CUPRIC AMMONIACAL THIOSULFATE LEACHING OF NATURAL ACANTHITE ORE IN A CONTINUOUS CIRCUIT

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Chih Wei Chao

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The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, a thesis/dissertation entitled:

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submitted by Chih Wei Chao	in partial fulfillment of the requirements for
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inMaterials Engineering	
Examining Committee:	
David Dreisinger, Materials Engineering	
Supervisor	
David Dixon, Materials Engineering	
Supervisory Committee Member	
Berend Wassink, Materials Engineering	
Supervisory Committee Member	
Matthias Militzer, Materials Engineering	
Additional Examiner	

Additional Supervisory Committee Members:

Supervisory Committee Member

Supervisory Committee Member

Abstract

Cyanidation has been the conventional way to leach silver ore for many years. However, environmental concerns regarding the use and disposal of cyanide have increased public concern. Now, regulations have emerged that prevent or limit cyanide usage in many regions. Finding an alternative lixiviant for silver leaching is necessary to leach silver ores in these locations. Among the proposed alternative leaching agents, cupric-ammoniacal thiosulfate system is a very attractive solution. Although the research on cupric-ammoniacal thiosulfate leaching system has been conducted for many years, most of the experiments were performed in batch fashion. It is difficult to find scale-up leaching data or experiments. This thesis study aims to engineer a lab-scale continuous leaching system that uses cupric ammoniacal thiosulfate as the leaching agent. The goal is to mimic the industrial process and collect useful data for further research and application. The experiments started with a series of batch leaching tests to obtain the optimized leaching conditions for treatment of an ore sample containing acanthite received from Pan American Silver. Next, the optimized leaching conditions were applied to the continuous leaching tests. After leaching, two different types of recovery methods were studied to separate the silver from the pregnant leach solution. The two recovery methods are ion exchange and cementation. The tests results show that the leaching ability of cupric-ammoniacal thiosulfate system is good. The continuous leaching tests were run for 3 days with a 24-hour retention time in leaching and achieved an 86% silver leaching efficiency. Furthermore, the leached silver was easily recovered 100% by cementation. The ion exchange tests were not successful in demonstrating silver recovery from the leachate.

Lay Summary

Due to the public concern about using cyanide to process silver ore, investigating alternative chemical agents is gaining more attention. Cupric ammoniacal thiosulfate is one of the most promising alternatives to replace cyanide for treating silver ore. This research examined the performance of cupric ammoniacal thiosulfate for taking the silver out from a silver sulfide ore received from Pan American Silver. The experiments were carried out continuously with multiple reactors in series. Two different methods were investigated to recover the silver in the solution: ion exchange and cementation. The test results indicated 86% of the silver was extracted from the ore sample. Silver can be recovered by adding both copper and zinc to the silver containing solution. Therefore, cupric ammoniacal thiosulfate has been shown to be a viable agent to replace cyanide in silver ore processing.

Preface

This thesis is a continuation of a Master of Applied Science conducted by Yueh Lai. The foundation of this project originates from the consultations with Pan American Silver, together with my thesis supervisor Prof. David Dreisinger and myself. The experimental design, analysis and data collection were completed by me. The IC analysis method was developed with the help from Dr. Renaud Daenzer. The general inputs, direction and safety strategies were provided by Dr. Bé Wassink. All the solid assays were conducted at Kemetco Limited.

The thesis was composed by me and edited by my thesis advisor Dr. David Dreisinger.

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List of Abbreviations

3T- trithionate

4T- tetrathionate

AAS- atomic absorption spectroscopy, an analytical method to determine the elements concentration in solution

AM- ammonia

EDTA- ethylenediaminetetraacetic acid

HSC - HSC is an Outotec software for thermodynamic calculation

IC- ion chromatography, an analytical method to determine the anion concentration in solution

ICP-OES - Inductively coupled plasma optical emission spectrometry, an analytical method to determine the composition of elements

LPM - liter per minute

ORP - oxidation reduction potential

RPM - revolutions per minute

TS- thiosulfate

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Dedication

For Yu Chang Chao and Yen Fang Chou

Chapter 1: Introduction

Silver is one of the important metals in modern society. It has some unique characteristics that make it widely used in different areas. For example, good conductivity and malleability make silver widely applied in electronic components. Moreover, silver nanoparticles show the unique ability of penetration inside bacteria cells. This makes it an effective antibacterial agent (Dakal, Kumar, Majumdar, & Yadav, 2016). The combination of ability to polish to a fine finish and malleability makes silver a popular material for silverware and jewellery. Further, silver is used as an investment commodity and trading medium. Although the physical demand for silver coins and bars is not as high as the demand for industrial fabrication, about 15% of total physical demand in 2017 was held as an investment (*WORLD SILVER SURVEY*, 2018).

In 2017, about 86% of the world silver supply came from mine production, the rest was from refinery operations (*WORLD SILVER SURVEY*., 2018). In the mining industry, the conventional way to extract silver from the ore is through cyanidation. Cyanide is the dominant lixiviant in both gold and silver leaching but in some cases is not effective or not permitted for use. For example, cyanide is not applicable to treatment of carbonaceous ore due to preg-robbing of the metal cyanide species. If the ore has a high copper content, it could cause excessive cyanide consumption and make the leaching process economically unfavorable. Another drawback for using cyanide in leaching is the toxicity of the chemical. Hydrogen cyanide, which is produced from cyanide salt under acidic conditions, is fatal to humans. Moreover, cyanide release to the surroundings can cause environmental damage as occurred in the 2000 Baia Mare cyanide spill in Europe (Batha, 2000). Therefore, with the increasing concern over the environmental safety of cyanide use, many regions have prohibited the cyanide leaching technology.

To mitigate the problems mentioned above, investigation of alternative leaching agents for silver recovery has been provoked. Many alternative lixiviants are proposed, such as thiosulfate, thiourea, thiocyanate

and chlorine. Among the alternatives, thiosulfate is one of the promising leaching agents for both silver and gold ores. The effectiveness and low toxicity of the chemical make it attractive.

The history of using thiosulfate to treat precious metals can be dated back to the 1860's. Le Neve Foster described a thiosulfate leaching process, known as the Patera process in detail (Le Neve Foster, 1861). From the description, the ores were roasted under chloridizing conditions before being leached with thiosulfate. Although the ability of thiosulfate to form stable complexes with silver has been known for more than 100 years, in-depth research into the application of using ammonium thiosulfate as the leaching medium for treating precious metals did not start until the late 1970s (Aylmore & Muir, 2001; Marsden & House, 2006). Since then, many researchers have conducted investigations on this leaching system. However, most of the leaching experiments were done in batch mode. There is a lack of scaling up data for thiosulfate leaching of ores. In other words, the thiosulfate leaching process is still at the starting stage in the mining industry.

There were two main objectives in this work. The first was to engineer a continuous leaching system with cupric-ammonia-thiosulfate medium. The second one was to find a feasible method to recover silver from the thiosulfate leaching solutions. Starting with batch leaching tests on the ore samples received from Pan American Silver, four factors: air flow rate, ammonia concentration, copper concentration and EDTA concentration were investigated to find an optimum leaching condition. The condition found was then used in the main part of this thesis, the continuous leaching experiments. A continuous leaching system with four reactors in series was constructed. Two different slurry pulp densities: 20% and 30% were tested. After the leaching was done, two recovery methods, cementation and ion-exchange were tested. From the continuous leaching tests, leaching data as well as the possible obstacles or challenges for larger scale thiosulfate leaching could be determined. Thus, these experiments can provide the data for later research and improvement.

This thesis is composed of four parts. First is the relevant background study in chapter 2. Second is the experimental materials and analytical methods used in this thesis, which are all in chapter 3. The third

part includes all the experimental results and discussion, from chapter 4 to chapter 6. The last part is the conclusion and some suggestions for future work, which can be found in chapter 7.

Chapter 2: Literature Review

2.1 Copper Ammoniacal Thiosulfate Leaching System

Most of the research on the thiosulfate leaching system focuses on metallic gold leaching. Thus, in this literature review some of the leaching reactions involve gold species. Gold can slowly dissolve in thiosulfate solution in alkaline or near neutral solution (White, 1905). Oxygen works as the oxidant in the reaction. The reaction is shown in Reaction 2.1.

Reaction 2-1

 $4\mathrm{Au} + 8S_2O_3^{2-} + O_2 + 2H_2O \leftrightarrow 4[Au(S_2O_3)_2]^{3-} + 4OH^-$

The reason for using alkaline solution is to prevent thiosulfate decomposition at low pH. Although thiosulfate has ability to form a stable complex with gold, the slow kinetics make it impractical for commercial purpose. In the late 1970s, researchers started to investigate the thiosulfate system with ammonia and copper present (Aylmore & Muir, 2001). Numerous researchers showed that with the presence of ammonia and copper, the leaching kinetics can be dramatically improved. In this system, copper acts as a catalyst for gold oxidation and ammonia stabilizes copper in the system.

In this leaching system, gold can be oxidized by cupric ammine. Reaction 2-2 shows the redox reaction of metallic gold dissolution.

Reaction 2-2

 $\mathrm{Au} + \mathrm{Cu}(NH_3)_4^{2+} + 5S_2O_3^{2-} \leftrightarrow \mathrm{Au}(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3$

The cupric and cuprous couple in ammoniacal thiosulfate solution catalyzes the leaching of gold. The cupric species is regenerated by reaction with oxygen in an aerated system as shown in Reaction 2-3.

$$2\operatorname{Cu}(S_2O_3)_3^{5-} + 8NH_3 + \frac{1}{2}O_2 + H_2O \leftrightarrow 2\operatorname{Cu}(NH_3)_4^{2+} + 6S_2O_3^{2-} + 2OH^{-1}$$

If Reaction 2-2 and 2-3 are combined, the overall reaction would be as follows:

Reaction 2-4

$$4\text{Au} + 8S_2O_3^{2-} + O_2 + 2H_2O \leftrightarrow 4\text{Au}(S_2O_3)_2^{3-} + 4OH^{-}$$

The overall reaction above shows that the copper acts as a catalyst in the system. Metallic silver follows a similar leaching reaction as gold in copper ammoniacal thiosulfate system, which is by oxidation (Zipperian, Raghavan, & Wilson, 1988). However, the leaching mechanism for silver sulfide appears to be different. It is reported to be the substitution of copper for silver in the solid sulfide (Briones & Lapidus, 1998). The reactions are shown in Reaction 2-5 and 2-6 (Aylmore & Muir, 2001).

Reaction 2-5

$$2Cu(S_2O_3)_3^{5-} + Ag_2S \rightarrow 2Ag(S_2O_3)_3^{5-} + Cu_2S \text{ (chalcocite)}$$

Reaction 2-6
 $Cu(NH_3)_4^{2+} + Ag_2S + 6S_2O_3^{2-} \rightarrow 2Ag(S_2O_3)_3^{5-} + CuS \text{ (covellite)} + 4NH_3$

Another way to explore the chemistry of the cupric-ammoniacal thiosulfate leaching system is through the metastable Eh-pH diagram, which shows the metastable species in the leaching range of interest. Note that thiosulfate is not thermodynamically stable but will persist in solution for an extended period. Figure 2.1 is the Eh-pH diagram for the system containing 1mM silver, 0.1 M thiosulfate and 0.7 M ammonia. The figure shows that the silver is readily soluble in the leaching system. As long as the potential is maintained at a certain level, silver thiosulfate is stable. If the potential is low, silver will precipitate as silver sulfide for the whole range of the pH. Note that ammonia species do not appear and hence ammonia is note required to keep Ag(I) in solution.



Figure 2.1 The Eh-pH diagram for Ag-S₂O₃²⁻-NH₃ system with 1mM silver, 0.1 M thiosulfate and 0.7 M ammonia (Lai, 2017)

The Eh-pH diagram for 1 mM copper, 0.1 M thiosulfate and 0.7 M ammonia is shown in Figure 2.2. In the Eh-pH range of interest for leaching, the dominant copper species can be cupric tetraamine complex or cuprous thiosulfate complexes depending on the solution potential. But if the potential drops to less than 0 mv, the copper could precipitate to form copper(I) sulfide.



Figure 2.2 The Eh-pH diagram for Cu-S₂O₃²⁻-NH₃ with 1mM copper, 0.1 M thiosulfate and 0.7 M ammonia (Lai, 2017)

Thiosulfate is a metastable anion that can undergo decomposition in solution. Many factors influence the stability of thiosulfate in solution, for example, concentration, pH of solutions, the presence of sulfur metabolising bacteria, certain metals and exposure to the ultraviolet light (Dhawale, 1993). Figure 2.3 shows the Eh-pH diagram for S-H₂O metastable system with 1 M sulfur species. Thus, the thermodynamically stable sulfur species, such as sulfate and bisulfate are omitted from the plot. The area for metastable thiosulfate in the Eh-pH diagram is relatively narrow. The oxidation of thiosulfate to tetrathionate is known to proceed rapidly at modest oxidation potentials. When comparing the previous two Eh-pH plots it can be concluded that silver and copper form thiosulfate complexes over a wide range while the metastable region of stability for thiosulfate is relatively small.



Figure 2.3 The Eh-pH diagram for metastable S-H₂O system with 0.1 M sulfur by HSC 6.0

The combination of copper, ammonia and thiosulfate increases the complexity of the system. For instance, copper can not only catalyze the silver dissolution, but also oxidize the thiosulfate. The thiosulfate oxidation by copper forms tetrathionates and makes the system even more complex. The simplified oxidation reaction can be found in Reaction 2-7 (P. L. Breuer & Jeffrey, 2000; Daenzer, 2017). The tetrathionate can undergo alkaline hydrolysis to form trithionate and thiosulfate. This is shown in Reaction 2-8.

Reaction 2-7 $8S_2O_3^{2-} + 2Cu(NH_3)_4^{2+} \leftrightarrow 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} + 8NH_3$ Reaction 2-8 $4S_4O_6^{2-} + 60H^- \leftrightarrow 2S_3O_6^{2-} + 5S_2O_3^{2-} + 3H_2O$ Another thiosulfate decomposition pathway is shown in Reaction 2-9 (Zhang & Senanayake, 2016). This reaction was found to be a first order reaction with thiosulfate being the rate determined factor.

Reaction 2-9

 $S_2O_3^{2-}+O_2+H_2O+2NH_3\leftrightarrow 2SO_3^{2-}+2NH_4^+$

Oxygen can oxidize thiosulfate; however, the oxidation in alkaline solution under normal temperature and pressure is very slow (P. Breuer, 2002). Another study showed the reaction occurs readily in the temperature range 75°C to 87°C (Rolia & Chakrabarti, 1982). The rate of oxidation increased with the increasing temperature. Reaction 2-10 shows the thiosulfate oxidation by oxygen.

Reaction 2-10

 $S_2 O_3^{2-} + 2O_2 + H_2 O \leftrightarrow 2SO_4^{2-} + 2H^+$

Even though direct thiosulfate oxidation by oxygen is very slow, oxygen can rapidly oxidize cuprous to cupric. The cupric continues oxidizing thiosulfate and increases the reaction rate between oxygen and thiosulfate. Hence, the thiosulfate decomposition rate increased (P. L. Breuer & Jeffrey, 2003). Reaction 2-11 shows the rapid reaction for Cu(I)/Cu(II) oxidation by oxygen.

Reaction 2-11

$$2Cu(I) + \frac{1}{2}O_2 + H_2O \leftrightarrow 2Cu(II) + 2OH^2$$

The copper ammoniacal thiosulfate leaching system is complex. The leaching rate can be affected by different variables, such as the ammonia/thiosulfate ratio, copper concentration and dissolved oxygen. Moreover, these factors could be interdependent.

2.2 Chemistry of EDTA in Cupric Ammoniacal Thiosulfate System

Ethylenediaminetetraacetic acid (EDTA) is a chelating agent that can bind with metal ions. It has been suggested as an additive to promote the cupric ammoniacal thiosulfate leaching system (Feng & van Deventer, 2010). EDTA can complex with cupric in leaching solution to reduce the oxidation of thiosulfate. Feng and Deventer showed that adding EDTA to the cupric ammoniacal thiosulfate leaching system can greatly increase gold extraction (Feng & van Deventer, 2010). However, adding too much

EDTA could be detrimental to the leaching reactions. In cupric ammoniacal thiosulfate system with EDTA, copper can complex with both ammonia and EDTA. The reactions with their log K values are shown below (Puente-Siller, Fuentes-Aceituno, & Nava-Alonso, 2014).

Reaction 2-12

 $Cu^{2+} + 4NH_3 \leftrightarrow Cu(NH_3)_4^{2+}$ log K=12.46

Reaction 2-13

 $Cu^{2+} + EDTA^{4-} \leftrightarrow Cu(EDTA)^{2-}$ log K=20.57

The log K values show that $Cu(EDTA)^{2-}$ is a stronger complex than $Cu(NH_3)_4^{2+}$. Therefore, the substitution of silver in silver sulfide with copper in Reaction 2-5 would be more difficult. Hence, the leaching process could be slowed down.

2.3 Ion-Exchange

Ion exchange is a process in which ions in solution exchange with ions present in the ion exchange adsorbent. The ion exchangers are insoluble materials with fixed ion exchange sites that contain exchangeable cations or anions. The exchanging ions between the solution and the ion exchangers are in stoichiometrically related. Ion exchangers can include natural materials such as soil and swelling clay. In hydrometallurgy, the common material used for ion exchange process is usually in the form of a synthetic resin particle. An ion exchange resin is composed of two parts: a polymer matrix which serves as a structural part and an ion-active group which acts as a functional part (Schmoker, 1996). There are three groupings of ion exchange resin based on their functional groups: cationic, anionic, and chelating. Cationic resin indicates its function group contains exchangeable cations for the ion exchange process. The same relationship holds for anionic resins. For chelating resins, the functional groups chelate to the ions. Since the goal is to separate the silver thiosulfate $(Ag(S_2O_3)_2^3)$ which is an anion, away from other species in solution, anionic resins were used in this work. A generalized anionic exchange reaction is shown below:

Reaction 2-14

$R^+A^- + B^- \leftrightarrow R^+B^- + A^-$

Where: R^+A^- is the functional group

 $R^{\scriptscriptstyle +} \text{is the fixed ion in the functional group}$

A⁻ is the exchangeable anion in the functional group

B⁻ is the exchangeable anion (target anion) in the solution

Under certain conditions, the selectivity for the target anion can be greater than for other anions in the solution. The proper exchange conditions are affected by the pH of the system, the species concentration in the solution and the mode of solution and resin contact.

Strong base resin has a quaternary ammonium functional group possessing a permanent positive charge.

Therefore, silver thiosulfate, which is an anion, can be extracted by a strong base ion exchange reaction.

Reaction 2-15 shows the ion exchange for gold thiosulfate (Schmoker, 1996).

Reaction 2-15

 $3|-NR_3^+A^- + Au(S_2O_3)_2^{3-} = (|-NR_3^+)_3Au(S_2O_3)_2^{3-} + 3A^-$

Where: |- is the matrix of the resin R is the methyl group A⁻ is the exchangeable anion in the functional group

2.4 Cementation of Silver from Thiosulfate System

Cementation is a technology that uses a metal as a reducing agent to electrochemically precipitate another metal. It is a common practice to recover silver by this method after a leaching process (Fabián, Ficeriová, Briančin, & Harvanová, 2013; Parga, Wan, & Miller, 1988; V. Figueroa Martinez, R. Parga Torres, L. Valenzuela García, C. Tiburcio Munive, & González Zamarripa, 2012). Zinc and copper are the typical cementing agents.

2.4.1 Copper Cementation of Silver

Copper as a cementing agent in the cupric-ammoniacal thiosulfate leaching system has benefits (Perez, Nacameri, & Stoll, 1987). Copper acts as a catalyst in the thiosulfate leaching system. Therefore, maintaining a certain level of copper in the leaching solution is important. Using copper as the cement material can replenish the loss of copper from the solution. When recycling the solution after cementation for further leaching process, the addition of copper may be reduced. Another benefit is not adding other ions (besides copper) as impurities to the recirculating solution that may be detrimental to the leaching process. Reaction 2-16 and Reaction 2-17 show the copper cementation reactions with silver thiosulfate.

Reaction 2-16

Reaction 2-18

Cu + 2[$Ag(S_2O_3)_2$]^{3−} → 2Ag + 4 $S_2O_3^{2−}$ + Cu^{2+} Reaction 2-17

 $Cu + [Ag(S_2O_3)_2]^{3-} → Ag + 2S_2O_3^{2-} + Cu^+$

2.4.2 Zinc Cementation of Silver

Zinc is a well-known cementing agent for recovery of gold from cyanide solution by the Merrill-Crowe process. One of the benefits for zinc over copper is the cost. The price of zinc is less than half of the copper price. In the ammoniacal system, the zinc ion could complex with ammonia forming zinc-ammonia complex quickly (Karavasteva, 2010; Navarro, Alvarez, Vargas, & Alguacil, 2004). Furthermore, the zinc-ammonia complex can undergo some reactions to form zinc oxide and zinc hydroxide. The reactions are shown below. Reaction 2-18 is the zinc cementation with silver thiosulfate. Reaction 2-19 is the zinc ion complex with the ammonia. Reaction 2-20 and 2-21 are the zinc-ammonia alkaline hydrolysis reactions with different products.

 $Zn + 2[Ag(S_2O_3)_2]^{3-} \rightarrow 2Ag + 4S_2O_3^{2-} + Zn^{2+}$ Reaction 2-19 $Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$ Reaction 2-20 $[Zn(NH_3)_4]^{2+} + 2OH^- \rightarrow ZnO + H_2O + 4NH_3$ Reaction 2-21 $[Zn(NH_3)_4]^{2+} + 2OH^- \rightarrow Zn(OH)_2 + 4NH_3$

As a relatively strong reducing agent, zinc can reduce thiosulfate and form insoluble zinc sulfide (Guerra, 1997). The precipitation of zinc sulfide on the metal surface can adversely impact the cementation. The reaction is shown below:

Reaction 2-22 $Zn + S_2 O_3^{2-} \rightarrow \text{ZnS} \downarrow + SO_3^{2-}$

2.5 Summary

The extraction of silver with copper-ammonium-EDTA-thiosulfate solutions appears well suited to treatment of silver ores containing acanthite mineral. The leaching conditions required must be optimized for maximum silver extraction, stability of silver in solution (avoidance of precipitation) and minimum consumption of thiosulfate reagent. Further, the recovery of silver from a thiosulfate leaching solution by ion exchange or cementation appears to be a promising route to complete the main elements of the thiosulfate processing of silver ores containing acanthite.

Therefore, the purpose of this study is to advance the leaching of a silver ore by thiosulfate leaching and demonstrating a continuous circuit for this purpose. The recovery of silver from the leachate by ion exchange or cementation were also investigated to complete the basic flowsheet development.

Chapter 3: Materials and Methods

3.1 Ore Preparation

The ore samples used for all experiments were provided by Pan American Silver. The samples were drawn from the Loma de la Plata deposit in Argentina within the Navidad Project site. The mineralogy data provided by Pan American Silver were provided in Table 3-1.

	Deep Composite, %	Pilot Plant Composite, %	Shallow Composite, %	
Silver Minerals	0.02	0.06	0.02	
Copper Sulphides	0.28	0.20	0.02	
Galena	0.10	0.14	0.04	
Goethite	1.50	2.23	1.50	
Pyrite	0.03	0.10	0.07	
Quartz	15.0	13.7	15.0	
Feldspars	51.1	47.8	46.6	
Micas	13.3	11.9	15.2	
Amphibole/Pyroxene	5.10	7.24	6.08	
Calcite	5.98	8.07	6.65	
Barite	1.50	3.02	2.69	
Garnet	1.03	1.21	2.10	
Apatite	0.50	0.41	0.50	
Kaolinite' (clay)	0.16	0.24	0.36	
Ti Minerals	1.93	1.81	1.41	
Others	2.45	1.81	1.76	
Total	100	100	100	

Table 3-1 The mineral composition of the Loma de la Plata sample

The table shows five most abundant minerals are feldspars, quartz, micas, amphibole/pyroxene, and calcite. In this Loma de la Plata deposit, silver is found mostly as silver sulfide (Lai, 2017). Also, silver oxide has been identified. The head assay for the copper and silver concentration are shown in Table 3-2. The head assay was done by Bureau Veritas.

Table 3-2 The head assay results for the ore sample

Element	Unit	
Cu	ppm	1338
Ag	ppm	300

The original particle size (P80) for the ore sample received is 508 μ m (Lai, 2017). Before leaching tests, the particle size for the ore samples was reduced by wet grinding. Grinding and sieving were conducted in the Coal and Mineral Processing Laboratory at UBC. The wet grinding was conducted in a rod mill with 20 rods inside. Each grinding batch had 1 kg of solid with 670 ml water, which was 60% solid. The speed of the rod mill was set to 30 rpm and the retention time for the grinding process was 30 minutes. After 30 minutes, the pulp was washed out from the mill and transferred to a pressure filter for filtration. The solid cake left in the pressure filter was then dried in an oven at 65°C. A roller was used to homogenize the dried samples after the solid cake was fully dried. Using coning and quartering, the dried samples were separated to the desired aliquots for the leaching tests. Also, a small portion of the solid was taken after coning and quartering for particle size analysis. The grinding process for the batch leaching tests and continuous leaching tests were performed separately. For the batch leaching tests, the particle size analysis was done by sieves. For the continuous leaching test, the particle size analysis was done using the Malvern Mastersizer 2000. Figure 3.1 show the particle size distribution for the two samples (for batch leaching test and the continuous leaching test).



Figure 3.1 Size distribution for the batch leaching test and continuous leaching test ground samples

The P80 values are summarized in Table 3-3.

Table 3-3 The P80 values for the batch leaching test and continuous leaching test samples

	P80 (µm)
Batch leaching	59
Continuous leaching	41

3.2 Analytical methods and Method Development

3.2.1 Sampling Procedure

Solution samples were withdrawn from leach reactors using auto-pipettes. The sample in the auto-pipette tip was then transferred into a luer-lock syringe connected to 0.2 µm nylon filter for filtration. The filtrate was recovered for silver, copper and polythionates analysis.

The solid samples preparation is described as follows. After the leaching test was done, the residue was filtered and washed with deionized water. The wet solid cake was then dried in an oven at 60°C. After the

residue was dried, a roller was used to homogenize the solids. A solid sample was taken from the homogenized residue and sent to the off-site laboratory for analysis.

3.2.2 Atomic Absorption Spectroscopy

AAS analysis was applied for determining the silver and copper concentration in solution. The analysis was conducted on a Varian AA420 AAS with an air-acetylene flame. For measuring the silver concentration, a silver hollow cathode lamp with a wavelength of 328.1 nm and a current of 4 mA was used. For copper analysis, a copper hollow cathode lamp with a wavelength of 324.8 nm and a current of 4 mA was used. Each AAS run for one sample provided three absorbance measurements with representative precisions of 1-2 % relative standard deviation. Usually, each sample would have two AAS runs under the same calibration curve if the volume of sample solution was enough. The average of the measurement was reported.

3.2.2.1 AAS Standard Solution Preparation

An AAS standard for silver analysis was prepared from Sigma-Aldrich Silver Standard for AAS with the concentration of 997 ± 5 mg/L. For copper AAS standard, SCP Science Copper AA Standard with the concentration of 1002 ± 5 mg/L was used. The original AAS standard was diluted to 100 ppm with DI water for both elements. These 100 ppm solutions of silver and copper were the stock solutions for making 1, 2, 4 and 5 ppm standard solutions. The stock solutions were prepared fresh every month. To match the solution matrix of the samples, the 1, 2, 4 and 5 ppm standard solutions contained the desired thiosulfate concentration. The desired thiosulfate concentration was the same value as the initial thiosulfate concentration of the leaching test. To make sure the thiosulfate did not decompose during the dilution, the pH of the volumetric amounts of standard solutions were increased from acidic condition to a slightly basic condition before adding thiosulfate salts. The pH adjustment was done by adding sodium hydroxide with the colour indicator phenolphthalein.

3.2.2.2 AAS Sample Preparation

After following the steps in Sampling Procedure section, a clear sample solution can be obtained. For the AAS analysis, the clear solution should be diluted to a concentration that is within the calibration range. In this project, both the silver and copper calibration ranges were between 1 ppm to 5 ppm. Moreover, the thiosulfate concentration of the AAS sample and the initial leaching test should be the same. Therefore, the AAS samples were diluted to desired thiosulfate concentration as mentioned in AAS Standard Solution Preparation section.

3.2.3 Ion Chromatography

Thiosulfate, trithionate and tetrathionate concentrations were analyzed by Ion Chromatography (IC). To avoid the problem of ongoing degradation of thiosulfate and other thiosalts species, all the IC tests were performed immediately after the sampling. The Dionex DX600 ion chromatograph and an AD25 absorbance UV-Vis detector were used. The wavelength was set to 214 nm. A 4x50 mm AG16 guard column and a 4x250 mm IonPac AS16 anion exchange analysis column were connected in series. The mobile phase was composed of a 0.2 M sodium perchlorate solution with a flow rate of 1 mL/min. The 0.2 M sodium perchlorate solution was prepared in 18.2 M Ω deionized water and was filtered with 0.2 µm membrane filter through vacuum filtration. Sodium perchlorate was chosen as the mobile phase due to its low UV absorbance. An example of a typical IC chromatogram is shown in Appendix A.

Chapter 4: Batch Leaching

4.1 Objectives and Approach

The objective of this set of experiments was to optimize the thiosulfate leaching condition for the ore received in order to maximize silver extraction. The optimum thiosulfate concentration for the ore sample used in this project was taken from the work of Lai (Lai, 2017). However, as mentioned in section 2.1, there are many factors affect the performance of the cupric ammoniacal thiosulfate leaching system. Therefore, four variables: air flow rate, ammonia concentration, copper concentration, and EDTA concentration were investigated to optimize the extraction to form the basis for the continuous leaching tests. The leaching conditions for each experiment are tabulated below.

Experiment ID	Base	Air	Cu1	Cu2	EDTA1	EDTA2	AM
Pulp density (w/w%)	20	20	20	20	20	20	20
pН	9	9	9	9	9	9	9
Temperature (°C)	30	30	30	30	30	30	30
Agitation (rpm)	700	700	700	700	700	700	700
Retention time (hour)	48	48	48	48	48	48	48
[TS] (M)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Total [AM] (M)	1	1	1	1	1	1	0.4
[Cu] (mM)	0.5	0.5	0.2	1	0.5	0.5	0.5
EDTA (mM)	0.5	0.5	0.5	0.5	0.25	1	0.5
Air flow rate (LPM)	0.1	0.2	0.1	0.1	0.1	0.1	0.1

Table 4-1 The experimental conditions for the batch leaching tests

The thiosulfate was added as ammonium thiosulfate. The source of ammonia was from ammonium thiosulfate and ammonium sulfate. The cupric was added as cupric sulfate.

4.2 Experimental Procedures

Leaching tests were conducted in a sealed 500-ml glass reactor with thermo-jacket. The temperature was controlled by a circulating water bath that maintained 30°C for all experiments. A pH electrode, a redox electrode, and an air sparging tube were inserted through the lid of the reactor. Mixing was carried out by overhead agitation with a Cole Parmer motor rotating at 700 rpm. All the redox potentials in this thesis

were reported as referred to the standard hydrogen electrode. The redox electrodes used in all experiments had a Ag/AgCl reference electrode with saturated KCl. The standard potential of Ag/AgCl reference electrodes can be expressed as a function of temperature, which is shown in equation 4-1 (Brajter-Toth, 1996).

Equation 4-1

$E = 199 - 1.01 \times (T - 25^{\circ}C)$

The reactor was initially filled with 100 g of ore sample and 350 ml deionized water. Then the reactor was sealed with the lid that had a pH probe, a redox probe and an air sparging tube inserted. The stirring motor was started at low speed for gentle mixing. The air sparge was started at this point. After the pulp was well mixed, the required amount of ammonium sulfate, cupric sulfate and EDTA were added to the reactor through the sampling port. The pH was adjusted to 9 by adding 8 N sodium hydroxide. After adjusting the pH, the required amount of ammonium thiosulfate was added to the reactor. The leach solution was topped up to 400 ml with deionized water and was adjusted to pH 9 again. Then the stirring speed was increased to 700 rpm to start the leaching test. The retention time for all batch leaching tests was 48 hours. For taking kinetic samples, a 15 ml slurry sample was taken from the leaching reactor without stopping the agitation. It was transferred into a test tube for centrifugation at 4000 rpm for two minutes. The clear solution was then pipetted out and filtered by the method mentioned in section 3.2.1. The remaining moist solid and the clear solution left were remixed by shaking the test tube vigorously. The mixed slurry was return to the reactor after shaking. Figure 4.1 shows the leaching reactor with the lid.



Figure 4.1 The batch leaching reactor apparatus

The content of Ag and Cu in solution were tested by AAS in this lab. The final residues were dried in an oven and then sent to Kemetco for chemical analysis by digestion and ICP-OES analysis. The polythionates concentration were determined by IC in this lab.
4.3 Results and Discussion

4.3.1 Effect of Air Flow Rate

The effect of air flow rate on the leaching system was investigated in two tests: one with 0.1 LPM air flow rate and another one with 0.2 LPM air flow rate. The leaching conditions are highlighted in Table 4-2.

Experiment ID	Base	Air
Pulp density (w/w%)	20	20
pH	9	9
Temperature (°C)	30	30
Agitation (rpm)	700	700
Retention time (hour)	48	48
[TS] (M)	0.2	0.2
Total [AM] (M)	1	1
[Cu] (mM)	0.5	0.5
EDTA (mM)	0.5	0.5
Air flow rate (LPM)	0.1	0.2

Table 4-2 The leaching condition for air flow rate tests

The pH and Eh for the two tests are shown in Figure 4.2. The graph shows that air flow rate did not affect the pH and Eh. The pH stayed at around 9 throughout the leaching tests. The Eh slightly increased over 48 hours for both air flow rates. The increment was less than 20 mV. Moreover, the Eh difference between the two tests was small. They were almost identical.



Figure 4.2 The pH and Eh for the air flow rate tests (0.2 M thiosulfate, 1 M total AM, 0.5 mM cupric, 0.5 mM EDTA, pH 9, 30°C and 700 rpm)

Silver and copper extraction with time are shown in Figure 4.3. The head assay and final residue assay for silver and copper are shown in Table 4-3. Both the extraction curves and solid assay values show that the lower air flow rate test had slightly higher silver extraction than the higher air flow rate test. The final silver extraction for 0.1 LPM air flow rate was 95%. Increasing the air flow rate to 0.2 LPM decreased the final extraction to 93%. These two values are close enough to conclude that there is little impact of aeration rate change. The aeration rate also had a small influence on copper extraction. Before 10 hours,

the two trending curves were very close to each other and then diverged slightly. In the end, the copper extraction was 22% for both 0.1 LPM and 0.2 LPM based on very similar residue assays.



Figure 4.3 The silver and copper extractions with time for different air flow rates (0.2 M thiosulfate, 1 M total AM, 0.5 mM cupric, 0.5 mM EDTA, pH 9, 30°C and 700 rpm)

Table 4-3 Initial feed and final resi	tue assay for silver and copp	er
---------------------------------------	-------------------------------	----

Experiment ID	Silver	(ppm)	Copper (ppm)	
Experiment ID	Initial	Final	Initial	Final
Base (0.1 LPM air flow rate)	301.4	12.7	650.0	473.2
Air (0.2 LPM air flow rate)	301.4	18.4	650.0	486.3

Higher air flow rate resulted in higher thiosulfate consumption. Figure 4.4 shows the concentration of polythionates for the two tests. After 48 hours, the 0.1 LPM air flow rate test had higher thiosulfate concentration, which was 14.2 g/L. Its trithionate and tetrathionate concentrations were lower compared to 0.2 LPM air flow rate test. This indicates higher air flow rate increased the thiosulfate oxidation. However, the increment of thiosulfate consumption was not severe. For 0.2 LPM air flow rate test, the final thiosulfate concentration was 12.4 g/L.



Figure 4.4 The polythionates concentration for different air flow rate (0.2 M thiosulfate, 1 M total AM, 0.5 mM cupric, 0.5 mM EDTA, pH 9, 30°C and 700 rpm)

Increasing the air flow rate from 0.1 LPM to 0.2 LPM did not affect silver and copper extraction much. However, almost half of the initial thiosulfate was consumed after leaching for the 0.2 LPM air flow rate test. The higher air flow rate raises the possibility of contact between cuprous and oxygen, which could promote the oxidation of cuprous to cupric. As a result, the thiosulfate decomposition by cupric oxidation is accelerated.

4.3.2 Effect of Copper Concentration

The effects of the initial copper concentration on the leaching system were examined. Three different copper concentrations: 0.2 mM, 0.5 mM and 1 mM were tested. The more detailed experimental conditions for the three tests are tabulated in Table 4-4.

Experiment ID	Base	Cu1	Cu2
Pulp density (w/w%)	20	20	20
pН	9	9	9
Temperature (°C)	30	30	30
Agitation (rpm)	700	700	700
Retention time (hour)	48	48	48
[TS] (M)	0.2	0.2	0.2
Total [AM] (M)	1	1	1
[Cu] (mM)	0.5	0.2	1
EDTA (mM)	0.5	0.5	0.5
Air flow rate (LPM)	0.1	0.1	0.1

Table 4-4 The leaching conditions for copper tests

The pH and Eh data are shown in Figure 4.5. From the graph, the initial copper concentration did not affect pH. All three tests had pH maintained around 9 throughout the leaching process. The Eh difference between the three tests was small. The number was within 20 mV, which can be considered insignificant. All three tests had Eh increased slightly after 48 hours. The increment was less than 10 mV.



Figure 4.5 The pH and Eh for different initial copper concentration (0.2 M thiosulfate, 1 M total AM, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Figure 4.6 shows the silver and copper extractions for different initial copper concentration. Table 4-5 summarizes the head assay and final residue assay for silver and copper. Higher copper concentration resulted in higher silver extraction. But the difference between 1 mM copper and 0.5 mM copper was small. The silver extraction for 0.5 mM and 1 mM copper were 95% and 96%, respectively. The 0.2 mM copper had the lowest silver extraction, which was 92%. In contrast to silver extraction, lower solution copper concentration resulted in higher copper extraction. However, the differences in copper extraction between the three tests were small. The final copper extraction for 0.2 mM, 0.5 mM and 1 mM copper were 23%, 22% and 20% respectively.



Figure 4.6 The silver and copper extraction for different copper concentration (0.2 M thiosulfate, 1 M total AM, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Europin ont ID	Silver (ppm)	Copper (ppm)		
Experiment ID	Initial	Final	Initial	Final	
Cu1 (0.2 mM Cu)	301.4	21.4	650.0	475.0	
Base (0.5mM Cu)	301.4	12.7	650.0	473.2	
Cu2 (1 mM Cu)	301.4	10.9	650.0	502.3	

Table 4-5 Initial feed and final residue assay for silver and copper

Figure 4.7 shows the polythionates concentrations for different initial copper concentrations. The 1 mM Cu test had the highest thiosulfate consumption. Its thiosulfate concentration dropped from 22.1 g/L to 11.4 g/L, which is almost half of the original concentration. As a result, the trithionate and tetrathionate concentrations were the highest among the three tests. The test with 0.2 mM Cu had the lowest thiosulfate consumption. After 48 hours the thiosulfate concentration dropped to 17.2 g/L, which is about 78% of its original concentration. This shows that the copper concentration affects the thiosulfate oxidation. Higher initial copper concentration in the leaching solution will result in more thiosulfate consumption.



Figure 4.7 The polythionates concentration for different copper concentration (0.2 M thiosulfate, 1 M total AM, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Copper plays an important role in the cupric ammoniacal thiosulfate leaching system. For silver sulfide leaching, the main leaching reaction is the substitution between copper and silver in the sulfide mineral (Reaction 2-5). From this perspective, higher initial copper concentration can make the leaching faster. However, copper can oxidize thiosulfate as well. Therefore, higher copper concentration will consume more thiosulfate and generate more trithionate and tetrathionate. For copper extraction, the high initial copper concentration in the solution can hinder the copper extraction.

4.3.3 Effect of EDTA Concentration

The effects of initial EDTA concentration on the leaching system were examined. Three different EDTA concentrations: 0.25 mM, 0.5 mM and 1 mM were tested. The leaching conditions for the EDTA tests are tabulated in Table 4-6.

Experiment ID	Base	EDTA1	EDTA2
Pulp density (w/w%)	20	20	20
pH	9	9	9
Temperature (°C)	30	30	30
Agitation (rpm)	700	700	700
Retention time (hour)	48	48	48
[TS] (M)	0.2	0.2	0.2
Total [AM] (M)	1	1	1
[Cu] (mM)	0.5	0.5	0.5
EDTA (mM)	0.5	0.25	1
Air flow rate (LPM)	0.1	0.1	0.1

Table 4-6 The leaching conditions for EDTA tests

The pH and Eh data for EDTA tests are shown in Figure 4.8. The graph shows that EDTA concentration did not affect pH. The pH stayed close to 9 throughout the leaching tests. For Eh, 0.25 mM EDTA and 1 mM EDTA have almost identical curves. The 0.5 mM EDTA test has the highest Eh curve, which is about 20 mV higher than 0.25 mM EDTA and 1 mM EDTA. The Eh increased slightly for all three tests.



Figure 4.8 The pH and Eh for different initial EDTA concentration (0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

The silver and copper extraction for different EDTA concentrations are shown in Figure 4.9. The solid assay for silver and copper from initial and final solids are tabulated in Table 4-7. The silver extraction curves are almost identical for 0.25 mM EDTA and 0.5 mM EDTA. The silver extraction was 95% for both 0.25 mM and 0.5 mM EDTA test. Solid assay also shows that final silver concentrations in the residues were very close for 0.25 mM and 0.5 mM EDTA tests. When the EDTA concentration was increased to 1 mM, the silver extraction slightly dropped to 93%. Moreover, the leaching kinetics is slower than the leaching kinetics of the two lower EDTA concentrations tests. The copper extraction had no big difference between the three EDTA concentrations tests. The highest extraction happened at the 1 mM EDTA, which was 24%. For 0.25 mM and 0.5 mM EDTA test, the copper extractions were 21% and 20% respectively.



Figure 4.9 The silver and copper extraction for different initial EDTA concentrations (0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Table 4-7 Initial feed and final residue assay for silver and copper

Exposiment ID	Silver (ppm)	Copper (ppm)		
Experiment ID	Initial	Final	Initial	Final	
EDTA1 (0.25 mM EDTA)	301.4	11.7	650.0	491.2	
Base (0.5 mM EDTA)	301.4	12.7	650.0	473.2	
EDTA2 (1 mM EDTA)	301.4	18.2	650.0	475.8	

The polythionates concentrations data are shown in Figure 4.10. The largest reduction of thiosulfate concentration was observed for the 1 mM EDTA test. The thiosulfate concentration dropped from 22 g/L to 11.4 g/L. Almost half of the initial thiosulfate was consumed. As a result, the final trithionate and tetrathionate concentrations for the 1 mM EDTA were the highest. The 0.5 mM EDTA test maintained the highest thiosulfate concentration after 48 hours, (14.2 g/L) and consequently the trithionate and tetrathionate concentrations were the lowest.



Figure 4.10 The polythionates concentration for different EDTA concentration (0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

EDTA can complex with cupric and form Cu(EDTA)²⁻. The reaction is shown in Reaction 4-1(Puente-Siller et al., 2014).

Reaction 4-1

 $Cu^{2+} + EDTA^{4-} \leftrightarrow Cu(EDTA)^{2-}$

The complexing reaction shows that the EDTA can stabilize the cupric species in the solution. Both the cupric EDTA complex and the cupric tetraamine can lead to copper substitution of the silver in the sulfide matrix. Reaction 4-2 and 4-3 demonstrate the substitute reactions (Puente-Siller et al., 2014).

Reaction 4-2 $Cu(NH_3)_4^{2+} + Ag_2S + 4S_2O_3^{2-} \rightarrow 2Ag(S_2O_3)_2^{3-} + CuS + 4NH_3$

Reaction 4-3

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

However, the cupric EDTA complex is more stable than cupric tetraamine. Therefore, the substitution would slow down if too much cupric EDTA complex exists in the leaching solution. Due to the slower substitution, the silver extraction for 1 mM EDTA was lower than the silver extraction of 0.25 mM and 0.5 mM EDTA.

The final extraction of silver was not really beneficially impacted by the addition of EDTA and higher levels of EDTA (1 mM) resulted in higher thiosulfate consumption.

4.3.4 Effect of Ammonia Concentration

The effects of initial ammonia concentration on the leaching system were examined. Two different ammonia concentrations: 0.4 M and 1 M were tested. The leaching conditions for the tests are summarized in Table 4-8. The higher ammonia concentration was set with ammonium sulfate.

Experiment ID	Base	AM
Pulp density (w/w%)	20	20
pН	9	9
Temperature (°C)	30	30
Agitation (rpm)	700	700
Retention time (hour)	48	48
[TS] (M)	0.2	0.2
Total [AM] (M)	1	0.4
[Cu] (mM)	0.5	0.5
EDTA (mM)	0.5	0.5
Air flow rate (LPM)	0.1	0.1

Table 4-8 The leaching conditions for different initial total ammonia concentration

The pH and Eh for the two tests are shown in Figure 4.11. The graph shows that the initial total ammonia concentration did not affect pH. The pH was maintained close to 9 throughout the leaching tests. The test at 1 M total ammonia had a higher Eh than 0.4 M ammonia; however, the difference was less than 10 mv. The Eh for both tests had increased slightly for over 48 hours.



Figure 4.11 The pH and Eh for two different ammonia concentrations (0.2 M thiosulfate, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

The silver and copper extraction are shown in Figure 4.12. The head and final solid assay for silver and copper are summarized in Table 4-9. The final silver extraction for 1 M ammonia and 0.4 M ammonia were close, which were 95% and 91% respectively. However, the silver leaching kinetics for 0.4 M ammonia was significantly slower than the kinetics for 1 M ammonia. The silver concentration in the final residues also show higher ammonia concentration benefits silver extraction. However, ammonia concentration has less effect on copper extraction compared to silver. The copper extraction for 0.4 M ammonia and 1 M ammonia were 18% and 22% respectively. The 1 M ammonia test had slightly faster leaching kinetics than 0.4 M ammonia.



Figure 4.12 The silver and copper extraction for different ammonia concentration (0.2 M thiosulfate, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Table 4-9 Initial	feed and final	residue assay f	for silver and	l coppei
		2		11

Europin ont ID	Silver (ppm)	Copper (ppm)		
Experiment ID	Initial	Final	Initial	Final	
Base (1 M total [AM))	301.4	12.7	650.0	473.2	
AM (0.4 M total [AM])	301.4	23.3	650.0	501.6	

Figure 4.13 shows the polythionates concentration for different initial total ammonia concentrations. The leaching test started with 1 M total ammonia had a lower thiosulfate concentration of 14.2 g/L after 48 hours. The 0.4 M initial total ammonia test had 17.2 g/L thiosulfate after 48 hours. The trithionate and tetrathionate concentrations for the 1 M ammonia test were higher than for the 0.4 M ammonia test. The results show that higher ammonia concentrations promoted the oxidation of thiosulfate.



Figure 4.13 The polythionates concentration for different ammonia concentration (0.2 M thiosulfate, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

The main role of ammonia in the thiosulfate leaching system is to stabilise cupric ion by forming cupric tetraamine (Aylmore & Muir, 2001). Stabilizing Cu(II) in the solution can promote the silver leaching.

4.3.5 Conclusion

The batch leaching test results show that pH and Eh were stable for all conditions. Almost no change in pH after 48 hours retention time for all tests. The Eh was stable for all tests as well. Figure 4.14 presents the pH and Eh for all batch leaching tests.



Figure 4.14 pH and Eh for all batch leaching tests

The potential of the system increased moderately with changes in variables as expected the increment was very small. Moreover, the potential differences between tests were small. From the graph, the potential differences were within 20 mV for all tests. The highest potential was observed for the base condition and it did not exceed 190 mV after 48 hours.

The results from these leaching tests show the cupric ammoniacal thiosulfate leaching system is robust. As long as the thiosulfate concentration starts at 0.2 M, changing other factors does not have a significant adverse impact on the leaching process. The silver extraction was higher than 90% for all batch tests. The copper extraction data show that silver preferably complexed over copper by thiosulfate. The silver extraction was higher than copper extraction in all tests. Table 4-10 summarized the leaching conditions, silver and copper extraction, and thiosulfate consumption for all batch tests.

Experiment ID	[TS] (M)	Total [AM] (M)	[Cu] (mM)	EDTA (mM)	Air flow rate (LPM)	Silver extraction (%)	Copper extraction (%)	Thiosulfate consumption (%)
Base	0.2	1	0.5	0.5	0.1	95.4	22.3	36.9
Air	0.2	1	0.5	0.5	0.2	92.8	22.4	48.0
Cu1	0.2	1	0.2	0.5	0.1	92.3	22.8	26.0
Cu2	0.2	1	1	0.5	0.1	96.0	20.8	47.3
EDTA1	0.2	1	0.5	0.25	0.1	95.1	20.7	42.5
EDTA2	0.2	1	0.5	1	0.1	92.7	23.9	53.4
AM	0.2	0.4	0.5	0.5	0.1	91.2	17.5	27.5

Table 4-10 Summary of batch leaching tests results

Silver extraction is not the only factor for determining the optimized leaching conditions. Another important factor is thiosulfate consumption. A condition that maximized the silver extraction without consuming too much thiosulfate reagent was selected for the continuous leaching tests. The Base condition selected was 0.1 LPM air flow rate, 1 M total initial ammonia, 0.5 mM EDTA and 0.5 mM copper. These conditions were applied in the continuous leaching experiments (Chapter 5).

4.3.5 Precipitation

After the leaching tests were completed, the pulp was filtered to separate the leachate and the residue. The leachate was transferred into a plastic bottle and stored in the refrigerator. However, after few days, the colour of the stored leachate became dark. A precipitate formed under low temperature conditions. Therefore, the leachate potential was monitored over time at room temperature. Figure 4.15 shows the potential of the pregnant leach solution over time.



Figure 4.15 The potential of the leachate over time

The graph shows that the potential dropped quickly for the first 90 minutes. After it reached around 80 mv, the potential became stable. The black precipitate was observed at 85 minutes after the filtration. The precipitate was collected and dissolved in concentrated nitric acid. The solution with the dissolved solid was then analyzed by AAS. The AAS analysis showed that the precipitate contained both copper and silver. The decreasing potential in solution is consistent with the formation of silver sulfide and copper sulfide. To prevent precipitation prior to analysis, all the samples for AAS analysis were treated with a standard addition of sodium cyanide to convert the silver and copper thiosulfates to silver and copper cyanide species in solution. Solvent extraction with DIBK was used to extract silver from the solution. The silver analysis was done with organic DIBK while copper was analyzed in cyanide form in aqueous solution.

Chapter 5: Continuous Leaching of Silver Ore

5.1 Objectives and Approach

The objective of this part of the study was to engineer a continuous leaching system for extracting silver from the Pan American Silver ore samples. Based on the continuous leaching tests, data for mimicking an industrial process can be obtained. The leaching conditions were chosen based on the results from batch leaching experiments. Table 5-1 shows the experimental conditions of continuous leaching tests.

Experiment ID	Pulp20	Pulp30
Pulp density (w/w%)	20	30
pН	9	9
Temperature	30	30
Agitation (rpm)	700	700
Residence time (hour)	24	24
[TS] (M)	0.2	0.2
Total [AM] (M)	1	1
[Cu] (mM)	0.5	0.5
EDTA (mM)	0.5	0.5
Air flow rate (LPM)	0.1	0.1

Table 5-1 The continuous leaching experiment conditions

5.2 Experimental Procedures

Leaching tests were conducted in the same sealed 500-ml glass reactor as in the batch leaching tests. The temperature was controlled by a circulating water bath that maintained 30°C for all experiments, which was the same as the batch leaching tests. A pH electrode, an Eh electrode, an air sparging tube, a pulp inlet tube, and a pulp outlet tube and a base addition tube were inserted through the lid of the reactor. The mixing was carried out by overhead agitation with a Cole Parmer motor at 700 rpm. Figure 5.1 illustrates the continuous leaching reactor with a lid.



Figure 5.1 The continuous leaching reactor with lid

In continuous leaching tests, pH was controlled by a Hach sc200TM universal controller at pH 9. When the pH dropped lower than the set point value, 8 M sodium hydroxide solution was pumped into the reactor to raise the pH.

The four reactors were connected in series. Fresh pulp and fresh leach solution were pumped into the first reactor (Reactor 1) separately. Then the pulp was transferred from reactor to reactor by pumps until it reached the collecting tank. The transferring of leach pulp between reactors and tanks was done by Masterflex I/P standard process pump. A simple flowsheet for the continuous leaching experiments is shown in Figure 5.2.



Figure 5.2 The continuous leaching flow sheet

The fresh pulp tank was sealed with a lid that had two openings. One was for an overhead agitator and the other was for the tube to transfer fresh pulp into Reactor 1. The fresh leach solution tank was loosely sealed with a rubber stopper containing one tube. The tube was for transferring fresh leach solution to Reactor 1. The agitation in the fresh leaching solution tank was provided by a magnetic stirrer. The speed of agitation was at 600 rpm. The collecting tank had three openings: one for the overhead agitator, one for the tube that pumped the pulp from Reactor 4 to the collecting tank, and the last one for inserting a tube to purge air into the pulp. The pulp in the collecting tank was filtered and sampled every 24 hours. It was found that if agitation and oxygen purging were not maintained in the collection tank, the potential of the slurry will drop, and precipitation would occur. Therefore, the agitation and the purging of air into the collecting tank were meant for the prevention of precipitation.

Due to the limitation of the equipment (wear on peristaltic tubing), it is not realistic to run the pump nonstop. Therefore, instead of transferring the pulp and solution continuously, all the pumps were controlled by a timer to turn on for one minute out of every 25 minutes. That is, the leaching tests were conducted in semi-continuous fashion. Before the pump started transferring the pulp and solution, the four reactors were filled with fresh pulp and leaching reagents. Once all the reactors and the tanks were fully mixed, the timer was started. The retention time for the pulp was 24 hours and the total running time for the leaching system was three days. Kinetic samples were taken every 12 hours. To monitor the pulp density in the four reactors, the fresh pulp tank and the collecting tank, the kinetics samples were taken in the following fashion. First, the empty sample tubes were weighed. Then a sample of 10 ml pulp was taken by pipette from each reactor and tank and put into sample tubes. The weight of the sample tube with pulp inside was recorded. The sample was centrifuged at the speed of 4000 rpm for two minutes to separate the solids and liquid. A sample of the clear solution was then pipetted for further analysis by the procedure described in section 3.2.1. The rest of the pulp in the sample tube was then dried in the oven. After the sample was fully dried, the weight of dry solid and the tube was recorded. Finally, the pulp density could be calculated from the data collected. Equation 5-1 shows the pulp density calculation.

Equation 5-1

Pulp density(w/w%) = $\frac{w_{tube+dry \ solid} - w_{tube}}{w_{tube+slurry} - w_{tube}}$

The solution samples from the pulp samples taken were analyzed by AAS for silver and copper concentrations and analyzed by IC for polythionates concentrations. The dried solid samples were sent to Kemetco Limited for assay. However, before putting the moist solid samples into the oven, there was no washing step to remove the leachate remained in the pulp. This was an error in the procedure. As a result, the silver and copper concentrations from the solid assay were biased to higher values due to the contamination from the unwashed leachate. To correct the error due to the excessive silver and copper in the solid assay, an extra calculation step was applied. The details are found in Appendix B.

After the leaching test was done, the pulp in each reactor was filtered and washed. The solid was dried in the oven and then sent to Kemetco Limited for ICP analysis. The solution was analyzed by AAS for silver and copper concentrations and IC for polythionates concentrations. The final washed solids represented a suitable basis for assessing overall silver and copper extractions.

5.3 Results and Discussion

5.3.1 Pulp20 Continuous Test

One of the important aspects of continuous leaching is to make sure the pump is transferring the slurry at a fixed pulp density. It is crucial to monitor the pulp density throughout the leaching test. In this test, the pulp density for fresh pulp tank was set to be 50%. For the four reactors and the collecting tank, the pulp density should be 20%. The pulp density throughout the leaching test is shown in Figure 5.3.



Figure 5.3 The pulp density for Pulp 20 test (20 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

The figure shows the pulp density for the fresh pulp tank was steady around 50% except in the end of the test. This is because the slurry in the fresh pulp tank was at a very low level in the end of the leaching test and the mixing might be affected. For the four reactors and the collecting tank, the pulp density was maintained around 20% throughout the test.

Figure 5.4 shows pH and Eh data from Pulp 20 test. The pH for the four reactors and the collecting tank was stable around 9 during the three days test. A total of 8.82 ml of 8 M sodium hydroxide was consumed

to maintain the pH. The potential was also stable in each reactor and collecting tank throughout the test. The differences between each reactor were small.



Figure 5.4 pH and Eh for Pulp 20 test (20 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Figure 5.5 shows the silver extraction based on the solid assay for Reactor 1 to 4 and the collecting tank. All reactors reached stable conditions after 12 hours except Reactor 1. Reactor 1 had the lowest extraction, which is 70.2% in the end. The extraction increased from Reactor 1 to Reactor 4. The final extraction for Reactor 4 was 86.2%. The increment of silver extraction from Reactor 1 to 4 is due to the different retention time. In Reactor 1, the solids were exposed to the leaching solution only for 6 hours. The exposure time increase along with the slurry transferred to the collecting tank. In Collecting tank, the silver extraction was close to the value from Reactor 4. The final extraction data are summarized in Table 5-2 below.



Figure 5.5 The silver extraction for each reactor as a function of run time (20 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Table 5-2 The final silver extraction for each reactor and collecting tank

	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Collecting tank
Silver Extraction (%)	70.2	77.1	83.8	86.2	86.4

Figure 5.6 shows the copper extraction for each reactor and the collecting tank. The graph shows that copper extraction was stable after 12 hours for all reactors. Moreover, the copper extraction curves were close to each other. The final copper extraction data for each reactor and the collecting tank are summarized in Table 5-3.



Figure 5.6 The copper extraction for each reactor (20 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Table 5-3 The final copper extraction for each reactor and the collecting tank

	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Collecting tank
Copper Extraction (%)	25.8	23.7	25.0	26.3	26.0

The copper concentration in each reactor is also important since copper is the catalyst in thiosulfate leaching mechanism. Figure 5.7 shows the copper concentration throughout the leaching test. After 12 hours, the copper concentration was stable in each reactor. Reactor 3 and Reactor 4 had a small drop between 12 hours and 36 hours, which can be considered insignificant. The copper concentration increased in the order; Reactor 1 had lowest copper concentration and Reactor 4 had the highest copper concentration.



Figure 5.7 Copper concentration in each reactor (20 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

The thiosulfate concentration data for Pulp 20 test are shown in Figure 5.8. The initial thiosulfate concentration for each reactor was 22 g/L and the initial thiosulfate concentration for the fresh leach solution tank was 30 g/L. These values were fixed and calculated by the amount of solid added. Figure 5.8 shows that the thiosulfate concentration dropped during the initial 12 hours in all four reactors and the leaching solution tank. After 12 hours, the thiosulfate concentration was stable. At 48 hours, the thiosulfate concentration in Reactor 1 was higher, but the value dropped back after 48 hours. In general, thiosulfate concentration decreased slightly from Reactor 1 to Reactor 4.



Figure 5.8 The thiosulfate concentration for Pulp 20 test (20 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Figure 5.9 and 5.10 show the trithionate and tetrathionate concentrations, respectively. Both graphs show the difference between the four reactors and leaching solution tank. The variations on trithionate and tetrathionate concentrations from Reactor 1 to Reactor 4 were obvious. The leaching solution tank had the lowest concentrations for the two species. The concentration of trithionate and tetrathionate increased with the increasing retention time. Therefore, the Reactor 4 had the highest trithionate and tetrathionate concentrations. Figure 5.11 shows the total sulfur content calculated from the polythionates concentrations. The graph shows the total sulfur from each reactor was constant. This indicates the analytical method for polythionates is reliable.



Figure 5.9 Trithionate concentration for Pulp 20 test (20 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)



Figure 5.10 Tetrathionate concentration for Pulp 20 test (20 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)



Figure 5.11 The total sulfur in each reactor for Pulp 20 test (20 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Table 5-4 shows the final thiosulfate concentration for the Pulp 20 test. The flow rate for fresh thiosulfate solution entering the leaching system was 50.0 ml/hr. And the flow rate for the solution that exited the leaching system was 66.7 ml/hr. Use the thiosulfate concentration in Table 5-4 and the flow rate, the amount of thiosulfate consumed per tonne ore treated can be calculated: 19.9 kg ammonium thiosulfate consumed per tonne ore treated.

Table 5-4 The final thiosulfate concentration for each reactor and tank in the end of the leaching test

	Fresh leaching solution tank	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Collecting tank
Thiosulfate Concentration, g/L	26.6	20.5	19.9	19.1	18.1	19.5

5.3.2 Pulp 30 Continuous Test

In the Pulp 30 test, the pulp density for the fresh pulp tank was set to 46% solids. For the reactors, the pulp density was set to be 30% solids. Figure 5.12 shows the pulp density for the Pulp 30 test. The fresh pulp tank maintained at a stable number around 46% throughout the test. Before 38 hours, there was a leak that happened between the fresh slurry tank and Reactor 1. During the leaking period, only fresh leach solution entered the leaching system. As a result, the pulp density in the Reactor 1 was influenced at 38 hours. The leaking slurry was recovered back to Reactor 1 as much as possible. The leakage affected the pulp density in Reactor 2 at 38 hours as well, which dropped to 21.8%. Fortunately, after recovery of the leakage, the system was returned back to steady state. In general, the pulp density of the reactors and the collecting tank was stable throughout the test.



Figure 5.12 Pulp density for Pulp 30 test (30 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Figure 5.13 shows the pH and Eh data for Pulp 30 test. The pH for all reactors was stable around 9 during the three-day test. A total of 26 ml of 8 M sodium hydroxide was consumed to maintain the pH. The potential was also stable for Pulp 30 test.



Figure 5.13 pH and Eh for Pulp 30 test (30 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

The silver extraction data based on the solid assay for each reactor are shown in Figure 5.14. All the reactors were stable after 12 hours. However, there were decreases in extraction after 24 hours. Reactor 2 and Reactor 3 had the most reduction in silver extraction, which was about 10% drop. The final silver extraction data are summarized in Table 5-5.



Figure 5.14 Silver extraction for Pulp 30 test (30 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Table 5-5 The final silver extraction for all the reactors and the collecting tank

	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Collecting tank
Silver Extraction, %	64.2	66.3	71.8	80.2	85.6

The copper extraction data are shown in Figure 5.15. The copper extraction was around 27% for all

reactors. Moreover, they all reached steady state after about 12 hours.



Figure 5.15 Copper extraction for Pulp 30 test (30 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Figure 5.16 shows the copper concentration in each reactor throughout the leaching test. The copper concentration had slightly increased until 60-hour. After that, the copper concentration was stable for all reactors. The final copper extraction data are summarized in Table 5-6.



Figure 5.16 Copper concentration in each reactor as a function of run time (30 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Table 5-6 The final copper extraction for all four reactors and the collecting tank

	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Collecting tank
Copper Extraction, %	27.3	27.0	28.0	26.7	26.9

Figure 5.17 shows the thiosulfate concentrations for the Pulp 30 test. The initial thiosulfate concentration for the fresh leaching solution was 45 g/L, and for the reactors was ~22 g/L. Again, the initial thiosulfate concentration was calculated by the amount of solid added to the reactors. Like the Pulp 20 test, the thiosulfate concentration dropped slightly during the first 12 hours. After 12 hours, the thiosulfate concentration was stable for all the reactors and the leaching solution tank. The thiosulfate concentration dropped across the circuit.



Figure 5.17 The thiosulfate concentration for Pulp 30 test (30 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Figure 5.18 and 5.19 show the trithionate and tetrathionate concentrations, respectively. The leaching solution tank had the lowest trithionate and tetrathionate concentration. For the four leaching reactors, the trithionate and tetrathionate concentrations increased from Reactor 1 to Reactor 4. The only exceptions happened at 24 hours and 60 hours where the trithionate concentration of leaching solution tank were higher than the trithionate concentration in Reactor 1 and Reactor 2. Figure 5.20 shows the total sulfur content calculated from polythionates concentration. The graph shows the total sulfur from each reactor was constant. This indicates the analytical method for polythionates is reliable.


Figure 5.18 Trithionate concentration for Pulp 30 test (30 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)



Figure 5.19 Tetrathionate concentration for Pulp 30 test (30 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)



Figure 5.20 The total sulfur in each reactor for Pulp 30 test (30 w/w% pulp, 0.2 M thiosulfate, 1 M total AM, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate, pH 9, 30°C and 700 rpm)

Table 5-7 shows the final thiosulfate concentration in each reactor. The flow rate for fresh thiosulfate solution that entered the leaching system was 25 ml/hr. And the flow rate for the solution exiting the leaching system was 50 ml/hr. Using the thiosulfate concentrations in Table 5-7 and the flow rates, the amount of thiosulfate consumed per tonne ore treated can be calculated: 14.9 kg ammonium thiosulfate consumed per tonne ore treated.

Fresh leaching Collecting Reactor 1 Reactor 2 Reactor 3 Reactor 4 solution tank tank Thiosulfate 41 20 19 17 17 14 Concentration, g/L

Table 5-7 Final thiosulfate concentration for each reactor and tank in the end of the leaching test

5.3.3 Conclusion

The continuous leaching tests show that thiosulfate leaching system is robust and effective. Even though there was a leak that happened during the Pulp 30 test, the system went back to normal soon after the problem was solved. The results for continuous leaching tests are summarized in Table 5-8. For 24 hours retention time, the silver extraction for Pulp 20 and Pulp 30 were 86.2% and 80.2% respectively. The data

show lower pulp density had higher silver extraction, as well as higher thiosulfate consumption. However, copper extraction was not affected by the pulp density. Both tests had about 26% copper extraction. The caustic consumptions were similar for Pulp 20 and Pulp 30.

Experiment ID	Pulp 20	Pulp 30
Pulp density (%)	20	30
[TS] (M)	0.2	0.2
Total [AM] (M)	1	1
[Cu] (mM)	0.5	0.5
EDTA (mM)	0.5	0.5
Air flow rate (LPM)	0.1	0.1
Silver extraction (%)	86.2	80.2
Copper extraction (%)	26.3	26.7
Thiosulfate consumed per tonne ore (kg/tonne)	19.9	14.9
Sodium hydroxide consumed per tonne ore (kg/tonne)	5.9	6.6

Table 5-8 Summary of continuous leaching tests

Comparing continuous leaching with batch leaching under the same pulp density (20%) and 24 hours retention time, batch leaching had slightly higher silver extraction and much more thiosulfate consumption. However, the continuous leaching test had higher copper extraction. Table 5-9 shows the comparison between batch leaching and continuous leaching tests.

Table 5-9 Comparison of batch leaching test and continuous leaching test

Experiment ID	Continuous	Batch
Pulp density (%)	20	20
[TS] (M)	0.2	0.2
Total [AM] (M)	1	1
[Cu] (mM)	0.5	0.5
EDTA (mM)	0.5	0.5
Air flow rate (LPM)	0.1	0.1
Silver extraction (%)	86.2	90.0
Copper extraction (%)	26.3	16.6
Thiosulfate consumed per tonne ore (kg/tonne)	19.9	26.5
Sodium hydroxide consumed per tonne ore (kg/tonne)	5.9	5.8

Chapter 6: Recovery Methods

6.1 Objectives and Approach

The objective of this part of the study was to find a feasible method to recover silver from the leachate. Ion exchange and cementation were investigated. For ion exchange, the testing program started with plotting the isotherm graph for the resins. After having the information for the resins, resin in pulp was conducted with the slurry generated from the continuous tests. For cementation, the tests were targeted at obtaining a suitable ratio (mole/mole) between the cementing agent and silver based on the reagent cost and the reaction time.

6.2 Ion exchange

6.2.1 Experimental Materials

Two different types of resins were chosen for the ion exchange experiments: Amberlite IRA400 and Purolite A500plus. The two resins were selected based on the previous research (Kononova, Shatnykh, Prikhod'ko, & Kashirin, 2009; Schmoker, 1996). The properties of the resins can be found in Table 6-1. All resins used were in their original chloride form.

Table 6-1 The properties of Amberlite IRA-400 and Purolite A500Plus

	Amberlite IRA400	Purolite A500Plus
Туре	Strong Base	Strong Base
Appearance	Spherical beads	Spherical beads
Physical structure	Gel	Macroporous
Polymer Structure	Polystyrene crosslinked with divinylbenzene	Polystyrene crosslinked with divinylbenzene
Functional Group	Quaternary Ammonium	Quaternary Ammonium

The synthetic leachate was used in the isotherm tests. The goal was to mimic the composition of the leachate from the leaching test. The concentration for each species is tabulated in Table 6-2.

Table 6-2 The synthetic leachate composition

Ag	70 ppm
Cu	54 ppm
Thiosulfate	0.2 M
Total AM	1 M

The inorganic salts used in the synthetic leachate preparation are ammonium thiosulfate $(NH_4)_2S_2O_3$, ammonium sulfate $(NH_4)_2SO_4$, copper sulfate CuSO₄.5H₂O and silver sulfate Ag₂SO₄. All the required pH adjustments were done by adding dropwise concentrated sodium hydroxide.

6.2.2 Experimental Procedures

6.2.2.1 Isotherm experiments

The first set of experiments was conducted in water bath shaker. Figure 6.1 shows the machine with two shaking bottles in it.



Figure 6.1 The water bath shaker

However, the water bath shaker was not available after the first set of experiment. The rest of the isotherm experiments were performed with an orbital shaker. Figure 6.2 shows the orbital shaker with one shaking bottle in it.



Figure 6.2 Orbital shaker

For both the shakers, the experimental procedure was the same. First, the required amount of resin was weighed and put into the shaking bottle. Then same volume of synthetic leachate was pipetted to each bottle and the shaking bottle was sealed with a cap. Once the shaking bottles were secured in the shaker, the experiment was started. The retention time was 24 hours for all isotherm experiments. After the shaker stopped, all the shaking bottles were taken out and the pH value was measured and recorded. Samples for AAS and IC analysis were also taken at that time. For AAS analysis sample, the preparation was as described in section 3.2.2.2.

The content of Ag and Cu in solution were tested by AAS in this lab. The polythionate concentrations were determined by IC in this lab.

6.2.2.2 Resin in Pulp

For the resin in pulp experiments, the required amount of resin was weighed and put into the fresh pulp generated from the continuous leaching test. The mixing was provided by overhead agitation. The sample procedure was similar to the bulk leaching tests. The slurry samples were taken from the leaching reactor without stopping the agitation. It was then transferred into a test tube for centrifuging at very high speed

for two minutes. The clear solution on the upper part was then pipetted out and filtered by the method mentioned in section 3.2.1. The remaining moist solid and solution were mixed by shaking the test tube vigorously. The mixed slurry was return to the reactor after shaking. For AAS analysis sample, the preparation was as described in section 3.2.2.2.

The content of Ag and Cu in solution were tested by AAS in this lab. The polythionate concentration were determined by IC in this lab.

6.2.3 Results and Discussion

6.2.3.1 Isotherm Experiments

The isotherm experiments started with the condition in Table 6-3. Note that the copper concentration was different than the synthetic leachate mentioned in Table 6-2, section 6.2.1. However, the higher copper concentration did not adversely affect the results since copper is less selectively loaded than silver on both Amberlite IRA400 and Purolite A500plus.

Table 6-3 The synthetic leachate components for the first set of isotherm experiment

Ag	70 ppm
Cu	108 ppm
Thiosulfate	0.2 M
Ammonia	1 M

Figure 6.3 shows the isotherm for the first set of experiments.



Figure 6.3 The isotherm for Amberlite IRA400 and Purolite A500plus from the first set of tests

The graph shows Amberlite IRA400 has higher silver loading capacity than Purolite A500plus. It also shows that the silver is more selectively loaded than copper for both types of resin. However, the silver isotherm for Purolite A500plus indicates that precipitation of silver may have occurred in samples indicated by circled points. This was also indicated by the darker colour of the solution and black solids appearing on the filter paper. To solve the precipitation problem, the thiosulfate concentration was increased for the rest of the isotherm tests. The effect of thiosulfate concentration on the ion-exchange can also be investigated. The summary of the isotherm experiments is tabulated in Table 6-4.

Experiment ID	Resin type	[TS], M	[Ag], ppm	[Cu], ppm
ISO 1	Amberlite IRA400	0.2	70	108
ISO 2	Purolite A500plus	0.2	70	108
ISO 3	Amberlite IRA400	0.3	70	54
ISO 4	Purolite A500plus	0.3	70	54
ISO 5	Amberlite IRA400	0.4	70	54
ISO 6	Purolite A500plus	0.4	70	54
ISO 7	Amberlite IRA400	0.5	70	54

Table 6-4 The summary of the isotherm experiments

Figure 6.4 shows the silver isotherm for Amberlite IRA400 with different thiosulfate concentrations (ISO 1, 3, 5, and 7).



Figure 6.4 The silver isotherm for Amberlite IRA400

The graph shows that the silver loading capacity increased with increased thiosulfate from 0.2 M to 0.4 M thiosulfate. When the thiosulfate concentration increased to 0.5 M, the silver loading capacity dropped. This may be due to competition by thiosulfate for the loading sites on the resin.

Figure 6.5 shows the silver isotherm for Purolite A500plus with different thiosulfate concentrations (ISO 2, 4, and 6).



Figure 6.5 The silver isotherm for Purolite A500plus

The precipitation problem was solved by increasing thiosulfate concentration. No precipitate was observed in the ISO 4 (0.3 M thiosulfate) and ISO 6 (0.4 M thiosulfate) experiments. For Purolite

A500plus, the silver loading capacity increased with the increasing thiosulfate concentration. But the increment in loading capacity between 0.3 M and 0.4 M thiosulfate is small.



The performance between the two resins, can be compared through the results in Figure 6.6.

Figure 6.6 The comparison of the silver isotherm between Amberlite IRA400 and Purolite A500plus

Both Amberlite IRA400 and Purolite A500plus had the highest loading capacity at 0.4 M thiosulfate in the starting solution. Therefore, the comparison between the two resins used the data from 0.4 M thiosulfate isotherm. Figure 6.6 shows the Amberlite IRA400 has better silver loading capacity than Purolite A500plus because with the same silver concentration in the solution, Amberlite IRA400 had more silver loaded on the resin.

6.2.3.2 Ion-exchange in Pulp

The isotherm experiments show Amberlite IRA400 has better silver loading capacity. Therefore, it was used in the resin in pulp experiment. Based on the isotherm, 16 g of Amberlite IRA400 should be sufficient for the silver recovery. Unfortunately, the resin performance was very poor. After 90 minutes retention time only 7.4% of silver was loaded on the resins. Figure 6.7 shows the result of the resin in pulp test.



Figure 6.7 The percentage silver loaded on Amberlite IRA400

The poor performance of ion exchange is likely caused by the polythionates in the system. The isotherm was generated by testing with the synthetic leachate. There was no trithionate and tetrathionate added to the synthetic solution. Using the published data for Amberlite IRA400 and the amount added to the pulp, the capacity can be calculated. The capacity of resin added to the pulp was 32 milliequivalents. However, literature studies show that tetrathionate can poison ion exchange resins (Daenzer, 2017). Table 6-5 shows the initial and final amounts of polythionates in the system. Also, the amount of polythionates loaded on resin and their amounts in milliequivalents are included in the table. The amount loaded on resin is calculated by subtracting the initial and final amounts of each species. Dividing the number by its molecular weight and multiplying by its valance number will give the milliequivalents.

	Thiosulfate (mg)	Trithionate (mg)	Tetrathionate (mg)
Initial	25611	15288	11112
Final	25173	13941	8970
Amount loaded on resin	438	1348	2142
Milliequivalents	7.8	14.0	19.1

Table 6-5 The amount of polythionates in the pulp before and after the ion exchange

Apparently, the effect of trithionate and tetrathionate on resin in pulp is significant. The two species took most of the capacity on the resin. The insufficient amount of resin for the ion exchange is the reason for the low silver recovery.

6.3 Cementation

6.3.1 Experimental Materials

Two metals, copper and zinc were picked for cementation experiments. The copper powder was obtained from Acros Organic. The purity was 99%. The particle size was less than 45 microns. The zinc powder was obtained from Fisher Scientific. The purity was also 99%. The particle size was less than 45 microns. Zinc metal powder was used as received. However, to avoid surface tension issues in the mixing of the copper metal powder into solution, the copper powder was washed with ethanol while vacuum filtering until the copper powder was dry.

The synthetic leachate was used in cementation experiments. The concentration for each component was tabulated in Table 6-6. Like the synthetic leachate used in ion-exchange experiments, the purpose was to mimic the leachate from leaching tests.

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Table 6 6	The cunthe	atic laacha	to come	1001t10n
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Ag	70 ppm
Cu	54 ppm
Thiosulfate	0.2 M
Ammonia	1 M

The inorganic salts used in the synthetic leachate preparation were ammonium thiosulfate $(NH_4)_2S_2O_3$, ammonium sulfate $(NH_4)_2SO_4$, copper sulfate $CuSO_{4.5}H_2O$ and silver sulfate Ag_2SO_4 . All the required pH adjustments were done by adding concentrated sodium hydroxide dropwise.

6.3.2 Experimental Procedures

The cementation test began with synthetic leachate preparation. 400 ml synthetic leachate was poured into the reactor and the reactor was then sealed with a lid. Nitrogen was purged into the system for 30 minutes to remove the oxygen in the system. After 30 minutes, the experiments were started by adding the metal powder into the reactor. Nitrogen was bubbling in the system throughout the cementation test. Kinetic samples were taken at the designated times. The sampling procedure is described in section 3.2.1. The

content of Ag and Cu in solution were tested by AAS in this lab. The polythionates concentration were determined by IC in this lab.

Before conducting the cementation experiments, the amount of the metal powder was determined. Generally, more metal powder in the cementation can accelerate the reaction time. However, more material used in the process raises the cost. Therefore, a reasonable proportion between the metal powder and the target metal for recovery should be investigated. Since the leaching solution contains silver and copper, the cementing reaction for each metal salt should be considered. Using this stoichiometry relationship, not only the required amount of metal powder can be calculated, but also an additional cost/silver-value ratio for each of the metals.

To simplify the calculation, reduction of $Ag(S_2O_3)_2^{3-}$ and $Cu(S_2O_3)_3^{5-}$ are the reactions included. Reaction 6-1 and 6-2 show the two redox reactions.

Reaction 6-1

$$M + 2Ag(S_2O_3)_2^{3-} \leftrightarrow 2Ag + 4S_2O_3^{2-} + M^{2+}$$

Reaction 6-2

 $M + 2Cu(S_2O_3)_3^{5-} \leftrightarrow 2Cu + 6S_2O_3^{2-} + M^{2+}$

Where M is the cementing agent. From Table 6-6, the initial silver and copper concentrations are known, which are 70 ppm and 54 ppm, respectively. Converting the unit from ppm to mol/L and using the stoichiometry relationship, the required mol/L of metal can be calculated. To make sure the system has enough cementing agent, two mole ratios were picked to test the efficiency, which were 1.5 and 10. Multiplying the mole ratios with the required mol/L metal will give the concentration for cementation tests.

Table 6-7 summarizes the designated concentration for cementing agents and the corresponding profit/cost ratio. The profit/cost ratio was calculated based on the metal price at the time. (Ag: \$473/kg, Cu: \$6.18/kg, and Zn: \$2.71/kg)

Table 6-7 The summary of the cementation experiments

Experiment ID	Metal powder, g/L	Profit/Cost
Cu1	0.07	74
Cu2	0.48	11
Zn1	0.07	166
Zn2	0.49	25

6.3.3 Results and Discussion

6.3.3.1 Cementation on Synthesis Leaching Solution

The results are shown in Figure 6.8.



Figure 6.8 The influence of cementing agent type and concentration on silver cementation Test Zn2 had the shortest reaction time. Test Cu1 had the longest reaction time, which was more than 60 minutes. Interestingly, test Cu2 and test Zn1 had similar reaction time. All the four silver cementation experiments followed first order kinetics. This can be observed from Figure 6.9, the plot of log([Ag]/[Ag]₀) with time.



Figure 6.9 The variation of $-log([Ag]/[Ag]_0)$ with time on copper and zinc

Since they are first order reactions, the slope in Figure 6.9 is the rate constant. Table 6-8 summarizes the rate constants for each experiment. A mathematical development of a first order reaction can be found in Appendix C.

Experiment ID	Metal powder, g/L	Rate constant, min ⁻¹
Cu1	0.07	0.03
Cu2	0.48	0.14
Zn1	0.07	0.11
Zn2	0.49	0.64

Table 6-8 The Rate constant for each cementation test

The table shows that with more metal powder, the rate constant increased. Comparing the ratios of the metal powder weights and the rate constants shows that adding more zinc powder can increase the cementation rate more efficiently. The comparison is shown in Table 6-9. In the table, W_{Cu2}/W_{Cu1} and W_{Zn2}/W_{Zn1} are the ratios of metal powder added for Cu1, Cu2, Zn1 and Zn2 tests. And k_{zn2}/k_{zn1} and k_{cu2}/k_{cu1} ratios are the rate constant ratios for the tests Cu1, Cu2, Zn1 and Zn2. For similar amounts of metal powder added, zinc has larger rate ratio (k_{zn2}/k_{zn1}) which was 5.8. For copper, the rate ratio

 (k_{cu2}/k_{cu1}) was 4.7. This indicates that the reaction rate for zinc cementation increases more per amount of cementing agent added.

W _{Cu2} /W _{Cu1}	6.9	WZn2/WZn1	7.0
k _{Cu2} /k _{Cu1}	4.7	kzn2/kzn1	5.8

Table 6-9 The amount ratio and rate ratio for copper and zinc cementation

Another aspect to consider is the final copper concentration in the solution. This is because after the cementation, the solids can be filtered, and the solution can be recycled back to the leaching circuit. If the copper maintained a certain level in the solution, it could reduce the extra copper addition to meet the leaching requirement. Table 6.10 shows the final copper concentration for each cementation test.

Table 6-10 The final copper concentration for each cementation test

Experiment ID	Final copper, ppm	Final silver, ppm	Retention time, minutes
Cu1	94	0.81	75
Cu2	126	0.12	20
Zn1	29	0.09	25
Zn2	0.28	0	4

For zinc, test Zn2 had almost no copper left in the solution after the cementation test. For copper, both tests Cu1 and Cu2 the final copper concentrations were higher than the copper concentrations in the leaching solution initially (which is about 32 ppm). Test Zn1 had the closest final copper concentration to the initial copper concentration of the leaching solution.

As mentioned in the section 2.4.2, zinc is a strong reducing agent. Thiosulfate can be reduced to sulfide by zinc. However, the initial and final thiosulfate concentration data showed the thiosulfate concentration was not affected during cementation. Table 6-11 shows the thiosulfate concentration at the beginning and the end of each cementation test. This is due to the short retention times for zinc cementation. The retention times for Zn1 and Zn2 were less than 25 minutes.

Experiment ID	Cu1	Cu2	Zn1	Zn2
Initial Thiosulfate, M	0.19	0.16	0.20	0.16
Final Thiosulfate, M	0.19	0.17	0.20	0.17

Table 6-11 The initial and final thiosulfate concentration for the cementation tests

6.3.3.2 Cementation on Real Leaching Solution

During Pulp 20 test, the collecting tank was filtered every 24 hours. The filtrate was then collected, and cementation performed. For each cementation test, 600 ml filtrate was poured into a glass reactor immediately after filtration. The reactor was sealed with a lid that had a pH probe inserted. The mixing was provided by an overhead agitator. 0.04 g of metal powder was added to the reactor. The cementation was started without purging any nitrogen before and during the tests. This permitted oxidation of metal powder during the cementation test. Figure 6.10 shows the cementation tests results on real leachate.



Figure 6.10 Silver precipitated for the cementation tests on real leachate

The graph shows that due to oxidation of during the cementation, both copper and zinc could not reach 100% silver recovery even after long retention times. Moreover, the silver recovery started to drop after a peak recovery. Therefore, excluding oxygen in the cementation system is crucial. Nitrogen should be introduced to the solution for a successful cementation process.

Chapter 7: Conclusions and Recommendations

7.1 Conclusions

A lab-scale continuous leaching system for studying the cupric-ammoniacal thiosulfate leaching of silver ore has been built. The leaching condition was defined following the evaluation of a series of batch leaching tests. Moreover, two different recovery methods were tested on the leaching system.

In the batch leaching tests, the optimized leaching conditions for the Navidad silver sulfide ore were found to be 0.1 LPM air flow rate, 0.5 mM Cu, 0.25 mM EDTA and 1 M total ammonia. The highest silver extraction was 95% for 48 hours retention time. The thiosulfate consumption for this leaching condition was 26.5 kg ammonium thiosulfate pre tonne ore treated and 5.8 kg sodium hydroxide was consumed per tonne of ore treated. Precipitation of silver occurred in the recovered pregnant solution. At room temperature, the precipitation happened at about 85 minutes after filtration. From the Eh-pH diagram, the precipitates were expected to be a mixture to silver sulfide and copper sulfide. The precipitation speed depends on the silver and copper concentration of the leachate and the temperature. Storing the solution in the refrigerator or diluting the leachate can slow down the precipitation.

In continuous leaching tests, two pulp densities, 20% and 30%, were investigated. The silver extraction for these two pulp density tests were close. The final extraction for 24 hours retention time was 86% for 20% pulp density test and 80% for 30% pulp density test. The thiosulfate concentration was moderately stable but lower than the initial value. The initial thiosulfate concentration was 22 g/L. After 24 hours, the thiosulfate concentration dropped to 20 g/L and stayed at this level throughout the test. The thiosulfate consumptions were 19.9 kg thiosulfate per tonne ore and 14.9 kg thiosulfate per tonne ore for 20% pulp density and 30% pulp density, respectively. To maintain the pH for the leaching process, about 6 kg of sodium hydroxide was required per tonne ore treated for both pulp densities.

Ion exchange and cementation were investigated for finding a viable silver recovery method. For ion exchange, absorption in the synthetic leachate shows that Amberlite IRA400 had better silver loading

capacity compared to Purolite A500plus. The highest loading occurred with 0.4 M thiosulfate leachate, which was 4 kg Ag/ tonne resin. However, the resin in pulp test showed poor results. Only 7.2% of silver was adsorbed on the resin after 90 minutes. This is due to the insufficient amount of resin in pulp to compensate for the presence of trithionate and tetrathionate. As a result, to recover silver from thiosulfate leachate a lot more resin would be needed, hence decreasing the loading capacity for silver dramatically.

The cementation tests on the synthetic leachate showed that both zinc and copper cementation for the silver followed first order kinetics. Metallic zinc cemented silver faster than metallic copper. However, zinc also reduced the copper in the leachate, whereas copper did not have this problem. Both copper and zinc cementation did not affect the thiosulfate concentration in the leachate. This might be due to the short reaction times for cementation.

The continuous leaching tests on cupric ammoniacal thiosulfate system showed that the silver sulfide ore can be leached rapidly. Moreover, the thiosulfate consumption for continuous leaching was lower than the consumption for batch leaching. Thiosulfate remained at a reasonable concentration throughout the continuous leaching tests. After leaching, the silver can be recovered from the leachate by cementation. Both copper and zinc cementation can recover silver. Zinc exhibits shorter reaction time, but it also recovers copper and introduces Zn(II) impurities into the system. Copper would be the better cementing agent for recycling the stripped leachate back to the leaching circuit.

7.2 Recommendations and Future Work

The three days continuous leaching experiments demonstrated the ability of the cupric ammoniacal thiosulfate system for silver extraction from silver sulfide ore. Furthermore, the cementation tests confirmed that copper or zinc can recover silver from the pregnant leachate. Copper is recommended as the cementing agent. The next step would be recycling the leaching solution after cementation back to the leaching system. However, before recycling the barren solution back to the leaching system, there are two problems to solve. First is the extra copper introduced during copper cementation. Another problem is the depleting of thiosulfate after leaching. A possible solution is adding hydrosulfide to precipitate the copper

in barren solution and to recover some thiosulfate. Performing the leaching test with the solution after hydrosulfide precipitation would provide better understanding of the leaching ability with the recycled solution. Moreover, the data for the continuous leaching test with recycled leaching solution can provide useful information for simple cost estimation of real operations.

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Appendices

Appendix A A Chromatograph Example

In this appendix, an example chromatograph from a typical IC analysis is shown. Three species of polythionates were determined: thiosulfate, trithionate and tetrathionate. Figure A.1 shows the three peaks that generated during IC. From left to right are thiosulfate, trithionate and tetrathionate. The area under the curve is used for calculated the concentration of each species based upon known standards. Note that a pentathionate peak was detected as well but the pentathionate species is difficult to quantify due to a lack of easily available standards.



Figure 7.1 The IC program window

Appendix B Calculation for Correcting the Kinetics Assay

First, assume the moisture content for the pulp was 40%. This assumption is based on the data from collecting tank. Both kinetic samples and final washed residues for collecting tank were send for assay. To make the recalculated kinetics assay of collecting tank close to its residue assay, 40% moisture content is the best assumption.

The volume of moist content ($V_{Moist content}$) in the pulp can be calculated by the dry solid weight ($W_{dry solid}$) and the solution density ($\rho_{solution}$).

 $V_{Moist content} = W_{dry solid}/(1-0.4)*0.4/(\rho_{solution})$

With the moisture content volume and the data of solution assay ($[Ag]_{solution}$), the silver amount (Ag_{moist} content) in the moist content can be calculated.

 $Ag_{moist\ content} = [Ag]_{solution} *\ V_{Moist\ content}$

Then subtract the silver amount in the moisture from the total silver amounts in the moist solid. This gives the corrected silver amount in the solid.

Appendix C First Order Reaction Rate Constant

The rate constant k for a first order reaction could be calculated from the experimental data. The derivation for the rate constant k is shown in this appendix.

First, the rate of a first order reaction can be expressed as:

Rate = k[A]

Where k is the rate constant and [A] is the concentration of the species A.

The rate can also be expressed in differential form as:

k[A] = -d[A]/dt

Rearrange the equation to give:

d[A]/[A]=-kdt

Integrate the equation for both sides to give:

$$\int_{[A]0}^{[A]t} \frac{1}{[A]} d[A] = -\int_{t0}^{t} k dt$$

After integration, the equation becomes:

 $\ln[A]_t - \ln[A]_0 = -kt$

Rearrange the equation to linear equation form give:

 $ln[A]_t = -kt + ln[A]_0$

Since the initial concentration of A is a known value, $\ln[A]_0$ is a constant. Then the slop of this straight

line is -k. Use the laws of logarithms to further arrange the equation as:

 $\ln([A]_t/[A]_0) = -kt$

Use the experimental data to plot $\ln([A]_t/[A]_0)$ versus time can find the value of rate constant k.

Appendix D Batch Leaching Experimental Results

In this appendix, the data from all the batch leaching were summarized in each table. In the column "Mass", there are two sub-columns: individual and overall. The individual is the multiplication of sample volume and assay. For example, at 50-hour the individual mass would be:

$$Mass_{individual,50\ hour}[mg] = Sample\ volume_{50\ hour}[ml] \times Assay_{50\ hour}[\frac{mg}{L}] \times \frac{1}{1000} \left[\frac{L}{ml}\right]$$

The overall mass is the summation of the metal mass in the solution at the sampling time and the sum of all the metal mass that was taken in the previous sampling time. For example, the total mass at 50-hour can be calculated by the equation below:

$$\begin{split} Mass_{overall,50\ hour}[mg] \\ &= \sum Sample\ volume_i[ml] \times Assay_i \left[\frac{mg}{L}\right] \times \frac{1}{1000} \left[\frac{L}{ml}\right] \\ &+ Total\ volume_{50\ hour}[ml] \times Assay_{50\ hour} \left[\frac{mg}{L}\right] \times \frac{1}{1000} \left[\frac{L}{ml}\right] \end{split}$$

In the Reaction, the i represents the sampling time before 50-hour, which are 1, 2, 4, 8, 24 and 32 hours. With the overall mass at each sampling time, the %Extraction can be calculated. The equation is shown below:

$$\% Extraction = \frac{Mass_{overall,i} [mg]}{Mass_{Head} (Cal.) [mg]} \times 100\%$$

The i in the equation represents each sampling time. The calculated head mass $Mass_{Head (Cal.)}$ can be expressed in the equation below:

$$Mass_{Head (Cal.)}[mg] = Mass_{overall,50 hour}[mg] + Mass_{wash}[mg] + Mass_{residue}[mg]$$

The calculated head assay is shown in the equation below:

$$Assay_{Head (cal.)}[\frac{mg}{kg}] = \frac{Mass_{Head (Cal.)}[mg]}{Ore \ Sample[g]} \times \frac{1000}{1} [\frac{g}{kg}]$$

The % weight loss is the percent difference between the ore sample and the residue based on the ore sample mass.

% weight loss =
$$\frac{Ore Sample[g] - Residue[g]}{Ore Sample[g]} \times 100\%$$

The Ag mass balance and Cu mass balance are the percentage of the calculated head mass over the direct head mass for silver and copper.

$$Ag, Cu \text{ mass balance} = \frac{Mass_{Head (Cal.)}[mg]}{Mass_{Head (dir.)}[mg]} \times 100$$

Product	Sample	Total	Assays, mg/L	Mas	ss Ag	% Extraction	Assays, mg/L	Mas	s Cu	% Extraction
	g, mL	g, mL	Ag	mg	mg	Ag	Cu	mg	mg	Cu
INPUT				_				_		
Ore sample		100.88	301.37	30.402			650.03	65.575		
Solution		403	0.00	0.000			31.56	12.709		
OUTPUT				Individual	Overall			Individual	Overall	
1 hour	2.5	403	36.79	0.092	14.816	54.5	46.38	0.116	5.971	9.9
2 hour	2.5	400	42.41	0.106	17.068	62.8	48.62	0.122	6.866	11.4
4 hour	2.5	398	48.83	0.122	19.618	72.2	51.13	0.128	7.866	13.1
8 hour	2.5	395	52.48	0.131	21.061	77.5	53.68	0.134	8.871	14.7
24 hour	2.5	393	61.18	0.153	24.478	90.0	56.59	0.141	10.015	16.6
32 hour	2.5	390	61.78	0.154	24.712	90.9	57.59	0.144	10.405	17.3
FINAL										
50 hour	2.3	353	63.95	0.144	23.335	95.4	63.75	0.143	10.582	22.3
Wash	707	707	3.677	2.599	2.599		4.00	2.826	2.826	
Residue	98.88	98.88	12.70		1.255		473.16		46.786	
Head (calc.)	100.88	100.88	269.53		27.190		596.70		60.195	
Head (dir.)	100.88	100.88	301.37		30.402		650.03		65.575	
Weight loss (%)	2.0									
Ag mass balance	89.4									

Table D-1 Base: 0.2M thiosulfate, 1 M ammonia, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate

(%)

(%)

91.8

Cu mass balance

Product	Sample	Total	Assays,			%	Assays,	G		%
			mg/L	Ag		Extraction	mg/L	Cu		Extraction
	g, mL	g, mL	Ag	mg	mg	Ag	Cu	mg	mg	Cu
INPUT				_				_		
Ore sample		100.03	301.37	30.146			650.03	65.023		
Solution		403	0.00	0.000			31.52	12.709		
OUTPUT				Individual	Overall			Individual	Overall	
1 hour	2.5	403	27.10	0.068	10.926	43.9	46.71	0.117	6.121	10.0
2 hour	2.5	401	33.64	0.084	13.545	54.4	49.81	0.125	7.363	12.0
4 hour	2.5	398	36.28	0.091	14.595	58.6	52.41	0.131	8.401	13.7
8 hour	2.5	396	45.68	0.114	18.315	73.5	55.62	0.139	9.669	15.8
24 hour	2.5	393	53.71	0.134	21.475	86.2	60.71	0.152	11.672	19.0
32 hour	2.5	391	53.95	0.135	21.567	86.6	61.73	0.154	12.070	19.7
FINAL										
50 hour	2.3	354	56.20	0.126	20.505	92.8	63.15	0.142	10.445	22.4
Wash	698	698	3.735	2.606	2.606		4.67	3.260	3.260	
Residue	97.83	97.83	18.43		1.803		486.25		47.570	
Head (calc.)	100.03	100.03	249.06		24.913		612.57		61.276	
Head (dir.)	100.03	100.03	301.37		30.146		650.03		65.023	
Weight loss (%)	2.2									
Ag mass balance (%)	82.6									
Cu mass balance	00 0									

Table D-2 Air1: 0.2 M thiosulfate, 1 M ammonia, 0.5 mM copper, 0.5 mM EDTA, 0.2 LPM air flow rate

Product	Sample	Total	Assays,	Δσ		% Extraction	Assays,	Cu		% Extraction
	g, mL	g, mL	Ag	mg	mσ	Ag	Cu	mg	mø	Cu
INPUT	8/	8/	0			8				
Ore sample		100.45	301.37	30.272			650.03	65.296		
Solution		401	0.00	0.000			12.68	5.084		
OUTPUT				Individual	Overall			Individual	Overall	
1 hour	2.5	401	29.50	0.074	11.832	43.2	28.12	0.070	6.194	10.2
2 hour	2.5	399	36.13	0.090	14.472	52.9	30.55	0.076	7.163	11.9
4 hour	2.5	396	42.13	0.105	16.848	61.6	32.84	0.082	8.069	13.4
8 hour	2.5	394	50.08	0.125	19.977	73.0	36.04	0.090	9.331	15.4
24 hour	2.5	391	58.50	0.146	23.272	85.1	40.75	0.102	11.171	18.5
32 hour	2.5	389	58.90	0.147	23.428	85.6	41.56	0.104	11.487	19.0
FINAL										
50 hour	2.3	529	43.08	0.097	23.462	92.3	31.86	0.072	12.287	22.8
Wash	556	556	3.223	1.793	1.793		2.65	1.473	1.473	
Residue	98.26	98.26	21.45		2.108		474.96		46.669	
Head (calc.)	100.45	100.45	272.40		27.362		601.59		60.430	
Head (dir.)	100.45	100.45	301.37		30.272		650.03		65.296	
Weight loss (%)	2.2									
Ag difference (%)	90.4									

Table D-3 Cu1: 0.2M thiosulfate, 1 M ammonia, 0.2 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate

Cu difference (%)

Product	Sample	Total	Assays,			%	Assays,	0		%
	· _	_	mg/L	Ag		Extraction	mg/L	Cu		Extraction
	g, mL	g, mL	Ag	mg	mg	Ag	Cu	mg	mg	Cu
INPUT				_				_		
Ore sample		100.29	301.37	30.224			650.03	65.192		
Solution		409	0.00	0.000			62.16	25.418		
OUTPUT				Individual	Overall			Individual	Overall	
1 hour	2.5	409	27.89	0.070	11.404	42.3	56.83	0.142	-2.181	-3.5
2 hour	2.5	406	42.64	0.107	17.399	64.5	77.61	0.194	6.268	10.1
4 hour	2.5	404	49.20	0.123	20.050	74.3	80.33	0.201	7.364	11.9
8 hour	2.5	401	55.03	0.138	22.388	83.0	82.12	0.205	8.084	13.1
24 hour	2.5	399	61.43	0.154	24.941	92.5	84.25	0.211	8.934	14.4
32 hour	2.5	396	61.40	0.154	24.932	92.5	84.39	0.211	8.989	14.5
FINAL										
50 hour	2.3	360	62.34	0.140	23.178	96.0	90.00	0.203	8.134	20.2
Wash	685	685	3.964	2.715	2.715		6.42	4.396	4.396	
Residue	98.37	98.37	10.93		1.075		502.29		49.411	
Head (calc.)	100.29	100.29	268.89		26.967		617.62		61.941	
Head (dir.)	100.29	100.29	301.37		30.224		650.03		65.192	
Weight loss (%)	1.9									
Ag mass balance (%)	89.2									
Cu mass balance	05.0									

Table D-4 Cu2: 0.2M thiosulfate, 1 M ammonia, 1 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate

Product	Sample	Total	Assays,			%	Assays,	G		%
	-	_	mg/L	Ag		Extraction	mg/L	Cu		Extraction
	g, mL	g, mL	Ag	mg	mg	Ag	Cu	mg	mg	Cu
INPUT				_				<u> </u>		
Ore sample		100.09	301.37	30.164			650.03	65.062		
Solution		403	0.00	0.000			31.53	12.709		
OUTPUT				Individual	Overall			Individual	Overall	
1 hour	2.5	403	29.34	0.073	11.824	50.2	46.36	0.116	5.977	9.8
2 hour	2.5	401	34.73	0.087	13.982	59.3	48.77	0.122	6.941	11.4
4 hour	2.5	398	37.78	0.094	15.196	64.5	51.16	0.128	7.893	13.0
8 hour	2.5	396	47.50	0.119	19.043	80.8	54.34	0.136	9.152	15.0
24 hour	2.5	393	54.26	0.136	21.701	92.1	58.31	0.146	10.709	17.6
32 hour	2.5	391	56.03	0.140	22.389	95.0	58.69	0.147	10.860	17.8
FINAL										
50 hour	2.3	353	54.99	0.124	20.052	95.1	58.68	0.132	8.791	20.7
Wash	574	574	4.125	2.367	2.367		6.64	3.812	3.812	
Residue	98.33	98.33	11.66		1.146		491.16		48.296	
Head (calc.)	100.09	100.09	235.45		23.566		608.45		60.899	
Head (dir.)	100.09	100.09	301.37		30.164		650.03		65.062	
Weight loss (%)	1.8									
Ag mass balance (%)	78.1									
Cu mass balance	026									

Table D-5 EDTA1: 0.2M thiosulfate, 1 M ammonia, 0.5 mM copper, 0.25 mM EDTA, 0.1 LPM air flow rate

Product	Sample	Total	Assays,			%	Assays,	C		%
			mg/L	Ag		Extraction	mg/L	Cu		Extraction
	g, mL	g, mL	Ag	mg	mg	Ag	Cu	mg	mg	Cu
INPUT				_				_		
Ore sample		100.78	301.37	30.372			650.03	65.510		
Solution		402	0.00	0.000			31.62	12.709		
OUTPUT				Individual	Overall			Individual	Overall	
1 hour	2.5	402	11.65	0.029	4.682	19.0	47.29	0.118	6.299	10.3
2 hour	2.5	399	28.71	0.072	11.497	46.7	50.26	0.126	7.482	12.2
4 hour	2.5	397	34.31	0.086	13.720	55.8	52.88	0.132	8.522	13.9
8 hour	2.5	394	41.81	0.105	16.678	67.8	56.29	0.141	9.870	16.1
24 hour	2.5	392	50.64	0.127	20.137	81.9	61.75	0.154	12.009	19.6
32 hour	2.5	389	53.44	0.134	21.227	86.3	63.16	0.158	12.556	20.5
FINAL										
50 hour	2.3	362	55.78	0.125	20.742	92.7	65.61	0.148	11.872	23.9
Wash	418	418	4.948	2.070	2.070		6.66	2.785	2.785	
Residue	98.12	98.12	18.19		1.785		475.77		46.682	
Head (calc.)	100.78	100.78	244.07		24.597		608.65		61.339	
Head (dir.)	100.78	100.78	301.37		30.372		650.03		65.510	
Weight loss (%)	2.6									
Ag mass balance (%)	81.0									
Cu mass balance	02.6									

Table D-6 EDTA2: 0.2M thiosulfate, 1 M ammonia, 0.5 mM copper, 1 mM EDTA, 0.1 LPM air flow rate

Product	Sample	Total	Assays,			%	Assays,	G		%
		_	mg/L	Ag		Extraction	mg/L	Cu		Extraction
	g, mL	g, mL	Ag	mg	mg	Ag	Cu	mg	mg	Cu
INPUT				_				_		
Ore sample		100.28	301.37	30.221			650.03	65.185		
Solution		402	0.00	0.000			31.62	12.709		
OUTPUT				Individual	Overall			Individual	Overall	
1 hour	2.5	402	23.40	0.059	9.404	36.3	42.49	0.106	4.369	7.3
2 hour	2.5	399	29.58	0.074	11.870	45.8	45.52	0.114	5.577	9.4
4 hour	2.5	397	35.94	0.090	14.396	55.6	47.54	0.119	6.380	10.7
8 hour	2.5	394	43.65	0.109	17.437	67.3	49.66	0.124	7.216	12.1
24 hour	2.5	392	49.48	0.124	19.720	76.1	53.68	0.134	8.789	14.7
32 hour	2.5	389	51.30	0.128	20.431	78.9	54.84	0.137	9.241	15.5
FINAL										
50 hour	2.3	333	61.06	0.137	20.947	91.2	60.03	0.135	8.045	17.5
Wash	765	765	3.487	2.668	2.668		3.12	2.387	2.387	
Residue	98.03	98.03	23.27		2.281		501.64		49.176	
Head (calc.)	100.28	100.28	258.24		25.896		594.42		59.608	
Head (dir.)	100.28	100.28	301.37		30.221		650.03		65.185	
Weight loss (%)	2.2									
Ag mass balance (%)	85.7									
Cu mass balance	01.4									

Table D-7 AM1: 0.2M thiosulfate, 0.4 M ammonia, 0.5 mM copper, 0.5 mM EDTA, 0.1 LPM air flow rate

Appendix E Continuous Leaching Experimental Results

All the solid assay results from Kemetco Limited for each continuous leaching experiment are summarized in the tables. The %extraction are calculated by the solid assay. The calculation is shown below:

$$\% Extraction_{Ag,Cu} = \left(1 - \frac{Solid Assay_{Ag,Cu}}{Head Assay_{Ag,Cu}}\right) \times 100\%$$

Table E-1 Solid assay for Pulp 20 (Ag)

Time (hr)	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Collecting tank
0	0	0	0	0	0
12	98.65	50.79	42.83	42.69	38.96
24	75.74	50.04	35.16	24.88	31.74
36	94.72	58.23	38.62	26.12	29.69
48	55.83	48.42	39.04	39.56	33.04
72	92.40	65.61	49.32	39.95	37.31
84	89.82	68.86	48.95	41.67	41.04

Table E-2 Solid Assay for Pulp 20 (Cu)

Time (hr)	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Collecting tank
0	0	0	0	0	0
12	522.92	527.41	525.11	546.84	513.85
24	523.09	529.00	520.56	529.28	492.35
36	535.26	503.61	502.67	477.37	490.15
48	515.92	496.88	474.77	476.52	491.42
72	524.42	520.16	498.37	482.61	473.52
84	482.06	495.85	487.71	479.24	494.03

Table E-3 Solid assay for Pulp 30 (Ag)

Time (hr)	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Collecting tank
0	0	0	0	0	0
12	117.98	71.11	60.83	48.66	
24	86.75	59.47	48.88	41.44	33.52
38	139.54	83.22	59.62	48.84	32.50
53	125.34	105.24	78.92	59.34	36.70
60	140.55	105.06	86.43	61.81	52.43
72	107.82	101.43	85.06	59.71	43.31

Time (hr)	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Collecting tank
0	0	0	0	0	0
12	501.86	498.30	474.81	483.73	
24	444.30	462.03	448.82	489.99	472.61
38	473.06	444.67	464.78	489.87	480.07
53	488.93	465.97	466.36	466.83	521.06
60	477.72	479.47	484.14	451.25	466.47
72	472.46	474.77	467.99	476.59	475.31

Table E-4 Solid assay for Pulp 30 (Cu)
Appendix F Ion Exchange Experimental Data

The results for isotherms tests are tabulated in Table F-1 to Table F-7. The %loaded for silver and copper can be calculated by the equation below:

$$\%$$
Loaded = $\frac{Ag, Cu \text{ in resin } [mg]}{Inital Ag, Cu [mg]} \times 100\%$

The loading capacity is calculated by the equation below:

$$Loading \ capacity \ \left[\frac{kg \ Ag, Cu}{tonne \ resin}\right] = \frac{Ag, Cu \ in \ resin \ [mg]}{Resin \ weight \ [g]} \times \frac{1}{10^6} \left[\frac{kg}{mg}\right] \times \frac{10^6}{1} \left[\frac{g}{tonne}\right]$$

The experiment results for resin in pulp test are summarized in Table F-8. In the table, the Amount Ag in solution and the %Ag loaded on resin are calculated by the equations below:

Amount Ag in solution
$$[mg] = Solution Volume [ml] \times [Ag]in solution [\frac{mg}{L}] \times \frac{1}{1000} [\frac{L}{ml}]$$

% Ag load on resin_t =
$$\frac{(Amount Ag \text{ in solution }_{t=0}[mg] - Amount Ag \text{ in solution }_{t}[mg])}{Amount Ag \text{ in solution}_{t=0}[mg]} \times 100\%$$

Bottle	Resin	[Ag] in	Ag in	Ag	Ag loading capacity	[Cu] in	Cu in	Cu	Cu loading capacity
Number	weight, g	solution, ppm	resin, mg	%loaded	(kg/tonne)	solution, ppm	resin, mg	%loaded	(kg/tonne)
1	1	32.88	2.07	55.7	2.07	92.25	1.07	18.8	1.07
2	2	10.10	3.21	86.4	1.60	68.05	2.28	40.1	1.14
3	4	2.31	3.60	96.9	0.89	33.85	3.99	70.2	0.99
4	8	1.03	3.66	98.6	0.46	19.50	4.71	82.8	0.59
5	10	0.87	3.67	98.8	0.36	15.20	4.92	86.6	0.49
6	12	0.72	3.68	99.0	0.31	12.60	5.05	88.9	0.42

Table F-1 Isotherm test: 0.2M thiosulfate, Amberlite IRA400, initial Ag = 3.71 mg, initial Cu = 5.68 mg

Table F-2 Isotherm test: 0.2M thiosulfate, Purolite A500plus, initial Ag = 3.79 mg, initial Cu = 5.25 mg

Bottle	Resin	[Ag] in	Ag in	Ag	Ag loading capacity	[Cu] in	Cu in	Cu	Cu loading capacity
Number	weight, g	solution, ppm	resin, mg	%loaded	(kg/tonne)	solution, ppm	resin, mg	%loaded	(kg/tonne)
1	0.5	45.8	1.5	39.6	3.26	101.84	0.16	3.0	0.34
2	0.7	49.0	1.3	35.4	2.04	100.25	0.24	4.5	0.36
3	0.8	50.3	1.3	33.7	1.68	99.30	0.28	5.4	0.37
4	0.9	46.8	1.5	38.3	1.63	98.24	0.34	6.4	0.38
5	1	40.4	1.8	46.8	1.64	95.11	0.49	9.4	0.46
6	2	13.4	3.1	82.3	1.48	65.61	1.97	37.5	0.93
7	4	2.8	3.7	96.4	0.90	25.93	3.95	75.3	0.98
8	10	0.7	3.8	99.1	0.37	8.50	4.82	91.9	0.48

Bottle	Resin	[Ag] in	Ag in	Ag	Ag loading capacity	[Cu] in	Cu in	Cu	Cu loading capacity
Number	weight, g	solution, ppm	resin, mg	%loaded	(kg/tonne)	solution, ppm	resin, mg	%loaded	(kg/tonne)
1	0.5	45.56	1.27	35.9	2.45	50.43	0.14	5.2	0.26
2	0.7	28.13	2.15	60.4	2.98	46.43	0.34	12.7	0.47
3	0.8	23.26	2.39	67.3	2.99	44.19	0.45	16.9	0.56
4	0.9	18.76	2.61	73.6	2.90	42.58	0.53	19.9	0.59
5	1	14.71	2.82	79.3	2.68	39.55	0.68	25.6	0.65
6	2	5.18	3.29	92.7	1.63	26.85	1.32	49.5	0.65
7	4	2.08	3.45	97.1	0.86	17.27	1.80	67.5	0.45
8	10	0.85	3.51	98.8	0.35	7.81	2.27	85.3	0.22

Table F-3 Isotherm test: 0.3M thiosulfate, Amberlite IRA400, initial Ag = 3.55 mg, initial Cu = 2.66 mg

Table F-4 Isotherm test: 0.3M thiosulfate, Purolite A500plus, initial Ag = 3.60 mg, initial Cu = 2.61 mg

Bottle	Resin	[Ag] in	Ag in	Ag	Ag loading capacity	[Cu] in	Cu in	Cu	Cu loading capacity
Number	weight, g	solution, ppm	resin, mg	%loaded	(kg/tonne)	solution, ppm	resin, mg	%loaded	(kg/tonne)
1	0.5	41.24	1.53	42.6	3.01	49.64	0.13	4.9	0.25
2	0.7	27.88	2.20	61.2	3.10	46.43	0.29	11.1	0.41
3	0.8	23.94	2.40	66.7	3.04	44.95	0.36	13.9	0.46
4	0.9	19.20	2.64	73.3	2.83	42.50	0.49	18.6	0.52
5	1	16.37	2.78	77.2	2.64	40.82	0.57	21.8	0.54
6	2	6.89	3.25	90.4	1.63	29.69	1.13	43.1	0.57
7	4	2.56	3.47	96.4	0.86	18.17	1.70	65.2	0.42
8	10	0.96	3.55	98.7	0.35	7.78	2.22	85.1	0.22

Bottle	Resin	[Ag] in	Ag in	Ag	Ag loading capacity	[Cu] in	Cu in	Cu	Cu loading capacity
Number	weight, g	solution, ppm	resin, mg	%loaded	(kg/tonne)	solution, ppm	resin, mg	%loaded	(kg/tonne)
1	0.5	28.76	2.20	60.5	4.08	47.63	0.09	3.5	0.16
2	0.7	22.94	2.49	68.5	3.67	46.04	0.17	6.8	0.25
3	0.8	18.26	2.73	74.9	3.37	44.03	0.27	10.8	0.33
4	0.9	15.53	2.86	78.7	3.11	42.55	0.34	13.8	0.37
5	1	12.25	3.03	83.2	2.63	40.08	0.46	18.8	0.40
6	2	6.30	3.32	91.3	1.63	33.29	0.80	32.6	0.39
7	4	3.07	3.49	95.8	0.88	24.98	1.22	49.4	0.31
8	10	1.31	3.57	98.2	0.36	13.22	1.81	73.2	0.18

Table F-5 Isotherm test: 0.4M thiosulfate, Amberlite IRA400, initial Ag = 3.64 mg, initial Cu = 2.47 mg

Table F-6 Isotherm test: 0.4M thiosulfate, Purolite A500plus, initial Ag = 3.57 mg, initial Cu = 2.63 mg

Bottle	Resin	[Ag] in	Ag in	Ag	Ag loading capacity	[Cu] in	Cu in	Cu	Cu loading capacity
Number	weight, g	solution, ppm	resin, mg	%loaded	(kg/tonne)	solution, ppm	resin, mg	%loaded	(kg/tonne)
1	0.5	37.49	1.69	47.5	3.32	50.86	0.09	3.5	0.18
2	0.7	28.26	2.16	60.4	3.08	48.78	0.20	7.4	0.28
3	0.8	24.58	2.34	65.6	2.92	47.54	0.26	9.7	0.32
4	0.9	21.96	2.47	69.2	2.78	46.57	0.31	11.6	0.34
5	1	18.25	2.66	74.4	2.46	44.85	0.39	14.9	0.36
6	2	8.53	3.14	88.0	1.47	35.99	0.83	31.7	0.39
7	4	4.03	3.37	94.4	0.84	26.89	1.29	49.0	0.32
8	10	1.59	3.49	97.8	0.34	13.52	1.96	74.3	0.19

Bottle	Resin	[Ag] in	Ag in	Ag	Ag loading capacity	[Cu] in	Cu in	Cu	Cu loading capacity
Number	weight, g	solution, ppm	resin, mg	%loaded	(kg/tonne)	solution, ppm	resin, mg	%loaded	(kg/tonne)
1	0.5	34.18	1.57	47.9	3.41	48.45	0.06	2.4	0.13
2	0.7	23.71	2.09	63.8	2.95	46.23	0.17	6.9	0.24
3	0.8	21.33	2.21	67.5	2.76	45.41	0.21	8.6	0.27
4	0.9	19.46	2.30	70.3	2.62	45.23	0.22	8.9	0.25
5	1	17.31	2.41	73.6	2.44	43.85	0.29	11.7	0.29
6	2	8.74	2.84	86.7	1.42	36.36	0.67	26.8	0.33
7	4	4.18	3.07	93.6	0.77	28.83	1.04	42.0	0.26
8	10	1.84	3.19	97.2	0.32	16.46	1.66	66.9	0.17

Table F-7 Isotherm test: 0.5M thiosulfate, Amberlite IRA400, initial Ag = 3.28 mg, initial Cu = 2.48 mg

Table F-8 Resin in Pulp

Time, min	Solution volume, ml	Sample taken, ml	[Ag] in solution, ppm	Amount Ag in solution, mg	% loaded on resin
0	1361		80.64	109.76	0.0
5	1361	3	77.60	105.62	3.8
10	1358	3	77.41	105.14	4.2
16	1355	3	77.78	105.40	4.0
31	1352	3	77.89	105.32	4.0
60	1349	3	76.48	103.18	6.0
90	1346	3	75.50	101.63	7.4

Appendix G Cementation Experimental Results

Table G-1 to G-4 show the results from cementation experiments. The $log(C_t/C_0)$ is for the kinetic calculation. C_t represents the concentration at time t. C_0 represents the initial concentration.

Time, minute	Ag in solution, ppm	$-\log(C_t/C_0)$
0	82.06	0.00
1	57.14	0.16
2	44.54	0.27
3	34.83	0.37
4	26.54	0.49
6	15.73	0.72
8	10.09	0.91
30	0.09	2.97

Table G-1 Zinc cementation with 0.07 g/L metallic zinc

Table G-2 Zinc cementation with 0.49 g/L metallic zinc

Time, minute	[Ag] in solution, ppm	$-\log(C_t/C_0)$
0	66.66	0.00
1	11.99	0.74
2	2.41	1.44
4	0.23	2.47

Table G-3 Copper cementation with 0.07 g/L metallic copper

Time, minute	[Ag] in solution, ppm	$-\log(C_t/C_0)$
0	68.60	0.00
5	51.61	0.12
10	42.05	0.21
15	31.37	0.34
30	8.83	0.89
45	3.48	1.29
60	0.76	1.96
75	0.45	2.19

Time, minute	[Ag] in solution, ppm	$-\log(C_t/C_0)$
0	66.66	0.00
1	46.88	0.15
3	25.93	0.41
5	15.44	0.64
10	2.99	1.35
15	0.29	2.36
20	0.11	2.79

Table G-4 Copper cementation with 0.48 g/L metallic copper