaline solutions. With this method, thiosulfate, trithionate, tetrathionate and pentathionate could all be detected within 7 minutes with the ability to quantify the former three species using freshly prepared standards (Figure 26).

Figure 26: Example chromatogram of an aged 150 mg/L standard solution showing species peaks and their retention times.

3.2.2.2 Sulfite and Sulfate Analysis

The Dionex DX600 ion chromatograph could also be configured with a conductivity detector and a suppressor in recycle mode for sulfate analysis using a 4 mm x 250 mm IonPac AS4A-SC analytical column and a 4 mm x 50 mm IonPac AG4A-SC guard column. The eluent used was a 1.8 mM
sodium carbonate/ 1.7 mM sodium bicarbonate solution and the recommended suppressor current was set to 27 mA. The sample loop was 25 μL and the eluent flow rate was set to 2 mL/min.

3.2.2.3 Method for Estimating Pentathionate Concentration

There is no commercially available pentathionate salt for use as a standard material. The synthesis of a pure pentathionate salt requires specialized equipment for cooling and concentrating solutions at reduced pressure (Kelly et al. 1994). Instead, a method was devised to estimate the concentration of pentathionate peaks detected during ion chromatography. The procedure consisted in monitoring multiple aged standard samples of different known original polythionate concentrations over time against freshly prepared standards. Over time, the formation of pentathionate peaks in aged standard samples were observed with corresponding changes in other polythionate solute concentrations. Sulfur mass balances between the initial and aged compositions of the samples were used to determine the concentration of pentathionate generated during ageing. These estimated concentrations were then plotted against their corresponding measured pentathionate peak areas into a scatter plot. A linear trendline was fitted through the scatter plot (Figure 27) whose resulting slope can be used to convert measured pentathionate peak areas into estimated concentrations.

![Figure 27: Pentathionate concentration to peak area correlation.](image-url)
3.2.3 Atomic Absorption Spectroscopy (AAS)

3.2.3.1 Gold Analysis Procedure

Previously observed issues with aqueous gold analysis using AAS were low absorption and resulting detection limits, complications with elements such as copper (O'Malley 2002) and burner flame interruptions due to the precipitation of sulfur due to thiosulfate present in the CaTS gold leaching system studied in this work. Furthermore, since experimental solutions contain CaTS, it is imperative to maintain a pH above neutral to hinder the degradation of thiosulfate into polythionates. At the onset, the aim of this work is to investigate the stability of the gold thiosulfate complex in artificial CaTS leaching solutions containing variable concentrations of polythionates over time. The gold concentration in aqueous aliquots of these experimental solutions must be representative of their time of sampling and should not be allowed to degrade and precipitate over time. Therefore, a method needed to be devised in which the current gold-thiosulfate concentration could be “frozen” in time, free of precipitates that would not alter until analysis. For the reasons outlined above, the following method makes the use of sodium cyanide to convert gold thiosulfate into the more stable aurocyanide complex and methyl isobutyl ketone (MIBK) as an organic gold solvent extractant to reduce the effects of the interfering elements, increase the sensitivity of gold and produce a stable gold sample.

3.2.3.1.1 Gold Solvent Extraction (SX) Sampling Method

Experimental solutions typically contain less than 8 mg/L Au in 0.1 M CaTS. In most instances for sampling, 4 mL of filtered solution (0.20 μm PTFE) was transferred into 15 mL centrifuge tubes to which 0.25 mL of 2 M sodium cyanide in 0.01 M NaOH were added to convert the gold-thiosulfate complex into a stable aurocyanide complex. Cyanide was always added in excess to initial thiosulfate at a 1.25 molar ratio.

After sampling, a known volume of MIBK containing 1 wt % Aliquat 336 was added to each aqueous aliquots already containing cyanide. The centrifuge tubes were capped and vigorously shaken for 10 minutes and then centrifuged at 2000 rpm until the phases separated. The gold bearing organic phase was transferred using disposable pipettes into a capped test tube awaiting analysis by AAS.
3.2.3.1.2 Standard Preparation

It is important to generate standards from solutions similar to that of the samples. The practice of matrix matching increases the accuracy of measurements by reducing matrix effects. To start, 5.00 mL of gold atomic absorption standard (Acros Organic, 1000 mg/L in 20 % HCl) was pipetted into a small beaker (30 mL) secured with a clamp. Deionized (DI) water was added up to the 15 mL mark and a rinsed, calibrated pH electrode was inserted into the solution. The pH of the acidic gold solution is slowly increased up to pH ~3 using 50 wt % NaOH and further up to pH 10.5 using 0.1 M NaOH. Subsequently, CaTS plus sodium cyanide at a 25 % excess to thiosulfate were added to the beaker and allowed to react. The gold chloride (yellow) was expected to be immediately reduced by cyanide to form gold(I) cyanide (clear) in a 0.1 M thiosulfate background. The pH electrode was carefully rinsed with DI water into the beaker and the solution was transferred quantitatively into a 50 mL volumetric flask filled to the mark with DI water. From the resulting 100 mg/L aqueous gold-cyanide solution, 25.00 mL were pipetted into a 50 mL centrifuge tube together with another 25.00 mL of organic MIBK with 1 wt % Aliquat 336. The two immiscible phases were shaken for 10 minutes and then allowed to separate again by centrifugation. At this stage, the recovered organic phase consisted of a 100 mg/L gold stock solution. Working gold standards (0.25, 1, 2.5 and 5 mg/L) were made by diluting appropriate amounts of this 100 ppm stock solution with the MIBK/Aliquat 336 organic solution. Details for this procedure can be found in the Appendix section A.2.

3.2.3.1.3 AAS analysis

Analysis was conducted on a Varian AA420 AAS with an air (3.5 L/min)-acetylene (1.5 L/min) flame, a gold hollow cathode lamp with a current of 4 mA, a wavelength of 242.8 nm and a deuterium lamp in operation for background correction. The instrument was recalibrated after every 40 samples and periodic quality control (QC) checks were made after every 5-10 samples throughout analysis to monitor instrument drift and apply a bracketing technique on the results. Each sample provided three absorbance measurements with typical precisions of 1-2 % RSD. In most cases enough sample volume remained for a second and sometimes third analysis run. Additional runs were either conducted on the same instrument using the same conditions within a short period of time (showing repeatability) or they were conducted using the same instrument on a different day showing reproducibility of the measurement. An average of the measured values was always reported. When faced with a potential blunder error or outlier, that is, an error that does not fall in
the systematic or random categories, QC checks were used to determine if the analytical run was still in control. The most common unintentional error experienced was an instrument clog identified by a significant drop in QC sample concentration. In this case, all measurements up to the previous QC sample in control were omitted.

### 3.2.3.2 Method Validation and Analytical Results

Table 15 shows measured readings using the SX method on gold standard solutions of known concentrations made up in CaTS or NaTS as starting solutions. In other words, these standard solutions were treated as depicted above in the “Standard Preparation” section.

<table>
<thead>
<tr>
<th>Sample/STD Checks</th>
<th>Conc. mg/L</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 ppm STD made in NaCN only (no TS)</td>
<td>0.44</td>
<td>3.1</td>
</tr>
<tr>
<td>5 ppm STD made in NaCN only (no TS)</td>
<td>4.79</td>
<td>0.3</td>
</tr>
<tr>
<td>5 ppm STD Check</td>
<td>4.94</td>
<td>0.8</td>
</tr>
<tr>
<td>1 ppm AuTS in 0.1 M CaTS (made from a 100 ppm AuTS stock)</td>
<td>0.92</td>
<td>1.5</td>
</tr>
<tr>
<td>4 ppm AuTS in 0.1 M CaTS (made from a 100 ppm AuTS stock)</td>
<td>4.12</td>
<td>0.5</td>
</tr>
<tr>
<td>1 ppm Au in 0.1 M CaTS</td>
<td>0.93</td>
<td>0.6</td>
</tr>
<tr>
<td>2.5 ppm Au in 0.1 M CaTS</td>
<td>2.63</td>
<td>0.9</td>
</tr>
<tr>
<td>0.25 ppm Au in 0.136 M NaTS</td>
<td>0.16</td>
<td>4.6</td>
</tr>
<tr>
<td>1 ppm Au in 0.136 M NaTS</td>
<td>0.92</td>
<td>1.7</td>
</tr>
<tr>
<td>2.5 ppm STD Check</td>
<td>2.52</td>
<td>1.9</td>
</tr>
<tr>
<td>0.25 ppm STD Check</td>
<td>0.24</td>
<td>3.8</td>
</tr>
<tr>
<td>0.25 ppm Au in 0.136 M CaTS</td>
<td>0.14</td>
<td>7</td>
</tr>
<tr>
<td>1 ppm Au in 0.136 M CaTS</td>
<td>0.94</td>
<td>0.2</td>
</tr>
<tr>
<td>2.5 ppm Au in 0.136 M CaTS</td>
<td>2.59</td>
<td>1</td>
</tr>
<tr>
<td>2.5 ppm STD Check</td>
<td>2.54</td>
<td>0.9</td>
</tr>
<tr>
<td>2.5 ppm STD Check</td>
<td>2.5</td>
<td>0.3</td>
</tr>
<tr>
<td>10 ppm NaTS plus 50 ppm Cu (2x diluted)</td>
<td>10.28</td>
<td>1.5</td>
</tr>
<tr>
<td>5 ppm Au in 0.136 M CaTS</td>
<td>5.1</td>
<td>0.3</td>
</tr>
<tr>
<td>2.5 ppm STD Check</td>
<td>2.47</td>
<td>2.1</td>
</tr>
<tr>
<td>1 ppm STD Check</td>
<td>0.93</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The results indicate that the MIBK procedure can successfully determine the concentrations of gold in solution complexed as either aurocyanide or aurothiosulfate species. Residual gold concentrations in the barren aqueous solutions were found to be less than 2%.

An added advantage of using MIBK as a solvent extractant is for the determination of the gold concentration in very dilute solutions. For instance, a small volume of the organic phase can be put into contact with a large volume of dilute gold concentration and effectively concentrate the gold for more accurate measurements.
3.2.3.2.1 Statistical Analysis

A thorough statistical analysis was conducted to determine the effects of shaking time on gold extraction by the organic phase from the aqueous solution during the AAS sample preparation procedure. Furthermore, the effects of pH (8.5 versus 10) and the use of an old versus freshly prepared gold stock solution were also examined. Details of this analysis can be found in the Appendix section A.3.

To summarize, it was determined that:

- The pH of the solution had no significant impact on the measured gold concentrations.
- An old gold stock solution was just as good for preparing samples as is a freshly prepared stock solution.
- The shaking for 10 minute resulted in significantly better gold extractions than 5 and 2 minutes of shaking respectively.

3.2.4 Fire Assay

A gold fire assay analysis method was used for head assaying of gold containing pressure oxidation discharge ores and for dried residue analysis post leaching. Fire assays were also conducted on dried, loaded and stripped resin materials. This method was also used to validate the efficiency of gold solvent extraction in the preparation of 100 mg/L organic gold standard solutions from aqueous standards. The fire assays were performed by AuTec in Vancouver, BC.
4 Stability of Synthetic Gold-Thiosulfate Solutions in the Presence of Polythionates and Additives

4.1 Introduction

Jeffrey et al. (2010) stated that the use of mixed polythionate solutions as an eluent for the recovery of gold from loaded resins (Fleming et al. 2003) has not been adopted due to stability issues and the observed precipitation of gold and copper from these solutions at high concentrations of tetrathionate. As mentioned in Section 2.3.2.3.1, Breuer et al. (2012) explained that a possible issue in the oxygen TS (CaTS-air) system was the instability of precious metals during leaching likely attributed to the precipitation as metal sulfides due to the oxidation of thiosulfate and sulfide minerals. Chu et al. (2003) also established that polythionates hindered the gold dissolution rate in oxygenated Cu-ATS solutions over time. As reviewed in Section 2.4, the oxidation of thiosulfate produces tetrathionate which then further decomposes by rearrangement to trithionate and pentathionate followed by their subsequent degradations influenced by solution pH and temperature. The key question to be answered is whether these degradations products may impact the stability of gold in solution or perhaps even reduce the gold thiosulfate complexes before adsorption onto the anion exchange resin as observed in Figure 5. It is therefore of interest to determine the role of polythionates in the precipitation of gold from solution onto preg-robbing carbon or onto other minerals or phases that may be present in the gold leaching slurry.

4.2 Objectives and Experimental Approach

The objective of the study was to investigate if gold losses from solution in the CaTS leaching system are caused by thiosulfate degradation products. A comprehensive testing program was initiated to investigate this possible mode of gold loss. The additions of various concentrations of polythionates to synthetic gold leach solutions was conducted. The aim was to investigate if these species contributed to the instability of soluble gold-thiosulfate complexes via complicated redox behaviours of the thiosalts, which could reductively precipitate gold. The reduction processes may also drive losses of gold onto preg-robbing carbon or other mineral phases in leaching slurries. These latter phenomena were investigated by the addition of mineral phases into the synthetic leaching system.
4.3 **Experimental Procedures**

### 4.3.1 Leaching Conditions

The composition and conditions of the synthetic leach solutions investigated were designed to resemble current industrial process solutions (Table 1) to be able to make meaningful comparisons with plant practice. The selected baseline solution composition consisted of 0.1 M CaTS, 5 mg/L gold as sodium aurothiosulfate, 50 mg/L cupric as copper sulfate and sodium hydroxide addition to control the pH at 8.5. The temperature and pH range investigated were 25-50 °C and pH 8.5-10 respectively. The various polythionate salts were added individually or in combination to test solutions. A polythionate concentration of 4 mM was targeted. This value represented a realistic concentration that had previously been found to interfere with effective gold leaching and recovery (Jeffrey et al. 2007, Oraby 2009). The effects of added minerals of interest were also investigated to complete this portion of the study (See Table 16).

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon (AC)</td>
<td>1.29 g/L</td>
<td>[C] = 0.43 wt % in carbonaceous ore originating from the Carlin Trend (Nelson et al. 1982)</td>
</tr>
<tr>
<td>Pyrite (Py)</td>
<td>8 g/L</td>
<td>Pyrite addition between 0.4-16 g/L in a study investigating its effect on gold dissolution rate (Feng et al. 2006)</td>
</tr>
<tr>
<td>Hematite (Hema)</td>
<td>8 g/L</td>
<td>Hematite addition between 1-12 g/L in a study to determine its effect on gold dissolution rate (Feng et al. 2007a)</td>
</tr>
<tr>
<td>Gypsum (Gyps)</td>
<td>4 g/L</td>
<td>Added in saturation. Solubility = 2.4 g/L</td>
</tr>
</tbody>
</table>

The activated carbon used (PICAGOLD® G208) was supplied by Univar Canada and has a specific surface area of 772 m²/g measured by N₂ physisorption. The pyrite sample was prepared by crushing and grinding a pure pyrite cube originating from Navajun, Spain. The purity of the pyrite sample was confirmed by XRD analysis (Rigaku MultiFlex) of the powder given in Figure 28. Moreover, the size distribution of the powder was determined by laser diffraction using a Malvern Mastersizer 2000. The averaged P80 of the pyrite used was 116 μm and the resulting particle size distribution is plotted in Figure 29. Laboratory grade hematite (Fisher Scientific) and gypsum (Alfa Aesar) were used.
4.3.2 Preparation of Synthetic CaTS Leaching Solutions

A 0.2 M copper stock solution as copper sulfate pentahydrate was prepared in advance and a 1250 mg/L gold stock solution as gold(I) sodium thiosulfate hydrate in 0.1 M CaTS was freshly prepared minutes before the start of the experiments. Briefly, a calculated amount of ~24 wt % CaTS solution was added to a 250 mL beaker partially filled with 18.2 MΩ nano pure water before addition of 1
mL copper and gold from each stock solution as well as any extra soluble additives such as polythionates. The pH was adjusted to the desired initial set point using 0.1 M NaOH. The solution was then transferred into a 250 mL volumetric flask whose volume was made up to the mark. After adequate mixing, the content of the volumetric flask was transferred into an Erlenmeyer flask reactor from which initial samples (t=0) were immediately taken. For experiments containing mineral additions, calculated amounts of each mineral were subsequently introduced into the reactors. The flasks were capped with rubber stoppers containing apertures for a pH electrode and a base inlet line and were submerged into a temperature controlled water bath sitting atop multiple magnetic plate stirrers for agitation (500 rpm). Where applicable, base additions of 0.1-1 M NaOH were made by a Jenco 3675 pH/ORP controller for automatic pH control.

4.3.3 Testing Procedures

The concentration and hence stability of gold in synthetic leach solution as well as changes in thiosulfate and polythionate concentrations were measured over time using the techniques described in Section 3.2.2. As the presence of pentathionate was deemed crucial in the outcomes of the tests, its quantification was estimated based on a pentathionate correlation method described in Section 3.2.2.3. At selected time intervals, sample aliquots were removed from the reactor and filtered using 0.22 μm PTFE filters. In some instances 0.02 μm filters (Whatman Anatop) were used capable of removing larger colloidal gold particles (+20 nm) if present.

4.4 Behaviour of Gold and Polythionates in CaTS Leach Solutions

4.4.1 Effect of pH at 25 °C

4.4.1.1 pH Drift Solutions

The initial aim of this work was to investigate the stability of the gold thiosulfate complex in artificial CaTS leaching solutions over time. This section describes the results generated while testing the stability of 5 mg/L gold-thiosulfate in 0.1 M CaTS solutions of varying polythionate compositions. The initial pH was adjusted to 8.5 and allowed to drift naturally as the ageing of the solutions progressed. Figure 30 A-F summarizes the collected data from which several conclusions can be drawn.
**4.4.1.1 Polythionate Stability**

As shown in Figure 30 E, it is evident that initial additions of polythionates decreased the pH over time in the order of no PolyTS < 3T < 4T < 3T & 4T. This indicates proton generating reactions were taking place. In the case of no PolyTS added, a little amount of tetrathionate was detected initially. This amount of tetrathionate originated from the oxidation of thiosulfate due to the reduction of 50 mg/L added cupric (See Section 3.1.2.2) and is to be present in all tests. However, an immediate thiosulfate catalyzed rearrangement reaction of tetrathionate into tri- and pentathionate occurred (Reaction 29). This was followed by their subsequent degradations comprising of the proton generating trithionate hydrolysis (Reaction 26) and the degradation (Reaction 30) and rearrangement of pentathionate (Reaction 40).

\[
2S_5O_6^{2-} \rightarrow S_4O_6^{2-} + S_6O_6^{2-} \quad 40
\]

As Zhang et al. (2010) pointed out, in the presence of thiosulfate and at near-neutral pH, the secondary reaction that dominates is the latter rearrangement of pentathionate. For Figure 30 A, C and D, initial tetrathionate present as a result of cupric reduction and artificial tetrathionate addition quickly rearranged with the products remaining constant over time. On the other hand, in the case of Figure 30 B, for trithionate addition alone, a steady decrease in trithionate concentration with a resulting increase in tetrathionate can be observed. A plausible reaction explaining this behaviour is given by Equation 41.

\[
S_3O_6^{2-} + S_2O_6^{2-} \rightarrow S_4O_6^{2-} + SO_3^{2-} \quad 41
\]

Equation 41 is accelerated by the presence of thiosulfate (reverse order of Reaction 28) and was shown to be more competitive at lower temperatures (Naito et al. 1975). This reaction was said to become more predominant at high concentrations of thiosulfate such as during thiosulfate leaching (Zhang et al. 2010) which bodes well with the present leach chemistry (0.1 M CaTS).

**4.4.1.2 Gold Stability**

Figure 30 F demonstrated that the gold concentrations in these solutions did not significantly change over the course of 48 hours of stability testing for each condition. Moreover, the gold concentrations remained stable after a total ageing time of 21 days.
Figure 30: Summary of drift pH stability tests with \([\text{Au}]_{\text{ini}} = 5 \text{ mg/L}, 0.1 \text{ M CaTS, 50 ppm Cu at 25 }°\text{C. A) No PolyTS addition, B) 4 mM 3T addition, C) 4 mM 4T addition, D) 4 mM 3T & 4T addition, E) pH profiles over time, F) Gold concentrations over time.}
4.4.1.2 pH 8.5 Controlled Solutions

Subsequent tests used automatic pH control to maintain the initial pH constant over time. Figure 31 E displays the constant pH 8.5 profiles during the stability testing. The drawback in these experiments were solution dilutions resulting from the added dilute base (NaOH) at the expense of worse pH control using concentrated base.

4.4.1.2.1 Polythionate Stability

Figure 31 A shows a replicated stability test at constant pH 8.5 without initial addition of polythionates. As can be seen, the same initial rearrangement reactions as discussed above occurred. It should be noted that the sulfur mass balance for all polythionate species present in solution initially equalled the theoretical sulfur mass balance as the added species. The observed rearrangement reactions also holds true for Figure 31 B, C and D for the first few hours after which, past the 12 hour mark, differences in the rates of tetrathionate decomposition were noticed compared to pH drift experiments.

4.4.1.2.2 Gold Stability

Unlike during the drift pH testing, some noticeable decreases in soluble gold were recorded during the stability testing at constant pH 8.5. Figure 31 F indicates lowered soluble gold measurements particularly between the 12 and 48 hour mark, in the order 3T & 4T addition < 4T ≈ 3T < TS. However this was partially attributed to the effects of solution dilution from automatic base addition which were in line with the decreases in pH observed during drifting experiments that followed the same order (Figure 30 E). In essence, there still remains a significant concentration of thiosulfate in solution to theoretically maintain all the gold in solution at all times. The interpretation of the apparent drops of soluble gold in Figure 31 F resulting from polythionate additions of 4 mM should be cautioned due to the lack of intermittent sodium hydroxide consumption data collected over time. Nonetheless, it is possible that soluble gold precipitated in the aforementioned early stages in the presence of polythionates before re-solubilizing as indicated by the higher final gold concentrations measured after 96 hours of testing.
Figure 31: Summary of pH 8.5 controlled stability tests with [Au]_{init} = 5 mg/L, 0.1 M CaTS, 50 ppm Cu at 25 °C. A) No PolyTS addition, B) 4 mM 3T addition, C) 4 mM 4T addition, D) 4 mM 3T & 4T addition, E) pH profiles over time, F) Gold concentrations over time.
4.4.1.3 pH 10 Controlled Solutions

For the pH 10 controlled gold stability test series, three test conditions were replicated to demonstrate reproducibility (Figure 32 to 34). These replicate tests confirm very good reproducibility in the conducted experiments and impart confidence in the quality of the collected data.

![Figure 32: TS and PolyTS concentrations for replicate stability tests A and B at constant pH 10 using 0.1 M CaTS, 4 mM 3T addition at 25 °C. Tests A and B are replicate tests (separate reactors) with each data point representing the average of two duplicate samples.](image)
Figure 33: TS and PolyTS concentrations for replicate stability tests A and B at constant pH 10 using 0.1 M CaTS, 4 mM 4T addition at 25 °C. Tests A and B are replicate tests (separate reactors) with each data point representing the average of two duplicate samples.

Figure 34: TS and PolyTS concentration profiles for replicate stability tests A and B at constant pH 10 using 0.1 M CaTS, 4 mM 3T & 4T addition at 40 °C. Tests A and B are replicate tests (separate reactors) with each data point representing the average of two duplicate samples. Gold data given in Figure 35.
Figure 35: Filtered gold concentration profiles for replicate stability tests A and B at constant pH 10 using 0.1 M CaTS, 4 mM 3T & 4T addition at 40 °C. Polythionate data given in Figure 34.

For the ease of comparison, the graphs A, B, C and D in Figure 36 combines the polythionate curves of the pH drift experiments given in Figure 30, the polythionate curves of the constant pH 8.5 experiments given in Figure 31 and the polythionate curves of the constant pH 10 experiments discussed in this section. Taken together, these combined graphs show the relationship between the pH of the solution and the degradation kinetics of the polythionates.

4.4.1.3.1 Polythionate Stability

The curves for the same species at every pH given in Figure 36 A-D consistently showed the same concentrations initially. From there on, the degradation of constituents varied according to the pH of the solutions. Initially, drift pH tests and pH 8.5 tests were expected to behave similarly before diverging as the pH continued to decrease in the pH drift tests. From Figure 30 E, the drift pH’s at the 48 hour mark for experiments with no initial PolyTS, 4 mM 3T, 4 mM 4T and 4 mM 3T & 4T additions were 7.1, 6.6, 5.3 and 4.6 respectively. With the exception of the drift test with 4 mM initial 3T, the polythionate concentrations for the other conditions remained constant during the time frame investigated. This changed when the pH was maintained constant at 8.5 or 10 with the latter increasing the rates of polythionate degradation the most. For controlled pH 10 experiments
containing initial tetrathionate, pentathionate was seen decomposing to trace amounts within 6 hours. It is generally accepted that higher polythionates decompose more readily at alkaline pH (Wagner et al. 1978, Varga et al. 2007, Zhang et al. 2010).

Figure 36: Comparison of pH drift (solid lines), pH 8.5 (dashed) and pH 10 (dotted) controlled stability tests with $[\text{Au}]_{\text{ini}}$ = 5 mg/L, 0.1 M CaTS and 50 ppm Cu at 25 °C. A) No PolyTS addition, B) 4 mM 3T addition, C) 4 mM 4T addition, D) 4 mM 3T & 4T addition, E) pH 10 profiles over time, F) pH 10 gold concentrations over time.
4.4.1.3.2 Gold Stability

Just as was indicated in experiments conducted at a constant pH 8.5, the interpretation of the decreases in soluble gold data analyzed during the gold stability tests at constant pH 10 (given in Figure 36 F) should be not be treated as definitive due to a lack of base consumption data collected over multiple time intervals. In total, the base consumption for the pH 10 stability tests after 72 hours amounted to volumes of 3.3, 7.3, 11.2 and 15.4 mL of 0.1 M NaOH for tests with no PolyTS, 4 mM 3T, 4 mM 4T and 4 mM of both 3T and 4T respectively. Despite this, the addition of 4 mM 3T and 4T resulted in a decrease in the filtered gold concentration from an initial 4.87 mg/L to 3.62 mg/L at the 10 hour mark. This decrease in the dissolved gold concentration (26 %) represents a considerably larger one than would be anticipated in the worst case due to solution dilution (6 %). Similarly, this argument can also be applied for the gold decreases measured in the case of 4 mM 3T (15 % vs. 3 %) and 4 mM 4T additions (11 % vs. 4 %). Conversely, in the absence of polythionate additions, a more stable gold concentration is measured over time with slight decreases (< 2 %) well within the experimental error of the analytical instrument. In subsequent tests, to account for the effects of dilution, gold concentration curves were modelled representing expected gold concentrations based on solution withdrawals due to sampling and solution dilution due to base additions.

4.4.2 Effect of pH at 40 °C

As was observed in tests conducted at room temperature, the pH of test solutions influences which decomposition reactions dominate in the CaTS leaching system. The series of graphs A-D in Figure 37 compare the effect of controlled pH 8.5 versus pH 10 on the behaviour of polythionate species in different synthetic CaTS leaching solutions at 40 °C. Graphs E and F display the filtered gold concentrations for pH 8.5 and 10 respectively over time for the different initial solution compositions given in A-D. The solid lines in Figure 37 E and F represent modelled gold concentration curves based on solution withdrawals from sampling and solution dilution from automatic base addition. Specifically, a modelled gold concentration curve relies on the starting gold concentration in solution for the given initial volume (250 mL). This gold mass balance was subsequently re-evaluated and plotted over time after every solution withdrawal of known volume and concentration (measured by AAS) as well as after incremental volume additions due to automatic base addition.
4.4.2.1 Polythionate Stability

In all cases with initially added polythionates, an increase in pH from 8.5 to 10 caused a faster decomposition of the polythionates species. Particularly in the presence of initial tetrathionate at pH 10, shown in Figure 37 C & D, tetrathionate and pentathionate concentrations rapidly decreased within the first three hours of the experiment. Again, this supports the fact that higher polythionates are less stable in alkaline solutions.

4.4.2.2 Gold Stability

The gold concentration data for tests containing no added initial polythionates at both pH values (Figure 37 E and F) remained stable throughout the stability testing period. Initial additions of 4 mM trithionate, tetrathionate, or both appear to have perturbed the gold stability at least initially as shown in Figure 37 E and F. After extended periods, the measured gold concentrations were back in line with expected gold values as predicted by the modelled curves. Gold measurements in tests reproduced on separate occasions (Figure 35) confirm the observed soluble gold behaviour is not due to random or systematic errors. From the results, it can be concluded that the presence of polythionates can at the very least temporarily remove soluble gold from solution.
Figure 37: Summary of pH 8.5 (dashed) and pH 10 (dotted) controlled stability tests with [Au]ini = 5 mg/L, 0.1 M CaTS, 50 ppm Cu at 40 °C. A) No PolyTS addition, B) 4 mM 3T addition, C) 4 mM 4T addition, D) 4 mM 3T & 4T addition, E) Filtered gold concentrations over time at pH 8.5, F) Filtered gold concentrations over time at pH 10 with modelled gold curves based on solution withdrawal and base addition.
4.4.3 Effect of Temperature

It was anticipated that the rates of polythionate degradation would be enhanced at higher temperatures (Fava et al. 1954, Naito et al. 1975). This was clearly shown for all combinations of initial polythionate additions (see Table 17) when comparing test solutions at 25 °C versus 40 °C for both pH 8.5 (Figure 39) and pH 10 (Figure 40).

### Table 17: List of figures and conditions being compared

<table>
<thead>
<tr>
<th>PolyTS Addition</th>
<th>Effect of Temperature</th>
<th>Effect of pH</th>
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<tbody>
<tr>
<td></td>
<td>pH</td>
<td>25 °C vs. 40 °C</td>
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<tr>
<td>TS only</td>
<td>8.5</td>
<td>Figure 39-A</td>
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<tr>
<td>4 mM 3T</td>
<td>Figure 39-B</td>
<td>Figure 36-B</td>
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<td>4 mM 4T</td>
<td>Figure 39-C</td>
<td>Figure 36-C</td>
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<tr>
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<td>Figure 39-D</td>
<td>Figure 36-D</td>
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<tr>
<td>4 mM 3T &amp; 4T</td>
<td>Figure 40-D</td>
<td>Figure 37-D</td>
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4.4.3.1 Trithionate Degradation

In previous work, Ahern (2005) determined the observed trithionate degradation reaction rate constant ($k_{obs}$) at 40 °C in water using an initial rate method. In its most basic form, the first order rate equation for the degradation of trithionate was expressed as in Equation (42) where $k_{obs}$ was found to be equal to 0.012 h$^{-1}$.

$$\frac{-d[S_2O_6^{2-}]}{dt} = k_{obs}[S_3O_6^{2-}]$$  \hspace{1cm} 42

The degradation of trithionate was found to generally follow the stoichiometry of Reaction (43) based on measured concentrations of trithionate, sulfate and thiosulfate.

$$S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + H_2O$$  \hspace{1cm} 43

In comparison, for the trithionate curve in Figure 37 B, where an initial 4 mM 3T was added at 40 °C at pH 8.5, a $k_{obs}$ of 0.0121 h$^{-1}$ was determined using the integrated rate method plotted in Figure 38. This values is in good agreement with the aforementioned previous work.
Figure 38: Linear plot for first order trithionate degradation reaction

\[ y = -0.0121x + 1.3106 \]
\[ R^2 = 0.9884 \]

Figure 39: Comparison of 25 °C (dashed) and 40 °C (solid) controlled stability tests with [Au]_{in} = 5 mg/L, 0.1 M CaTS, 50 ppm Cu at pH 8.5. A) No PolyTS addition, B) 4 mM 3T addition, C) 4 mM 4T addition, D) 4 mM 3T & 4T addition.

Figure 39: Comparison of 25 °C (dashed) and 40 °C (solid) controlled stability tests with [Au]_{in} = 5 mg/L, 0.1 M CaTS, 50 ppm Cu at pH 8.5. A) No PolyTS addition, B) 4 mM 3T addition, C) 4 mM 4T addition, D) 4 mM 3T & 4T addition.
4.4.4 Effect of High Concentrations of Polythionate Additions to CaTS Leach Solutions

In this section the results from stability tests at 40 °C using concentrated polythionates additions in the order of 25 mM are presented in Figure 41. This concentration represent a 25 % fraction of the initial 100 mmoles/L of thiosulfate present as CaTS throughout this work. From previous experimentation, it was predicted that considerable base would be required to maintain a constant pH and therefore the lower pH set point of 8.5 was selected. Firstly, the base consumption (mmoles) is plotted together with the actual volume of base (mL) used to control the pH in Figure 41 D. It can be seen that the addition of polythionates consumed more base in the order of 25 mM 3T alone, 25 mM 4T alone and 25 mM each of 3T and 4T. Base addition was switched to 1 M NaOH for the latter two cases which explains the levelling off in terms of volume added into the system. It is apparent that these leach solutions were significantly diluted, particularly in the case of 25 mM 3T addition.

Figure 40: Comparison of 25 °C (dashed lines) and 40 °C (solid lines) controlled stability tests with [Au]_{init} = 5 mg/L, 0.1 M CaTS, 50 ppm Cu at pH 10. A) No PolyTS addition, B) 4 mM 3T addition, C) 4 mM 4T addition, D) 4 mM 3T & 4T addition.
where the pH was controlled using 0.1 M NaOH. As such, the interpretation of the polythionate and gold concentration data should be done in a qualitative way and with caution.

Figure 41: Summary of polythionate additions during pH 8.5 controlled stability tests with [Au]_{ini} = 4.16 mg/L, 0.1 M CaTS, 50 ppm Cu at 40 °C. A) 25 mM 3T addition, B) 25 mM 4T addition, C) 25 mM 3T & 4T addition, D) Base consumption (in mmoles and mL) E) Filtered gold concentrations over time with modelled gold curves based on solution withdrawal and base addition.
4.4.4.1 Polythionate Stability

An analysis of the sulfur mass balance in terms of the measured polythionate species as a function of time remaining in the reaction and extracted from the reactor was conducted. The results showed that after 120 hours of stability testing, the measured sulfur species excluding sulfate still made up over 90% of the initial mass balance. The sulfur and gold mass balances for experiments A, B and C of Figure 41 are shown in the Appendix A.1 as bar graphs in Figures A4, A5 and A6.

Figure 41 A shows the trithionate decomposition occurring steadily right after the addition of 25 mM trithionate. Reaction (43) can be re-written as a trithionate hydrolysis reaction given as Reaction (44) where one mole of reacted trithionate results in one mole thiosulfate and sulfate and two moles of protons, of which the latter would require base addition to maintain the pH set point. In this case, the calculated molar ratio of reacted trithionate over consumed hydroxide after 120 hours was 0.57, close to the theoretical ratio of 0.5 based on the stoichiometry of Reaction (44).

\[ S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \]  \hspace{1cm} 44

However, the tetrathionate concentration increased slightly to 2 mM up to the 48 hour mark before decreasing again due to its own degradation over time. The presence of tetrathionate likely results from Reaction (41) which is promoted in the presence of thiosulfate and a low pH. If this side reaction was taken into account, the moles of trithionate hydrolyzed by Reaction (44) would decrease and the above calculated molar ratio would be closer to 0.5. Unfortunately, it should be noted that sulfate and sulfite are reaction products that were not included in the chemical analysis nor in the experimental sulfur mass balance.

Figure 41 B shows the behaviour of the polythionates after an initial addition of 25 mM tetrathionate. The decomposition reactions are well captured by the frequent sampling. Initially, tetrathionate was seen quickly rearranging into trithionate and pentathionate as per Reaction (29). The moles of tetrathionate reacted and the moles of trithionate generated during the first time interval followed the expected stoichiometry of Reaction (29). Within that same time interval, pentathionate generation was also clearly observed but had already begun to quickly degrade according to the pentathionate degradation reaction (Reaction 30). As the pH of the solution was maintained at 8.5, Reaction (30) occurred faster than the trithionate hydrolysis reaction (Reaction 44). Both Reactions (30) and (44) generate thiosulfate which was seen increasing significantly as soon as pentathionate degradation began.
Figure 41 C combines the addition of both 25 mM 3T and 4T initially. The moles of polythionate added into this system amounted to 50 % of the initial moles of thiosulfate. A combination of the aforementioned reactions were expected to occur over time. The initial sampling captured a small increase of trithionate above its initially added concentration together with an increase in pentathionate. This was taken as evidence of the fast initial tetrathionate rearrangement reaction (Reaction 29). This rearrangement reaction coupled with the subsequent fast pentathionate degradation (Reaction 30) explains the sharp decreases in both the tetrathionate and pentathionate concentrations over time. The products of these reactions were thiosulfate and trithionate with the latter undergoing slow hydrolysis (Reaction 44) where additional thiosulfate was generated.

4.4.4.2 Gold Stability

Figure 41 E displays the measured soluble gold concentrations over time as well as the modelled gold concentration curves. The modelled curves were based on accurate and frequent measurements of the volume of base added to the reactor over time as well as accounting for the removal of solution from the reactors for gold and polythionate analysis. The filtered soluble gold concentration data points are shown to lie below the predicted values represented by the model. This trend of gold decreases associated with polythionate additions continues as observed in previous cases. This phenomenon is further discussed later.

4.5 Behaviour of Gold and Polythionates in the Presence of Mineral Additions in CaTS Leach Solutions

The testing condition used to observe the effects of added minerals in synthetic CaTS leaching solutions containing polythionates was a pH of 10 and a temperature of 40 °C. This experimental condition in the absence of minerals, previously plotted in Figure 37 and Figure 40, was considered as the baseline to which subsequent experiments containing mineral additions were compared.

4.5.1 Gypsum

As given in Table 16, gypsum additions of 4 g/L along with varying compositions of initial polythionate additions were made to 0.1 M CaTS solutions controlled at pH 10 and 40 °C with initial soluble gold-thiosulfate concentrations of ~5 mg/L. The results from these tests are summarized in Figure 42 where polythionate concentration curves in the presence of gypsum (dashed lines) are plotted together with the baseline test (solid lines).
Figure 42: Comparison of 4 g/L gypsum additions (dashed lines) and no mineral additions (solid lines) during stability tests with [Au]$_{ini}$ = ~5 mg/L, 0.1 M CaTS, 50 ppm Cu at 40 °C and pH 10. A) No PolyTS addition, B) 4 mM 3T addition, C) 4 mM 4T addition, D) 4 mM 3T & 4T addition, E) Base consumption, F) Filtered gold concentrations over time in the presence of gypsum and modelled gold curves based on solution withdrawal and base addition.

4.5.1.1 Polythionate Stability

Figure 42 A-D show similar trends in terms of polythionate concentrations in solution over time for tests with and without gypsum addition. However, it should be noted that the polythionate curves in
the presence of the added mineral appear to fluctuate more than the baseline. Figure 42 E show base consumptions are also in good agreement with the exception of the baseline test with 4 mM 3T & 4T additions past the 48 hour mark. This side effect of solution dilution can also be observed in Figure 42 D where the decrease in thiosulfate concentration diverged more severely past the 48 hour mark compared to the test with gypsum addition.

4.5.1.2 Gold Stability

Figure 42 F displays the measured gold concentrations over time compared to the expected modelled gold concentrations. Of note are overall lower gold concentrations in tests with added polythionates in the order of 3T & 4T < 4T < 3T < no PolyTS in line with base consumption data displayed in Figure 42 E. However, soluble gold concentrations from filtered aliquots measured shortly after gypsum addition in solutions containing added initial polythionates strayed significantly from the expected concentrations based on the modelled curves. This trend is reversed after extended periods where the last measured gold concentrations are in better agreement with the expected gold values.

4.5.2 Activated Carbon

Activated carbon (AC) was added to test solutions at a concentration of 1.29 g/L (Table 16). This represents a typical concentration of carbon in a slurry of 25 % pulp density containing a typical Carlin Trend type preg-robbing ore with 0.43 wt % carbon content. In this series, only the cases without polythionate additions (Figure 43 A) and both 4 mM 3T and 4T (Figure 43 B) were considered.
Figure 43: Comparison of 1.29 g/L activated carbon additions (dashed lines) and no mineral additions (solid lines) during stability tests with $[\text{Au}]_{\text{ini}} \approx 5 \text{ mg/L}$, 0.1 M CaTS, 50 ppm Cu at 40 °C and pH 10. A) No PolyTS addition, B) 4 mM 3T & 4T addition, C) 0.1 M base consumption, D) Filtered gold concentrations over time in the presence of activated carbon and modelled gold curves based on solution withdrawal and base addition.

4.5.2.1 Polythionate Stability

As was observed for gypsum addition, the presence of activated carbon did not generally alter the behaviour of the polythionate concentrations in solution over time. Although the trends were the same, the presence of the added mineral seem to have perturbed the system particularly initially, as more fluctuations in the collected polythionate data were observed as shown in Figure 43 B.

4.5.2.2 Gold Stability

The measured gold concentrations from filtered aliquots in the activated carbon test solution without added polythionates followed the predicted gold concentration closely (Figure 43 D). On the other hand, fluctuations in soluble gold concentrations are recorded in the system containing initial additions of 4 mM 3T and 4T. The measured gold concentrations seem to diverge from the expected
concentrations based on the modelled curves past the 48 hour mark. Activated carbon was previously shown to have a slight affinity for aurothiosulfate (Gallagher et al. 1990) which can also contribute to the lowered gold concentrations after long periods of stability testing.

4.5.3 Hematite

The next mineral of interest in this section is hematite. It was shown that this mineral has the propensity to catalyze the oxidative decomposition of thiosulfate to polythionates as well as to form passivating iron oxide coatings on gold surfaces (Feng et al. 2007a). The former characteristic is of greater interest during an investigation on the effects of polythionates on the stability of aurothiosulfate in synthetic CaTS leaching solutions.

4.5.3.1 Polythionate Stability

The addition of 8 g/L hematite incurred a similar outcome in terms of polythionate behaviour as in the case of activated carbon addition. Figure 44 A shows a slight increase in trithionate formation in the synthetic leach solution without initial polythionates contacted with hematite compared to the case without mineral addition. As for the introduction of 4 mM 3T and 4T into the system (Figure 44 B), although the same general polythionate decomposition pathways were followed, hematite appears to have disrupted the polythionate decomposition reactions more than without the presence of a mineral addition.

4.5.3.2 Gold Stability

The measured soluble gold concentrations in the absence of initial polythionates closely follows the modelled gold curve. Once more, in the presence of the polythionates, some fluctuations were recorded whereby gold values were considerably lower than expected. These intermittent gold decreases could be related to the complex redox behaviours exhibited by the polythionate species during the same time frame discussed later.
Figure 44: Comparison of 8 g/L hematite additions (dashed lines) and no mineral additions (solid lines) during stability tests with \([\text{Au}]_\text{ini} \approx 5 \text{ mg/L}, 0.1 \text{ M CaTS}, 50 \text{ ppm Cu at 40 } ^\circ\text{C and pH 10. A) No PolyTS addition, B) 4 mM 3T & 4T addition, C) 0.1 M base consumption, D) Filtered gold concentrations over time in the presence of hematite and modelled gold curves based on solution withdrawal and base addition.}

4.5.4 Pyrite

For the baseline stability tests without mineral additions and all previous tests with mineral additions at pH 10 and 40 °C, the pH was adjusted using 0.1 M sodium hydroxide. For the subsequent tests, investigating the effects of 8 g/L pyrite addition into the leaching system, 1 M sodium hydroxide was employed to further limit solution dilution. Therefore, comparison of the polythionate data between the pyrite addition tests and the baseline tests without mineral additions is cautioned.
4.5.4.1 Polythionate Stability

Figure 45 A compares the polythionate concentrations over time for tests without initial polythionate additions in the presence of pyrite (dashed lines) to the baseline test without mineral additions (solid lines). A sharp rise in trithionate was observed with a corresponding drop in thiosulfate concentration in the presence of pyrite. A known mechanism for the catalyzed decomposition of thiosulfate onto the surface of pyrite (Section 2.5.2) results in the generation of tetrathionate. This latter species was very briefly detected before its fast rearrangement according to Reaction (29). The generated trithionate continued to accumulate as its hydrolysis (Reaction 44) was slower than the pyrite catalyzed degradation of thiosulfate. On the other hand, the generated pentathionate, which was also briefly detected initially, quickly reacted according to Reaction (30) thereby regenerating thiosulfate and resulting in significant base consumption initially (Figure 45 C). In the case of the
initial addition of 4 mM 3T & 4T into the leaching system (Figure 45 B), the pyrite catalyzed thiosulfate decomposition was less apparent as the concentration of thiosulfate remained constant. The subsequent decomposition of polythionates followed the same previously discussed tetrathionate rearrangement and pentathionate degradation reactions. It should be emphasized that the initially measured pentathionate concentration appeared to have rapidly reacted in the alkaline conditions and is therefore under represented vis-à-vis trithionate.

4.5.4.2 Gold Stability

Figure 45 D shows a sharp decrease in soluble gold concentration shortly after the addition of pyrite into the system. As will be discussed later, the initial generation and brief appearance of pentathionate in the system can possibly account for the gold losses. Nonetheless gold appears to have re-leached over time returning to expected values based on the gold concentration model.

The fresh iron sulfide surface area may have adsorbed the \( \text{Au}(S_2O_3)_2^{3-} \) complex leading to the precipitation of gold (Lengke et al. 2006). The reductive nature of sulfide surfaces was shown to be responsible for slowing down gold extractions by ATS (Xia 2008). Moreover, this type of reduction in gold dissolution has previously been posited to be due to the reductive iron sulfide surface where a co-precipitation mechanism was used to explain the role of iron in the gold-thiosulfate reduction (Xia et al. 2005). In short, the dissolution of pyrite can contribute to dissolved ferrous ions in solution and create defected surfaces on the sulfide. Gold complexes may physically adsorb onto those defected surface sites and immediately reduce to elemental gold. At the same time, the dissolved ferrous ions can form ferrous species such as \( \text{Fe(OH)}_2 \) acting as reducing agents for gold-thiosulfate whereby a redox reaction results in the co-precipitation of elemental gold and ferric hydroxide on the surface of the pyrite (Reaction 45).

\[
\text{Au}(S_2O_3)_2^{3-} + \text{Fe(OH)}_2 + \text{OH}^- \rightarrow \text{Au}^0 + 2S_2O_3^{2-} + \text{Fe(OH)}_3
\]  

Over time, given enough remaining lixiviant, gold may eventually re-dissolve to yield anticipated levels as was seen in Figure 45 D.

4.6 Effect of Mineral Additions without Polythionates on Gold Stability

Up to this point, suspected decreases in soluble gold concentrations have occurred in solutions containing added initial polythionates. The effect of mineral additions alone on gold solubility was further investigated in 0.1 M CaTS solutions at room temperature and pH 10. Briefly, to this end,
solutions were prepared using a similar procedure as used for the former gold stability tests with the main difference being a focus on duplicate initial gold sampling followed by duplicate gold concentration sampling post mineral addition over time as well as reproducibility (repeated tests). Initial pH 10 adjustments were made by base additions and the solution pH was allowed to drift.

### 4.6.1 Gypsum and Hematite

Figure 46 displays the filtered gold concentrations for repeat tests involving gypsum and hematite additions.

![Figure 46: Filtered soluble gold concentrations before (initial) and after mineral additions (t≥0) (Hematite 8 g/L, Gypsum 4 g/L). Error bars = 5%. Conditions: 0.1 M CaTS, 50 ppm Cu, pH_{ini.} = 10.](image)

The results show the tests are reproducible and more importantly, that both hematite and gypsum additions in the absence of initial polythionates did not sequester gold from solution.

### 4.6.2 Activated Carbon

Figure 47 displays the filtered gold concentrations for repeat tests before and after 1.29 g/L activated carbon additions.
The replicated tests demonstrate reproducibility of drops in soluble gold contacted with activated carbon past the 68 hour mark. This confirms the affinity of \( \text{Au} \left( \text{S}_2\text{O}_3 \right) \) complexes with activated carbon over extended periods of time. It was previously reported that thiosulfate only slightly adsorbed onto activated carbon hence its suitability as a lixiviant for carbonaceous ores (Gallagher et al. 1990). The uptake of aurothiosulfate by naturally occurring carbon in during the leaching of preg-robbing ores could pose an additional challenge for effective gold recovery. However, these effects may be overcome when considering the total residence time in a typical leaching circuit is limited to 24 hours (Choi et al. 2012a).

### 4.6.3 Pyrite

Figure 48 compares the dissolved gold stabilities for replicated synthetic CaTS leaching solutions using two separately and freshly prepared gold-thiosulfate stock solutions labelled as Stock A and B. Figure 48 shows that anticipated drops in gold concentration right after pyrite addition \((t=0)\) that occurred in Figure 45 D were not observed. It is possible that the sampling procedure failed to capture the initial gold precipitation from solution right after pyrite addition by allowing enough time for re-leaching to occur. Another possibility for this can be linked to the drifting pH that is decreasing with time thereby changing the pathways and rates of polythionate degradations. Nonetheless, lowered soluble gold concentrations were measured after extended periods of time in solutions containing pyrite. The presence of 50 mg/L copper appears to accelerate the decrease in soluble gold concentration after extended times \((t=168)\). This was best illustrated by comparing tests.
Py2 and Py2-Cu and seeing the accelerated decrease in soluble gold for the latter starting at the 68 hour mark. The blank test (BLK) containing neither pyrite nor copper addition remains constant throughout the stability test.

![Filtered [Au] with Pyrite over Time](image)

**Figure 48:** Filtered soluble gold concentrations before (initial) and after 8 g/L pyrite additions (t≥0). Different fresh Au-stock solutions were used (A & B). Error bars = 5%. Conditions: 0.1 M CaTS, 50 ppm Cu added, pH_{ini} = 10.

Figure 49 shows the accelerated decomposition of 0.1 M initial thiosulfate when contacted with pyrite compared to the stable thiosulfate in the blank experiment. The sulfur (S⁰) mass balance in terms of thiosulfate and polythionate species remained constant at all times with a maximum 3 % deviation from the initial mass balance. As mentioned earlier, results from other researchers indicated decreased gold extractions in the presence of pyrite with higher thiosulfate consumptions (Xia et al. 2005). Although no polythionate additions were made initially, the presence of 8 g/L pyrite in this synthetic leaching system contributed to the formation of appreciable levels of polythionates providing a solution chemistry that resembles the ones found in Figure 36 B-D.
The results suggest an interaction between the pyrite mineral’s surface and the dissolved aurothiosulfate complexes where the latter may be adsorbed and even reduced which is enhanced by the presence of 50 mg/L copper. Pyrite was previously shown to have preg-robbing characteristics in the ATS leaching system whereby gold was lost from solution when contacted with pyrite in the absence of free thiosulfate (Feng et al. 2001). The adsorption process was fast and found to be countered by increasing the free thiosulfate content. Moreover, the presence of increasing initial cupric ion concentration enhanced the preg-robbing attributed to the oxidation of free thiosulfate. The study did not consider the possible additional effects of the thiosulfate oxidation products which would also be present in solution. The involvement of polythionates in redox reactions occurring at the surface of the mineral cannot be ruled out where these species could act as reducing agents in the precipitation of aurothiosulfate as elemental gold.

### 4.7 Discussion

Figure 50 is composed of Eh-pH reduction lines at equilibrium in a system composed of 0.1 M thiosulfate, 5 mg/L gold and polythionate concentrations of 4 mM. These types of lines are the basis for the construction of Pourbaix diagrams that give equilibrium stability regions for phases and species. For instance, the gold thiosulfate reduction line represents the Eh and pH conditions at which the aurothiosulfate (AuTS) is in equilibrium with reduced gold. Above this line, the oxidized gold complex is the dominant phase and is considered to be stable. Conversely, below the line, elemental gold is the dominant phase. When, vis-à-vis the gold line, a reducing agent with $Eh < Eh_{AuTS(aq)/Au(s)}$ is added, it will donate its electrons to the oxidant, namely AuTS. Gold(I) accepts the
electron and reduces to elemental gold given its higher reduction potential. Figure 50 contains several Eh-pH lines of redox half reaction involving polythionates. Above pH 7.7, the Eh of all half reactions lie below that of the AuTS/Au$^0$ line and therefore could, in principle, be involved in the reduction of gold. The half reactions at equilibrium that involve pentathionate ($\Delta G^\circ = -956$ kJ/mol, (Bard et al. 1985)) lie well below the gold line demonstrating its reducing strength. Although pentathionate is unstable in alkaline solutions, it can still be present in solution at least transiently as shown in Figure 41 B.

Figure 50: Eh-pH lines for possible redox reactions involving polythionates at 25 °C with 0.1 M TS, 0.004 M PolyTS, 5 ppm Au.

4.8 Partial Conclusions

First and foremost, the experimental body of work performed in this chapter was designed to follow the fate of soluble gold-thiosulfate in synthetic leaching solutions at various conditions (pH, temperature) in the presence of artificially added polythionate concentrations while also closely monitoring the latter. In all situations, the degradation of polythionates followed known mechanisms established in the literature. Decreases in soluble gold concentrations were never observed in solutions in the absence of polythionate additions. On the other hand gold concentrations below anticipated levels, in some cases despite solution dilution from base additions, were constantly recorded during stability testing of leaching solutions containing initially added polythionates.
Extended leaching times often resulted in the re-dissolution of gold to expected levels based on the gold mass balance measurements (e.g.: Figures 31 F, 35 and 37 F, 41 E).

The addition of mineral phases such as gypsum, activated carbon and hematite to synthetic leaching solutions only had a slight impact on the polythionate degradations reactions whereby more fluctuations in the measured data were observed than in the absence of the mineral additions. Soluble gold concentrations were also affected in stability tests involving minerals with polythionate additions (Figures 42 F, 43 D, 44 D). The introduction of pyrite into a synthetic leach solution had a much more pronounced effect on the degradation of thiosulfate and an even greater effect on the initial gold stability capable of temporarily reducing gold (Figure 45 D).

In the absence of synthetically added polythionates, gypsum and hematite were found not to contribute to gold losses. On the other hand, activated carbon was confirmed to have a slight affinity for aurothiosulfate complexes after extended times. Pyrite was found to negatively impact gold stability as a result of its role in the catalytic decomposition of thiosulfate resulting in the generation of polythionates which were shown to reduce gold concentrations.
5 Stability of Gold-Thiosulfate during the Leaching of a Preg-robbing Ore in the Presence of Polythionates

The previous chapter focused on the stability of gold in synthetic CaTS leaching solutions with polythionate and mineral additions. The natural progression of this work is to incorporate an actual preg-robbing ore into the CaTS leaching system mimicking the industrial conditions presently encountered in the world’s only thiosulfate gold leaching plant. As such, the subsequent effects of polythionate additions on the stability of gold in this complex system can be further investigated.

5.1 Experimental Procedures

The preg-robbing material used in the following experiments was provided by the Barrick Gold Corporation subsidiary AuTec (see Appendix A.6 for details). The material consists of a gold-bearing double refractory sulfidic and carbonaceous ore that was pre-treated by pressure oxidation. This autoclave discharge slurry was filtered and dried in an oven at 60 °C. The density of the dried autoclave discharge was calculated as the average value of five measurements using a pycnometer giving a density of 2.7 g/mL. The gold concentration in this material determined by fire assay was 2.96 g/t ore. Experiments involving this preg-robbing feed material were prepared by addition of a predetermined volume of a stock leaching reagent solution (0.1 M CaTS, 50 mg/L copper as cupric sulfate and, optionally, 6-7 mg/L aurothiosulfate) to a calculated mass of dry material based on its density to yield an overall slurry pulp density of 30 wt %. The initial pH was set and controlled automatically at pH 8.5 for the duration of the tests. The modelling of expected gold concentrations in these experiments due to solution withdrawals from sampling and solution addition for pH control were ruled out owing to the preg-robbing nature of the feed material combined with its leachable gold content.

The first series of tests in this section involved the addition of polythionates to 30 wt % slurries of pre-treated gold bearing feed material (2.96 ppm) together with an artificial source of initial gold thiosulfate (6-7 mg/L). The aim was to observe how artificially introduced soluble gold would behave in contact with a feed materials of known preg-robbing characteristics. Subsequently, polythionate additions into this leaching system were made to examine their added effect on the gold preg-robbing behaviour of the system. To this end, polythionate additions of 25 mM as trithionate (Conc3T), tetrathionate (Conc4T) or both tri- and tetrathionate (ConcPT) were made after an initial gold sample was taken unless otherwise stated.
The second series of tests used the same aforementioned conditions, however without an artificial source of initial gold. Any soluble gold measured in these trials result from the leaching of the gold contained in the autoclave discharge itself. The intention of these leaching tests was to determine the impact of polythionate additions on the gold stability shortly after the start of leaching, and on the overall gold extraction.

### 5.2 Effects of Polythionate Additions to a Preg-robbing Ore

#### 5.2.1 Leaching Tests with Initial Synthetic Gold

##### 5.2.1.1 Baseline Leaching

In this series of tests, the absence of initially added polythionates was considered as the baseline. Baseline tests contained a small initial amount of polythionates due to the added copper sulfate discussed in Section 4.4.1.1.1. Figure 51 displays the gold and polythionate concentrations of replicate baseline tests using identical leaching conditions. The results indicated excellent reproducibly over the first 24 hours with some divergence at extended leach times. For each baseline test, the soluble gold concentration was seen increasing slightly initially due to the fast leaching of gold contained in the feed material. Subsequently, it appears that the gold was preg-robbed to levels below the initially added artificial soluble gold concentration. The adsorption of aurothiosulfate onto activated carbon was previously shown in Section 4.6.2. The naturally occurring carbon in the feed material with similar properties as activated carbon is the likely culprit for this sequestration of the initially added soluble gold observed.
5.2.1.2 Leaching with Polythionate Addition

As described in the procedure above, the aim in this section was to determine the effects of polythionate additions on the stability of soluble gold added initially to CaTS leaching slurries containing a preg-robbing feed material. To trigger and capture a measurable effect on the stability of gold in this system, exaggerated levels of polythionates concentrations were introduced into the leaching system at concentrations matching those used in Section 4.4.4. As done previously, an emphasis was placed on generating reproducible results to rule out random errors. Figure 52 displays the gold and polythionate concentrations for two replicate leach tests with 25 mM trithionate and tetrathionate additions using identical leaching conditions. Once again, the results prove to be reproducible in terms of species concentrations over time. In particular, the behaviour of the soluble gold concentration must be highlighted, where upon the addition of the thiosalts, significant drops in gold concentrations were recorded. This observation is clearly not manifested in the case of the baseline leaching tests.
Figure 52: Replicate leach tests on a preg-robbing gold ore (2.96 ppm Au) with artificial gold in the presence of 25 mM 3T and 4T additions (30 wt % PD, 0.1 M CaTS, [Au]$_{ini}$ = ~7 mg/L, 50 ppm Cu, pH 8.5, 50 °C).

To further illustrate the contribution of polythionate additions to the observed gold drops from solution, Figure 53 combines the soluble gold concentration data of the baseline experiments together with that of leaching experiments containing added polythionates. As can be seen, gold losses from solution were consistently intensified after polythionate additions. In all cases with initial polythionate additions, a significant reduction in soluble gold was observed with a minimum dissolved gold concentration reached between 2-6 hours. This indicates the precipitation of gold from solution due to the preg-robbing material and the thiosulfate degradation products. Over time, the precipitated gold re-dissolved back into solution to levels similar to the baseline tests.
The interaction between the preg-robbing material in contact with initial soluble gold and polythionates was made evident by conducting detailed gold mass balances for such tests, namely Conc4T-A and ConcPT-B. Figure 54 shows the decreases in soluble gold measured from filtered solution fractions by AAS corresponded well to the increases in gold found in the fire assays of the solid fractions from slurry aliquots sampled over time. As such, this shows the introduction of polythionate salts into the leaching system promoted the reduction of gold from solution onto the preg-robbing material which subsequently re-dissolved back into solution.
The polythionate concentration profiles in Figure 52 bear a resemblance to the ones recorded for Figure 41 C. It follows that the same redox reactions discussed in Section 4.7 can occur with the likely ability to reduce the aurothiosulfate gold complexes. A possible mechanism for gold reduction may be the adsorption of the gold complex on the large surface to volume area of the fine preg-robbing feed material that serves as a suitable site for gold reduction.

The observed re-dissolution of gold over time in Figure 53 for tests containing polythionate additions could be partially explained by an increase in the thiosulfate concentration resulting from the degradation and rearrangement of higher polythionate into thiosulfate. Normally such a significant increase of the gold lixiviant concentration would increase the gold leaching rate. Yet in this case it serves to partially revert the reduced gold back into solution. This is best demonstrated in Figure 55 where the thiosulfate concentration for test ConcPT-A is seen increasing relative to that of baseline test A.

![Comparison of Baseline Test with ConcPT Addition](image)

Figure 55: Gold and polythionate concentration profiles of baseline test A (no polythionates) compared to a test with 25 mM tri- and tetrathionate additions (ConcPT-A) at the 30 minute mark (30 wt % PD, 0.1 M CaTS, [Au]ini = ~7 mg/L, 50 ppm Cu, pH 8.5, 50 °C).

Similarly, the polythionate and gold concentration profiles for tests Conc3T and Conc4T-A with 25 mM trithionate and tetrathionate additions respectively are displayed in Figure 56.
As previously discussed, after an initial introduction of 25 mM tetrathionate into the leaching system (Conc4T-A), tetrathionate quickly rearranges into tri- and pentathionate (Reaction 29). Following the rearrangement reaction, both trithionate hydrolysis (Reaction 44) and pentathionate degradation (Reaction 30) resulted in the generation of appreciable amounts of thiosulfate.

In the case of 25 mM trithionate addition (Conc3T), the predominant reaction leading to the generation of thiosulfate was the trithionate hydrolysis reaction (Reaction 44). However, other side reactions were occurring concomitantly as evidenced by the increase in tetrathionate up to the 9 hour mark. A likely reaction generating tetrathionate could be the oxidation of thiosulfate by oxygen which can be enhanced by the presence of sulfidic minerals (Reaction 32). One cannot discount redox reactions discussed in Section 4.7 where the observed reduction of gold came at the expense of polythionate oxidation half reactions for example Reactions 46 and 47:

\[
2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \tag{46}
\]

\[
4S_2O_3^{2-} + 6H_2O \rightarrow 5S_4O_6^{2-} + 12H^+ + 10e^- \tag{47}
\]

Lastly, revisiting Reaction 41 can also afford another plausible side reaction for the generation of tetrathionate in solution as discussed in Section 5.3.
5.2.1.2.1 Short Term Leaching and Sampling

Results thus far for extended leaching times indicated that gold solubility decreased significantly shortly after addition of polythionates into the leach slurry. Figure 53 shows that this occurred within the first 6 hours. The slurry residence time in a real leaching reactor is commonly in the range of 3-4 hours with a total leaching circuit residence time of 10-24 hours (Choi et al. 2012a). As such, it is of interest to investigate the leaching behaviour of the system in a shorter time frame. To this end, a set of bench top leach experiment with more frequent sampling over the course of 9 hours was designed to follow initial soluble gold data without polythionate addition (Baseline C) and with 25 mM tetrathionate addition (Conc4T-C). For each sampling time, the reactor’s stirring was paused to allow the slurry to partially settle. An overhead solution aliquot containing some fines in suspension was pipetted, filtered and partitioned for both gold and polythionate analysis (described in Section 3.2). For polythionate analysis, the clear sample was diluted and promptly injected into the Ion Chromatograph for immediate analysis thereby preventing any possibility for further sample degradation.

Figure 57 displays the soluble gold and polythionate concentrations profiles revealing once more gold losses associated with the introduction of tetrathionate into the system.
5.2.2 Leaching Tests without Initial Synthetic Gold

The second series of tests presented in this section did not involve the addition of initial synthetic gold. As such, any soluble gold values measured resulted directly from the leaching of gold contained in the feed material.

5.2.2.1 Baseline Leaching

Figure 58 displays the rates of gold leaching as well as the concentration of polythionates over time for two baseline replicate tests. Gold was seen leaching rapidly and uninterruptedly before levelling off past the 9 hour mark. Baseline tests A and B resulted in the leaching of 58 and 62 % of the gold contained in the feed respectively by means of analyzing the leach residues by fire assay. The replicate tests showed good agreement in terms of polythionate concentrations. Both sulfur mass balances remained constant within 1 % error up to the 24 hour mark.

Figure 58: Replicate baseline leach tests (A & B) of a preg-robbing gold ore (2.96 ppm Au) in the absence of initial gold and polythionate additions (30 wt % PD, 0.1 M CaTS, 50 ppm Cu, pH 8.5, 50 °C).

5.2.2.2 Leaching with Polythionate Addition

Figure 59 displays the concentrations of soluble gold over time for leaches of the refractory preg-robbing ore in the absence of initial gold. All curves showed fast initial gold leaching kinetics. However, it should be noted that for tests with tetrathionate additions, a drop in soluble gold was also observed. In Figure 59 A, compared to test Baseline B, the introduction of 25 mM tetrathionate
into the leach solution at the 30 minute mark, represented by Conc4T, led to a distinct drop in the soluble gold concentration. The same observation was made in Figure 59 B for a second set of leaches distinguished from the first by the incorporation of air-sparging into the system. As was also shown in leaching tests with initial synthetic gold additions, the introduction of polythionate species into the leaching system resulted in repeatable negative impacts on the stability of soluble gold.

![Figure 59: Effect of 25 mM 4T addition (Left) and 25 mM 4T addition in combination with air-sparging (Right) on gold dissolution during the leaching of a preg-robbing gold ore (30 wt % PD, 0.1 M CaTS, 50 ppm Cu, pH 8.5, 50 °C).](image)

Table 18 shows that despite lower soluble gold concentrations and the observed reduction of gold from solution, tests with tetrathionate additions had a higher final gold extraction based on final residue fire assays. Table 18 also indicates that tests with added tetrathionate (Conc4T) required more base addition than the baseline tests resulting in a slight dilution of the leach solutions and possibly accounting for the lower soluble gold concentrations measured in Figure 59. Moreover, tests with aeration (Figure 59 B) were more prone to evaporation and therefore concentration of the leach solutions over extended times, which may also have had an effect on solution analysis. Nonetheless, measures were taken to reduce the uptake of moisture from the reactor by first bubbling the air in a separate water reactor as a pre-humidifying step.

### Table 18: Gold extraction for preg-robbing ore leaching tests

<table>
<thead>
<tr>
<th>Test</th>
<th>Gold extraction (%)</th>
<th>Base consumption (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline B</td>
<td>61.8</td>
<td>2.31</td>
</tr>
<tr>
<td>Conc4T</td>
<td>66.9</td>
<td>13.19</td>
</tr>
<tr>
<td>Baseline + Air Sparging</td>
<td>62.5</td>
<td>2.32</td>
</tr>
<tr>
<td>Conc4T + Air Sparging</td>
<td>63.2</td>
<td>11.75</td>
</tr>
</tbody>
</table>

The addition of 25 mM tetrathionate during the leaching of the preg-robbing ore also resulted in the aforementioned increase in thiosulfate concentration. As shown in Figure 60, thiosulfate was generated through the rearrangement and degradation reactions of higher polythionates. This
significant increase in the thiosulfate reagent concentration can also explain the re-dissolution of the precipitated of gold and the overall higher gold extraction.

![Figure 60: Gold and polythionate concentration profiles of a baseline test (B-no polythionate addition) compared to a test with 25 mM tetrathionate addition at the 30 minute mark (Conc4T) during the leaching of a preg-robbing gold ore (30 wt % PD, 0.1 M CaTS, 50 ppm Cu, pH 8.5, 50 °C).](image)

### 5.3 Discussion

The reduction of gold from solution was consistently observed during the leaching of the preg-robbing ore with and without synthetically added gold shortly after introduction of polythionate salts. The formation of complex solutions containing various polythionate species tend to change in composition over time. When exposed to dissolved oxygen or other oxidants, these solutions will degrade into sulfate. In the absence of strong oxidants, these solutions will take time to reach equilibrium while the metastable species continue to interact and disproportionate. Metastable sulfoxy anions undergo two types of reactions, namely redox and bimolecular nucleophilic displacement ($S_N^2$) reactions (Moses et al. 1984). In addition to this, polythionates can undergo hydrolysis reactions (Druschel et al. 2003).

An aqueous mixture of sulfite, thiosulfate and polythionates is known as Wackenroeder’s solution and is represented by Reaction (48):

$$S_nO_6^{2-} + S_2O_3^{2-} \overset{pH < 7}{\Rightarrow} S_{n+1}O_6^{2-} + SO_3^{2-}$$

$$pH > 7$$

111
Moses et al. (1984) described Wackenroeder’s reaction as a metastable equilibrium whose species are easily removed from the system, therefore making it difficult to predict the behaviour of the solution by applying thermodynamic relationships or even by experimental measurements. For instance, sulfite is a good reducing agent which requires a stabilizer such as glycerol or formaldehyde (Lindgren et al. 1982) to prevent it from oxidizing before analysis. The direction of Reaction (48) depends on the nucleophilicity of the intermediate sulfur species which increase in the order \( \text{SO}_3^{2-} > \text{S}_2\text{O}_3^{2-} > \text{HSO}_3^- > \text{S}_n\text{O}_6^{2-} \) (Moses et al. 1984). Since the \( \text{pK}_a \) of bisulfite lies near pH 7, bisulfite becomes the predominant phase versus sulfite at a pH lower than 7 and thiosulfate becomes the stronger nucleophile to drive the reaction to the right through \( \text{SN}_2 \) reactions known as S-chain lengthening. Reaction (48) is known to be catalyzed by thiosulfate (Zhang et al. 2010) and is thus driven to the right in the presence of relatively high initial concentrations of thiosulfate as in the leaching conditions of this work. Furthermore, the uptake of sulfite from solution by any another process would also favour the chain-lengthening mechanism.

Reaction (48) is the basis for the frequently mentioned thiosulfate catalyzed disproportionation reaction of tetrathionate into tri- and pentathionate (Reactions 27 to 29) described by Zhang and Jeffrey (2010). However, it cannot be ruled out that sulfite, a well-known reducing agent, be also involved in other side reactions which could possibly lead to the reduction of gold from solution as exemplified by Reaction (49).

\[
2\text{Au(S}_2\text{O}_3)_2^{3-} + \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow 4\text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{Au}^0
\]  

49

In the experimental results, aside from the slow hydrolysis of trithionate over time, the polythionate concentration profiles for leaching solutions that contained initially added trithionate showed increases in tetrathionate (e.g. Figure 56). These rises in tetrathionate indicate the possible chain-lengthening mechanism represented by Reaction (48) which also generates the reactive sulfite into the solution. Subsequently, as per Reaction (49), sulfite may be an important contributor to the observed gold precipitation.

Similarly, Aylmore et al. (2014) stated that the mechanisms and pathways for the decomposition of tetrathionate species depended on the \( \text{E}_\text{h} \) and pH of the solutions outlining several reactions for oxygen and alkaline decomposition of tetrathionate from the literature (e.g. Reactions 24 and 25). They proposed a mechanism for the precipitation of gold onto a pyrite mineral in the presence of tetrathionate in an ATS leaching system based on the products of polythionate decomposition.
reactions. It was suggested that the adsorption of tetrathionate on the surface of pyrite could promote the formation of sulfide ions whereby the rate of oxygen consumption by the decomposing tetrathionate would exceed the rate of oxygen mass transfer from solution. Without immediately oxidizing, the resulting reactive sulfide ions may subsequently reduce gold from solution as a gold-sulfide precipitate.

In leaching solutions containing initially added tetrathionate alone or together with trithionate, a fast tetrathionate rearrangement reaction into trithionate and pentathionate was consistently observed. The presence of pentathionate was captured analytically and in each instances was found to react very quickly. In particular, the disappearance of pentathionate during the leaches of the preg-robbing ore is consistently associated with gold losses (Figure 52, Figure 56, Figure 57, Figure 60). It is posited that the oxidation of pentathionate results in the reduction of gold-thiosulfate as per Reaction (50).

\[
10Au(S_2O_3)_2^3^- + 4S_5O_6^{2-} + 6H_2O \rightarrow 5S_4O_6^{2-} + 20S_2O_3^{2-} + 12H^+ + 10Au^0
\]  

5.3.1 Thermodynamic considerations

The feasibility of gold precipitation through redox reactions involving polythionates and other sulfur species can be assessed by conducting basic thermodynamic calculations. The first step is to write out possible reactions and calculate the standard free energies of those reactions using the free energies of formation for each species. Using the temperature and pH of the experimental conditions as well as the concentrations of the species as an estimate of their activities at any moment in time, a non-standard reaction potential can be subsequently calculated.

The standard Gibbs free energy for Reaction (49) was calculated to be −20.9 kJ/mol emphasizing that this reaction is thermodynamically feasible. The standard reaction potential (E°) related to the standard free energy of the reaction by \( \Delta G^\circ = −nF\Delta E^\circ \), is equal to 0.10 V. The reaction potential in non-standard conditions can be calculated using the Nernst Equation given by Reaction (51).

\[
\Delta E = \Delta E^\circ - \frac{RT}{nF}\ln Q
\]  

The constant R is the gas constant (8.314 J/mol K), T is the temperature in K, n is the number of moles of electrons participating in the redox reaction (moles e−/mole), F is Faraday’s constant (96485 C/mol e−) and Q is the reaction quotient. The reaction quotient is equal to the multiplication
of the activities (or concentrations) of the products divided by that of the reactants with each component raised to the power of their stoichiometric coefficient. Given the pH of leach tests are held constant, the activity of the protons can be estimated as the concentration of the $[H^+]$ by taking the antilog of the negative pH of the solution. By selecting a moment in time and the corresponding concentrations from experimental data with the given experimental conditions, an instantaneous non-standard reaction potential can be estimated.

In the case of Reaction (50), the standard reduction potential of the reaction, $E^\circ$, is equal to $-0.14$ V which is unfavorable. However, the calculated non-standard state potential at $50 \, ^\circ C$ and pH $8.5$ using the initial concentrations of test Conc4T-A (Figure 56) becomes favorable with a reaction potential, $E$, of $0.36$ V.

The resulting thermodynamically feasible Reactions (49) and (50) bode well with the experimental data showing gold precipitation initiated shortly after polythionate additions. It is suspected that after the depletion of pentathionate through redox (e.g. Reaction 50) and degradation (e.g. Reaction 30) reactions, gold re-dissolution may be initiated. This process appears to be facilitated by the increased thiosulfate concentration arising from its generation through polythionate degradations.

### 5.4 Partial Conclusions

It appears that surface interactions between preg-robbing minerals and additions of polythionates have the propensity to reduce gold. The reduction of gold from leach solution through redox reactions involving sulfite and/or pentathionate was determined to be thermodynamically possible in the experimental conditions employed. In the case of initial trithionate additions, gold precipitation may be indirectly induced via reaction with generated sulfite through a thiosulfate catalyzed chain-lengthening reaction (Reaction 48). In the case of tetrathionate addition, the precipitation of gold can be ascribed to a reaction with pentathionate formed through a tetrathionate rearrangement reaction (Reaction 29). In stability and leach tests where both tri- and tetrathionate additions were made, a combinations of both reactions could have contributed to the gold losses.

Gold losses from solution reported in the solid phase during the leaching of preg-robbing ores containing added initial gold and polythionate additions. This was well indicated by the gold mass balances of these experiments (Figure 54). Moreover, in the absence of added polythionates, it was
clearly observed that the feed material displayed a gold preg-robbing behaviour over time (Figure 51).

Baseline leaching of the preg-robbing ore without initial synthetic gold resulted in acceptable gold dissolution rates. However, the introduction of 25 mM tetrathionate shortly after the start of leaching results in a visible reduction in soluble gold. This gold reduction is attributed to the reactivity of the strong reductant, pentathionate, arising from the tetrathionate rearrangement reaction. A clear hindrance in the gold dissolution process can be expected if solutions containing polythionates with appreciable concentrations (e.g. recycled streams, entrainment of downstream solutions with resin movement upstream) are contacted with a gold leaching slurry.

The coaction of the adverse effects of higher polythionates on gold stability and the preg-robbing character of the feed material complicates the recovery of gold from solution. In order to mitigate gold losses during the leaching of such solutions two actions are necessary. Firstly, gold that is dissolved needs to be immediately recovered. This is presently achieved in the industry using RIL versus RIP. Secondly, leaching solutions should be maintained at minimum levels of higher order polythionates particularly tetrathionate and pentathionate. This requires careful monitoring of the polythionates in the leach solutions as well as pre-treatment (regeneration) of recycled reagent streams that contain appreciable concentrations of these thiosulfate degradation products.
6 Loading Behaviour of Polythionates on Strong Base IX Resin and their Effects on Gold-thiosulfate Recovery

6.1 Introduction

Zhang and Dreisinger (2002a) suspected that trithionate, formed during the loading, adsorbed strongly onto the resins and replaced the already loaded metal species. However, this observation was not further investigated. More recently, as summarized in Section 2.3.2.4, researchers have determined that trithionate competes strongly with the adsorption of gold-thiosulfate and is therefore considered as the most important counter-anion and may even be used as an eluent (Jeffrey et al. 2010). Moreover, trithionate was deemed to be a baseline species for multi-polythionate systems, where its concentration on resin was in certain proportion to the amount of resin and independent of gold in solution (Muslim 2010a). Clearly, the impact of the presence of polythionates on the loading behaviour of gold on resins is still not completely understood and more importantly has not yet been investigated in the CaTS leaching system. In an industrial context, it was shown that the addition of resin-in-leach mitigated the loss of gold from solution (Figure 4). However, the mechanisms by which gold losses are avoided in the presence of the resin are unknown and will be studied. The aim of this section is to investigate the pathways to gold loss identified in Chapter 4 in the presence of the strong base anion exchange resin, Purolite A500 (Table 14), and the mechanisms by which the simultaneous loading of polythionates may avoid the loss of gold.

6.2 Objectives

The first goal of this chapter is to determine the loading rates of each polythionate species. The rate of adsorption of a polythionate species into a resin bead can be limited by the mass transfer of the anionic species to the ion exchange sites (film diffusion) or by the diffusion of the anionic species within the resin material (intraparticle diffusion). The second objective is to determine the loading distribution coefficients of thiosulfate and polythionates in the CaTS system in combinations with other competing anions. The distribution of a solute between two phases in an ion exchange system is described by \( K \), the distribution coefficient, and is equal to the concentration of the solute in the resin over that in the bulk loading solution (See Section 2.3.2.4.1). Subsequently, the detrimental effect of increasing levels of thiosulfate degradation species on the adsorption rates and effective loading of gold onto Purolite A500 resin from CaTS leaching solution will be investigated. The final objective is to construct aurothiosulfate loading isotherms in the presence of increasing initial
concentrations of polythionates at different polythionate species combinations to further elucidate
the negative effect these species have on gold loading. The gold loading trials were carried out in
typical CaTS leaching conditions using Purolite A500 as the ion exchange material. These loading
isotherms were replicated using an actual industrial recycled barren resin.

6.3 Thiosulfate and Polythionate Loading Rates on Purolite A500

6.3.1 Experimental Procedures

Three 10 g batches of Purolite A500 strong base anion exchange resin were prepared as detailed in
Section 3.1.3.1.1 to be used for loading tests. From such a batch of resin stored in DI water, a transfer
pipette was used to measure out 1 mL of swollen and pre-treated resin into a graduated glass
cylinder. Upon closing in on the targeted volume of beads, the cylinder was lightly tapped onto a
hard working surface to promote bead settling and compacting. Once an accurate volume of resin
was measured, it was transferred into a small plastic weigh boat with any retained DI water drawn
out by a pipette.

Calculated amounts of either calcium thiosulfate stock solution, sodium trithionate or sodium
tetrathionate salt (Table 10) were added to 200 mL volumetric flasks to prepare 4 mM initial
solutions of thiosalts ([S_{x}O_{y}^{2−}]_{0}). The initial solution compositions were measured by ion
chromatography after a 10 times dilution of a 1 mL sample aliquot. The solutions were then
transferred into Erlenmeyer flasks with various agitation options. The first type of agitation was
provided by a temperature controlled shaking water bath (SWB) maintained at 20 °C and a shaking
rate of 100 rpm. Magnetic stirring (MAG) with a two inch stirring rod at rates of 100 and 500 rpm
was also investigated. Lastly, loading tests with overhead agitation (AGI) using a two blade pitched
impellor at rates of 100, 150, 250 and 500 rpm were conducted in beakers. In the case of magnetic
and overhead stirring, solutions were also kept in a water bath regulated at 20 °C. Contact of the 1
mL resin with the solution marked the onset of the loading experiment. Initially, frequent 1 mL
aliquots of solution were extracted and analyzed using the IC to monitor anion concentrations over
time. Gradually, the time in-between sampling was increased accordingly towards the tail end of the
experiments until a stable anion equilibrium concentration ([S_{x}O_{y}^{2−}]_{eq}) was reached. In some
instances, the loading of species on the resin from solution analysis was confirmed by resin stripping
as outlined in Section 3.1.3.1.3.
6.3.2 Results

6.3.2.1 Species Loading

The loading curves for each species at various agitation conditions are grouped together. Figure 61 shows the rates of thiosulfate loading onto the resin over time plotted together with a linear approach to equilibrium model represented by Equation (17) in Section 2.3.2.4.1. The model rate constants $k_1$ for all loading tests were determined by a least square method using Excel’s Solver routine and are reported in Table 19. Figure 62 and 63 show the same types of curves for the loading of trithionate and tetrathionate respectively. It was quickly evident that the rates of loading were directly dependent on the type and rates of agitation employed. The most gentle type of agitation was provided by the shaking water bath which can be best described as a swirling motion with the resin beads slightly shuffling and accumulating at the bottom of the flask. The agitation by means of overhead stirring with a small pitched blade impellor went from gentle at 100 rpm with the resin beads collecting in the center of the beaker and moving upwards towards the blades, to turbulent at 500 rpm where resin beads were well dispersed throughout the beaker. Magnetic agitation at 100 and 500 rpm both provided dispersion of the resin beads throughout the flask with the latter generating a vortex.

Figure 61: Thiosulfate loading rates on Purolite A500 resin as a function of type and rate of agitation. Curves represent the linear approach to equilibrium model fitted to the data points.
Figure 62: Trithionate loading rates on Purolite A500 resin as a function of type and rate of agitation. Curves represent the linear approach to equilibrium model fitted to the data points.

Figure 63: Tetrathionate loading rates on Purolite A500 resin as a function of type and rate of agitation. Curves represent the linear approach to equilibrium model fitted to the data points.
The modelled thiosulfate loading curves for all mixing conditions in Figure 61 showed good fits with the actual concentrations of the species remaining in solution over time. The linear approach to equilibrium engineering model is typically applied to describe film diffusion (McKevitt et al. 2012). An ion-exchange process whose rate is governed by film diffusion control will exhibit increases in loading rates with increasing rates of agitation (Helfferich 1962). As such, the rate constants for thiosulfate loading are indeed seen increasing with more vigorous mixing conditions (Figure 65).

On the other hand, for trithionate (Figure 62) and tetrathionate (Figure 63) loading, the linear approach to equilibrium loading model was a good fit for the measured concentrations at slower and gentler agitation conditions (e.g. 100 rpm AGI). The goodness of the fit for the modelled curves at higher mixing rates decreased as shown by the increasing root mean squared errors given in Table 19.

<table>
<thead>
<tr>
<th>Type of Agitation</th>
<th>k constants (min⁻¹)</th>
<th>k constants (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k-TS</td>
<td>RMS Error</td>
</tr>
<tr>
<td>Muslim et al. (2009) 100 RPM</td>
<td>0.058</td>
<td>-</td>
</tr>
<tr>
<td>SWB 100 RPM</td>
<td>0.006</td>
<td>0.06</td>
</tr>
<tr>
<td>AGI 100 RPM</td>
<td>0.018</td>
<td>0.04</td>
</tr>
<tr>
<td>AGI 150 RPM</td>
<td>0.056</td>
<td>0.03</td>
</tr>
<tr>
<td>AGI 250 RPM</td>
<td>0.084</td>
<td>0.06</td>
</tr>
<tr>
<td>MAG 100 RPM</td>
<td>0.104</td>
<td>0.04</td>
</tr>
<tr>
<td>AGI 500 RPM</td>
<td>0.123</td>
<td>0.05</td>
</tr>
<tr>
<td>MAG 500 RPM</td>
<td>0.138</td>
<td>0.02</td>
</tr>
</tbody>
</table>

During film diffusion control, beyond a critical agitation rate, as the rate of agitation reaches a limiting hydrodynamic efficiency, no further increases in the ion-exchange rate should be observed (Helfferich 1962). At this stage, the rate-limiting step is instead governed by particle diffusion. An engineering model frequently used to describe the rate of diffusion of ions through an ion exchanger is Vermeulen’s quadratic approach to equilibrium given by Equation (52) (Fleming et al. 1980, McKevitt et al. 2012).
\[
[S_xO_y^{2-}]_t = [S_xO_y^{2-}]_0 - \left( \sqrt{1 - \exp(-4k_vt)} \times \left( [S_xO_y^{2-}]_0 - [S_xO_y^{2-}]_{eq} \right) \right)
\]

where \( y = 6 \) if \( x \geq 3 \) (polythionates) or \( y = 3 \) if \( x = 2 \) (thiosulfate)

and \( k_v = \frac{\pi^2 D_p}{d_p^2} \)

As shown in Figure 64, the Vermeulen model for intraparticle diffusion fitted the solution data of tetrathionate loading at a high agitation rate much better than the linear approach to equilibrium model.

![Model Comparisons](image)

**Figure 64:** Comparison of models fits for the loading of tetrathionate onto 1 mL Purolite A500 resin mixed by an overhead agitator at 500 rpm.

The same observations can be made for trithionate loading at more vigorous agitation conditions as summarized in Table 20.
Table 20: Qualitative assessment of the better fit curve for the experimental data between the Linear (L) and the Vermeulen (V) models.

<table>
<thead>
<tr>
<th>Type and Rate of Agitation</th>
<th>Mixing Condition</th>
<th>TS</th>
<th>3T</th>
<th>4T</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWB 100 RPM</td>
<td>Gentle</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>AGI 100 RPM</td>
<td></td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>AGI 150 RPM</td>
<td></td>
<td>L</td>
<td>V/L</td>
<td>V</td>
</tr>
<tr>
<td>AGI 250 RPM</td>
<td></td>
<td>L</td>
<td>V</td>
<td>V</td>
</tr>
<tr>
<td>MAG 100 RPM</td>
<td></td>
<td>L</td>
<td>V</td>
<td>V</td>
</tr>
<tr>
<td>AGI 500 RPM</td>
<td></td>
<td>L</td>
<td>V</td>
<td>V</td>
</tr>
<tr>
<td>MAG 500 RPM</td>
<td>Vigorous</td>
<td>L</td>
<td>V</td>
<td>V</td>
</tr>
</tbody>
</table>

This qualitative assessment of the better fit curve between the two models is in good agreement with the plotting of the calculated rate constants, $k_l$, as a function of increasingly more vigorous mixing condition given in Figure 65. There, the thiosulfate rate constant is seen continually increasing indicating the mass transfer process is under film diffusion control. As for trithionate and tetrathionate, the rate constants appear to stabilize starting with 150 rpm overhead agitation indicating the rate-limiting step switches to the diffusion of the anions through the ion exchange particles.

![Figure 65](attachment:image.png)

Figure 65: Graphical representation of calculated rate constants ($k_l$) using a linear approach to equilibrium model for species loading (TS, 3T & 4T) ordered by increasingly more vigorous mixing conditions.

Figure 65 also displays that once a reasonably fast mixing condition has been reached, the loading rates for the smaller trithionate molecules are consistently faster than that of the larger tetrathionate...
molecules. This is to be expected as the rate constant, \( k_v \), in Equation (52) is proportional to the diffusivity, \( D_p \), of the anion which is a physical constant that in part depends on the size of the ionic species.

### 6.3.2.2 Species Stripping

In most cases, after the loading of the target species from solution, the resin material was collected and stripped twice with 0.2 M sodium perchlorate and analyzed (See Section 5.1.2.6). Table 21 summarizes the species loading on the resin by means of the strip solution analysis compared to the loading solution mass balance. The two methods are in good agreement with an average calculated error of 2.5 %. Moreover, the average target species loading on the resin reported in milli-equivalents per liter is very close to the theoretical capacity of the resin (1150 meq/L).

Table 21: Calculated thiosulfate and polythionate loadings on 1 mL Purolite A500 resin by strip solution analysis compared to loading solution mass balance.

<table>
<thead>
<tr>
<th>Loading Test</th>
<th>Strip Solution Mass Balance</th>
<th>Loading Solution Mass Balance</th>
<th>Target Species Resin Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Target Species ( \mu )moles</td>
<td>Other Species ( \mu )moles (hrs(_{eq}))</td>
<td>All Species ( \mu )moles</td>
</tr>
<tr>
<td>TS AGI 100</td>
<td>515</td>
<td>6.1 (8.0)</td>
<td>539</td>
</tr>
<tr>
<td>TS AGI 150</td>
<td>511</td>
<td>2.7 (3.0)</td>
<td>528</td>
</tr>
<tr>
<td>TS AGI 250</td>
<td>504</td>
<td>5.4 (4.1)</td>
<td>511</td>
</tr>
<tr>
<td>TS AGI 500</td>
<td>522</td>
<td>5.9 (5.4)</td>
<td>545</td>
</tr>
<tr>
<td>TS SWB 100</td>
<td>517</td>
<td>6.6 (45.8)</td>
<td>528</td>
</tr>
<tr>
<td>3T AGI 100</td>
<td>604</td>
<td>28.2 (22.4)</td>
<td>619</td>
</tr>
<tr>
<td>3T AGI 150</td>
<td>607</td>
<td>1.6 (6.4)</td>
<td>616</td>
</tr>
<tr>
<td>3T AGI 250</td>
<td>590</td>
<td>1.8 (5.9)</td>
<td>626</td>
</tr>
<tr>
<td>3T AGI 500</td>
<td>649</td>
<td>1.6 (5.0)</td>
<td>651</td>
</tr>
<tr>
<td>3T MAG 100</td>
<td>616</td>
<td>29.1 (23.6)</td>
<td>649</td>
</tr>
<tr>
<td>3T MAG 500</td>
<td>600</td>
<td>36.9 (24.1)</td>
<td>618</td>
</tr>
<tr>
<td>3T SWB 100</td>
<td>611</td>
<td>6.3 (46.3)</td>
<td>637</td>
</tr>
<tr>
<td>4T AGI 500</td>
<td>635</td>
<td>1.3 (7.3)</td>
<td>618</td>
</tr>
<tr>
<td>4T SWB 100</td>
<td>600</td>
<td>0.9 (46.3)</td>
<td>602</td>
</tr>
<tr>
<td>Average</td>
<td>577</td>
<td>9.6</td>
<td>592</td>
</tr>
</tbody>
</table>

Table 1 shows evidence that species other than the targeted ones were also loaded onto the resin from the loading solution. This was determined to be a result of the degradation of the initial solution composition over time where the degradation products also loaded onto the resin. For each target species, there is a correlation between the time taken to reach equilibrium (hrs\(_{eq}\)) and the amount of other species loaded on the resin. The rate of agitation also plays a role but to a much lesser degree (e.g. TS AGI 100 vs. SWB 100).
These results show that once loaded onto the ion exchange material, the polythionate species remain stable and their elution from the ion exchanger can be used for mass balancing purposes.

6.3.3 Discussion

Although the leaching system differed slightly (sodium thiosulfate vs. CaTS), the thiosulfate, tri- and tetrathionate loading rate constants determined by Muslim et al. (2009) (Table 19) are dependent on the type and rate of agitation selected (100 rpm overhead stirring) where the diffusion of ions in the adherent films was likely rate-limiting. Therefore, the rate constants measured by Muslim et al. (2009) appear to be underestimated as the mixing regime was mild enough to be characterized by film diffusion in comparison with the rate constants measured in this work. Nonetheless, the rate constants obtained from the work herein are within the same order or magnitude and follow the same trend in that the rates of species loading onto the resin increase in the order of tetrathionate, trithionate and thiosulfate.

6.4 Competitive Loading of Polythionate Species on Resin

In the previous section it was confirmed that the loading of thiosulfate anions from calcium thiosulfate solutions on Purolite A500 resin occurred at a faster rate than both trithionate and tetrathionate with the latter anions having the slowest loading rates. In the following section, the competitive adsorption between any solutes for ion exchange sites was investigated. Similar to the work initiated by Muslim et al. (Section 2.3.2.4.1), it is important to investigate the competitive loading behaviour of polythionates with respect to one another and with respect to the gold-thiosulfate complex. As these types of fundamental studies have yet to have been conducted on the CaTS leaching system, an opportunity exists to compare and build upon the limited knowledge regarding the behaviour of the various thiosalt species and the gold-thiosulfate complex.

As pointed out by O’Malley (2002) several models fail in describing the loading of particular combinations of complexes on anion exchange resins such as in the case of gold cyanide anions in the presence of zinc cyanide. Of these species, the gold complex is initially the first to be loaded but is soon displaced by the zinc cyanide anions. This phenomenon is due to the differences in the rate of diffusion of the various species in both the Nernst diffusion layer and in the resin matrix. In the aforementioned case the gold cyanide adsorption through the diffusion layer is initially favoured due to its higher surface diffusion coefficient. However, zinc cyanide gradually displaces the gold
complex because of a greater equilibrium constant on the resin. As demonstrated in this case, the competitive adsorption on resin between polythionates and gold-thiosulfate may also result in complicated interactions between the anions.

**6.4.1 Experimental Procedures**

Similarly to the single species loading experiments, 200 mL solutions were prepared containing 4 mM of an anion species (4 mM $S_xO_y^{2−}$). To such initial solutions, increasing concentrations of a competing anion (1, 2, and 4 mM $S_aO_b^{2−}$) were added before taking an initial solution sample and transferring the solution into a reactor. To each reactor, a specific volume of Purolite A500 resin was added marking the onset of the competitive loading process. Mixing was provided by a pitched blade impellor connected to an overhead agitator set to 500 rpm to maximize mass transfer as attested by the results in the previous section. Periodic sampling of the loading solutions were made until a stable equilibrium was reached. This procedure was applied for three different initial resin volumes namely 1, 0.75 and 0.5 mL. Using the methods described in Section 2.3.2.4.1, the equilibrium concentration of the target species loaded on the resin ([R$_2S_xO_y^{2−}$]) was plotted over the equilibrium concentration of that same species remaining in solution ([S$_xO_y^{2−}$]) in the presence of an increasing concentration of initial counter-anion ([S$_aO_b^{2−}$]). Data from each equilibration test plotted in these loading isotherms were subsequently used as a data points for the construction of equilibrium plots. In these equilibrium plots, the slope of the trendline passing through the origin gives the distribution coefficient between the two competing anions.

**6.4.2 Results**

6.4.2.1 Competitive loading in a two solute system

**6.4.2.1.1 Thiosulfate Loading in the Presence of Trithionate Counter-anions**

The thiosulfate loading isotherms given in Figure 66 show the equilibrium concentration of thiosulfate on the resin was greatly decreased by increasing levels of trithionate as the counter-anion. Accordingly, as less thiosulfate was loaded or conversely, previously loaded thiosulfate was being displaced by trithionate, the equilibrium concentration of thiosulfate left in solution remained relatively unchanged from its initial concentration (~4 mM).
Figure 66: Equilibrium loading isotherms for initial solutions containing 4 mM thiosulfate in the presence of increasing concentration of trithionate as a counter-anion.

The attainment of equilibrium by the resin during the loading process was followed by periodic sampling of the loading solutions containing increasing initial amounts of counter-anions in contact with variable volumes of resin. Such curves for the loading of thiosulfate in the presence of trithionate are gathered in Figure 67 A-C. These curves demonstrate several loading behaviours. Firstly, as the resin volumes increased, more exchange sites were available for molecular adsorption and thus overall more anionic species could be taken up from solution. However, the loading systems were designed to contain enough solutes initially such that upon adsorption onto the given resin volume and reaching an equilibrated concentration based on the resin capacity, a balance of solutes would remain in solution. For example, given the minimum initial moles of solutes in a solution was 1 mmole (4 mM TS plus 1 mM 3T in 0.2 L) and the largest volume of resin in contact with such loading solutions was 1 mL (1150 meq/L capacity), a minimum 42.5 % of all initial solutes should remain in solution. In the case of an initial 4 mM of both TS and 3T in contact with 0.5 mL resin, a maximum of 82 % of all initial solutes are expected to remain in solution. Therefore, a competition for ion exchange sites is always to be expected in a loading system comprised of two solutes with different loading rates. Ultimately, the species that are preferentially loaded will occupy more loading sites and be more strongly adsorbed.

Figure 67 A shows that fast initial thiosulfate loading occurred during the first 15 minutes of contact with the resin at all resin volumes in the presence of 1 mM trithionate. At the same time trithionate
was also being removed from solution although slower than its counterpart. In the case of the higher loading capacity of 1 mL resin, as the loading progressed and the resin capacity was reached by the one hour mark, all initial trithionate ions (1 mM) were adsorbed from solution with the balance of the ion exchange sites being occupied by a constant thiosulfate concentration. However, at lower resin volumes of 0.5 and 0.75 mL and hence an overall lower number of functional sites available for adsorption, thiosulfate anions were displaced and released back into solution to preferentially load remaining trithionate. Similarly, as the initial concentration of trithionate was increased to 2 mM and 4 mM as given by Figure 67 B and C respectively, increasing fractions of faster and earlier loaded thiosulfate were released back into solution to make way for trithionate.
Figure 67: Graphical representation of the competitive loading process on resin between competing anions. Initial [TS] = 4 mM with increasing initial [3T] counter-anion (1, 2, 4 mM for A, B & C). Resin volumes range from 0.5 mL to 1 mL.
Table 22 summarizes the final loading capacities based on resin stripping and the percentages of each solute loaded on the resin. Clearly evident was the increasing trithionate occupancy on the resin as a function of initial trithionate concentration and the secondary effect of decreasing the volume of resin on the preferential loading of trithionate over thiosulfate. The latter point is explained by the higher concentrations of trithionate remaining in solution for lower resin volumes resulting in greater concentration gradients and therefore more driving force for trithionate adsorption. Moreover, at equimolar initial concentrations of trithionate and thiosulfate (4 mM each), Table 22 convincingly shows the preferential loading of trithionate by occupying over 97% of all ion exchange sites on the resin. Lastly, the averaged resin capacity for all loading tests was 1166 meq/L, which is in good agreement with the theoretical resin capacity of 1150 meq/L. The discrepancies in individually measured capacities (SD= 80.7) was attributed to the difficulty in accurately preparing small measured initial resin volumes using graduated cylinders.

<table>
<thead>
<tr>
<th>[3T]_{ini} (mM)</th>
<th>Resin Volume (mL)</th>
<th>Final Capacity (meq/L)</th>
<th>TS Loading (%)</th>
<th>3T Loading (%)</th>
<th>3T Remaining in Sol. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1113</td>
<td>63.2</td>
<td>36.8</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>0.75</td>
<td>1048</td>
<td>48.4</td>
<td>51.6</td>
<td>1.6</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>1236</td>
<td>35.3</td>
<td>64.7</td>
<td>3.7</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1188</td>
<td>34.7</td>
<td>65.3</td>
<td>1.9</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>1124</td>
<td>14.2</td>
<td>85.8</td>
<td>8.5</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>1288</td>
<td>6.6</td>
<td>93.4</td>
<td>24.2</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1186</td>
<td>3.1</td>
<td>96.9</td>
<td>26.4</td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>1057</td>
<td>1.6</td>
<td>98.4</td>
<td>49.8</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>1254</td>
<td>1.3</td>
<td>98.7</td>
<td>61.7</td>
</tr>
</tbody>
</table>

**6.4.2.1.2 Thiosulfate Loading in the Presence of Tetrathionate Counter-anions**

Figure 68 shows the loading isotherms for 4 mM thiosulfate in the presence of increasing levels of tetrathionate. After equilibration with low initial tetrathionate concentrations of 1 mM, all of the counter-anions (4T) loaded together with discernable levels of thiosulfate as measured from the resin stripping solutions.
This was also confirmed via Figure 69 showing the complete adsorption of tetrathionate from solution in equilibrium with thiosulfate within three hours. On the other hand, at higher initial tetrathionate concentrations of 2 and 4 mM, very low thiosulfate concentrations were stripped from the resin beads. This implies that tetrathionate was preferentially loaded onto the resin occupying the majority of loading sites with excess tetrathionate beyond the resin's capacity remaining in solution during equilibration together with thiosulfate. In fact, equilibrium solution analyses indicated the generation of thiosulfate in surplus to the initial 4 mM thiosulfate present in solution as well as the emergence of small amounts of trithionate. This can be attributed to the decomposition of tetrathionate into both thiosulfate and trithionate as per Reaction (31). This decomposition reaction is known to be catalyzed by the presence of thiosulfate (Zhang et al. 2010). The stoichiometry of this reaction could not be confirmed as the initial anions present in solution as well as those being generated through the decomposition reaction were simultaneously being loaded into the anion exchange material. However, the presence of trithionate species were also detected in the stripping solutions of the equilibrated resin. Taken together, the competitive loading process of 2 or 4 mM tetrathionate over 4 mM thiosulfate proceeded with the fast initial uptake of thiosulfate followed by its displacement by the more strongly adsorbed tetrathionate species. Afterwards, excess tetrathionate remaining in solution to equilibrate with thiosulfate was seen decomposing into additional thiosulfate and trithionate. In the case of 1 mM initial tetrathionate, all tetrathionate anions
were loaded onto the resin thereby preventing its decomposition during the attainment of equilibrium (Figure 69).

![Graphical representation of the competitive loading process on resin between competing anions. Initial [TS] = 4 mM with initial [T] = 1 mM as counter-anion. Resin volumes range from 0.5 mL to 1 mL.](image)

**6.4.2.1.3 Trithionate Loading in the Presence of Tetrathionate Counter-anions**

In the two previous competitive loading scenarios, increasing concentrations of tri- and tetrathionate were added as counter-anions into solutions containing 4 mM thiosulfate as CaTS with varying volumes of resin. Although fast initial loading of thiosulfate occurred, both counter-anions displayed extremely preferential loading relative to thiosulfate at equilibrium. The following loading scenario aims at determining the competitive loading on Purolite A500 resin between trithionate and tetrathionate.

The loading isotherm given in Figure 70 shows that upon addition of increased concentrations of counter-anions, in this case tetrathionate, the loading of trithionate onto the resins decreased significantly.
The introduction of tetrathionate anions was expected to compete with trithionate for ion exchange sites on the resin until an equilibrium between the two species on the resin and in solution could be reached. Figure 71 shows the loading process between the two solutes. During thiosulfate loading in the presence of either 1 mM trithionate (Figure 67 A) or tetrathionate (Figure 69), both the counter-anions ended up being much more preferentially loaded onto the resin versus thiosulfate and were therefore completely removed from solution. In comparison, Figure 71 shows that 1 mM trithionate added as the counter-anion to 4 mM initial tetrathionate was not completely removed from solution. Instead, a clear equilibrium between the two solutes was reached.

<table>
<thead>
<tr>
<th>Distribution Coefficients</th>
<th>Work Herein</th>
<th>Muslim et al. (2009)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{4/2}$</td>
<td>226</td>
<td>N/A</td>
</tr>
<tr>
<td>$K_{3/2}$</td>
<td>179</td>
<td>95.1</td>
</tr>
<tr>
<td>$K_{4/3}$</td>
<td>2.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**Figure 70:** Equilibrium loading isotherms for initial solutions containing 4 mM trithionate in the presence of increasing concentration of tetrathionate as a counter-anion.
6.4.2.2 Distribution Coefficients

The degree of preferential loading on the resin between an anion, $S_xO_y^{2-}$, and a competing anion, $S_aO_b^{2-}$, is given by the distribution coefficient $K_{a/x}$ as reviewed in Section 2.3.2.4.1. To determine the coefficient’s value, an equilibrium plot was constructed using as data points the concentration of a solute loaded on the resin ($[R_SxO_y^{-}]$, determined by means of resin stripping) divided by its concentration remaining in solution at equilibrium ($[S_xO_y^{2-}]$) plotted over that of the counter-anion ($[R_aS_bO_b^{2-}]$/$[S_aO_b^{2-}]$) for several equilibrium tests. The slope of the trendline passing through the origin gives the distribution coefficient between the two competing anions. Figures 72 and 73 yielded distribution coefficients $K_{3/2} = 179$ and $K_{4/2} = 226$ respectively. These values indicate that tetrathionate loads more strongly than trithionate on the resin relative to thiosulfate. As a result, it was anticipated that $K_{4/3}$ be greater than 1 which would indicate stronger tetrathionate loading on the resin relative to trithionate. Figure 74 confirmed this by yielding a value of 2.39 for the slope representing $K_{4/3}$. These results confirm the order of relative affinities for anions loading onto Purolite A500 at equilibrium as: $S_4O_6^{2-} > S_3O_6^{2-} > S_2O_3^{2-}$ (Choi et al. 2012a). Table 23 compares the coefficients measured here with values established by Muslim et al. (2009) in a sodium thiosulfate system that appears to have been limited by mass transfer. The values from the literature are within the same order of magnitude as those determined in this work but are lower as was suspected due to mass transfer limitations.
Figure 72: Equilibrium plot giving the distribution coefficient $K_{3/2}$ as the slope of the trendline.

Figure 73: Equilibrium plot giving the distribution coefficient $K_{4/2}$ as the slope of the trendline.

Figure 74: Equilibrium plot giving the distribution coefficient $K_{4/3}$ as the slope of the trendline.
6.5 Effect of Polythionates on the Loading of Gold-Thiosulfate

In a continuous gold-thiosulfate leaching process where the leaching is occurring concurrently with recovery by resin-in-leach, fresh feed material and either fresh or regenerated resin are being pumped into the first reaction vessel. The best gold recovery results are achieved when soluble gold is immediately adsorbed thus preventing it from precipitating or being preg-robbed. Therefore, it is of interest to determine the rates of gold loading and observe the effects of competing anions that are known to be present in solution. An effective gold loading process will limit the overall exposure of soluble gold to higher polythionates which have the potential to reduce gold from solution as was shown in Chapter 4.

6.5.1 Experimental Procedures

Gold loading experiments were performed by introducing set volumes of resin (5 or 10 mL) into 2 L of 0.1 M synthetic calcium thiosulfate leaching solutions initially containing 8 mg/L gold as sodium aurothiosulfate and 50 mg/L cupric with increasing levels of polythionates (1, 2 or 4 mM 3T or 4T). The natural pH of the solutions was 8 and the reactors were maintained at 25 °C using a water bath. Overhead agitation was provided by a four blade pitched impellor rotating at 500 rpm and the solutions were allowed to equilibrate for 24 hours with periodic sampling of gold and polythionates from solution. Upon reaching equilibrium, a final solution sample was taken and the resin was separated and rinsed. The gold content in the resin was determined by fire assay or via resin stripping (See Section 3.1.3.1.3) with the latter method also giving the loading of polythionates on the resin.

6.5.2 Results

6.5.2.1 Gold Loading in the Presence of Increasing Concentrations of Tetrathionate

The following sections present the effects of increasing levels of tetrathionate on AuTS loading from synthetic gold-CaTS solutions with varying initial resin volumes.

6.5.2.1.1 10 mL Purolite A500

The loading process of gold onto an anion exchange resin material from a typical CaTS leaching solution in the presence of increased initial tetrathionate concentrations was captured by periodic sampling of the loading solutions. Figure 75 shows the resulting gold uptake on 10 mL resin as a
function of time. Each set of data points were successfully fitted with the Vermeulen approximation model for intraparticle diffusion indicating that the gold loading process was limited by the diffusion of the gold complexes inside the macroporous resin material. It appears that the gold loading process reached equilibrium before the six hour mark for initial tetrathionate concentrations of 1 and 2 mM with close to complete adsorption of gold. In the case of 4 mM tetrathionate, the time for equilibrium shifted to approximately the 12 hour mark. Figure 75 clearly shows that increasing the initial concentration of tetrathionate hindered the gold loading rate as well as the overall gold uptake by the resin as summarized by Table 25.

Furthermore, it was found that the loading of gold was much more favorable in the presence of 4 mM tetrathionate when the background solution of 0.1 M CaTS was removed as displayed by Figure 76. Conversely, with a 0.1 M CaTS background solution, the high concentration of thiosulfate anions, which also have an affinity for adsorption sites albeit a weaker one, can successfully compete with tetrathionate against the relatively low concentration of aurothiosulfate complexes and occupy a significant portion of the adsorption sites. To further illustrate this, the thiosulfate loading
measured by resin stripping was 178.6 meq/L for the loading solution with a 0.1 M CaTS background compared to just 3.1 meq/L without the background solution.

The concentrations in solution for all other constituents during the loading process on 10 mL resin at increasing initial concentrations of tetrathionate are shown Figure 77. A first important observation was the emergence of both pentathionate and trithionate concentrations in 0.1 M CaTS solutions upon addition of the initially targeted levels of tetrathionate. This is recognized to be a result of the previously discussed tetrathionate rearrangement reaction (Reaction 29) which is known to be accelerated by the presence of thiosulfate. In light of this, the tetrathionate rearrangement reaction did not occur in the absence of the 0.1 M CaTS background solutions as shown by Figure 77 D.

As fresh resin material was introduced into each loading solution (2 L), all solutes present had the potential to be adsorbed initially. The rate at which solutes were loaded was limited to their individual diffusion rates through the macroporous resin material which is correlated to their size and charge. The smaller thiosulfate molecules with a higher loading rate constant (Table 19) were quickly adsorbed initially to the extent that drops in thiosulfate solution concentrations were
noticeable. Considering the comparably large initial thiosulfate concentrations (100 mM) in contrast to all other solutes, small changes in thiosulfate concentrations resulted in significant loadings on the given 10 mL resin volume. In the case of 1 mM initial 4T (Figure 77 A), all polythionate species and aurothiosulfate complexes were successfully removed from solution at equilibrium. The initially loaded thiosulfate, on the other hand, was gradually displaced by larger polythionate species as they slowly diffused and preferentially adsorbed onto the active sites inside the resin matrix. At initial tetrathionate concentrations of 2 and 4 mM, the total loading capacity of the resin was reached before all higher polythionates could be adsorbed from solutions. As a result of the competition of higher polythionates for adsorption sites, some initially loaded trithionate was gradually displaced from the resin back into solution in favor of preferentially loaded tetrathionate and pentathionate. The fate of the detected pentathionate is difficult to interpret in these equilibrium tests. Firstly, although its presence was confirmed from analysis using ion chromatography, its quantification was based on a linear correlation established in Section 3.2.2.3. This method may introduce some uncertainty when scaled up to greater pentathionate peak areas observed in strip solutions. As such, two values are given in Table 25 for the total loading capacities on the resin, namely one that takes into account pentathionate which overestimates the theoretical capacity and another without pentathionate which underrepresents the theoretical capacity. Secondly, before loading, pentathionate may also degrade via Reaction (30) thereby contributing to the generation of excess thiosulfate. Figure 77 C displays the complex adsorption-desorption process of higher polythionates towards reaching equilibrium over the course of 24 hours. In this case, pentathionate loading on the resin closely rivaled the tetrathionate loading on the resin. This is demonstrated in Table 24 in terms of solute loading fractions on the resin where pentathionate loaded to similar levels as tetrathionate albeit a much lower initial concentration. This implies pentathionate has a stronger affinity than tetrathionate for resin ion-exchange sites.
Figure 77: Gold and polythionate solution concentrations during the loading process onto 10 mL resin with increasing initial [4T] (A = 1 mM, B = 2 mM, C = 4 mM) with a 0.1 M CaTS background. D = 4 mM 4T without a CaTS background.

### Table 24: Fractional breakdown of measured resin capacity by solute.

<table>
<thead>
<tr>
<th>Volume Resin (mL)</th>
<th>Polythionate</th>
<th>Fraction of Total Capacity by Solute</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Polythionate]</td>
<td>% TS</td>
</tr>
<tr>
<td>10</td>
<td>4 mM 4T*</td>
<td>0.24</td>
</tr>
<tr>
<td>10</td>
<td>4 mM 4T</td>
<td>12.40</td>
</tr>
<tr>
<td>10</td>
<td>2 mM 4T</td>
<td>34.18</td>
</tr>
<tr>
<td>10</td>
<td>1 mM 4T</td>
<td>58.59</td>
</tr>
<tr>
<td>5</td>
<td>4 mM 4T</td>
<td>8.48</td>
</tr>
<tr>
<td>5</td>
<td>2 mM 4T</td>
<td>18.12</td>
</tr>
<tr>
<td>5</td>
<td>1 mM 4T</td>
<td>38.94</td>
</tr>
<tr>
<td>5</td>
<td>4 mM 3T</td>
<td>14.91</td>
</tr>
<tr>
<td>5</td>
<td>2 mM 3T</td>
<td>28.36</td>
</tr>
<tr>
<td>5</td>
<td>1 mM 3T</td>
<td>47.42</td>
</tr>
</tbody>
</table>

*no 0.1 M CaTS background, 0.4 mM thiosulfate introduced initially by aurothiosulfate stock solution.

### 6.5.2.1.2 5 mL Purolite A500

The same experimental conditions previously used for synthetic gold-CaTS loading solution were reproduced with less resin, namely 5 mL. The resulting loading rates of aurothiosulfate onto the Purolite A500 resin in the presence of increased initial tetrathionate concentrations is shown in
Figure 78. As expected, the rates of loading and the overall uptake of gold from solution followed the same trends as with 10 mL resin (Figure 75) but in a slower and less efficient way. The rate constants \( k_v \), Equation 52) determined by a least square method and given in Table 25 show that the adsorption of gold was hindered by the presence of competing anions as well as by the reduced number of available active sites due to the decrease in resin volume.

![Graph](image)

Figure 78: Aurothiosulfate loading rates on 5 mL Purolite A500 resin in the presence of increasing levels of tetrathionate (4T) in 0.1 M CaTS solutions containing 50 mg/L cupric. Curves represent the Vermeulen approximation model fitted to the data points.

The concentrations in solution for all other constituents during the loading process on 5 mL resin at increasing initial concentrations of tetrathionate are shown in Figures 79 to 81. The same observations as described above for the loading process onto 10 mL resin are also valid.
Figure 79: Gold and polythionate solution concentrations during the loading process onto 5 mL resin with 1 mM initial 4T.

Figure 80: Gold and polythionate solution concentrations during the loading process onto 5 mL resin with 2 mM initial 4T.

Figure 81: Gold and polythionate solution concentrations during the loading process onto 5 mL resin with 4 mM initial 4T.
6.5.2.2 Gold Loading in the Presence of Increasing Concentrations of Trithionate

The following section presents the effects of increasing levels of trithionate on AuTS loading from synthetic gold-CaTS solutions with an initial resin volume of 5 mL.

**6.5.2.2.1 5 mL Purolite A500**

Based on the results from Section 6.4 confirming the greater affinity of tetrathionate on the resin over trithionate ($K_{4/3} = 2.4$), it should be predictable that trithionate would have a lesser impact than tetrathionate in obstructing the gold loading process. This was accurately demonstrated in Figure 82 for gold-CaTS loading solutions of increasing initial tri- or tetrathionate concentrations each containing 5 mL of ion exchange resin beads.

![Figure 82](image)

At equal molarities, tetrathionate was consistently more detrimental to gold loading than trithionate. This is also evident in Table 25 where higher loading rate constants determined for trithionate go in hand with lower equilibrium gold concentrations which ultimately resulted in higher final resin gold loadings compared to loading tests involving tetrathionate.
Table 25: Summary of gold loading rate constants, gold loadings on a dry resin basis and total resin loadings for equilibrium loading tests with increasing initial polythionate concentrations and resin volumes.

<table>
<thead>
<tr>
<th>Volume Resin (mL)</th>
<th>[PolyTS]</th>
<th>Equilibrium [Au] (mg/L)</th>
<th>Rate Constant $k_v$ (1/min)</th>
<th>Au Resin Loading (mg/kg)</th>
<th>Total Resin Loading Excl. [5T] (meq/L)</th>
<th>Total Resin Loading Incl. [5T] (meq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4 mM 3T</td>
<td>1.82</td>
<td>1.56E-03</td>
<td>5743</td>
<td>1219</td>
<td>1238</td>
</tr>
<tr>
<td>5</td>
<td>2 mM 3T</td>
<td>0.57</td>
<td>2.03E-03</td>
<td>7470</td>
<td>1205</td>
<td>1217</td>
</tr>
<tr>
<td>5</td>
<td>1 mM 3T</td>
<td>0.12</td>
<td>2.60E-03</td>
<td>8089</td>
<td>1208</td>
<td>1219</td>
</tr>
<tr>
<td>5</td>
<td>4 mM 4T</td>
<td>3.66</td>
<td>1.16E-03</td>
<td>4267</td>
<td>873</td>
<td>1376</td>
</tr>
<tr>
<td>5</td>
<td>2 mM 4T</td>
<td>1.27</td>
<td>1.30E-03</td>
<td>6558</td>
<td>962</td>
<td>1345</td>
</tr>
<tr>
<td>5</td>
<td>1 mM 4T</td>
<td>0.25</td>
<td>2.01E-03</td>
<td>7509</td>
<td>1073</td>
<td>1307</td>
</tr>
<tr>
<td>10</td>
<td>4 mM 4T*</td>
<td>0.04</td>
<td>7.18E-03</td>
<td>3459</td>
<td>1241</td>
<td>1312</td>
</tr>
<tr>
<td>10</td>
<td>4 mM 4T</td>
<td>1.04</td>
<td>1.93E-03</td>
<td>2923</td>
<td>947</td>
<td>1441</td>
</tr>
<tr>
<td>10</td>
<td>2 mM 4T</td>
<td>0.19</td>
<td>3.69E-03</td>
<td>3552</td>
<td>1054</td>
<td>1337</td>
</tr>
<tr>
<td>10</td>
<td>1 mM 4T</td>
<td>0.05</td>
<td>6.06E-03</td>
<td>4082</td>
<td>1082</td>
<td>1225</td>
</tr>
</tbody>
</table>

*no 0.1 M CaTS background, 0.4 mM thiosulfate introduced initially by aurothiosulfate stock solution.

The concentrations in solution of all constituents during the loading process on 5 mL resin at increasing initial concentrations of trithionate are shown in Figures 83 to 85. The average total loading on the resin at equilibrium for these three equilibration tests, determined by resin stripping, was 1238 meq/L (theoretical resin capacity 1150 meq/L).

Several observations can be made by comparing the three loading processes. Firstly, in the presence of only 1 mM trithionate (Figure 83), fast initial uptake of thiosulfate from the bulk solution was observed which is related to its higher loading rate constant (See Figure 65). At 2 mM (Figure 84) and 4 mM initial trithionate (Figure 85) less thiosulfate was removed from solution below its initial concentration. In fact, for the latter two cases, it can be seen that thiosulfate increased above its initial concentration by the 1.5 hour mark. The generation of thiosulfate is attributable to the trithionate hydrolysis (Reaction 26) which can still occur at the same time as trithionate is being loaded onto the resin. The fraction of loading sites occupied by trithionate on the resin at equilibrium were 40, 58 and 69 % for increasing initial trithionate concentrations of 1, 2 and 4 mM respectively. Based on solution analysis however, the differences in initial and final trithionate solution concentrations converted into resin loadings would have resulted in even higher loading fractions. Using this method, trithionate anions would have occupied 50, 78 and 103 % of the actual measured resin loading capacity for initial 3T concentrations of 1, 2 and 4 mM respectively. This suggests that trithionate degradation also played a role in the later decrease of trithionate in solution ($t > 6$ hours) as evidenced by slight increases in tetrathionate (observed in Figures 83 to 85) based on Reaction (41) previously discussed in Section 4.4.1.1.1. Nonetheless, it can be presumed that the trithionate
loading on the resin achieved by the six hour mark remained unchanged for the remaining equilibration time.

Unlike loading tests with initial additions of tetrathionate, those with added trithionate contained only trace amount of pentathionate loadings on the resin (Table 24).

Figure 83: Gold and polythionate solution concentrations during the loading process onto 5 mL resin with 1 mM initial 3T.

Figure 84: Gold and polythionate solution concentrations during the loading process onto 5 mL resin with 2 mM initial 3T.
Figure 85: Gold and polythionate solution concentrations during the loading process onto 5 mL resin with 4 mM initial 3T.

6.5.3 Discussion

The theoretical capacities of 5 and 10 mL resin are 2.88 and 5.75 mmoles of anions respectively with a charge of −2 (e.g. thiosulfate and polythionates). It follows that the moles of tetrathionate anions contained in a 2 L gold-thiosulfate solution with 4 mM tetrathionate surpasses the theoretical loading capacities of both resin volumes while ignoring thiosulfates (~200 mmoles). Conversely, the 8 mg/L gold in solution as \( \text{Au(S}_2\text{O}_3\text{)}_2^{3-} \) represents only 4.24 and 2.12 % of the loading capacities of 5 and 10 mL resin respectively. Therefore, at high polythionate concentrations in solution, the larger gold-thiosulfate ions must compete for adsorption sites during their slower diffusion through the macroporous structure of the resin material. The efficient recovery of gold-thiosulfate complexes from recycled CaTS leaching solutions will not only heavily rely on the selectivity of the gold-thiosulfate complexes over thiosulfate degradation products but on the latter’s concentrations. To address this problem, a leaching process requires the supply of sufficient resin volumes to be present in solution in order to promote gold-thiosulfate recovery. In the CaTS loading system studied in this section, a general trend is discernible from the data contained in Table 24 and Table 25: In order to maintain an equilibrium gold concentration below 0.5 mg/L, the fractional loading of all polythionates on the resin must be maintained below 65 %. At higher overall polythionate contents gold loading is considerably obstructed. Practically, to achieve a lower polythionate content on the resin (as a percentage of total loading sites), the concentration of resin (typically in mL resin per L slurry) added into a RIL reactor must simply be increased. Alternatively, the gold leach solution can be treated with a reductant such as sulfite to reduce the concentration of higher polythionates (Ji et
al. 2003, Senanayake 2005a). Although sulfite would indeed reduce higher polythionates and regenerate thiosulfate in solution, this practice is not be advisable as gold-thiosulfate may also be reduced as given by Reaction (49). The detrimental effect of sodium sulfite addition on gold extraction during ammoniacal thiosulfate gold leaching (0.3 M NaTS, 0.03 M Cu(II), 1 M NH₃, pH 10, 4 hrs) was recently shown whereby the extraction and thiosulfate consumption decreased from 72.7 % and 42.4 % to 23.5 % and 5.7 % respectively above 0.06 M sulfite (Xu et al. 2015). Moreover, the addition of sulfite, aimed to remove tetrathionate which was posited to promote gold and silver adsorption onto mineral phases, was shown to work for goethite and pyrite (Aylmore et al. 2014). For goethite, the sulfite addition decreased trithionate levels (unclear mechanism) and for pyrite it reduced any tetrathionate present. The sulfite addition had no effect on precious metal losses due to kaolinite or activated carbon. On the other hand, the same authors pointed out a decrease in soluble gold and silver by 10 % after addition of 5 mM sulfite to ATS solutions without minerals (10 mg/L Au and Ag, 0.4 M NH₃, 0.05 M TS, pH 9.5) initially containing 10 mM trithionate. This serves as additional evidence as to how sulfite can decompose and precipitate gold and silver from solution.

6.6 Gold Loading Isotherms in the CaTS Leaching System

Gold loading isotherms are typically generated by preparing several identical synthetic gold leaching solutions, adding varying amounts of resin in each batch and allowing them to reach equilibrium. Alternatively, a single batch experiment may be used where resin is incrementally added to the solution and allowed to equilibrate in between additions (Zhang et al. 2002a). The initial and final solution concentrations of gold for each equilibrium test is analyzed and the gold loading can be deduced by Equation (53) (O'Malley 2002).

\[
[Au]_{r, eq} = \frac{([Au]_{s, ini} - [Au]_{s, eq})V_s}{M_r \text{ or } V_r}
\]

Where \([Au]_{r, eq}\) = Concentration of gold on the resin at equilibrium (mg/kg or mg/L)

\([Au]_{s, ini} \text{ & } [Au]_{s, eq}\) = Initial and equilibrium gold concentration in solution (mg/L)

\(V_s\) = Volume of solution (L)

\(M_r \text{ or } V_r\) = Mass (kg) or volume (L) of resin

In cases where large solution volumes are in contact with small resin volumes, small changes between the initial and final gold solution concentrations may be difficult to measure. Therefore, the
stripping of the resin material followed by analysis of the strip solution by AAS is preferable. Alternatively, the collected resin material can be analysed for gold by fire assay.

In this section, gold loading isotherms in the presence of various total concentrations of polythionates and combinations of polythionates were constructed to elucidate the detrimental effects of these thiosulfate degradation production on the gold loading performance on resin. These loading tests were carried out in typical CaTS leaching solution compositions (0.1 M CaTS, 50 mg/L Cu). Loading isotherms are usually reported in the literature as the mass of gold loaded per mass dry resin (mg Au/kg Resin) versus the equilibrium concentration in solution (Jeffrey et al. 2007). These types of graphs can be useful a tool in the design of separation processes in similar systems.

### 6.6.1 Experimental Procedures

Solutions for baseline equilibration tests containing increasing soluble gold concentrations (0.25, 1, 2.5, 8 mg/L) as aurothiosulfate in 0.1 M calcium thiosulfate with 50 mg/L cupric were prepared in 2 L volumetric flasks. These solutions were transferred into 2.5 L baffled glass reactors mixed by four blade pitched impellors affixed to overhead agitators rotating at 500 rpm. The reactors were placed inside a water bath controlled at 25 °C. This set-up ensured optimal mixing conditions at a constant temperature. Similarly, for equilibration tests containing various initial polythionate concentrations (4 mM 3T, 4 mM 4T, 4 mM 4T and 4 mM 3T), calculated amounts of each thiosalt were added to the volumetric flasks. To these solutions, 0.5 mL of swollen Purolite A500 resin previously conditioned with chloride were added to the reactors and allowed to reach equilibrium. Upon reaching equilibrium, the final solution concentration was measured and the resin material was filtered, rinsed and twice stripped with 50 mL of 0.5 M sodium perchlorate for one hour.

This same procedure was subsequently repeated using an industrial resin sample, GSBR, described in Section 3.1.3.2.

### 6.6.2 Results

#### 6.6.2.1 Commercial Purolite A500

Figure 86 contains four gold isotherm curves each with varying degrees of polythionate additions.
It is immediately evident that as little as 4 mM of trithionate can have a severe impact on the uptake of gold onto the resin compared to the baseline isotherm not containing initially added polythionates. Gold loadings on the resin with respect to an equilibrium gold concentration in solution were calculated using a best fit trendline for the constructed curves. At a gold equilibrium concentration of 1 mg/L, the gold loading on the resin dropped from 3245 to 1078 mg/kg with 4 mM trithionate. The gold loading further drops an order of magnitude to 333 mg/kg when 4 mM tetrathionate was added to the system. Simultaneous additions of 4 mM tri- and tetrathionate additions resulted the lowest gold loading on the resin at 223 mg/kg.

6.6.2.2 Industrial Purolite A500 (GSBR)

Figure 87 shows the resulting gold loading isotherms using the Goldstrike barren resin. The baseline curve contains no added polythionates in a 0.1 M CaTS background solution containing 50 mg/L cupric. As was observed with the commercial resin, the addition of 4 mM trithionate or tetrathionate clearly decreases the loading of gold loading onto the GSBR material.
From the generated GSBR gold isotherms, the calculated gold loadings on the GSBR at equilibrium with 1 mg/L gold in solution was 4386 mg/kg without polythionate additions decreasing down to 1453 and 626 mg/kg in the presence of 4 mM trithionate and 4 mM tetrathionate respectively. Higher gold loadings were achieved with the GSBR compared to the fresh A500 resin in the presence of equal levels of polythionate additions. The reason for this unclear but could be due to the preconditioning of the GSBR which contained some thiosulfate and sulfates (See Table 26). On the other hand, the commercial Purolite A500 resin was pre-treated in chloride media as described in Section 3.1.3.1.1. As a point of reference, typical tetrathionate and higher polythionate concentrations in CaTS leaching solutions range between 0.22 and 0.89 mM and between 1.43 and 1.95 mM for trithionate. Furthermore, a high gold loading of about 706 mg/kg resin was measured from the second co-current leach tank (see Section 2.1.1) although no equilibrium gold concentration in solution nor polythionate concentrations were reported (Choi et al. 2012a).
6.7 Partial Conclusions

As was portrayed in the literature review, the CaTS gold leaching system is a relatively new process which affords new research opportunities. This chapter provided some fundamental loading rate constants for polythionate species and compared them to the few values available in the literature. Subsequently, the competitive loading between different polythionate species was further quantified by establishing new distribution coefficients for the CaTS system. It was shown that the higher the number of sulfur atoms the polythionate species had, the slower it loaded onto the resin material. It was also shown that over time, the higher polythionates displaced lower polythionates and ultimately proved to have the highest affinities for adsorption sites. The gold thiosulfate loading rate on the resin was shown to be considerably affected by small amounts of tri- or tetrathionate in the concentration range of 2-4 mM. The uptake of gold from typical CaTS solution was shown to be reduced by a whole order of magnitude with addition of 4 mM tetrathionate alone or with 4 mM trithionate. The presence of 4 mM trithionate alone decreased the gold loading by a factor of 3.
7 CaTS Leaching of Refractory Ores in the Presence of Polythionates with Goldstrike Plant Resin

In Chapter 5, several leaching tests were performed on a preg-robbing feed material with and without initially added gold thiosulfate to observe the gold leaching behaviour in the presence of polythionate additions. Chapter 6 introduced the loading behaviour of gold thiosulfate complexes onto ion exchange materials from synthetic CaTS leaching solutions in the presence of polythionates. The aim of this chapter is to combine CaTS leaching of industrial gold-bearing preg-robbing ores with the simultaneous recovery of the dissolved gold from solution onto an ion exchange resin. As such, the subsequent batch leaching tests mimic the conditions used in the first leaching tank of a continuous resin-in-leach process where the residence time ranges from 1-5 hours but more commonly 3-4 hours per tank (Choi et al. 2012a).

7.1 Materials and Experimental Conditions

CaTS gold leaching and recovery experiments were conducted on two similar alkaline pressure oxidation (AlkPox) discharge materials received at different times (July 2015 and April 2016). Leaching tests including gold recovery were conducted with the addition of a pre-treated Goldstrike barren resin (GSBR) for adsorption. Additionally, 4 mM tetrathionate or 4 mM trithionate was added into the leaching system to observe the effect on the gold loading.

7.1.1 Refractory Preg-robbing Ore

Two distinct refractory preg-robbing materials with similar properties originating from the Goldstrike mine were investigated (Appendix Table A 9). These ores were pre-treated in an alkaline autoclave process to partially break down sulfides to liberate gold and allow the generated acid to react with carbonates and other acid consumers (Langhans et al. 2012). The first feed material consisted of an aged stockpiled alkaline pressure oxidation discharge from autoclaves 4, 5, 6 received in July 2015 (July’15 AlkPox). The second, represented a more recently pre-treated ore by alkaline pressure oxidation received in April 2016 (Apr.’16 AlkPox).

7.1.1.1 July’15 AlkPox

This alkaline pressure oxidation discharge was received from AuTec as a wet slurry (50% pulp density). It was vacuum filtered and dried overnight at 60 °C. The dried material was split to yield representative and appropriately sized fractions for experiments. The gold head fire assay of this
material conducted at AuTec was determined to be 4.98 ppm. Leaching experiments using the July’15 AlkPox are denoted by “J”.

7.1.1.2 Apr.’16 AlkPox

A little over 1 kg of this alkaline pressure oxidation discharge was received from AuTec as a ground and dried sample. It was twice split into four representative ~255 g fractions allowing for four leaching experiments. The average gold head assay provided by AuTec was 3.9 ppm (SD = 0.09). Leaching experiments using the Apr.’16 AlkPox are denoted by “A”.

7.1.2 Ion Exchange Material

The resin material used in these experiments originated from the Goldstrike plant and was received by UBC through AuTec in March 2016. The circa 200 mL batch of Purolite A500 resin labelled “Barren Resin GS Aug. 2015” was presumably taken from the post elution step at the plant. In the following test work, GSBR denotes Goldstrike Barren Resin. The theoretical resin loading capacity is 1150 meq/L Resin. Table 26 shows the average concentration of polythionates and sulfate measured after twice stripping four 1 mL GSBR samples in 50 mL of 0.5 M sodium perchlorate. The averaged measured molar equivalent of species loaded per liter of resin amounts to 81.42 % of the theoretical capacity of the resin.

Table 26: Average measured polythionate and sulfur loadings on GSBR from four stripping tests

<table>
<thead>
<tr>
<th>GSBR Strip Analysis</th>
<th>TS Loading mmole/L</th>
<th>3T Loading mmole/L</th>
<th>4T Loading mmole/L</th>
<th>5T Loading mmoles/L</th>
<th>SO₄²⁻ Loading mmole/L</th>
<th>Total Loading meq/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Concentration</td>
<td>77.17</td>
<td>0.06</td>
<td>0.02</td>
<td>0.03</td>
<td>390.89</td>
<td>936.34</td>
</tr>
</tbody>
</table>

From Table 26, it can be seen that the stripping procedure used on the GSBR released only trace amounts of polythionates together with some thiosulfate and a large proportion of sulfate. This suggests that after gold elution by trithionate, the GSBR sample was indeed treated with sulfide to convert trithionate back to thiosulfate as was shown by Equation (4) and discussed in Section 2.1.2.2. Moreover, no detectable concentrations of gold were measured in the sodium perchlorate strip solutions after GSBR stripping. On the other hand, a duplicated fire assay analysis conducted on two large representative GSBR samples (8 mL) resulted in an averaged “locked gold” resin concentration of 1392.4 mg of Au/kg resin. It is hypothesized that this gold content was not recovered during the stripping procedure at the plant nor during the stripping procedure used to characterize the resin as given by Tables 29 and 31.
7.1.3 Leaching Procedure

A 0.1 M CaTS leaching solution was prepared in a volumetric flask by appropriately diluting a fresh CaTS stock solution (23.83 wt %) together with a targeted concentration of 50 mg/L copper added from a copper sulfate stock solution. For Tests J3 & A3, a pre-determined amount of trithionate was weighed and added to the reagent solution to yield an initial 4 mM concentration of trithionate. Similarly, for Tests J4 & A4, a pre-determined amount of tetrathionate was weighed and added to the reagent solution to yield an initial 4 mM concentration of tetrathionate. Leach slurries were prepared by adding a mass of dry preg-robbing material (density: 2.51 g/mL) together with the resin material when applicable into a 1 L baffled reactor which was subsequently filled with the CaTS reagent to yield a 30 wt % pulp density. For leach experiments using the July’15 AlkPox discharge (Tests J2, J3, J4), Goldstrike Barren Resin (GSBR) was added into the reactor on a wet volume basis at 3.4 mL/L slurry. This concentration represents the typical amount of resin added into the first of two co-current leaching tanks in the RIL process (Choi et al. 2012a). For leach experiments using the Apr.’16 AlkPox discharge (Tests A2, A3, A4), GSBR was added into the reactor at 15 mL/L slurry. This increased resin concentration represents the typical resin level found in the second of two co-current leaching tanks (Choi et al. 2012a). The start of leaching was marked by the introduction of the reagent. Test J1 and A1 containing the July’15 AlkPox and Apr.’16 AlkPox materials respectively served as baseline tests without additions of polythionates and resin beads. Moreover, all Apr.’16 AlkPox leaching tests were conducted with air-sparging at a flow rate of 0.2 LPM. No aeration was used in the July’15 AlkPox tests. Mixing was provided by overhead agitation of a four blade pitched impellor rotating at 500 rpm. The pH set-point of all slurries was set to 8.5 to be adjusted by NaOH with an automated pH controller and the temperature was controlled at 50 °C with a water bath. A summary of the experiments and their respective conditions are summarized in Table 27.
Table 27: Summary of Preg-robbing Material Leach Tests

July’15 AlkPox Tests (Designated as J)

<table>
<thead>
<tr>
<th>Test</th>
<th>Description</th>
<th>Air Sparging (LPM)</th>
<th>Resin (mL/L)</th>
<th>Ore (g/L)</th>
<th>[3T] mM</th>
<th>[4T] mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>July’15 AlkPox</td>
<td>Ø</td>
<td>Ø</td>
<td>370</td>
<td>Ø</td>
<td>Ø</td>
</tr>
<tr>
<td>J2</td>
<td>July’15 AlkPox with GSBR</td>
<td>Ø</td>
<td>3.4</td>
<td>370</td>
<td>Ø</td>
<td>Ø</td>
</tr>
<tr>
<td>J3</td>
<td>July’15 AlkPox with 3T and GSBR</td>
<td>Ø</td>
<td>3.4</td>
<td>370</td>
<td>4</td>
<td>Ø</td>
</tr>
<tr>
<td>J4</td>
<td>July’15 AlkPox with 4T and GSBR</td>
<td>Ø</td>
<td>3.4</td>
<td>370</td>
<td>Ø</td>
<td>4</td>
</tr>
</tbody>
</table>

April’16 AlkPox Tests (Designated as A)

<table>
<thead>
<tr>
<th>Test</th>
<th>Description</th>
<th>Air Sparging (LPM)</th>
<th>Resin (mL/L)</th>
<th>Ore (g/L)</th>
<th>[3T] mM</th>
<th>[4T] mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Apr.’16 AlkPox-Air</td>
<td>0.2</td>
<td>Ø</td>
<td>370</td>
<td>Ø</td>
<td>Ø</td>
</tr>
<tr>
<td>A2</td>
<td>Apr.’16 AlkPox with GSBR and Air</td>
<td>0.2</td>
<td>15</td>
<td>370</td>
<td>Ø</td>
<td>Ø</td>
</tr>
<tr>
<td>A3</td>
<td>Apr.’16 AlkPox with 3T, GSBR and Air</td>
<td>0.2</td>
<td>15</td>
<td>370</td>
<td>4</td>
<td>Ø</td>
</tr>
<tr>
<td>A4</td>
<td>Apr.’16 AlkPox with 4T, GSBR and Air</td>
<td>0.2</td>
<td>15</td>
<td>370</td>
<td>Ø</td>
<td>4</td>
</tr>
</tbody>
</table>

7.1.4 Resin Stripping Procedure

The shut-down procedure for leaching tests with resin required the separation of resin beads from the leached slurry. This was accomplished by passing the final well stirred slurry through a 400 μm screen, followed by a rinsing stage of the collected beads using DI water. Subsequently, 1 mL of the recovered resin was twice stripped in a beaker with magnetic agitation for one hour with ~40 mL of 0.5 M sodium perchlorate solution. The strip solution was quantitatively transferred into a 50 mL volumetric flask by thoroughly rinsing the stripped resin with DI water. The contents of the volumetric flask was filled to the mark and this solution was analysed via ion chromatography for polythionate species concentrations and AAS for gold concentrations.

7.2 Results

7.2.1 July’15 AlkPox

The first series of CaTS leach tests on an alkaline pressure oxidation discharge ore with simultaneous gold recovery onto recycled plant resin (GSBR) was conducted using the following conditions: 0.1 M CaTS, 50 ppm Cu, 50 °C and pH 8.5. Resin was added at a volume of 3.4 mL/L slurry which represents the targeted amount for the first tank of a continuous co-current and counter current RIL process for gold leaching (Choi et al. 2012a).

7.2.1.1 Gold Loading Behaviour

Figure 88 displays the loading behaviour of gold onto resin when present in terms of its soluble concentration remaining in solution. Tests J2 and J4 indicated fast gold leaching rates within the first 15 minutes. This is also assumed to have been the case for leaching Tests J1 and J3, whose first
data points were only taken after 1 hour. The baseline leach Test J1 that did not include resin nor initial polythionate additions quickly established an average soluble gold value of 0.92 mg/L (avg. $[\text{Au}]_{t=1-4\,\text{hrs}}$).

Comparing to this baseline leach, Figure 88 shows the addition of 3.4 mL resin/L slurry in Test J2 resulted in the uptake of gold onto the resin past the 15 minute mark. The loading of gold continued down to a minimum soluble gold concentration of 0.37 mg/L at the two hour mark before increasing again. This latter increase in dissolved gold can be attributed to the release of gold from the resin back into solution due to the competitive loading of polythionate species onto the resin. On the other hand, relative to the baseline (Test J1) and assuming equally fast gold leaching rates, the presence of 4 mM 3T (Test J3) appears to have further hindered the gold loading process on the resin. This was shown by the slow increase of gold-thiosulfate in solution past the 1 hour mark resulting from the release of any gold-thiosulfate loaded on the resin prior that point. The detrimental effect of 4 mM initial 4T additions on gold loading (Test J4) was even more pronounced whereby upon fast leaching, any soluble gold remained in solution at identical levels to the baseline test without uptake onto the GSBR.

Figure 88: Concentration of soluble gold (mg/L) for July'15 AlkPox leaching tests.
7.2.1.2 Effect of Resin on Gold Loading Without Polythionate Additions

Although no polythionate additions were made in the following leach solutions, the initial presence of tetrathionate came from the addition of 50 ppm copper as cupric sulfate into the system. This resulted from the known redox reaction where cupric is reduced to cuprous by thiosulfate oxidation into tetrathionate (See Section 3.1.2.2). At the given testing conditions (pH 8.5), tetrathionate is known to rearrange to form trithionate and pentathionate with the latter degrading further to thiosulfate (See Section 2.4). It is therefore difficult to solely attribute the loss of tetrathionate from solution in Test J2 simply due to resin loading.

For Test J2 shown in Figure 89, it appears that both tetrathionate and trithionate anions were loaded onto the resin compared to the baseline Test J1 not containing resin. Beyond the two hour mark, the generation of polythionates in the solution and their simultaneous accumulation on the resin commenced the displacement of aurothiosulfate complexes.

Figure 89: Gold and polythionate concentrations in solution over time during the leaching of 30 wt % July'15 AlkPox using 0.1 M CaTS, 50 ppm Cu, pH 8.5, 50 °C. Test J1 is resin-less and Test J2 contains 3.4 mL resin/L slurry.
Table 28: Calculation estimating the loading of Au, 3T and 4T on the resin in Test J2.

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Δ[AuTS] on Resin (mmoles/L)</th>
<th>Δ[3T] on Resin (mmoles/L)</th>
<th>Δ[4T] on Resin (mmoles/L)</th>
<th>Loading on Resin (meq/L)</th>
<th>% Resin Capacity (1.15 eq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.25</td>
<td>81.4</td>
<td>76.6</td>
<td>319.9</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>1.32</td>
<td>186.7</td>
<td>158.7</td>
<td>694.7</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>1.34</td>
<td>329.8</td>
<td>88.1</td>
<td>840.0</td>
<td>73</td>
</tr>
<tr>
<td>4</td>
<td>0.99</td>
<td>419.3</td>
<td>95.1</td>
<td>1031.9</td>
<td>90</td>
</tr>
</tbody>
</table>

To further investigate this, a basic calculation given in Table 28 was conducted. The differences at each time interval in the soluble concentrations of gold, trithionate and tetrathionate between Test J1 and J2 was assumed to have been loaded on the resin present in the latter test. Given the initial volume of reagent and resin, this molar difference was converted into an estimated loading value given in milli-equivalents/L, which in turn was used to calculate a percent loading on the resin based on its theoretical capacity. This calculation assumes no degradation or rearrangements reactions, that the differences in soluble concentrations between the two tests are only due to resin loading and that the remaining loading sites are occupied by thiosulfate and higher polythionates. Firstly, it can be seen that gold contributed relatively little to the overall loading on the resin (<0.35 %). Secondly, as the sum of trithionate and tetrathionate loading surpassed 60 % of the resin capacity, gold started to be displaced from the resin into solution. This value is similar to the previously established cut-off value of 65 % resin capacity for polythionate loading on the resin to maintain a soluble gold concentration below 0.5 mg/L established in Section 6.5.3.

7.2.1.3 Polythionate Additions during Simultaneous Gold Leaching and Loading

Figure 90 shows the gold and polythionate solution concentrations during the resin-in-leach Tests J2 and J4, the latter of which contained 4 mM of initially added tetrathionate. It is clear that Test J4 continued to maintain a high concentration of soluble gold even in the presence of resin (3.4 mL/L slurry). In fact, as seen in Figure 88, soluble gold concentrations for Test J4 closely resembles those of the blank and resin-less Test J1, particularly for the first three hours. This indicates that as gold leached and became available, its loading onto the resin was immediately inhibited. Instead Figure 90 shows that for Test J4, tetrathionate was gradually removed from solution due to its preferential loading onto the ion exchange resin confirmed by resin stripping (Table 29). At the same time, the decrease in tetrathionate from solution can also be partially attributed to its degradation or, rather, its rearrangement to tri- and pentathionate (Reaction 29). Indeed, as observed in Figure 90, this rearrangement reaction results in a gain in trithionate and pentathionate both of which can also load onto the resin. The trithionate concentration in solution however is seen gradually increasing over
time compared to its pentathionate counterpart which is preferentially loaded on the resin together with tetrathionate. Taken together, the total amount of initial polythionates present in solution for Test J4 is high enough to completely inhibit gold-thiosulfate adsorption.

![Figure 90: Gold and polythionate concentrations in solution over time during leaching of 30 wt % July'15 AlkPox with 3.4 mL GSBR/L using 0.1 M CaTS, 50 ppm Cu, pH 8.5, 50 °C. Test J4 contains 4 mM 4T added initially.](image)

Table 29 shows the values of individual species concentrations stripped from the GSBR after loading during the RIL Tests J2, J3 and J4 compared to the initial concentrations in the barren GSBR. As expected, the combined loading of higher polythionates (3T, 4T & 5T) in Test J4 surpasses that of Test J2 with 97 % of the theoretical resin capacity occupied compared to just 59 %.

<table>
<thead>
<tr>
<th>Species Loading on GSBR Samples</th>
<th>TS mmoles/L Resin</th>
<th>3T mmoles/L Resin</th>
<th>4T mmoles/L Resin</th>
<th>5T mmoles/L Resin</th>
<th>PolyTS Loading meq/L Resin</th>
<th>PolyTS Loading % Theo. Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Barren Strip</td>
<td>77.17</td>
<td>0.06</td>
<td>0.02</td>
<td>0.03</td>
<td>0.23</td>
<td>0.02</td>
</tr>
<tr>
<td>J2 Strip</td>
<td>222.4</td>
<td>71.3</td>
<td>133.3</td>
<td>136.7</td>
<td>682.7</td>
<td>59.4</td>
</tr>
<tr>
<td>J3 Strip (4 mM 3T)*</td>
<td>111.3</td>
<td><strong>183.4</strong></td>
<td>148.4</td>
<td>125.0</td>
<td>913.5</td>
<td>79.4</td>
</tr>
<tr>
<td>J4 Strip (4 mM 4T)</td>
<td>87.2</td>
<td>108.6</td>
<td><strong>203.4</strong></td>
<td>245.0</td>
<td>1113.8</td>
<td>96.9</td>
</tr>
</tbody>
</table>

*5 hours of loading

The total loadings for Test J2 and J4 including thiosulfate were 1127 meq/L and 1288 meq/L respectively, which are close to the theoretical loading capacity of the resin of 1150 meq/L. Table
29 and Figure 90 indicate that Test J4 was still in the process of approaching a steady state when the experiment was terminated at the 4 hour mark. This is supported by the fact that the loading of gold onto 2.5-5 mL resin/L solution containing 0.1 M CaTS with 4 mM tetrathionate was previously shown to take approximately 12 hours (See Section 6.5.2.1). Therefore, with additional leaching time, further changes in the concentration of species loaded onto the resin would have been expected, driven by the concentration gradients of said species in solution and the differences in the affinities of each competing species for adsorption sites.

Also included in Table 29 are the higher polythionate species loadings for Test J3 (4 mM 3T), which contributed close to 80% of the theoretical resin capacity whereas the total species loading reached 1136 meq/L. It should be noted the duration of Test J3 was five hours compared to four for the other leaches using the July’15 AlkPox ore. In Test J3 trithionate initially loaded preferentially over tetrathionate, which is the reverse trend observed for Test J4 (See Figure 91). In this case, there was a greater driving force for the uptake of trithionate onto the resin due to its higher initial concentration in solution. However, past the two hour mark, trithionate was released back into solution as well as the initially adsorbed gold-thiosulfate. The release of trithionate due to the preferential loading of tetrathionate was previously shown in Figure 71 in Section 6.4.2.1.3. Although not shown, the same preferential loading process is expected for pentathionate over trithionate. The resin strip results for Test J3 (Table 29) reveal that pentathionate was an important constituent in the total solute loading owing to its high affinity for loading sites. This also explains the eventual release of lower polythionates of lower affinity back into solution.
From the polythionate data measured from the resin strip solutions, the following conclusions can be drawn:

1. At equal initial concentrations, tetrathionate adsorbed more strongly and faster (Test J4) than trithionate (Test J3).

2. Tetrathionate is known to degrade over time by first rearranging to form trithionate and pentathionate over time. This allowed for pentathionate to load onto the resin as it formed (Test J4) resulting in a higher resin pentathionate loading (245 mmoles 5T/L Resin) and virtually no gold-thiosulfate loading based on solution analysis.

3. Four hours of leaching was enough time for 3.4 mL resin/L slurry to be loaded to capacity however a stable state was not fully achieved.

7.2.1.4 Resin Gold Loading and Gold Mass Balance

Table 30 displays the percent gold leached based on the head fire assays and final residue assays. It also shows the final loaded gold content measured by fire assay on the resin after leaching with the barren resin initially containing 1392.4 mg Au/kg resin. Also given are the soluble gold
concentrations after four hours of leaching, the recovery of gold by resin and the calculated final gold mass balances.

Test J1, without resin, leached 52.5 % of the gold from the Pox discharge with a maximum soluble gold concentration of 0.89 mg/L. A good closure of the total gold mass balance was observed with 98.5 % of the gold taken into account. Test J2, with resin, leached 50.8 % of the available gold which compares favorably to the resin-less leach Test J1. Figure 88 showed soluble gold dropping from solution due to its adsorption onto the resin which is confirmed in Table 30 by an increase in gold concentration on the resin (1792 mg/kg) and the resulting 25 % gold recovered by resin. The balance of gold that remained in solution as leached gold was measured to be 0.5 mg/L after four hours. Most of all the gold was taken into account with a final gold mass balance of 93 %.

Table 30: Summary for July’15 AlkPox leaching Tests: Residue fire assays, final resin gold loadings, four hour soluble gold concentrations and gold mass balances.

<table>
<thead>
<tr>
<th>July’15 AlkPox Test</th>
<th>Leached Au (%-FA)</th>
<th>[Au]$_{GSBR}$ (mg/kg- FA)</th>
<th>[Au]$_{hrs}$ in Solution (mg/L)</th>
<th>Au Recovered by Resin (%)</th>
<th>Au Mass Bal. % $[(Au_{out}/Au_{in})*100%]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1 (no resin)</td>
<td>52.5</td>
<td>N/A</td>
<td>0.89</td>
<td>N/A</td>
<td>98.5</td>
</tr>
<tr>
<td>J2 (Blank)</td>
<td>50.8</td>
<td>1792</td>
<td>0.50</td>
<td>25.0</td>
<td>93.0</td>
</tr>
<tr>
<td>J3 (4 mM 3T)*</td>
<td>56.8</td>
<td>777</td>
<td>0.96</td>
<td>Net Loss</td>
<td>75.7</td>
</tr>
<tr>
<td>J4 (4 mM 4T)</td>
<td>37.3</td>
<td>480</td>
<td>1.08</td>
<td>Net Loss</td>
<td>71.6</td>
</tr>
</tbody>
</table>

Tests J3 and J4 are more complex due to their initial additions of 4 mM 3T and 4T respectively. The interpretation of the data should be cautioned as a significant portion of initial gold into the system is unaccounted for in the final gold mass balances. However, Table 30 shows that in the presence of 4 mM trithionate (Test J3) and tetrathionate (Test J4), the final gold concentration on the resin decreased to 777 and 480 mg/kg respectively down from 1392.4 mg/kg initially. These net losses of gold from the resin materials are corroborated in Figure 88 by a surplus in gold concentrations in solution after four hours of leaching exceeding the value of leach Test J1 which utilized optimal leaching condition (no initial polythionate additions).

In terms of overall leaching by final residue fire assays, Test J4 performed the worst with 37 % of gold leached. Test J3 leached 57 % of the gold but had the benefit of an additional hour of leaching for a total of five. It is presumed that the overall leaching in Test J3 at the four hour mark would fall between that of Tests J4 and J2. For this series of tests and conditions, it is suggested that the maximum gold leaching for the July’15 AlkPox discharge is in the low 50 % (See Tests J1 and J2).
The following consist of additional partial conclusions based on the measured gold concentrations and resin fire assays:

1. Available gold was quickly dissolved into solution from the preg-robbing material as evidenced in Test J1 and J2 (Figure 88).
2. In a leach containing 3.4 mL resin/L slurry, as the percentage of the total resin capacity occupied by higher polythionates reached 60%, only half of the leached gold adsorbed onto the resin (Test J2).
3. In the absence of initial polythionate additions (Blank Test J2), the presence of >0.8 mM 3T and 4T due to natural reagent degradation and decomposition was seen to adversely affect gold-thiosulfate uptake by the resin.
4. In a leach containing 3.4 mL resin/L slurry of recycled pre-treated resin, 4 mM 3T or 4T in solution did not only prevent the uptake of any newly leached soluble gold from the feed material, but also partially stripped any previously loaded or “locked” gold present on the resin initially (Figure 91).
   a. With 4 mM 3T addition into this system (Test J3), newly leached gold was slowly taken up by the resin before being displaced by the uptake of trithionate and pentathionate (time 1-4 hours).
      i. Beyond the 4 hour mark, “locked” gold desorbed back into solution.
   b. With 4 mM 4T addition into this system (Test J4), newly leached gold never seemed to load onto the resin by the fast preferential uptake of tetrathionate (within 15 minutes).
      i. Beyond the 2 hour mark, “locked” gold began desorbing back into solution.

The above results for the leaching and recovery of gold from a preg-robbing material demonstrated the significant detrimental effects of even small amounts of initial polythionates concentrations on the gold loading process. It was found that at an initial resin volume of 3.4 mL per liter of slurry, even the natural generation of polythionates through the decomposition of the CaTS reagent was sufficient to severely reduce the total gold recovery (See Test J2). Moreover, the initial artificial addition of 4 mM trithionate or tetrathionate was deemed too high for the aforementioned resin volume to recover any of the leached gold. In fact, upon loading of the polythionates species, “locked” gold initially contained in the resin material was displaced and reported into solution. It must be emphasized that the observed increase of dissolved gold in Test J4 from the release of
“locked” gold from the resin gives the appearance of a high gold extraction but in reality it was only 37 %. It may be possible that a fraction of the released gold precipitated out from solution and reported in the solid phase thereby indirectly affecting the residue assays and the calculated extraction. In order to promote gold adsorption to achieve higher overall gold recoveries on the resin and avoid the release of gold back into solution, a larger volume of resin must be employed. A greater volume of resin can reduce the adverse effects the polythionates have on the loading of the dissolved gold complexes.

7.2.2 Apr.’16 AlkPox – With Aeration (0.2 LPM)

The second series of CaTS leach tests on an alkaline pressure oxidation discharge ore with simultaneous gold recovery onto recycled plant resin (GSBR) used the same conditions as the first series with the addition of air sparging at 0.2 LPM. To mitigate the detrimental effects of polythionate additions observed in the previous section, a larger volume of resin, namely 15 mL/L slurry, was employed. As a reminder, this resin volume represents the targeted amount for the second co-current tank of a continuous co-current and counter current RIL process for gold leaching (Choi et al. 2012a).

7.2.2.1 Effect of Air-sparging

The added aeration in Test A1 (Apr.’16 AlkPox) does not appear to enhance the decomposition of thiosulfate when compared to the baseline Test J1 (July’15 AlkPox) that had no air sparging (See Figure 92). The underwhelming rate of thiosulfate oxidation by air sparging in Test A1 is supported by other works reviewed that showed the resistance of thiosulfate to oxidation (Zhang et al. 2016). For instance, thiosulfate and polythionate solutions aerated at pH 7 under sterile conditions for four months showed less than 10 % changes in concentrations (Rolia et al. 1982). It was also reported that stirred thiosulfate solutions lost less than 1 % of thiosulfate due to oxidation during the course of 24 hours at pH 6-12 (Jiang et al. 1996). Therefore the contribution of air sparging to the generation of polythionates in the subsequent tests involving the Apr.’16 AlkPox materials within the investigated timeframes can be considered to be negligible.
7.2.2.2 Gold Loading Behaviour

Figure 93 shows the gold loading behaviours on 15 mL GSBR/L slurry for Tests A2, A3 and A4 compared to the resin-less Test A1. From these soluble gold curves, it can be seen that gold leached from the preg-robbing feed material very quickly (Test A1) and was immediately and completely taken up by the GSBR in the absence of initial polythionates (Test A2). No soluble gold was detected in sample aliquots taken in Test A2. Compared to Test A2, the soluble gold loading onto the resin for A3 was hampered starting with the first sampled aliquot at the 19 minute mark due to the presence and fast uptake of the initially added 4 mM trithionate. Similarly, Test A4, containing 4 mM tetrathionate, sees its initially adsorbed soluble gold concentration competitively displaced from the resin back into solution beyond the two hour mark.
7.2.2.3 Effect of Resin on Gold Loading Without Polythionate Additions

Figure 94 displays the gold and polythionate concentrations during leach Tests A1 (no resin) and A2 (15 mL GSBR/L slurry). In the case of no resin addition, limited amounts of tri-, tetra- and pentathionate decomposition products were present initially due to Cu(II) reduction (~0.4 mM 4T) and generated by the oxidation of thiosulfate.
Figure 94: Gold and polythionate concentrations in solution over time during the leaching of 30 wt % Apr.’16 AlkPox using 0.1 M CaTS, 50 ppm Cu, pH 8.5, 50 °C, 0.2 LPM air sparging. Test A2 contains 15 mL resin/L slurry.

For Test A2 containing GSBR at 15 mL/L slurry, gold and trithionate never accumulated in solution due to their immediate uptake by the resin. Tetrathionate was seen dropping from an initial 0.33 mM to 0.11 mM within the first hour before slowly increasing to 0.14 mM after five hours. Similarly, pentathionate solutes were also seen loading from solution onto the resin material. The resin volume was large enough to allow for a significant fraction of thiosulfate loading without displacement. This was confirmed by the highest thiosulfate loading values measured in the resin strip solutions given in Table 31.

7.2.2.4 Polythionate Additions during Simultaneous Gold Leaching and Loading

Figure 95 compares the solution polythionate and gold concentrations as a function of time for Tests A3 and A4 containing 4 mM trithionate and 4 mM tetrathionate initially, respectively. At similar initial concentrations, tetrathionate (Test A4) loaded to a greater extent than trithionate (Test A3) beyond the one hour mark. However, although not visible in Figure 95, trithionate loaded faster than tetrathionate due to its higher loading rate constant (Table 19 in Chapter 6). To some extent, this fast initial preferential trithionate loading can explain the delayed gold adsorption observed.
Even with over four fold the concentration of GSBR compared to the first series of Tests (July’15 AlkPox), 15 mL resin/L slurry were still not enough to maintain the leached gold loaded onto the resin in the presence of 4 mM 3T or 4T.

Table 31 summarizes the loading of individual species stripped from the GSBR after 5 hours of leaching and loading (except Test A3 which was for 4 hours). In Tests A4, gold was first seen being released back into solution past the 2 hour mark ending up with a final soluble gold concentration of 0.12 mg/L. This represents an instance just past a threshold value where the polythionate loading on the resin begins to adversely affect gold loading. It should be noted that, based on the upward soluble gold trend observed in Test A4 (Figure 93), if the leaching were to have continued beyond 5 hours, an even greater displacement of gold would have been expected. At the end of Test A4, 61 % of the resin capacity was occupied by polythionates. This value compares favorably to the 59 % of final polythionate loading in Test J2 (Table 29) where gold changed from loading onto the resin to being released into solution mid-way though the leach test (Figure 88).

Table 31 reveals that Test A3 nearly reached the theoretical loading capacity within 4 hours with 96 % compared to 88 % for Test A4 after 5 hours. This is due to the relatively large fraction of

![Figure 95: Gold and polythionate concentrations in solution over time during the leaching of 30 wt % Apr.’16 AlkPox with 15 mL GSBR/L using 0.1 M CaTS, 50 ppm Cu, pH 8.5, 50 °C, 0.2 LPM air sparging. Test A3 and Test A4 have an additional 4 mM 3T and 4T added initially respectively.](attachment:image.png)
thiosulfate anions still occupying adsorption sites after 4 hours of loading that are being slowly exchanged by the more favorably loaded trithionate anion. It remains puzzling that Test A3 (4 mM 3T) released gold into solution prior to Test A4 (4 mM 4T) as this is the reversed trend in the leach tests using lower resin concentrations (See the July’15 AlkPox section). However, as mentioned previously, this can be partially attributed to the faster loading rates of trithionate onto the resin (compared to tetrathionate) which could have had a more immediate impact on the displacement of the initially loaded \( \text{Au(S}_2\text{O}_3)\text{)}^3^-\) complexes.

Table 31: Stripping of loaded GSBR used in Tests A2 (Blank), A4 (4 mM 4T) and A3 (4 mM 3T). PolyTS loading includes 3T, 4T and 5T.

<table>
<thead>
<tr>
<th>Species Loading on GSBR Sample</th>
<th>TS mmoles/L Resin</th>
<th>3T mmoles/L Resin</th>
<th>4T mmoles/L Resin</th>
<th>5T mmoles/L Resin</th>
<th>PolyTS Loading meq/L Resin</th>
<th>PolyTS Loading % Theo. Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Barren Strip</td>
<td>77.2</td>
<td>0.06</td>
<td>0.02</td>
<td>0.03</td>
<td>0.23</td>
<td>0.02</td>
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<tr>
<td>A2 Strip</td>
<td>301.8</td>
<td>17.1</td>
<td>45.4</td>
<td>60.1</td>
<td>245.2</td>
<td>21.3</td>
</tr>
<tr>
<td>A3 Strip (4 mM 3T)*</td>
<td>255.9</td>
<td>112.5</td>
<td>93.5</td>
<td>88.0</td>
<td>587.9</td>
<td>51.1</td>
</tr>
<tr>
<td>A4 Strip (4 mM 4T)</td>
<td>159.6</td>
<td>61.9</td>
<td>128.5</td>
<td>158.4</td>
<td>697.6</td>
<td>60.7</td>
</tr>
</tbody>
</table>

*4 hours of loading

7.2.2.5 Resin Gold Loading and Gold Mass Balance

Table 32 summarizes relevant data pertaining to the gold loading on the recovered resin after leaching the Apr.’16 AlkPox feed material. The main difficulty in reaching good overall gold mass balances comes from the large amounts of resin (15 mL/L) used and its high initial “locked” gold content (1392.4 mg/kg) which contains over six times more gold than included in the feed material used. Moreover, fire assay results were not always in agreement, where for instance, the leached residue fire assay of Test A2 suggested 63 % of the gold was leached whereas the assay of the recovered gold loaded resin amounted to 54 % of the initial gold in the feed. A possible source for these kinds of discrepancies could be from the attrition and breakage of the gold loaded resin beads whose gold contents may end up reporting in the fire assays of leached residues. Another example was the residue fire assay of Test A1 resulting in 54 % of gold leached whereas solution analysis of the filtered pregnant solution and wash water suggested 69 % of the total gold in the feed material was leached. In this case, in the absence of resin beads in the leach, emphasis should be placed on the residue assays.

The extraction of gold in the absence of resin (A1 - 54 %) was clearly lower than in the presence of 15 mL/L resin (A2 - 63 %) which validates the use of a RIL for the recovery of gold from preg-robbing ores and to mitigate gold losses. Test A3 (4 mM 3T) yielded a net gain in resin loading
(1453 mg/kg) albeit lower than Test A2 (1510 mg/kg). This was to be expected as some gold was left in solution (Figure 93). On the other hand Test A4 (4 mM 4T), which has less soluble gold remaining in solution than A3 at the end of leaching, encountered a net loss in resin loading as measured by fire assay (1245 mg/kg). In this case, a release of initially “locked” gold contained on the GSBR should have resulted in a net increase in the final solution gold concentration which was not observed. Conversely, if the “locked” gold released from the GSBR into solution precipitated, then it should have reported in the leached residue which was not observed either. As the overall gold leaching for A4 measured by way of residue fire assay resulted in 63 % gold leaching which is close to that of baseline Test A2, the GSBR fire assay result is likely unrepresentative.

Table 32: Summary for Apr.’15 AlkPox leaching tests: Residue fire assays, final resin gold loadings, five hour soluble gold concentrations and gold mass balances.

<table>
<thead>
<tr>
<th>July'15 AlkPox Test</th>
<th>Leached Au (%-FA)</th>
<th>[Au]_{GSBR} (mg/kg-FA)</th>
<th>[Au]_{Solv} in Solution (mg/L)</th>
<th>Au Recovered by Resin (%)</th>
<th>Au Mass Bal. [(Au_{out}/Au_{in})*100%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 (no resin)</td>
<td>54.4</td>
<td>N/A</td>
<td>0.92</td>
<td>N/A</td>
<td>114.2</td>
</tr>
<tr>
<td>A2 (Blank)</td>
<td>62.9</td>
<td>1510</td>
<td>0.00</td>
<td>53.5</td>
<td>96.2</td>
</tr>
<tr>
<td>A3 (4 mM 3T)*</td>
<td>41.5</td>
<td>1453</td>
<td>0.22</td>
<td>24.3</td>
<td>92.9</td>
</tr>
<tr>
<td>A4 (4 mM 4T)</td>
<td>62.6</td>
<td>1234</td>
<td>0.12</td>
<td>Net Loss</td>
<td>80.6</td>
</tr>
</tbody>
</table>

*4 hours of loading

7.3 Conclusions

This chapter summarized the results of CaTS gold leaching experiments with simultaneous gold recovery on resin from a preg-robbing alkaline pressure oxidation discharge feed material. Leach tests were performed at identical conditions with the exception of the introduction of 4 mM tetrathionate or trithionate into some of the leaches. The purpose of adding these polythionates was to cause an interference (competing anion) during the in-situ gold loading onto the resin material as soluble gold thiosulfate becomes available during leaching. It was expected that tetrathionate and even possibly trithionate retards or even prevents gold from loading onto the resin by being preferentially loaded onto the resin adsorption sites. It was found that the presence of 4 mM tetrathionate or trithionate has the potential to elute gold initially contained in the GSBR. Furthermore, it was shown that when more than ~60 % of the total resin loading capacity was occupied by polythionates there was an adverse effect on the gold loading from the leach slurry. This was previously concluded in Section 6.5.3 and was found applicable during the leaching and recovery of gold-thiosulfate from actual preg-robbing ores.
7.3.1 July’15 AlkPox

The CaTS leaching of the July’15 AlkPox residue resulted in ~50 % gold dissolution. The addition of GSBR at 3.4 mL/L slurry resulted in 25 % gold recovery by the resin. The presence of > 0.8 mM trithionate and tetrathionate due to calcium thiosulfate reagent degradation was enough to prevent further gold loadings on the resin. Additions of 4 mM 3T or 4T severely affected the uptake of fast dissolved “new” gold from the feed material. Eventually, negative gold loadings occurred which translated into a release of any previously contained or “locked” gold from the GSBR into solution.

7.3.2 Apr.’16 AlkPox

The leach tests conducted with 15 mL resin /L slurry in the presence of 4 mM 3T or 4T also saw adverse effects of gold loadings albeit to a lower degree than with a resin volume of 3.4 mL/L. The additional introduction of air sparging at 0.2 LPM in the Apr.’16 AlkPox leach trials did not significantly enhance thiosulfate oxidation. The polythionate analysis on the final resin products suggest greater than 60 % polythionate loadings onto the resin material as the threshold value before adverse effects on gold loadings are observed.
8 Summary and Recommendations

8.1 Review of Objectives

The research conducted in this dissertation was focused on determining the modes for gold loss in the calcium thiosulfate leaching system. It began with simple synthetic gold leaching solution with polythionate additions and transitioned into more complex solutions containing mineral additions (Chapter 4). The results showed that the presence of tri- and tetrathionate alone or in combination affected the solubility of the gold-thiosulfate complex during gold stability tests. This was posited to be due to complex redox reactions between polythionate species and their interactions with the gold complex shown to be thermodynamically feasible at non-standard states in the given leaching conditions. Metastable pentathionate was perceived as a highly reactive by-product of tetrathionate rearrangement reactions which is believed to be a contributing factor to the reduction of gold from solution. In addition, solutions initially containing trithionate were subjected to chain lengthening reactions resulting in sulfite and tetrathionate. Therefore, gold-thiosulfate complexes may have been reduced by a combination of sulfite and pentathionate species generated during polythionate degradation reactions. The mineral pyrite was shown to increase the rates of thiosulfate degradation and hence contribute to gold instability issues with the added generation of polythionates. The minerals hematite and gypsum did not sufficiently affect solution compositions over time and therefore did not affect the gold stability unless polythionates were added to the leach resulting in the aforementioned redox reactions. A similar behaviour was observed with the addition of activated carbon coupled with a slight adsorption of the dissolved gold over extended times due to the weak affinity of the gold complex for active surface sites in the carbon and its high surface area to volume ratio.

Eventually, current industrial CaTS leaching conditions were applied to an actual preg-robbing material, that is, an ore that displays double refractory properties that act as barriers to conventional processing by cyanidation (Chapter 5). The entire CaTS process was specifically designed to be able to dissolve and recover gold from this type of ore. The first barrier to this process was to liberate the gold particles that are locked inside of a refractory sulfide mineral requiring an autoclave pre-treatment. The second barrier to the process that needed to be overcome was the selection of a suitable reagent for the dissolution of the gold without losing it to the naturally occurring carbonaceous matter contained in the ore – a phenomenon called preg-robbing – unlike with
cyanidation. This is where CaTS came into play, capable of leaching the autoclave pressure oxidized discharge material. Although using thiosulfate as an alternative reagent to solubilize the gold was already proven, the resulting aurothiosulfate complex is not as stable as the aurocyanide complex and losses in gold have been reported. The introduction of trithionate and/or tetrathionate directly into CaTS leaching slurries of preg-robbing material either with or without artificially added aurothiosulfate presented clear evidence of the loss of gold from solution. The aforementioned complex redox reactions occurring with initial tetrathionate formed important detectable levels of pentathionate and in the case of initial trithionate, tetrathionate was generated likely with sulfite. Possible mechanisms for gold reduction by pentathionate and sulfite were subsequently proposed.

The current practice to limit gold losses during thiosulfate leaching is to introduce an anion exchange resin material directly into the leach corresponding to a resin-in-leach process. The aim of the strong base anion exchange resin, Purolite A500, is to provide 1.15 equivalents of per liter resin of loading capacity to adsorb and “collect” the dissolved gold-thiosulfate \((\text{Au(S}_2\text{O}_3)_2^{3-})\) complexes. In reality thiosulfate and polythionate species also simultaneously adsorb and compete for resin loading sites. The rates of loading for each species were determined as well as the distribution coefficients between two competing solutes (Chapter 6). It was shown that at faster agitation rates, the loading process of polythionates becomes limited by intraparticle diffusion and that higher polythionates ultimately exhibited the highest affinities for loadings sites and therefore displaced lower polythionates and gold-thiosulfate over time. It was subsequently established that polythionate loadings on to the resin above 60 % of its designed capacity lead to adverse effects on gold loadings and recovery.

In the penultimate Chapter, the CaTS leaching of an industrial gold bearing preg-robbing ore and the simultaneous recovery of gold onto an industrial resin material were combined. The effects of polythionate additions into these leaching systems were observed resulting in reduced gold loadings and adverse recoveries. The relationship between polythionate loadings beyond the threshold limit of 60 % of the total resin capacity and the onset of the detrimental effects of these species on gold loadings was reinforced. As a rule of thumb, exceeding this polythionate loading value on the resin is not recommended in order to yield reasonable gold loadings. The operation of the leaching circuit therefore requires careful monitoring of the polythionate species loadings on the resin and ideally their removal from loading solutions to ensure an economically viable process.
8.2 Future Work Recommendations

As was proposed in this dissertation, the transient appearance of the pentathionate anion was deemed to play an important role in the stability of dissolved gold in CaTS leaching solutions. As such, further research into this reactive polythionate species is encouraged. Aside from limited work on its degradation kinetics in alkaline solutions (Pan et al. 2011, Pan et al. 2013) and its detection and presence in ATS and CaTS leaching solutions as a product of tetrathionate rearrangement reactions, no current research program has yet to have investigated the direct effect of pentathionate on gold stability. Firstly, a pure form of this thiosalt should be successfully synthesized by the methods outlined by Kelly et al. (1994) which requires specialized equipment for cooling and concentrating solutions at reduced pressure. This step alone will benefit the accurate measurements of pentathionate anions from solutions by providing a standard material for ion chromatography (IC). Subsequently, the experiments conducted in this work can be reproduced with the use of the pentathionate salt to further elucidate its involvement in the reduction of gold-thiosulfate from both synthetic CaTS leaching solutions and actual CaTS leaching slurries. Furthermore, the loading rates of this anion on IX resin can be determined for modelling purposes as well as its distribution coefficient in solutions containing another polythionate counter-anion.

Similarly, a second area of interest should be the continued development of a method to stabilise sulfite ions for detection using IC. The sulfite ion was suspected to have formed together with tetrathionate during trithionate decomposition capable of causing documented decreases in gold concentration from leach solutions. The challenge encountered was twofold: Firstly, it was difficult to obtain a representative solution aliquot potentially containing sulfite and to stabilize this ion of interest with additives such as formaldehyde or glycerol to prevent its oxidation (Lindgren et al. 1982). Secondly, it was imperative for the treated sample to remain stable long enough to conduct its analysis. With the available equipment during this thesis work, after polythionate analysis by UV-Vis detection, the IC needed to be converted for use with an alternative IX column and eluent, suitable for sulfate and sulfite, in line with a conductivity suppressor and detection by conductivity. This procedure was attempted but the results did not achieve complete oxidation prevention thus leading to erroneous data for sulfite analysis. Some alternative solutions are the use of a second IC instrument to conduct simultaneous polythionate and sulfite analysis without unnecessary delays or to invest into a more modern high-performance liquid chromatography (HPLC) instrument capable of analyzing all sulfur anions at once (Ji et al. 2015).

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A third relevant area of research would be to expand the CaTS leaching and gold recovery by IX of preg-robbing ores into a continuous, multistage set-up that closely mimics the industrial process (Choi et al. 2012a). There are many challenges for this endeavour to further investigate the effect of polythionates on the stability and extraction gold-thiosulfate from continuously leached slurries. The first that comes to mind is the management and preparation of large amounts of solids and reagent solution volumes as well as the higher consumption of non-commercially available reagents such as trithionate and possibly pentathionate. The effective transfer of the resin material from one reactor to another in a counter-current fashion is also seen as a hurdle requiring good experimental design and execution. Another possible limiting factor is the complex control and automation of the process to maintain and measure pH, ORP and temperature. Without getting into the specifics, lots of preparation would have to go into the effective extraction and analysis of representative solution and resin samples for gold and polythionate concentrations. The operation of such a mini-pilot plant to further investigate the effects and behaviours of polythionate species on the stability of gold is seen as an excellent opportunity for continued research in this domain.

A final research topic deemed worthy of perusing is the development of a comprehensive model making use of the measured thiosalt loading rates and their distribution coefficients to describe the gold loading process in the presence of polythionate species on anion exchange resins. Publications from other research groups (CSIRO) indicate this is currently an ongoing objective.
8.3 Concluding Remarks

The CaTS leaching system has been successfully applied for a niche application at the BGC Goldstrike mine to deal with double refractory sulfide ores. The technological development of this process was driven by the need for an alternative reagent to the otherwise futile cyanidation-CIL process to leach gold from autoclave treated discharge materials due to the preg-robbing effect of the contained Total Carbonaceous Matter (TCM). Moreover, from an economic point of view, the commercialization of the CaTS leaching system was aided by the renewed use of already existing capital assets in the form of the otherwise obsolete autoclaves. This unique set of circumstances provided BGC with the platform to design and construct the first industrial thiosulfate leaching process. This CaTS leaching technology will not be replacing conventional cyanidation any time soon yet represents an important step or leap towards establishing new alternative, environmentally safe and economical ways to treat ever more complex gold ores bodies.

The modus operandi for BGC hitherto has been to establish the best operating conditions and to increase production using this new technology. Operational challenges were soon encountered and a root cause for reduced gold extractions was identified as the management of the complex chemistry associated with the thiosulfate reagent degradation products. The work performed in this dissertation played a small part of the larger picture to help fundamentally understand the process. Ultimately, the continuation of these research endeavors will help ensure and solidify the optimal performance of this leaching process. Hopefully this technology can eventually be applied for the treatment of Carlin-type gold deposits elsewhere in the world.
References


Appendix

A.1 Supporting Figures

Figure A 1: Elution curve of a mixed polythionate sample. Elution flow rate was 0.5 cc/sec. (Iguchi 1958).

Figure A 2: Effect of various sulfur anions at 0.05 M on the kinetics of the loading of gold on Amberjet 4200 at an initial gold concentration of 20 mg/L. (O’Malley 2002).

Figure A 3: Effect of tetrathionate on Au loading onto various strong base resins. Loading solutions: 0.1 M ATS + 10 ppm Au + x M Na₂S₄O₆·2H₂O; pH = 9. Resins concentration: 1 g/L for IRA-910 and 0.5 g/L for the rest of resins (Zhang et al. 2002a).
Figure A 4: Sulfur and gold mass balance for gold stability test (Figure 41 A) with initial addition of 25 mM trithionate.

Figure A 5: Sulfur and gold mass balance for gold stability test (Figure 41 B) with initial addition of 25 mM tetrathionate.
Figure A 6: Sulfur and gold mass balance for gold stability test (Figure 41 C) with initial addition of both 25 mM tri- and tetrathionate.

Figure A 7: Comparison of CaTS leaching tests of July’15 AlkPox without air sparging (J4) and Apr.’16 AlkPox with air sparging (A4) in the presence of 4 mM tetrathionate with increasing resin additions. Test J4 and A4 contain 3.4 and 15 mL resin/L slurry respectively.
A.2 Organic AAS Gold Stock Solution Procedure

The following procedure outlines the steps used to prepare a 100 mg/L organic gold stock solution to be used for organic gold standard preparations.

a. Weigh a calculated amount of CaTS (typically 0.1 M) in a clean 50 mL vol. flask and NaCN (in 25% molar excess to TS) in a small weighing boat
b. Clamp small clean 50 mL beaker used for gold standard preparations only
c. Calibrate a pH electrode and place in beaker
d. Fill beaker with just enough ultra pure water (18.2 MΩ) to submerge the pH electrode tip (junction)
e. Pipette 5 mL of gold atomic absorption standard (Acros Organic, 1000 mg/L in 20 % HCl) into beaker
f. Neutralize solution from pH ~0.75 to pH 3 using dropwise addition of 50 wt % NaOH

g. Continue neutralizing up to pH 10.5 using 0.1 N NaOH and record pH

Figure A 8: Comparison of CaTS leaching tests of July’15 AlkPox without air sparging (J3) and Apr.’16 AlkPox with air sparging (A3) in the presence of 4 mM trithionate with increasing resin additions. Test J3 and A3 contain 3.4 and 15 mL resin/L slurry respectively.
h. Quantitatively add weighed amount of NaCN by rinsing the weighing boat’s content into the beaker, stir in with electrode and dissolve completely, wait 10 minutes, record pH
i. Rinse pH electrode carefully and thoroughly with as little 18.2 MΩ water as possible: Hold pH electrode vertically and rinse downwards while being careful not to splash. No not exceed 35 mL total volume
j. Quantitatively transfer solution into the 50 mL volumetric flask containing CaTS by rinsing the beaker a minimum of four times. Make up the remaining volume of the flask to the meniscus with nano water
k. Seal the flask with parafilm or cap and flip upside down 20 times
l. Draw out 25 mL of aqueous gold solution with pipette for aqueous use only into 50 mL centrifuge tube
m. Draw out 25 mL of MIBK with 1 % Aliquat 336 with pipette for organic use only and add it to the 50 mL centrifuge tube containing aqueous gold solution
n. Vigorously manually shake the centrifuge tube for 10 minutes
o. Centrifuge the 50 mL tube and subsequently separate the 100 ppm gold organic phase (top) into a new sealable tube using a transfer pipette. Properly discard the remaining solution in the centrifuge tube consisting of the gold-less aqueous solution (bottom) and a thin meniscus of organic (top) with a cruddy phase in-between
p. Prepare working gold standards (0.25, 1, 2.5 and 5 mg/L) by diluting appropriate amounts of the 100 ppm stock solution with the MIBK/Aliquat 336 organic solution

A.3 Statistical Analysis for Gold Solvent Extraction in MIBK

A.3.1 Objective

Several tests were conducted to determine if shaking time had an effect on gold extraction by the organic phase (MIBK) from the aqueous sample during the AAS sample preparation procedure. Furthermore, the effects of pH and the use of an older versus newer stock solution was also examined.

A.3.2 Procedure

Two 100 mg/L gold stock solutions, one old and one new, were each used to prepare two 250 mL solutions containing 5 mg/L of gold in 0.1 M CaTS with pH’s of 8.5 and 10. From these aqueous
solutions, samples of 4 mL were drawn into test tubes containing 0.25 mL of an excess of cyanide (2 M NaCN, giving an CN⁻/TS molar ratio of 1.25) followed by the addition of 8 mL of MIBK containing 1 % Aliquat. These samples were then shaken for periods of 2, 5 or 10 minutes before being placed in a centrifuge for phase separation at 2000 rpm for 12 minutes. For each sample, the organic phase was then transferred into a test tube using a disposable pipette. A calibrated AAS was run in organic mode with standards prepared from a 100 mg/L stock solution prepared in the same fashion as the AAS samples for matrix matching.

### A.3.3 Results

Table A 1 contains the raw data adjusted to take dilution factors into consideration. During the AAS analysis, a standard check was made every 9 samples. These standard checks were used in a bracketing technique to minimize the effects of instrumental drift. Each sample was analyzed twice and the average of the two measurements is given in Table A 1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Avg. (mg/L)</th>
<th>Sample ID</th>
<th>Avg. (mg/L)</th>
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<td>10-2-O2</td>
<td>0.62</td>
<td>10-2-N2</td>
<td>0.87</td>
</tr>
<tr>
<td>10-5-O1</td>
<td>4.58</td>
<td>10-5-N1</td>
<td>4.58</td>
</tr>
<tr>
<td>10-5-O2</td>
<td>4.57</td>
<td>10-5-N2</td>
<td>4.60</td>
</tr>
<tr>
<td>10-5-O3</td>
<td>4.56</td>
<td>10-5-N3</td>
<td>4.60</td>
</tr>
<tr>
<td>10-10-O1</td>
<td>4.55</td>
<td>10-10-N1</td>
<td>4.67</td>
</tr>
<tr>
<td>10-10-O2</td>
<td>4.63</td>
<td>10-10-N2</td>
<td>4.68</td>
</tr>
<tr>
<td>10-10-O3</td>
<td>4.58</td>
<td>10-10-N3</td>
<td>4.61</td>
</tr>
</tbody>
</table>

All statistics were conducted using IBM SPSS Statistics software version 21. For analysis requiring a level of significance alpha, the widely accepted standard value of 0.05 was selected (95% confidence interval).
A.3.3.1 Effect of pH

A.3.3.1.1 Independent T-Test

The independent T-test compared the means between two unrelated groups (pH 8.5 and pH 10) on the same continuous dependent variable (gold concentration).

<table>
<thead>
<tr>
<th>Table A 2: Independent Samples Test.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levene's Test for Equality of Variances</td>
</tr>
<tr>
<td>F</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>mgd. Equivariances assumed</td>
</tr>
<tr>
<td>mgd. Equivariances not assumed</td>
</tr>
</tbody>
</table>

Here, the Levene’s test for equality has a P value of 0.891 indicating that the variances are equal and that the resulting P value for the T-test for the equality of means assuming equal variances, given on the same line, is equal to 0.975. Therefore we must accept the null hypothesis indicating that the means for gold concentration of the two pH values are equal.

A.3.3.2 Effect of Old Gold Stock vs. New Gold Stock

A.3.3.2.1 Independent T-Test

The test summarized in Table A 3 shows that the means of gold concentrations for samples made up from new or old gold stock solutions are not significantly different (P= 0.937).

<table>
<thead>
<tr>
<th>Table A 3: Independent Samples Test.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levene's Test for Equality of Variances</td>
</tr>
<tr>
<td>F</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>mgd. Equivariances assumed</td>
</tr>
<tr>
<td>mgd. Equivariances not assumed</td>
</tr>
</tbody>
</table>

This result can be interpreted as saying that samples prepared from an old gold stock solutions still yield the same gold concentrations as samples prepared from a freshly prepared gold stock solution. This also confirms that a 1250 mg/L gold stock solution made up in 0.1 M CaTS is quite stable.

A.3.3.3 Effect of Shaking Time

A.3.3.3.1 One Way ANOVA for Shaking Times

The null hypothesis for this analysis is that the gold concentrations after shaking samples for time periods of 2, 5 and 10 minutes are equal. Thus $H_0: t_{2\min} = t_{5\min} = t_{10\min}$.  

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The P value for this ANOVA was 1.67E−42 which is smaller than alpha (P<0.05) and therefore the null hypothesis must be rejected. This concludes that shaking time has a significant variance on the gold concentration when comparing three difference shaking times.

Table A 4: One way ANOVA for Shaking Times.

<table>
<thead>
<tr>
<th></th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>89.521</td>
<td>2</td>
<td>44.760</td>
<td>11017.082</td>
<td>1.686567E-42</td>
</tr>
<tr>
<td>Within Groups</td>
<td>.118</td>
<td>29</td>
<td>.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>89.639</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### A.3.3.3.2 T-Tests

To further analyze the effects of shaking times, a T-test can help identify if the gold concentrations from samples with different shaking times are significantly different from one another. A T-test determines if the means of two sample groups are the same or different.

#### A.3.3.3.2.1 T-Test 2 Minutes vs. 10 Minutes

This T-test, where equal variances are not assumed (P=0.007 < 0.05 .: Reject the null hypothesis), gives a P value of 3.73E−13 indicating that the means of the two time periods are significantly different from one another. This is an expected results based on the initial observation of the data which differs greatly.

#### A.3.3.3.2.2 T-Test 2 Minutes vs. 5 Minutes

Similarly to the previous T-test, there is a significant difference between the means of the samples shaken of 2 minutes versus those shaken for 5 minutes (P=2.74E−12).

#### A.3.3.3.2.3 T-Test 5 Minutes vs. 10 Minutes

This T-test, where equal variances are not assumed (P=0.038 < 0.05 .: Reject the null hypothesis), gives a P value of 0.029 indicating that the means of the two time periods are significantly different from one another. This result was surprising but holds with a confidence interval of 95%. This can
be explained by looking at the descriptive statistics indicating a very small variance and therefore standard deviation for each data set.

**Table A 6: Independent Samples Test (5 minutes vs. 10 minutes shaking).**

<table>
<thead>
<tr>
<th>mg/L</th>
<th>Equivariances assumed</th>
<th>Equivariances not assumed</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.64</td>
<td>.038</td>
<td>2.415</td>
</tr>
<tr>
<td></td>
<td>4.59</td>
<td>4.62</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std. Error of Mean</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std. Deviation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Variance</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**A.3.3.4 Descriptive Statistics**

**Table A 7: Case summaries.**

<table>
<thead>
<tr>
<th>min</th>
<th>2 mg/L</th>
<th>5 mg/L</th>
<th>10 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>8</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Mean</td>
<td>0.74</td>
<td>4.59</td>
<td>4.62</td>
</tr>
<tr>
<td>Median</td>
<td>0.74</td>
<td>4.60</td>
<td>4.63</td>
</tr>
<tr>
<td>Grouped Median</td>
<td>0.74</td>
<td>4.60</td>
<td>4.63</td>
</tr>
<tr>
<td>Std. Error of Mean</td>
<td>0.04</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Sum</td>
<td>5.94</td>
<td>55.09</td>
<td>55.44</td>
</tr>
<tr>
<td>Range</td>
<td>0.32</td>
<td>0.05</td>
<td>0.13</td>
</tr>
<tr>
<td>Std. Deviation</td>
<td>0.12</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Variance</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
A.3.4 Conclusions

To summarize, it was determined that:

- The pH of the solution has no significant impact on the measured gold concentrations.
- An old gold stock solution is just as good for preparing samples as is a freshly prepared stock solution.
- 10 minute shaking results in significantly better gold extraction than 5 and 2 minutes respectively.

A.4 Goldstrike Loaded Resin (GSLR) Characterization

Together with an industrial barren resin material (GSBR - see Section 7.1.2), a sample of an industrially loaded resin (GSLR) was also obtained through AuTec. Although no loading experiments were performed using this resin material, several stripping experiments were conducted on it to determine its gold and polythionate contents. Table A 8 gives the average loading values of thiosulfate, polythionates and sulfate stripped from four separate resin fractions.

<table>
<thead>
<tr>
<th>GSLR Strip Analysis</th>
<th>TS Loading</th>
<th>3T Loading</th>
<th>4T Loading</th>
<th>5T Loading</th>
<th>SO$_4^{2-}$ Loading</th>
<th>Total Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Concentration</td>
<td>0.94</td>
<td>9.08</td>
<td>50.94</td>
<td>82.39</td>
<td>389.05</td>
<td>1064.78</td>
</tr>
</tbody>
</table>

As anticipated, in comparison the GSBR materials (Table 26), the GSLR contains a much higher fraction of loaded polythionate species amounting close to 25 % of the theoretical loading capacity. Figure A 9 shows the resulting elution profile of a stripping procedure where a bed volume of 5 mL GSLR contained inside a burette was continuously eluted at a rate of 10 mL/hr using 0.5 M sodium perchlorate. This elution profile confirms trithionate as the most weakly adsorbed species following by tetrathionate and eventually pentathionate. The small concentrations of thiosulfate measured in every later BV’s are likely present due to its regeneration from polythionate degradation reactions rather than from actual elution from the resin material.
A.5 Gold Loading Isotherms and the Interpretation of Available Data

There are few publications that include data showing the effects of polythionates on the adsorption of gold on ion exchange resins. A particular publication of interest (Muslim 2010a) contains valuable tables with increasing gold and respective polythionate concentrations in non-ammoniacal solutions before (initial) and after addition of 0.5 g Purolite A500/2788 IX resin and equilibration (final). This data was used to plot curves of % gold loading versus equilibrium gold solution concentration giving a linear relationship with a trendline equation. Knowing the total capacity of this resin in the Cl$^-$ form is 1.15 eq/L and that the adsorbing gold species are in the form of Au(S$_2$O$_3$)$_3^-$, one can determine the capacity for gold to be 75.50 g Au/L resin. Next, with the given trendline equation, the gold loading percentage corresponding to a given solution gold concentration in equilibrium can be determined. The gold loading percentage can easily be converted to a gold loading value in mg Au/L resin using the known total capacity of the resin. Finally, by using the given tabulated initial and final gold solution concentrations and rearranging Equation (53) (O'Malley 2002), the volume of resin used in these equilibrium loading tests can be back calculated. From the data provided by Muslim (2010a), the average resin volume calculated by this manner was 0.755 mL. This volume is equal to 0.493 g by reference to the ratio of 1 mL per 0.653 g of Purolite A500 resin given by Muslim (2010a) collaborators Jeffrey et al. (2007). This average back-calculated mass of resin of 0.493 g is very close to the targeted 0.5 g described in the procedure for these loading experiments and confirms the validity of using the linear trendline equation to generate loading isotherms for non-tabulated experimental data.
Plots of $[\text{Au}]_{r, \text{eq}}$ versus $[\text{Au}]_{s, \text{eq}}$ such as Figure 14 and Figure 21 are usually reported in the literature and are a useful tool in the design of separation processes.

### A.6 Summary of Preg-robbing Materials Used

Table A 9 summarizes the similar preg-robbing materials used for the various leaching experiments presented in this thesis. Also included in the table are the initial masses of the autoclave discharge materials received, their densities measured via pycnometer and finally head assays determined by fire assay.

<table>
<thead>
<tr>
<th>ID</th>
<th>Initial Mass (g)</th>
<th>Density (g/mL)</th>
<th>Head Assay (ppm)</th>
<th>Tests Associated with Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov. '14 PR2</td>
<td>388</td>
<td>2.7</td>
<td>2.96</td>
<td>A(Figure 51, 53, 55)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ConcPT-A (Figure 52, 53, 55)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Baseline A (Figure 58)</td>
</tr>
<tr>
<td>Jan. '15 PR2</td>
<td>1564</td>
<td>2.7</td>
<td>2.96</td>
<td>B (Figure 51, 53)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C (Figure 57)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conc3T (Figure 53, 56)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conc4T-A (Figure 53, 54, 56)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conc4T-B (Figure 53, 54)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conc4T-C (Figure 57)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ConcPT-B (Figure 52, 53)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Baseline B (Figure 58, 59 A, 60)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conc4T (Figure 59 A, 60)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Baseline + Air Sparging (Figure 59 B)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conc4T + Air Sparging (Figure 59 B)</td>
</tr>
<tr>
<td>July '15 AlkPox</td>
<td>1995</td>
<td>2.5</td>
<td>4.98</td>
<td>J1 (Figure 88, 89, 92); J2 (Figure 88, 89, 90); J3 (Figure 88, 91); J4 (Figure 88, 90, 91)</td>
</tr>
<tr>
<td>Apr. '16 AlkPox</td>
<td>1017</td>
<td>2.5</td>
<td>3.9 (SD = 0.09)</td>
<td>A1 (Figure 92, 93, 94); A2 (Figure 93, 94); A3 (Figure 93, 95); A4 (Figure 93, 95)</td>
</tr>
</tbody>
</table>
Table A 10 gives the elemental analysis of the PR2 preg-robbing material used.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>≤ 10</td>
<td>mg/L</td>
<td>Mg</td>
<td>2.15</td>
<td>%</td>
</tr>
<tr>
<td>Al</td>
<td>0.37</td>
<td>%</td>
<td>Mn</td>
<td>0.02</td>
<td>%</td>
</tr>
<tr>
<td>As</td>
<td>0.03</td>
<td>%</td>
<td>Mo</td>
<td>0.00</td>
<td>%</td>
</tr>
<tr>
<td>Au (FA)</td>
<td>2.96</td>
<td>mg/L</td>
<td>Na</td>
<td>0.21</td>
<td>%</td>
</tr>
<tr>
<td>Ba</td>
<td>0.07</td>
<td>%</td>
<td>Ni</td>
<td>0.04</td>
<td>%</td>
</tr>
<tr>
<td>Bi</td>
<td>≤ 0.001</td>
<td>%</td>
<td>P</td>
<td>0.15</td>
<td>%</td>
</tr>
<tr>
<td>Ca</td>
<td>4.49</td>
<td>%</td>
<td>Pb</td>
<td>0.00</td>
<td>%</td>
</tr>
<tr>
<td>Cd</td>
<td>0.00</td>
<td>%</td>
<td>S</td>
<td>0.87</td>
<td>%</td>
</tr>
<tr>
<td>Co</td>
<td>0.00</td>
<td>%</td>
<td>Sb</td>
<td>0.00</td>
<td>%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05</td>
<td>%</td>
<td>Se</td>
<td>≤ 0.001</td>
<td>%</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01</td>
<td>%</td>
<td>S total</td>
<td>0.90</td>
<td>%</td>
</tr>
<tr>
<td>Fe</td>
<td>1.61</td>
<td>%</td>
<td>Ti</td>
<td>0.00</td>
<td>%</td>
</tr>
<tr>
<td>Hg</td>
<td>13.00</td>
<td>mg/L</td>
<td>W</td>
<td>≤ 0.020</td>
<td>%</td>
</tr>
<tr>
<td>K</td>
<td>0.13</td>
<td>%</td>
<td>Zn</td>
<td>0.04</td>
<td>%</td>
</tr>
</tbody>
</table>