THIOSULFATE LEACHING OF NATURAL ACANTHITE ORE IN COPPER-AMMONIA-AMMONIUM SULFATE MEDIUM

by

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B.Sc., University of Alberta, 2014

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

MASTER OF APPLIED SCIENCE
in
THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

April 2017

Abstract

Silver is commonly present in acanthite in nature. Reagents like cyanide are used to extract silver from acanthite ores. However, cyanide can potentially damage human health and environment. The use of cyanide is tightly regulated, thus forcing the industry to seek for alternatives. Thiosulfate is currently the most promising alternative. The leaching chemistry of silver with thiosulfate is complex and maybe supplemented with additives such as ammonia, copper and even ethylenediaminetetraacetic acid. The efficiency of silver leaching is improved with the use of these additives.

The use of cyanide for silver leaching in Navidad project in Argentina is not permitted, so the use of thiosulfate leaching as an alternative was investigated. The application of thiosulfate leaching to Navidad ores containing acanthite was the focus of this thesis. This thesis provides experimental evidence that supports the use of thiosulfate with additives as a promising alternative to conventional cyanidation method for the Navidad deposits and for similar deposits, wherever found.

Thiosulfate leaching of silver is known for two pathways: silver in acanthite is substituted by cupric or by cuprous ion. The cupric pathway is thermodynamically more favourable, but various factors may affect extraction. Batch leaching tests showed that Navidad ore samples may be leached using thiosulfate, with silver extraction affected by variables including thiosulfate concentration, ammonia concentration, initial copper addition, pH, temperature, EDTA addition and the presence or absence of air sparging. The most significant variables were thiosulfate concentration, ammonia concentration, copper addition and pH. Cyanidation yielded 91.2% extraction of silver from a sample of Loma de la Plata, and thiosulfate leaching with 0.2 M of thiosulfate and 1.0 M of ammonia yielded comparable extractions: 92.1% and 87.0%, respectively. Initial copper addition increases extraction rate from 66.2% to 72.3% after 72 hours, and air sparging increases extraction rate to 84.8% after 72 hours. Other samples from the Navidad Project were also tested and found to be amenable to thiosulfate leaching. LDLPMC and Connector Zone (CZMC) sample were found to have potential for thiosulfate leaching to achieve a high silver extraction.

Preface

This thesis is original, unpublished, independent work by the author, Yueh (Yves) Lai.

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List of Symbols and Abbreviations

Standard, or multiples of, SI units and International Union of Pure and Applied Chemistry (IUPAC) approved abbreviations were used wherever applicable. In the case where the convention in scientific literature of the field uses alternative units (e.g., ppm), these are used. A list of major symbols and abbreviations used:

Acronyms and Abbreviations

AAS – atomic absorption spectroscopy (chemical technique) or atomic absorption spectrophotometer (apparatus)

ACS – American Chemical Society

AM - ammonia

BL - baseline

CZMC – Connector Zone Master Composite

DI – deionized water

EDTA – ethylenediaminetetraacetic acid

ERC – endpoint recognition criterion

ICP-MS - inductively coupled plasma mass spectrometry

LDLPMC – Loma de la Plata Master Composite

MEDUSA – make equilibrium diagrams using sophisticated algorithms

NHMC – Navidad Hill Master Composite

ORP – oxidation reduction potential

RPM – revolutions per minute

SHE – standard hydrogen electrode

TS - thiosulfate

XRD – X-ray diffraction

USD – United States Dollar

Letters

C or c – concentration (M)

E^o – standard reaction potential (V)

ΔG^o – standard Gibbs free energy change at 25°C (kJ/mol)

ΔH^o – standard enthalpy change at 25°C (kJ/mol)

P80 – 80% quartile for a particle size distribution

R – gas constant (8.314 J/mol/K)

S^o – entropy (valid at 25°C) (J/mol/K)

t – time (hours)

T – temperature (°C or K)

Acknowledgements

I would like to sincerely thank my supervisor, Dr. David Dreisinger, for guidance, support, encouragement, understanding and helpful feedback throughout the study. It is my great honor to be a student of yours.

I would also like to express my sincere gratitude to Dr. Bé Wassink, who provided training and persistent feedback with respect to my procedures and analytical methods, as well as answering all my questions with great patience. Thank you to senior fellows in our lab and department like Renaud Daenzer, Dr. Jianming Lu, Meng Li, Dr. Alex Burns, Dr. Zihe Ren, Hongxing Liang and Jackie Zhou for your sharing, suggestion, support and assistance in all aspects. Another thank you to technicians in our departments like Jacob Kabel and Dave Torok for providing support for equipment. I greatly appreciate the help and support of Chih-Wei Chao in conducting many experiments. I wish you all the best in graduate school. Sincere thanks are due to Dr. Jared Deutsch for prompt email correspondence in relation to my numerous questions and for kindly arranging a face to face meeting during my stay in Edmonton.

In addition, my sincere thanks to Dr. Dreisinger, the Department of Materials Engineering at University of British Columbia, Pan American Silver and Mitacs Accelerate for providing the financial assistance necessary to undertake this thesis.

Many thanks to my loyal friends I have met in Vancouver, Edmonton, Toronto and Shanghai. Encounters with you have enriched my life experience. You are always there to support me, even

when we are apart and have not seen each other for a long time. Best of luck to all of you and I hope we all strive towards a bright future.

I want to also thank my undergraduate professors in Department of Chemical and Materials Engineering in University of Alberta, Dr. Jing-Li Luo, Dr. Stojan Djokić, Dr. Suzzane Kresta, Dr. Hao Zhang, Dr. Qi Liu, Dr. Chad Liu, Dr, Hani Henein, Dr. Ivey Douglas and Dr. Thomas Etsell for helping me to realize my ambition to pursue my graduate degree.

Finally, I would like to express my deepest gratitude to my parents, Roger and Maureen, my sister Bernice, and Grace for their love, encouragement, support and suggestions. Without you I would not have gone this far.

Dedication

“Your story may not have such a happy beginning, but that doesn’t make you who you are.

It is the rest of the story, who you choose to be.”

— Soothsayer *Kung Fu Panda 2*

We don’t need to think about rescuing the world, but do our best on every single piece.

Maybe one day, the world will change for you.

— Ke Hua

我們不需要夢想著拯救世界；但是做好點點滴滴，或許有一天，這個世界將會為你而變。

—— 格華居士

“On and on stretched my road, long it was and far;

I would go high and go low, in this search that I made.”

— Qu Yuan (340 BC – 278 BC) *Li Sao (Encountering Sorrow)*

「路漫漫其修遠兮，吾將上下而求索。」

—— 屈原《離騷》

Chapter 1: Introduction

The leaching of gold and silver ores in alkaline cyanide solution is widely applied. More than 90% of gold is extracted using cyanide, and 6% of the 1.1-million-tonne annual production of hydrogen cyanide is converted into sodium cyanide for the use of the mining industry (Laitos, 2012). Cyanide may be used safely in this application. However, there is ongoing public concern related to the use of cyanide due to the highly toxic nature of this chemical and a number of historical industrial disasters related to cyanide spills. If the cyanide containing waste solutions and slurries used in precious metal recovery are not treated properly then there may be a hazard to human and animal health. (Eisler, 2007) There are some jurisdictions that have banned the use of cyanide for precious metal leaching such as the state of Montana and the country of Argentina. (Laitos, 2012) To enable gold and silver leaching in these places, the industry must seek for alternatives to cyanide. There are other reasons for developing non-cyanide lixiviants such as to treat ores and concentrates having excessively high consumption of cyanide or containing "preg-robbing" materials (H. G. Zhang et al., 2005). There are several lixiviants that have received significant interest to as a replacement for cyanide. Thiosulfate is a leading candidate. Thiosulfate has been used in the Patera process for silver sulfide leaching in the past (Fleming, 2007). At present, thiosulfate leaching of gold from a preg-robbing ore has been commercialized by Barrick Gold's Goldstrike plant in Nevada, USA (M. D. Adams, 2016). However, there are limited applications of thiosulfate for silver leaching in industry. This thesis focuses on investigating thiosulfate leaching with additives to treat a natural silver sulfide ore. To enhance the performance for thiosulfate leaching on precious metals, past studies have indicated that additives like ammonia and copper can be introduced into the leaching system to enhance leaching (Abbruzzese et al., 1995; Aylmore et al., 2001; Molleman et al., 2002), but the majority of the research on thiosulfate leaching focuses only on gold due to its higher value and larger market compared to silver. An extensive number of the latest research works on thiosulfate leaching are primarily interested in gold rather than silver (Aazami et al., 2014; Baron et al., 2011; Lampinen et al., 2015; Smith et al., 2016; Xu et al., 2015; Y.-b. Yang et al., 2015), and among those studies which concentrate on silver sulfide most have used synthetic silver sulfide or tailing materials from a mining process (Aylmore et al., 2014; Deutsch et al., 2013a, 2013b; Puente-Siller et al., 2013, 2014; Salinas-Rodríguez et al., 2016). Little has been reported regarding thiosulfate leaching of a naturally occurring silver sulfide ore.

Additionally, cupric ammoniacal thiosulfate leaching system is complex and the mechanism is still not fully understood (Puente-Siller et al., 2014). Ammonium thiosulfate has been used as the primary reagent due to its relatively inexpensive cost as well as providing an extra source of ammonia to the system (John O. Marsden et al., 2006; Muir et al., 2004). A study showed that the silver dissolution rate can be affected by addition of ammonium sulfate (Ibarra-Galvan et al., 2014). Other variables including temperature, initial thiosulfate concentration, initial copper concentration and initial ammonia concentration were investigated to determine the impact on the silver dissolution rate (Oraby et al., 2014). Ethylenediaminetetraacetic acid (EDTA) was also considered and tested as a lixiviant in the cupric-ammonia-thiosulfate leaching system (Puente-Siller et al., 2014).

In this thesis, a series of fundamental leaching tests with cupric ammonia thiosulfate system on a natural silver ore from the Navidad deposit in Chubut, Argentina were conducted. Using a batch reactor setup, the effects of reagent concentrations, temperature, and air-sparging were each investigated separately.

The remainder of the thesis is divided into 5 chapters. Chapter 2 covers the relevant literature background information about thiosulfate leaching; Chapter 3 discusses ore characterization and preparation including the process of size reduction; Chapter 4 focuses on the leaching performance of the samples under different conditions; Chapter 5 provides conclusions and recommendation for future work.

Chapter 2: Background and Literature Review

2.1 Silver and Human Society

2.1.1 Silver in History

Silver is one of the eight precious metals and is one of the most important and well-known metals in human society. Metallic silver has high reflectivity and this makes it popular for jewelry and tableware (Bringas et al., 2003). Silver has also been used in human history as an antimicrobial agent for six millennia since its discovery (Alexander, 2009). The monetary use of silver was initiated back in ancient Egypt and Mesopotamia for financial transactions, where the metal was not native in either region (Bernholz et al., 2014). Discovery and use of silver can be traced back to 4000 B.C., after the discovery of gold and copper (Hill et al., 1939). In the earlier period, silver was mostly mined and smelted from lead ores by means of cupellation (Patterson, 1972). The first silver production was established in Anatolia, Turkey in about 3000 B.C., and the center of silver production shifted to Greece in 1200 B.C. The Roman Empire adopted silver as part of the standard coinage in 269 B.C., which strengthened the important standing of silver in human society. The total world silver production peaked at 30,000 metric tons during 50 B.C. to 100 A.D. then shrank to one-eighth of that number during 300 A.D. to 400 A.D. (Patterson, 1972) The silver production trend intimately aligned with the collapse of the Roman Empire, as the Empire fell economically due to the depletion of silver-lead ore. Spain overtook the title for center of silver production in around 100 A.D., and dominated the production for a millennium. With the Moor invasion and occupation of Spain starting in the 8th century, it necessitated the European countries to seek for alternative source of silver, principally in Central Europe. Discovery of silver mines in Austria-Hungary, Germany and Eastern Europe led to an increase of silver production from 750 A.D. to 1200 A.D. After the Spanish conquest of the New World, the newly founded silver mines in Mexico, Bolivia and Peru contributed 85% of the world silver production from 1500 to 1800. Approximately 3 million troy ounces (103 metric tons) of silver were mined in Bolivia annually from 1500 to 1800; Peru produced another 3 million troy ounces of silver annually from 1600 to 1800; 9 million troy ounces (309 metric tons) of silver were produced in Mexico annually in the 1700s. Technological innovation and exploitation of new regions, steam-assisted drilling, dewatering and improved haulage for example, exploded during the period from 1876 to 1920, leading to silver production in different countries, with the most notable one being Comstock Lode area in Nevada, U.S. The annual world silver production increased to 190 million troy ounces (5,909.7 metric tons) during the period 1900 to 1920. (Patterson, 1972; Sim et al., 2011; The Silver Institute, 2004)

2.1.2 Silver in Contemporary Society

At present, silver as a precious metal still maintains its importance in human society. Even though silver is not used as a structural material like steel, it is still a very critical non-ferrous metal to human society. Silver has wide usage in various applications due to its physical and chemical properties: electronics, dentistry, aerospace, chemical industries, etc. (Bringas et al., 2003). Of all the demands on silver, industrial use of silver occupies the greatest portion, where electrical and electronics requires the largest amount among all industries. Jewelry use comes second and silver coins and bars are the third (The Silver Institute, 2014b). The world mine production of silver steadily increased from 613.6 million ounces to 886.7 million ounces from 2004 to 2015. The price of silver increased from 6.658 USD/oz. to 23.790 USD/oz. in this period. The highest silver price since 1985 was 49.80 USD/oz. on April 25, 2011 (The Silver Institute, 2014a). A massive quantity of silver is stored in the form of bullion bars through historical accumulation for investment. Theoretically, there should be a huge stock of silver that overhangs the market; about 22 million oz of scrap silver, old silver coins and silverware were drawn out of the market when its price was artificially as high as \$40 USD/oz in 1980 (LaBorde, 2016; Mohide, 2014). With Hunts brothers' attempt to cornering silver market to push the silver price, Commodity Exchange Inc. (COMEX) and Commodity Futures Trading Commission (CFTC) eventually intervened. The Hunts brothers went bankrupt as they were not able to buy out all the silver before they ran out of cash along with the intervention of government. Besides, an approximation of 34% of the stock is held in vaults of the central banks around the world. (Mohide, 2014) The top 10 silver production countries in the world are Mexico, China, Peru, Australia, Chile, Russia, Poland, Bolivia, U. S. and Canada, where more than half of the total production of the top 10 countries is contributed by Latin American countries (USGS, 2016). The Latin American countries have dominated silver production in the past, and with more new silver mines being discovered, they will continue to play a major role in the world's silver production in the near future.

2.2 Silver Production from Minerals

2.2.1 Mineralogy of Silver Ore

Silver may exist in nature as elemental silver, silver alloys or a variety of silver minerals. Besides the native elemental silver, silver ore may contain minerals such as ceragyrite or chlorargyrite ($AgCl$), argentite, or more correctly acanthite (Ag_2S), freibergite ($(Ag, Cu, Fe, Zn)_{12}(Sb, As)_4S_{13}$), pyrargyrite ($Ag_3SbS_3$), proustite ($Ag_3AsS_3$), embolite ($AgCl$, $AgBr$) and bromyrite ($AgBr$) (Australia, 2015; Chamberlain et al., 1984; Cotton, 1997; RRUFF, 2005). Silver sulfide has a strong affinity for galena (PbS), a possible host sulfide mineral, and is mostly abundant in the form of "exsolved, black, minute, invisible specks in large host metal sulfide crystals" (Nissen et al., 1915; Patterson, 1971). Silver can also be affiliated to galena if antimony and/or bismuth are present in a significant amount (Amcoff, 1984).

2.2.2 Leaching of Silver with Cyanide

Elsner discovered the requirement for oxygen in the dissolution of gold in cyanide solution in 1846, which led to the famous Elsner equation (Habashi, 1997):

$$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4Na[Au(CN)_2] + 4NaOH$$

However, it was not until 1887 that its value was recognized, when McArthur and Forrest patented the process and initiated cyanide leaching on gold ores. Cyanidation of silver ore is accomplished in a similar fashion because of the similar chemical properties of silver compared to that of gold and favourable economics. Cyanidation of elemental silver can be achieved by via aeration of the cyanide containing solution (Habashi, 1997):

$$4Ag + 8NaCN + O_2 + 2H_2O \rightarrow 4Na[Ag(CN)_2] + 4NaOH$$

Acanthite reacts slower in comparison to elemental silver and follows the reaction (Habashi, 1997):

$$2Ag_2S + 10NaCN + O_2 + 2H_2O \rightarrow 4Na[Ag(CN)_2] + 2NaSCN + 4NaOH$$

Depending on the grade of the silver ore, a variety of leaching processes can be used including heap leaching or agitated tank leaching. For agitated tank leaching, the silver ore is first crushed and wet-ground, then treated with 5-10 g/L of sodium cyanide solution for several days in a Pachuca tank. (Habashi, 1997) A thickener and filter removes the unreacted solid residue, and then zinc powder is introduced for cementation. (Habashi, 1969) The pregnant leach solution must be deoxygenated before cementation to ensure that zinc will not be oxidized into $Zn(CN)_4^{2-}$ by oxygen (Swaddle, 1990). The cementation process, which is also called the Merrill Crowe Process, follows the reaction (Parga et al., 1988):

$$Zn_{(s)} + 2Ag(CN)_2^-{}_{(aq)} \rightarrow Zn(CN)_4^{2-}{}_{(aq)} + 2Ag_{(s)}$$

There are other methods of recovery of silver from cyanide solution, including ion exchange, electrolytic reduction and adsorption of silver cyanide complex onto activated carbon, but these alternatives have not achieved the same level of importance and productivity comparing to their counterparts in gold recovery (Habashi, 1997).

Cyanidation has several disadvantages even though it performs well when leaching precious metals. In the case of heap leaching, cyanidation of silver ore is relatively slower and yields a lower recover when compared with cyanidation of gold ore under the same typical conditions of conventional cyanidation method (M. D. Adams, 2016; Habashi, 1967, 1997; Hiskey et al., 1990). With sodium cyanide concentration higher than 1mM, the silver leaching rate is lower than the gold leaching rate, typically only 80-90% of that of gold (Habashi, 1967). However, in extremely diluted cyanide solution (e.g., 2.33 mM of cyanide) the dissolution rate of elemental silver can be significantly higher than that of elemental gold (Dai et al., 2013), which agrees with the higher silver leaching rate at extremely low concentration range by Barsky et al. (1934) and Habashi (1967). In some cases, the lower extraction of silver can be attributed to the different form of gold and silver in the natural deposits, as gold is usually in elemental form and silver may be in various mineral forms, some of them being cyanide insoluble (M. D. Adams, 2016). Other metals and minerals may be present in natural ores with silver and may react in aerated dilute alkaline cyanide solutions. These reactions may consume cyanide and oxygen and thus reduce the efficiency of silver cyanidation (John O. Marsden et al., 2006). Cyanide has been the primary leaching agent used in the mining of gold and the current industry has been able to safely and responsibly manage it in most cases (Laitos, 2012). However, cyanide has still raised public concern about industrial application due to high toxicity and the consequences of spills in the past. In the case of Navidad ore from Argentina, the ore has a high content of copper, which significantly increases the consumption of cyanide. Due to the legislative regulation in Chubut Province, Argentina (Anes et al., 2008; Laitos, 2012), cyanide cannot be used and alternative methods of silver recovery must be identified.

2.2.3 Leaching of Silver with Alternatives to Cyanide

A large body of research on alternative lixiviants to cyanide for the leaching gold and silver was initiated in the 1990s. The major alternatives include thiosulfate, thiourea, thiocyanate and halides. (John O. Marsden et al., 2006)

In the traditional cyanidation process, a significant amount of lime is used to maintain the high pH of the alkaline cyanide solution. With progression on developing refractory sulfide ore projects, more and more interest has risen on using acidic media to avoid high neutralization cost. (John O. Marsden et al., 2006). Thiourea, a lixiviant that can be used under acidic conditions, complexes with silver by the reaction (Baláž et al., 1996):

$$Ag^{+} + 3CS(NH_2)_2 \rightleftharpoons Ag[CS(NH_2)_2]_3^{+}$$

A study by Pesic et al. (1990) using the rotating disc technique showed that silver only dissolves in thiourea with the presence of ferric ion, and foreign ions such as copper have a dramatically negative effect on the dissolution of silver. Strong oxidants like manganese dioxide and hydrogen peroxide are also detrimental as thiourea is oxidatively degraded. An excess of ferric sulfate will passivate the silver surface with formation of a solid silver-thiourea complex and hinder further dissolution. Even though thiourea is a possible carcinogen, and it dissolves heavy metals beside gold and silver (John O. Marsden et al., 2006). Thiourea has been found to have a high reagent consumption compared to cyanidation. No large-scale commercial application using thiourea for silver leaching has been conducted. (John O. Marsden et al., 2006)

Thiocyanate is another option to substitute for the cyanidation of silver. (S.-H. Yang et al., 2010) Thiocyanate complexing of silver follows the reaction:

$$Ag^{+} + nSCN^{-} \rightleftharpoons Ag(SCN)_{n}^{1-n}$$

where n = 2, 3, 4 depending on the conditions of reaction. The optimum conditions yielding highest silver extraction were obtained with 1.5 M NH_4SCN, 0.5 g/L lignin, 2 g/L Fe^{3+}, 200 g/L concentrate, 1.2 MPa oxygen pressure, 130 °C and 3 hours leaching time. The silver extraction was 94% and only 7% of ammonium thiocyanate was lost. (S.-H. Yang et al., 2010). Acidic thiocyanate shows potential for industrial application, but more work needs to be accomplished on optimization of conditions and minimization of reagent consumption (John O. Marsden et al., 2006).

The chlorination system was applied extensively in the 1800s before the introduction of cyanidation. This process is now no longer used for leaching, but there are proposed chloride-based processes for treating refractory or semi-refractory ore to replace cyanide. (John O. Marsden et al., 2006). The chloride system is also proven to be effective to leach silver sulfide in an acidic environment with the presence of ferric ion (Dutrizac, 1994). A study has also suggested high silver leaching rate even without addition of ferric ion at elevated temperatures (Almeida et al., 1995). The dissolution of insoluble silver chloride in excess chloride ion follows the reaction (Dutrizac, 1994):

$$AgCl + 3Cl^{-} \rightarrow AgCl_{4}^{3-}$$

The dissolution of silver sulfide may be inhibited by formation of an insoluble AgCl surface layer as well as by the formation of a passive sulfur layer on the sulfide surface. The Ag-Cl complexes can be trapped in the pores of such a passive layer, thus reducing the rate of dissolution (Dutrizac, 1994). The chloride system may be potentially promising due to this high recovery on silver comparable to cyanidation as well as other valuable metals even without ferric ion (Almeida et al., 1995; Jeffrey et al., 2001). The chloride system is limited by the requirement of a high concentration of chloride to promote silver solubility. The chloride solutions are corrosive to industrial equipment especially at high temperature.

Other halides systems like bromine-bromide, iodine-iodide, and bromine-chloride have been investigated for gold leaching, but these systems suffer from high reagent cost, high material cost and industrial hygiene and health issues. Other leaching systems using cyanamide, cyanoform, organic nitrile and malononitrile-related compounds were only studied academically (John O. Marsden et al., 2006).

None of these alternatives are comparable to thiosulfate, which is the most promising, technically and economically viable alternative to cyanide. Thiosulfate-based leaching systems will receive the most attention in industry in the 21st century. (John O. Marsden et al., 2006)

2.2.4 Leaching of Silver with Thiosulfate

The thiosulfate leaching process, also called the Patera Process, was developed in Europe in the 1800s. The process has further received attention in Central and South America, then North America due to its low cost and high recovery comparing to the traditional amalgamation process. The common concentration range used for the process is 2.5-25 g/L, in which excess thiosulfate prevents formation of the sparingly-soluble silver-thiosulfate precipitate $Na[Ag(S_2O_3)]$. Besides sodium thiosulfate, calcium thiosulfate and sodium copper thiosulfate are alternatives for the process. However, the Patera Process was later replaced by cyanidation due to its lower yield in comparison. (Habashi, 1969) There are still places in Mexico that use thiosulfate for silver leaching (Dreisinger, 2016), but thiosulfate leaching is not as common as cyanidation.

The dramatic discontinuation and rediscovery of thiosulfate versus cyanide on leaching of precious metals is mostly dependent on economics and human factors. Cyanide overtook the dominant Patera Process for silver leaching due to its favourable economics in the early 20th century (Habashi, 1969) and it was not until the 1970s that thiosulfate leaching has drawn more serious attention again. There was a dramatic increase of research on thiosulfate leaching in the 1990s due to public concerns about use of cyanide. Thiosulfate has particular advantages on leaching ores containing carbonaceous preg-robbing materials, cyanide-consuming copper and sulfur species and refractory sulfides (John O. Marsden et al., 2006). Different aspects of thiosulfate leaching will be discussed in detail in Section 2.3: Cupric-Ammonia Thiosulfate Leaching Systems.

2.3 Cupric-Ammonia Thiosulfate Leaching Systems

The cupric-ammonia-thiosulfate system has been widely studied due to its potential to leach silver and gold (Abbruzzese et al., 1995; Aylmore et al., 2001; Breuer et al., 2002). About a century after the invention of Patera Process, interest on thiosulfate leaching revived. Berezowsky et al. (1979) treated residues of ammoniacal oxidation leaching of sulfide copper concentrates with atmospheric ammoniacal thiosulfate and managed to recover more gold and silver compared to that recovered by cyanidation. Umetsu et al. (1972) identified $[Cu(NH_3)_4]^{2+}$

as a catalyst for the dissolution of gold, and formation of a CuS coating as causing inhibition of gold dissolution. Flett et al. (1983) discovered that the leaching of silver sulfide improves with an increase of cuprous and thiosulfate concentration, but higher copper concentration yields higher thiosulfate decomposition. An excess amount of thiosulfate was necessary to prevent silver re-precipitation, and a layer of Cu_2S may passivate the mineral surface. Zipperian et al. (1988) investigated the leaching of gold and silver in a rhyolite ore, and concluded that proper E_h-pH conditions are critical to prevent Cu_2S passivation. Other studies have discovered more advantages of the ammonia-thiosulfate leaching system over the traditional process. Ammoniacal thiosulfate leaching is found to be less sensitive than cyanidation to undesired cations (Aylmore et al., 2001), and an excess of ammonia hinders the dissolution of silicates and carbonates (Abbruzzese et al., 1995). If using a leaching system with a pH greater than 9.5, a number of unwanted compounds in the ore like CaO and Fe_2O_3 may precipitate out, avoiding any interference with leaching (Perez et al., 1987). Starting in the 1990s, research on the cupric-ammonia thiosulfate leaching system focused on testing how leaching performance is affected by various conditions, with reference to the E_h-pH diagrams and basic chemical reactions developed. In this section, the foundation of chemistry of the copper-ammonia thiosulfate leaching system will be discussed.

2.3.1 Chemistry of Cupric-Ammonia Thiosulfate Leaching System

The copper-ammonia thiosulfate system is mostly used for the leaching of gold, and in fewer cases it has been applied to leach silver. Most of the past research focuses on leaching of metallic gold and silver, and in some cases leaching of gold ore is tested as well. There are only a limited number of past research studies on the leaching of acanthite using thiosulfate. In the initial work by Berezowsky et al. (1979) on thiosulfate leaching, the chemical reactions for thiosulfate leaching on gold and silver were described. A sample calculation of Gibbs free energy of reaction will be included in the Appendix.

$$4Au + 8S_2O_3^{2-} + 2H_2O + O_2 \rightleftharpoons 4Au(S_2O_3)_2^{3-} + 4OH^- \qquad \Delta G° = -97.92 \text{ kJ/mol}$$

$$4Ag + 8S_2O_3^{2-} + 2H_2O + O_2 \rightleftharpoons 4Ag(S_2O_3)_2^{3-} + 4OH^- \qquad \Delta G° = -131.52 \text{ kJ/mol}$$

Gold and silver can form different thiosulfate complexes by bonding with various numbers of thiosulfate ions, but $Au(S_2O_3)_2^{3-}$ is the most stable (Massey et al., 1973) and $Ag(S_2O_3)_2^{3-}$ is theoretically the most stable since it has the lowest Gibbs free energy of formation (Aylmore et al., 2001). The silver-thiosulfate oxidation and complexation reaction can be written:

$$4Ag + 12S_2O_3^{2-} + 2H_2O + O_2 \rightleftharpoons 4Ag(S_2O_3)_3^{5-} + 4OH^- \qquad \Delta G° = -161.52 \text{ kJ/mol}$$

which has a more negative Gibbs free energy of reaction comparing to the reaction to form the dithiosulfate complex of silver. The latter reaction is more thermodynamically favourable. Figure 2.1 shows the distribution of 1 mM total silver in solution with the presence of ammonia and thiosulfate. It shows that if the thiosulfate concentration is higher than about 50 mM, silver and thiosulfate will complex to form $Ag(S_2O_3)_3^{5-}$, which supports the view that this complex is most stable in the presence of excess thiosulfate.

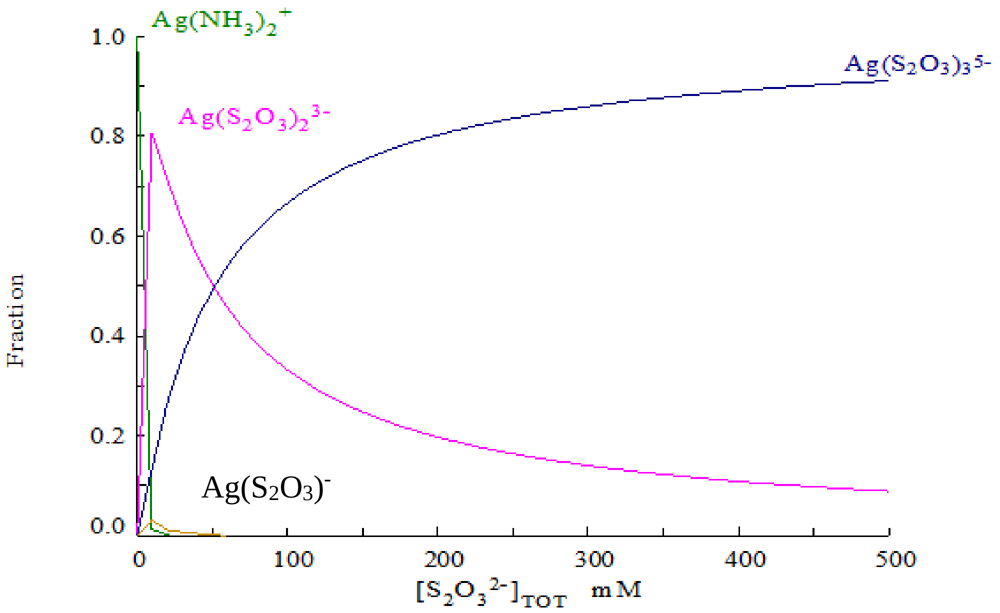


Figure 2.1 Speciation of 1 mM silver complexes at 0.7 M total ammonia, pH of 9.5 at 25 °C for various thiosulfate concentrations by MEDUSA

Even though the above reactions are all thermodynamically favourable, the study of the kinetics of the reaction suggested that these reactions are slow and ammonia and copper can catalyze the reaction (Aylmore et al., 2001; Flett et al., 1983; Umetsu et al., 1972; Zipperian et al., 1988). In a gold leaching system, the catalyzed reaction can be described as follows (Zipperian et al., 1988):

$$Au + 5S_2O_3^{2-} + Cu(NH_3)_4{}^{2+} \rightleftharpoons Au(S_2O_3)_2^{3-} + 4NH_3 + Cu(S_2O_3)_3^{5-} \quad \Delta G° = -16.08 \text{ kJ/mol}$$

Similarly, dissolution of silver in copper-ammonia thiosulfate undergoes the reaction (Ibarra-Galvan et al., 2014):

$$Ag + Cu(NH_3)_4{}^{2+} + 4S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-} + 4NH_3 + Cu(S_2O_3)_2^{3-} \quad \Delta G° = -7.70 \text{ kJ/mol}$$

or with formation of more stable thiosulfate complexes:

$$Ag + Cu(NH_3)_4{}^{2+} + 6S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_3^{5-} + 4NH_3 + Cu(S_2O_3)_3{}^{5-} \quad \Delta G° = -23.58 \text{ kJ/mol}$$

in which $Cu(NH_3)_4^{2+}$ substitutes for oxygen in the role of oxidant.

Since the chemistry of the copper-ammonia thiosulfate leaching system is complicated and not fully understood at present, the remainder of the section will discuss the possible chemistry of the leaching system based on the existing thermodynamics data from past studies of Aylmore et al. (2001) and Speight (2005). Eh-pH diagrams and speciation diagrams will be drawn using HSC 6.0 by Outokumpu (2009) and MEDUSA by Puigdomenech (2004).

Sulfur in water can form a number of metastable species, including thiosulfate and other polythionates. Figure 2.2 shows the predominance area diagram of some of the metastable sulfur species, which excludes sulfate and $S_3O_6^{2-}$ so that the stability regions of these species can be revealed (Zhang, 2004). It is shown that thiosulfate is dominant in an alkaline and slightly reducing environment. Thiosulfate may be oxidized into tetrathionate, dithionate and sulfite during leaching. Formation of multiple sulfur species complicates the study for such a leaching system.

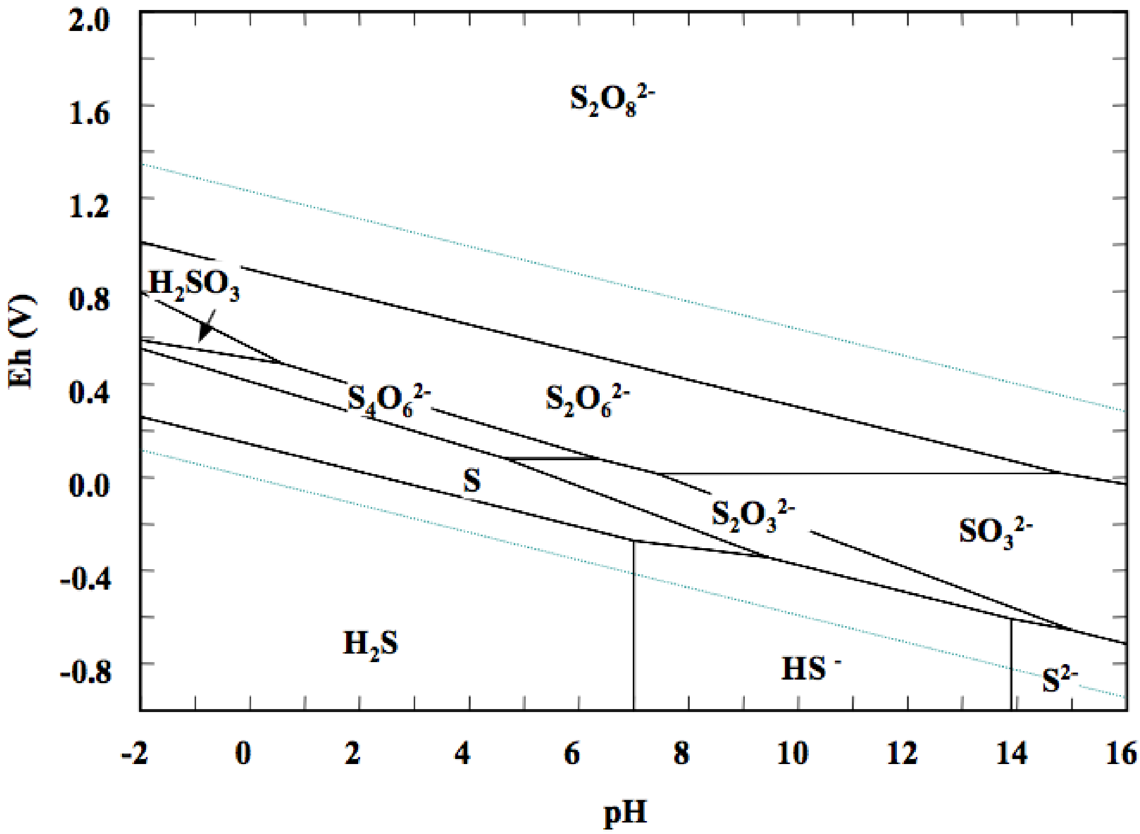


Figure 2.2 Eh-pH diagram for metastable sulfur species at 25 °C (excludes sulfate and some stable polythionates) with 0.1m sulfur (Zhang, 2004)

Figure 2.3 shows an Eh-pH diagram for nitrogen species, another important set of components in the leaching system under different Eh-pH conditions. The hydroxylamine derivatives are not significant, and nitrogen will mostly present in solution in form of nitrate, nitrite, ammonium ion and aqueous ammonia. The figure shows that in an oxidizing environment, ammonium ion and aqueous ammonia may be oxidized into nitrite and nitrate ion, which do not complex with copper and silver. In past studies related to silver or gold leaching, there is no noticeable sign that ammonia will break down and form nitrate over an extended period, which would hinder complexation and dissolution of copper thus affecting dissolution of precious metals (Briones et al., 1998; Ibarra-Galvan et al., 2014; S. Zhang et al., 2005). Besides, to accomplish oxidation of ammonia to nitrate, ammonia needs to be firstly oxidized into nitrogen oxides, which typically requires very high temperatures and catalysts (Il'Chenko et al., 1975; Nowak, 1966; Sadykov et al., 2000). It is highly unlikely that ammonia will be oxidized even though the Eh-pH diagram in Figure 2.3 shows that nitrite and nitrate are more thermodynamically stable. Therefore, it can be assumed that the nitrogen in such leaching system mostly exists in form of ammonium ion and aqueous ammonia. Ammonium ion will dominate below the buffer point and aqueous ammonia will dominate above the buffer point (pH ~ 9.23 in the figure below).

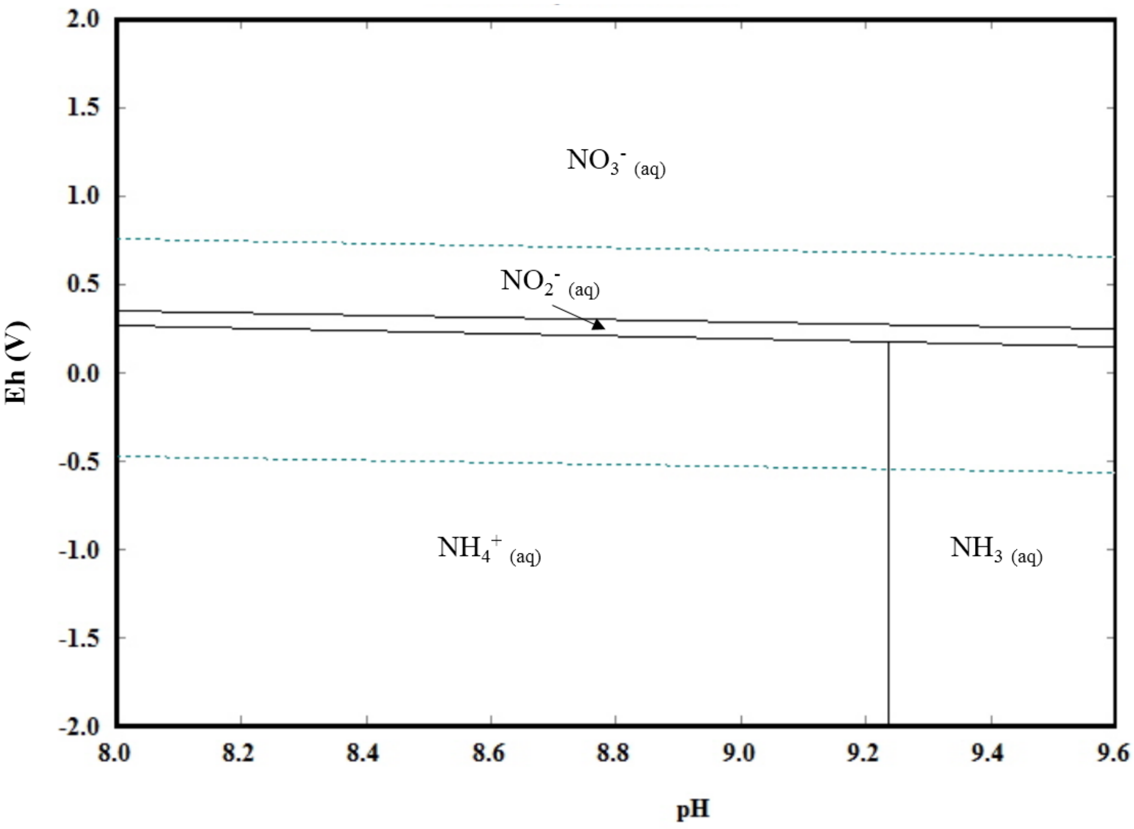


Figure 2.3 Eh-pH diagram for ammonia-water system at 25 °C with 0.7 m nitrogen by HSC 6.0

Figure 2.4 shows the dominant form of silver compounds and complexes of 1×10^{-3} m Ag, 0.1 m of thiosulfate and 0.7 m of ammonia. Silver sulfide is readily soluble in thiosulfate and forms the most thermodynamically stable $Ag(S_2O_3)_3^{5-}$ complex in a more oxidative environment in aqueous solution. The silver-ammonia complexes were also considered, but they do not appear on the Eh-pH diagram. It can be concluded that they are not significant to the leaching process due to their low stability relative to the thiosulfate complex of silver.

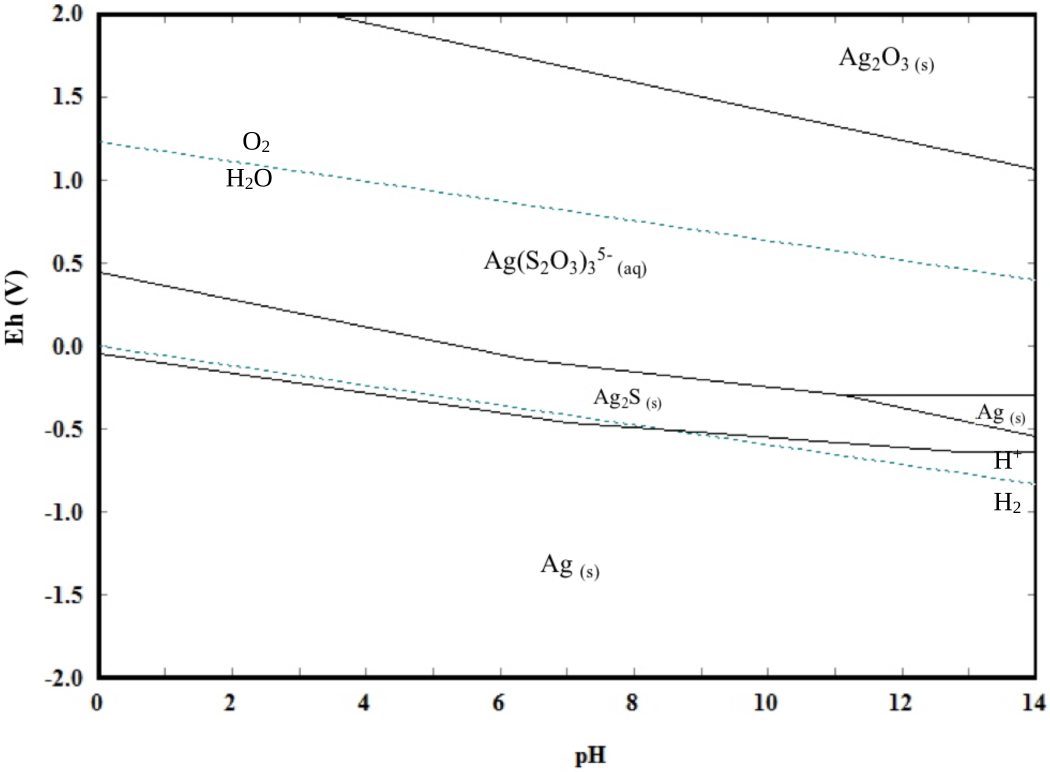


Figure 2.4 Eh-pH diagram for 1×10^{-3} m silver, 0.1 m thiosulfate and 0.7 m ammonia by HSC 6.0

The dominant region for copper compounds and complexes are shown in Figure 2.5. In past research, there were indications that copper will precipitate in the form of CuS and/or Cu_2S (Abbruzzese et al., 1995; Flett et al., 1983; Umetsu et al., 1972). This is confirmed by the presence of copper sulfides in the lower potential areas of the water stability region. However, if the system is sufficiently oxidizing and contains an excess of thiosulfate, copper should be complexed with thiosulfate and will dissolve in aqueous solution. In the leaching range of interest, copper can be present in the form of the most thermodynamically stable copper-thiosulfate complex $Cu(S_2O_3)_3^{5-}$, and if the system becomes more oxidative, the tetraamminecopper(II) ion will be dominant. There are possibilities that cupric-thiosulfate complexes form, but they are not regarded as thermodynamically stable and are quickly converted into cuprous-thiosulfate complexes (Trachevskii et al., 2008).

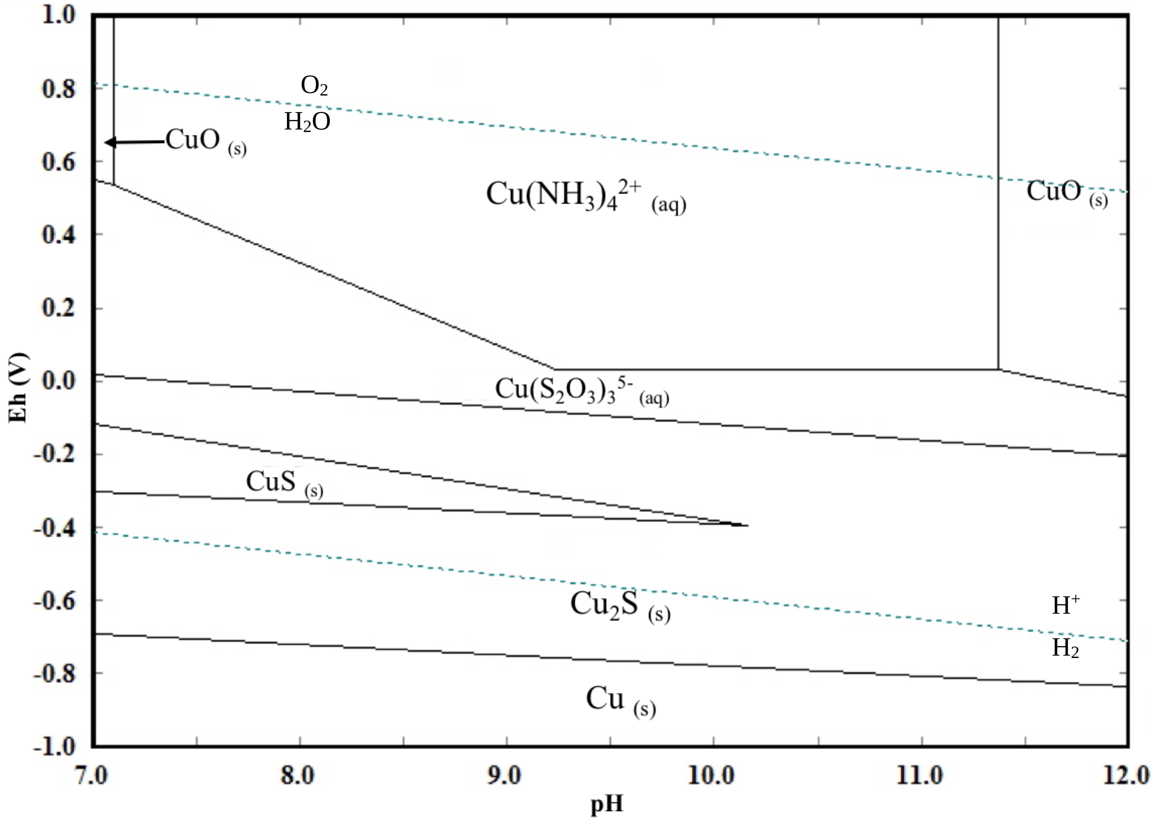


Figure 2.5 Eh-pH diagram for 1×10^{-3} m copper, 0.1 m thiosulfate and 0.7 m ammonia by HSC 6.0

Figure 2.6 demonstrates the speciation of the system at a constant Eh. As an aside, the Eh of the thiosulfate leaching system used in this study is relatively stable throughout the leaching tests at around 300 mV. If pH is higher than around 8.5, $Cu(NH_3)_4^{2+}$ becomes dominant in the leaching system. At a pH higher than 11 copper will precipitate in the form of CuO. Once cupric ion complexes with thiosulfate, it forms the cuprous-thiosulfate complex (Zhang, 2004). An alkaline leaching system is desired since thiosulfate decomposes under acidic condition, but pH should be kept under 11. When pH is greater than 8, up to 4% of triammine copper(II) ion will form.

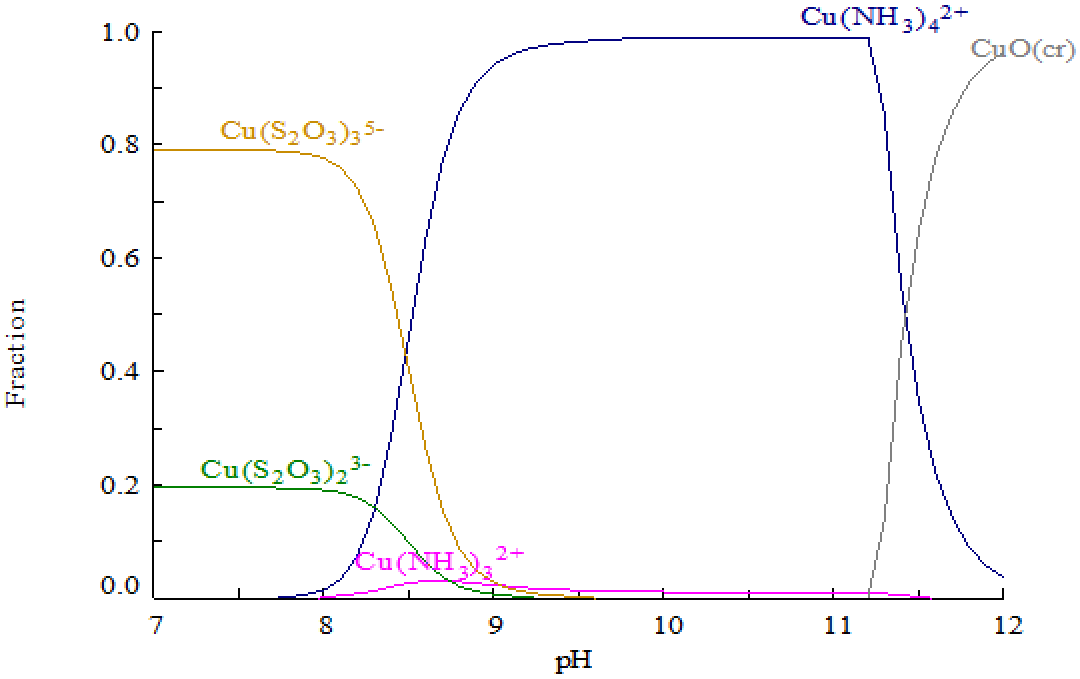


Figure 2.6 Speciation of copper compounds and complexes at 0.1 M thiosulfate, 0.7 M total ammonia, 1 mM total copper, 300 mV vs SHE at 25 °C for alkaline pH range by MEDUSA

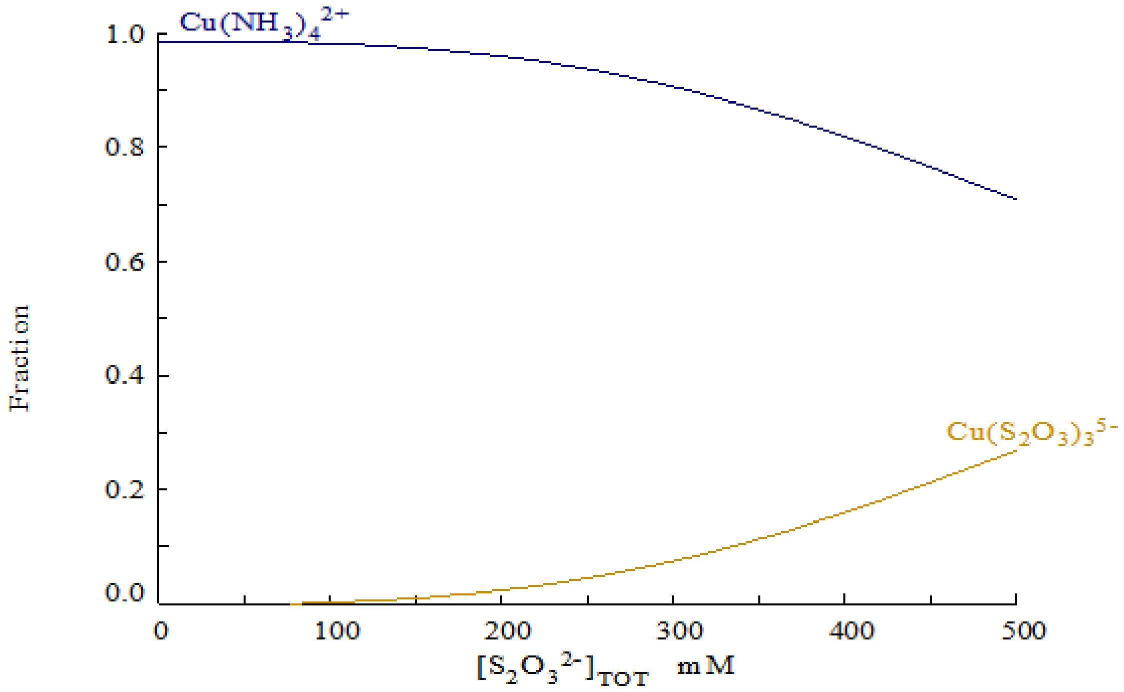


Figure 2.7 Speciation of copper complexes at 0.7 M total ammonia, 1 mM total copper, 300 mV vs SHE, pH of 9.5 at 25 °C for various thiosulfate concentrations by MEDUSA

Figure 2.7 illustrates the speciation of copper complexes under different thiosulfate concentrations. With an increase of thiosulfate in the system, $Cu(S_2O_3)_3^{5-}$ becomes more dominant in solution, as more tetraamminecopper(II) ions are converted to the cuprous thiosulfate species. The more thiosulfate available in the system, the more silver and copper it can dissolve and the more stable the thiosulfate complexes. In industrial application, increase of thiosulfate concentration is equivalent to increase of reagent cost. Thus, a moderately high concentration will be desired to keep the system stable.

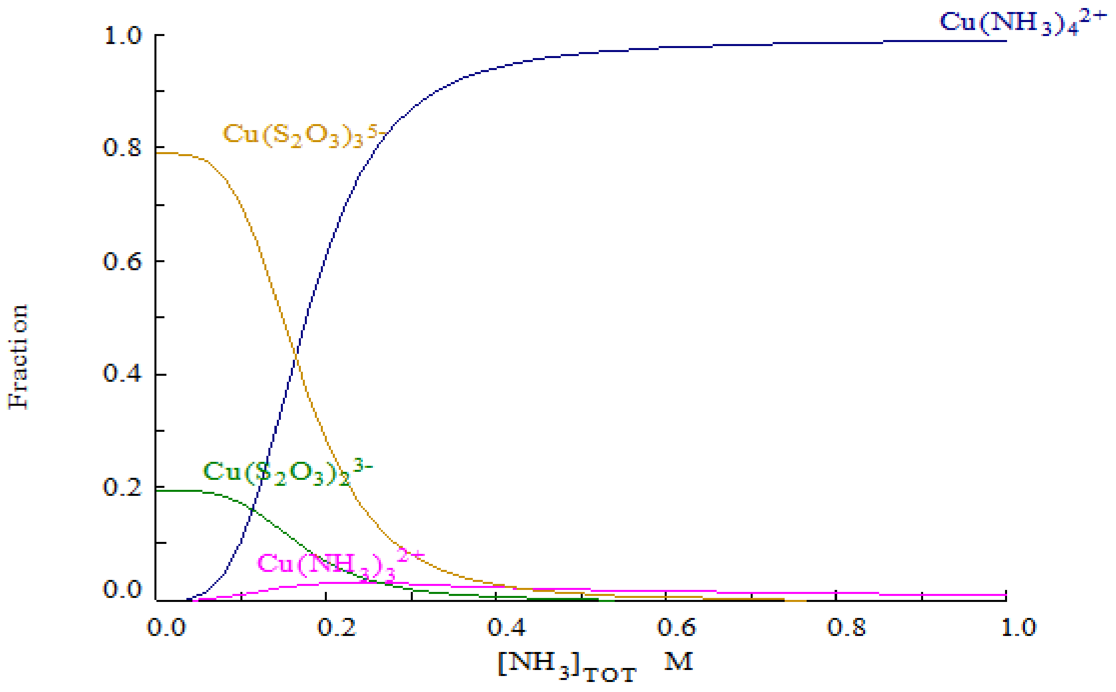


Figure 2.8 Speciation of copper complexes at 0.1 M thiosulfate, 1 mM total copper, 300 mV vs SHE, pH of 9.5 at 25 °C for various total ammonia concentrations by MEDUSA

Speciation can also change due to different total ammonia concentrations. Figure 2.8 shows the speciation of copper complexes regarding a range of total ammonia concentrations. With more than 0.2 M of ammonia available in solution, the copper-tetraammine complex prevails over copper-thiosulfate complexes under the conditions specified.

The leaching system is more oxidative with higher concentration of tetraamminecopper(II) ion while the leaching system is more reductive with higher concentration of copper-thiosulfate complexes. Since thiosulfate is metastable and can potentially be oxidized by lots of species (discussed in 2.3.3), the amount of thiosulfate and ammonia added to the system should be carefully balanced. Also by comparing Figure 2.7 and Figure 2.8, a change in thiosulfate concentration has a lesser effect on the speciation distribution compared to the change in ammonia concentration.

2.3.2 Application to Leaching of Silver Sulfide

The copper-ammonia thiosulfate leaching system for silver sulfide was firstly studied by Flett et al. (1983). A mass of 0.124 g of synthetic silver sulfide was used for all leaching tests, with uncontrolled pH and a leaching tank open to air. Flett et al. (1983) found that the amount of silver leached increased with both increasing thiosulfate and cuprous concentrations. The reaction chemistry indicated that silver sulfide complexes with thiosulfate competes with that of re-precipitation of silver sulfide, thus an excess of thiosulfate is necessary to keep silver in solution. The stoichiometry of chemical reaction without air is one silver to one copper, as copper is kept at an oxidation state of +1 (Flett et al., 1983). The stoichiometry of chemical reaction with the presence of air is one copper to two silver as copper exists in form of Cu^{2+} since cuprous ion is quickly oxidized to cupric ion by oxygen (Flett et al., 1983).

The two proposed chemical reactions by Flett et al. (1983) were re-written by Deutsch (2012) using the prevalent species in such alkaline leaching system:

$$Ag_2S + 2Cu(S_2O_3)_3^{5-} \rightleftharpoons 2Ag(S_2O_3)_3^{5-} + Cu_2S \qquad \Delta G° = 7.01 \text{ kJ/mol}$$

$$\begin{aligned} Ag_2S + Cu(NH_3)_4{}^{2+} + 8S_2O_3^{2-} + 2NH_4{}^{+} + \frac{1}{2}O_2 \\ \rightleftharpoons 2Ag(S_2O_3)_3^{5-} + CuS + S_4O_6{}^{2-} + 6NH_3 + H_2O \end{aligned} \qquad \Delta G° = -113.29 \text{ kJ/mol}$$

The second reaction above is a combination of two independent reactions, which makes the ΔG° value not very meaningful. The reaction ought not to be considered as a single reaction. Thus, the cupric reaction was further refined by Deutsch (2012) to the following chemical reactions:

$$Ag_2S + Cu(NH_3)_4{}^{2+} + 6S_2O_3^{2-} \rightleftharpoons 2Ag(S_2O_3)_3^{5-} + CuS + 4NH_3$$ ΔG°= -5.69 kJ/mol

$$2S_2O_3^{2-} + \frac{1}{2}O_2 + 2H^+ \rightleftharpoons S_4O_6{}^{2-} + H_2O$$ ΔG°= -213.2 kJ/mol

$$2NH_4{}^+ \rightleftharpoons 2NH_3 + 2H^+$$ ΔG°= 105.6 kJ/mol

It appears that ammonia is not thermodynamically favourable to dissociate, but of course the solution is acidic under standard condition; under high alkaline pH, ammonium can form ammonia.

In Figure 2.9, the dominant species in the ammonia-ammonium system under different pH values are shown. The distribution changed at pH of about 9.24. Aqueous ammonia is the dominant species above such pH while ammonium ion is the dominant species below such pH. The concentrations of ammonium and ammonia are of course similar around the pH of 9.25.

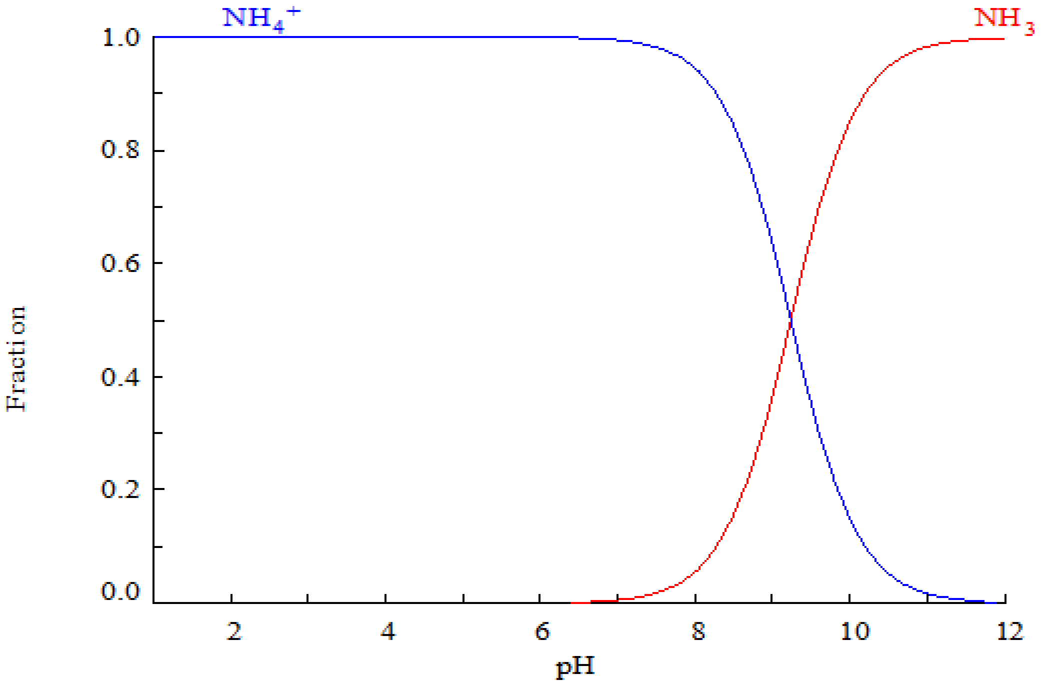


Figure 2.9 Speciation of ammonia at 25 °C for various pH by MEDUSA

The formation of copper tetraammine complex by ammonia/ammonium is as following:

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4{}^{2+} \qquad \Delta G° = -71.15 \text{ kJ/mol}$$

$$Cu^{2+} + 4NH_4{}^{+} \rightleftharpoons Cu(NH_3)_4{}^{2+} + 4H^{+} \qquad \Delta G° = 140.05 \text{ kJ/mol}$$

The formation of cupric tetraammine is thermodynamically favourable through reaction with aqueous ammonia under standard condition. Since the ΔG° value of second reaction is so large, it is impossible for such reaction to become spontaneous. It requires suitable conditions to form cupric tetraammine complex, for example, sufficiently high pH. It is an indication that cupric tetraammine will only be dominant with high ammonia concentration. With pH higher than 9.24, ammonia is more dominant than ammonium (Figure 2.3, Figure 2.9), thus a higher pH is desired to yield higher concentration of copper-tetraammine complex to catalyze the reaction between acanthite and thiosulfate. Higher concentration of such complex will drive the reaction equilibrium between silver sulfide and cupric-tetraammine to the left, thus enhancing leaching. However, an excessively high pH is not desired by the industry due to excess reagent cost, so the range of pH should be carefully controlled in industrial practice, so that it maintains a sufficient but not excess amount of ammonia to complex with copper.

Flett et al. (1983) also found that loss of thiosulfate is more significant with an increase of the copper concentration, temperature and pH. A passive layer of Cu_2S on silver sulfide may hinder the progression of reaction.

In the cuprous thiosulfate reaction with acanthite, copper in the thiosulfate complex substitutes for silver in sulfide, allowing silver to dissolve in solution. In the cupric tetraammine reaction with acanthite, the chemistry is more complicated, copper eventually forms sulfide as covellite.

With the presence of oxygen, it is almost impossible to have stabilized cuprous ion reduced from cupric ion in significant amount. The cupric chemical reaction is more thermodynamically favourable compared to the first one. Thus, a ratio of silver to copper in the final product can be used to indicate the extent of the two reactions. The first reaction can occurs under oxygen-deficient environment. High concentration of cuprous thiosulfate complex and low concentration of silver thiosulfate complex are necessary to drive the reaction to the right. It has been found that the leaching reaction is a mixture of the two reactions, as the dissolved silver to copper ratio ranges from 1.1:1 to 1.4:1 with no oxygen and up to 1.9:1 with oxygen. With presence of oxygen, the cuprous pathway is probabily inhibited as cuprous is less stable and is prone to be oxidized. In the case of leaching systems exposed to air, the second reaction can be expected to be dominant. (Baron et al., 2011; Briones et al., 1998; Deutsch, 2012; Flett et al., 1983)

Zipperian et al. (1988) conducted silver leaching tests using rhyolite ore samples. Silver sulfide was mostly associated with manganese dioxide in the ore. Zipperian tested the impact of different parameters on the effect of leaching of silver and gold, including temperature, concentration of thiosulfate, concentration of ammonia and concentration of copper. Throughout the tests, it was found that silver leaching is more sensitive to temperature as compared to gold. Like the study by Flett et al. (1983), extraction is always increased with an increase of the thiosulfate concentration. Excess thiosulfate is necessary to keep silver-thiosulfate complex stable (Flett et al., 1983). Silver leaching is also more sensitive to ammonia than gold, since with a range of ammonia concentration (0.7% to 14%), silver extraction ranges from 30% to 60%, whereas only a minor extraction difference of gold was detected with the same range of ammonia concentration (Zipperian et al., 1988). A similar effect was observed in later studies and is claimed to be caused by decrease of activity of cupric tetraammine with increase of ammonia (Deutsch et al., 2013a). Silver is also much more sensitive to addition of copper compared to gold, yet an excess of copper suppresses silver leaching. Copper is reported to be accelerate the leaching (Zipperian et al., 1988).

Briones et al. (1998) found that under a deoxygenated environment, silver sulfide leaching is performed by the cuprous substitution reaction, and this is significantly different from gold thiosulfate leaching. In theory, the copper-silver substitution reaction is favourable in terms of its similar structure and the rapid diffusivity of Ag^+ and Cu^+. The formation of a mixed product of covellite and chalcocite is suggested, possibly digenite ($Cu_{1.8}S$). Ore samples were tested for silver leaching with variation of conditions of copper, thiosulfate and ammonia concentrations. A moderate copper concentration yields the best extraction rate, and silver extraction increases with an increase of thiosulfate concentration. Excessively high ammonia concentration in fact suppresses the extraction of silver.

Deutsch et al. (2013a) used a rotating disk electrode to measure the leaching rate of synthetic silver sulfide. Using the rotating disk method, the mass transport can be precisely controlled so that the leaching reaction rate can be studied. It was found that the leaching reaction is under pure diffusion control, since the square root of the rotational speed had a linear effect on silver dissolution rate. The major oxidant in the system, cupric-tetraammine complex, is also involved as the rate limiting reagent, since its molar ratio is 1:100 to thiosulfate. The other effects on leaching have also been tested, including concentration of thiosulfate, ammonia and copper. Thiosulfate concentration is found to enhance initial leaching rate up to 0.125 M, and further addition of thiosulfate will reduce tetraamminecopper(II) ion into cuprous-thiosulfate complex ion. Since an excess of thiosulfate concentration in fact suppresses formation of cupric ion, the cupric leaching reaction is faster than cuprous leaching reaction, which is also confirmed by the fact that higher cupric to cuprous ratio yields higher initial leaching rate. The activation energy was found to be 7.4 kJ/mol. Such a low value indicates that the reaction is under diffusion control, and relatively unaffected by increase of temperature. Moreover, an increase in temperature increases the consumption of ammonia due to more volatilization. Deutsch also discovered that silver extraction decreases if the concentration is lower than 0.35 M, since sufficient ammonia is necessary to stabilize the system. If ammonia concentration is higher than 0.35 M, the excess ammonia decreases the activity of tetraamminecopper(II) ion, thus resulting in a lower silver extraction rate. Increasing the pH of the system over 9.50 will yield a drop of solution potential, which led to a small decrease in silver leaching rate. Extra addition of EDTA is not favourable in leaching of silver, even though copper is stabilized in the EDTA system. Deutsch et al. (2013b) also compared the original leaching system and ferric-EDTA system and found out that all ferric-aided leaching systems were less effective.

2.3.3 Consumption of Copper and Thiosulfate

Thiosulfate is a metastable sulfur species. Thiosulfate oxidation by oxygen is slow due to the slow oxygen oxidation kinetics and limited solubility of oxygen. With the presence of soluble oxidants, thiosulfate is more readily oxidizable to polythionates like tetrathionate, and eventually will be converted to the most thermodynamically stable sulfate ion. Even if the Eh-pH system is altered to allow formation of metastable species, thiosulfate still has a limited predominance region and cannot tolerate an acidic environment (see Figure 2.2). As the major reagent used for silver leaching, limiting the consumption of thiosulfate is critical to its industrial application from an economical perspective. In a copper-ammonia-thiosulfate leaching system, typical sources of oxidation of thiosulfate are oxygen and cupric-tetraammine:

$$4S_2O_3^{2-} + O_2 + 2H_2O \rightleftharpoons 2S_4{O_6}^{2-} + 4OH^- \qquad \Delta G° = -106.4 \text{ kJ/mol}$$

$$2Cu{(NH_3)_4}^{2+} + 8S_2O_3^{2-} \rightleftharpoons 2Cu(S_2O_3)_3^{5-} + S_4{O_6}^{2-} + 8NH_3 \qquad \Delta G° = -19.76 \text{ kJ/mol}$$

The first thiosulfate oxidation reaction can also be split into two half-cell reactions:

$$2S_2O_3^{2-} \rightleftharpoons S_4{O_6}^{2-} + 2e^- \qquad \Delta G° = 24.0 \text{ kJ/mol}$$

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad \Delta G° = -154.4 \text{ kJ/mol}$$

The standard reduction potential for the second reaction in an alkaline solution is calculated as 0.4 V. From the perspective of thermodynamics, thiosulfate oxidation is promoted by the spontaneous oxidation-reduction reaction. However, oxidation of thiosulfate in alkaline solution by dissolved oxygen is kinetically slow (Breuer, 2002).

With the presence of copper, cupric tetraammine ion substitutes oxygen for the role of oxidant. Even though the cuprous-silver substitution reaction still occurs to a certain extent, with the presence of oxygen, cupric tetraammine plays a more important role in leaching (see Section 2.3.2). In the presence of thiosulfate, the reduction of cupric to cuprous by thiosulfate is rapid (Black, 2006). The formation of cuprous will consume cupric tetraamine in the leaching system, thus depleting the copper(II) in solution (Deutsch et al., 2013a). In order to catalyze the leaching reaction consistently, oxygen is required to re-oxidize the cuprous back to cupric, thus maintaining a certain concentration of cupric tetraammine; exposing the leaching system to air is sufficient (Aylmore et al., 2001). Another possibility is that cupric can be reduced by sulfite and polythionates, but this is not significant as compared to thiosulfate due to its high concentration.

(Breuer et al., 2003) Reduction of cupric ion by other sulfur oxo-anions does occur such as sulfite (Lappin, 1994):

$$2Cu^{2+} + SO_3^{2-} + 2OH^- \rightarrow 2Cu^+ + {SO_4}^{2-} + H_2O \qquad \Delta G° = -210.2 \text{ kJ/mol}$$

$$Cu^{2+} + SO_3^{2-} \rightarrow Cu^+ + \frac{1}{2}S_2{O_6}^{2-} \qquad \Delta G° = -981.3 \text{ kJ/mol}$$

Cuprous cannot persist in solution on its own without complexation. Breuer et al. (2003) discovered that oxidation of 2 mM sulfite requires 3 mM of cupric ion, and considering the consumption of some cupric ion by thiosulfate, he thus argued that copper to sulfite ratio is in fact 1:1, therefore formation of dithionate is more prevalent. Thermodynamically, the dithionate reaction is also more favourable. Interestingly, Breuer also discovered that oxidation of tetrathionate and trithionate are more rapid by cupric as compared to thiosulfate. The system can be expected to be finally stable with the formation of the sulfate ion. Breuer also discovered that phosphate ion can almost completely cease copper reduction by thiosulfate. Phosphate readily complexes with copper(II) ion and prevents thiosulfate to substitute into inner coordinate sphere of copper(II). Since it is necessary to reduce copper to catalyze the leaching system, thus such impurity should be avoided.

Under all circumstances, thiosulfate is being consumed over time, despite partial regeneration of thiosulfate. In some cases it is possible to regenerate thiosulfate from the polythionates formed under oxidative leaching conditions. The major oxidation product is tetrathionate ($S_4O_6^{2-}$), and there are side products including trithionate ($S_3O_6^{2-}$) and sulfite (SO_3^{2-}) (Ahern, 2005), and eventually all sulfur oxo-anions will be oxidized to the most thermodynamically stable sulfate

(Breuer et al., 2003). From Figure 2.10, it can be found that most of the ultimate oxidation production is aqueous solution is sulfate.

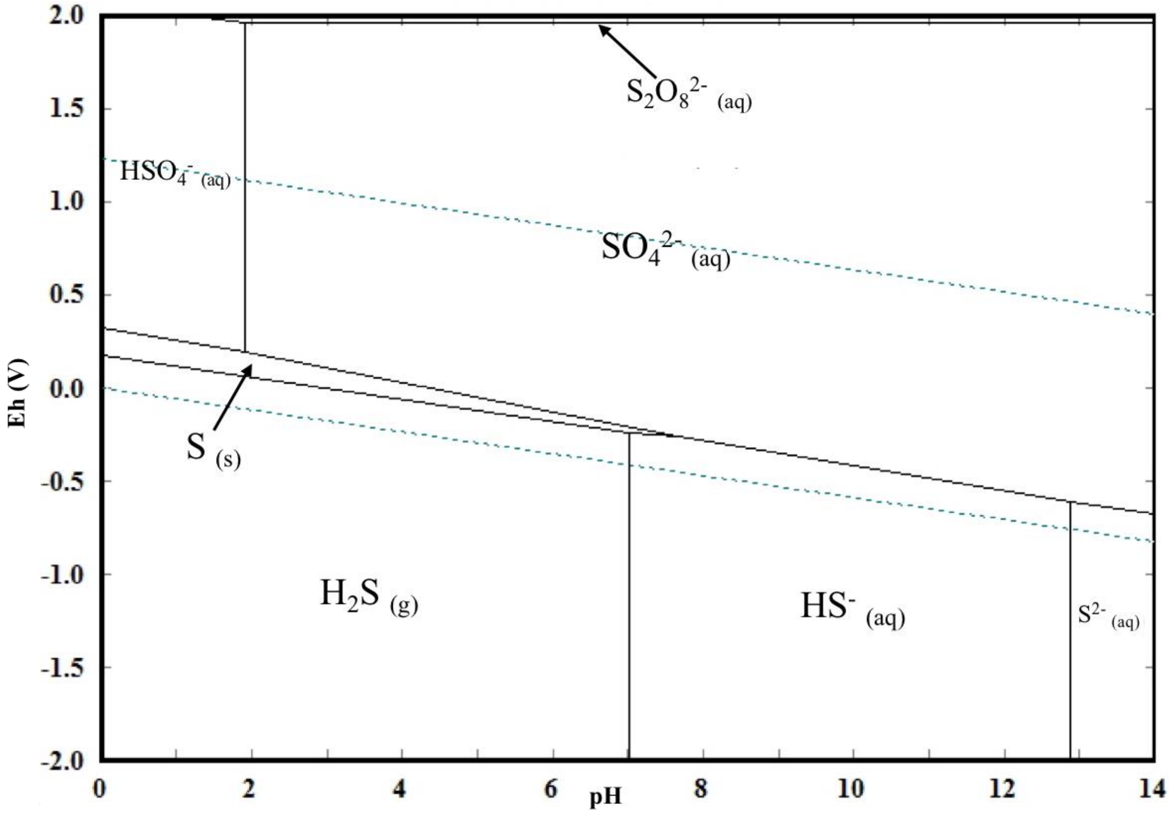


Figure 2.10 Eh-pH diagram for sulfur species at 25 °C with 0.1m sulfur by HSC 6.0

Byerley et al. (1973) proposed the primary oxidation reaction of thiosulfate by tetraamminecopper(II) ion as following:

$$2Cu^{2+} + 2S_2O_3^{2-} \rightarrow 2Cu^{+} + S_4O_6{}^{2-} \qquad \Delta G° = -5.54 \text{ kJ/mol}$$

in which the ligands are omitted.

When thiosulfate reacts with the cupric-tetraammine complex, it substitutes on the axial site of the distorted octahedral complex to replace water (Breuer et al., 2003). Copper ion is known to have sp^3d^2 type coordination orbit, thus possessing six coordination bonds, but due to Jahn-Teller effect, the axial sites move farther apart to cancel out degeneracy of orbitals. This results in octahedron shape of copper ion transforming into an elongated octahedron geometry. With such distortion of the geometry, the total energy of copper ion reduces and the ion becomes more stable. The axial sites are more distant from the central atom than planar site, thus the axial ligands are easier to be replaced. The schematic of the reaction is shown as Figure 2.11.

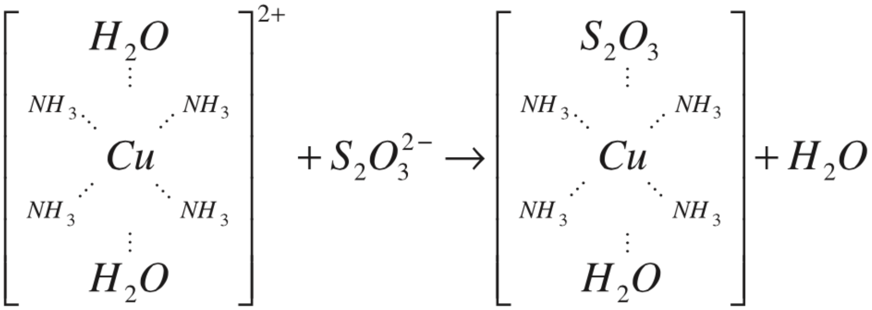
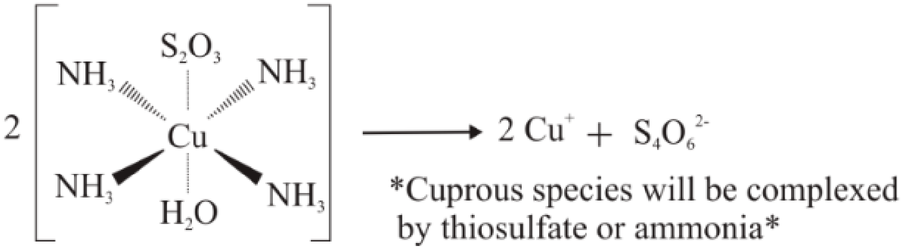


Figure 2.11 Schematic of thiosulfate substitution on axial site of tetraamminecopper(II) ion (Breuer et al., 2003)



Cuprous species will be complexed by thiosulfate or ammonia

Figure 2.12 Schematic of reaction of cupric-tetraammine-thiosulfate complex (Deutsch, 2012)

Deutsch (2012) developed the schematic for oxidation of $[Cu(NH_3)_4(S_2O_3)]^0$ complex (Figure 2.12) which elucidates the step that copper reduction takes place. Breuer et al. (2003) indicated that this is an inner sphere reaction, meaning that only by connecting the thiosulfate ion to the central copper atom can the electron transfer from thiosulfate to copper. Byerley et al. (1975) also proposed another possible mechanism in which thiosulfate can substitute on the planar site with access of oxygen, thus forming the complex $[Cu(NH_3)_4(OH_2)(S_2O_3)(O_2)]^0$. The ligand water can be easily substitute by thiosulfate ion (Figure 2.13). Since cupric-thiosulfate complexes are not thermodynamically stable and will decompose into cuprous-thiosulfate complexes rapidly (Black, 2006), with a sufficient amount of dissolved oxygen, oxidation of thiosulfate in solution will be enhanced by such mechanism.

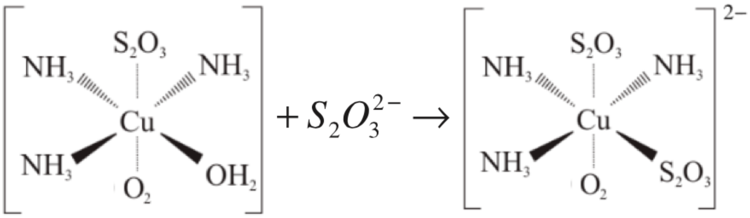


Figure 2.13 Formation of copper-ammonia-thiosulfate complex containing planar thiosulfate ligand (Deutsch, 2012)

Regeneration of thiosulfate can be achieved to a certain extent. The reaction of disproportion of tetrathionate into thiosulfate and trithionate enables recycling of some thiosulfate, and minimizing the effect of polythionates on further processing of pregnant leach solution. The disproportion reaction of tetrathionate is described as (Byerley et al., 1973):

$$2S_4O_6{}^{2-} + 3OH^- \rightarrow \frac{5}{2}S_2O_3^{2-} + S_3O_6^{2-} + \frac{3}{2}H_2O \qquad \Delta G° = -91.66 \text{ kJ/mol}$$

Since the leaching system is still complicated and not fully understood, there are further ongoing studies on thiosulfate degradation in the copper-ammonia-thiosulfate leaching system.

2.4 Alternative Thiosulfate Leaching Systems

Besides copper-ammonia thiosulfate leaching system, there are other efforts on investigating alternative conditions and additives on the leaching system. These include the study on copper thiosulfate leaching without ammonia and the use of EDTA.

2.4.1 Cupric Thiosulfate Leaching without Ammonia

Ammonia is known as a copper stabilizer in the copper-ammonia thiosulfate leaching system, and it maximizes copper's presence in aqueous solution in the form of cupric-tetraammine. Copper-tetraammine serves as catalyst for silver leaching either by substitution or by taking the role of oxidant. Surprisingly, Cui et al. (2011) found an effective silver sulfide leaching system without ammonia. The study compared the leaching performance under different ammonia concentrations with 0.048 M cupric ion, 0.12 M thiosulfate, 25 °C, 250 RPM and pH of 9. After 3 hours of leaching, it was found that the leaching extraction is the highest (95.1%) without ammonia and silver leaching rate decreases with increase of ammonia. Cui et al. also found the cupric to thiosulfate ratio an important factor in leaching, as increases in the ratio enhances silver extraction. However, the study did not mention the consumption of thiosulfate. It has also been mentioned that addition of ammonia can reduce the degradation of thiosulfate complexes (Deutsch, 2012).

2.4.2 Cupric-Ammonia Thiosulfate Leaching with addition of EDTA

Ethylenediaminetetraacetic acid (EDTA or H_4EDTA, 2,2',2'',2'''-(Ethane-1,2-diyldinitrilo) tetraacetic acid, $C_{10}H_{16}N_2O_8$ or $C_{10}H_{16}N_2O_8^{4-}$) is an organic "six-toothed" ligand and chelating agent. EDTA can complex with various heavy metal ions as a hexadentate ligand due to its structure. The whole organic molecule binds the metal ion thus stabilizing the metal in aqueous solution (Figure 2.14). Feng et al. (2010) investigated addition of EDTA to cupric-ammonia thiosulfate leaching system and discovered that EDTA lowered cupric/cuprous equilibrium potential, thus decreasing the interaction between copper and thiosulfate, and hence lowers the thiosulfate consumption. EDTA helps to stabilize copper in solution, especially when ammonia concentration is low. Excess EDTA is found to decrease gold dissolution. In the case of leaching of sulfide ores, EDTA enhances gold and silver leaching dissolution and the leaching kinetics, especially with higher EDTA concentrations. It is achieved by increasing sulfide minerals dissolution and copper stabilization, while preventing passivation and isolating of foreign heavy metal ions.

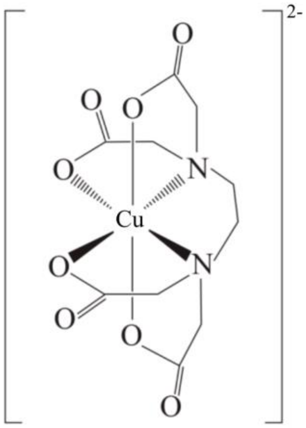


Figure 2.14 Schematic of cupric EDTA complex $CuC_{10}H_{12}N_2O_8^{2-}$ (Deutsch, 2012)

The leaching performance with introduction of Ferric-EDTA was investigated by Deutsch et al. (2013b) as well, along with citrate and oxalate. It was found that the ferric complexes have low interaction with thiosulfate due to slow kinetics, but ferric-EDTA shows potential for its higher extraction rate. Lower thiosulfate consumption is observed comparing to the copper ammonia-thiosulfate system. In the case of ore leaching, ferric-EDTA is found to be the most efficient as it leaches out the cyanide-soluble silver. Addition of EDTA into the cupric-ammonia thiosulfate system not only enhances leaching performance but also decreases thiosulfate consumption.

Puente-Siller et al. (2014) investigated the copper-ammonia-thiosulfate-EDTA/citrate leaching system. The copper-EDTA complex $Cu(EDTA)OH^{3-}$ is observed to work similarly as $Cu(NH_3)_4^{2+}$ with presence of ammonium hydroxide. A layer of copper oxide and sulfide was found on the residue particles after leaching, indicating that passivation had occurred. In the copper-ammonia-thiosulfate-EDTA system, $Cu(EDTA)^{2-}$ is more dominant in the system than copper-tetraammine. Copper-EDTA complex leaching of silver sulfide in the same way as copper-tetraammine(Puente-Siller et al., 2014):

$$Cu(EDTA)^{2-} + Ag_2S + 4S_2O_3^{2-} \rightarrow 2Ag(S_2O_3)_2^{3-} + CuS + EDTA^{4-}$$

A disadvantage of using EDTA is that $Cu(EDTA)^{2-}$ is less reactive than $Cu(NH_3)_4^{2+}$, thus the kinetics and thermodynamics of the reaction may not be as favourable for leaching. Even though citrate is observed to have a higher leaching rate than EDTA, it is less stable under extended leaching time. (Puente-Siller et al., 2014)

2.5 Recovery of Silver from Thiosulfate Leaching Solution

Silver recovery is mainly achieved by cementation, electrowinning, ion exchange and carbon adsorption. (Habashi, 1969) Cementation is currently the most common industrial practice, whereas other alternatives are not fully developed.

Cementation of gold and silver from thiosulfate solution can be accomplished with addition of a powder of copper, zinc, iron, aluminum or soluble sulfides (Aylmore et al., 2001). As mentioned in Section 2.2.2, Merrill-Crowe process used in cyanidation of silver shares the same principle with cementation in thiosulfate solution. The cementation reaction of gold and silver in the copper-ammonia thiosulfate media using zinc can be represented as the following:

$$4Au(S_2O_3)_2^{3-} + 2Zn^0 + 4NH_3 \rightleftharpoons 4Au^0 + 6S_2O_3^{2-} + Zn(S_2O_3)_2^{2-} + Zn(NH_3)_4{}^{2+}$$

$$4Ag(S_2O_3)_3^{5-} + 2Zn^0 + 4NH_3 \rightleftharpoons 4Ag^0 + 10S_2O_3^{2-} + Zn(S_2O_3)_2^{2-} + Zn(NH_3)_4{}^{2+}$$

Due to the presence of copper in solution, the final cementation product contains a mixture of silver and copper, which may need further processing to obtain pure products.

Electrowinning is an alternative for gold and silver recovery from thiosulfate solution (Abbruzzese et al., 1995). The cathodic reactions for gold and silver deposition are:

$$Au(S_2O_3)_2^{3-} + e^- \rightleftharpoons Au + 2S_2O_3^{2-} \qquad E° = 0.15\ V$$

$$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag + 2S_2O_3^{2-} \qquad E° = 0.01\ V$$

A major parasitic cathodic reaction is reduction of water:

$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \qquad E° = -0.828\ V$$

Evolution of oxygen will take place at anode:

$$4OH^- \rightleftharpoons O_2 + 2H_2O + 4e^- \qquad E° = 0.40\ V$$

Electrowinning of gold thiosulfate is kinetically faster than that of gold cyanide, but electrowinning is not attractive for thiosulfate leaching due to the complex chemistry of thiosulfate at the anode and cathode. (Aylmore et al., 2001)

Past studies have mentioned the possibility of adsorption of silver using strong and weak base resin (Grosse et al., 2003; Paiva, 2000). A variety of resins can achieve very high recoveries including weak base IRA-68, IRA-67 and GT-73 resins. The eluent used is 1 M sodium thiosulfate on weak base resins and sulfuric acid on strong base resins. (Deutsch, 2012)

To develop a full recovery process for thiosulfate leaching on acanthite, these options need to be further studied and tested. Cementation from thiosulfate solution may be a viable option.

2.6 Acanthite in Navidad Samples in Chubut Province, Argentina

2.6.1 Mineralogy of Acanthite

As described in Section 2.2.1, silver sulfide (Ag_2S) is one of the primary forms that silver is found in nature. Silver sulfide is one of the most common silver-containing mineral due to the chalcophilic nature of silver, and even other forms of silver mineral are frequently associated with sulfur to a certain extent. Acanthite is mostly found in sulfur ore of other elements, especially galena (PbS), and it is present in the form of very fine inclusions in the matrix. The silver minerals concentrate more on Earth's surface rather than deeper in the crust, as silver does not alloy with iron and nickel. The average content of silver in earth's crust is about 0.05-0.1 ppm, which is 100 to 1000 times more concentrated than gold and platinum. (Cotton, 1997; Habashi, 1997)

Historically, silver sulfide has identified as two minerals that contains the exact same elemental composition: acanthite and argentite. Acanthite and argentite are independent mineral species, and argentite only exists above 180 °C (Emmons et al., 1926). At room temperature, the monoclinic acanthite is the only stable form of silver sulfide mineral, as the cubic structure of argentite distorts under cooling from above 173 °C. The opaque black to lead-gray argentite is the dimorphous form of the black and streak shiny acanthite. (Anthony et al., 2001-2005; Emmons et al., 1926; Manutchehr-Danai, 2013)

The ionically-bonded silver sulfide has a silver composition between 86.4% to 87.2% and a sulfur composition between 12.0% to 12.94%, and a small portion of mineral can be associated with copper or selenium (Anthony et al., 2001-2005). In the case of Loma de la Plata deposit in Project Navidad, silver is found both in form of disseminated grains and coarse grains. Silver mostly presents as silver sulfide, but silver oxide phase has also been identified. Another silver carrier in the ore body is stromeyerite (AgCuS). The silver phases are discovered in association with primarily plagioclase ($NaAlSi_3O_8$-$CaAl_2Si_2O_8$), orthoclase ($KAlSi_3O_8$) and quartz (SiO_2). Chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4) and barite ($BaSO_4$) associate with a minor portion of the silver minerals. (Anes et al., 2008)

Association of silver minerals with other mineral phases can potentially cause problems during leaching. A significant problem is existence of other cyanide-soluble minerals (especially copper) causing an increase of reagent cost. Dissolution of heavy metals (especially mercury) is another significant problem for waste management (De Lacerda et al., 2012).

2.6.2 Geology of Navidad Project

The ore samples used in this thesis were provided by the Pan American Silver Corporation from the Navidad Project. The Navidad Project is located in the north central Chubut Province in Argentina. Geologically, it locates on the southwest edge of the Northern Patagonia Massif, which is coincident with the “Gastre Fault System”. The “Gastre Fault System” is a structure formed by continental-scale northeast to southwest extension. Deposits of silver, lead, zinc and copper have been identified on the property. The rocks on the property are composed of Mamil Choique Formation, overlain by acid pyroclastics, volcanic agglomerates and lavas of the Lonco Trapial Formation. Parts of the ore body has been undergone mineralogical characterization, and deposits from Loma de la Plata, Navidad Hill, Connector Zone, Calcite Hill and Calcite Northwest are found to have potential for silver leaching. The Navidad mineralization is found to be epithermal because its gangue materials (mostly carbonate and barite) possess widespread open space-filling crustiform and cockade textures. High grade mineralization is usually found in permeable host rocks, mostly coarse volcaniclastic rocks and autobrecciate lava flows. Other secondary porosities include crackle brecciation of the brittle lava flows, hydrothermal eruption breccias and tectonic breccias. (Anes et al., 2008; M3 Engineering & Technology Corporation, 2010)

Due to relatively high content of cyanide-soluble copper in the deposits, cyanide consumption turned out to be relatively high. A current law in Chubut Province prohibits open cut mining and the use of cyanide has highly restricted the development of this mining project. Therefore, alternatives such as copper-ammonia thiosulfate leaching on the deposits have the potential to allow the further development of the Navidad Project without use of cyanide.

The objective of this thesis is to investigate the use of ammonium thiosulfate leaching for silver recovery from ore samples from the Navidad project in order to create an economic pathway to silver recovery from these ores.

Chapter 3: Preparation for Leaching of Acanthite

3.1 Introduction

A number of mineral samples from the Navidad Project were received from Pan American Silver. The samples were provided as a series of 13 composites drawn from different zones of mineralization (7 Loma de la Plata, 3 Navidad Hill and 3 Connector Zone). Each composite was blended on site and the splits of the sample were used to create three master composites: Loma de la Plata, Navidad Hill and Connector Zone. (Heinen, 2013) The master composites were used for leaching tests to investigate the potential of using thiosulfate as an alternative lixiviant for silver recovery in the Navidad Project. To accomplish the leaching tests, the ore samples were ground so the sample particles were fine enough for leaching of silver.

3.2 Preparation of Ore Samples

3.2.1 Determination of Particle Size Distribution of Original Samples

The initial samples were received as rough rock powder (see Figure 3.1). Loma de la Plata Master Composite (LDLPMC) appears grey, whereas Navidad Hill Master Composite (NHMC) appears dark red-ish and Connector Zone Master Composite (CZMC) possesses a light brown yellow colour.

Figure 3.1 Appearance of ore samples (a) Loma de la Plata Master Composite (LDLPMC) (b) Navidad Hill Master Composite (NHMC) and (c) Connector Zone Master Composite (CZMC)

Since the original ore samples are already in the form of relatively finely ground material the process of ore crushing was not required. In the preliminary cyanidation testing by Pan American Silver Corp., a range of particle sizes (P_{80}) from 45 μm to 106 μm was used. With the consideration of project economics to minimize energy consumption on grinding, an initial particle size of approximately 100 μm was selected for thiosulfate leaching test.

In order to determine the extent of grinding necessary, the original particle sizes for the ore samples need to be identified first. The samples were received in multiple labelled bags; the samples with the same labels were homogenized on a tarp by coning and quartering, then split into multiple sub-samples. The sub samples are further split into smaller sizes of sub samples to fit into a smaller splitter and dry sieves. After a series of riffle splitting, the sub samples are small enough to fit into the equipment, yet still being representative of its original sample. The dry sieve analysis was then performed on the sub samples. Three different sub samples from the same original sample were tested using a series of dry sieves and their results are compared to ensure the homogeneity of the mixed ore samples.

Figure 3.2 shows the results of particle size distribution of for three random sub samples of LDLPMC. The three particle size distribution curves follow the same pattern and are close to each other, which is an indication of homogeneity. The average particle size (P_{80}) of the original sample was determined to be 508 µm from these three trials, with the variation among them less than 5%.

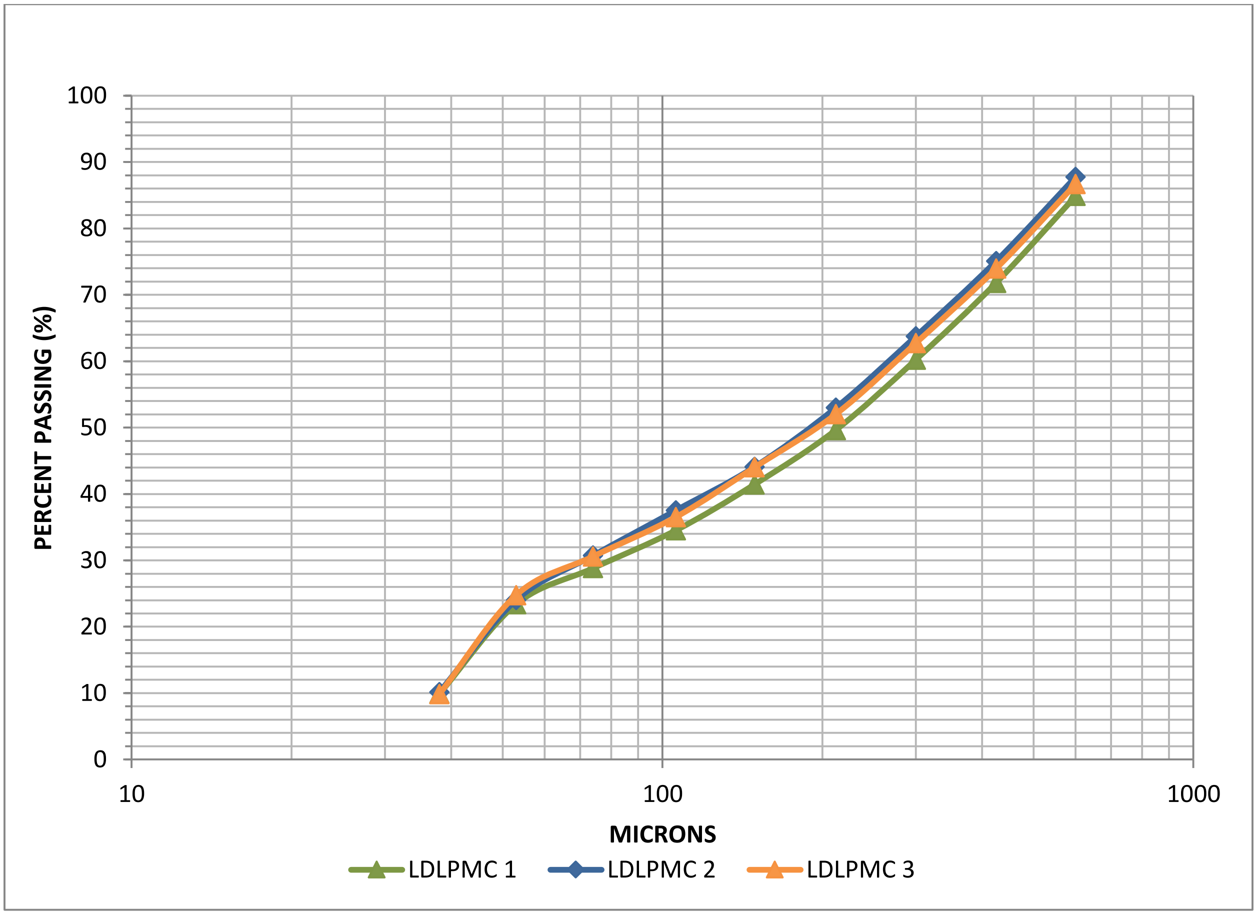


Figure 3.2 Particle size distribution of three randomized LDLPMC sub samples

From Figure 3.3, it can be determined that the average particle size (P_{80}) of the three representative sub samples of NHMC is 455 µm, with the variation among the three trials less than 5%. The three particle size distributions are almost identical to each other, indicating the homogeneity of the original mixed sample.

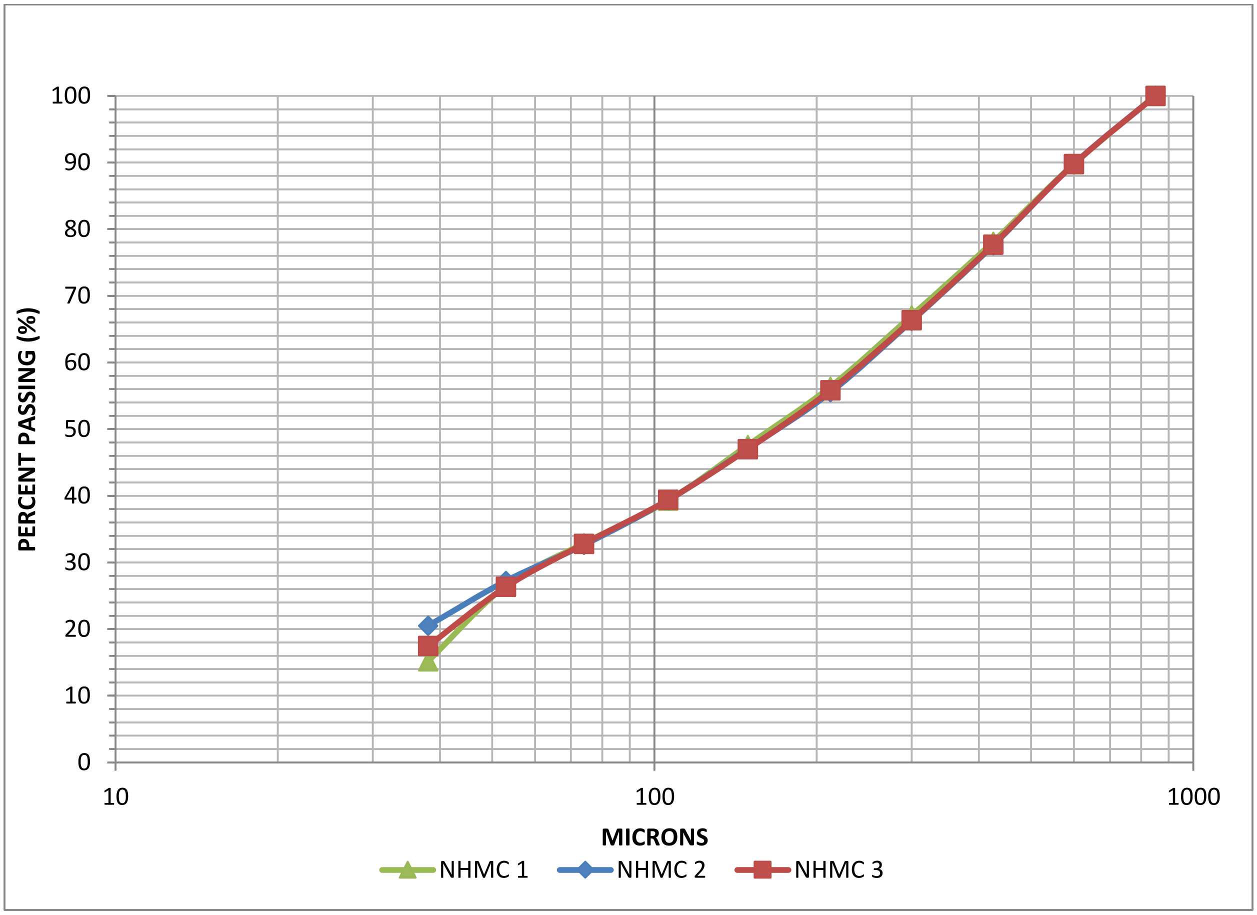


Figure 3.3 Particle size distribution of three randomized NHMC sub samples

As demonstrated in Figure 3.4, the particle size distribution and average particle size (P_{80}) of the three random trials using randomized CZMC samples are identified. The average particle size (P_{80}) is found to be 418 µm, and the three particle size distribution curves are almost identical. It indicates that the bulk sample of CZMC was well homogenized, and the P_{80} determined is the particle size of the original sample.

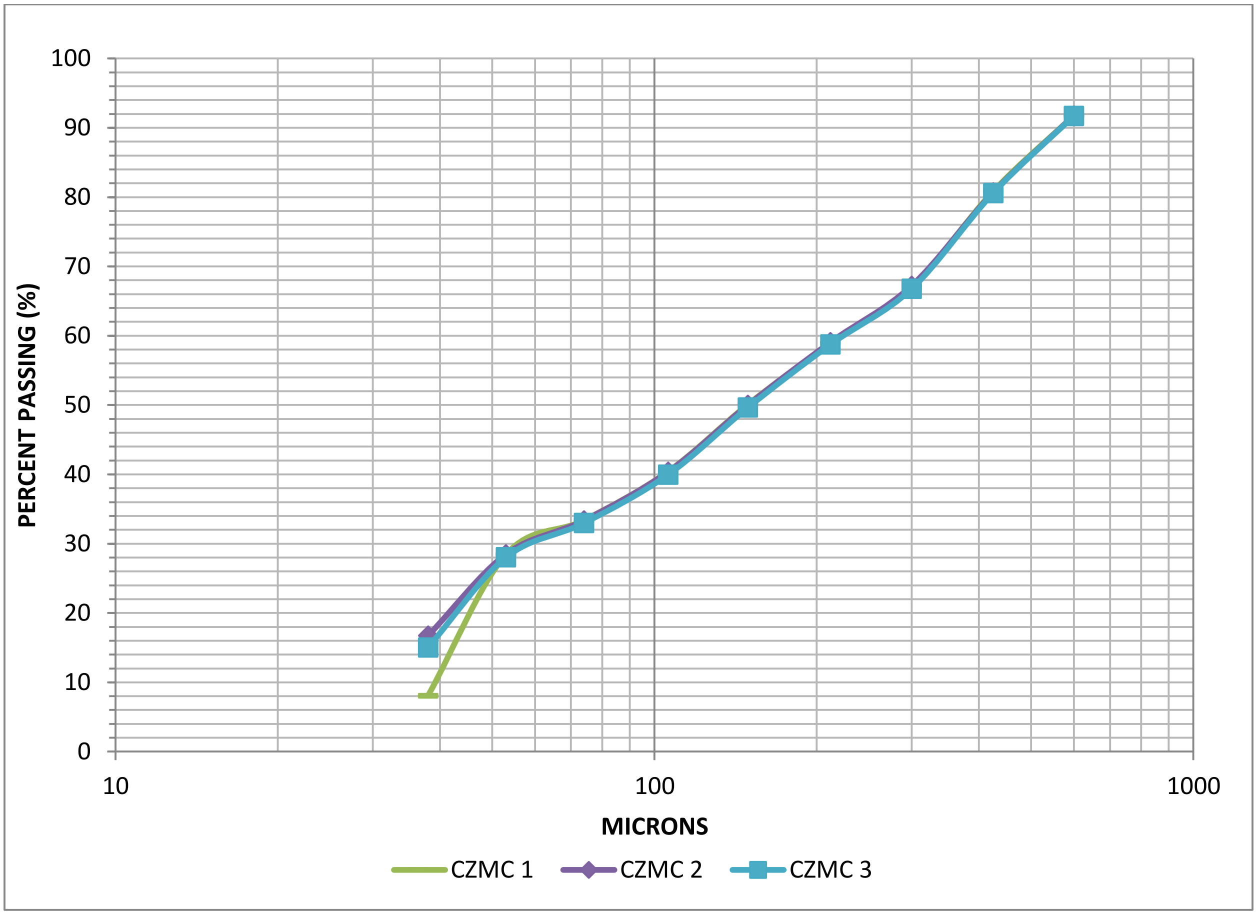


Figure 3.4 Particle size distribution of three randomized CZMC sub samples

The original samples are in general too coarse to be processed for leaching, as all sample have a particle size above 400 µm. Ultimately, further grinding is necessary to successfully leach most of the silver in the samples even if the operational cost will increase. As mentioned before, ultra-fine grinding might not be necessary due to its high mechanical and energy cost; in preliminary tests done by Pan American Silver Corp., leaching performance of some samples are not sensitive to grinding (Heinen, 2013). Therefore, the extent of grind should be carefully controlled so the desired particle size (P_{80}) can be achieved.

3.2.2 Wet Grinding

Wet grinding in a rod mill was selected for the purpose of size reduction of the samples (Figure 3.5). The wet grinding mill rotates so the ore particles in slurry can contact with the steel rods inside the mill, and the impact between the rods and the rods and the mill wall breaks the particles.

Figure 3.5 Wet grinding mills

During grinding, a batch of the original samples was used. Each batch was ground with 20 rods in the mill, and a slurry of 60% pulp density was used. The sample was ground inside the mills for around 15 minutes. The ground slurry was washed out from the mill, and transferred into a pressure filter. After filtration, the solid residue in the filter was collected and dried in an oven overnight at 80 °C. The dried residue was lightly crushed using a roller, then homogenized. Using coning and quartering again, a portion of the powder was sent through dry sieve analysis again, to make sure the sample particle size is close to the desired value.

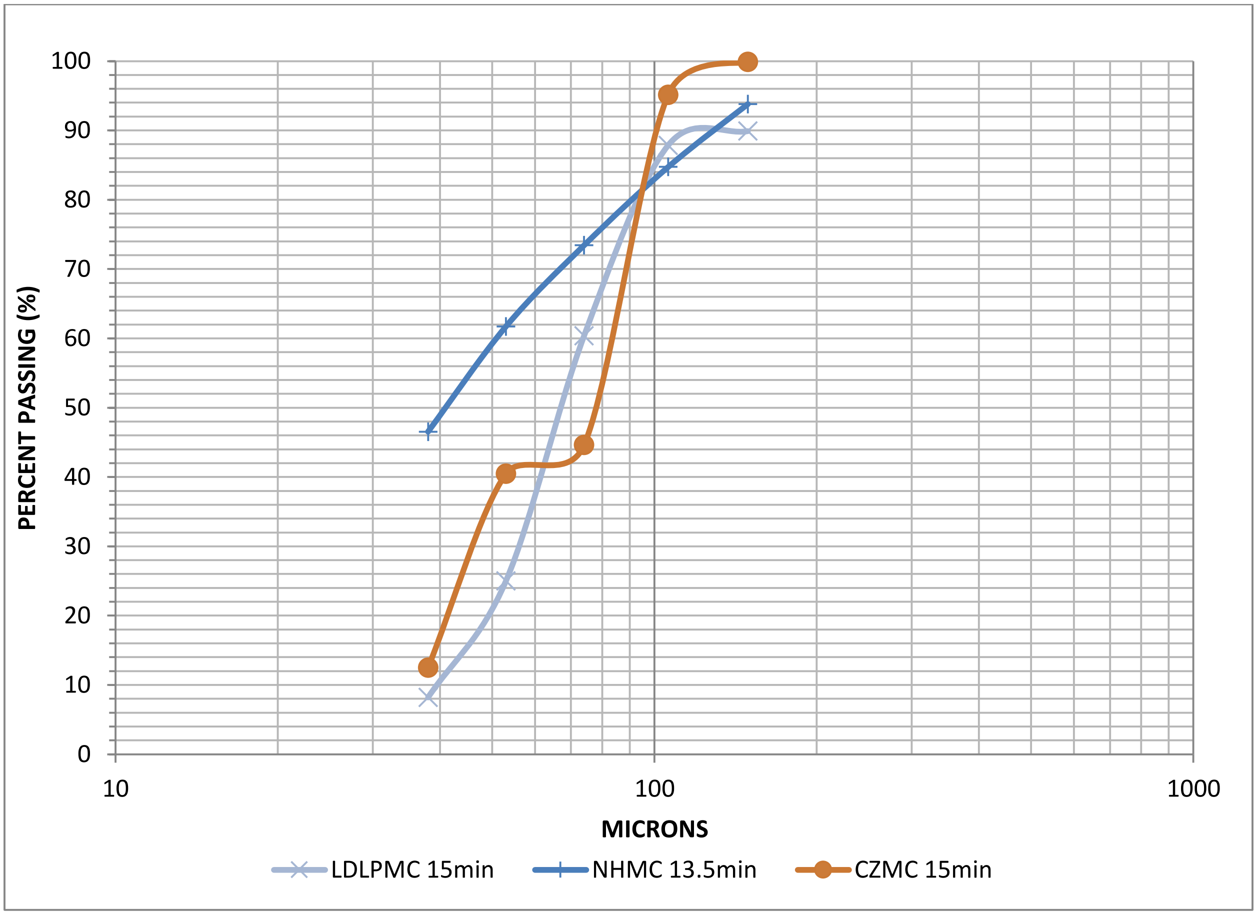


Figure 3.6 Particle size distribution for LDLPMC, NHMC and CZMC with grinding time

From Figure 3.6, the particle size (P_{80}) of LDLPMC, NHMC and CZMC are identified as 97, 92 and 98 µm respectively, which are close enough to the required particle size. It can also be concluded that the grinding time shown in Figure 3.6 is sufficient for grinding these samples.

3.3 Methodology for Leaching Test

The leaching tests were carried out using a batch reactor. A 500 mL baffled glass reactor (obtained from CANSCI) was used as the leaching tank. The baffled reactor ensured that the slurry was well mixed. A Cole-Parmer Compact Digital Mixer was suspended over the reactor tank to mix the slurry. For the preliminary tests, the reactor was uncovered and exposed to the atmosphere. The setup was further adjusted to have a three-hole lid on top of the reactor to prevent evaporation since the prolonged leaching time increases exposure to the atmosphere. The intermediate samples were extracted from the stock leaching slurry in the baffled reactor to measure the concentration for silver and copper. The pH and oxidation-reduction potential (ORP) of the solution were also measured using an Oakton pH 110 Hand-held pH/mV Meter and probe. Since thiosulfate is metastable and it is important to control the consumption of reagents in industrial application, the solution samples were also analyzed for thiosulfate concentration. After the leaching test was completed, the final slurry was poured into a vacuum filter to separate the final leachate and the suspended solid. The pregnant leach solution was once again analyzed. The solid was retained on the filter as a filter cake, then was washed using 100 to 200 mL deionized (DI) water. The leachate and wash solution was analyzed separately. The residual solid was placed in an oven overnight at 60 °C. After the solid was dried, it was crushed using a roller and shipped to Bureau Veritas for analysis using digestion and inductively coupled plasma mass spectrometry (ICP-MS) analysis.

Figure 3.7 Experimental setup of leaching tank

3.4 Analytical Methods

As mentioned in Section 3.3, several chemical analytical techniques were used in this study. The metal concentrations were measured using Atomic Absorption Spectroscopy (AAS), and the thiosulfate concentration was measured using potentiometric iodometric titration.

AAS is a typical chemical technique used for accurate measurement of metal concentrations in aqueous or organic solution. The solution samples from this study were assayed using a Varian 240 AAS instrument with an air-acetylene flame.

Thiosulfate concentration was determined by potentiometric iodometric titration. Titration is a quantitative chemical method used to quickly and accurately determine the concentration of species in aqueous solution. Traditionally, titration was performed manually with glass buret containing titrant, but due to the instability of thiosulfate with presence of copper and exposure to oxygen, the sample can quickly breakdown during the process. Therefore, a Metrohm 888 Titrando auto-titrator was introduced to simplify the method. By monitoring the solution potential simultaneously with addition of standard titrant, the endpoint of the titration reaction can be accurately determined within a short period. Figure 3.8 shows an example of such titration technique with plots of solution potential versus titrant volume and Endpoint Recognition Criterion (ERC) vs titrant volume. The ERC curve is defined as a derivative of the titration curve, and where the sharp peak occurs indicates the endpoint of titration. A vertical line in the figure indicates the endpoint titrant volume. The manual titration results were also compared with the auto-titration results, and it was found that auto-titration agreed with the manual results.

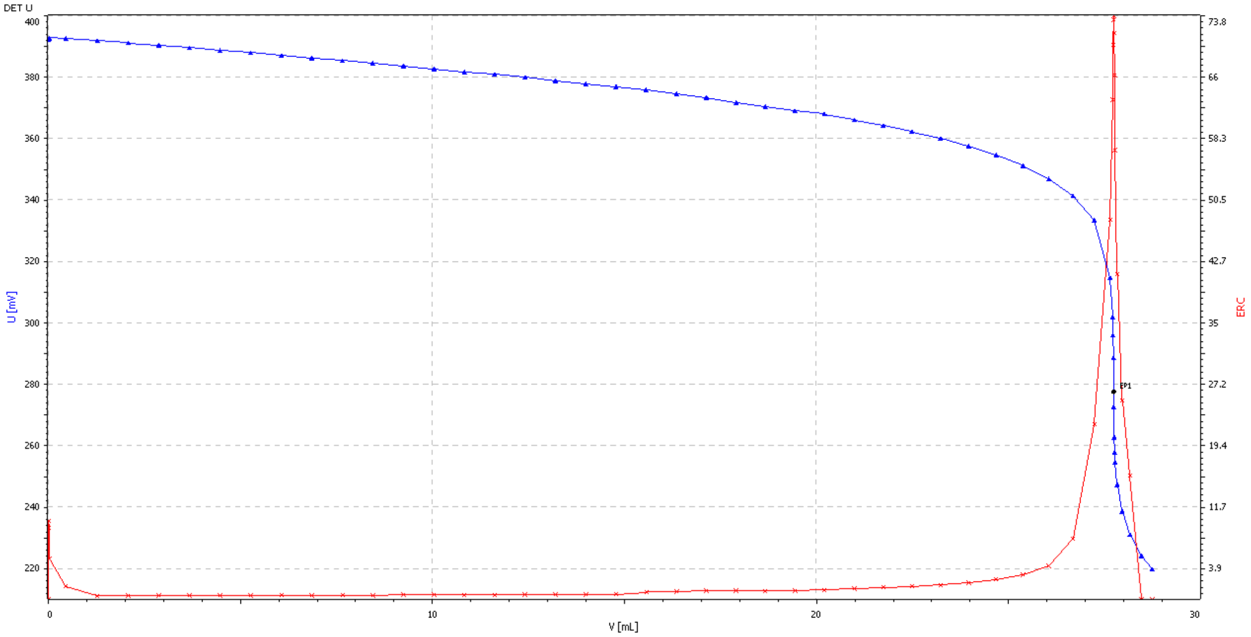


Figure 3.8 Potentiometric iodometric titration curve

The principal reaction of iodometric titration is shown as the following:

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

In this chemical reaction, the free thiosulfate in the sample solution is oxidized by dark brown-yellow iodine, forming colourless tetrathionate and iodide. Near the endpoint of this reaction, the dark brown-yellow colour of the solution will fade into light yellow, and when the endpoint has reached the solution becomes colourless. However, it is difficult to examine the actual endpoint of such a reaction as the human eye cannot distinguish such a minor colour change. For iodometric titrations, starch solution may be used as redox indicator for the endpoint, and with presence of free iodine, the solution takes on a dark blue-black colour (Speight, 2005). With the use of potentiometric titration, the auto-titrator determines the endpoint directly according to the change of solution potential, which removes the requirement of such a colour-change indicator.

The reaction proceeds quickly and quantitatively. However, the drawback of the iodometric titration is also present, because there are different species that can potentially be present in solution and be oxidized by iodine. These side reactions interfere with the titration and can cause the method to be inaccurate.

One potential species that can form in the sample solution is sulfite ion, and its conjugate acid bisulfite:

$$SO_3{}^{2-} + I_2 + H_2O \rightarrow SO_4{}^{2-} + 2H^+ + 2I^-$$

$$HSO_3{}^{-} + I_2 + H_2O \rightarrow SO_4{}^{2-} + 3H^+ + 2I^-$$

Moreover, metal-thiosulfate complexes can also release thiosulfate (Sneed, 1961):

	K
$Cu(S_2O_3)_2^{3-} \rightleftharpoons Cu(S_2O_3)^- + S_2O_3^{2-}$	1.2×10^{-2}
$Cu(S_2O_3)_2^{3-} \rightleftharpoons Cu^+ + 2S_2O_3^{2-}$	5.5×10^{-13}
$Cu(S_2O_3)^- \rightleftharpoons Cu^+ + S_2O_3^{2-}$	4.5×10^{-11}
$Cu(S_2O_3)_3^{5-} \rightleftharpoons Cu^+ + 3S_2O_3^{2-}$	2.3×10^{-14}
$Cu(S_2O_3)_3^{5-} \rightleftharpoons Cu(S_2O_3)_2^{3-} + S_2O_3^{2-}$	3.6×10^{-2}

The small K values of these reactions indicates that the complexes do not dissociate to a very significant extent. However, the presence of such complexes can contribute error to titration results (Wassink, 2011). The best practice is to use strong base ion exchange resin to load the anions and strip off only the thiosulfate ion for titration. The method used in this study which was developed by Wassink (2011) and altered by Deutsch (2012) was adopted, and is briefly described below.

A mass of 50 g of Amberlite IRA 400 resin in the Cl form was placed in a 500 mL buret. Then, 200 mL of 1 M sodium nitrate solution at pH of 8, and a further 200 mL of DI was passed through the column. The flow rate of solution to the column was controlled under 8 mL/min. The resin was then converted from its original chloride form into nitrate form. The treated resin was then stored for later use.

For loading the anions and stripping off only the thiosulfate ion so that other impurities are isolated, 7.5 g of treated Amberlite IRA 400 was placed in a 25 mL buret, and the sample containing thiosulfate solution was passed over the resin. The anions in the solution are then loaded onto the resin. The resin column was then rinsed with 30 mL of DI, and the same sodium nitrate solution was used to eluate off only sulfide, sulfite, sulfate and thiosulfate ions. All other complex ions are strongly retained on resin. (Wassink, 2011) The flow rate was controlled approximately at 2 mL/min. The error of titration for free thiosulfate using such method was less than 1.5%.

After the process of loading and stripping, the only possible interfering species is sulfite (Wassink, 2011), and it can be sequestered with formaldehyde (Wassink, 2011):

$$H_2CO + SO_3^{2-} + H_2O \rightarrow HOCH_2SO_3^{-} + OH^{-}$$

As mentioned above, sulfite and sulfate ions will also be eluted into the titration solution, but they do not interfere with iodometric titration.

The pH and ORP of the solution are the two other variables measured throughout the tests. The pH measurements were accomplished with a Fisher single junction Ag/AgCl pH combination electrode. ORP measurements were performed using a Cole Parmer sealed, double junction saturated Ag/AgCl reference electrode with a platinum pin. The reading of the probe is approximately 206 mV in Thermo Scientific Orion 967901 ORP Standard solution. The pH was measured when the intermediate sample was taken, and ORP was measured for every 24 hours. The reagents used in this study were all ACS grade, and a complete list of the reagents used in the experiments is included in Appendix.

Chapter 4: Leaching of Natural Acanthite

4.1 Introduction

Leaching tests of acanthite ore from Navidad Project were conducted using the setup mentioned in Section 3.3. For preliminary testing, no lid was used to cover the reactor, and with subsequent tests the three-hole lid was added. The reaction time varies depending on the condition of trial carried out; during the preliminary tests, 72 hours was used as default leaching time. LDLPMC samples were reacted for at least 48 hours, while NHMC and CZMC were reacted for less than 24 hours in the subsequent tests. The rotational speed of the overhead stirrer was controlled at 400 rpm for preliminary tests, and in order to maximize mixing effect without spilling slurry out of reactor, it was fixed at 500 rpm in subsequent tests.

Cyanidation was also carried out on the samples, so a maximum extraction rate can be referenced. Thiosulfate is usually expected to yield a lower extraction comparing to cyanide. Various cyanide concentrations have been used throughout the project, and the stirring rate of cyanidation is fixed at 400 rpm or 500 rpm to ensure maximum mixing effect.

As for AAS measurement, the aliquot of sample extracted was initially diluted in DI, so the metal concentrations in the sample fall in the detectable range of AAS. However, a better method was adopted halfway through the study as low thiosulfate concentration may be subject to oxidation by atmospheric oxygen causing solution instability. Instead of diluting in DI, the aliquot was diluted in a prepared solution with similar composition of baseline leaching solution, so sample was matched to the prepared AAS standards. The results of the two analytical methods were compared in some chosen trials, and it was shown that the results were sufficiently close, with error normally within 5%. The latter analytical method always yields a slightly higher silver concentration than the original method, as the original method underestimates silver dissolution to a small extent. Excess thiosulfate in the prepared AAS solution ensures all silver remains dissolved, thus yielding slightly higher silver concentration. Details will be discussed further in this chapter.

All experiments were performed on the three samples: LDLPMC, NHMC and CZMC. The initial conditions of these trials are described in the following table:

Table 4.1 Conditions for preliminary leaching tests

Ore Samples	LDLPMC, NHMC, CZMC
Thiosulfate Concentration (M)	0.1
Total Ammonia Concentration (M)	0.7
Total Copper Concentration (mM)	1
pH	9.5
Temperature (ºC)	25
Reaction Time (hour)	72
Rotational Speed (rpm)	400

The relevant compositions of the samples are listed in the following table:

Table 4.2 Relevant head assay of the Navidad Project samples

	LDLPMC	NHMC	CZMC
Silver (ppm)	296.1±5.4	303.5±39.2	316.8±8.6
Copper (ppm)	759.1±118.3	5995±194.0	1732.3±83.6
Lead (ppm)	473.3±13.2	1362.3±179.4	15326.4±316.7
Arsenic (ppm)	48.55±9.3	240.0±20.4	724.6±21.2
Selenium (ppm)	<0.5	<0.5	1.60±0.14
Mercury (ppm)	0.05±0.02	2.11±0.14	0.51±0.07
Cadmium (ppm)	1.25±0.14	20.95±0.76	8.16±0.41
Total Sulfur (%)	0.10	0.10	0.69±0.18

From Table 4.2, the copper contents of the samples are found to vary rather significantly. Silver contents are more uniform across the sample. The presence of relatively high copper content is beneficial to thiosulfate leaching of silver, since abundant copper complexes with ammonia to form cupric tetraammine ion which is the reactant that accelerates leaching reaction by changing the nature of reaction. It also becomes unnecessary to introduce copper into the initial leaching solution, which reduces the reagent cost in industrial practise. Lead and arsenic are relatively high in the samples, especially in NHMC and CZMC. Dissolution of these elements in leaching solution is potentially a concern when handling the aqueous solution, as they can contaminate the environment if not treated properly. Other toxic elements like selenium, mercury and cadmium are not significant and are unlikely to dissolve during leaching. It was discovered that the contents of these toxic elements in the leaching residue are approximately the same as the head assay, indicating that the toxic elements are not dissolved during leaching.

4.2 Results of Preliminary Tests

Three leaching tests were executed in the cupric-ammonia thiosulfate leaching system with the initial leaching condition: 0.1 M total thiosulfate, 0.7 M total ammonia, 1 mM total copper, 25 °C, pH 9.5, air atmosphere and 35% pulp density. The leaching time was controlled at 72 hours. The reactor was open to air without lid.

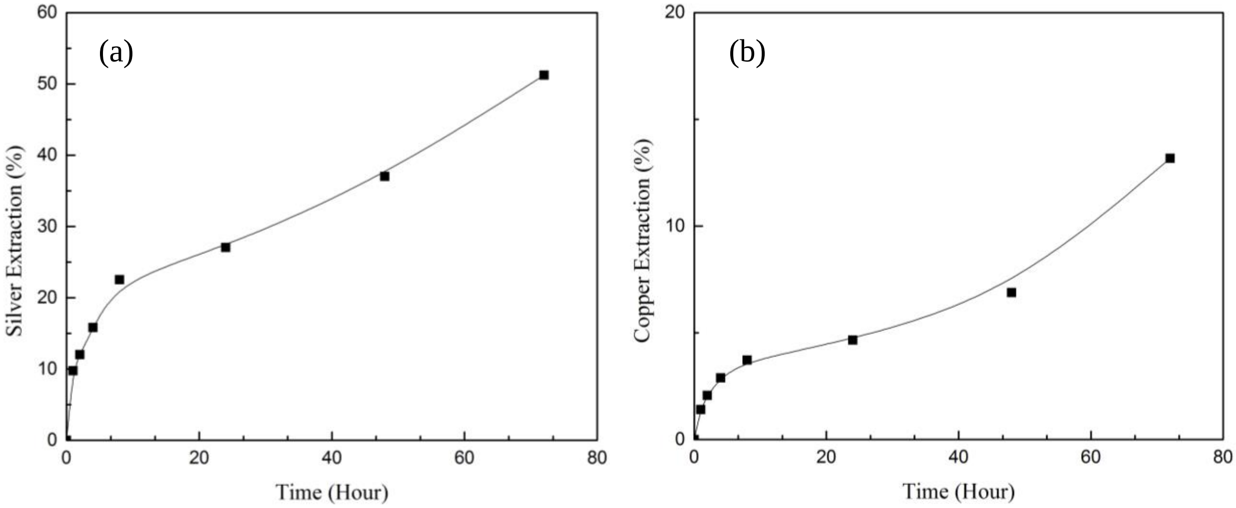


Figure 4.1 Extraction of (a) silver and (b) copper of preliminary test on LDLPMC (Initial condition of 35% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Figure 4.1 shows simultaneous dissolution of silver and copper from the LDLPMC sample. Thiosulfate leaches about 51% of silver and 14% of copper, however the concentration of the dissolving metals was still increasing drastically after 24 hours. Considering it is possible that silver is still leaching, it can also be possible that the solution was becoming more concentrated due to evaporation. The tendency of slope of curves becoming steeper at high silver and copper concentration after extended hours is abnormal. If leaching tests were performed within 24 hours, evaporation of leachate is not significant; but with such an extended period, a more significant portion of solution was evaporated. The measured concentrations within 24 hours were more accurate and reflect true concentration of leaching of silver and copper. Following the trend line indicated by the black solid line in Figure 4.1 in the first 24 hours, the supposed leaching plateau on the leaching curve is established at around 26% dissolution of silver and 5% dissolution of copper.

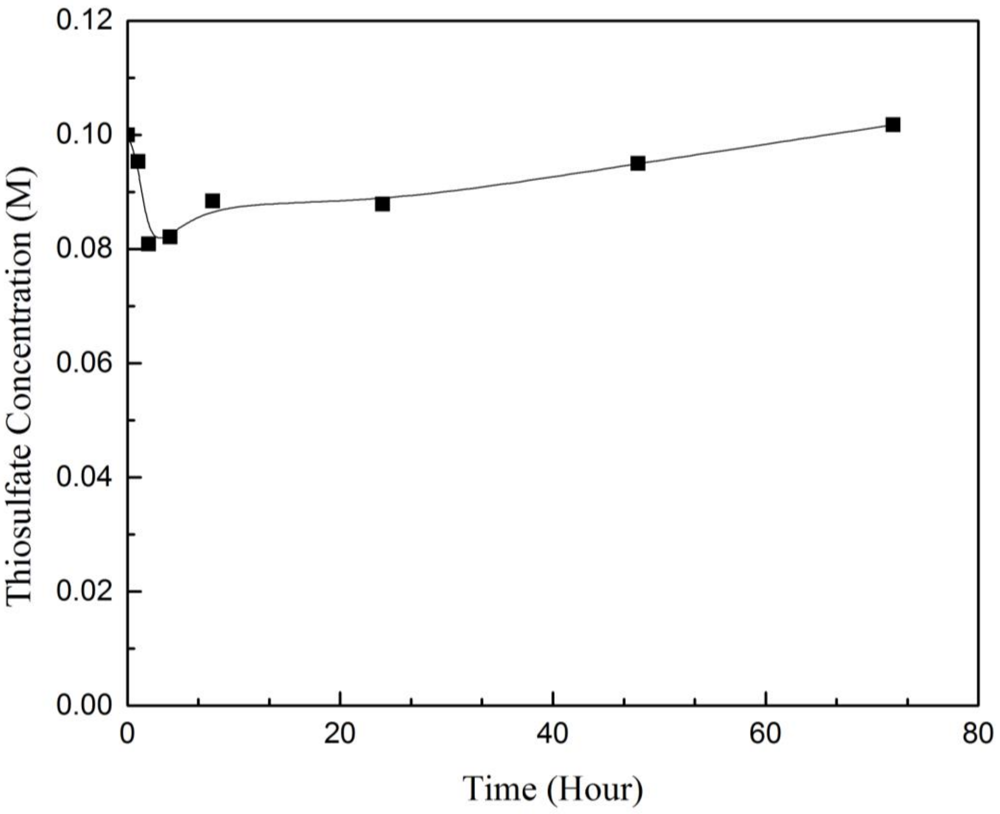


Figure 4.2 Thiosulfate concentration throughout preliminary leaching test on LDLPMC (Initial condition of 35% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Figure 4.2 shows that thiosulfate concentration decreases in the first 8 hours, indicating that most of the silver leaching occurs in such time frame. The concentration recovers gradually over time after 24 hours. Regeneration of thiosulfate is possible from certain sulfur oxoanions mentioned in Section 2.3.3, but not to such an extent that the final concentration becomes comparable to initial concentration. It can be concluded that thiosulfate concentration was affected by evaporation. With less water present in solution, thiosulfate becomes more and more concentrated over time. A side point of Figure 4.2 is that even after such extended exposure to air with presence of copper, thiosulfate is still present in a significant amount, indicating that leaching silver from LDLPMC does not consume excessively high ammonium thiosulfate. Thiosulfate leaching in industrial practice usually accompanies higher reagent consumption comparing to its cyanide counterpart; thus, thiosulfate leaching on this particular sample is apparently promising.

During the experiment, pH also dropped to 7.6 from its original pH of 9.5, and Eh of the solution increased to 271.4 mV from 248.3 mV. The decrease of pH indicates loss of a significant amount of ammonia due to the open-to-air experimental setup. As discussed in Section 2.3.2, ammonia complexes with cupric ion to form cupric tetraammine ion and accelerates silver dissolution; with loss of significant amount of ammonia, dissolution of both silver and copper will be reduced. This explains the low extraction rate of silver and copper in Figure 4.1. Increase of Eh indicates the leaching system was oxidizing throughout the test,

As for NHMC and CZMC, the leaching behaviors are different than that of LDLPMC. It can be predicted that evaporation occurs in these two trials as well, but besides that the concentration of silver and copper decrease over time after 24 hours (Figure 4.3).

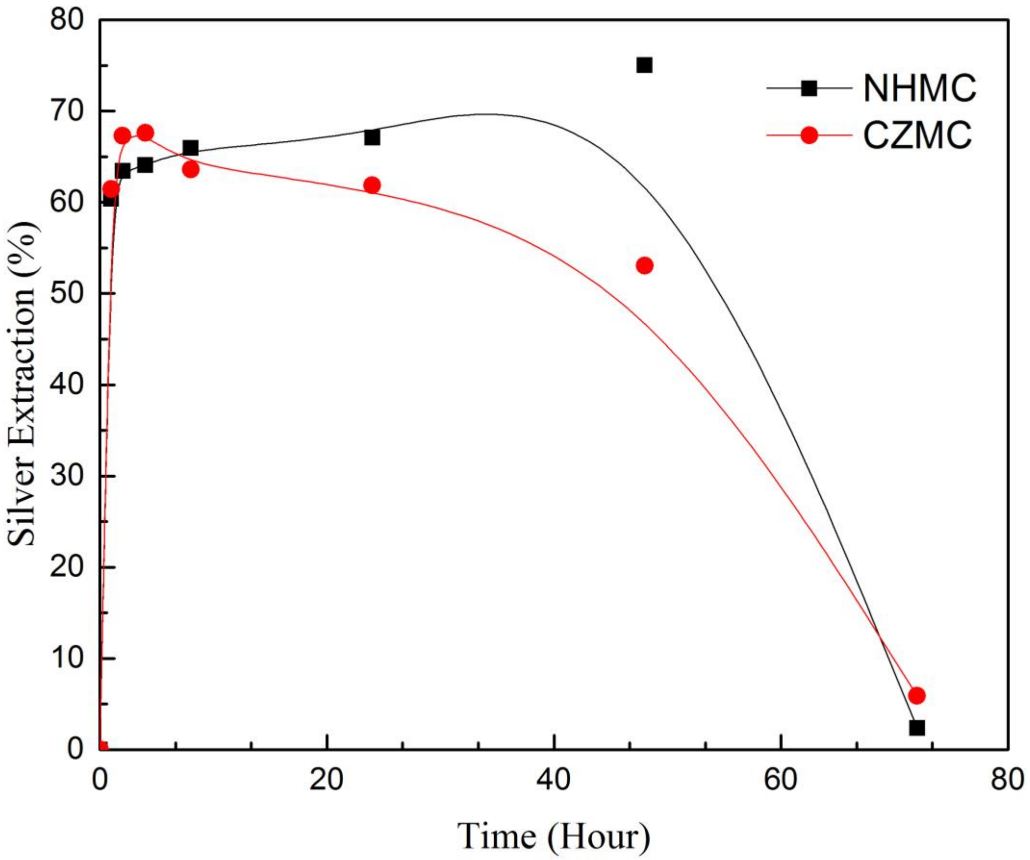


Figure 4.3 Extraction of Silver of preliminary tests on NHMC and CZMC (Initial condition of 35% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

From Figure 4.3, silver extraction appears to complete within 24 hours, as the curves plateau out after 8 hours. However, silver concentrations in solutions decrease after 24 hours, which is significantly different from the silver behavior of LDLPMC.

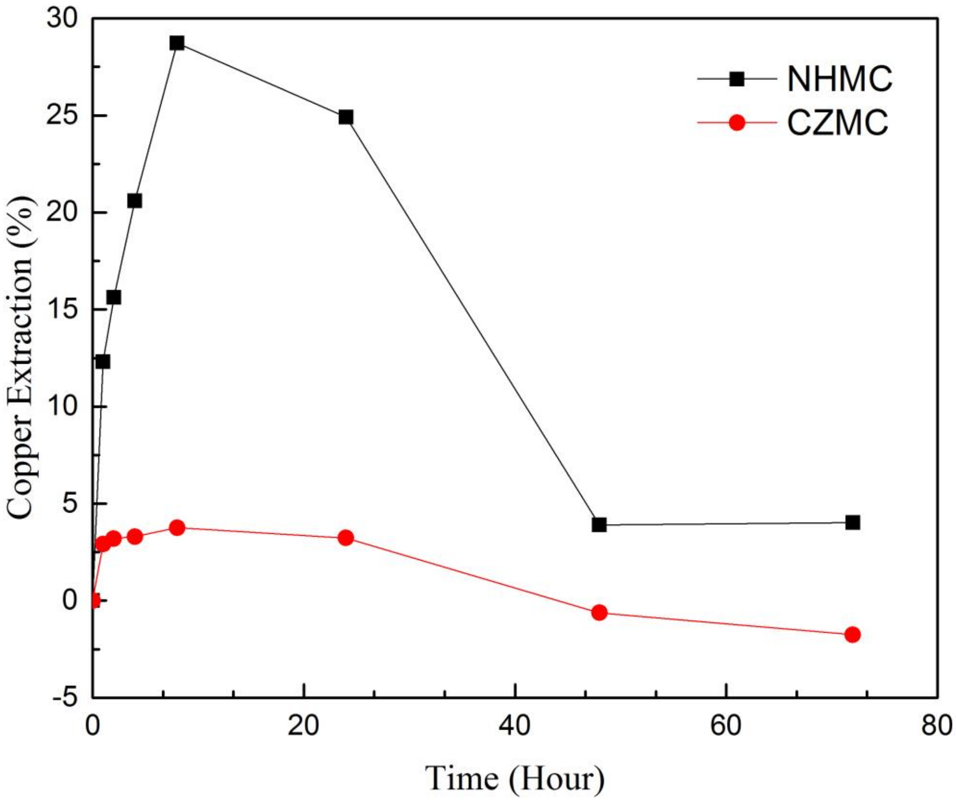


Figure 4.4 Copper Extraction throughout preliminary leaching tests on NHMC and CZMC (Initial condition of 35% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Copper dissolution shows a similar trend, as the leaching curves decline drastically after 8 hours (Figure 4.4). In ammonia thiosulfate leaching system, silver dissolution is highly dependent on the thiosulfate concentration in the leachate. Excessive free thiosulfate ions ensure dissolution of silver (Habashi, 1967), thus precipitation of silver indicates depletion of free thiosulfate in the system, which is also confirmed by the measurement of thiosulfate concentration in Figure 4.5.

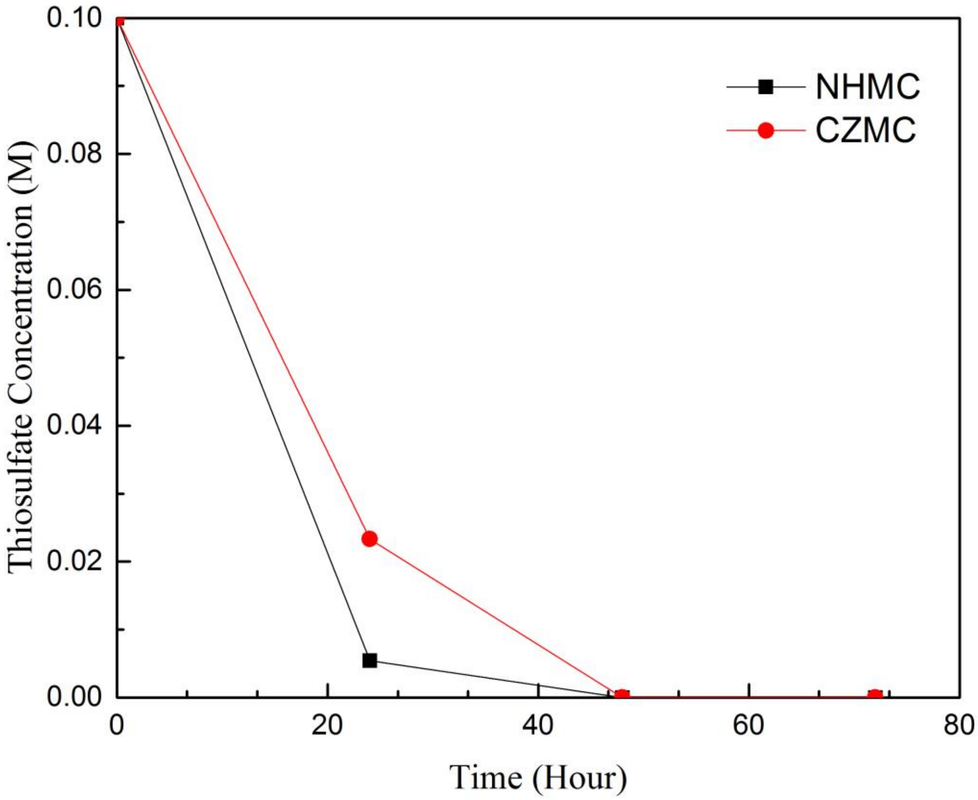


Figure 4.5 Thiosulfate concentration throughout preliminary leaching tests on NHMC and CZMC (Initial condition of 35% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Copper dissolution is definitely affected by thiosulfate; however, it has been discussed in Chapter 2 that copper dissolution in the system is more dependent on total ammonia. With such extended exposure of leachate to air, it can be expected that much ammonia has escaped from the system. Figure 4.6 indicating a significant pH drop from 9.5 to around 7.5 for both ores confirms the destruction of ammonia-ammonium buffer system in the leachate.

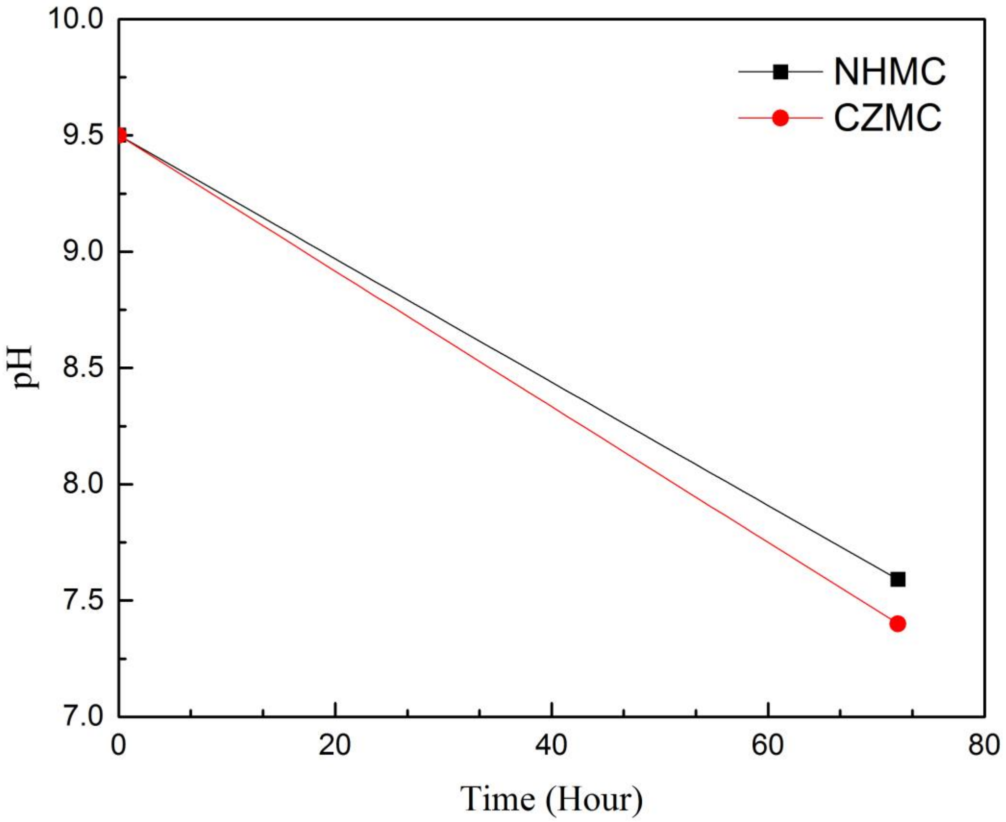


Figure 4.6 pH throughout preliminary leaching tests on NHMC and CZMC (Initial condition of 35% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Throughout the preliminary leaching tests on NHMC and CZMC, Eh of the two systems increases from approximately 200 mV to more than 350 mV. Increase of Eh relates to oxidation of thiosulfate throughout the tests. CZMC ends with an Eh of 374 mV and NHMC yields a final Eh of 398 mV. Such difference in Eh shows that the NHMC leach slurry is more oxidized comparing to CZMC, as the two started at the same condition. It also corresponds to a lower thiosulfate concentration in leachate after 24 hours (Figure 4.5).

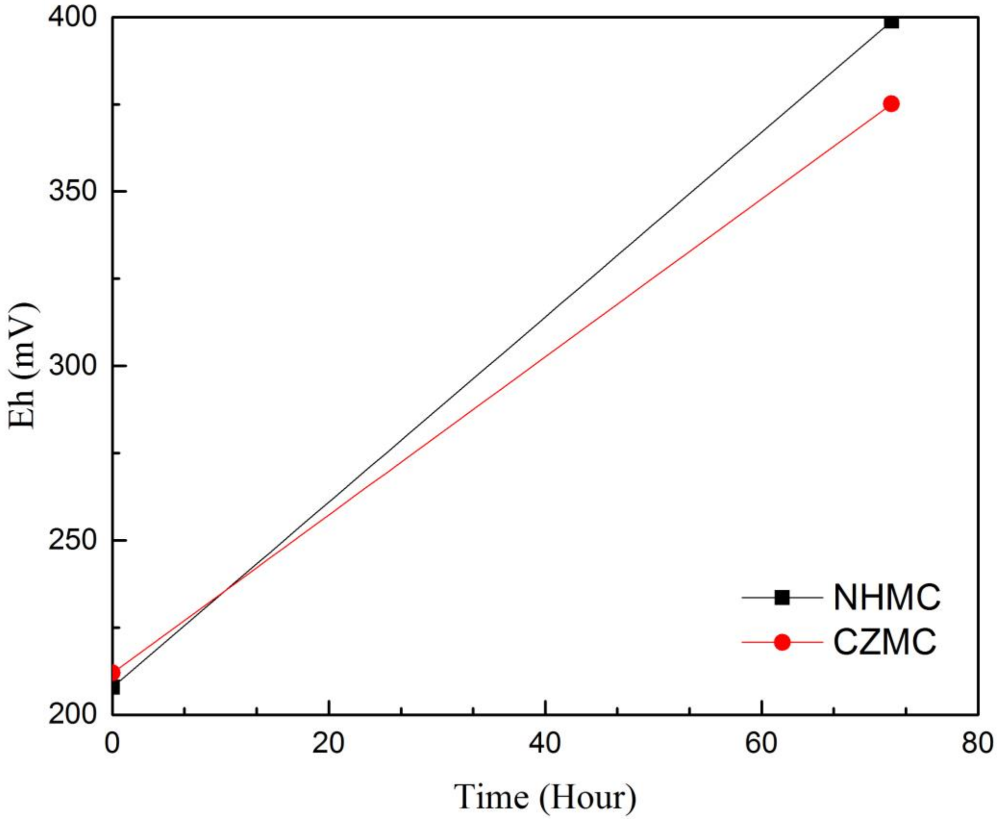


Figure 4.7 Eh throughout preliminary leaching tests on NHMC and CZMC (Initial condition of 35% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Figure 4.4 suggests a much higher dissolution of copper from NHMC comparing to CZMC, and considering NHMC has three times more of copper than CZMC, NHMC has more leachable copper than CZMC. With more copper present in solution, more thiosulfate will be oxidized into tetrathionate, which accelerates the process of thiosulfate leaching but also consumes more reagents. The literature review in Chapter 2 highlighted that a moderate copper concentration is necessary to enhance silver leaching, but not to consume excessive thiosulfate. From such perspective, high content of copper present in NHMC and CZMC is not only troublesome in the cyanidation system, but also catalyzes the consumption of reagent under thiosulfate leaching.

Thiosulfate leaching is often not as effective as cyanide leaching. Thiosulfate only leaches the metal contents that are accessible to cyanide. In order to compare these results to maximum cyanide-leachable silver and copper, cyanidation tests on these samples were conducted.

4.3 Cyanidation

4.3.1 Preliminary Cyanidation

The preliminary cyanidation tests were carried out using the same setup as preliminary thiosulfate leaching tests. The initial cyanidation conditions were set as 4 g/L sodium cyanide for LDLPMC and CZMC, 5 g/L sodium cyanide for NHMC, pH of 11, rotational speed of mixer as 500 rpm to maximize mixing effect, pulp density of 35%, water bath temperature of 25 °C. The pH was as adjusted using 40% lime throughout the leaching trial to avoid generation of highly toxic HCN. NHMC is expected to consume more cyanide by copper dissolution, thus a higher cyanide concentration was adopted.

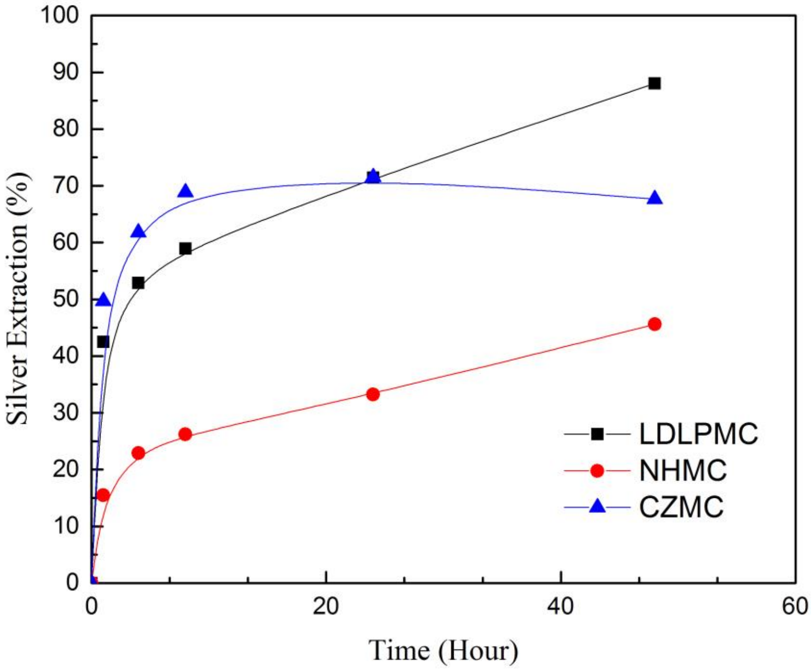


Figure 4.8 Silver extraction throughout preliminary cyanidation tests on LDLPMC, NHMC and CZMC

Figure 4.8 shows the leaching performance of the three samples in cyanidation. It can be seen that LDLPMC leaches most the silver (88%) while NHMC leaches the least silver (57%). The steeper rise of the curves after 24 hours may be an indication that extraction percentages is affected by evaporation.

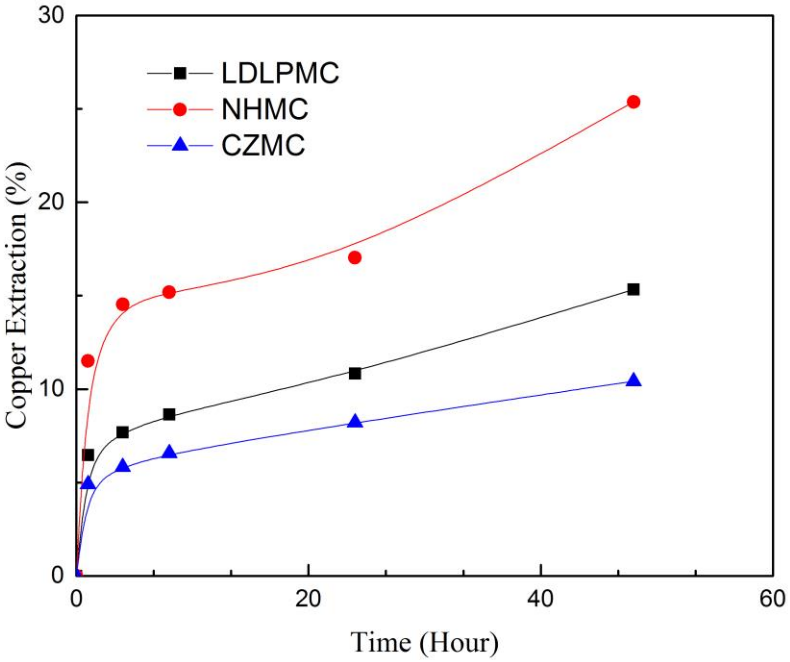


Figure 4.9 Copper extraction throughout preliminary cyanidation tests on LDLPMC, NHMC and CZMC

Cyanide loss can be attributed to different reasons: evaporation in form of HCN, but this is less likely under highly alkaline pH; bonding with base metals; reaction with sulfides; oxidation to form cyanate (Section 2.2.2) (M. Adams, 1990). From Figure 4.9, NHMC can be concluded to dissolve most copper (25%) while CZMC leaches the least (10%). LDLPMC leaches 15% of its total copper content. In NHMC, besides the fact that copper content was found to be the highest, cyanide-soluble copper was also the highest among all samples. Such high leachable copper content explains the reason that NHMC depletes thiosulfate in preliminary thiosulfate test that rapidly because high copper concentration not only consumes more thiosulfate, but accelerates degradation of thiosulfate. The copper leaching curves are still rising sharply after 24 hours, following the same trends as previous results. This indicates either presence of evaporation of solution in these trials, which concentrates the pregnant leach solutions, or continuous dissolution of copper with extended period of time. The copper curve of CZMC also rises at the end, which suggests that either it also underwent evaporation or continuous copper dissolution. Further tests with setup preventing evaporation should be conducted, so that the results can be compared to confirm the existence of evaporation.

In these preliminary cyanidation tests, the consumption of sodium cyanide is determined. LDLPMC consumes 7.1 kg/tonne ore, NHMC consumes 9.175 kg/tonnes ore, and CZMC consumes 6.522 kg/tonne ore, respectively. Consumption of cyanide aligns well with consumption of thiosulfate in thiosulfate leaching tests. Preliminary cyanidation results show that LDLPMC has the highest potential to leach silver while only consuming moderate amount of reagent. Cyanide leaching is known to have issue with leaching high copper content precious metal ore, and apparently similar problem persists using thiosulfate.

Thiosulfate leaching does not appear that promising thus far, which can be attributed to open-to-air leaching atmosphere that allows ammonia to freely escape. Moreover, evaporation of the leaching solution affects concentration in the preliminary results. It is necessary to cover the leach reactors to prevent ammonia loss while still allowing for some air ingress to oxidize cuprous to cupric ion.

4.3.2 Cyanidation with Adjusted Setup

In order to measure cyanide leaching efficiency with better control, a three-hole lid was introduced to the reactor during leaching. The lid was placed on top of the rim of the reactor, with stoppers in the holes. The presence of the lid was found to be effective in limiting evaporation, and all trials with such setup had less than 5% of evaporation as determined by changes in weight of the initial and final slurries.

The leaching condition of the adjusted cyanidation tests were the same as preliminary tests, except that the stirring rate was lowered to 500 rpm to avoid splashes, and solid percentage was lowered to 20% to extract clear intermediate sample solutions easier. The initial cyanide concentrations were also adjusted as suggested by Pan American Silver Corp. 4.25 g/L of sodium cyanide was used for LDLPMC, 25 g/L of sodium cyanide was used for NHMC, and 7.4 g/L of sodium cyanide was used for CZMC. The concentrations were determined according to the copper content in the samples. The loose parafilm seal on the lid allows oxygen to diffuse into the reactor under extended period while preventing some evaporation.

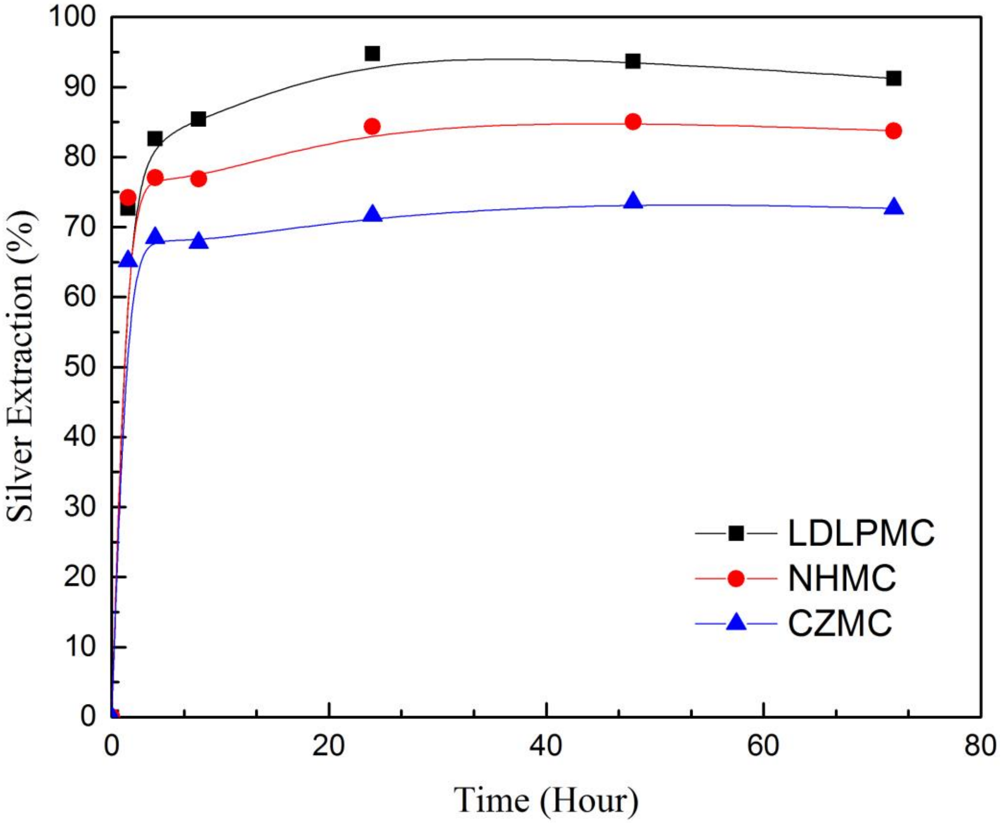


Figure 4.10 Silver extraction throughout cyanidation tests on LDLPMC, NHMC and CZMC

With adjustment of experimental setup, silver extraction was relatively stable after 24 hours for all samples. From Figure 4.10, LDLPMC yields about 90% extraction, while NHMC yields 80% extraction, and CZMC yields about 70% extraction. This result set a baseline of cyanide-leachable silver present in each ore, and thiosulfate leaching is targeting to leach silver to the same extent. Compared to Figure 4.8, the leaching curves flat out after 24 hours, rather than increasing significantly with steeper slope. This indicates the leaching reactions has ceased. The total mass before and after leaching was measured, and less than 5% of mass loss has been discovered, which mean no significant evaporation has taken place.

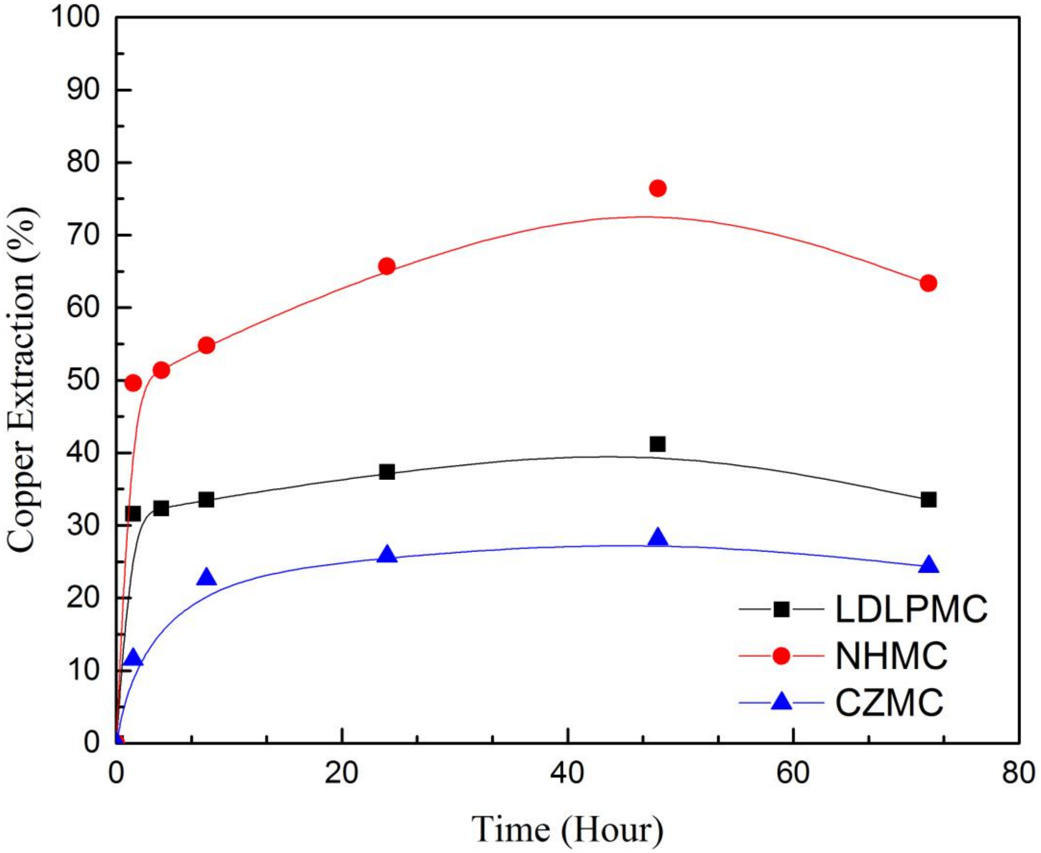


Figure 4.11 Copper extraction throughout cyanidation tests on LDLPMC, NHMC and CZMC

Copper extraction follows a similar trend as that in preliminary tests but peaked after 48 hours. NHMC leaches most copper out due to its high content of cyanide-soluble copper. Approximately 65% of copper dissolved in NHMC, whereas only 35% and 25% of copper dissolved in LDLPMC and NHMC respectively. These results create a baseline for maximum soluble copper during thiosulfate leaching, even though it is unlikely that copper leaching can come close to these values, since thiosulfate is not as stable or reactive toward copper minerals.

The cyanide consumption has been determined for these tests. Sodium cyanide consumption is the highest for NHMC as in preliminary test (64 kg/tonne of ore). CZMC and LDLPMC consume 17 kg/tonne of ore and 9.8 kg/tonne of ore respectively. The difference in cyanide consumption between current results and preliminary results is likely due to the very high dosage used in current results, as higher concentration of cyanide drives more metals out of solid; the adjusted setup avoids evaporation and splash effectively, bringing more credibility to the results. In later plots regarding silver and copper extraction, this set of data is used to compare with the thiosulfate leaching results.

4.4 Thiosulfate Leaching Tests

The thiosulfate leaching tests were then conducted in the reactor with the lid. Variables of the leaching tests include initial thiosulfate concentration, initial total ammonia concentration, initial pH, temperature of water bath and initial copper concentration. Tests with additional air sparging and EDTA are carried out to compare the effect of these two factors. The leaching tests were executed with varying one variable at a time (OVAT), with values of all other variables being the same as the baseline condition. The combined effect of changing multiple variables simultaneously are ignored in this study.

According to the preliminary studies as well as the cyanidation results, it can be seen that LDLMPC is the sample with the most leaching potential. The following tests will mainly be focusing on this sample.

The following table summarizes all variables and the conditions involved in the study:

Table 4.3 Conditions studied for cupric thiosulfate leaching on LDLPMC

Variables	Baseline	Conditions		
Thiosulfate Concentration (M)	0.1	0.2	0.3	0.5
Total Ammonia Concentration (M)	0.7	0.35	0.2	1.0
Cupric Concentration (mM)	1	0		
pH	9.5	9.0	8.5	
Temperature (°C)	25	35	45	
EDTA (mM)	0	0.5		
Air Sparging	No	Yes		
% Solid	20%			

As mentioned in the discussion of the cyanidation tests, higher concentration of reagents is favourable to extract more metals from the ore, so higher concentrations of thiosulfate are investigated. Ammonia also plays a critical role in leaching, as it interacts with copper, a critical reactant of the system. Introducing copper in the initial leaching solution may be necessary to enhance initial silver dissolution; however, addition of excessive copper is unnecessary since high concentration of copper oxidize thiosulfate rapidly. Dissolution of copper also occurs throughout the test, which suggests that very diluted initial copper concentration or zero addition of copper is still possible to leach silver. This is critical to industrial practice as introducing less copper into the leaching system reduces down reagent cost significantly. Thiosulfate leaching is usually being criticized for high reagent cost, and the possibility of reduce reagent cost raises its competitiveness to cyanidation. According to Figure 2.2, thiosulfate is stable across a pH range from 4.7 to 15, but typical thiosulfate leaching tests are carried out under pH from 9 to 11, with the optimum conditions achieved between 9 and 10 (John O Marsden et al., 2006). In order to cut down the usage of pH conditioner, pHs lower than baseline value are investigated. pH is also critical to speciation in solution, and in order to maintain a decent amount of copper catalyst present in solution, the solution pH still needs to be maintained in the alkaline region. Higher temperature yields faster kinetics, but it can also drive off ammonia from the system (Deutsch et al., 2013a). EDTA is known to be one of the additives to copper ammonia thiosulfate leaching system that can help leach silver (Deutsch et al., 2013b; Puente-Siller et al., 2014); it might be helpful to investigate its interaction with an actual ore. Air sparging is a typical condition to be used to oxidize the ore and enhances leaching, but in the case of thiosulfate leaching, such condition is expected to consume more thiosulfate.

4.4.1 Reproducibility of Tests

Throughout the time span of the project, various duplicate tests of baseline condition were conducted, and the results of these tests were compared to ensure the reproducibility of the tests. Three baseline test results are presented in Figure 4.12 to Figure 4.16.

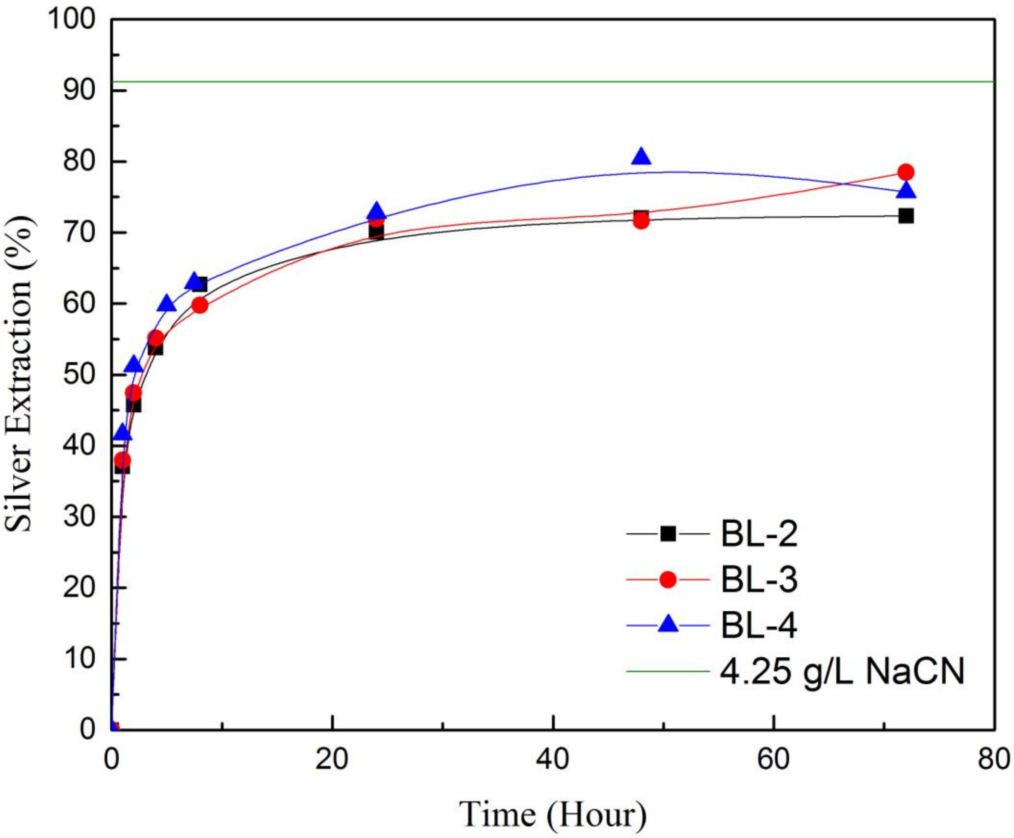


Figure 4.12 Silver extraction throughout baseline tests on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

It can be seen that the silver extraction of the three trials follows the same trend and approximately the same silver concentration at all time intervals. BL-4 yields slightly higher silver dissolution than the other two trials due to adapting the new sample solution handling method, as discussed in Section 4.1. Most of the points obtained at the same time agree within 5%.

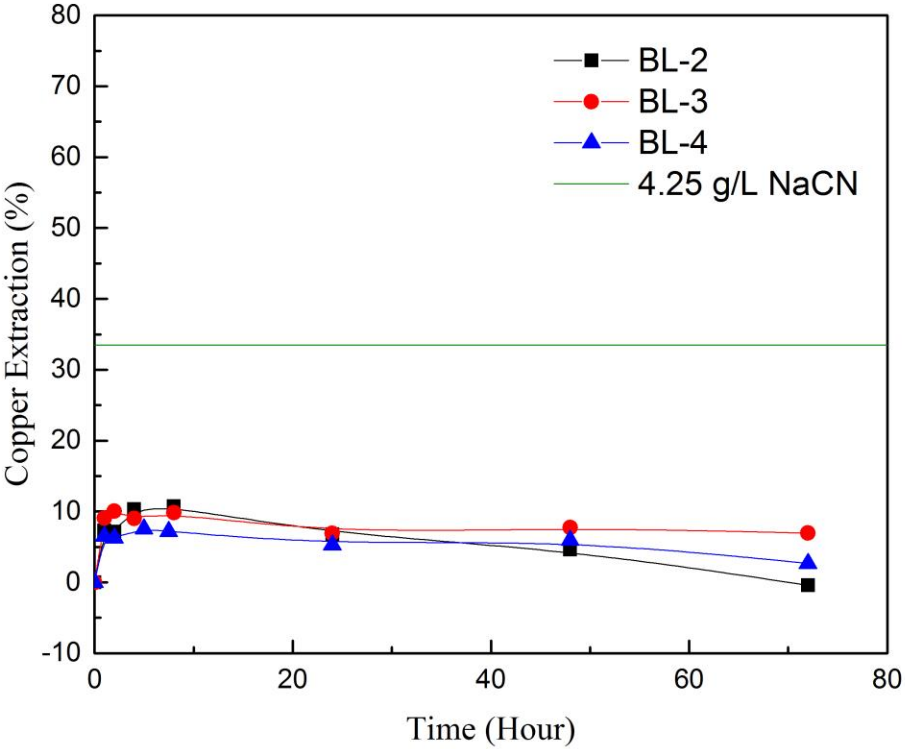


Figure 4.13 Copper extraction throughout baseline tests on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Figure 4.13 shows the copper concentration in intermediate samples extracted at different time. Most of the points the three trials exert similar trend in copper extraction rate: all concentrations peak around first 8 hours, then becoming stable with fluctuation. The major source of error for leaching of copper is attributed to large variation of the copper assays in the head ore.

Figure 4.12 and Figure 4.13 suggest a significant difference between thiosulfate leaching and cyanidation. Thiosulfate leaching is very selective towards silver, whereas cyanide leaches all available silver and copper, which increases the reagent cost of leaching.

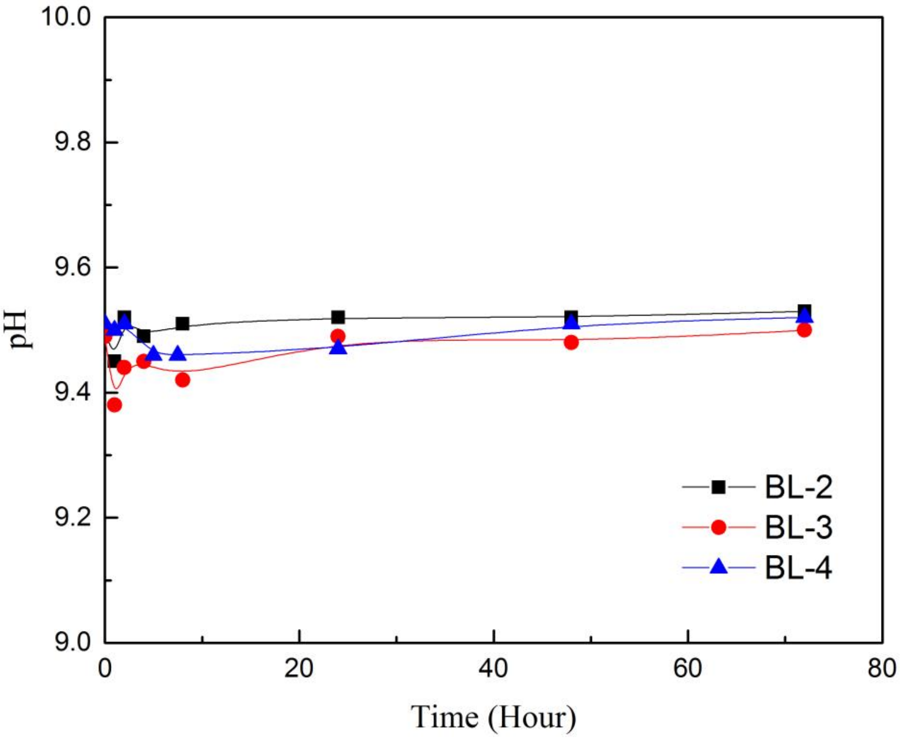


Figure 4.14 pH throughout baseline leaching tests on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

The pH throughout the baseline tests are rather stable, with a variation between 9.4 and 9.5 for most of the time, as shown in Figure 4.14. The pH measurements show that it is not necessary to control pH throughout the trial, which eliminates the cost of pH conditioner and related equipment in industrial practice. The ammonium/ammonia buffer is also serving well for buffering pH change of the system, as long as ammonia loss is under control.

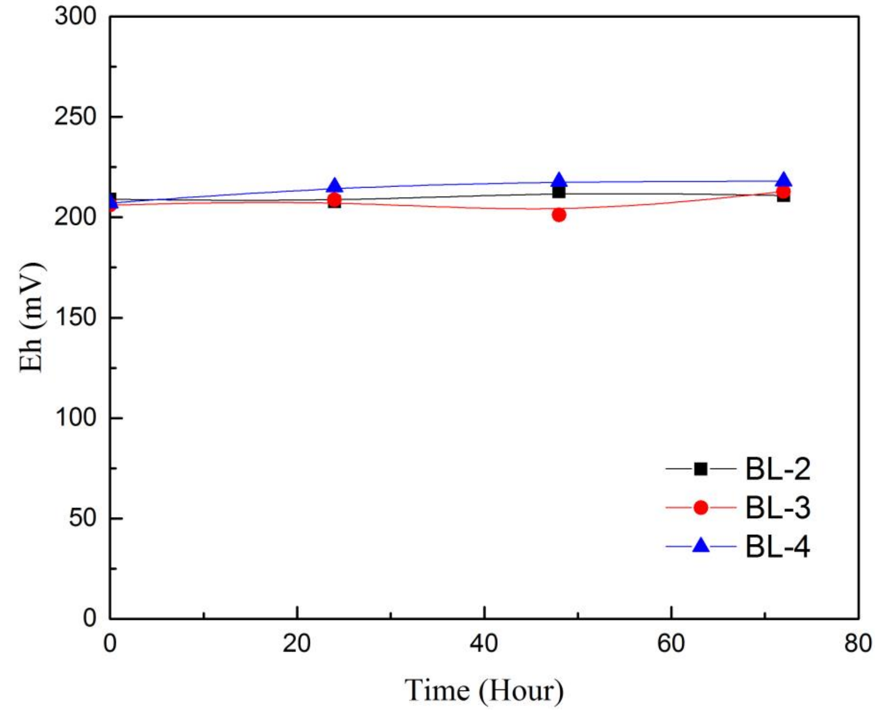


Figure 4.15 Eh throughout baseline leaching tests on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Figure 4.15 shows the Eh change throughout the trials. It turns out that Eh stays around 210 mV throughout the experiments. Compared to the preliminary tests, as long as Eh of the system is stable, thiosulfate ought to be present in excess; this ensures dissolution of silver and, to some extent, copper. The major aqueous redox reaction couples taking place in the system are listed as following (in reduction form):

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad E° = 0.40\ V$$

$$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-} \qquad E° = 0.12\ V$$

$$Cu(NH_3)_4{}^{2+} + 3S_2O_3^{2-} + e^- \rightleftharpoons Cu(S_2O_3)_3^{5-} + 4NH_3 \qquad E° = 0.23\ V$$

Accounting for concentration using Nernst equation, the actual potential of these couple are calculated as below:

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad \text{E= 0.61 V}$$

$$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-} \qquad \text{E= 0.01 V}$$

$$Cu(NH_3)_4{}^{2+} + 3S_2O_3^{2-} + e^- \rightleftharpoons Cu(S_2O_3)_3^{5-} + 4NH_3 \qquad \text{E= 0.19 V}$$

Since the Eh value falls between 0.19 V and 0.61 V, it is concluded that the oxygen/hydroxyl ion couple and cupric tetraammine/cuprous trithiosulfate couple manifest the Eh.

The thiosulfate concentrations of the leaching solutions are demonstrated in Figure 4.16. The three set of results exhibit the same trend of decrease in thiosulfate concentration over time, but even after 72 hours around 70% of the thiosulfate is still present. The initial thiosulfate concentrations are lower than 0.1 M because some thiosulfate ions have been complexed by the initial addition of copper into the original leaching solution. Due to the solution pretreatment, thiosulfate in cuprous thiosulfate complexes were not indicated, which accounts some of the loss of thiosulfate. In addition, differences in delays prior to titration was performed may have allowed for some loss of thiosulfate due to oxidation by oxygen. The average ammonium thiosulfate consumption is determined as 16.9 kg/tonne ore for such sample ore.

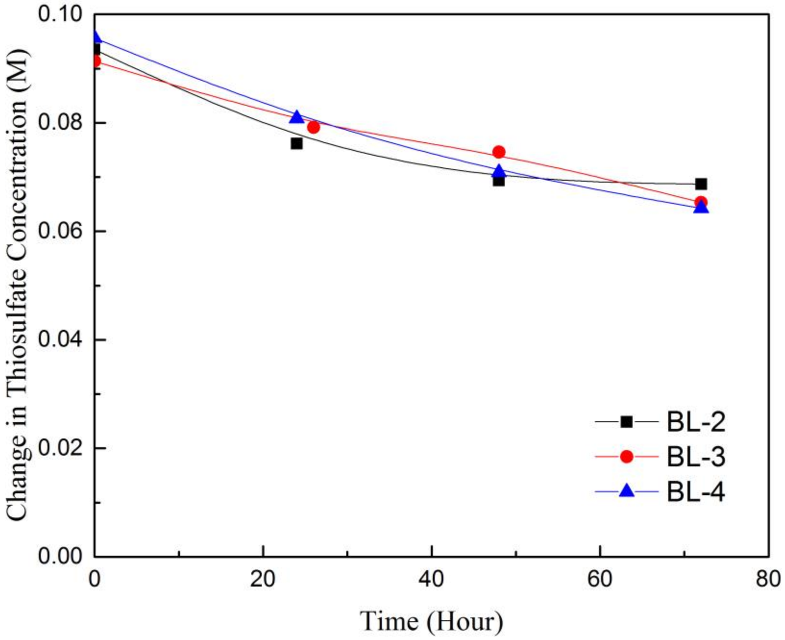


Figure 4.16 Thiosulfate concentration throughout baseline leaching tests on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

The various conditions of leaching test on LDLPMC were carried out, and their results are compared with the baseline condition. The comparison will assist to investigate the factors that impact the leaching performance the most, as well as finding the best condition under each variable.

There are two methods to calculate the extraction percentage. The first method is to calculate the total mass of metal extracted, which is the sum of metals in all intermediate sample solutions, the final filtrate and wash. By subtracting away the initial metal content that was added to the solution (e.g. Cu), the total metal mass extracted can be calculated. This value divide by the mass of metal in the head ore (based on the solid assay and the mass of ore used) gives percent extraction. This is percent extraction by solutions basis. The second method is to calculate the ratio of difference between final mass of total metal in tail residue and initial mass of total metal in head ore to the initial mass of total meal in head ore. Such calculated ratios are the percent extractions by solids basis. Ideally, the results from these two methods should be the same but in reality the values can differ. As mentioned in this section before, variation of copper content in the head assay is quite high. This can yield greater differences between the two values. In this thesis the extraction calculation is based on solutions basis. Sample calculations of how head assay affects extraction percentage are shown in Appendix.

4.4.2 Initial Concentration of Thiosulfate

Thiosulfate as the major complexing agent with silver is critical to the performance of the leaching system. Higher concentration of thiosulfate helps to increase the driving force of leaching reaction, but also risks increasing reagent cost in industrial practice. Therefore, a sufficiently high but also economically viable thiosulfate concentration is desired. A series of thiosulfate (0.1 to 0.5 M) concentrations were investigated, with measuring their silver and copper dissolution over time, change of pH, Eh and thiosulfate concentration. The maximum leachable silver and copper are also included for comparison. In 0.5 M of thiosulfate, with 0.7 M of total ammonia present, the maximum thiosulfate concentration achievable with mere source of thiosulfate being ammonium thiosulfate is 0.35 M. Additional thiosulfate is introduced in the form of sodium thiosulfate pentahydrate to compensate for the difference.

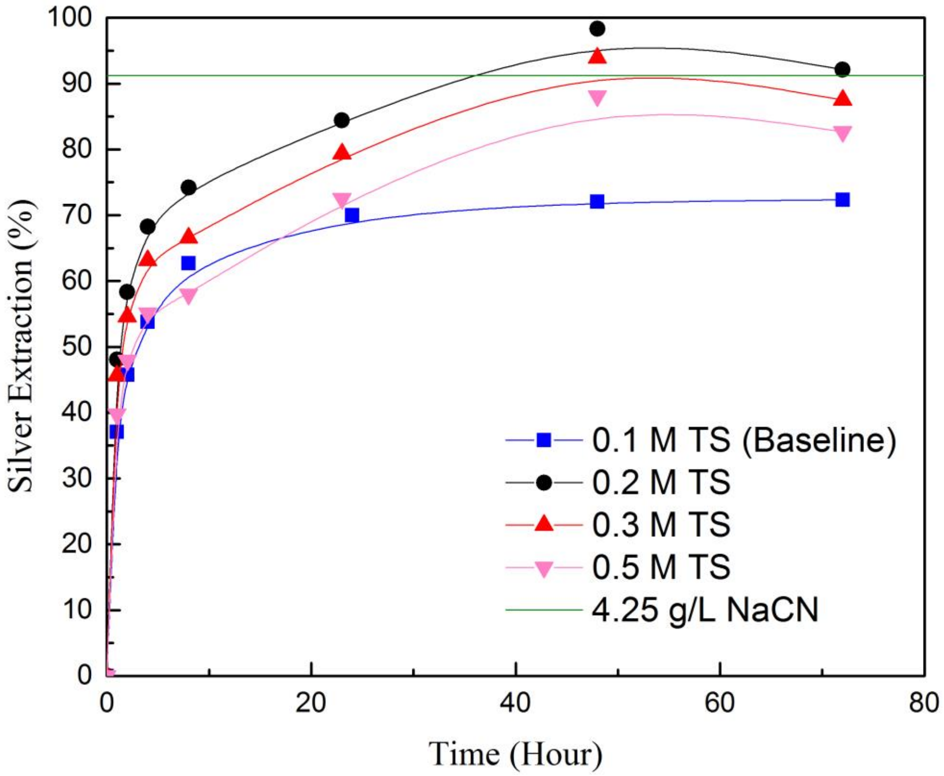


Figure 4.17 Silver extraction throughout tests with various thiosulfate concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

From Figure 4.17, it is found that the condition that yields the highest silver dissolution is 0.2 M of thiosulfate. Higher concentrations beyond this value only yield lower silver extraction. Initial concentrations of 0.2 M and 0.3 M of thiosulfate yield 92% and 87% of silver dissolution respectively, whereas 0.1 M and 0.5 M of thiosulfate only yield around 72% and 83% of extraction respectively. Impressively, 0.2 and 0.3 M of thiosulfate yield silver extractions that are comparable to that of cyanidation. Higher reactant concentration usually yields higher kinetics; however, 0.5 M result in lower kinetics that is the opposite. From Figure 2.7, it is known that concentration of cupric tetraammine, the catalyst of leaching reaction, will decrease with increase of thiosulfate concentration. Low kinetics and extraction by 0.5 M of thiosulfate can be attributed to the suppressed concentration of the catalytic cupric tetraammine. The competition of increasing leaching kinetics with more thiosulfate and decreasing leaching kinetics with less cupric tetraammine complicates the comparison. Effect of increasing extraction and kinetics by increasing thiosulfate concentration can be seen from 0.1 to 0.2 M; from 0.2 M to 0.5 M the suppression effect by increasing concentration of thiosulfate dominates the system.

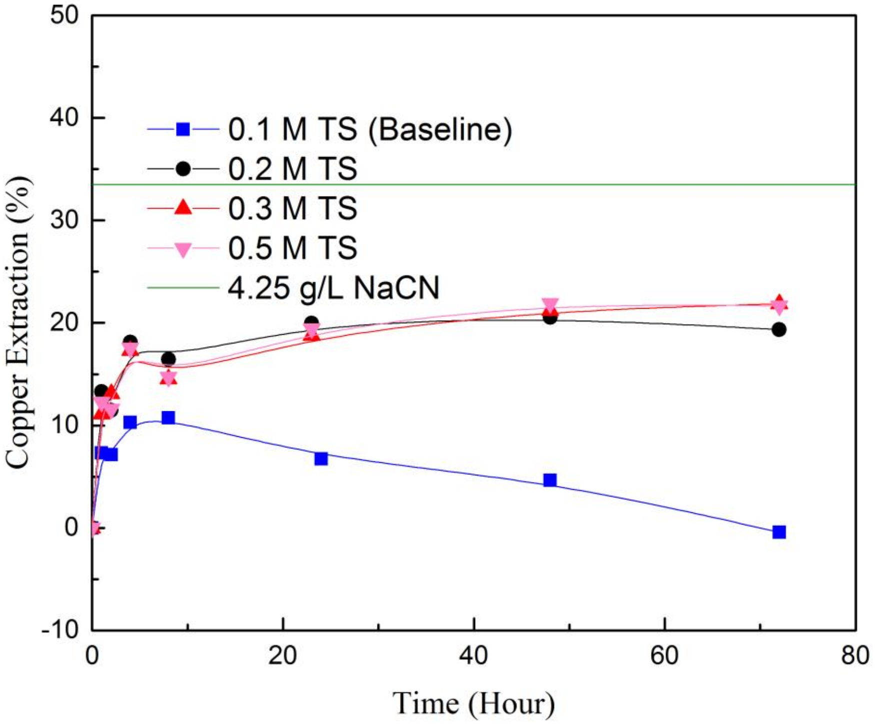


Figure 4.18 Copper extraction throughout tests with various thiosulfate concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Extraction of copper is proportional to concentration of thiosulfate. Once in contact, cupric reacts with thiosulfate rapidly; it is not surprising that higher concentrations of thiosulfate yield higher extraction of copper. Copper extraction appears to become constant after 24 hours, indicating that copper leaching is completed. Copper concentration is still low in solution compared to that in cyanidation, even at around 20% extraction. Only maximum of 133 ppm of copper (equivalently 2 mM) is dissolved in solution. As cyanide is a more effective complex agent than thiosulfate with metals, thiosulfate cannot leach the same amount of copper. Moreover, as discussed in Chapter 2, copper also precipitates and may form chalcocite and covellite when cupric substitutes silver; therefore, some copper will eventually end up in the leach residue, which is another factor that reduces copper extraction via thiosulfate. In industrial practice, in order to maintain consistent condition of leachate, copper needs to be removed from the leachate periodically. The use of zinc cementation for silver recovery would allow removal of copper with the silver.

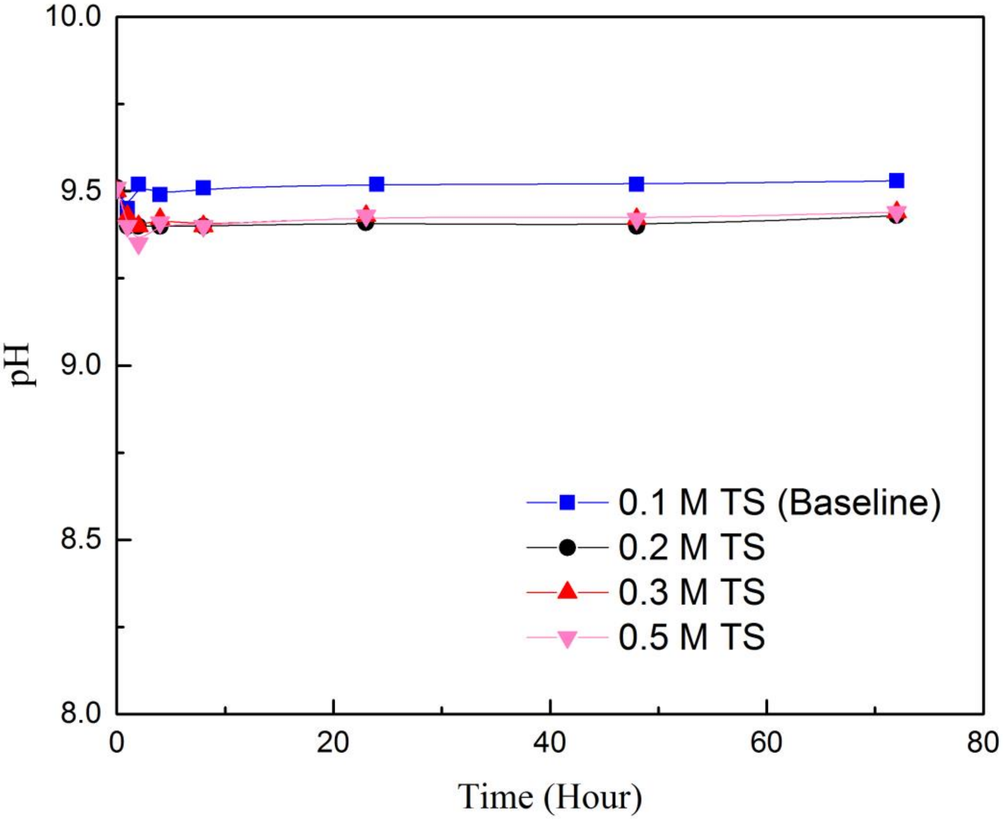


Figure 4.19 pH throughout tests with various thiosulfate concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

The pH of increased thiosulfate concentrations are stable throughout the tests at around 9.4, which is close to stable pH value (9.5) of the baseline.

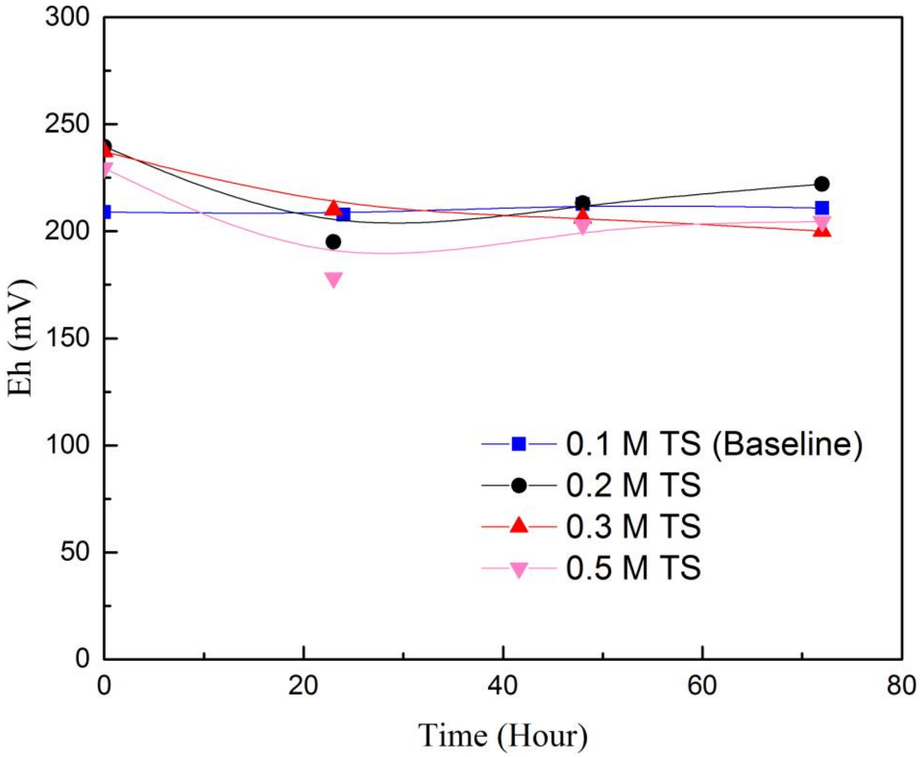


Figure 4.20 Eh throughout tests with various thiosulfate concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Overall, Eh of the increased thiosulfate concentration tests all have a trend of decrease in Eh compared to the initial value, but the overall decrease is rather small. 0.2, 0.3 and 0.5 M all have a significant decrease in the first 24 hours, which can be attributed to the consumption of tetraamminecopper(II) ion for leaching silver. A lower concentration of such ion exhibits a lower Eh in cupric tetraammine thiosulfate leaching system (Breuer et al., 2002). In comparison, Eh of the trials are relatively stable after 24 hours, indicating that the systems start to converge to type of steady state. Along with Figure 4.17, most of the leaching takes place in the first 48 hours.

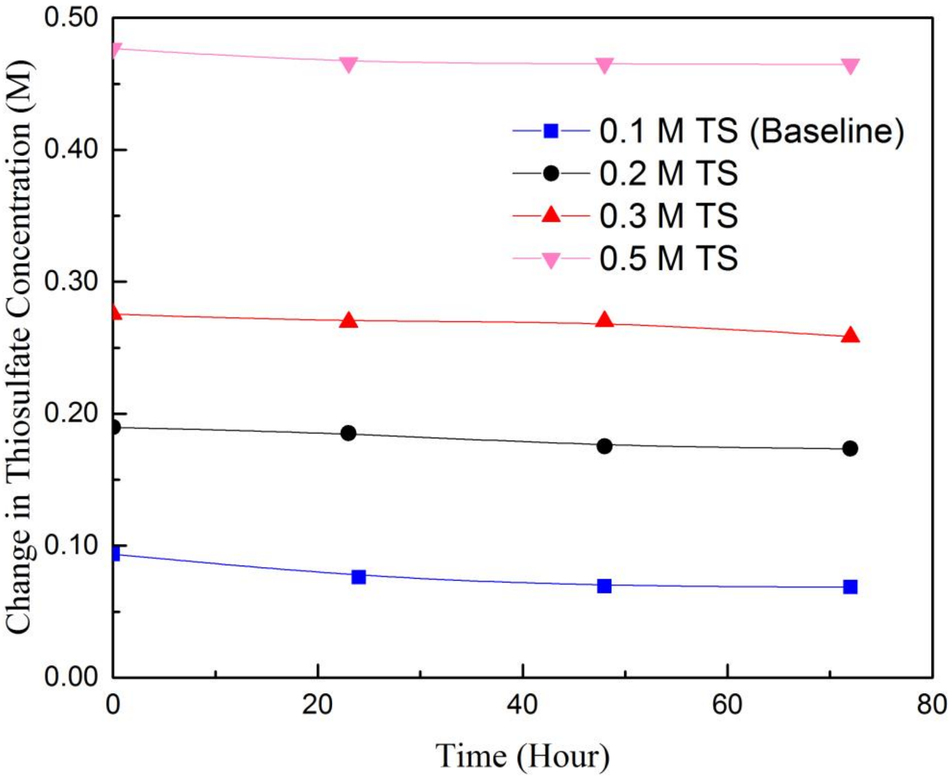


Figure 4.21 Thiosulfate concentration throughout tests with various thiosulfate concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Change of thiosulfate concentration for different trials are depicted in Figure 4.21. Similar to the baseline tests, the initial thiosulfate concentrations are slightly lower than their designated value, which may be attributed to complexation between cupric and thiosulfate, accelerated initial oxidation of thiosulfate with presence of oxygen and amplified error in analytical method due to dilution of concentrated thiosulfate samples (loading and stripping method was designed for 0.1 M of thiosulfate). The decrease of thiosulfate concentration throughout the trials are relatively small, which is beneficial to keep the whole leaching system stable for extended period. In general, change in thiosulfate concentration increases with increase of initial thiosulfate concentration. This may be attributed to increase of thiosulfate concentration decreases reduction potential of tetrathionate reaction ($S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$), which is the anodic half-cell reaction of thiosulfate oxidation reaction in alkaline solution ($4S_2O_3^{2-}+O_2+2H_2O \rightarrow 2S_4O_6^{2-}+4OH^-$). The potential of such reaction decreases with decrease of its anodic reaction potential. This suggests that the extent of this reaction is greater at higher thiosulfate concentrations. The ammonium thiosulfate consumption for the tests with 0.2, 0.3 and 0.5 M thiosulfate were calculated as 17.9 kg/tonne ore, 10.1 kg/tonne ore, and 7.05 kg/tonne ore, respectively.

The 0.2 M of initial thiosulfate concentration is the most promising leaching condition among all thiosulfate concentrations. It yields highest silver extraction with moderate consumption of ammonium thiosulfate.

4.4.3 Initial Concentration of Total Ammonia

Besides thiosulfate, another critical component for cupric tetraammine thiosulfate leaching system is ammonia. Zipperian et al. (1988) concluded in his study that silver leaching is more sensitive to ammonia concentration compared to gold leaching. As discussed in Chapter 2, ammonia complexes with cupric ion to form cupric tetraammine and becomes the catalyst of silver leaching; concentration of total ammonia is also another critical factor that affects the speciation of system (Figure 2.8). A sufficiently high ammonia concentration is necessary to maintain the availability of tetraamminecopper(II) ions, but excessively high concentration is not only unnecessary as resulting in high reagent cost but also increase the safety concern for such operation (Puente-Siller et al., 2014). The presence of ammonium and ammonia acts as a buffer of the system, therefore the use of an additional pH conditioner like lime addition in the case of cyanidation can be eliminated. The downside of such is that aqueous ammonia is prone to evaporation at high pH, thus equipment design of preventing evaporation becomes critical; in the case of this study, addition of lid is sufficient. Various total ammonium concentrations (0.2 M, 0.35 M and 1.0 M) were investigated, and their results will be discussed in this section.

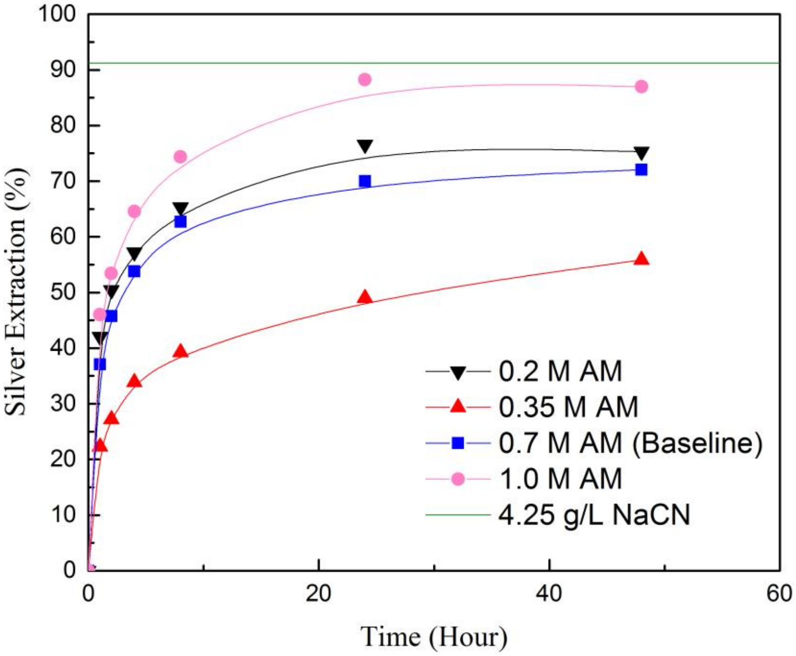


Figure 4.22 Silver extraction throughout tests with various ammonia concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 1 mM copper, pH 9.5, 25 °C)

Silver extraction is measured at various time intervals for different ammonia concentrations. From Figure 4.22, it can be seen that silver dissolution increases with increase of ammonia concentration from 0.35 M to 1.0 M, with exception of 0.2 M ammonia. 1.0 M ammonia dissolves the most silver among all conditions.

As for copper extraction, it increases with increase of ammonia concentration. 0.2 M and 0.35 M of total ammonia yields negative copper extraction, indicating that these two conditions do not contain sufficient ammonia in solution to dissolve copper (and in fact added copper is precipitated). In the leaching reaction, cupric ion in solution forms tetraamminecopper(II) ion and cuprous thiosulfate ion first, then both ions react with silver compounds and form cuprous or cupric sulfide. With higher concentration of ammonia, it is possible that those copper sulfides can redissolve; at lower concentrations it is more difficult, thus leading to precipitation of copper as shown in Figure 4.23.

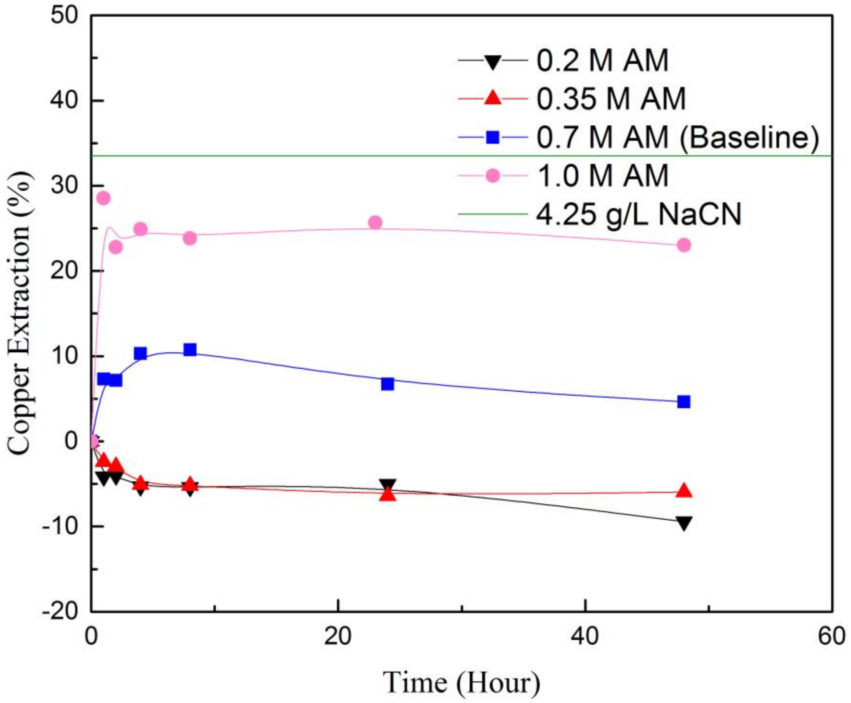


Figure 4.23 Copper extraction throughout tests with various ammonia concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 1 mM copper, pH 9.5, 25 °C)

The pH change of various tests with different ammonia concentrations are depicted in Figure 4.24. Overall, pH stays stable in the range of 9.4 to 9.6 for all tests. At 1.0 M of ammonia has a slight decrease of pH after 24 hours, which can be attributed to minor loss of ammonia due to its high concentration.

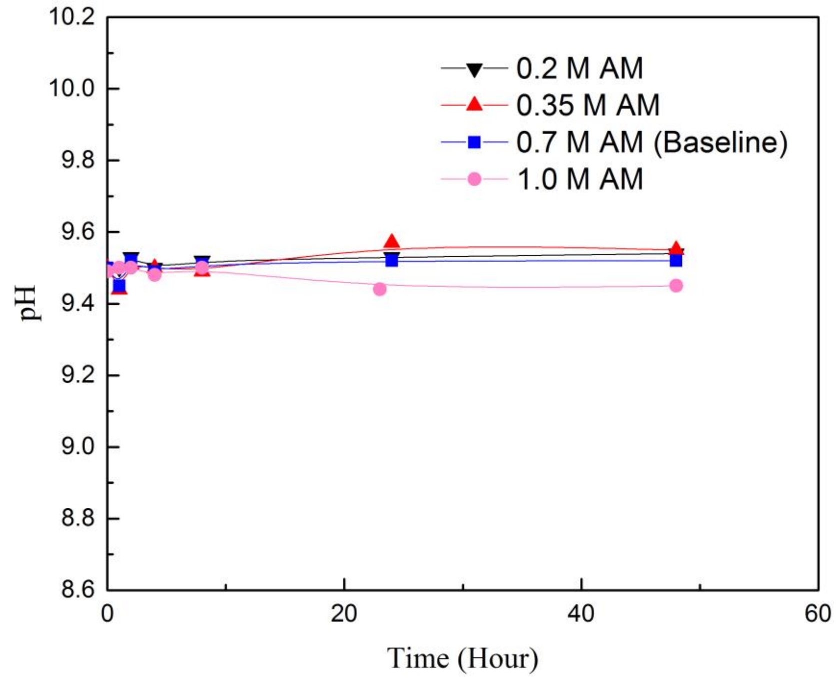


Figure 4.24 pH throughout tests with various ammonia concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 1 mM copper, pH 9.5, 25 °C)

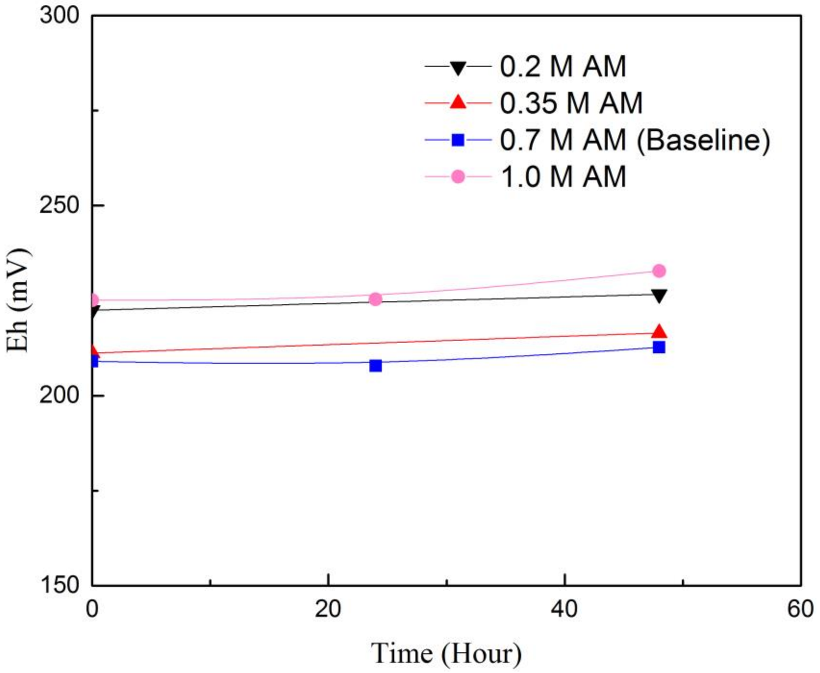


Figure 4.25 Eh throughout tests with various ammonia concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 1 mM copper, pH 9.5, 25 °C)

Eh of the leaching conditions does not change greatly throughout the experiments. The conditions that yields higher silver extractions (0.2 and 1.0 M) exhibits higher Eh throughout the trial.

Change of thiosulfate concentration throughout the experiments are similar, as shown in Figure 4.26. The consumption of ammonium thiosulfate are 15.7 kg/tonne ore, 13.7 kg/tonne ore and 20.0 kg/tonne ore for 0.2 M, 0.35 M and 1.0 M of ammonia, respectively.

The optimum ammonia concentration is determined as 1.0 M of ammonia, with moderate consumption of ammonium thiosulfate. A starting concentration of 0.2 M of ammonia is also attractive, as silver leaching extraction is comparable to that achieved at 1.0 M ammonia, while it has a lower reagent consumption.

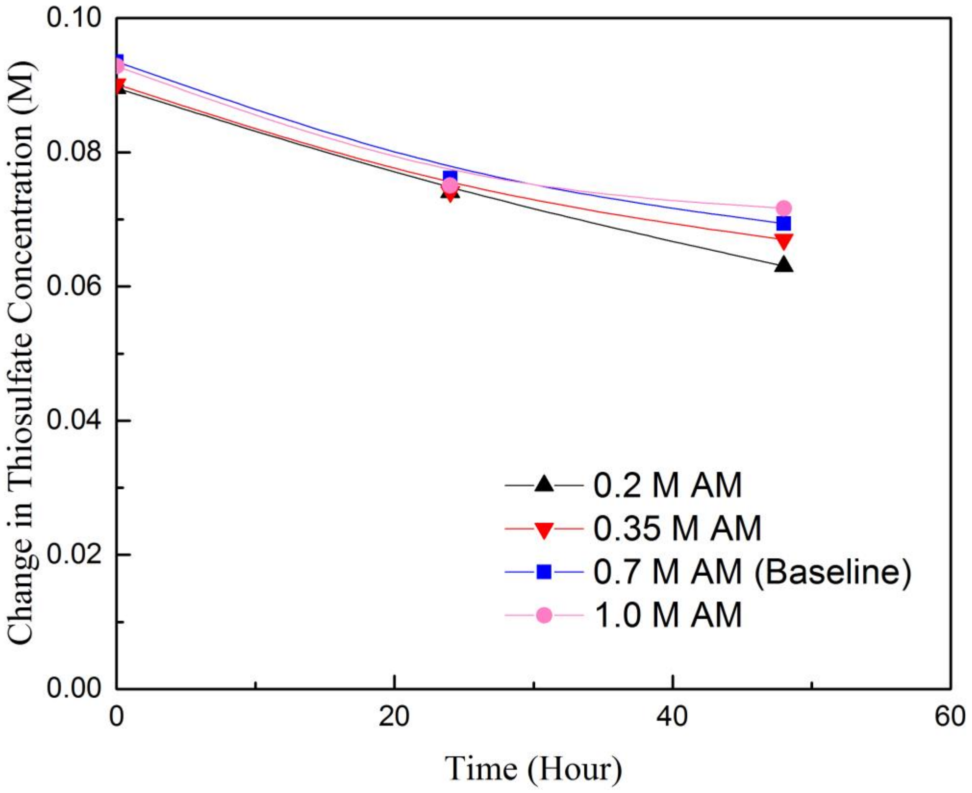


Figure 4.26 Thiosulfate concentration throughout tests with various ammonia concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 1 mM copper, pH 9.5, 25 °C)

4.4.4 Initial pH

The speciation diagrams and Eh-pH diagrams in Chapter 2 already indicated the importance of pH as it affects the speciation of the system and their location on Eh-pH diagram. Besides, higher pH in industrial practice needs more pH conditioner to maintain, thus increases the reagent cost; it is more favourable to leach silver at a lower pH. Deutsch (2012) also indicated that higher pH may dramatically decrease silver dissolution beyond 9.5. A range of pH (8.5 to 9.5) was investigated in this section and their results were analyzed.

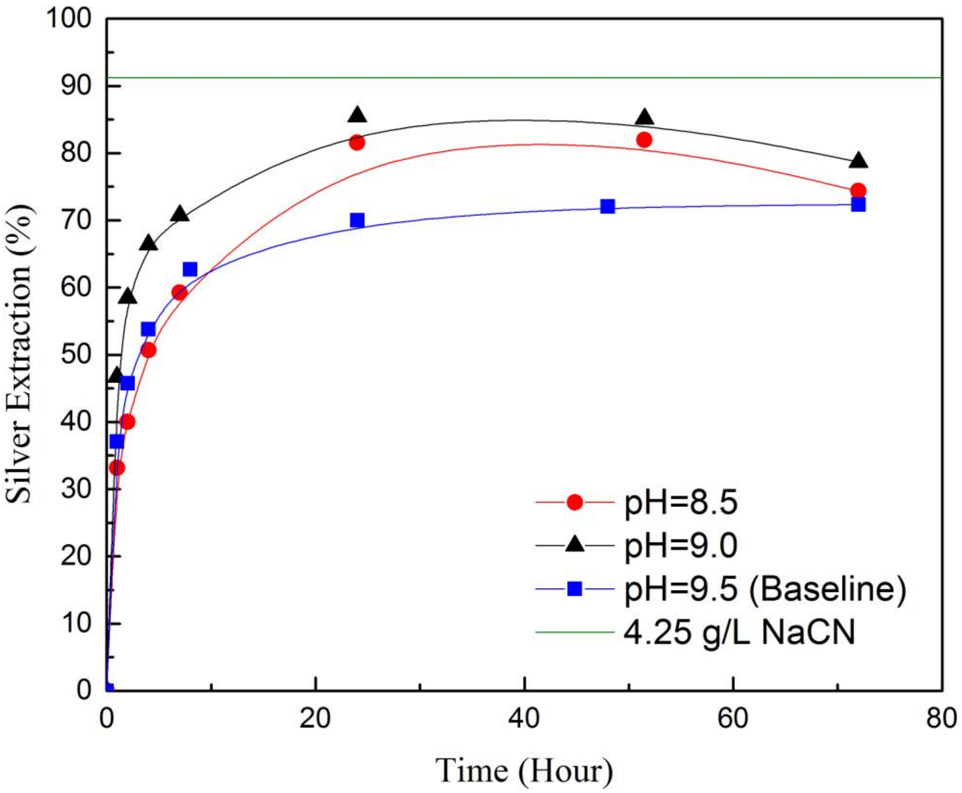


Figure 4.27 Silver extraction throughout tests with various pH on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, 1 mM copper, 25 °C)

Figure 4.27 shows the silver leaching performance with different initial pH. With initial pH of 9.0, silver extraction is the highest (87%), which is even comparable to that of cyanidation. pH of 8.5 still results in a higher silver extraction than baseline, but the extraction rate is only slightly higher than that of baseline.

Lower pH also dissolves more copper than that in the baseline test, according to Figure 4.28. Decrease of pH corresponds to the increase of copper dissolution, in the range of 8.5 to 9.5. It can be seen that dissolution of copper is a function of pH, as lower pHs dissolve more copper. In fact, minerals like copper oxides can dissolve in ammonium solution to some extent. An example of such a chemical reaction follows:

$$CuO + 2NH_3 + 2NH_4^+ \rightarrow Cu(NH_3)_4{}^{2+} + H_2O$$

Thus, dissolution of copper is thus higher comparing to the higher pH of baseline.

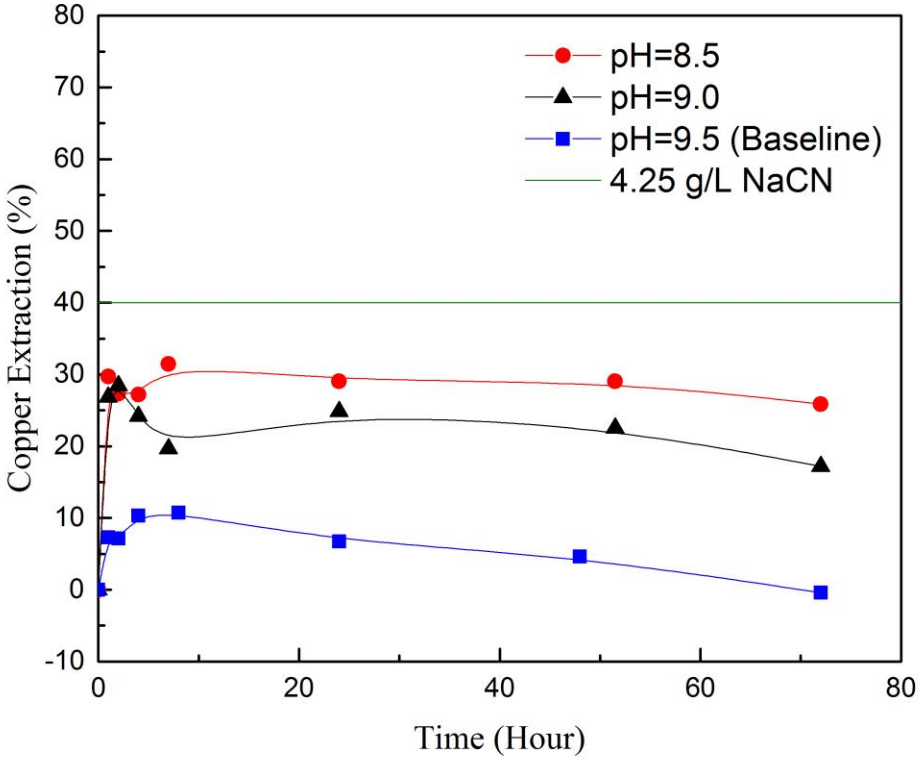


Figure 4.28 Copper extraction throughout tests with various pH on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, 1 mM copper, 25 °C)

It can be observed in Figure 4.29 that pH stays relatively stable, except that an increase of 0.2 is observed in pH of 8.5. This phenomenon agrees with the phenomena observed by Deutsch (2012) that lower pH tests yields larger pH increase. Such phenomenon may due to higher reaction potential (E) of oxygen reduction reaction in alkaline solution (O_2+H_2O+4$e^-$$\rightarrow$4$OH^-$). Since dissolved oxygen concentration do not differ significantly across the tests, pH has a higher effect on the concentration correcting term in Nernst equation, thus yielding a lower E with higher [OH^-] in solution. Higher E produces more hydroxyl ion, increasing the solution pH over time. Besides, the buffer point in ammonia-ammonium system occurs at pH of 9.26, and since pH of 8.5 is less buffered than 9.0 and 9.5, thus change in pH is more significant for the other two conditions.

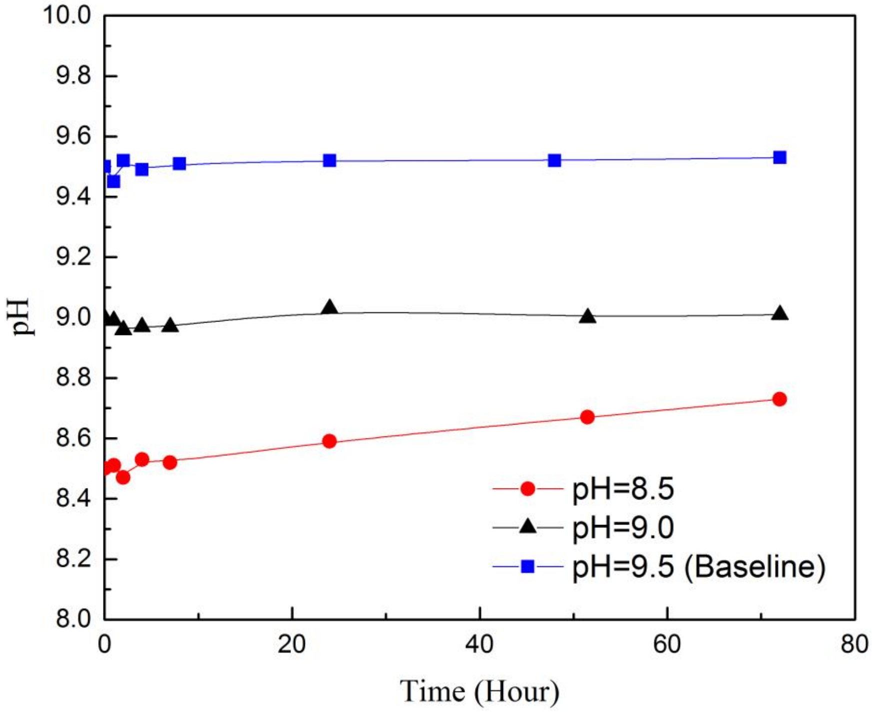


Figure 4.29 pH throughout tests with various pH on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, 1 mM copper, 25 °C)

The Eh of different pH conditions remains the same except pH of 8.5, as indicated in Figure 4.30. In the case of pH 8.5, Eh decreases over time and eventually stabilizes at 240 mV. This is an indication of different reaction mechanism in the case of pH of 8.5 and the other two. From the speciation diagrams in Chapter 2, lower pH increase concentration of cuprous thiosulfate in the system, thus the reaction where cuprous thiosulfate directly substitute silver sulfide becomes more favourable. A decrease of Eh also indicates decrease of concentration of cupric tetraammine. In the other two pH experiments, tetraamminecopper(II) ions are more abundant, which results in direct oxidation of silver sulfide by cupric tetraammine.

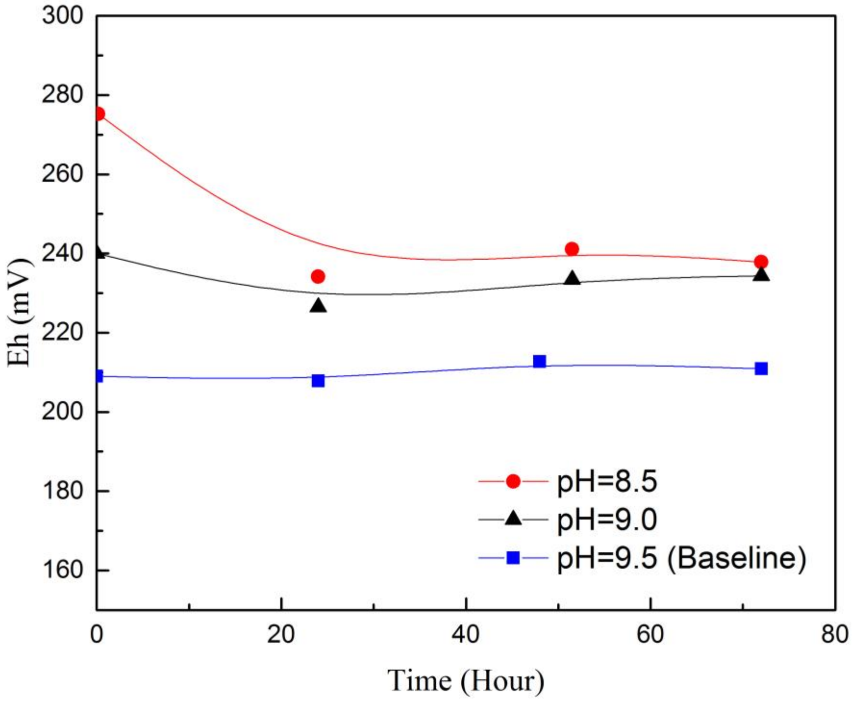


Figure 4.30 Eh throughout tests with various pH on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, 1 mM copper, 25 °C)

As for thiosulfate concentration, from Figure 4.31 the residual thiosulfate concentrations after 72 hours are significantly lower than that of baseline. According to the reaction mentioned in Chapter 2 ($2S_2O_3^{2-} + \frac{1}{2}O_2 + 2H^+ \rightleftharpoons S_4{O_6}^{2-} + H_2O$), lower pH increases hydrogen ion concentration, which may be responsible for the acceleration of the oxidation of thiosulfate. As mentioned in the discussion of the results in Figure 4.29, lower pH tends to show a greater increase in pH throughout the experiment, such increase helps to reduce thiosulfate oxidation, which is reflected by higher residual thiosulfate concentration of pH of 8.5 than that of pH of 9.0. The calculated ammonium thiosulfate consumption were 14.3 kg/tonne ore and 14.4 kg/tonne ore for pH of 8.5 and 9.0, respectively.

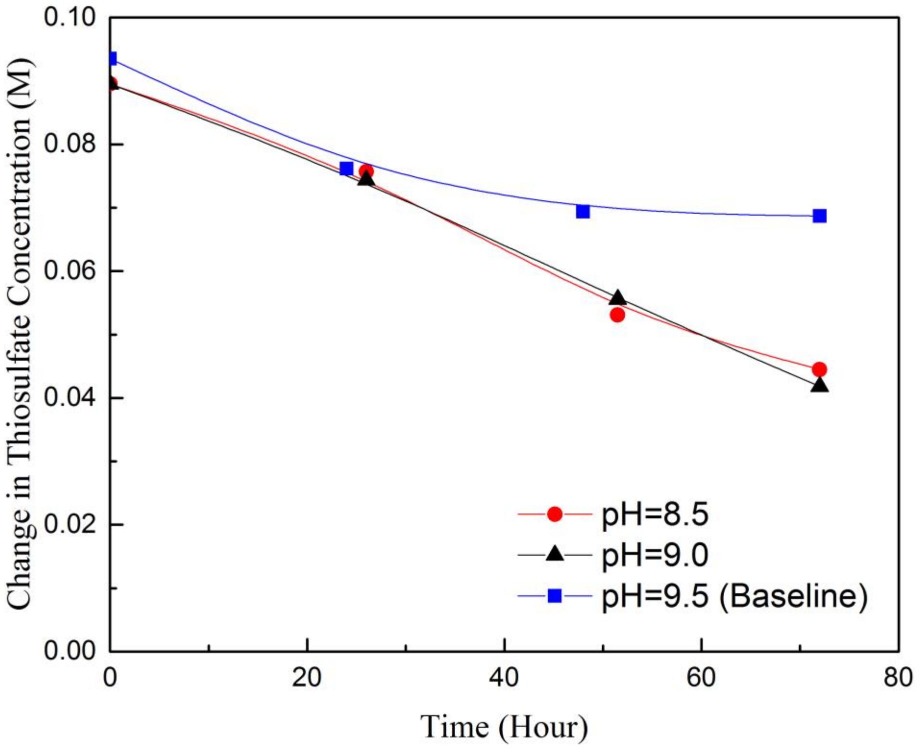


Figure 4.31 Thiosulfate concentration throughout tests with various pH on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, 1 mM copper, 25 °C)

4.4.5 Temperature

In general, higher temperatures increase the kinetics of reaction. In industry, higher temperature also increases the energy cost for operation. Therefore, an optimum temperature that balances the output and energy consumption is critical for industrial application. Temperatures of 25 ºC, 35 ºC and 45 ºC are tested for silver leaching, and the results are described in the following paragraphs.

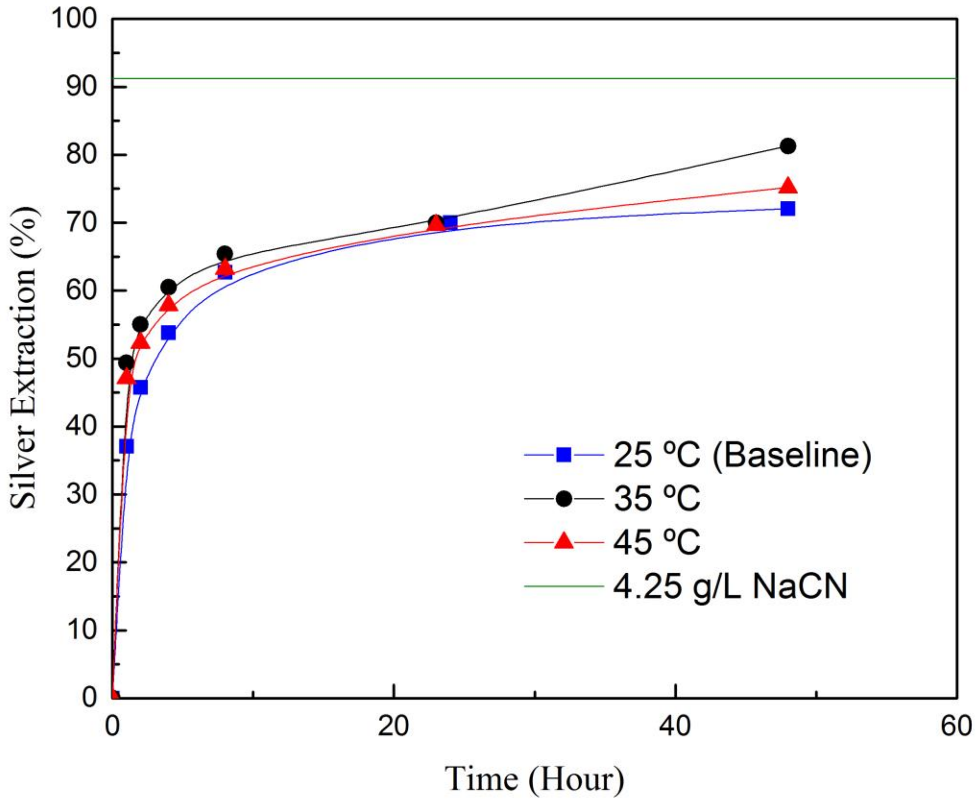


Figure 4.32 Silver extraction throughout tests with various temperature on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper)

Figure 4.32 demonstrates the silver extraction of different temperature. Silver extraction peaks at 35 ºC, and decreases at 45 ºC; silver extraction at 45 ºC is still higher than baseline condition. Silver extraction kinetics is enhanced by increase of temperature, but higher temperature may suffer loss of ammonia, which reduces the amount of cupric tetraammine in solution (Deutsch et al., 2013a).

Copper extraction is more directly related to total ammonia concentration in solution. Figure 4.33 shows the same trend of copper extraction with respect to increase of temperature, and 35 ºC yields the lowest copper extraction.

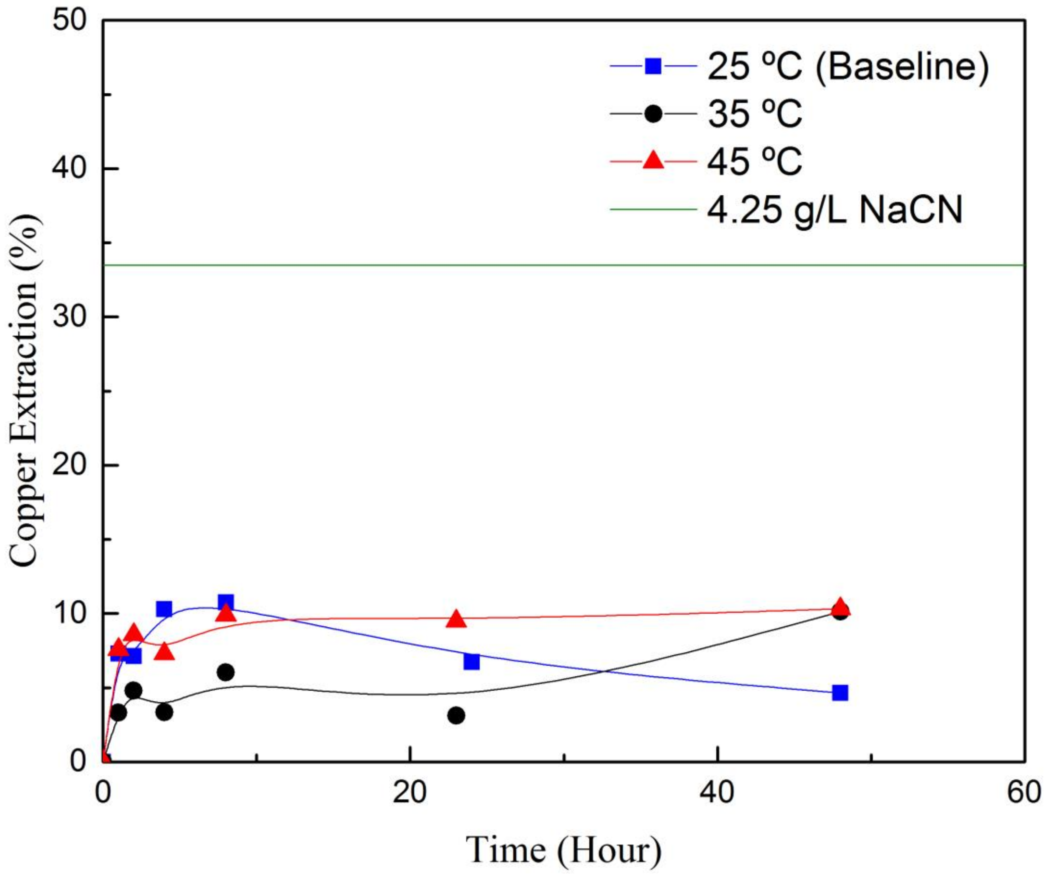


Figure 4.33 Copper extraction throughout tests with various temperature on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper)

Presence of ammonia can be reflected by the pH of solution. As an ammonia/ammonium buffer, pH of such system cannot be changed easily, unless loss of ammonia becomes significant. Figure 4.34 shows that higher temperature promotes more significant decrease of pH over time, which can be attributed to higher temperature increasing the evaporation of ammonia from the system.

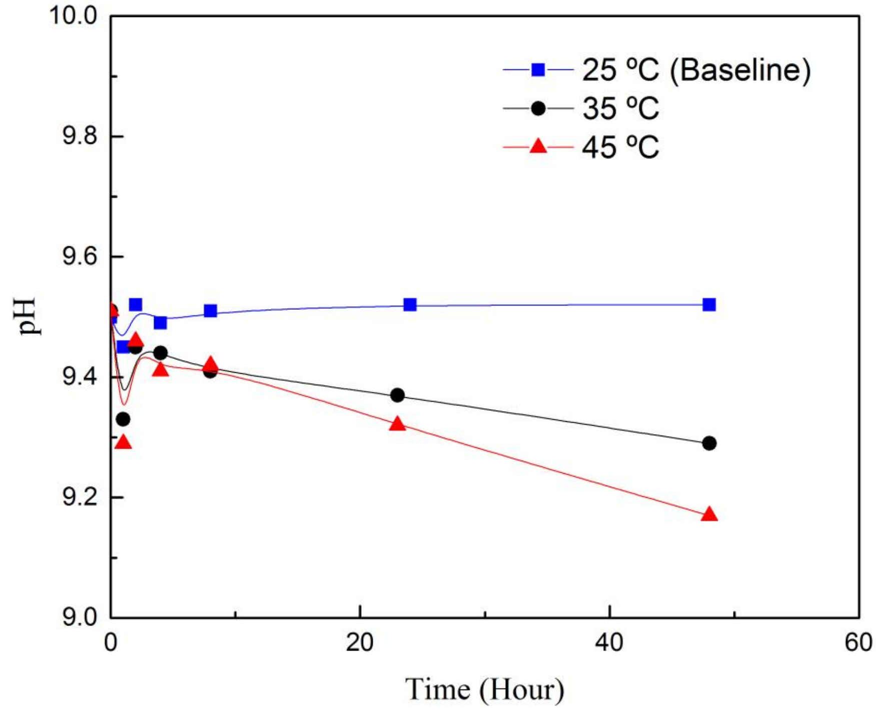


Figure 4.34 pH throughout tests with various temperature on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper)

In Figure 4.35, Eh of solution decreases over time at higher temperature, which is significantly different than the case of baseline. Since higher temperature reduces concentration of total ammonia in the system, cupric tetraammine ions are less dominant, which reduces the solution potential throughout the period of reaction.

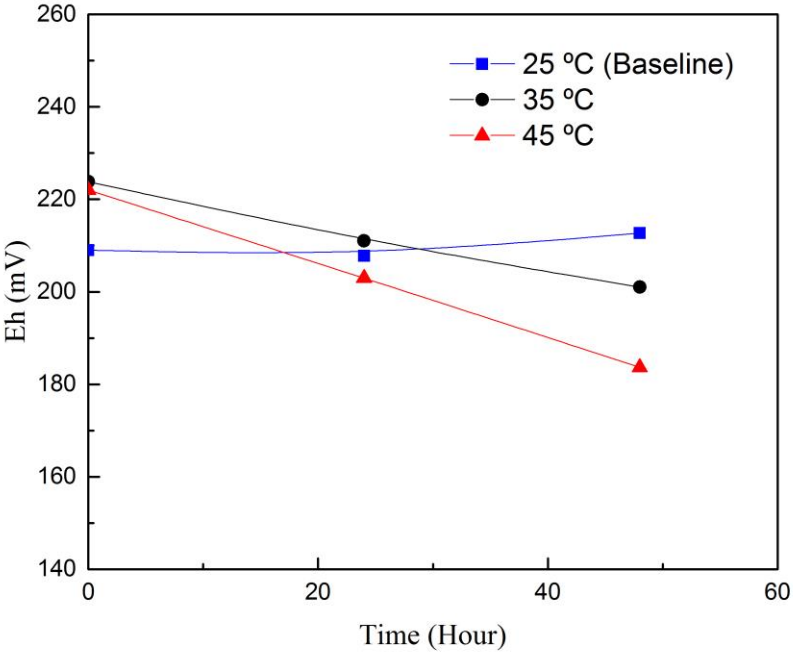


Figure 4.35 Eh throughout tests with various temperature on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper)

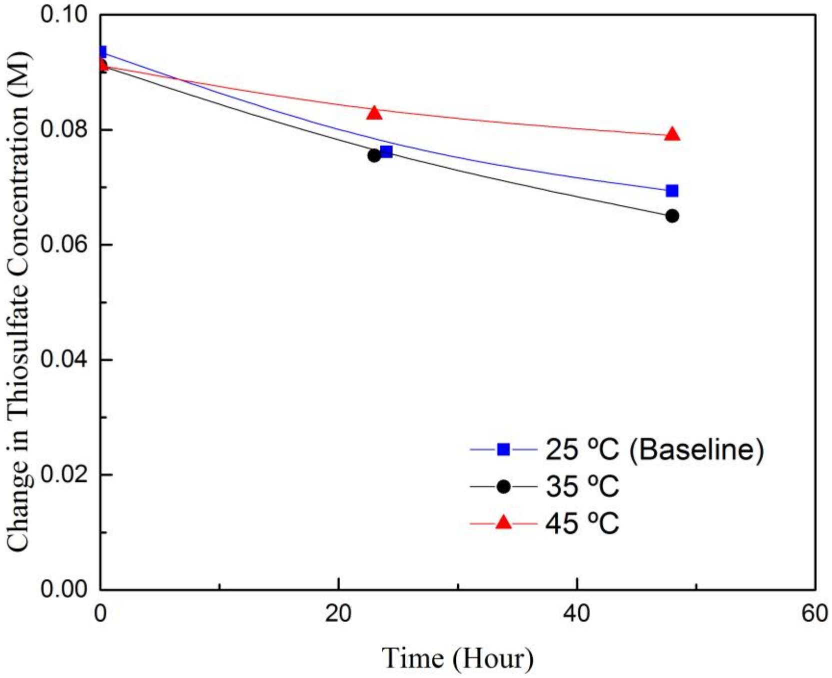


Figure 4.36 Thiosulfate concentration throughout tests with various temperature on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper)

From Figure 4.36, thiosulfate concentration decreases the most at 35 ºC, which corresponds to highest silver extraction. 45 ºC has significantly less thiosulfate degradation, due to lack of cupric tetraammine ions that catalyzes oxidation of thiosulfate. The reagent consumption of the 35 ºC and 45 ºC are 14.4 kg/tonne ore and 6.05 kg/tonne ore respectively.

4.4.6 Initial Copper Addition

Initial copper addition is intended to catalyze the leaching reaction, by means of complexing the cupric ion with ammonia to form the critical catalyst, tetramminecopper(II) ion. Since the ore samples are already rich in copper, the possibility appears that initial copper can be avoided to decrease the reagent cost. Copper that is leached from the ore can complex with the ammonia in solution and catalyze the system. The initial leaching kinetics might be less favourable, due to lack of catalyst.

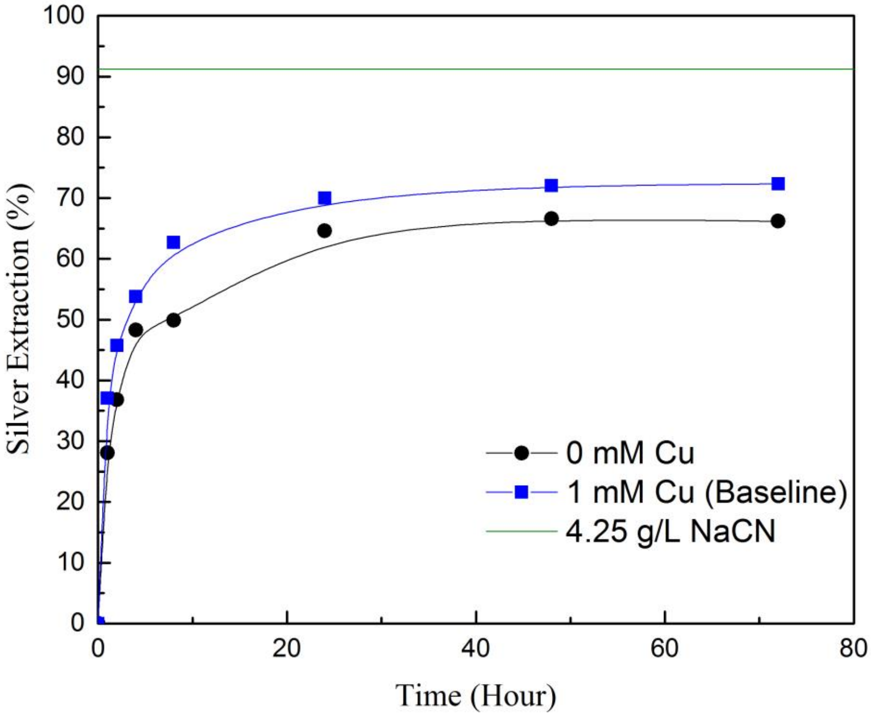


Figure 4.37 Silver extraction throughout tests with various copper concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 25 °C)

Silver extraction under different initial conditions with respect to copper addition was investigated, and the results are shown in Figure 4.37. With no initial addition of cupric ion, the kinetics of leaching is slower than that of baseline, and the final extraction of silver is below 70%. Lack of initial copper addition clearly yields lower silver extraction comparing to baseline; as discussed in Chapter 2, two pathways of silver sulfide are available: the cupric tetraammine reaction ($Ag_2S + {Cu(NH_3)_4}^{2+} + 6S_2O_3^{2-} \rightleftharpoons 2Ag(S_2O_3)_3^{5-} + CuS + 4NH_3$) with negative ΔG° and the cuprous thiosulfate reaction ($Ag_2S + 2Cu(S_2O_3)_3^{5-} \rightleftharpoons 2Ag(S_2O_3)_3^{5-} + Cu_2S$) with positive ΔG°, and such results shown in Figure 4.37 indicate that baseline follows cupric pathway while no initial copper addition follows cuprous pathway, which yields lower silver extraction. This phenomenon agrees with observation by Briones et al. (1998) and Aylmore et al. (2001) that addition of copper enhances silver leaching. With progression of leaching, increase of copper dissolution may enhance silver leaching by forming increased concentration of copper tetraammine.

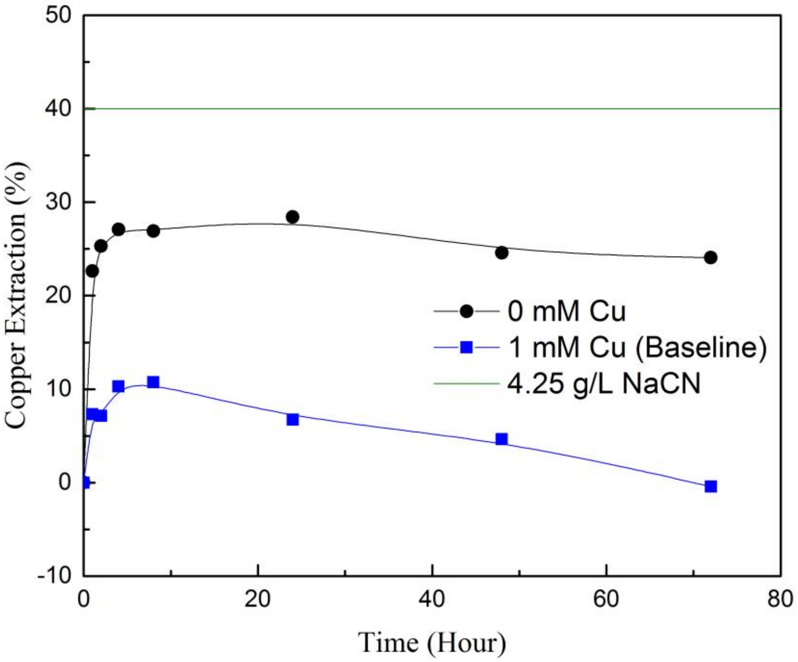


Figure 4.38 Copper extraction throughout tests with various copper concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 25 °C)

Copper extraction in Figure 4.38 for the two scenarios are significantly different, as no copper addition leaches out 25% of copper, whereas baseline in comparison only leaches 5%. Lack of copper in initial leaching solution enhances copper leaching, but suppresses silver leaching. This phenomenon agrees with the work established by Wejman-Gibas et al. (2015) that no initial copper addition enhances copper leaching.

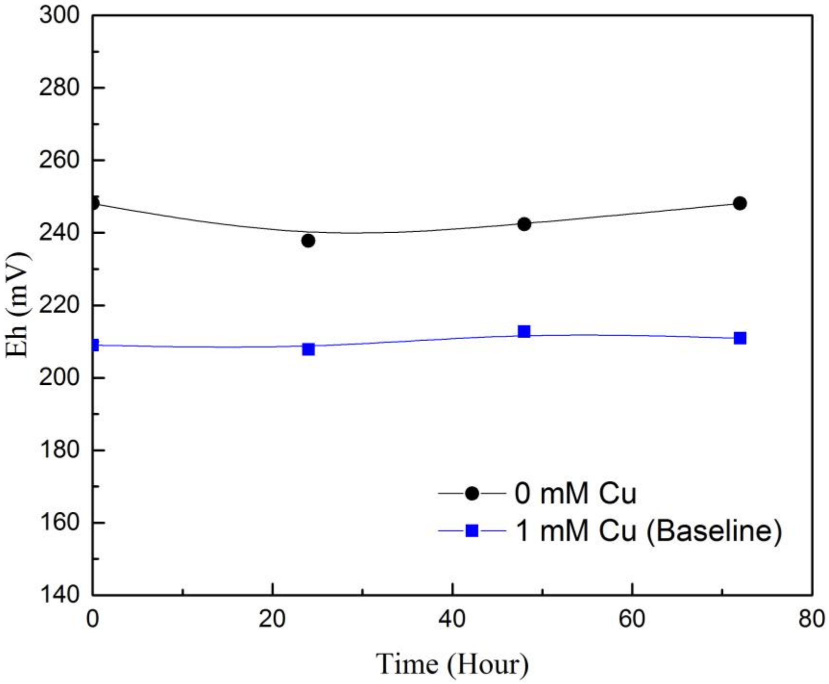


Figure 4.39 Eh throughout tests with various copper concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 25 °C)

The Eh of solution (Figure 4.39) with no initial copper addition is stable around 250 mV, which is significantly higher than the baseline Eh. The constant and high Eh suggest higher concentration in copper tetraammine comparing to baseline, which corresponds to higher copper extraction rate under such condition.

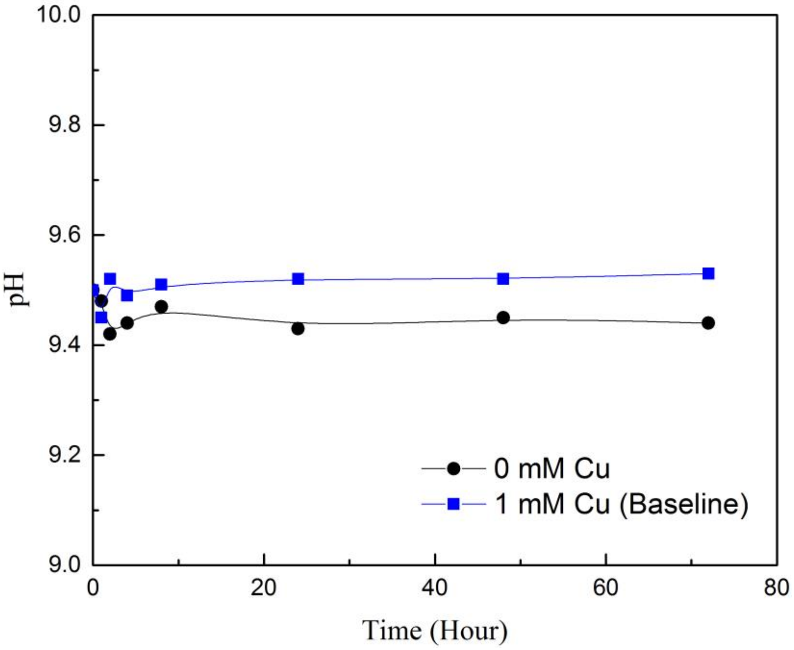


Figure 4.40 pH throughout tests with various copper concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 25 °C)

The pH of the two tests, in comparison, are not as large, as shown in Figure 4.40. The pH with no initial copper addition are slightly lower than 9.5, whereas that of baseline is slightly higher than 9.5. The constant pH difference after 8 hours are below 0.1.

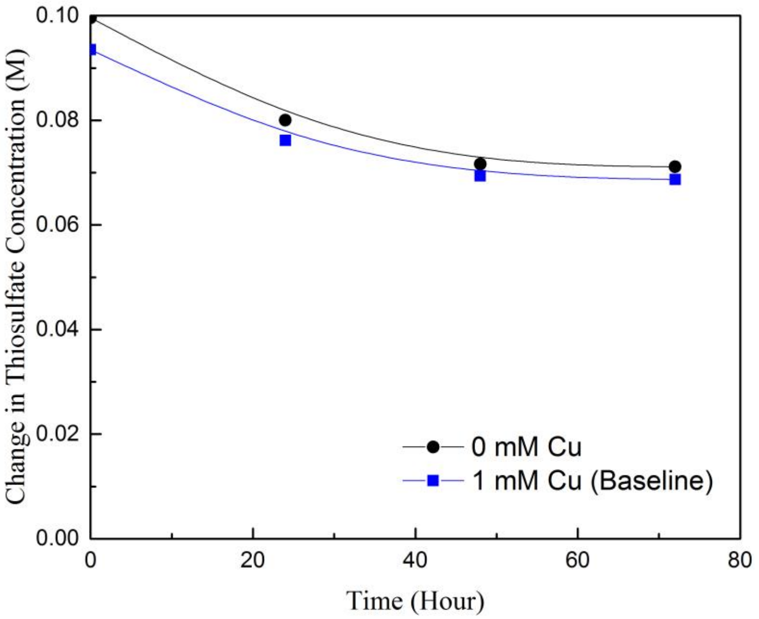


Figure 4.41 Thiosulfate concentration throughout tests with various copper concentrations on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 25 °C)

Thiosulfate concentration curves in Figure 4.41 follow the same trend. Higher residual thiosulfate concentration after 72 hours may be attributed to lower consumption of thiosulfate by silver leaching due to its lower extraction. The experiment with no initial copper addition has a reagent consumption of 16.9 kg/tonne ore.

4.4.7 Air Sparging

Air sparging is used in industrial application to help oxidizing the ore, thus enhances metal leaching. In thiosulfate leaching, increasing oxygen concentration in solution may help to oxidize the ore, but also risk increasing oxidation of thiosulfate, thus increasing reagent cost. Air sparging may drive out ammonia in the solution, thus decreasing the effectiveness of silver leaching. Therefore, the air source is conditioned with fresh 1 L ammonium sulfate solution with pH 9.5 solution before passing into solution. The air flow rate was controlled around 19.62 mL/min. Since reaction ratio of acanthite and oxygen is 2:1, and with such low silver content in the ore, the flow rate with ten times excess is still too low; such flow rate is selected to be sufficiently low but stable based on allowance of the equipment.

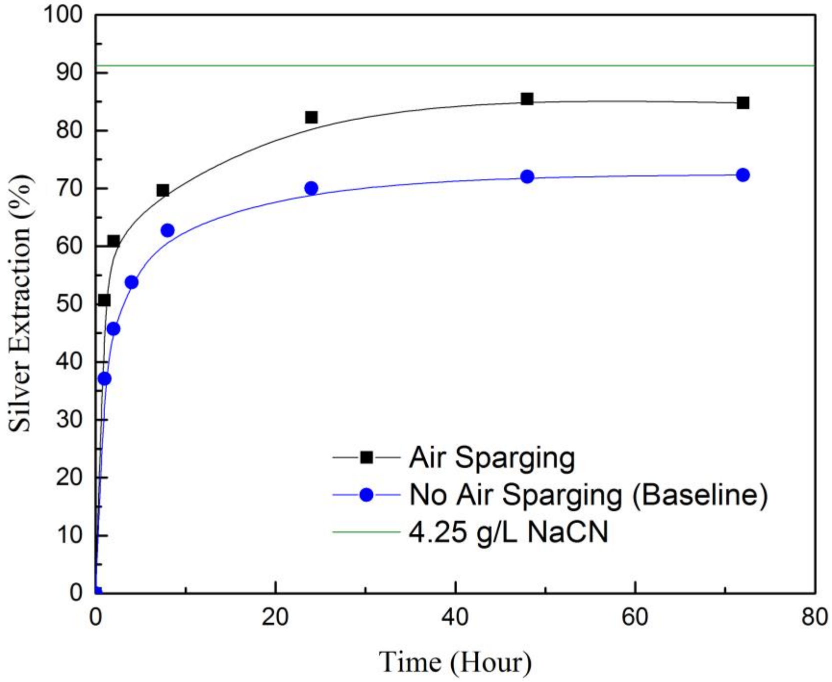


Figure 4.42 Silver extraction throughout tests with and without air-sparging on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.42 shows silver leaching curves with and without air sparging. Air sparging marginally increases silver leaching performance, by less than 5%. Theoretically, abundance of oxygen in solution helps to re-oxidize the reduced cuprous ion into cupric and form cupric tetrammine ion, and the increase amount of such catalyst results in higher silver extraction. Overdose of oxygen may reduce thiosulfate concentration, which leads to insufficient thiosulfate in solution to keep metals soluble.

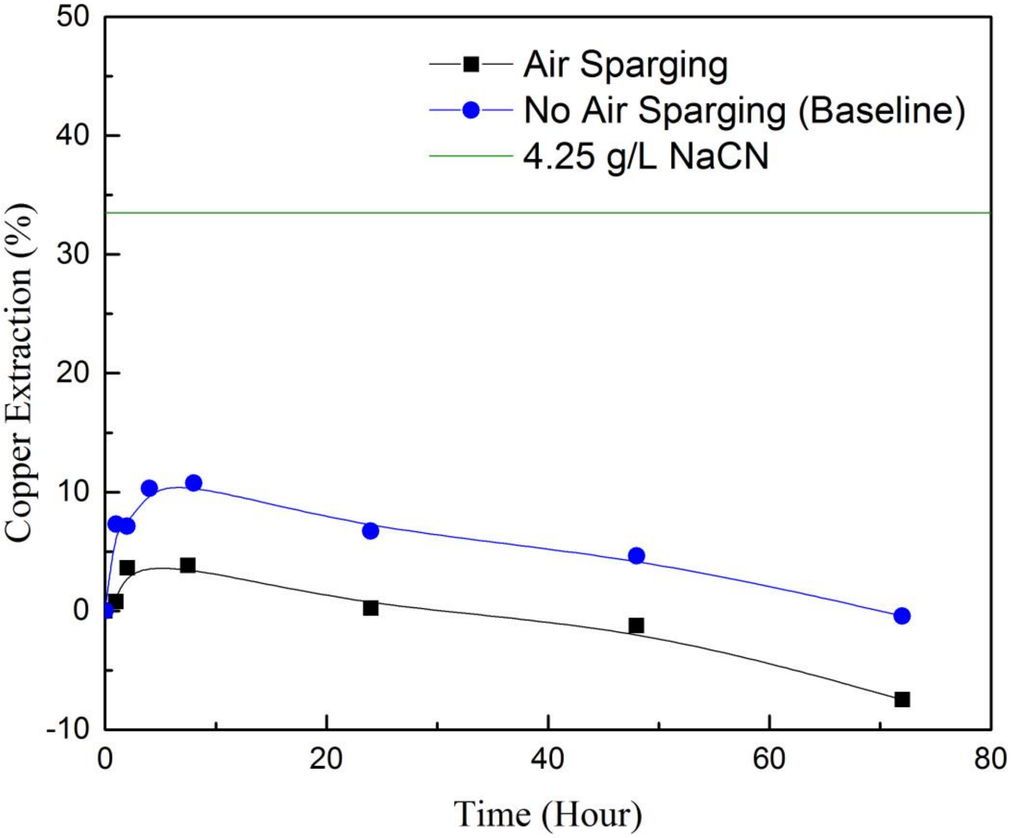


Figure 4.43 Copper extraction throughout tests with and without air-sparging on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.43 shows copper extraction under different condition with and without air sparging. The two results follows the same trend, while Air sparging has the effect of depressing copper extraction. This may attribute to increase of oxygen partial pressure in solution with air flow, and with limited solubility in solution, ammonia partial pressure decreases more compared to the case without air sparging. Similar phenomenon was also found by Bidari et al. (2015).

Figure 4.44 shows the change of Eh for the two different conditions. Higher oxygen concentration in leaching solution makes the leaching environment more oxidizing, which is reflected on the increasing Eh over time.

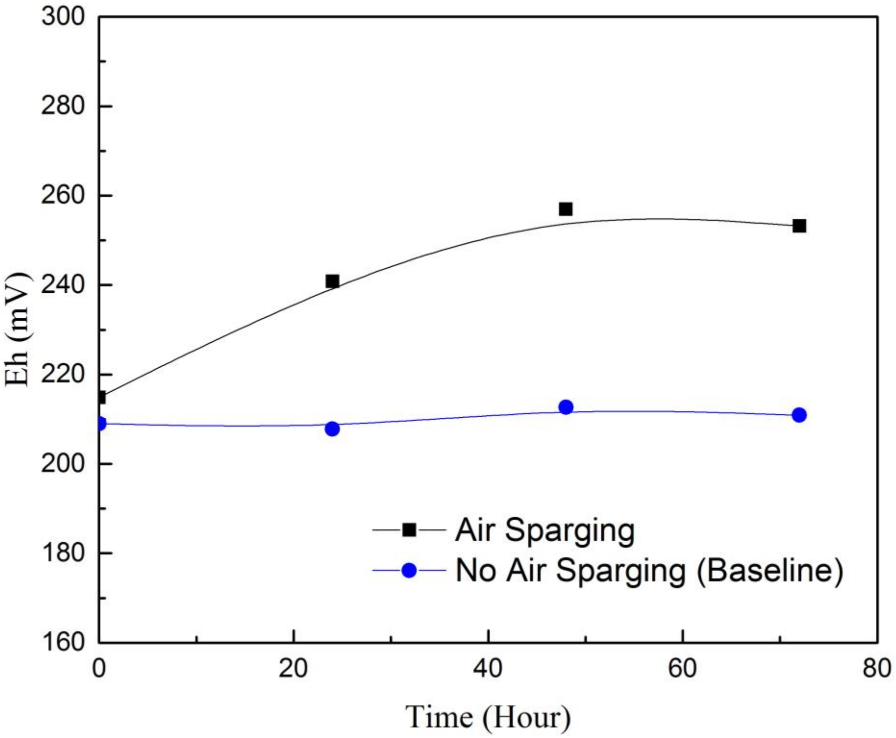


Figure 4.44 Eh throughout tests with and without air-sparging on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.45 shows pH change of the two tests, and no significant change of pH has been observed throughout the period of experiments. Even though no significant change of pH occurred throughout the course of reaction, there still can be ammonia loss with presence of air flow. The consistent pH only shows that ammonia loss does not increase to an extremely high extent, but such loss may still be significant to affect the already-low copper dissolution.

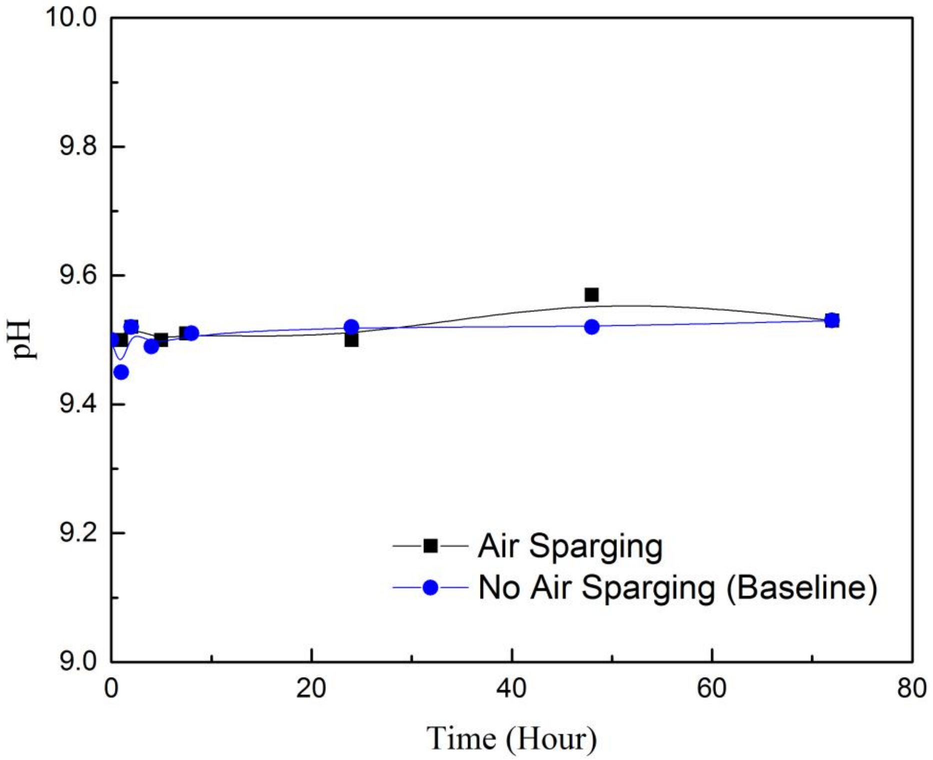


Figure 4.45 pH throughout tests with and without air-sparging on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.46 demonstrates the thiosulfate concentration change with time. Thiosulfate concentration decreases drastically with air-sparging, as high oxygen content in leaching solution accelerates thiosulfate oxidation, and with extended time thiosulfate will be depleted. The ammonium thiosulfate consumption with air sparging is calculated as 35.5 kg/tonne ore.

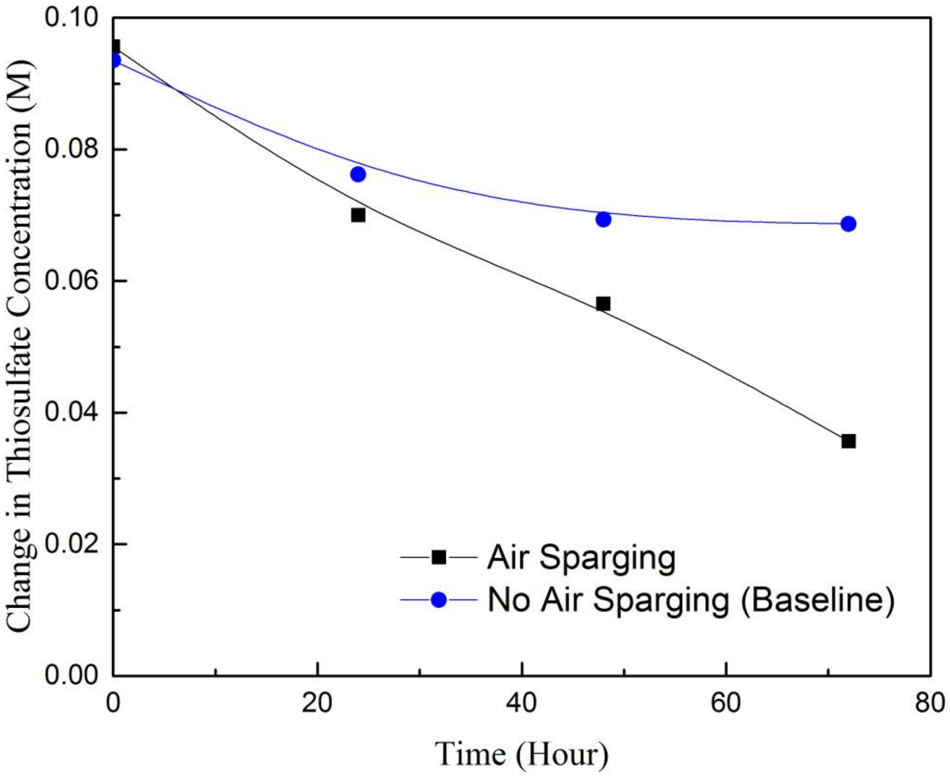


Figure 4.46 Thiosulfate concentration throughout tests with and without air-sparging on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

4.4.8 EDTA

EDTA as one of the additives to thiosulfate leaching system, has been found to enhance silver leaching by stabilizing copper in solution, event at low ammonia concentration. EDTA has been reported to decreases the consumption of thiosulfate in various studies. This section will investigate the effect of addition of EDTA into the leaching system.

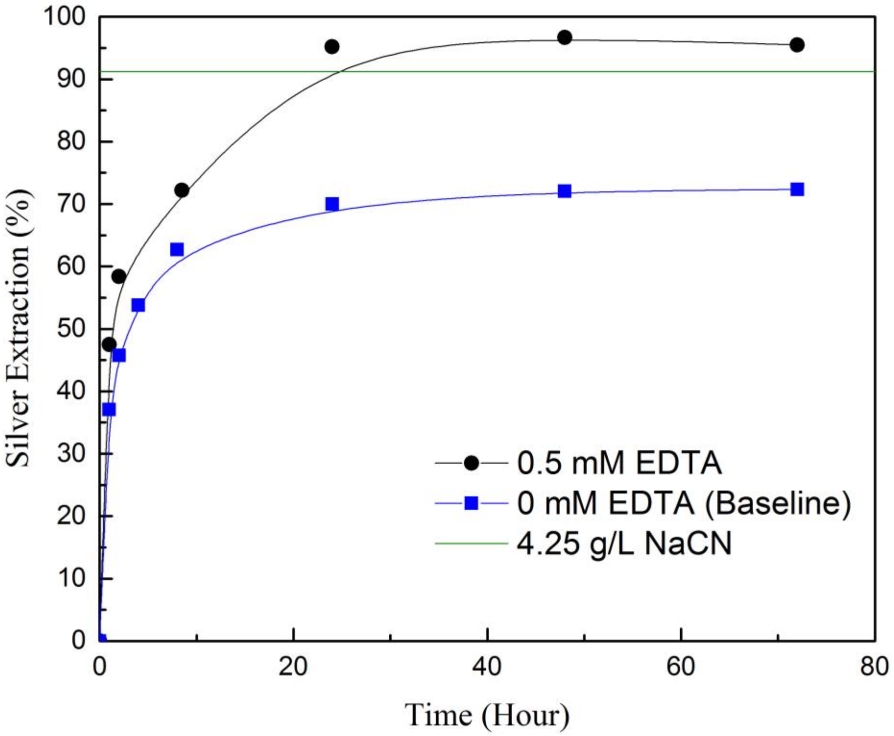


Figure 4.47 Silver extraction throughout tests with and without EDTA on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

In Figure 4.47, 0.5 mM of EDTA in solution increases silver leaching drastically comparing to baseline, and the extraction is even higher than that of cyanidation. Considering EDTA addition is minimal, it is extremely effective in enhancing silver leaching.

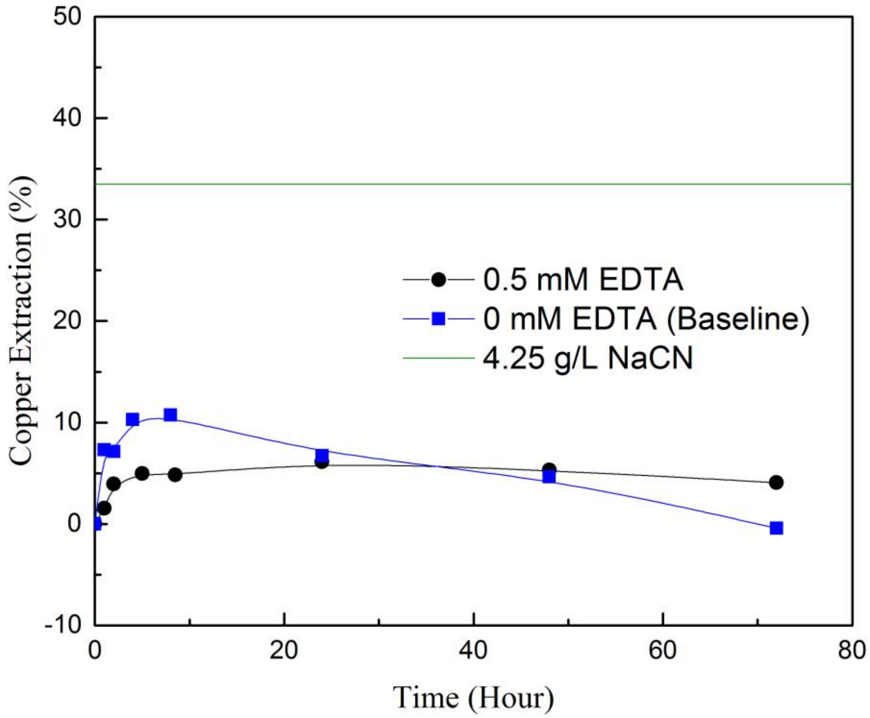


Figure 4.48 Copper extraction throughout tests with and without EDTA on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.48 shows copper extraction of the two tests, and it can be seen that with EDTA in solution, copper extraction is relatively stable comparing to that of baseline after 8 hours, which agrees with the conclusion drawn by Feng et al. (2010). The copper extraction is suppressed by addition of EDTA, which can be attributed to the chemical structure of EDTA that encapsulated copper ion thus decreases its activity.

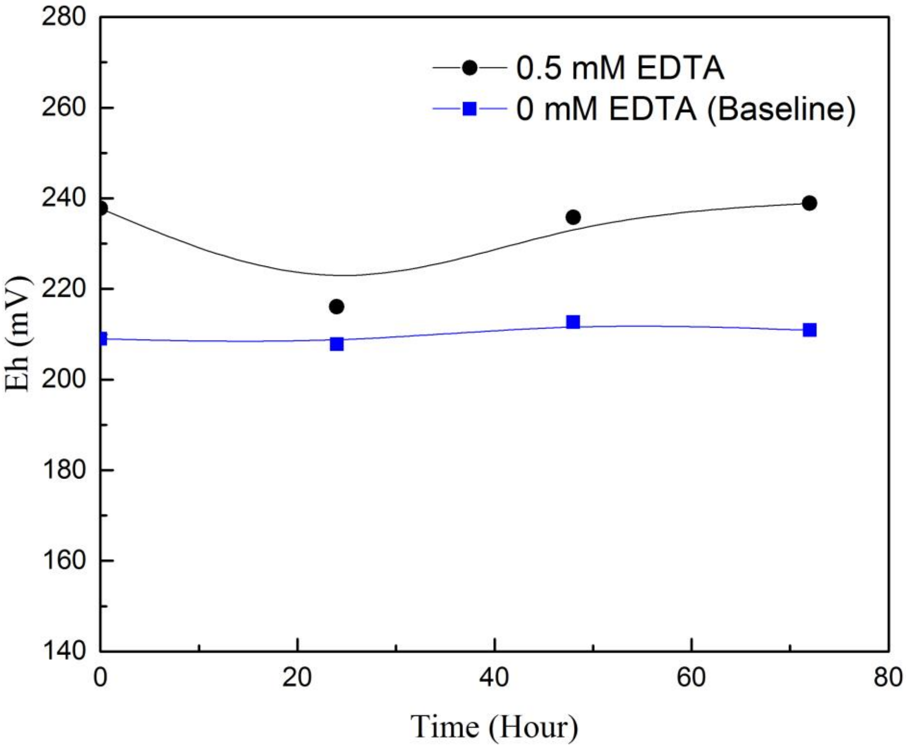


Figure 4.49 Eh throughout tests with and without EDTA on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.49 shows that addition of EDTA increases the leaching solution potential for about 30 mV, which can be attributed to formation of copper-EDTA complex. The Eh of leaching solution remains stable in general throughout the trial.

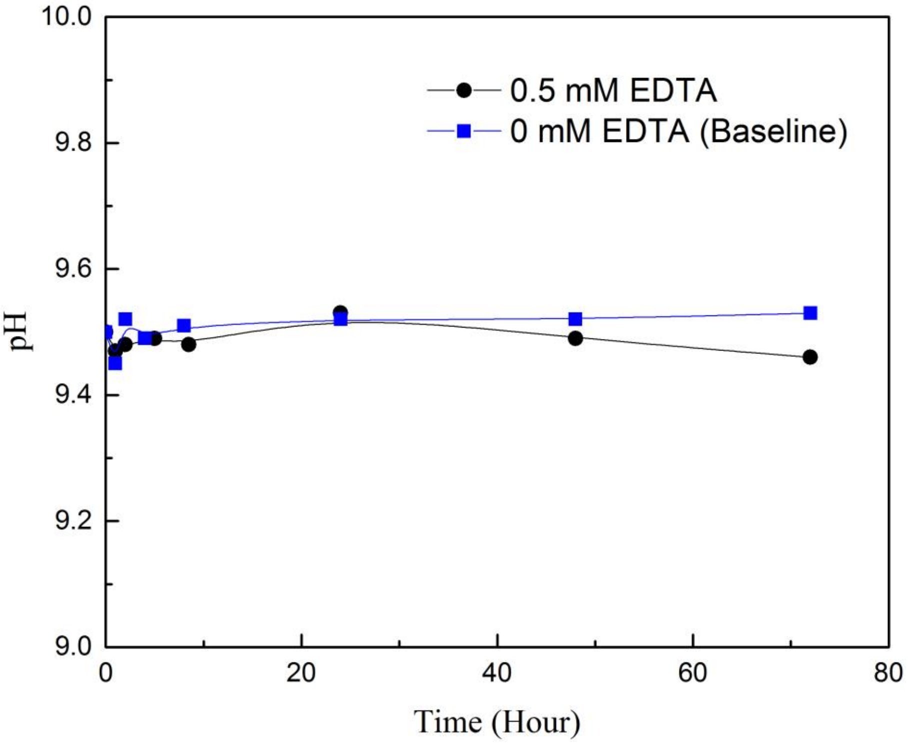


Figure 4.50 pH throughout tests with and without EDTA on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

From Figure 4.50, the pH of the two conditions do not change much during the experiment. A minor drop in pH is observed in test with EDTA after 24 hours.

Figure 4.51 shows the change in thiosulfate concentration with the two conditions discussed in this section. With addition of EDTA, the residual thiosulfate concentration after 72 hours is lower than that of baseline. The reagent consumption is 19.7 kg/tonne ore.

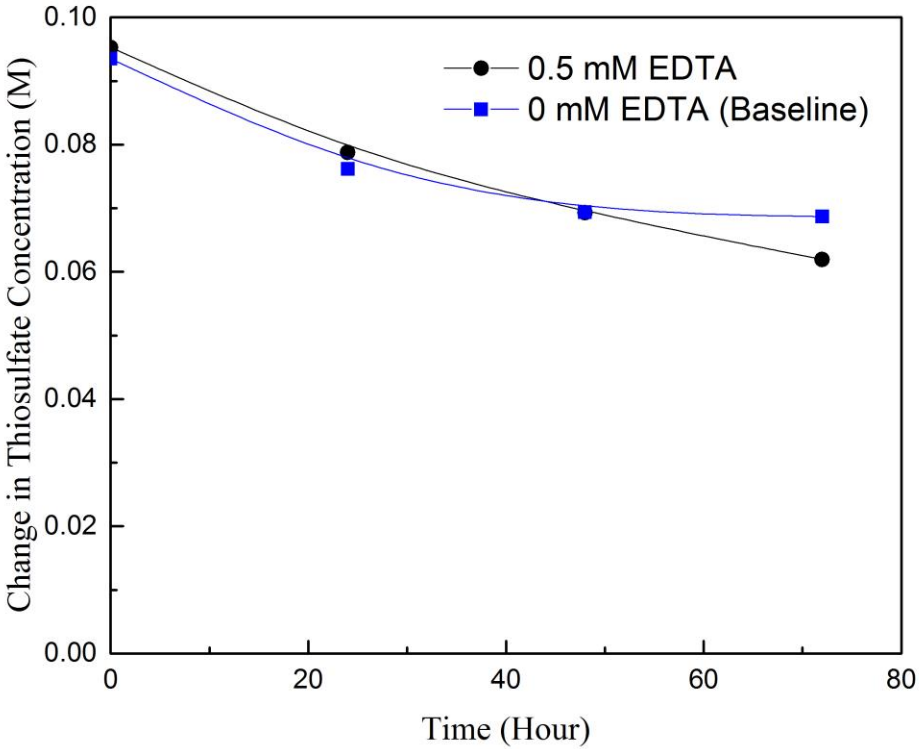


Figure 4.51 Thiosulfate concentration throughout tests with and without EDTA on LDLPMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

4.4.9 Different Ore Samples

The adjusted setup has also been applied on the other ore samples: NHMC and CZMC. The baseline condition used on LDLPMC is also used on these two deposits. According to the preliminary study results, these leaching tests with these two samples oxidized thiosulfate rather rapidly, therefore the leaching time of the two were reduced to 24 hours. The results for leaching on these samples will be discussed in this section.

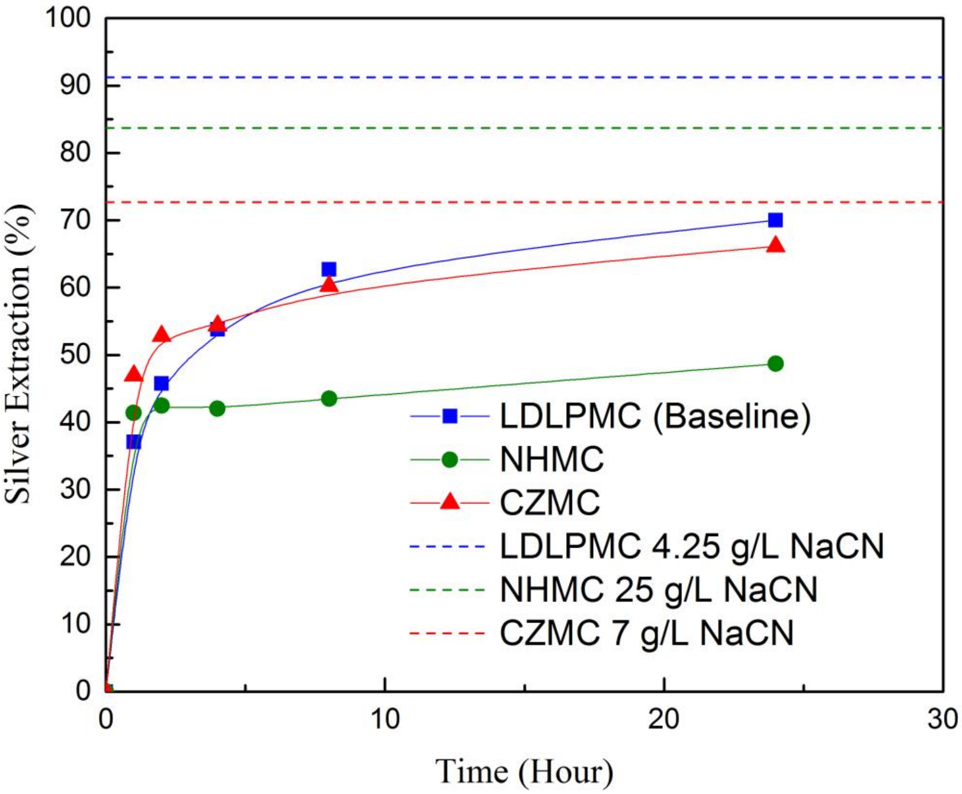


Figure 4.52 Silver extraction throughout tests on LDLPMC, NHMC and CZMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

In Figure 4.52, the baseline condition on these three deposits leaches 74%, 49% and 60% of silver on LDLPMC, NHMC and CZMC respectively for the first 24 hours. It can be seen that leaching on NHMC and CZMC are completed as their extraction at 8 hours is very close to that at 24 hours. NHMC and CZMC has a faster kinetics in leaching in the first 4 hours, as their leaching curves are steeper comparing to that of LDLPMC. CZMC has a silver concentration drop after 8 hours, indicating that the leaching system is not as stable.

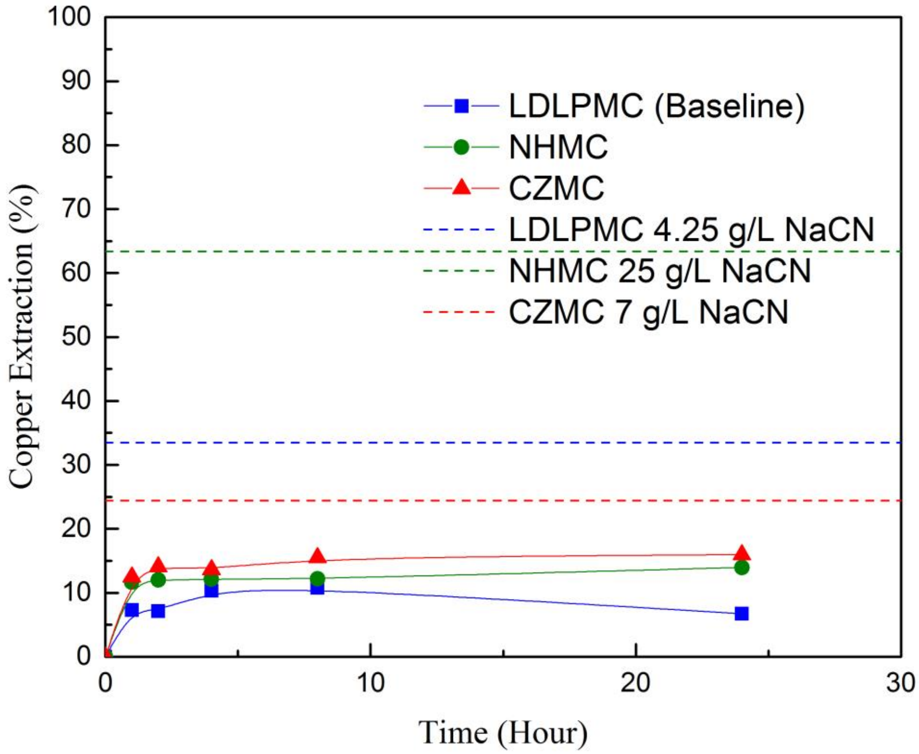


Figure 4.53 Copper extraction throughout tests on LDLPMC, NHMC and CZMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.53 shows that NHMC and CZMC only leaches 10% and 15% of their total copper content in the ore, which are drastically lower than that of their counterparts in cyanidation. Both NHMC and CZMC leach out more copper comparing to LDLPMC, which can potentially consume more thiosulfate during the leaching process.

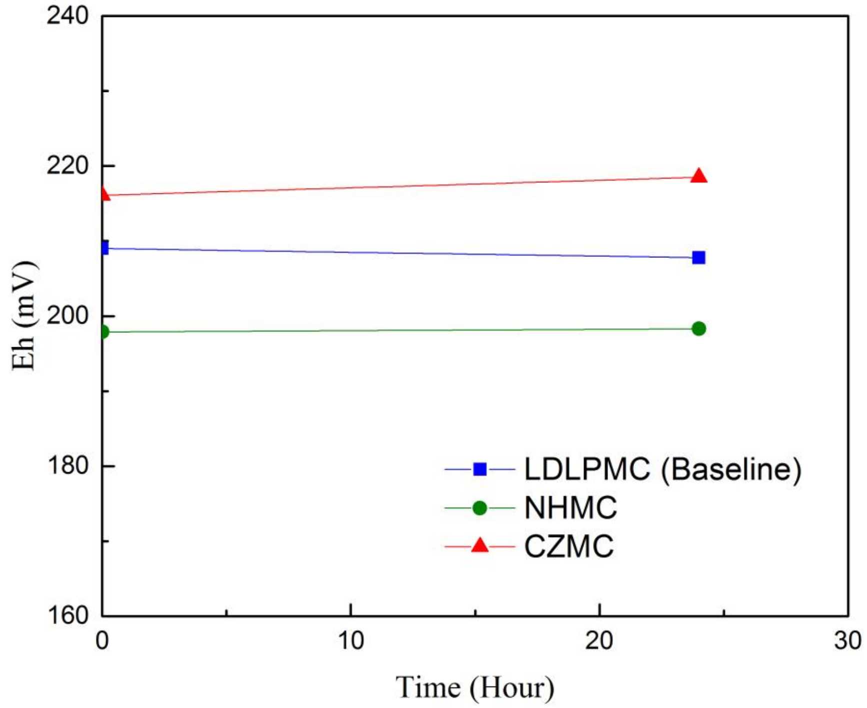


Figure 4.54 Eh throughout tests on LDLPMC, NHMC and CZMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.54 shows the Eh of the three ore in 24-hour leaching test. Eh remains almost constant throughout the process.

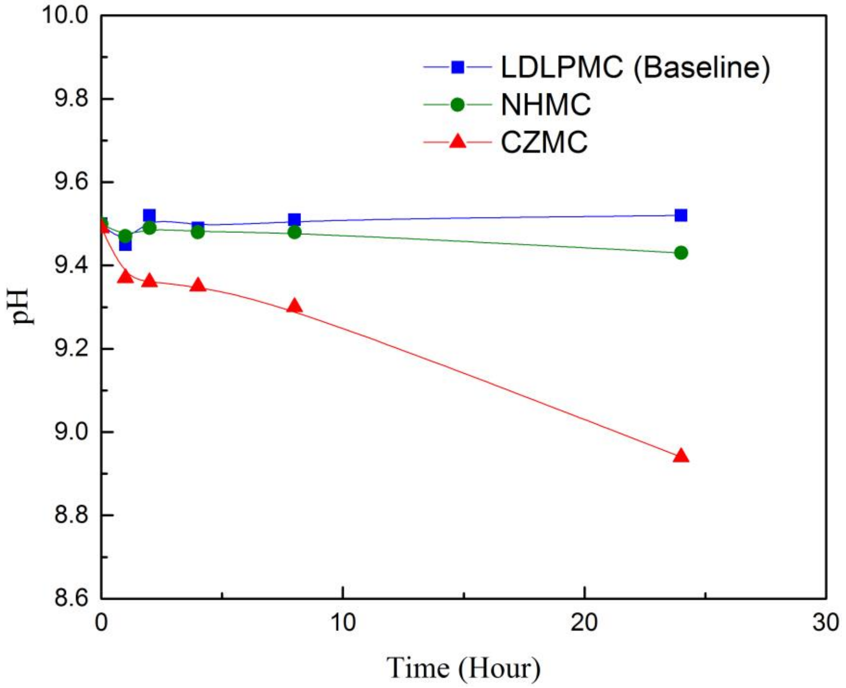


Figure 4.55 pH throughout tests on LDLPMC, NHMC and CZMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.55 shows change of pH of the three tests in the first 24 hours. Both NHMC and CZMC have a decrease of pH, but CZMC is drastically lower than the other two after 24 hours. It may be attributed to generation of acid, which destroys the ammonia/ammonium buffer in the solution. NHMC may generate a small portion of acid during the process of leaching as well. Such phenomenon agrees with the fast depletion of thiosulfate in preliminary study on these two samples. Such pH drop of CZMC aligns with the drop of silver extraction.

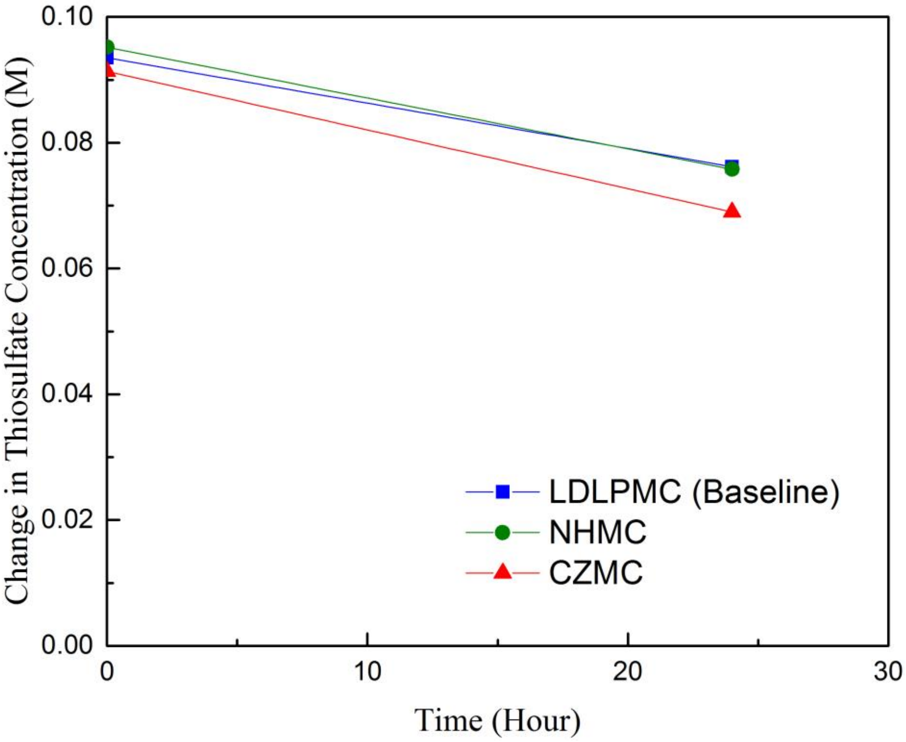


Figure 4.56 Thiosulfate concentration throughout tests on LDLPMC, NHMC and CZMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.56 depicts drop of thiosulfate concentration after 24 hours. NHMC and CZMC yields lower residual thiosulfate concentration, and CZMC is significantly lower than the other two. Such results align with the trend of pH on these three samples. The thiosulfate consumption at 24 hours for NHMC and CZMC are 11.5 kg/tonne ore and 13.3 kg/tonne ore.

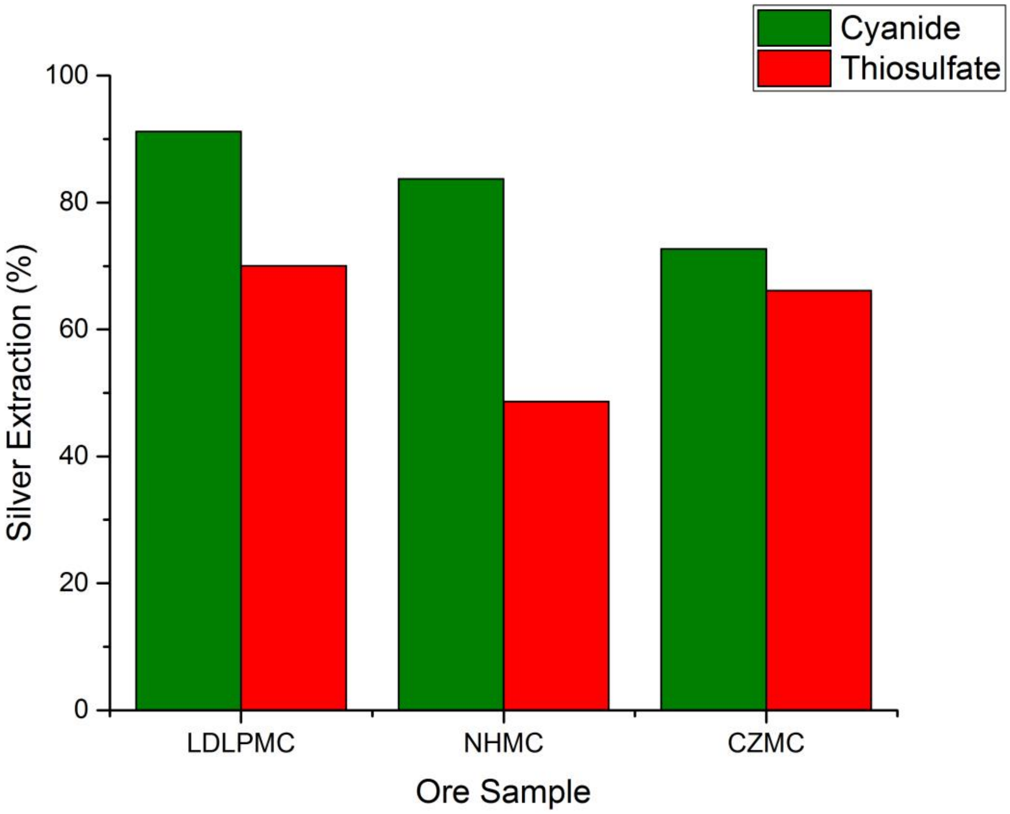


Figure 4.57 Bar chart of 24-hour silver extraction through different reagents on LDLPMC, NHMC and CZMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.57 demonstrates the silver extraction by thiosulfate and cyanide in baseline condition. It can be observed that in the case of CZMC most of cyanide soluble silver is leached out by thiosulfate, and the least in NHMC. LDLPMC is already identified to have potential for leaching; from such aspect, CZMC may also have value for leaching, if not considering the drop of silver extraction after 8 hours.

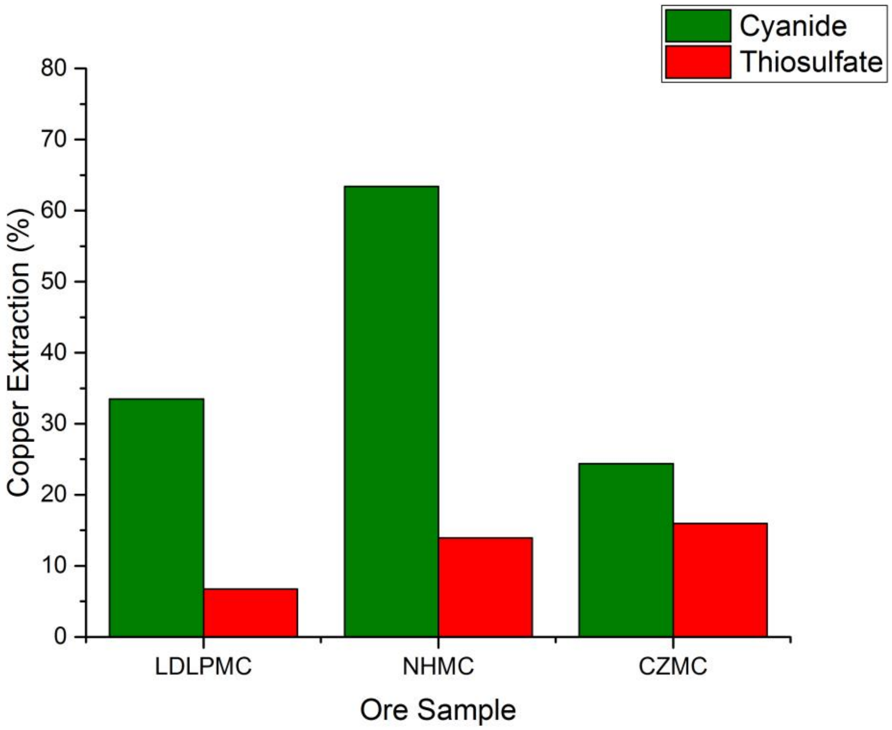


Figure 4.58 Bar chart of 24-hour copper extraction through different reagents on LDLPMC, NHMC and CZMC (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

Figure 4.58 shows the copper extraction by thiosulfate and cyanide in baseline condition. Thiosulfate is the most selective for leaching silver on LDLPMC, whereas CZMC is the least. With extended period of leaching, CZMC may suffer high reagent consumption and high copper concentration in leachate. Periodic removal of copper in CZMC pregnant leach solution becomes more critical if it were to be leached.

4.4.10 XRD Phase Analysis

XRD analysis was performed on the head and tail residue of LDLPMC, NHMC and CZMC. It was found that with treatment of thiosulfate or cyanide under different conditions, no significant phase changes have been detected. No silver and copper phases were detected as well, which is due to their low concentration in the ore compared to the detection limit (5%). The head XRD patterns are shown in this section. Additional XRD patterns will be listed in appendix.

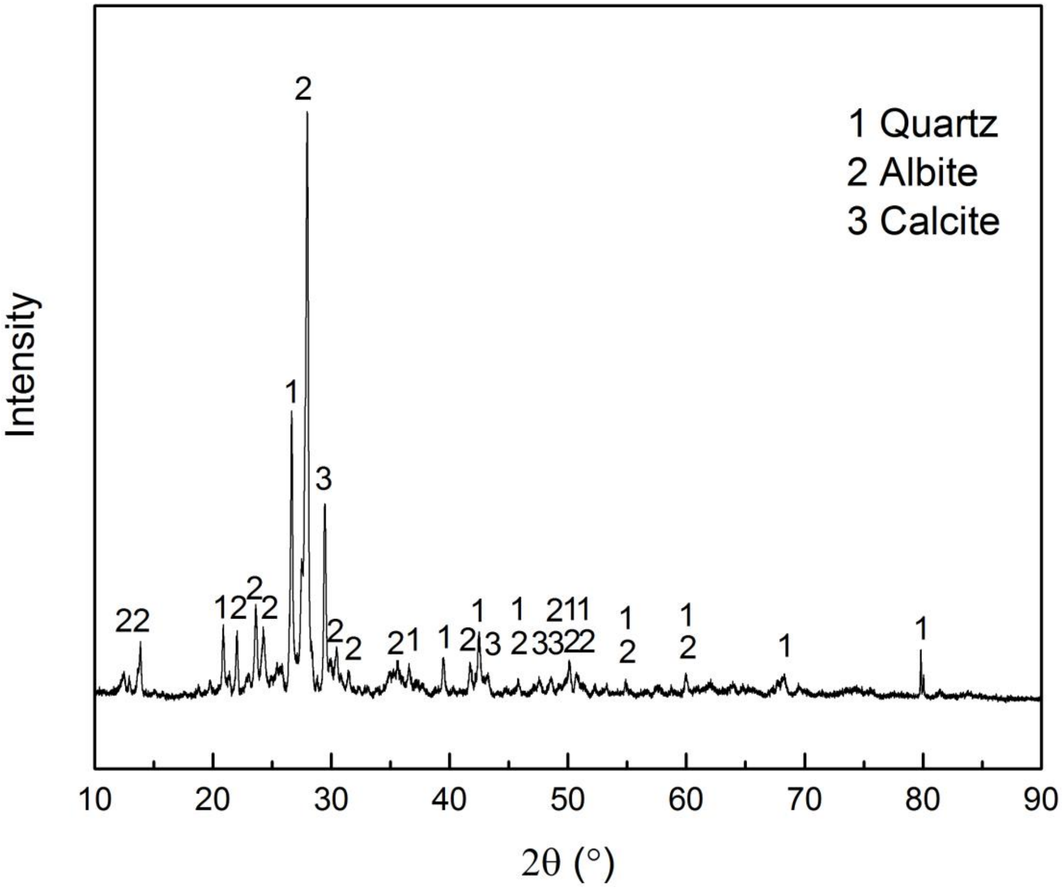


Figure 4.59 Sample XRD pattern for LDLPMC head ore

As shown in Figure 4.59, the three major phases in LDLPMC are quartz, albite and calcite. These three phases remain before and after leaching. The silver and copper minerals reported by Pan American Silver cannot be detected due to their low content. These phases themselves are not reactive with cyanide or thiosulfate, thus no major phase changes were detected.

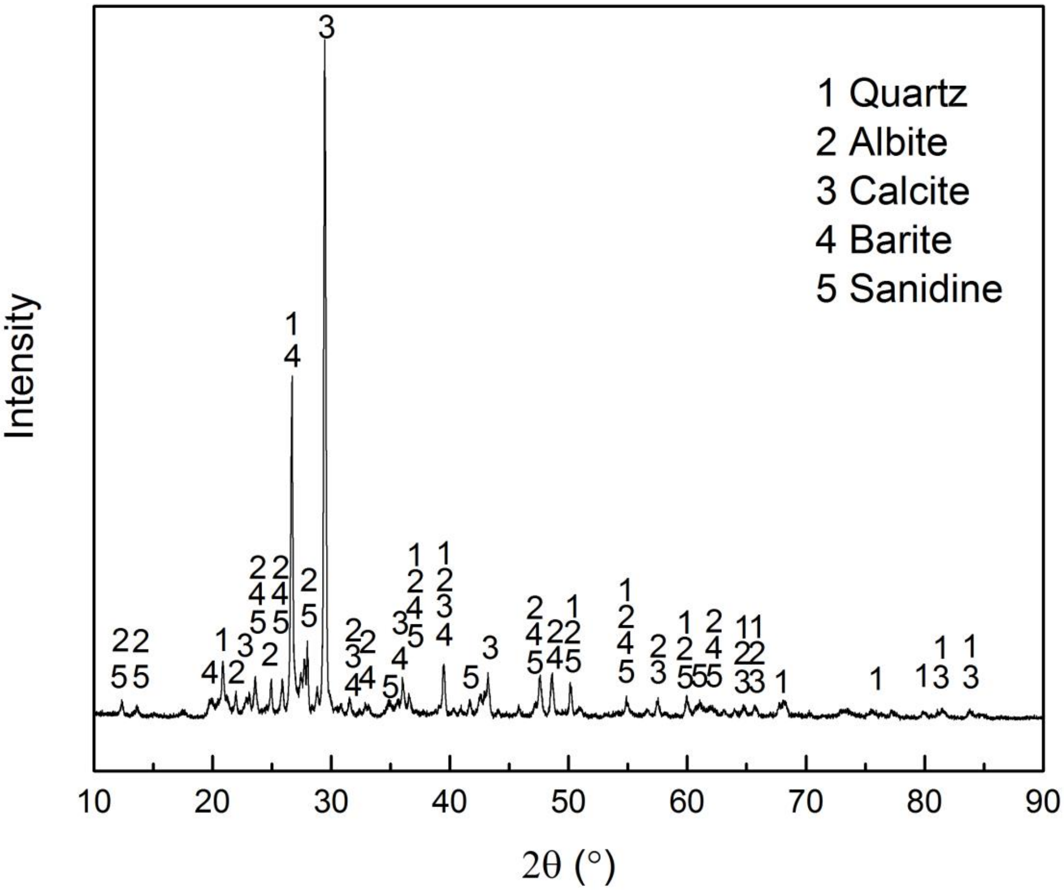


Figure 4.60 Sample XRD pattern for NHMC head ore

Figure 4.60 describes the major phases for NHMC head sample. The major phases present in NHMC are quartz, albite, calcite, barite and sanidine. These phases themselves do not react with thiosulfate and cyanide, and remain the same after leaching. Like LDLPMC, no silver and copper phases are detected due to their low concentrations.

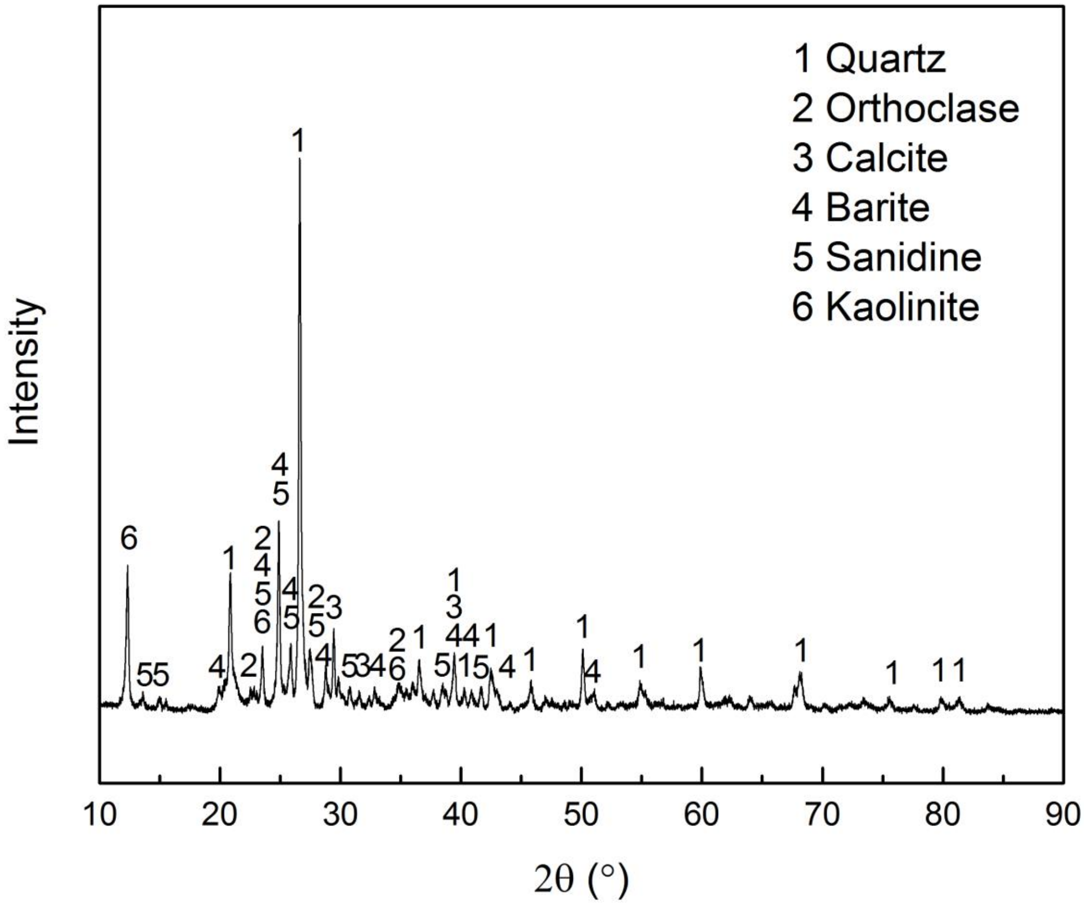


Figure 4.61 Sample XRD pattern for CZMC head ore

From Figure 4.61, it can be seen that CZMC has similar phase composition with NHMC, which agrees with the results in Section 4.4.9. CZMC has major phases of quartz, orthoclase, calcite, barite, sanidine and kaolinite. As in the other two samples, none of these phases themselves are known to react with cyanide and thiosulfate, and silver and copper phases are too dilute to be detected.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

Leaching of natural acanthite using the cupric ammoniacal thiosulfate system was studied, with variation of conditions and on different ore samples. LDLPMC is the sample with most leaching potential, thus it has been used in thiosulfate leaching tests with different conditions.

Variation of initial thiosulfate concentration has a relatively significant effect on leaching. As the major leaching agent in reaction, its concentration affects the speciation in system. Higher concentration not only suppresses formation of catalytic cupric tetraammine, but also increases reagent cost in industrial practice. 0.2 M of thiosulfate yields the highest silver extraction, with moderately high ammonium thiosulfate consumption (17.9 kg/tonne ore).

Initial total ammonia concentration also has a significant effect on silver leaching. Ammonia helps to stabilize the copper in the system, as well as catalyzing the leaching reaction. Sufficient ammonia is necessary to dissolve copper in solution for catalyzing the system. 1.0 M of total ammonia yields the highest silver extraction, with moderate ammonium thiosulfate consumption (20.0 kg/tonne ore).

Starting pH of the reaction affects silver leaching greatly as well. The pH not only controls speciation of system, but also determines the amount of pH conditioner needed for industrial application. An alkaline pH value is a must; however, there is no need for excessively high pH. pH of 9.0 gives the best silver extraction, with relatively high ammonium thiosulfate consumption (14.4 kg/tonne ore).

Temperature moderately affects leaching performance. Higher temperature increases reaction kinetics, but also consumes more energy and drives off ammonia from system. 35 ºC is the optimal temperature for silver leaching, with moderate reagent consumption (14.4 kg/tonne ore).

Copper is not the major focus of leaching, but it plays a critical role in thiosulfate leaching. Initial copper addition affects leaching greatly as well. A difference in 1 mM of copper yields significant different extraction rate. Silver extraction is highest with 1 mM of initial addition of copper, even though it means higher reagent cost in industrial practice.

Air sparging only affects leaching to relatively small extent. Air sparging provides the air to oxidize sulfide mineral, but also risks consuming more thiosulfate. Air sparging does result in higher silver extraction, but results in high reagent consumption (35.5 kg/tonne ore). No air sparging is more ideal to leach silver in such case.

EDTA as an additive moderately affects silver leaching. With EDTA, silver extraction increases around 5%, with a moderate ammonium thiosulfate consumption of 19.7 kg/tonne ore. 0.5 mM EDTA seems beneficial to such leaching system.

Copper extraction varies greater comparing to silver extraction, even when the leaching system is stabilized. A certain extent of copper leaching has been detected in most of the conditions, which is different from the past studies, where copper was depleted over time. Using high copper content acanthite is not beneficial for cyanidation, but in case of thiosulfate leaching where it needs copper to catalyze the system, it becomes beneficial. Low copper extraction is being detected (5-10%).

In NHMC and CZMC, copper extractions are significantly higher than that in LDLPMC. In NHMC, silver is not as accessible as in the case of cyanidation; in CZMC most of the cyanide-leachable silver can be leached. Both these samples showed complete silver leaching in 24 hours. In the same time interval, thiosulfate consumption of the two samples was higher than that of LDLPMC, which are 20.59 and 23.19 kg/tonne ore.

5.2 Recommendations and Future Work

The chemical aspect of leaching the natural acanthite ore has been studied using a batch reactor. In order to investigate the economic feasibility of leaching such ore in a full industrial scale, a scale-up design of reactor is necessary (i.e., cascade series of leaching tanks). This study has proven the feasibility of leaching such ore from aspect of chemistry, but more work is necessary from the engineering aspect. For example, if elevated temperature is necessary, an improved setup that prevents ammonia loss should be introduced. In the new setup, leaching condition without ammonia can be tested as well since it was not tested in the scope of this thesis.

In terms of analytical technique, a more simplified method (automate) to isolate thiosulfate from other interfering ions can be introduced. Loading and stripping of thiosulfate ions is effective and accurate; a slurry with natural ore is more difficult to predict than slurry with synthetic silver sulfide, and if a new method is to be introduced, it should be compared to the results from loading and stripping. Analysis of ammonia should be done, and genuinely sealed the leaching system so minimal ammonia losses can be achieved.

Finally, it is worth investigating downstream of leaching – purification of pregnant leach solution and electrowinning/cementation. The leachate can be collected to test for the process of purification by means of ion exchange or solvent extraction, and either electrowinning or cementation can be carried out to test for the recovery of silver, and possibly copper.

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Appendices

Appendix A Analytical Methods

The supplementary information regarding analytical methods are documented here. The chemical analytical methods used in this study are AAS and iodometric potentiometric titration. All water used was deionized water and chemicals were ACS grade. Bureau Veritas Commodities Canada Ltd. in Richmond, BC performed ICP-MS for elemental assay in head sample and leaching solid residues.

A.1 Atomic Absorption Spectrophotometry (AAS)

As described in Chapter 3, two different methods of AAS sample preparation were involved in the study. In the earlier part of the study, DI was used to dilute the intermediate sample solutions, whereas synthetic baseline leaching solution was used to dilute the intermediate sample solutions later. Solution properties can have a significant effect on AAS absorbance values, since the physical properties of the standards or samples will change the amount of solution that is atomized by nebulizer, as well as the dispersion droplet size. The more similar the properties of standards and samples, the more accurate the measurement.

Preparation of Standards

Original AAS standards obtained from Sigma-Aldrich has a concentration of 1000 ppm, and it is not suitable for direct measurement due to nitric acid in the solution. Therefore, volumetric amounts of standard solutions were neutralized by drops of phenolphthalein and sodium hydroxide first, then addition of ammonium sulfate and sodium thiosulfate to approximate the concentrations of baseline solution but without copper addition.

Preparation of Samples

The extracted aliquots of solution from the batch reactor were first filtered using VWR Syringe Filters with Polypropylene Housing to avoid suspension in solution to block the nebulizer of AAS machine. In earlier part of the thesis, the clear solutions were then diluted using DI so that they fall into the range of measurement of AAS standards (0 to 5 ppm). In later part of the study, to provide a better match for sample solutions to standards in terms of their physical properties, synthetic solutions with baseline condition but no copper addition were prepared to dilute the sample. Random trial results were selected to adopt two different methods on their intermediate samples, to compare the difference. The trials selected were 0 mM Cu in initial leaching solution and 1.0 M of ammonia in initial leaching solution, respectively.

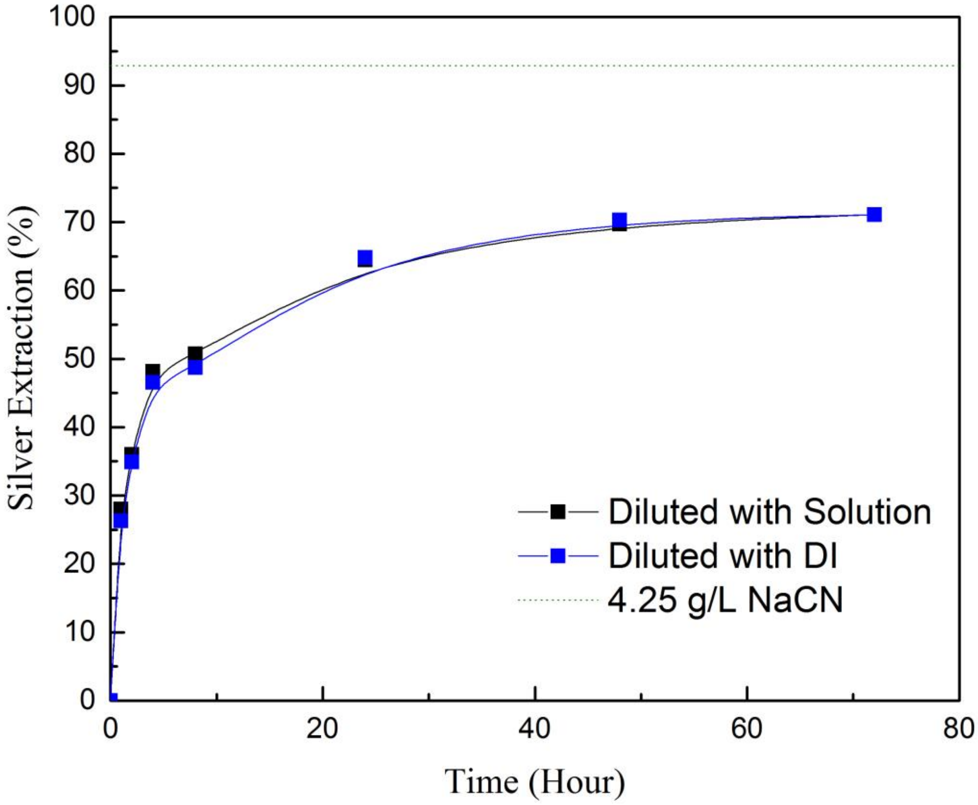

Figure A.1 Silver extraction with various sample preparation methods on LDLPMC on test of no initial copper addition (0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 0 mM copper, 25 °C)

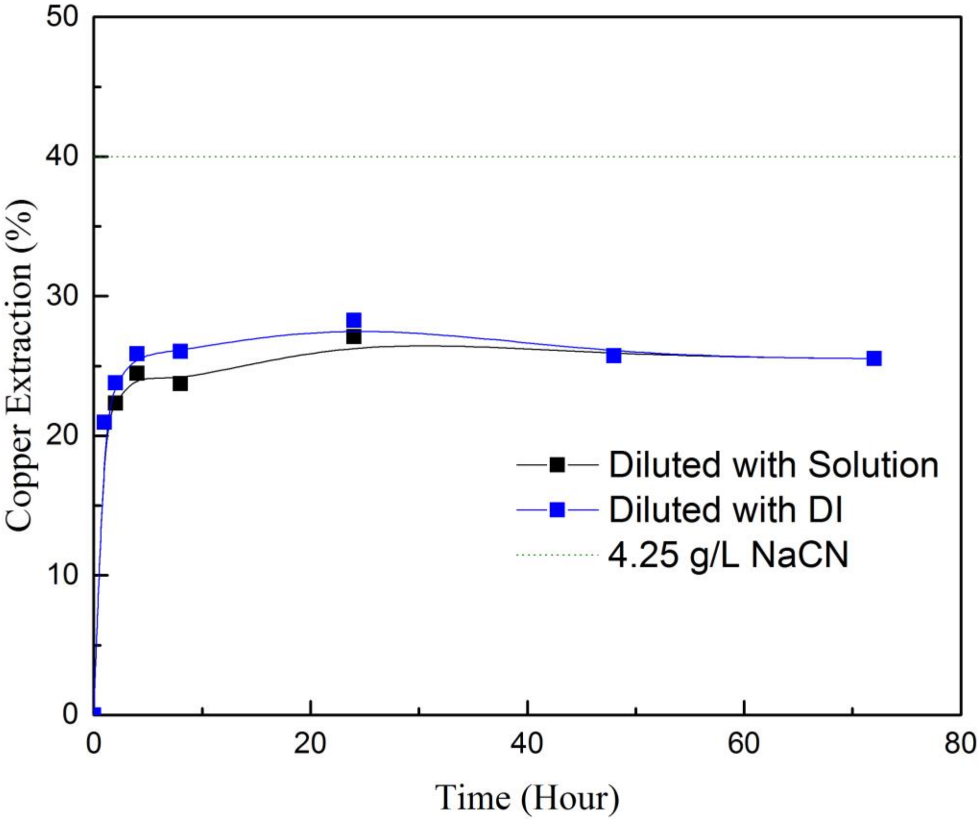

Figure A.2 Copper extraction with various sample preparation methods on LDLPMC on test of no initial copper addition (0.1 M of thiosulfate, 0.7 M total ammonia, pH 9.5, 0 mM copper, 25 °C)

From Figure A.1 and Figure A.2, it can be seen that silver extractions using two different methods barely have any differences. In copper extractions, the results differ a bit greater, but the final extractions after 24 hours are still very similar.

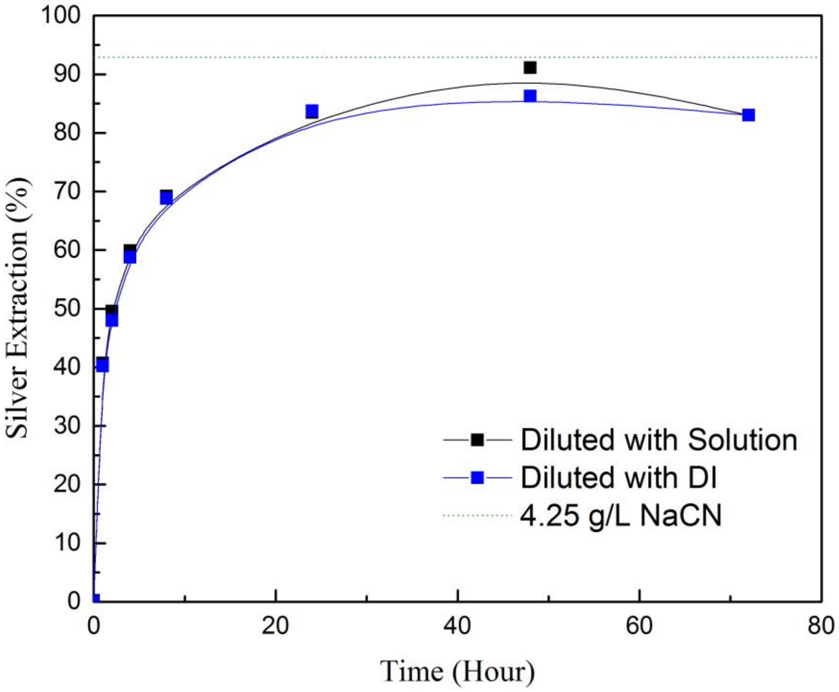

Figure A.3 Silver extraction with various sample preparation methods on LDLPMC on test of 1.0 M of ammonia (0.1 M of thiosulfate, 1.0 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

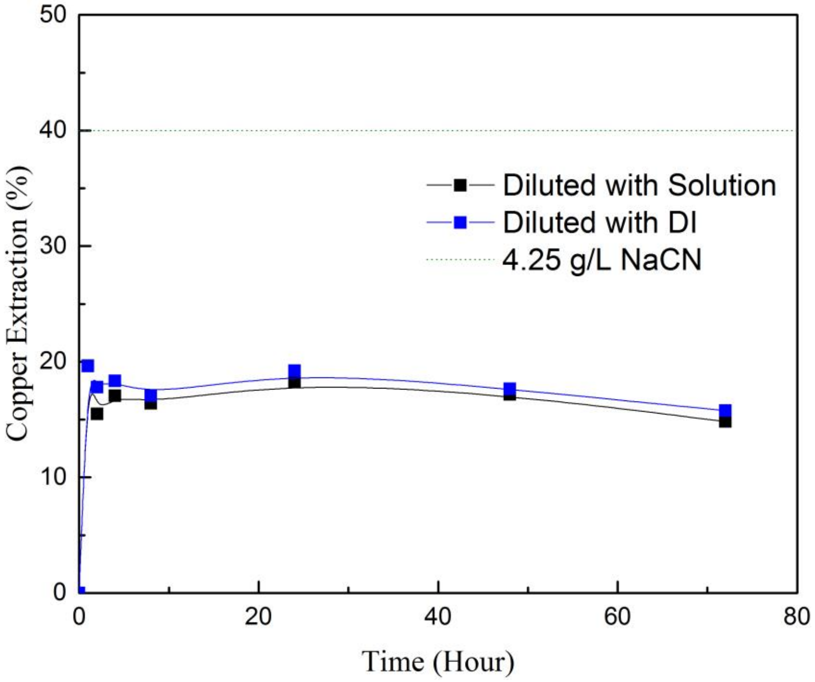

Figure A.4 Silver extraction with various sample preparation methods on LDLPMC on test of 1.0 M of ammonia (0.1 M of thiosulfate, 1.0 M total ammonia, pH 9.5, 1 mM copper, 25 °C)

In Figure A.3 and Figure A.4, similar trends were observed as in the case of trial 0 mM copper. Silver extraction does not seem to vary differently with the two methods; copper extraction with the new method appear to have slightly higher extraction. At the points where silver extractions are different, the new method always yields higher extraction. This is because of excessive thiosulfate in sample solution dissolves all copper and silver. In the samples diluted by DI, silver and copper are still soluble, but with the solution exposed to air with high oxygen content, there are possibility that traceable amount of silver and copper precipitates out; using thiosulfate solution for dilution can totally avoid such issue.

A.2 Reagent Specifications

The sources and grades of primary reagent used in this study are specified in the following table.

Chemical Name	Grade/Purity	Source
Amberlite IRA 400-Cl	-	Sigma-Aldrich
Ammonium sulfate	ACS	Fisher Scientific
Ammonium thiosulfate	ACS	Sigma-Aldrich
Calcium hydroxide	ACS	BDH Chemicals
Cupric sulfate pentahydrate	ACS	Sigma-Aldrich
Mercury iodide	99.0+% ACS	Fisher Scientific
Potassium iodate	99.5+% ACS	BDH Chemicals
Potassium iodide	ACS	Fisher Scientific
Sodium thiosulfate pentahydrate	ACS	Fisher Scientific
Sodium hydroxide	ACS	Fisher Scientific
Sodium cyanide	ACS	Fisher Scientific
Sulfuric acid	ACS	Fisher Scientific

Appendix B Sample Calculations

This Appendix shows the main calculations used in this thesis.

B.1 Thermodynamic Calculations

Thermodynamic data used in this study was adopted from Aylmore et al. (2001), Martell et al. (1974), HSC, MEDUSA, Speight (2005) and Deutsch (2012). The sample calculation shown below is the chemical reaction selected from 2.2.4 Leaching of Silver with Thiosulfate.

Table B.1 Thermodynamic data used

Formula	ΔG° (kJ/mol)	Formula	ΔG° (kJ/mol)	Formula	ΔG° (kJ/mol)
Ag	0	Cu	0	S	0
Ag^+	77.2	Cu^+	50.208	S^{2-}	91.9
AgO	10.9	Cu^{2+}	64.978	$S_2O_3^{2-}$	-532.2
Ag_2O	-10.8	CuO	-127.194	SO_3^{2-}	-486.5
Ag_2O_3	87.0	Cu_2O	-146.356		
AgOH	-92.0	$Cu(OH)_2$	-356.895		
Ag_2S	-40.5	CuS	-48.953		
$Ag(S_2O_3)^-$	-506.3	Cu_2S	-86.190		
$Ag(S_2O_3)_2^{3-}$	-1058.6	$Cu(S_2O_3)^-$	-540.991		
$Ag(S_2O_3)_3^{5-}$	-1598.3	$Cu(S_2O_3)_2^{3-}$	-1084.07		
$Ag(NH_3)^+$	31.8	$Cu(S_2O_3)_3^{5-}$	-1624.65		
$Ag(NH_3)_2^+$	-17.5	$Cu(NH_3)^+$	-10.293		
NH_3 (aq)	-26.7	$Cu(NH_3)^{2+}$	14.477		
NH_4^+ (aq)	-79.5	$Cu(NH_3)_2^{2+}$	-32.259		
H_2O	-237.2	$Cu(NH_3)_3^{2+}$	-73.212		
O_2	0	$Cu(NH_3)_4^{2+}$	-112.968		
OH^-	-157.28				

Reaction:

$$4Ag + 12S_2O_3^{2-} + 2H_2O + O_2 \rightleftharpoons 4Ag(S_2O_3)_3^{5-} + 4OH^-$$

Calculation:

$$\Delta G^{\circ}_{reaction} = 4\Delta G^{\circ}_{Ag(S_2O_3)_3^{5-}} + 4\Delta G^{\circ}_{OH^-} - 4\Delta G^{\circ}_{Ag} - 12\Delta G^{\circ}_{S_2O_3{}^{2-}} - 2\Delta G^{\circ}_{H_2O} - \Delta G^{\circ}_{O_2}$$

$$= 4\times(-1598.3) + 4\times(-157.28) - 4\times 0 - 12\times(-532.2) - 2\times(-237.2) - 0$$

$$= -161.52\ kJ/mol$$

B.2 Calculations of Extraction

In order to calculate silver and copper extraction, the calculated head of the two elements are necessary. Both copper and silver follow the same calculation. The calculation of total silver dissolved is a function of silver dissolved at time *i* (where current sample is *j*) when the sample was taken, the initial solution volume V_0, the concentration of element C_i at time *i*, the volume of sample V_i taken at time *i*:

$$Ag_{dis}(j) = \sum_{i=1}^{j} C_i V_i + C_j \left(V_0 - \sum_{i=1}^{j-1} V_i \right)$$

where *i*=1, 2, 3, …, *n*.

For the last sample *n*, which is also the time leaching is due, the total silver dissolved in solution, $Ag_{dis}(n)$, can be calculated. The calculated head of silver can be represented as:

$$Ag_{calc-head} = Ag_{dis}(n) + Ag_{solid}(final\ residue)$$

The silver extraction at time *i* is calculated as the ratio of total dissolved silver over total silver calculated head assay:

$$Ag\%(i) = \frac{Ag_{dis}(i)}{Ag_{calc-head}}$$

Copper follows the same idea except initial addition of copper complicates the equations. The total dissolved copper is calculated as:

$$Cu_{dis}(j) = \sum_{i=1}^{j-1} C_i V_i + C_j \left(V_0 - \sum_{i=1}^{j-1} V_i \right)$$

The calculated head of copper can be represented as:

$$Cu_{calc-head} = Cu_{dis}(n) + Cu_{solid}(final\ residue)$$

The copper extraction at time *i* is calculated as the ratio of total dissolved copper over total silver calculated head assay:

$$Cu\%(i) = \frac{Cu_{dis}(i) - C_0V_0}{Cu_{calc-head}}$$

where C_0 is the initial concentration of copper in leaching solution.

B.3 Calculations of Ammonium Thiosulfate Consumption

Ammonium thiosulfate consumption was calculated for each test based on mass of ore sample used, initial solution volume and change in thiosulfate concentration. A sample calculation of trial 0.2 M ammonia is shown as following:

V_0 = 0.398 L

M_{ore} = 99.39 g

$C_{TS,0}$ = 0.08958 M

$C_{TS,final}$ = 0.06304 M

$$Consumption = \frac{(0.08958 - 0.06304)\ mol}{L} \times \frac{0.398\ L}{99.39\ g\ ore} \times \frac{148.21\ g\ (NH_4)_2S_2O_3}{mol}$$

$$\times \frac{1000000\ g\ ore}{tonne\ ore} \times \frac{1\ kg\ (NH_4)_2S_2O_3}{1000\ g\ (NH_4)_2S_2O_3} = 15.75\ kg(NH_4)_2S_2O_3/tonne\ ore$$

Appendix C Supplemental XRD Results

The additional XRD results of the leaching residues of LDLPMC, NHMC and CZMC are listed in this section.

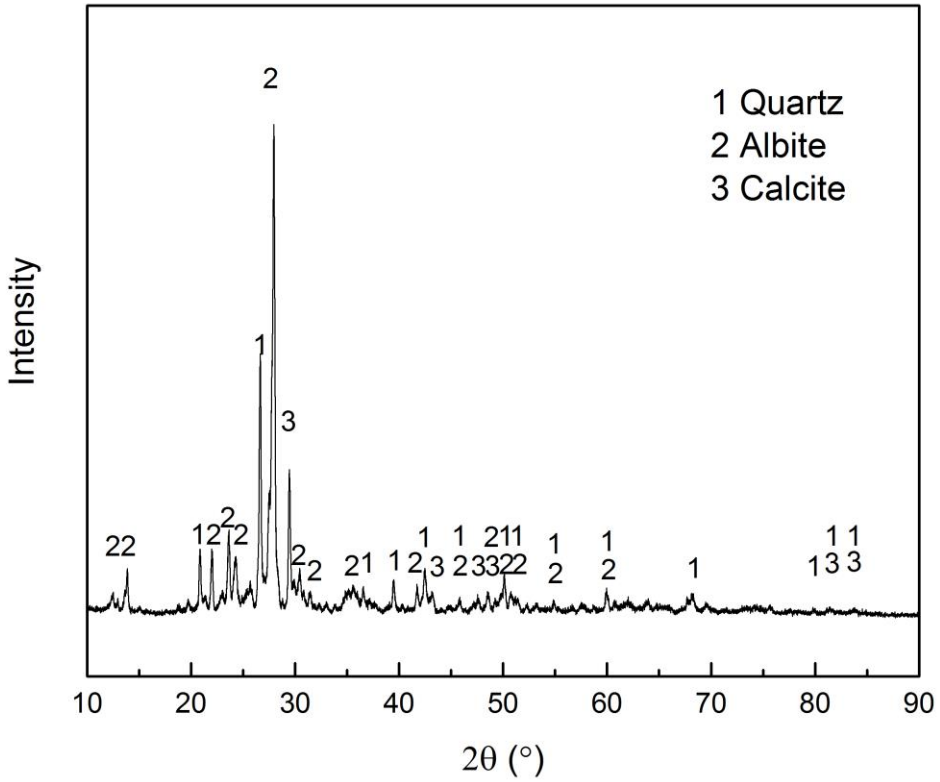

Figure C.1 XRD results of LDLPMC cyanidation residue

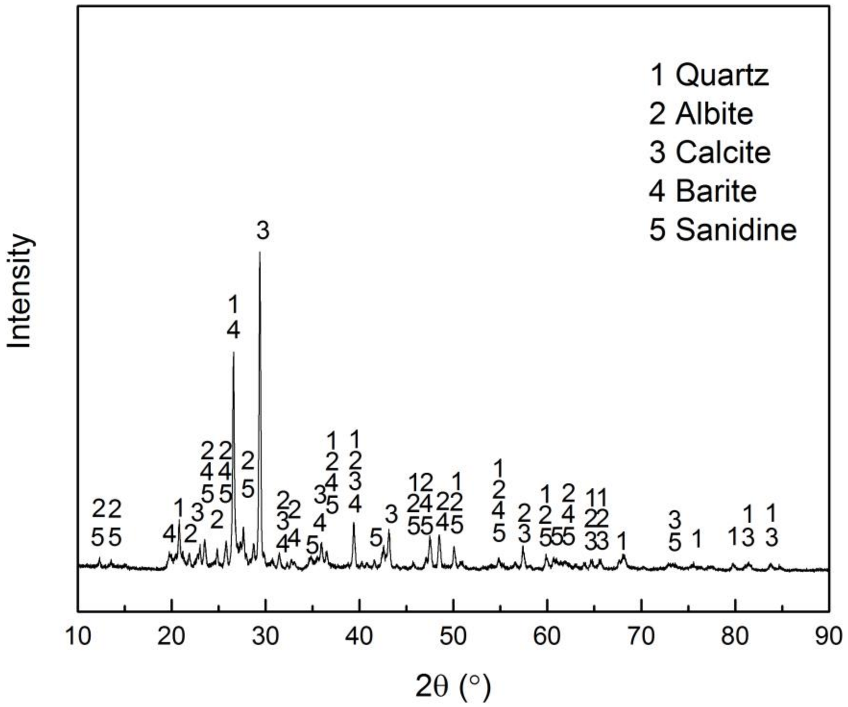

Figure C.2 XRD results of NHMC cyanidation residue

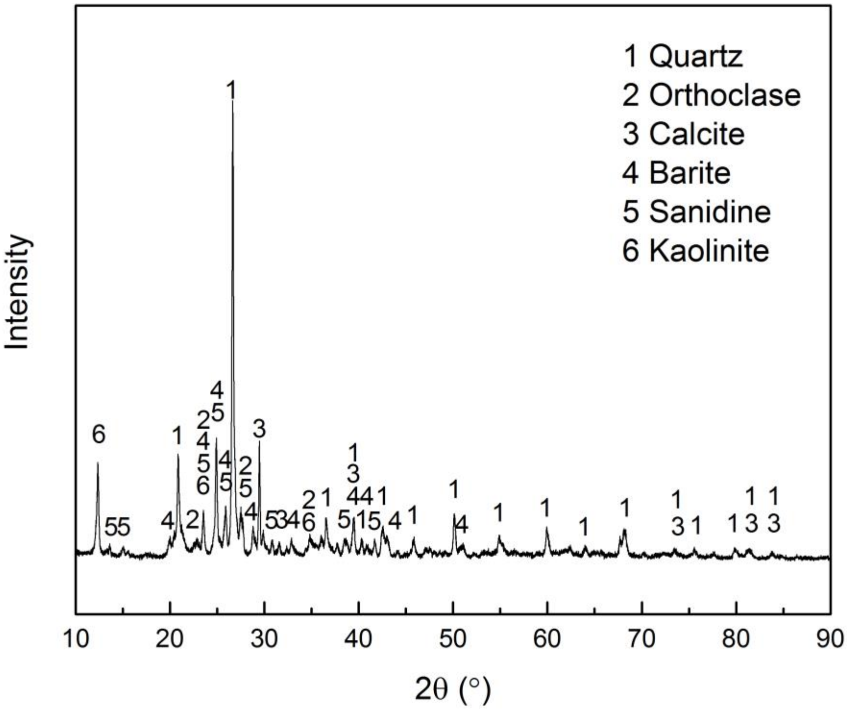

Figure C.3 XRD results of CZMC cyanidation residue

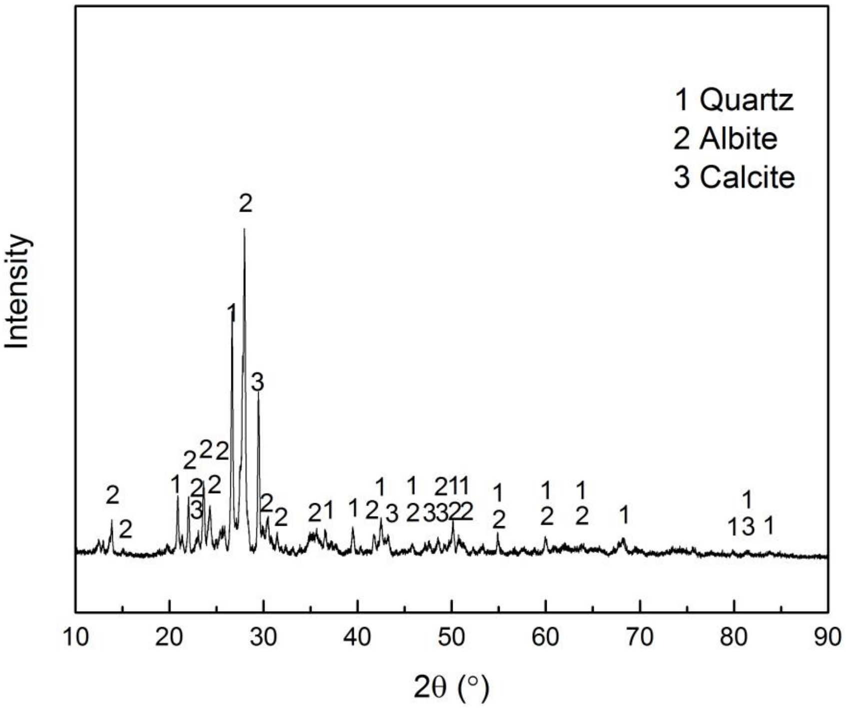

Figure C.4 XRD results of LDLPMC baseline residue

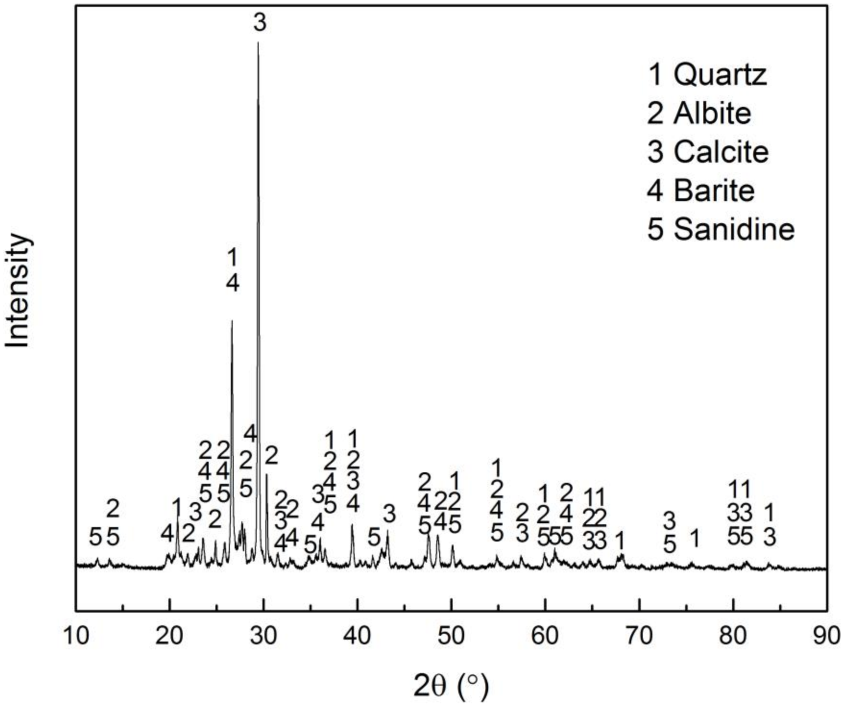

Figure C.5 XRD results of NHMC baseline residue

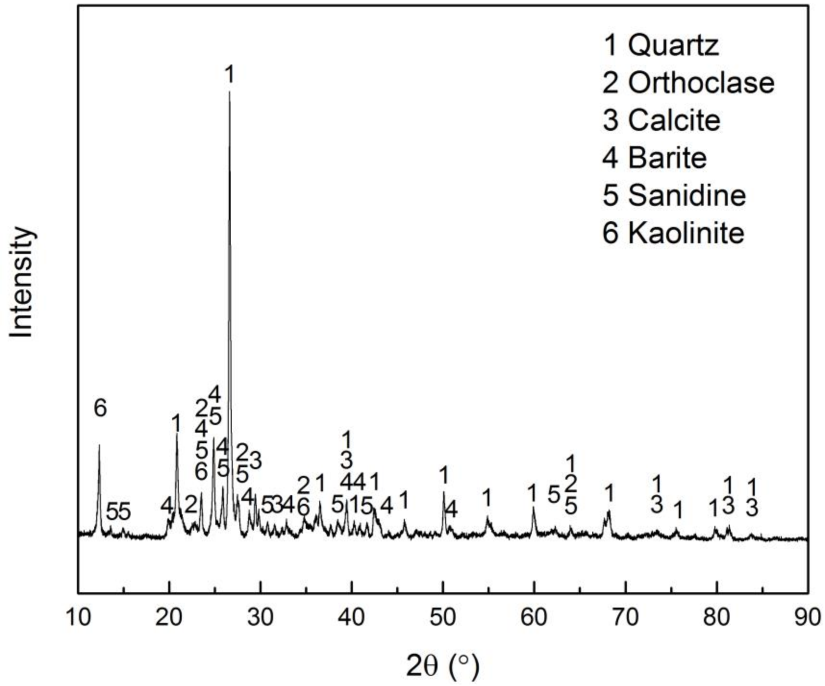

Figure C.6 XRD results of CZMC baseline residue

These XRD results show that the major phases in the samples did not change after treatment with cyanide and thiosulfate, indicating that the phases that leached are minor phases, possibly lower than the 5% detection limit of XRD. No silver and copper phases were detected.

Appendix D Sample Calculation for Extraction with Variation of Head Assay

The following tables show a sample calculation with an initial copper head assay of 673.2 ppm. All aqueous copper is the sum of copper content in all intermediate solutions, the filtrate and the wash. The initial copper mass is the copper added in solution at time 0. Extracted copper is the difference between all aqueous copper and initial added copper mass, and the % extraction is the ratio of extracted copper to copper in ore.

Mass ore (g)	100
Cu assay ore (ppm)	673.2
Cu in ore (g)	0.06732
aqoues solution vol (mL)	400

samples	Vol mL	[Cu] ppm	Cu mass g
t=0		73.62	
t=1h	5	97.5	0.0004875
t=2h	2	97.6	0.0001952
t=4h	2	108.4	0.0002168
t=8h	2	104.25	0.0002085
t=24h	3	113.6	0.0003408
t=48h	3.665	120	0.0004398
filtrate	344	133.2	0.0458208
wash	140	57	0.00798

All aqueous Cu (g)	0.055689
Initial Cu mass (g)	0.029448
Extracted Cu (g)	0.026241
% extraction Cu	38.98%

Cu residue mass (g)	99.1
Cu residue (ppm)	532.1
% extraction by solids	21.7%

It can be seen that the % extraction by solids basis is quite different from % extraction copper on solutions basis. However, they would be very close if the head assay were to have been 790 ppm.

The range of copper head assay values was 600 to 900 ppm. Therefore, the discrepancies between the two types of percent extraction calculations can be attributed to variations in head assays.

Mass ore (g)	100
If the Cu assay is: (ppm)	**790**
Cu in ore (g)	0.079
aq soln vol (mL)	400

samples	Vol mL	[Cu] ppm	Cu mass g
t=0		73.62	
t=1h	5	97.5	0.0004875
t=2h	2	97.6	0.0001952
t=4h	2	108.4	0.0002168
t=8h	2	104.25	0.0002085
t=24h	3	113.6	0.0003408
t=48h	3.665	120	0.0004398
filtrate	344	133.2	0.0458208
wash	140	57	0.00798

All aqueous Cu (g)	0.055689
Initial Cu mass (g)	0.029448
Extracted Cu (g)	0.026241
% extraction Cu	**33.22%**

Cu residue mass (g)	99.1
Cu residue (ppm)	532.1
% extn by solids	**33.3%**

The difference between the two extraction values is very small. This demonstrates the effect of variations in head assay copper content on percent extraction calculations.

Appendix E Mass Balance Tables

The mass balance tables of the tests presented in this thesis are listed in this section.

Table E.1 Mass balance table for preliminary CZMC cyanidation test (35% solid, 4 g/L NaCN)

Mass Balance			
Input			
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	317.80	1673.85
	Element in feed, mg	31.78	167.39
Mass of Feed Solution, g	Element in feed, ppm	0.00	0.00
185.7	Element in solution, mg	0.00	0.00
	Element mass total, mg	31.78	167.39
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	107.76	37.84
5	Element in samp., mg	0.54	0.19
4h sampling, sol. vol, mL	Element in sampling, ppm	134.00	44.87
3	Element in samp., mg	0.40	0.13
8h sampling, sol. vol, mL	Element in sampling, ppm	149.45	50.55
2	Element in samp., mg	0.30	0.10
24h sampling, sol. vol, mL	Element in sampling, ppm	155.25	63.30
1	Element in samp., mg	0.16	0.06
48h lechate, sol. vol, mL	Element in sampling, ppm	146.80	80.32
103	Element in samp., mg	15.12	8.27
Volume of Wash, mL	Element in wash, ppm	7.00	11.00
600	Element in wash, mg	4.20	6.60
	Element in solutions, mg	20.72	15.36
Mass of Residue, g	Element in residue, ppm	102.50	1365.80
96.6	Element in residue, mg	9.90	131.94
	Element mass total, mg	30.62	147.30
Extraction			
Calculated Head, g	Element in feed, ppm	306.17	1472.97
100	Element mass total, mg	30.62	147.30
Extraction	%	67.7%	10.4%
Balance Check	(Ouput-Input)/Input, %	-3.66	-12.00

Table E.2 Mass balance table for repeated CZMC cyanidation test (20% solid, 7.4 g/L NaCN)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	322.00	1817.50
	Element in feed, mg	32.20	181.75
Mass of Feed Solution, g	Element in feed, ppm	0.00	0.00
400.0	Element in solution, mg	0.00	0.00
	Element mass total, mg	32.20	181.75
Output			
1.5h sampling, sol. vol, mL	Element in sampling, ppm	52.50	20.00
5.000	Element in samp., mg	0.26	0.10
4h sampling, sol. vol, mL	Element in sampling, ppm	55.96	40.00
2.500	Element in samp., mg	0.14	0.10
8h sampling, sol. vol, mL	Element in sampling, ppm	55.90	50.00
2.000	Element in samp., mg	0.11	0.10
24h sampling, sol. vol, mL	Element in sampling, ppm	60.10	50.00
2.000	Element in samp., mg	0.12	0.10
48h sampling, sol. vol, mL	Element in sampling, ppm	63.10	50.00
2.000	Element in samp., mg	0.13	0.10
72h lechate, sol. vol, mL	Element in sampling, ppm	63.65	122.90
333	Element in samp., mg	21.20	40.93
Volume of Wash, mL	Element in wash, ppm	25.95	53.60
114	Element in wash, mg	2.96	6.11
	Element in solutions, mg	24.91	47.54
Mass of Residue, g	Element in residue, ppm	88.40	1380.60
99.57	Element in residue, mg	8.80	137.47
	Element mass total, mg	33.72	185.00
Extraction			
Calculated Head, g	Element in feed, ppm	337.16	1850.02
100	Element mass total, mg	33.72	185.00
Extraction	%	73.9%	25.7%
Balance Check	(Ouput-Input)/Input, %	4.71%	1.79%

Table E.3 Mass balance table for preliminary LDLPMC cyanidation test (35% solid, 4 g/L NaCN)

Mass Balance			
Input			
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	288.65	682.30
	Element in feed, mg	28.87	68.23
Mass of Feed Solution, g	Element in feed, ppm	0.00	0.00
185.7	Element in solution, mg	0.00	0.00
	Element mass total, mg	28.87	68.23
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	107.76	37.84
11	Element in samp., mg	1.19	0.42
4h sampling, sol. vol, mL	Element in sampling, ppm	134.00	44.87
3	Element in samp., mg	0.40	0.13
8h sampling, sol. vol, mL	Element in sampling, ppm	149.45	50.55
2	Element in samp., mg	0.30	0.10
24h sampling, sol. vol, mL	Element in sampling, ppm	181.00	63.30
1	Element in samp., mg	0.18	0.06
48h lechate, sol. vol, mL	Element in sampling, ppm	223.10	89.60
40	Element in samp., mg	8.92	3.58
Volume of Wash, mL	Element in wash, ppm	23.80	9.30
620	Element in wash, mg	14.76	5.77
	Element in solutions, mg	25.75	10.07
Mass of Residue, g	Element in residue, ppm	36.10	572.00
97.2	Element in residue, mg	3.51	55.60
	Element mass total, mg	29.26	65.66
Extraction			
Calculated Head, g	Element in feed, ppm	292.56	656.64
100	Element mass total, mg	29.26	65.66
Extraction	%	88.0%	15.3%
Balance Check	(Ouput-Input)/Input, %	1.36	-3.76

Table E.4 Mass balance table for repeated LDLPMC cyanidation test (20% solid, 4.25 g/L NaCN)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	295.30	817.00
	Element in feed, mg	29.53	81.70
Mass of Feed Solution, g	Element in feed, ppm	0.00	0.00
400.0	Element in solution, mg	0.00	0.00
	Element mass total, mg	29.53	81.70
Output			
1.5h sampling, sol. vol, mL	Element in sampling, ppm	53.70	20.00
5.000	Element in samp., mg	0.27	0.10
4h sampling, sol. vol, mL	Element in sampling, ppm	61.88	40.00
2.500	Element in samp., mg	0.15	0.10
8h sampling, sol. vol, mL	Element in sampling, ppm	64.55	50.00
2.000	Element in samp., mg	0.13	0.10
24h sampling, sol. vol, mL	Element in sampling, ppm	72.65	50.00
2.000	Element in samp., mg	0.15	0.10
48h sampling, sol. vol, mL	Element in sampling, ppm	73.20	50.00
2.000	Element in samp., mg	0.15	0.10
72h lechate, sol. vol, mL	Element in sampling, ppm	75.00	85.60
335	Element in samp., mg	25.13	28.68
Volume of Wash, mL	Element in wash, ppm	31.93	35.63
83	Element in wash, mg	2.65	2.96
	Element in solutions, mg	28.62	32.13
Mass of Residue, g	Element in residue, ppm	25.90	543.90
99.84	Element in residue, mg	2.59	54.30
	Element mass total, mg	31.21	86.44
Extraction			
Calculated Head, g	Element in feed, ppm	312.05	864.36
100	Element mass total, mg	31.21	86.44
Extraction	%	91.7%	37.2%
Balance Check	(Ouput-Input)/Input, %	5.67%	5.80%

Table E.5 Mass balance table for preliminary NHMC cyanidation test (35% solid, 4 g/L NaCN)

Mass Balance			
Input			
Mass of Feed Solid, g	Element	Ag	Cu
100.01	Element in feed, ppm	292.00	6026.20
	Element in feed, mg	29.20	602.68
Mass of Feed Solution, g	Element in feed, ppm	0.00	0.00
185.9	Element in solution, mg	0.00	0.00
	Element mass total, mg	29.20	602.68
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	63.84	1082.80
5.000	Element in samp., mg	0.32	5.41
4h sampling, sol. vol, mL	Element in sampling, ppm	94.54	1368.08
2.500	Element in samp., mg	0.24	3.42
8h sampling, sol. vol, mL	Element in sampling, ppm	108.05	1430.00
2.000	Element in samp., mg	0.22	2.86
24h sampling, sol. vol, mL	Element in sampling, ppm	137.20	1604.00
1.000	Element in samp., mg	0.14	1.60
48h sampling, sol. vol, mL	Element in sampling, ppm	188.20	2388.00
1.000	Element in samp., mg	0.19	2.39
72h lechate, sol. vol, mL	Element in sampling, ppm	235.20	3235.50
18.0	Element in samp., mg	0.24	3.24
Volume of Wash, mL	Element in wash, ppm	25.30	303.40
465	Element in wash, mg	11.76	141.08
	Element in solutions, mg	12.86	156.77
Mass of Residue, g	Element in residue, ppm	99.65	3561.45
97.4	Element in residue, mg	9.71	346.89
	Element mass total, mg	22.57	503.65
Extraction			
Calculated Head, g	Element in feed, ppm	225.65	5036.02
100.01	Element mass total, mg	22.57	503.65
Extraction	%	57.0%	31.1%
Balance Check	(Ouput-Input)/Input, %	-22.72	-18.04

Table E.6 Mass balance table for repeated NHMC cyanidation test (20% solid, 25 g/L NaCN)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	295.10	6158.40
	Element in feed, mg	29.51	615.84
Mass of Feed Solution, g	Element in feed, ppm	0.00	0.00
400.0	Element in solution, mg	0.00	0.00
	Element mass total, mg	29.51	615.84
Output			
1.5h sampling, sol. vol, mL	Element in sampling, ppm	54.74	200.00
5.000	Element in samp., mg	0.27	1.00
4h sampling, sol. vol, mL	Element in sampling, ppm	57.56	200.00
2.500	Element in samp., mg	0.14	0.50
8h sampling, sol. vol, mL	Element in sampling, ppm	57.80	500.00
2.000	Element in samp., mg	0.12	1.00
24h sampling, sol. vol, mL	Element in sampling, ppm	63.75	500.00
2.000	Element in samp., mg	0.13	1.00
48h sampling, sol. vol, mL	Element in sampling, ppm	64.60	500.00
2.000	Element in samp., mg	0.13	1.00
72h lechate, sol. vol, mL	Element in sampling, ppm	66.95	1152.00
318	Element in samp., mg	21.29	366.34
Volume of Wash, mL	Element in wash, ppm	38.87	666.80
105	Element in wash, mg	4.08	70.01
	Element in solutions, mg	26.16	440.85
Mass of Residue, g	Element in residue, ppm	48.55	2283.00
98.86	Element in residue, mg	4.80	225.70
	Element mass total, mg	30.96	666.55
Extraction			
Calculated Head, g	Element in feed, ppm	309.61	6665.47
100	Element mass total, mg	30.96	666.55
Extraction	%	84.5%	66.1%
Balance Check	(Ouput-Input)/Input, %	4.92%	8.23%

Table E.7 Mass balance table for 0.2 M ammonia LDLPMC test (Initial condition of 20% solid to liquid, 0.2 M of thiosulfate, 0.2 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
99.39	Element in feed, ppm	293.20	754.00
	Element in feed, mg	29.14	74.94
Mass of Feed Solution, g	Element in feed, ppm	0.00	62.66
397.6	Element in solution, mg	0.00	24.91
	Element mass total, mg	29.14	99.85
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	30.64	54.54
5	Element in samp., mg	0.15	0.27
2h sampling, sol. vol, mL	Element in sampling, ppm	37.22	55.46
5	Element in samp., mg	0.19	0.28
4h sampling, sol. vol, mL	Element in sampling, ppm	42.80	53.68
2.5	Element in samp., mg	0.11	0.13
8h sampling, sol. vol, mL	Element in sampling, ppm	49.20	53.92
2.5	Element in samp., mg	0.12	0.13
24h sampling, sol. vol, mL	Element in sampling, ppm	58.25	55.20
7	Element in samp., mg	0.41	0.39
48h lechate, sol. vol, mL	Element in sampling, ppm	61.35	48.80
333	Element in samp., mg	20.43	16.25
Volume of Wash, mL	Element in wash, ppm	14.27	14.96
106	Element in wash, mg	1.51	1.59
	Element in solutions, mg	22.92	19.04
Mass of Residue, g	Element in residue, ppm	50.00	830.70
97.96	Element in residue, mg	4.90	81.38
	Element mass total, mg	27.82	100.42
Extraction			
Calculated Head, g	Element in feed, ppm	279.88	1010.33
99.39	Element mass total, mg	27.82	100.42
Extraction	%	82.4%	19.0%
Balance Check	(Ouput-Input)/Input, %	-4.54%	0.57%

Table E.8 Mass balance table for 0.2 M thiosulfate LDLPMC test (Initial condition of 20% solid to liquid, 0.2 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	300.00	673.20
	Element in feed, mg	30.00	67.32
Mass of Feed Solution, g	Element in feed, ppm	0.00	76.82
400.0	Element in solution, mg	0.00	30.72
	Element mass total, mg	30.00	98.04
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	36.08	96.04
5.000	Element in samp., mg	0.18	0.48
2h sampling, sol. vol, mL	Element in sampling, ppm	44.35	94.20
2.000	Element in samp., mg	0.09	0.19
4h sampling, sol. vol, mL	Element in sampling, ppm	52.20	106.15
2.000	Element in samp., mg	0.10	0.21
8h sampling, sol. vol, mL	Element in sampling, ppm	57.15	104.00
2.000	Element in samp., mg	0.11	0.21
23h sampling, sol. vol, mL	Element in sampling, ppm	65.85	111.50
4.500	Element in samp., mg	0.30	0.50
48h sampling, sol. vol, mL	Element in sampling, ppm	78.60	115.30
4.500	Element in samp., mg	0.35	0.52
72h lechate, sol. vol, mL	Element in sampling, ppm	74.15	129.40
339	Element in samp., mg	25.14	43.87
Volume of Wash, mL	Element in wash, ppm	24.51	38.77
102	Element in wash, mg	2.50	3.95
	Element in solutions, mg	28.77	49.93
Mass of Residue, g	Element in residue, ppm	34.00	550.00
98.7	Element in residue, mg	3.36	54.29
	Element mass total, mg	32.13	104.22
Extraction			
Calculated Head, g	Element in feed, ppm	321.30	1349.41
100	Element mass total, mg	32.13	134.94
Extraction	%	89.6%	59.8%
Balance Check	(Ouput-Input)/Input, %	7.10%	6.29%

Table E.9 Mass balance table for 0.3M thiosulfate LDLPMC test (Initial condition of 20% solid to liquid, 0.3 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	300.00	673.20
	Element in feed, mg	30.00	67.32
Mass of Feed Solution, g	Element in feed, ppm	0.00	72.76
400.7	Element in solution, mg	0.00	29.15
	Element mass total, mg	30.00	96.47
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	34.24	95.66
5.000	Element in samp., mg	0.17	0.48
2h sampling, sol. vol, mL	Element in sampling, ppm	41.50	100.30
2.000	Element in samp., mg	0.08	0.20
4h sampling, sol. vol, mL	Element in sampling, ppm	48.25	108.05
2.000	Element in samp., mg	0.10	0.22
8h sampling, sol. vol, mL	Element in sampling, ppm	51.15	103.90
2.000	Element in samp., mg	0.10	0.21
23h sampling, sol. vol, mL	Element in sampling, ppm	61.45	112.10
3.665	Element in samp., mg	0.23	0.41
48h sampling, sol. vol, mL	Element in sampling, ppm	73.75	118.00
3.665	Element in samp., mg	0.27	0.43
72h lechate, sol. vol, mL	Element in sampling, ppm	72.60	132.40
342	Element in samp., mg	24.83	45.28
Volume of Wash, mL	Element in wash, ppm	29.41	51.72
79	Element in wash, mg	2.32	4.09
	Element in solutions, mg	28.10	51.31
Mass of Residue, g	Element in residue, ppm	38.00	533.00
98.7	Element in residue, mg	3.75	52.61
	Element mass total, mg	31.85	103.92
Extraction			
Calculated Head, g	Element in feed, ppm	318.52	1330.71
100	Element mass total, mg	31.85	133.07
Extraction	%	88.2%	60.5%
Balance Check	(Ouput-Input)/Input, %	6.17%	7.72%

Table E.10 Mass balance table for 0.5 M thiosulfate LDLPMC test (Initial condition of 20% solid to liquid, 0.5 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	300.00	673.20
	Element in feed, mg	30.00	67.32
Mass of Feed Solution, g	Element in feed, ppm	0.00	73.62
400.0	Element in solution, mg	0.00	29.45
	Element mass total, mg	30.00	96.77
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	29.84	97.50
5.000	Element in samp., mg	0.15	0.49
2h sampling, sol. vol, mL	Element in sampling, ppm	36.40	97.60
2.000	Element in samp., mg	0.07	0.20
4h sampling, sol. vol, mL	Element in sampling, ppm	42.15	108.40
2.000	Element in samp., mg	0.08	0.22
8h sampling, sol. vol, mL	Element in sampling, ppm	44.60	104.25
2.000	Element in samp., mg	0.09	0.21
23h sampling, sol. vol, mL	Element in sampling, ppm	56.40	113.60
3.000	Element in samp., mg	0.17	0.34
48h sampling, sol. vol, mL	Element in sampling, ppm	69.75	120.00
3.665	Element in samp., mg	0.26	0.44
72h lechate, sol. vol, mL	Element in sampling, ppm	70.30	133.20
344	Element in samp., mg	24.18	45.82
Volume of Wash, mL	Element in wash, ppm	17.76	57.00
140	Element in wash, mg	2.49	7.98
	Element in solutions, mg	27.49	55.69
Mass of Residue, g	Element in residue, ppm	52.50	532.10
99.1	Element in residue, mg	5.20	52.73
	Element mass total, mg	32.69	108.42
Extraction			
Calculated Head, g	Element in feed, ppm	326.93	1378.68
100	Element mass total, mg	32.69	137.87
Extraction	%	84.1%	61.8%
Balance Check	(Ouput-Input)/Input, %	8.98%	12.04%

Table E.11 Mass balance table for 0.5 mM EDTA LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, 0.5 mM EDTA, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	304.00	817.00
	Element in feed, mg	30.40	81.70
Mass of Feed Solution, g	Element in feed, ppm	0.00	64.30
400.0	Element in solution, mg	0.00	25.72
	Element mass total, mg	30.40	107.42
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	36.10	67.44
5.000	Element in samp., mg	0.18	0.34
2h sampling, sol. vol, mL	Element in sampling, ppm	44.95	73.30
2.000	Element in samp., mg	0.09	0.15
5h sampling, sol. vol, mL	Element in sampling, ppm	57.25	75.80
2.000	Element in samp., mg	0.11	0.15
8.5h sampling, sol. vol, mL	Element in sampling, ppm	56.15	75.90
2.000	Element in samp., mg	0.11	0.15
24h sampling, sol. vol, mL	Element in sampling, ppm	74.55	79.15
7.000	Element in samp., mg	0.52	0.55
48h sampling, sol. vol, mL	Element in sampling, ppm	77.25	79.00
7.000	Element in samp., mg	0.54	0.55
72h lechate, sol. vol, mL	Element in sampling, ppm	78.85	77.65
335	Element in samp., mg	26.41	26.01
Volume of Wash, mL	Element in wash, ppm	21.95	25.55
119	Element in wash, mg	2.61	3.04
	Element in solutions, mg	30.59	30.95
Mass of Residue, g	Element in residue, ppm	43.35	629.50
98.84	Element in residue, mg	4.28	62.22
	Element mass total, mg	34.87	93.17
Extraction			
Calculated Head, g	Element in feed, ppm	348.71	1188.88
100	Element mass total, mg	34.87	118.89
Extraction	%	87.7%	47.7%
Balance Check	(Ouput-Input)/Input, %	14.71%	-13.27%

Table E.12 Mass balance table for 0.35 M ammonia LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.35 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
99.23	Element in feed, ppm	293.20	754.00
	Element in feed, mg	29.09	74.82
Mass of Feed Solution, g	Element in feed, ppm	0.00	61.76
396.9	Element in solution, mg	0.00	24.51
	Element mass total, mg	29.09	99.33
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	16.20	57.24
5	Element in samp., mg	0.08	0.29
2h sampling, sol. vol, mL	Element in sampling, ppm	20.06	57.00
5	Element in samp., mg	0.10	0.29
4h sampling, sol. vol, mL	Element in sampling, ppm	25.28	54.12
2.5	Element in samp., mg	0.06	0.14
8h sampling, sol. vol, mL	Element in sampling, ppm	29.52	54.32
2.5	Element in samp., mg	0.07	0.14
24h sampling, sol. vol, mL	Element in sampling, ppm	37.20	52.70
7	Element in samp., mg	0.26	0.37
48h lechate, sol. vol, mL	Element in sampling, ppm	44.85	47.60
330	Element in samp., mg	14.80	15.71
Volume of Wash, mL	Element in wash, ppm	8.32	5.65
175	Element in wash, mg	1.46	0.99
	Element in solutions, mg	16.84	17.91
Mass of Residue, g	Element in residue, ppm	110.55	739.15
98.28	Element in residue, mg	10.86	72.64
	Element mass total, mg	27.70	90.55
Extraction			
Calculated Head, g	Element in feed, ppm	279.16	1159.58
99.23	Element mass total, mg	27.70	115.07
Extraction	%	60.8%	36.9%
Balance Check	(Ouput-Input)/Input, %	-4.79%	-8.84%

Table E.13 Mass balance table for 0 mM copper LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 0 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	300.00	673.20
	Element in feed, mg	30.00	67.32
Mass of Feed Solution, g	Element in feed, ppm	0.00	0.00
400.2	Element in solution, mg	0.00	0.00
	Element mass total, mg	30.00	67.32
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	23.56	47.96
5.000	Element in samp., mg	0.12	0.24
2h sampling, sol. vol, mL	Element in sampling, ppm	30.28	51.08
5.000	Element in samp., mg	0.15	0.26
4h sampling, sol. vol, mL	Element in sampling, ppm	40.50	56.00
4.000	Element in samp., mg	0.16	0.22
8h sampling, sol. vol, mL	Element in sampling, ppm	42.65	54.30
4.000	Element in samp., mg	0.17	0.22
24h sampling, sol. vol, mL	Element in sampling, ppm	54.25	62.00
9.000	Element in samp., mg	0.49	0.56
48h sampling, sol. vol, mL	Element in sampling, ppm	58.65	58.85
9.000	Element in samp., mg	0.53	0.53
72h lechate, sol. vol, mL	Element in sampling, ppm	59.80	58.35
311	Element in samp., mg	18.60	18.15
Volume of Wash, mL	Element in wash, ppm	16.04	16.56
140	Element in wash, mg	2.25	2.32
	Element in solutions, mg	22.46	22.49
Mass of Residue, g	Element in residue, ppm	88.00	619.40
98.86	Element in residue, mg	8.70	61.23
	Element mass total, mg	31.16	83.72
Extraction			
Calculated Head, g	Element in feed, ppm	311.61	837.23
100	Element mass total, mg	31.16	83.72
Extraction	%	72.1%	26.9%
Balance Check	(Ouput-Input)/Input, %	3.87%	24.37%

Table E.14 Mass balance table for 1.0 M ammonia LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 1.0 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	297.00	837.20
	Element in feed, mg	29.70	83.72
Mass of Feed Solution, g	Element in feed, ppm	0.00	75.22
400.2	Element in solution, mg	0.00	30.11
	Element mass total, mg	29.70	113.83
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	35.22	40.00
10.000	Element in samp., mg	0.35	0.40
2h sampling, sol. vol, mL	Element in sampling, ppm	42.88	40.00
5.000	Element in samp., mg	0.21	0.20
4h sampling, sol. vol, mL	Element in sampling, ppm	51.84	40.00
5.000	Element in samp., mg	0.26	0.20
8h sampling, sol. vol, mL	Element in sampling, ppm	59.88	40.00
5.000	Element in samp., mg	0.30	0.20
24h sampling, sol. vol, mL	Element in sampling, ppm	72.20	50.00
9.000	Element in samp., mg	0.65	0.45
48h sampling, sol. vol, mL	Element in sampling, ppm	78.85	50.00
9.000	Element in samp., mg	0.71	0.45
72h lechate, sol. vol, mL	Element in sampling, ppm	71.80	136.40
300	Element in samp., mg	21.54	40.92
Volume of Wash, mL	Element in wash, ppm	34.65	74.56
83	Element in wash, mg	2.88	6.19
	Element in solutions, mg	26.90	49.01
Mass of Residue, g	Element in residue, ppm	55.00	688.70
98.1	Element in residue, mg	5.40	67.56
	Element mass total, mg	32.30	116.57
Extraction			
Calculated Head, g	Element in feed, ppm	322.96	1165.70
100	Element mass total, mg	32.30	116.57
Extraction	%	83.3%	42.0%
Balance Check	(Ouput-Input)/Input, %	8.74%	2.41%

Table E.15 Mass balance table for 35 °C LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 35 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	293.20	754.00
	Element in feed, mg	29.32	75.40
Mass of Feed Solution, g	Element in feed, ppm	0.00	63.20
413.7	Element in solution, mg	0.00	26.15
	Element mass total, mg	29.32	101.55
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	35.98	68.74
5	Element in samp., mg	0.18	0.34
2h sampling, sol. vol, mL	Element in sampling, ppm	40.70	72.34
5	Element in samp., mg	0.20	0.36
4h sampling, sol. vol, mL	Element in sampling, ppm	45.40	70.80
2.5	Element in samp., mg	0.11	0.18
8h sampling, sol. vol, mL	Element in sampling, ppm	49.56	76.40
2.5	Element in samp., mg	0.12	0.19
24h sampling, sol. vol, mL	Element in sampling, ppm	54.10	72.50
6	Element in samp., mg	0.32	0.44
48h lechate, sol. vol, mL	Element in sampling, ppm	60.20	81.75
336	Element in samp., mg	20.23	27.47
Volume of Wash, mL	Element in wash, ppm	22.34	31.26
115	Element in wash, mg	2.57	3.59
	Element in solutions, mg	23.74	32.57
Mass of Residue, g	Element in residue, ppm	32.90	631.70
98.99	Element in residue, mg	3.26	62.53
	Element mass total, mg	27.00	95.10
Extraction			
Calculated Head, g	Element in feed, ppm	269.98	1212.50
100	Element mass total, mg	27.00	121.25
Extraction	%	87.9%	48.4%
Balance Check	(Ouput-Input)/Input, %	-7.92%	-6.35%

Table E.16 Mass balance table for 45 ºC LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 45 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	293.20	754.00
	Element in feed, mg	29.32	75.40
Mass of Feed Solution, g	Element in feed, ppm	0.00	63.20
400.1	Element in solution, mg	0.00	25.29
	Element mass total, mg	29.32	100.69
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	34.56	76.36
5	Element in samp., mg	0.17	0.38
2h sampling, sol. vol, mL	Element in sampling, ppm	38.92	79.16
5	Element in samp., mg	0.19	0.40
4h sampling, sol. vol, mL	Element in sampling, ppm	43.68	78.08
2.5	Element in samp., mg	0.11	0.20
8h sampling, sol. vol, mL	Element in sampling, ppm	48.24	83.56
2.5	Element in samp., mg	0.12	0.21
24h sampling, sol. vol, mL	Element in sampling, ppm	54.40	84.80
6	Element in samp., mg	0.33	0.51
48h lechate, sol. vol, mL	Element in sampling, ppm	66.25	98.75
300	Element in samp., mg	19.88	29.63
Volume of Wash, mL	Element in wash, ppm	18.39	23.56
118	Element in wash, mg	2.17	2.78
	Element in solutions, mg	22.97	34.10
Mass of Residue, g	Element in residue, ppm	44.60	625.80
98.65	Element in residue, mg	4.40	61.74
	Element mass total, mg	27.37	95.83
Extraction			
Calculated Head, g	Element in feed, ppm	273.68	1211.18
100	Element mass total, mg	27.37	121.12
Extraction	%	83.9%	49.0%
Balance Check	(Ouput-Input)/Input, %	-6.66%	-4.82%

Table E.17 Mass balance table for air sparging LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	304.00	817.00
	Element in feed, mg	30.40	81.70
Mass of Feed Solution, g	Element in feed, ppm	0.00	58.28
399.9	Element in solution, mg	0.00	23.31
	Element mass total, mg	30.40	105.01
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	38.52	59.52
5.000	Element in samp., mg	0.19	0.30
2h sampling, sol. vol, mL	Element in sampling, ppm	46.85	64.85
2.000	Element in samp., mg	0.09	0.13
5h sampling, sol. vol, mL	Element in sampling, ppm	57.70	65.45
2.000	Element in samp., mg	0.12	0.13
7.5h sampling, sol. vol, mL	Element in sampling, ppm	54.25	65.90
2.000	Element in samp., mg	0.11	0.13
24h sampling, sol. vol, mL	Element in sampling, ppm	64.70	60.65
7.000	Element in samp., mg	0.45	0.42
48h sampling, sol. vol, mL	Element in sampling, ppm	68.90	59.75
7.000	Element in samp., mg	0.48	0.42
72h lechate, sol. vol, mL	Element in sampling, ppm	71.05	52.00
336	Element in samp., mg	23.87	17.47
Volume of Wash, mL	Element in wash, ppm	8.78	5.20
216	Element in wash, mg	1.90	1.12
	Element in solutions, mg	27.21	20.13
Mass of Residue, g	Element in residue, ppm	45.70	686.00
98.35	Element in residue, mg	4.49	67.47
	Element mass total, mg	31.71	87.60
Extraction			
Calculated Head, g	Element in feed, ppm	317.09	875.96
100	Element mass total, mg	31.71	87.60
Extraction	%	85.8%	23.0%
Balance Check	(Ouput-Input)/Input, %	4.31%	-16.58%

Table E.18 Mass balance table for preliminary 0.1 M thiosulfate LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance

Input

Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	294.00	653.50
	Element in feed, mg	29.40	65.35
Mass of Feed Solution, g	Element in feed, ppm	0.00	63.55
185.7	Element in solution, mg	0.00	11.80
	Element mass total, mg	29.40	77.15
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	37.37	94.92
8	Element in samp., mg	0.30	0.76
2h sampling, sol. vol, mL	Element in sampling, ppm	46.01	109.63
8	Element in samp., mg	0.37	0.88
4h sampling, sol. vol, mL	Element in sampling, ppm	60.50	128.12
7	Element in samp., mg	0.42	0.90
8h sampling, sol. vol, mL	Element in sampling, ppm	86.24	146.64
6	Element in samp., mg	0.52	0.88
24h sampling, sol. vol, mL	Element in sampling, ppm	103.52	167.65
10	Element in samp., mg	1.04	1.68
48h sampling, sol. vol, mL	Element in sampling, ppm	141.61	217.24
10	Element in samp., mg	1.42	2.17
72h sampling, sol. vol, mL	Element in sampling, ppm	195.99	294.25
7	Element in samp., mg	1.37	2.06
Volume of Lechate and Wash, mL	Element in wash, ppm	23.40	0.04
430	Element in wash, mg	10.06	0.02
	Element in solutions, mg	15.49	9.34
Mass of Residue, g	Element in residue, ppm	151.50	632.00
97.34	Element in residue, mg	14.75	61.52
	Element mass total, mg	30.24	70.86
Extraction			
Calculated Head, g	Element in feed, ppm	302.40	708.56
100	Element mass total, mg	30.24	70.86
Extraction	%	51.2%	13.2%
Balance Check	(Ouput-Input)/Input, %	2.86	-8.16

Table E.19 Mass balance table for baseline LDLPMC test 2 (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100.09	Element in feed, ppm	293.20	754.00
	Element in feed, mg	29.35	75.47
Mass of Feed Solution, g	Element in feed, ppm	0.00	71.68
403.8	Element in solution, mg	0.00	28.95
	Element mass total, mg	29.35	104.41
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	25.94	86.21
5.000	Element in samp., mg	0.13	0.43
2h sampling, sol. vol, mL	Element in sampling, ppm	32.42	87.10
5.000	Element in samp., mg	0.16	0.44
4h sampling, sol. vol, mL	Element in sampling, ppm	38.71	94.55
2.565	Element in samp., mg	0.10	0.24
8h sampling, sol. vol, mL	Element in sampling, ppm	45.60	96.42
2.500	Element in samp., mg	0.11	0.24
24h sampling, sol. vol, mL	Element in sampling, ppm	52.02	90.43
7.000	Element in samp., mg	0.36	0.63
48h sampling, sol. vol, mL	Element in sampling, ppm	55.85	90.00
7.000	Element in samp., mg	0.39	0.63
72h sampling, sol. vol, mL	Element in sampling, ppm	58.60	82.99
7.000	Element in samp., mg	0.41	0.58
96h sampling, sol. vol, mL	Element in sampling, ppm	56.35	73.70
7.000	Element in samp., mg	0.39	0.52
120h lechate, sol. vol, mL	Element in sampling, ppm	59.95	71.60
301	Element in samp., mg	18.04	21.55
Volume of Wash, mL	Element in wash, ppm	23.02	43.12
127	Element in wash, mg	2.92	5.48
	Element in solutions, mg	23.03	30.74
Mass of Residue, g	Element in residue, ppm	41.10	779.25
97.7	Element in residue, mg	4.02	76.13
	Element mass total, mg	27.05	106.87
Extraction			
Calculated Head, g	Element in feed, ppm	270.24	1356.93
100.09	Element mass total, mg	27.05	135.82
Extraction	%	85.2%	43.9%
Balance Check	(Ouput-Input)/Input, %	-7.83%	2.35%

Table E.20 Mass balance table for baseline LDLPMC test 3 (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
99.99	Element in feed, ppm	304.00	957.70
	Element in feed, mg	30.40	95.76
Mass of Feed Solution, g	Element in feed, ppm	0.00	76.40
402.4	Element in solution, mg	0.00	30.74
	Element mass total, mg	30.40	126.50
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	28.83	98.52
5.000	Element in samp., mg	0.14	0.49
2h sampling, sol. vol, mL	Element in sampling, ppm	36.51	102.21
5.000	Element in samp., mg	0.18	0.51
4h sampling, sol. vol, mL	Element in sampling, ppm	42.97	100.93
2.500	Element in samp., mg	0.11	0.25
8h sampling, sol. vol, mL	Element in sampling, ppm	46.88	103.62
2.500	Element in samp., mg	0.12	0.26
24h sampling, sol. vol, mL	Element in sampling, ppm	56.79	102.09
7.000	Element in samp., mg	0.40	0.71
48h sampling, sol. vol, mL	Element in sampling, ppm	55.40	106.23
7.000	Element in samp., mg	0.39	0.74
72h lechate, sol. vol, mL	Element in sampling, ppm	58.55	103.93
377	Element in samp., mg	22.06	39.15
Volume of Wash, mL	Element in wash, ppm	13.29	29.08
135	Element in wash, mg	1.79	3.93
	Element in solutions, mg	25.19	46.05
Mass of Residue, g	Element in residue, ppm	62.30	724.10
98.48	Element in residue, mg	6.14	71.31
	Element mass total, mg	31.32	117.36
Extraction			
Calculated Head, g	Element in feed, ppm	313.25	1481.18
99.99	Element mass total, mg	31.32	148.10
Extraction	%	80.4%	51.9%
Balance Check	(Ouput-Input)/Input, %	3.04%	-7.23%

Table E.21 Mass balance table for baseline LDLPMC test 4 (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	304.00	817.00
	Element in feed, mg	30.40	81.70
Mass of Feed Solution, g	Element in feed, ppm	0.00	58.28
400.0	Element in solution, mg	0.00	23.31
	Element mass total, mg	30.40	105.01
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	35.16	71.68
5.000	Element in samp., mg	0.18	0.36
2h sampling, sol. vol, mL	Element in sampling, ppm	43.82	72.08
2.000	Element in samp., mg	0.09	0.14
5h sampling, sol. vol, mL	Element in sampling, ppm	51.50	75.22
2.000	Element in samp., mg	0.10	0.15
7.5h sampling, sol. vol, mL	Element in sampling, ppm	54.55	74.96
2.000	Element in samp., mg	0.11	0.15
24h sampling, sol. vol, mL	Element in sampling, ppm	63.95	71.90
7.000	Element in samp., mg	0.45	0.50
48h sampling, sol. vol, mL	Element in sampling, ppm	72.85	75.54
7.000	Element in samp., mg	0.51	0.53
72h lechate, sol. vol, mL	Element in sampling, ppm	69.75	71.35
320	Element in samp., mg	22.32	22.83
Volume of Wash, mL	Element in wash, ppm	20.96	19.02
140	Element in wash, mg	2.93	2.66
	Element in solutions, mg	26.69	27.33
Mass of Residue, g	Element in residue, ppm	43.10	716.10
98.74	Element in residue, mg	4.26	70.71
	Element mass total, mg	30.94	98.04
Extraction			
Calculated Head, g	Element in feed, ppm	309.43	1213.48
100	Element mass total, mg	30.94	121.35
Extraction	%	86.2%	41.7%
Balance Check	(Ouput-Input)/Input, %	1.79%	-6.64%

Table E.22 Mass balance table for pH 8.5 LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 8.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	295.30	817.00
	Element in feed, mg	29.53	81.70
Mass of Feed Solution, g	Element in feed, ppm	0.00	80.64
400.0	Element in solution, mg	0.00	32.25
	Element mass total, mg	29.53	113.95
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	24.50	141.40
5.000	Element in samp., mg	0.12	0.71
2h sampling, sol. vol, mL	Element in sampling, ppm	29.97	138.37
3.000	Element in samp., mg	0.09	0.42
4h sampling, sol. vol, mL	Element in sampling, ppm	38.28	139.40
2.500	Element in samp., mg	0.10	0.35
7h sampling, sol. vol, mL	Element in sampling, ppm	45.15	149.60
2.000	Element in samp., mg	0.09	0.30
24h sampling, sol. vol, mL	Element in sampling, ppm	63.30	147.20
7.000	Element in samp., mg	0.44	1.03
51.5h sampling, sol. vol, mL	Element in sampling, ppm	66.25	153.25
7.000	Element in samp., mg	0.46	1.07
72h lechate, sol. vol, mL	Element in sampling, ppm	63.80	151.95
309	Element in samp., mg	19.71	46.95
Volume of Wash, mL	Element in wash, ppm	18.68	44.24
120	Element in wash, mg	2.24	5.31
	Element in solutions, mg	23.26	56.13
Mass of Residue, g	Element in residue, ppm	39.70	614.60
98.53	Element in residue, mg	3.91	60.56
	Element mass total, mg	27.17	116.69
Extraction			
Calculated Head, g	Element in feed, ppm	271.73	1166.91
100	Element mass total, mg	27.17	116.69
Extraction	%	85.6%	48.1%
Balance Check	(Ouput-Input)/Input, %	-7.98%	2.40%

Table E.23 Mass balance table for pH 9.0 LDLPMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.0, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	295.30	817.00
	Element in feed, mg	29.53	81.70
Mass of Feed Solution, g	Element in feed, ppm	0.00	80.64
400.0	Element in solution, mg	0.00	32.26
	Element mass total, mg	29.53	113.96
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	34.52	135.60
5.000	Element in samp., mg	0.17	0.68
2h sampling, sol. vol, mL	Element in sampling, ppm	43.76	140.68
5.000	Element in samp., mg	0.22	0.70
4h sampling, sol. vol, mL	Element in sampling, ppm	50.36	133.60
2.500	Element in samp., mg	0.13	0.33
7h sampling, sol. vol, mL	Element in sampling, ppm	54.10	125.10
2.000	Element in samp., mg	0.11	0.25
24h sampling, sol. vol, mL	Element in sampling, ppm	66.20	137.80
7.000	Element in samp., mg	0.46	0.96
51.5h sampling, sol. vol, mL	Element in sampling, ppm	68.00	137.15
7.000	Element in samp., mg	0.48	0.96
72h lechate, sol. vol, mL	Element in sampling, ppm	64.55	124.70
321	Element in samp., mg	20.72	40.03
Volume of Wash, mL	Element in wash, ppm	15.65	36.54
160	Element in wash, mg	2.50	5.85
	Element in solutions, mg	24.79	49.77
Mass of Residue, g	Element in residue, ppm	31.10	685.90
98.64	Element in residue, mg	3.07	67.66
	Element mass total, mg	27.86	117.42
Extraction			
Calculated Head, g	Element in feed, ppm	278.57	1174.23
100	Element mass total, mg	27.86	117.42
Extraction	%	89.0%	42.4%
Balance Check	(Ouput-Input)/Input, %	-5.66%	3.04%

Table E.24 Mass balance table for preliminary baseline CZMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input			
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	276.00	5658.03
	Element in feed, mg	27.60	565.80
Mass of Feed Solution, g	Element in feed, ppm	0.00	63.55
185.7	Element in solution, mg	0.00	11.80
	Element mass total, mg	27.60	577.61
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	91.33	152.30
5	Element in samp., mg	0.46	0.76
2h sampling, sol. vol, mL	Element in sampling, ppm	102.77	165.44
5	Element in samp., mg	0.51	0.83
4h sampling, sol. vol, mL	Element in sampling, ppm	106.20	173.36
5	Element in samp., mg	0.53	0.87
8h sampling, sol. vol, mL	Element in sampling, ppm	102.84	193.56
5	Element in samp., mg	0.51	0.97
24h sampling, sol. vol, mL	Element in sampling, ppm	103.04	181.44
3.25	Element in samp., mg	0.33	0.59
48h sampling, sol. vol, mL	Element in sampling, ppm	90.13	50.85
3.25	Element in samp., mg	0.29	0.17
72h sampling, sol. vol, mL	Element in sampling, ppm	10.21	11.76
3.25	Element in samp., mg	0.03	0.04
Volume of Lechate and Wash, mL	Element in wash, ppm	3.30	3.40
538	Element in wash, mg	1.78	1.83
	Element in solutions, mg	4.45	6.05
Mass of Residue, g	Element in residue, ppm	186.80	1742.50
94.6	Element in residue, mg	17.67	164.84
	Element mass total, mg	22.12	170.89
Extraction			
Calculated Head, g	Element in feed, ppm	221.23	1708.86
100	Element mass total, mg	22.12	170.89
Extraction	%	20.1%	3.5%
Balance Check	(Ouput-Input)/Input, %	-19.84	-70.41

Table E.25 Mass balance table for repeated baseline CZMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
55.02	Element in feed, ppm	317.60	1682.40
	Element in feed, mg	17.47	92.57
Mass of Feed Solution, g	Element in feed, ppm	0.00	71.68
220.1	Element in solution, mg	0.00	15.78
	Element mass total, mg	17.47	108.34
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	39.50	127.52
5	Element in samp., mg	0.20	0.64
2h sampling, sol. vol, mL	Element in sampling, ppm	42.56	133.24
5	Element in samp., mg	0.21	0.67
4h sampling, sol. vol, mL	Element in sampling, ppm	45.60	135.84
2.5	Element in samp., mg	0.11	0.34
8h sampling, sol. vol, mL	Element in sampling, ppm	50.20	138.12
2.5	Element in samp., mg	0.13	0.35
24h leachate, sol. vol, mL	Element in sampling, ppm	24.81	110.80
174	Element in samp., mg	4.32	19.28
Volume of Wash, mL	Element in wash, ppm	10.37	20.84
160	Element in wash, mg	1.66	3.33
	Element in solutions, mg	6.63	24.60
Mass of Residue, g	Element in residue, ppm	105.63	1519.10
54.44	Element in residue, mg	5.75	82.70
	Element mass total, mg	12.38	107.30
Extraction			
Calculated Head, g	Element in feed, ppm	224.93	2236.96
55.02	Element mass total, mg	12.38	123.08
Extraction	%	53.5%	32.8%
Balance Check	(Ouput-Input)/Input, %	-29.18%	-0.96%

Table E.26 Mass balance table for repeated baseline CZMC test 3 (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
99.61	Element in feed, ppm	328.25	1822.25
	Element in feed, mg	32.70	181.51
Mass of Feed Solution, g	Element in feed, ppm	0.00	76.40
398.4	Element in solution, mg	0.00	30.44
	Element mass total, mg	32.70	211.96
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	38.44	132.76
5	Element in samp., mg	0.19	0.66
2h sampling, sol. vol, mL	Element in sampling, ppm	43.82	142.20
5	Element in samp., mg	0.22	0.71
4h sampling, sol. vol, mL	Element in sampling, ppm	45.80	142.08
2.5	Element in samp., mg	0.11	0.36
8h sampling, sol. vol, mL	Element in sampling, ppm	51.28	152.60
2.5	Element in samp., mg	0.13	0.38
24h leachate, sol. vol, mL	Element in sampling, ppm	31.25	89.60
315	Element in samp., mg	9.84	28.22
Volume of Wash, mL	Element in wash, ppm	25.62	77.60
402	Element in wash, mg	10.30	31.20
	Element in solutions, mg	20.80	61.53
Mass of Residue, g	Element in residue, ppm	114.00	1399.35
97.1	Element in residue, mg	11.07	135.88
	Element mass total, mg	31.87	197.41
Extraction			
Calculated Head, g	Element in feed, ppm	319.91	1981.80
99.61	Element mass total, mg	31.87	197.41
Extraction	%	65.3%	31.2%
Balance Check	(Ouput-Input)/Input, %	-2.54%	-6.86%

Table E.27 Mass balance table for preliminary baseline NHMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input			
Mass of Feed Solid, g	Element	Ag	Cu
100	Element in feed, ppm	276.00	5658.03
	Element in feed, mg	27.60	565.80
Mass of Feed Solution, g	Element in feed, ppm	0.00	63.55
185.7	Element in solution, mg	0.00	11.80
	Element mass total, mg	27.60	577.61
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	84.18	431.42
5	Element in samp., mg	0.42	2.16
2h sampling, sol. vol, mL	Element in sampling, ppm	90.46	530.80
5	Element in samp., mg	0.45	2.65
4h sampling, sol. vol, mL	Element in sampling, ppm	100.63	678.90
5	Element in samp., mg	0.50	3.39
8h sampling, sol. vol, mL	Element in sampling, ppm	106.64	922.30
5	Element in samp., mg	0.53	4.61
24h sampling, sol. vol, mL	Element in sampling, ppm	111.71	807.80
3.25	Element in samp., mg	0.36	2.63
48h sampling, sol. vol, mL	Element in sampling, ppm	127.49	179.89
3.25	Element in samp., mg	0.41	0.58
72h sampling, sol. vol, mL	Element in sampling, ppm	4.08	120.08
3.25	Element in samp., mg	0.01	0.39
Volume of Lechate and Wash, mL	Element in wash, ppm	0.85	7.50
635	Element in wash, mg	0.54	4.76
	Element in solutions, mg	3.24	21.18
Mass of Residue, g	Element in residue, ppm	248.00	6155.20
82.2	Element in residue, mg	20.39	505.96
	Element mass total, mg	23.69	527.14
Extraction			
Calculated Head, g	Element in feed, ppm	236.86	5271.37
100	Element mass total, mg	23.69	527.14
Extraction	%	13.9%	4.0%

Balance Check	(Ouput-Input)/Input, %	-14.18	-8.74

Table E.28 Mass balance table for repeated baseline NHMC test (Initial condition of 20% solid to liquid, 0.1 M of thiosulfate, 0.7 M of total ammonia, 1 mM copper, pH 9.5, 25 °C)

Mass Balance			
Input		**Volume**	
Mass of Feed Solid, g	Element	Ag	Cu
98.65	Element in feed, ppm	292.00	6037.30
	Element in feed, mg	28.81	595.58
Mass of Feed Solution, g	Element in feed, ppm	0.00	74.30
394.6	Element in solution, mg	0.00	29.32
	Element mass total, mg	28.81	624.90
Output			
1h sampling, sol. vol, mL	Element in sampling, ppm	30.16	250.12
5	Element in samp., mg	0.15	1.25
2h sampling, sol. vol, mL	Element in sampling, ppm	31.70	261.12
5	Element in samp., mg	0.16	1.31
4h sampling, sol. vol, mL	Element in sampling, ppm	32.56	273.52
2.5	Element in samp., mg	0.08	0.68
8h sampling, sol. vol, mL	Element in sampling, ppm	35.76	290.48
2.5	Element in samp., mg	0.09	0.73
24h leachate, sol. vol, mL	Element in sampling, ppm	37.68	305.60
319	Element in samp., mg	12.02	97.49
Volume of Wash, mL	Element in wash, ppm	10.76	79.88
186	Element in wash, mg	2.00	14.86
	Element in solutions, mg	14.50	116.31
Mass of Residue, g	Element in residue, ppm	135.05	5348.65
95.44	Element in residue, mg	12.89	510.48
	Element mass total, mg	27.39	626.79
Extraction			
Calculated Head, g	Element in feed, ppm	277.65	6650.83
98.65	Element mass total, mg	27.39	656.10
Extraction	%	52.9%	22.2%
Balance Check	(Ouput-Input)/Input, %	-4.91%	0.30%