THE STUDY OF THE KINETICS OF GOLD LEACHING IN THE AMMONIUM THIOSULFATE SYSTEM IN THE PRESENCE OF COPPER

by

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ABSTRACT

The kinetics of gold leaching in ammonium thiosulfate solution in the presence of copper have been studied by electrochemical polarization and direct rotating disk leaching methods. The effects of pH, temperature, rotating velocity and the concentrations of different reagents on the gold leaching rate have been investigated.

It was found that the anodic oxidation of gold in ammonium thiosulfate solution is complex. Ammonia, thiosulfate and copper species all affect the anodic process. The anodic process is under surface reaction control. The above species plus oxygen are involved in the cathodic process. The role of copper species are facilitating oxygen reduction through the $Cu(S_2O_3)_3^{5-}/Cu(NH_3)_4^{2+}$ couple. The gold leaching rate in ammonium thiosulfate in the presence of copper species is mainly controlled by the cathodic process, which is under diffusion or mixed kinetics control.

The results of the rotating gold disk leaching study are consistent with those from the electrochemical study. The gold leaching process in ammonium thiosulfate solution is under diffusion or mixed kinetics control. The gold leaching rate can be correlated with different parameters as follows. The application of this rate equation is limited to the range of conditions used in this study.

$$r \propto [NH_3]^{1.557} \times [S_2O_3^{2-}]^{-0.63} \times [OH^-]^{0.447} \times [Cu]_T^{0.647} \times \omega^{0.675} \times T^{-3.72}$$

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NOMENCLATURE

C _b	bulk concentration (mole dm ⁻³)
Cs	surface concentration (moledm ⁻³)
D	diffusion coefficient ($cm^2 s^{-1}$)
E	potential of the electrode (V)
E°	standard potential (V)
F	Faraday constant, 96487 A s mol ⁻¹
Ι	current density (A cm ⁻²)
Iı	limiting current density (A cm ⁻²)
iL	limiting current (A)
κ	rate constant
М	molarity (mol dm ⁻³)
n .	number of electrons transferred
pH	negative logarithm to base of the activity of hydrogen ion
ppm	part per million
R	gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
r	corrosion rate (mol $m^2 s^{-1}$)
Re	Reynold number
SCE	standard calomel electrode
SHE	standard hydrogen electrode
Т	temperature (°C)
υ	kinematic viscosity ($cm^2 s^{-1}$)
ω	rotating velocity (revolutions per minutes)

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Х

1. INTRODUCTION

The most common leaching process for gold dissolution is cyanidation, a process that has been practiced for over a century and will continue to dominate the gold industries in the foreseeable future [Li and Miller, 1996]. However, more and more research activities have focused on alternative processes using non-cyanide lixiviants due to the following reasons:

- Environmental and social concern on the toxicity of cyanide. Expensive posttreatment processing is necessary to ensure environmental safety.
- Cyanidation is not economically feasible for some refractory ores, such as carbonaceous ores and copper-bearing gold ores.

One of current research areas is the leaching of gold with ammonium thiosulfate (ATS) in the presence of copper. Although ATS is not as effective as cyanide for oxide ores it may be superior for the leaching of certain refractory ores, which were listed above. Generally speaking, high gold extraction can be achieved in the ATS system (Jiang et al. 1993(1)). Unlike cyanidation, which has been conducted for over a hundred years, ATS technology has not been studied in detail. The solution chemistry of the gold leaching in ATS system has been studied by Li and Miller, et al. (1996). An extensive research program on ATS leaching gold from preg-robbing carbonaceous ores had been done at the Newmont metallurgical services laboratory (Wan, 1997). Since 1992, a total of three pilot plant scale tests and three demonstration plant tests have been completed using ammonium thiosulfate heap leaching technology for carbonaceous sulphidic refractory ores at Newmont gold company.

The gold leaching rate in the ATS system has been studied by several researcher (Block-Bolten & Torma, 1986; Gong et al, 1993(1), (2)) from ores/concentrates. It was reported that gold leaching kinetics were dominated by mineralogy of ores/concentrates studied (Gong et al, 1993 (1), (2)). Therefore, it is not surprising that some discrepancy exists in the literature regarding the effects of some parameters on gold leaching kinetics in ATS system due to the diversity of the mineralogy of ores/concentrates studied.

The object of this work is to investigate the effects of different parameters (rotating velocity, pH, temperature, and concentration of different reagents) on the gold leaching rate in the ATS system in the presence of copper in a pure gold system. Polarization and gold disk leaching methods have been used in this study.

This thesis contains five chapters. Chapter two provides a review of existing literature on the ATS system for gold recovery, mainly focusing on gold leaching and its kinetics. The experimental methods are described on chapter three. Chapter four summarizes the experimental results and discussion. The conclusions of this study are provided in chapter five.

2. LITERATURE REVIEW

2.1. Solution Chemistry

Thiosulfate salts are compounds containing the group $S_2O_3^{2-}$ which is a structural analog of sulfate with one oxygen atom replaced by a sulfur atom. Therefore, the two sulfurs atom in thiosulfate are not equivalent and the sulfide-like sufur is responsible for the reducing properties and complexing abilities of thiosulfate. Thiosulfate is stable in alkaline solution, but decomposes in acid solution:

$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + S + SO_2 + H_2O$

Equation 2.1

It is well known that thiosulfate is easily oxidized by O_2 (in the presence of catalyst), Cu^{2+} and H_2O_2 , and this issue will be addressed later. Thiosulfate can form complex ions with many metals, such as gold, silver and copper ion. The most famous application is using sodium thiosulfate to dissolve silver bromide. Thiosulfate can also form metal sulfide precipitate with copper, silver and mercury. Thiosulfate is a moderate reductant:

 $S_4O_6^{2-} + 2e \rightarrow 2S_2O_3^{2-}$ $E^0 = 0.09 V_{SHE}$, Equation 2.2

Iodine can oxidize thiosulfate to tetrathionate, and this reaction is widely used in analytical chemistry.

From the above description, it can be seen that thiosulfate is reactive in solution. Thiosulfate is not stable thermodynamically. Thiosulfate has no dominant stability region in aqueous solution. By removing from consideration more stable species

such as sulfate ions, the characteristic features of the metastable species can be examined (Figure 2.1). As we can see, the dominant metastable region of thiosulfate exists in a narrow range: pH from 4-14, Eh 0-0.25. V_{SHE} .



Figure 2.1 Eh-pH diagram for the metastable system S-H₂O at 25°C (after Molleman, 1998)

By ignoring more stable species such as sulfate and nitrogen, Li & Miller (1996) plotted the metastable Eh-pH diagram of gold-ammonia-thiosulfate system (Figure 3.6). During calculation, only the following species are considered: NH_4^+ , NH_3 , $H_2S_2O_3$, $HS_2O_3^-$, $S_2O_3^{2-}$, H_2S , HS^- and S^{2-} . According to this pH-Eh diagram, under alkaline operating condition (pH> 9), $Au(NH_3)_2^+$ is the most stable gold species instead of $Au(S_2O_3)_2^{3-}$, which is considered to be more stable by most other researchers (Hu and Gong, 1991; Cai, 1997). The same authors (Li, & Miller 1996) suggested that the predominant gold species is $Au(S_2O_3)_2^{3-}$ in the leaching condition since the gold rest

potential varied with thiosulfate concentration instead of ammonia concentration. The discrepancy may derive from the nonideal behavior of the gold complexes since activities of species are not necessarily equal to the concentrations of species; or the experimental errors in the determination of the equilibrium constants could be blamed for the discrepancy. Molleman (1998) found that the free energy value for thiosulfate in the literature varied from -518.8 kJ/mol to -532.2 kJ/mol. Figure 2.2 adopted the latter value. However if the former value is adopted, the Eh-pH diagram is totally different as presented in Figure 2.3: the gold (I) thiosulfate complex predominates in the whole pH range. This example shows that Eh-pH diagrams for these systems have to be interpreted with caution.



Figure 2.2 Gold-ammonia-thiosulfate-water systems under following conditions: 0.1 M S₂O₃²⁻, 0.1M NH₃, 5×10^{-4} M Au, $\Delta G_1^{0}(S_2O_3^{2-}) = -532.2$ kJ/mol (After Li, et al, 1995)

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The thermodynamic stability diagrams have been constructed for Au/Silver-cyanide, -halogen, -thiourea and –thiosulfate systems by Wang (1992). Due to the deficiency of some thermodynamic data for mixed species, the estimated stability constants were used in calculation. It was shown that the stability constant of a mixed-ligand metal complexed(A_mB_n) in solution can be estimated from the stability constants of the parents complexes, A_{m+n} , B_{m+n} by using the following equation:

$$log \beta_{A_m B_n} = \frac{m log \beta_{A_{m+n}} + n log \beta_{B_{m+n}}}{m+n} + log(\frac{(m+n)!}{m!*n!})$$
 Equation 2.3
Excellent agreement can be obtained between estimated and determined data from the Au-Br-Cl system. Applying this method:

 $Au^+ + NH_3 + S_2O_3^{2-} \rightarrow AuNH_3S_2O_3^{-1} \log \beta = 26.55$ Equation 2.4

As a result, $AuNH_3S_2O_3^-$ is dominant over broad range of pH and Eh, including the typical gold leaching condition: pH 9-10, E_h 200 mV_{SHE}. However, no evidence was presented to verify the existence of this species.

From either of the Eh-pH diagrams, it is critical to maintain the solution potential above 0.05 V_{SHE} to keep gold in solution as dictated by the following half cell reaction:

$$Au(S_2O_3)_2^{3-} + e \rightarrow Au + 2S_2O_3^{2-} E^0 = 0.153 V_{SHE}$$
 Equation 2.5

The rate of gold leaching is enhanced greatly by a catalytic copper reaction (Cai, 1997; Cao, et al, 1992). Unlike the relatively simple cyanide system, the ammonium thiosulfate system is a significantly more complex system. Normally it has

three indispensable components: ammonia, thiosulfate and copper ions. Many reactions may occur among these species and with gold. Molleman (1998) and Li & Miller (1996) studied the copper–ammonia-thiosulfate-water system recently and the Eh-pH diagram is presented in Figure 2.4. It shows that copper(I)thiosulfate is the predominant species in solution at most common potentials and appears to be in equilibrium with copper(II) ammine. At low potential, the decomposition of thiosulfate leads to the precipitation of copper sulfide. These precipitates are observed as black precipitates in solution containing ammonia, thiosulfate and copper (Li and Miller, 1996).

It is generally agreed that gold dissolution can be represented by the following overall reaction:

$2Au + 4S_2O_3^{2-} + 1/2 O_2 + H_2O \rightarrow 2Au(S_2O_3)_2^{3-} + 2OH^-$ Equation 2.6

However, conflicting opinions exist on the exact role of the copper in the leaching chemistry. Under ambient condition, generally the gold extraction in the absence of copper is far less than that in the presence of copper; however, an excess amount of copper is detrimental to gold leaching from gold bearing ore/concentrate (Cai, 1997, Hu and Gong, 1991). Li and Miller (1996) verified this effect of Cu(II) on the gold leaching rate in pure gold–ammonia-thiosulfate-water system as shown in Figure 2.5 and attribute the detrimental effect on copper to the following reasons:



Figure 2.3 Eh-pH diagram of the gold-thiosulfate-ammonia-water system at 25°C. The activities of the species are 2.5 ×10-5 M Au, 0.2 $S_2O_3^{2-}$ and 0.4 M NH₃. $\Delta G_f^{o}(S_2O_3^{2-}) = -518.8 \text{ kJ/mol}$ (After Molleman, 1998)



Figure 2.4 Copper-ammonia-thiosulfate-water system at 25°C, 0.1 M thiosulfate, 0.1 M ammonia, 5×10⁻⁴ M copper (after Li and Miller, 1996)

- Copper ion complexes with thiosulfate leading to a lack of lixiviant left for gold dissolution
- Copper ions accelerate the decomposition of thiosulfate

From the thermodynamic analysis and kinetic studies, Li and Miller (1996) modified the equation 2.6 to highlight the catalytic effect of copper:

Au + 5 S₂O₃²⁻ + Cu(NH₃)₄²⁺
$$\rightarrow$$
 Au(S₂O₃)³⁻ + Cu(S₂O₃)₃⁵⁻ + 4 NH₃ Equation 2.7
Oxidant

The regeneration of Cu(II) is suggested to be very important. From the above equation, it is suggested that it is vital to keep the molar concentration ratio of ammonia to thiosulfate in a certain range in order to regenerate the cupric species. Increasing the concentration of single ligands will have a limited positive effect on gold leaching and will eventually decrease the gold leaching rate. This effect is illustrated in Figure 2.6. However, it is not clear if the pH was fixed or not during the experiments; if not, the effect of $[NH_3]/[(NH_4)_2S_2O_3]$ molar ratio on the gold leaching rate may be due to the effect of pH, which was reported to have great impact on the gold leaching rate. Gong and Hu (1994) also reported that high concentration of thiosulfate prevent the regeneration of Cu(II) and maintaining the proper Cu:NH_3:S_2O_3²⁻ ratio is very critical.



Figure 2.5 Effect of copper sulfate concentration on gold leaching rate (after Li and Miller, 1996)



Figure 2.6 Effect of concentration ratio of ammonia to thiosulfate on gold leaching rate (after Li and Miller, 1996)

Thiosulfate ions are metastable and tend to undergo chemical decompositions in aqueous solutions. Numerous factors affect the system stability. Depending on the solution potential and pH, two types of thiosulfate degradation may occur in the system: oxidative and reductive decomposition with elemental sulfur and copper sulfides forming as confirmed by XRD analysis (Li & Miller, 1996). The possible reactions are:

 $Cu^{2+} + S_2O_3^{2-} + 6H^+ + 6e^- \rightarrow S + CuS + 3H_2O$ Equation 2.8 $2Cu^+ + S_2O_3^{2-} + 6H^+ + 6e^- \rightarrow S + Cu_2S + 3H_2O$ Equation 2.9

Such reactions are not desirable; they not only consume thiosulfate and copper but also may block the surface of gold and inhibit further reaction.

In the case of oxidative decomposition of thiosulfate, a series of stable or metastable sulfur-oxygen species may form. These include $S_5O_6^{2-}$ (+2), $S_2O_3^{2-}$ (+2), $S_4O_6^{2-}$ (+5/2), $S_2O_4^{2-}$ (+3), $S_3O_6^{2-}$ (+10/3), SO_3^{2-} (+4), $S_2O_6^{2-}$ (+5), SO_4^{2-} (+6), $S_2O_8^{2-}$ (+7), SO_5^{2-} (+8). Thermodynamically, sulfate is the stable species under the preferred leaching conditions: Although the oxidative degradation appears to be rather complicated due to the existence of many species, the reactions can be generally represented as following:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$$
 Equation 2.10

Equation 2.11

 $S_4O_6^{2-} + 10 H_2O \rightarrow 4SO_4^{2-} + 20 H^+ + 14e$

Since thiosulfate is not stable thermodynamically, the loss of the lixiviant is inevitable. Additives such as sulfite and sulfate(Gong and Hu, 1989, 1991,1994) have

been suggested to stabilize the thiosulfate ions in solution according to the following reactions:

$$4SO_{3}^{2-} + 2S^{2-} + 3H_{2}O \rightarrow 3S_{2}O_{3}^{2-} + 6OH^{-}$$
Equation 2.12
$$SO_{4}^{2-} + S^{2-} + H_{2}O \rightarrow S_{2}O_{3}^{2-} + 2OH^{-}$$
Equation 2.13

Hu and Gong (1994) studied the oxidation of sulfite and thiosulfate in ammonium solution with addition of Cu(II). It was found that the oxidation could be divided into two stages: initial stage and continuing stage. The initial oxidation rate is two orders of magnitude higher than the continuing stage. Addition of sulfate can reduce the oxidation rate of both stages. The initial stage of sulfite oxidation is under chemical reaction control, the main oxidant is Cu(II); the continuing stage is under oxygen diffusion control, the main oxidant is oxygen, Cu[II] has no effect on the oxidation rate. The initial stage of thiosulfate oxidation is also under chemical control and the continuing stage is under mixed control.

Electro-oxidation of thiosulfate ion on a gold electrode by means of cyclic voltammetry and Auger electron spectrosopy (AES) was studied by Pedraza et al (1988). The solution contained 0.01 M Na₂S₂O₃. A current peak at 0.44 V_{SHE} is identified as thiosulfate oxidation. As a result of oxidation, elemental sulfur was found to be deposited in the gold surface by both electrochemical analysis and AES detection. This sulfur film hinders the further oxidation. It was also found that thiosulfate ions decomposed when in contact with gold at open circuit potential, leaving a film of several sulfur-containing species, which were not reported to block the oxidation of thiosulfate.

However, as mentioned earlier, the ATS system is very complicated and the exact degradation pathway for thiosulfate is still open to further investigation. Many reactions are possible between existing and generated species in solution. The reactions quoted in the literature do not reflect this complexity. Obviously further fundamental studies are needed.

Jiang et al (1997) studied the anodic oxidation of thiosulfate on a gold electrode by electrochemical methods. The oxidation peak of thiosulfate is around 620 mV vs SHE in the absence of ammonia. Peak current of thiosulfate oxidation increases with thiosulfate concentration in the absence of copper ion and ammonia. The cyclic polarization studies showed that the oxidation of thiosulfate is irreversible. The introduction of copper and ammonia change the thiosulfate oxidation rate significantly: The oxidation rate of thiosulfate is far less than that in the absence of ammonia and copper above a certain potential; peak potential shifts negatively to 350 mV Vs SHE in the presence of ammonia and copper. However, the current density in the presence of copper ion and ammonia is actually more than that in the absence of ammonia and copper when the potential is less than 400 mV vs SHE. This means that under leaching condition, thiosulfate oxidation would be accelerated in the presence of ammonia and copper. The same result can be obtained in the presence of ammonia but without copper ion and it is concluded that this effect is mainly caused by free ammonia. It was found that thiosulfate is most stable at pH 10 and either an increase or decrease the pH will accelerate thiosulfate degradation. The addition of sulfite was found to have no significant effect on thiosulfate oxidation rate.

2.2. Leaching of Gold in The Thiosulfate System

The use of thiosulfate for the recovery of gold was first proposed in the 19th century and is know as "Patera Process". In this process, gold and silver bearing ores were first treated by a chloridizing roast followed by thiosulfate leaching (Zhu, 1993).

Berezowsky and Gormely (1978) developed an atmospheric ammoniacal thiosulfate leach system to recover gold and silver from ammoniacal oxidative pressure leach residues of sulfidic copper concentrate. The residues were comprised predominantly of hydrated ferric oxides and unleached sulfides. Extractions of 88-95% for gold and 83-98% for silver were achieved after 2 hours leaching with 0.4-0.8 M $S_2O_3^{2-}$ at 40 – 60°C.

Kerley (1981,1983) patented a process for the recovery of precious metals from refractory ores; particularly those containing manganese and/or copper, by lixiviation using ammonium thiosulfate leach solution. The main feature of the patent is the addition of sulfite ions to control the stability of the solutions during leaching. Kerley claimed that the sulfite ions inhibit the decomposition of thiosulfate and thus prevent the precipitation of metal sulfides. However, Molleman (1998) closely examined the Eh-pH diagram and found that this reaction is not thermodynamically favorable in the leaching condition: $1.2 \sim 1.35$ M S₂O₃²⁻, $1 \sim 4$ g/L Cu²⁺, pH \geq 7.5 (adjusted by ammonia).

The process patented by Kerley was commercialized in Mexico, but the scale-up from the laboratory to full scale plant failed. Perez and Galaviz (1987) described the modifications required to make plant operation feasible. The most important process adjustment was the pH value that should be maintained at a minimum level of pH 9.5 instead of 7.5.

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The higher pH inhibits the action of iron and ferric salts that are present in the lixiviating solution as a result of grinding the ore in a ball mill prior to lixiviating. According to Perez and Galaviz (1987) the ferric ion accelerates the oxidation of thiosulfate to tetrathionate:

$$2S_2O_3^{2-} + 2Fe^{3+} \rightarrow 2Fe^{2+} + S_4O_6^{2-}$$

The ferrous ion in turn displaces silver and gold from solution:

 $FeO + Ag_2S_2O_3 \rightarrow Ag_2S + FeSO_4$

At high pH (9.5 and higher) ammonia hydrolysis produces hydroxide ions which react with the ferrous ions and thus preventing iron from displacing silver and gold from solution:

 $Fe^{2+} + 2NH_3 + 2H_2O \rightarrow Fe(OH)_2 + 2NH_4^+$

 $Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3(S)$

Ter-Arakelyan et al. (1984) reviewed the research in gold leaching in the thiosulfate system in the former USSR. It was suggested the effect of NH_3 in the system is to reduce the formation of sulfide precipitates and this effect is only valid during

15

Equation 2.15

Equation 2.17

Equation 2.16

Equation 2.14

leaching in autoclave but not ambient condition. Experiments were carried out on the mill tailing with 2 g/t Au in a glass pachuca tank with compressed air. The results confirmed that the addition of sulfite does increase the degree of extraction of gold. It was found that the filtrates obtained with the addition of sodium sulfite remain clear in several days, which is contrary to the filtrates obtained without sulfite addition. The simultaneously addition of copper sulfate with sodium sulfite promotes the extraction of gold. In the absence of sodium sulfite, the copper sulfate reduced the gold extraction. The processes that occur with or without the presence of sodium sulfite are suggested as following:

 $CuSO_4 + 2 Na_2S_2O_3 + 1\frac{1}{2} Na_2SO_3 + \frac{1}{2} H_2O + \frac{1}{2} O_2$

$$\rightarrow$$
 Na₃[Cu(S₂O₃)₂] + ¹/₂ H₂SO₄ + 2 Na₂SO₄

1.1.1

Equation 2.18

 $CuSO_4 + 3 Na_2S_2O_3 + H_2O + O_2 \rightarrow CuS + 3 Na_2SO_4 + H_2SO_4$ Equation 2.19

The effects of reagent concentration, such as thiosulfate, copper (II), sulfite and ammonia on the gold and silver extraction from gold concentrate, were studied by Zhang and Li (1987). It was shown that maintaining proper $[S_2O_3^{2^-}]/[Cu^{2^+}]$ and $[S_2O_3^{2^-}]/[SO_3^{2^-}]$ is very critical. The gold leaching kinetics were fitted with shrinking core model; the activation energy was calculated to be less than 5 kcal/mol.

Zipperian and Raghavan (1998) identified the parameters of importance in the dissolution of gold and silver values from a rhyolite ore with a high manganese content using ammonium thiosulfate solution containing copper. The effects of thiosulfate, ammonia concentration, temperature, and copper sulfate addition were studied. Optimum conditions were established at 2 M $S_2O_3^{2^-}$, 4.1 M NH₃, 6 g/L Cu²⁺, 50 $^{\circ}$ C, and 2 hours leaching in the absence of oxygen. In the absence of cupric ions only 14% of gold was extracted. Increasing cupric ion concentration enhanced the initial rate of gold extraction, but the ultimate extraction was not influenced by the cupric ion concentration in the range of studies (up to 6 g/l Cu). Furthermore, it was concluded that maintaining optimal pH and Eh conditions (pH 10 and 200 mV) are necessary to prevent precipitation of copper as Cu₂S. Half of the thiosulfate in the lixiviant solution at pH 9.5-10 was consumed during the dissolution process.

Hemmati et al (1989) studied the application of ammonium thiosulfate leaching for gold recovery on various types of ores. It was found that the highest gold extractions were achieved at 0.7 M S₂O₃²⁻, 3M NH₃, pH 10.5, 35 °C (cover the range 25 ~35 °C) and oxygen partial pressure of 103 kPa. 73% of gold was extracted under these conditions. No impact was found on either gold extraction or thiosulfate consumption by variation of the oxygen pressure in the range of 0 ~ 206 kPa. Hemmati et al (1989) concluded that the efficiency of thiosulfate leaching depends upon ore type. For treating carbonaceous ores, thiosulfate was found to be chemically superior and economically advantageous over cyanide.

Langhans et al (1992) focused on maximizing gold extraction while minimizing thiosulfate consumption at low reagent concentrations and ambient temperature and a pH range between 9 and 11. The range of the thiosulfate concentration

tested was $0.05 \sim 0.2$ M. The research was conducted on low-grade oxidized gold ores with application to heap, dump, or in-situ leaching techniques and found to be competitive with conventional cyanidation. After leaching for 48 hours, 83% gold extraction was achieved with 0.2 M S₂O₃²⁻, 0.09 M NH₃, 0.00625 M sulfite, 63.5 ppm Cu²⁺ with 0.4 kg/t S₂O₃²⁻ consumption. It was concluded that these results compare favorably with 86% gold extraction after 24 hours with 0.21 kg CN⁻/t consumption using standard cyanidation.

The research group of the Institute of Chemical Metallurgy (ICM) in China have systematically studied thiosulfate technology for gold and silver(Cao et al, 1992, 1994; Gong et al, 1993(1), 1993(2), 1994; Hu et al, 1989, 1991,1994).

Hu and Gong (1991) studied the solution chemistry of the thiosulfate system. It was found that the existence of both sulfite and sulfate can reduce the consumption of thiosulfate and sulfate is more favorable since sulfite itself is not stable under the leaching condition. It was also determined that reducing Cu(II) and oxygen addition are critical to reduce thiosulfate consumption. There must be a trade off between the gold extraction and thiosulfate consumption.

The kinetics of gold and silver leaching from gold sulfide concentrates in thiosulfate solution was studied and compared with the kinetics of pyrite and chalcopyrite anodic polarization in ammonia-ammonium sulfate solution by Gong et al., 1993(1), 1993(2), 1994. It was found that both gold and silver leaching kinetics are similar to the kinetics of pyrite anodic oxidation. The author concluded the dissolution of gold and

silver from gold sulfide concentrate was closely associated with the pyrite corrosion. Further mineralogical studies (Cao et al. 1994) showed that, without of the presence of the free ammonia, copper minerals remained untouched even in the presence of ammonium. When in the presence of free ammonia, copper mineral was attacked. It was concluded that, in the leaching process, ammonia first attack the gold bearing minerals and expose gold to the leaching solution and then gold was oxidized in associated with thiosulfate.

Cai, (1997) studied the effect of different parameters on gold extraction using ammonium thiosulfate from oxide ores, in which, S_T = 0.73%, gold = 1.28 ppm. It was reported that, in the absence Cu²⁺, NH₃ and S₂O₃²⁻, the gold extraction is negligible. In the presence of 2M NH₃ and 0.12 M CuSO₄, gold extraction increased up to 70% extraction. The introduction of agitation increase the gold extraction with (from 60-72%) or without (20 to 30%) CuSO₄ (0.12 M) addition. Cai (1997) also reported that, the presence of copper species can significantly increases the gold leaching rate. The author suggested that in the ATS system, oxygen alone is not sufficient to oxidize gold from the ore sample. Without ammonia and cupric ion, the gold extraction with ammonium thiosulfate was strongly affected by temperature. In the presence of ammonia and cupric ions, gold extraction was also affected by temperature, but in less significant way. This was consistent with Jiang et al (1993). It was found the extraction was preferably carried out at temperature of 60°C.

Only 9% of the gold was extracted in the absence of ammonia. Gold extraction increased dramatically with increase of ammonia from 0-2 mol/L (NH₃/ S₂O₃²⁺ from 0 ~ 7), beyond which gold extraction was not increased significantly. When the ammonia over 4 mol/L, lower extraction were obtained. Cai (1997) suggested that addition of ammonia may lead to dissolving some sulfide precipitates, such as CuS, Cu₂S and FeCuS₂. These sulfides are easily formed due to the nature of ores and the decomposition of thiosulfate. The formation of some precipitates such as (NH₄)₅Cu(S₂O₃)₃, which could cover the ore's surface and hinder the attachment of thiosulfate to the ore, was suggested to explain the detrimental effect of ammonia over 4 mol/L. Cai (1997) also found that the introduction of ammonium sulfate does increase the gold extraction rate. It was also found gold extraction was increased from pH 7.5 to 10.5, then leveled off. However, it can also be considered as the effect of ammonia instead of pH since higher pH leads to higher free ammonia concentration.

Li and Kuang (1998) report that: in thiosulfate leaching of gold from both oxide and sulfide ores, adding of NaCl instead of Cu(II) significantly increased the gold extraction. It is suggested that the formation of intermediate $[AuCl_2]^2$ facilitate the gold oxidation:

$[AuCl_2]^- + 2 S_2O_3^{2-} \rightarrow [Au(S_2O_3)_2]^{3-} + 2Cl^-$ Equation 2.20

However it is questionable since the standard reduction potential of $Au/[AuCl_2]$ is as high as 1.154 (Molleman, 1998) and without strong oxidant, it is very unlikely to form $[AuCl_2]$ in solution. It is more likely that, as the introduction NaCl, more copper in ores was leached out and this was responsible for the increasing of gold leaching rate. This can also explain the fact that the gold extraction decreased as [NaCl] was increased over 1 mol/L: oxidation of thiosulfate due to the high Cu(II) concentration in solution reduced the rate of gold leaching. The effects of $[S_2O_3^{2^-}]$, [NaCl], [NH₃] and temperature on gold leaching were also studied by Li and Kuang (1998) and the results were compatible with those of Cai(1997). It is noted that the optimum $[NH_3]/[S_2O_3^{2^-}]$ ratio was around 1. It was also reported that the addition of sodium dodecyl sulphonate (SDS) significantly increased the gold extraction. This was reported to be due to the fact that SDS can decrease the solution surface tension, and increase the leaching rate.

Newmont Gold Company evaluated the application of ammonium thiosulfate on a demonstration heap leach of 327,000 metric tonnes of low-grade carbonaceous sulfide ores that was pretreated by bio-oxidation. The average gold recovery for thiosulfate heap leach at a particle size of minus 1.9 cm was found to be approximately 55%. Ammonium thiosulfate consumption was about 5 kg/t carbonaceous ores (without bio-oxidation) and 12-15 kg/t for bio-oxidized ores. Typical leaching solutions used contained 0.1 M $S_2O_3^{2^-}$, 0.1 M NH₃, and 30 ppm Cu²⁺ [Wan, 1997].

The application of a thiosulfate salt lixiviant to recover gold from an oxidative pressure leaching slurry is described in a patent granted to Marchbank et al (1996). Ore slurry of refractory sulfidic and refractory carbonaceous ores is subjected to pressure oxidation in an autoclave under neutral or alkaline conditions followed by leaching with thiosulfate salt in stirred tank reactors. Typical leaching conditions are

0.0025 to 0.1 M (NH₄)₃S₂O₃, 50 to 100 ppm Cu²⁺, 40 -55 °C, and a minimum sulfite concentration of 0.0001 M, while maintaining a pH between 7 and 8.7.

2.3. Gold Recovery From Thiosulfate Solution

Thiosulfate leaching of gold has not been commercialized yet and there is no predominant method for ultimate gold recovery in this system. Some research studies on recovery of gold from thiosulfate have been published and several methods have been suggested: cementation; carbon adsorption; direct electrowinning; reductive precipitation; ion exchange; solvent extraction.

Zhao et al (1996, 1997, 1998(1), 1998(2)) intensively studied the solvent extraction of gold from thiosulfate solution with alkyl phosphorus ester, amines and mixed amines. Gold can be extracted effectively from gold- thiosulfate solution. However, no literature was found which reported the selective extraction of gold from a thiosulfate solution.

Awadalla and Ritcey (1991) reported the use of sodium borohydride for the reduction of gold and silver in acidic solution at pH 5 \sim 7. Impurities can be removed through precipitation. However, in the case of copper-gold thiosulfate solution, the precipitation of copper is undesirable and pH adjustment could be expensive.

Gallagher (1987) reported that activated carbon has a very low affinity for the gold(I) thiosulfate complex. This behavior makes thiosulfate leaching superior to cyanidation in treating carbonaceous "preg-robbing" ore, but the standard CIP/CIL technology in cyanidation is not applicable to thiosulfate system. However Mckee and Lulham (1991) found the gold was effectively recovered by the addition of a stoichiometric amount of cyanide to the leaching solution, enabling the recovery of the gold cyanide complex by activated carbon.

Abbruzzese et al. (1995) explored the possibility of direct electrowinning of a gold thiosulfate leach solution onto a steel cathode. The kinetics of electrowinning was reported to be very fast and gold recovery was as high as 99%. The current efficiency was 4%. Thermodynamic analysis showed that the directly electrowinning is viable and there is some industrial practice on electrowinning of silver from thiosulfate solution (Ouyang, 1999).

Hu and Gong (1989) studied the recovery of gold from thiosulfate solution by copper powder, activated carbon, iron powder and zinc powder. It was reported the first two methods are not viable for gold recovery. Zinc powder will precipitate both gold and copper from solution. Iron powder can precipitate gold and maintain most copper in solution. Guerra and Dreisinger (1999) studied the factors affecting copper cementation of gold from ammoniacal thiosulfate solution. It was found the cementation was under diffusion control. Increased temperature and high pH/ammonia concentration enhance cementation performance while the presence of sulfite and copper ions in solution negatively affect the cementation.

The use of anion exchange resins for the selective recovery of gold and silver from simulated thiosulfate leach liquors containing copper, gold and silver was studied by Atluri (1987). Marchbank et al, 1996 and Thomas et al, 1998, patented a process to recover gold and copper from thiosulfate solution using ion exchange resin. Copper is recovered from the resin by elution with a thiosulfate solution; gold is recovered from the resin by elution with a thiocyanate. Unfortunately only poor selectivity can be obtained for gold or silver over copper.

The recovery of gold from thiosulfate system is also very complicated, and more researches need to be done before commercial technology is available.

2.4. Kinetics Studies

Since the gold-ammonia-thiosulfate system is not stable thermodynamically, the solution chemistry as was discussed in 2.1 is inevitably associated with kinetics in this system. The focus of this review is the gold leaching rate in ammonia-thiosulfate system.

2.4.1. Electrochemical studies

The electrochemical basis of metal dissolution is well established (Nicol, 1993). The center of such theoretical treatment of such reactions is the recognition that the rate of electrochemical reactions are functions of the electrochemical potential in addition to the concentrations of species taking part in the rate determining process. Here, the reaction rate is in the form of current, which can be converted to corrosion rate by Faraday's law:

- $r = \frac{i}{nF}$ Equation 2.21 where r is corrosion rate (mol/cm²s), i is the current density (A/cm²), n is the number of electron transferred and F is the Faraday constant (96487 A s/mol).
- A typical dissolution reaction can be treated as two coupled electrochemical processes which, under freely-dissolving conditions, occur at equal rates. For example, gold leaching in cyanide solution can be divided into anodic and cathodic reactions, which can be represented as following:

Anodic:	$Au + 2CN \rightarrow Au(CN)_2 + e$ -	Equation 2.22		
Cathodic:	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	Equation 2.23		
These two half reactions can be studied respectively by polarization technology as shown				

in Figure 2.7.



Figure 2.7 Current-voltage curves for gold and oxygen in 0.1% KCN solution (after Wadsworth, 1991)

According to the mixed potential theory, the total rate of oxidation must equal the rate of reduction. As we can see from Figure 2.7, there is an intersection point of anodic and cathodic polarization curve, where cathodic current is equal to anodic current. The potential at this intersection point is the mixed potential.

Kudryk & Kellogg (1954) first applied this method to study the kinetics of gold leaching, including both the anodic dissolution of gold as well as oxygen discharge at the gold – solution interface and successfully correlated the mixed potential to the leaching kinetics. It was found that the gold leaching rate was either controlled by the rate of diffusion of cyanide or oxygen. After Kudryk and Kellogg (1954), similar methods were applied for gold and silver or alloy dissolution in cyanide system: Tshilombo & Sandenbergh (1999) studied the influence of impurities in the dissolution of
gold in cyanide solutions; Woods (1991) determined the leaching rate of precious metals by the corrosion potential and voltammograms of the anodic oxidation reaction; Guan and Han (1994) studied the dissolution behavior of gold/copper alloy. Hiskey and Sanchez (1990) investigated the factors influencing the dissolution kinetics of pure silver in cyanide solution in terms of an electrochemical mechanism. Satisfactory results can usually be obtained. Electrochemical mechanisms are generally applicable to metal or metal sulfide minerals dissolution and the electrochemical studies of gold leaching in cyanide solution were successful.

2.4.2. Direct leaching

As was discussed in the electrochemical studies section of an electrochemical process, the rate is measured as current and then the current can be converted into leaching rate by Faraday's law. However, either the anodic or the cathodic processes or both can be composed of several reactions, and it is impossible to identify what fraction of each reaction account for the currents. Therefore it is important to complement the electrochemical studies with direct leaching tests to compare and verify the results. In the first place, Kudryk and Kellogg (1954) realized the importance of direct leaching studies; the gold specimen for the direct leaching was identical to the electrochemical studies. The results were in good agreement to that obtained from the electrochemical studies, which further verified that the mechanism of gold leaching in cyanide is electrochemical mechanism.

Direct leaching can be imposed on the ores/concentrates or pure metals/minerals. However, while considering the kinetics of leaching ores/concentrates,

the behavior of associated minerals and gangue is hard to distinguish from the leaching behavior of the main metals/minerals studied. Since electrochemical studies are generally applied on the pure metals/minerals, it makes sense to perform the direct leaching studies in the same way.

Since the working electrodes (Gold) have a fixed shape, the working surface areas are kept constant during electrochemical experiments. It is therefore better to use the same geometry electrode as that used in electrochemical studies during direct leaching studies. For example, if metal power is used during direct leaching, it is hard to eliminate the effect of surface area on the metal leaching since the surface area changes continuously during experiments.

The dissolution of metals in aqueous solution can be broken down into five steps (Guan and Han, 1993):

- Diffusion of the reactant(s) from the bulk of the solution to the metal surface through the boundary layer;
- 2. Adsorption of the reactant(s) onto the metal surface;
- 3. Chemical reaction at the surface;
- 4. Desorption of the soluble product(s);
- 5. Diffusion of the product(s) through the boundary layer back to the bulk solution.

In most cases, one or several of these steps are slower than the other. The slowest step alone practically controls the overall reaction rate. It is therefore of great importance to determine the limiting step of the overall reaction solution. If step 1 or 5 is the slowest step in the sequence, then the reaction is under diffusion control; if step 2, 3 or 4 is the slowest step, then the reaction is under chemical control. In the study of the dissolution rate of metals and sulfides, the rotating disc geometry has been widely used in many cases (Guan and Han, 1993; Pesic and Seal, 1990; Chen et al, 1980; Choi et al, 1991). Although it is not a practical geometry, it is a convenient geometry since hydrodynamics of the rotating disk are well established. When mass transfer controls the dissolution of metals or sulfides, the equation derived by Levich is used to describe the overall leaching process:

$$\frac{dC_{b}}{dt} = 0.62 (A/V) D^{2./3} v^{-1/6} w^{1/2} (C_{s} - C_{b})$$

= $k_{m} (C_{s} - C_{b})$ Equation 2.24

where:

 $k_m = 0.62(A/V)D^{2./3}v^{-1/6}w^{1/2}$

D is the diffusivity of the limiting reactant or product metal ion

 ω is the angular velocity of the rotating disc

 υ is the kinematic viscosity of the solution

 C_b is the concentration of the limiting reactant/product metals ion in the bulk solution C_s is the concentration of the limiting reactant/product metals ion in the surface of electrode

A is the projected area of the rotating disc

V is the volume of the solution

It should be emphasized that in the case of the diffusion-controlling mechanism, the overall rate will be directly proportional to the concentration of the limiting reactant or product and the square root of the angular velocity. In addition, the corresponding activation energy will be relatively small (2-5 kcal/mole).

If a heterogeneous chemical reaction at the surface of the metal disc is the controlling factor, the reaction temperature should have a significant effect on the overall reaction rate, the activation energy is usually high (10-20 kcal/mole), and the dissolution rate will not be affected by the stirring speed. Due to the electrochemical nature of the reaction, the rate expression can be obtained by using the Butler-Volmer equation. It should be noted that the reaction order with respect to the limiting reagent, is usually about 0.5.

In the case of mixed control, the corresponding activation energy could be in the range of 5-10 kcal/mole, and the slope of the log(rate) vs. the log(angular velocity) will be between 0-0.5.

2.4.3. Kinetics studies of the thiosulfate leaching of gold from ores and concentrates

In section 2.2, the literatures about gold leaching in ammonium thiosulfate system were reviewed in detail. It was concluded that acceptable gold extraction rates can be achieved using thiosulfate in the presence of ammonia and copper(II). However, regarding the effects of different parameters on the extraction rate, sometimes, different authors came up with different results. This shows that fundamental kinetics studies are needed. A former Soviet Union scientist studied the dissolution kinetics of gold and silver in thiosulfate using rotating disk, the activation energy of gold was found to be 17.55 kJ/mol. During the experiments, elemental sulfur was found on gold disk after 15

-30 min agitation (0.09 ~0.19 M Na₂S₂O₃, 65 °C); the addition of sulfite can prevent the formation of elemental sulfur and other sulfur species in the gold surface (Zhu, 1993).

The kinetics of Au extraction from Pb-Zn sulfide flotation tailings by thiosulfate leachants has been investigated by Block-Bolten & Torma (1986). The order of reaction as well as the overall reaction rate constant were, with respect to thiosulfate concentration, calculated to be n = 0.75 and $k = 1.05 \times 10^{-6} \text{ mol}^{1/4} \text{ dm}^{5/4} \text{ min}^{-1}$ The apparent activation energy was found to be 48.53 kJ/mol. Optimum leach temperature of 50 °C was established. Gold extractions as high as 99% were realized in two-step counter current leaching.

The kinetics of gold leaching from gold sulfide concentrates in thiosulfate solution was studied and compared with the kinetics of pyrite and chalcopyrite oxidation in ammonia-ammonium sulfate solution (Gong et al 1993(1), (2)). The gold dissolution can be divided into two stages: in the first 5 minutes, gold dissolution was very fast (k_5); and then gold dissolution rate decreased significantly, which can be fitted with the solid reaction products layer diffusion model (k_s). The gold leaching rate can be related to the experimental parameters as follows:

$$k_{5} = k_{1} [Cu^{2+}]^{0.69} [NH_{3}]^{0.2} [(NH_{4})_{2} SO_{4}]^{0.14} [(NH_{4})_{2} S_{2}O_{3}]^{0.05} \omega^{1/2} \frac{1}{\overline{d}} e^{-3.1/RT}$$

Equation 2.25

$$k_{s} = k_{2} [Cu^{2+} J^{0.76} [NH_{3} J^{1.53} [(NH_{4})_{2} SO_{4} J^{0.12} [(NH_{4})_{2} S_{2} O_{3} J^{0.21} \omega^{1/2} Q_{O_{2}}^{n} \frac{1}{H} \frac{1}{\overline{d^{2}}} e^{-10/RT}$$

Equation 2.26

The gold sulfide mineral has been characterized and it was found that the most gold was embedded in pyrite and others are non-associated gold or embedded in chalcopyrite. Xray and SEM analysis showed that both pyrite and chalcopyrite are attacked by solution. It is suggested that, in the first 5 minutes, gold dissolution only occurs in non-associated gold or gold embedded in chalcopyrite or pyrite but exposed to solution. And then, solid product layer envelops the particles and the reaction is under diffusion control. Leaching reagents were first diffused through the product layer and react with gold bearing minerals to expose the gold. The pyrite anodic polarization current in ammoniaammonium sulfate solution was related to the reaction parameters as follow. This correlation is similar to κ_5 , which shows gold dissolution is closely associated with pyrite.

$i = k [NH_3]^{0.18} [(NH_4)_2 SO_4]^{0.14} e^{-12.1/RT}$ Equation 2.27

Similar observation were found for silver extraction from the same concentrates (Hu and Gong, 1994). Therefore it is not strange that there is much variation on the effect of some parameters on the gold dissolution (extraction) rate, since most studies of thiosulfate leaching were performed on the gold bearing ores/concentrates.

2.4.4. The kinetics of gold leaching studied by Tozawa et al (1981)

Pure gold (annealed in 520-540 °C) plate was used in the studies of gold dissolution in thiosulfate solution in an autoclave by Tozawa et al. (1981). The rate of gold leaching was studied over a 3 hr period with the assumption that the gold leaching

rate is linear with time. Baseline conditions were as follows: $T = 65^{\circ}C$, T = 3 hrs, $S_2O_3^{2-}$ = 0.25 M, NH₃ = 1.0 M, Cu(II) = 0.04 M, PO₂ = 2 kg/cm², stirring velocity: 200 rpm.

The rate of gold leaching increases as rotating velocity increases from 0-200 rpm, then decreases with increasing rotating velocity. The authors suggested that, increase in stirring velocity strongly promotes the oxidation of thiosulfate ions and thus results in a decrease of leaching kinetics at high stirring velocity.

Gold leaching rate increases as oxygen partial pressure increases from 0 - 1 kg/cm^2 , beyond that, gold dissolution decreases. Again the oxidation of thiosulfate at higher oxygen partial pressure is blamed for the decline of gold dissolution rate.

The effect of thiosulfate ion concentration was studied in the range from 0.1 to 0.53 M. NH₃ concentration is set to 1.0 M (the corresponding molar ratio of $[NH_3]/[S_2O_3^{2^-}]$ varied from 10 to 2). The gold leaching rate increases substantially from 0.1 to 0.44 $S_2O_3^{2^-}$ ($[NH_3]/[S_2O_3^{2^-}]$ molar ratio from 10 to 2.44) and then leveled off.

The increase of ammonia concentration promotes gold dissolution from 0-0.5 M ($[NH_3]/[S_2O_3^2]$ ratio from 0- 2); beyond that, there was a negative effect on the gold dissolution rate. It was stated that the excess of ammonia results in an increase of pH which suppresses the dissolution of gold.

Gold leaching rate increased as temperature was increased from $20 - 65^{\circ}$ C Over this range, solution was blue, which indicated that Cu(NH₃)₄²⁺ is predominant in solution. From 65- 100 °C, gold leaching rate decreased, the solution was colorless and at the surface of gold, black precipitate formed, which was identified as CuS. The decrease of thiosulfate concentration by oxidation, the decrease of Cu(II) by reduction by thiosulfate and the passivation of gold surface by cupric sulfide were responsible for the decrease of gold leaching rate.

$$Cu^{2+} + S_2O_3^{2-} + H_2O \rightarrow CuS + SO_4^{2-} + 2 H^+$$
 Equation 2.28
 $Cu(S_2O_3)_2^{3-} + H_2O + \frac{1}{2}O_2 \rightarrow 2CuS + S_3O_6^{2-} + 2 OH^-$ Equation 2.29

From 100 to 140 °C, gold leaching rate increased again. It was suggested that it was due to the dissolution of CuS and the regeneration of thiosulfate and cupric amine complex ions on the gold surface by the following reaction:

 $2CuS + 8 NH_3 + 2 O_2 \rightarrow 2Cu(NH_3)_4^{2+} + S_2O_3^{2-} + 2OH^-$ Equation 2.30 Above 140 °C, the rate of oxidation of thiosulfate exceeds the rate of regeneration of

thiosulfate and the gold leaching rate decreased again.

It was found that there exists one optimum copper concentration, which is dependent on the concentration of thiosulfate.

2.4.5. Mechanism of silver sulfide dissolution

Flett et al. (1983) investigated silver sulfide leaching using solutions of thiosulfate that contained copper sulfate and proposed a reaction mechanism that emphasizes the importance of the presence or absence of air for the formation of the

product as cupric or cuprous sulfide. In the absence of air, these authors proposed that the following reaction are involved in the process: firstly, the reduction of copper by thiosulfate in the bulk solution:

$5(NH_4)_3S_2O_3 + 2CuSO_4 \rightarrow CU_2S_2O_3 \cdot 2(NH_4)_2S_2O_3 + (NH_4)_2SO_4 + (NH_4)_2S_4O_6$

Equation 2.31

Later, within the mineral particle, silver is substituted by copper in the sulfide molecule:

$Cu_2S_2O_3 \cdot 2(NH_4)_2S_2O_3 + Ag_2S \rightarrow Cu_2S(s) + Ag_2S_2O_3 + 2(NH_4)_2S_2O_3$

Equation 2.32

Briones and Lapidus (1998) verified the above mechanism and considered the tetrathionate disproportionate reaction:

$2(NH_4)_2S_4O_6 + NH_4OH \rightarrow (NH_4)_2S_3O_6 + 2/5 (NH_4)_2S_2O_3 + 2H_2O$

Equation 2.33

The experimental thiosulfate consumption was very close to that of the theoretical value predicted by the above equations, although it was found that the reduction of cupric was not complete. It was also found the thiosulfate and its derivatives (tetrathionate) themselves have no ability to dissolve silver sulfide. However if with the addition of copper sulfate ($0.1 \text{ M S}_2\text{O}_3^{2^-}$, $0.1 \text{ M NH}_4\text{Cl}$, pH 9.5, 0.003 M Cu^{2^+}), a substantial amount of silver sulfide was leached out and there exists a marked relationship between the amounts of copper precipitated and the silver leached out. The molar ratio of them is close to 1.5

It was found that the silver leaching kinetics from silver sulfide increase with the increase of concentration of thiosulfate and copper ion and decrease with the increment in the ammonia concentration. This behavior is believed due the decrease of cuprous to silver ratio at the reaction boundary.

2.4.6. Electrochemical investigation of gold leaching by Jiang

The electrochemistry of leaching gold with thiosulfate has been studied systematically using electrochemical techniques by Jiang et al (1993,(1)). Stationary gold electrode was used in this study.

For the anodic dissolution, two current peaks were identified at 50 mV and 620 mV Vs _{SHE} respectively. It was suggested that the gold dissolution occurs at 50 mV and thiosulfate oxidation occurs at 620 mV. Ammonia remarkably improves the anodic dissolution rate of gold and reduces the passivation as well as making the current peak shift negatively. Cupric ions and cupric ammonium complex ions were found to have no effect on the gold dissolution rate. Cyclic voltammogram studies showed that the anodic dissolution of gold in thiosulfate solution is characteristic of electrochemical-chemical (EC) reaction. A current step technique was used to investigate the role of ammonia in anodic process and the adsorption mechanism of ammonia was excluded. The author proposed the following anodic dissolution mechanism of gold:

Au → Au⁺ + e Au⁺ + 2NH₃ → Au(NH₃)₂⁺ Au(NH₃)₂⁺ + 2S₂O₃²⁻ → Au(S₂O₃)₂³⁻ + 2 NH₃

Equation 2.34 Equation 2.35 Equation 2.36

For the cathodic processes, the addition of cupric ammonium ions entirely changed the behavior of the cathodic process. There is no current peak of cathodic process in the range of 0 ~ -900 mV Vs _{SHE}. A peak appears at -400 mV V_{SHE} in the presence of 0.1 mol/L cupric ammonium ions. It was found that free ammonia has no effect on the cathodic process. The current peak in – 400 mV Vs SHE still exists in the absence of thiosulfate, but the current density is much higher. It is suggested thiosulfate is not involved in the cathodic process and the effect of thiosulfate on the peak current is the results of a reduced aqueous diffusion coefficient in the presence of thiosulfate. However, it is more likely due to the decrease of Cu(II) species by thiosulfate reduction. In the absence of oxygen (protected by nitrogen), the peak at -400 mV Vs_{SHE} still exists, as the oxygen content increases, the peak current increases. It was suggested that cupric (II) ammine is reduced at the gold surface and oxygen is involved in the cathodic process indirectly: for example, oxygen oxidized reduced copper species. Cyclic voltammetry investigations had been performed and it was concluded that the cathodic process is characteristic of quasi-reversible process in the presence of nitrogen and catalytic reaction in the presence of oxygen. Based on the results above, the mechanism of cathodic process of gold leaching of ammoniacal thiosulfate was put forward as follows:

 $Cu(NH_{3})_{4}^{2+} + e \rightarrow Cu(NH_{3})_{2}^{+} + 2NH_{3}$

Equation 2.37

$Cu(NH_3)_2^+ + 2NH_3 + \frac{1}{4}O_2 + \frac{1}{2}H_2O \rightarrow Cu(NH_3)_4^{2+} + OH^-$ Equation 2.38

Combining the cathodic and anodic processes, Jiang et al (1993 (1)) schematically proposed the mechanism shown in Figure 2.8.

Jiang et al (1993(2)) used the Tafel curve technique and leaching test to study the kinetics of gold leaching with thiosulfate. The exchange current density (i_{cor}) was utilized to identify the dissolution of gold. It is found that the i_{cor} increased with thiosulfate concentrate (0.01 ~ 1.0 M); i_{cor} increased as pH increased from 7 to 10, and then dropped slightly at pH > 10. As [Cu(NH₄)₄²⁺] increased from 0.001 to 0.1, i_{cor} increased dramatically(from 5.62 ~ 573.82 μ A/cm²). However, it is hard to believe that the current increase is 100% due to the gold dissolution since the thiosulfate degradation is accelerated in the presence of cupric ion. It was found that i_{cor} did increase with the increase of temperature and the dissolution activation energy is reduced from 27.99 KJ/mol to 15.54 KJ/mol in the presence of 0.01 M Cu(NH₄)₄²⁺ and 0.5 M ammonia. The catalytic effect of copper ion and ammonia was verified.



Figure 2.8 The mechanism of gold dissolution in Ammonia-thiosulfate-water system

(after Jiang et al. 1993(1))

2.4.7. Electrochemical investigation of Zhu (1994)

The dissolution of gold in aqueous thiosulfate solution and the effect of the presence of ammonia in the solution were investigated with the methods of voltammetry and electrochemical impedance spectroscopy (EIS) by Zhu et al. (1994). The electrochemical impedance spectra of gold in the sodium thiosulfate solution in absence of ammonia accords with the active-passive electrochemical process on the metal surface. The authors attribute this to the formation of elemental sulfur and thus the elemental sulfur at the gold surface passivates the gold dissolution:

Equation 2.39

Equation 2.40

$S_2O_3^{2-} + 6OH \rightarrow SO_3^{2-} + 2S^{2-} + 3H_2O$

The elemental sulfur may absorb on the gold surface and anodic process may occur on the gold electrode surface as:

$$S^{2-} + Au \rightarrow Au | S^{0} + 2e$$

 $S_{2}O_{3}^{2} \rightarrow S^{0} + SO_{3}^{2}$

Equation 2.41

The presence of ammonia eliminates the passivation phenomena even in the absence of copper ion. It was explained that the ammonia prevent the gold electrode from passivation with sulfur coating by being preferentially adsorbed on the gold surface to bring gold to dissolve as amine complex, as was suggested by Jiang et al. (1993, 1). This explanation was supported by the fact that aqueous ammonia addition was superior to ammonium sulfate addition. Ammonia in large excess was found to hinder the thiosulfate leaching of gold in the presence of copper due to its precipitation with ammonia and thiosulfate, possibly as NaCu(NH₃)₄.Cu(S₂O₃)₂ or (NH₄)₅Cu(S₂O₃)₃. However, no inhibition can be observed by excessive ammonia within the studies in the absence of copper.

2.4.8. Breuer and Jeffrey's works

The oxidation of gold in thiosulfate solutions containing copper and ammonia was studied by Breuer and Jeffrey (2000 (1)) using a rotating electrochemical quartz crystal microbalance (REQCM). With REQCM, mass change can be measured simultaneously with current. The quartz electrode was coated with gold/silver alloy that contained 2wt% silver by electroplating. All potentials were measured relative to SCE but were reported relatively to the SHE. The results are introduced below.

The gold oxidation half reaction was studied using linear sweep voltammetry, and Figure 2.9 showed the resultant voltammogram for gold in 0.1 M thiosulfate solutions. Figure 2.9 also showed the electrode mass change which is measured as a function of potential; it is clear from this data that the mass decreases as the potential is scanned above 150 mV, indicating that gold is being oxidized to soluble gold thiosulfate. These mass changes can be converted into a calculated equivalent current density for gold oxidation using Faraday's Law. The calculated current density is also shown in Figure 2.9 as a dashed line. It is clear that at potentials less than 300 mV, the calculated current density matches the measured current density; such a result implies that in this potential region thiosulfate oxidation does not occur to a large extent.

However, the gold oxidation process is obviously hindered. It has been suggested that thiosulfate can disproportionate in alkaline solutions to form sulfite and sulfide ions (Zhu, et al, 1994). Once in solution, sulfide ions can be readily oxidized to form sulfur on the



Figure 2.9 Linear sweep voltammogram of gold oxidation. Also shown is the mass change measured using the REQCM, and the calculated current density derived from this. Experimental conditions: 0.1M $Na_2S_2O_3$, pH=11.4 (NaOH), 30°C (after Breuer and Jeffrey, 2000 (1))

gold surface. This deposition is suggested responsible for the sluggish oxidation kinetics of gold in thiosulfate solutions. At potentials more positive than 300 mV, it can be seen from Figure 2.9 that the calculated current density deviates from the measured current density; this implies that thiosulfate oxidation has commenced.

Figure 2.10 shows the calculated current densities for gold oxidation at various ammonia concentrations. It was found that the ammonia not only reduces the passivation observed at potentials greater than 300 mV, but also enhances gold oxidation below 300 mV. The standard reduction potential of $Au(NH_3)_2^+$ is 0.572 V, which is considerably more positive than the potentials shown in Figure 2.10. Thus, Breuer & Jeffery suggested that the action of ammonia is to alter the surface of the gold electrode, reducing the effect of the surface passivation.





Further studies showed ammonium ions enhance the gold oxidation process in the absence of ammonia, although in a less significant way. However even added in ammonium form, the effect is possibly due to an increase of free ammonia concentration since it is well known that there is a solution equilibrium between ammonia and ammonium.

As the thiosulfate concentration is increased, the gold oxidation reaction occurs more readily, as expected. However, as the thiosulfate concentration increases, the rate of thiosulfate oxidation also increases.

As temperature increases, there is a significant increase in the calculated current density of gold dissolution. It was suggested that the gold oxidation process remains hindered to some extent even in the presence of ammonia, and with increasing temperature, this passivation becomes less important.

Figure 2.11 showed the effect of initial copper(II) concentration on the calculated voltammogram for gold oxidation in thiosulfate solutions shortly after preparation so that the majority of copper is present as copper(II). It was clear that the presence of copper(II) enhances the gold oxidation process; in other words, the author claimed the copper does not solely act as an oxidant. However it may be due to heterogeneous chemical dissolution of gold as followes:

Au $+5S_2O_3^{2-} + Cu(NH_3)_4^{2+} \rightarrow Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3$ Equation 2.42

Also some evidence showed that the products of either the thiosulfate/copper(II) reaction or subsequent reactions bring about passivation of the gold surface.



Figure 2.11. Effect of copper(II) concentration on gold oxidation. Experimental conditions: 0.4M NH₃, 0.1M Na₂S₂O₃, 30°C (after Breuer and Jeffrey, 2000 (1)).

Breuer & Jeffrey (2000(2)) further studied the thiosulfate leaching kinetics of gold in the presence of copper and ammonia using rotating electrochemical quartz crystal microbalance (REQCM). Since cupric ion is not stable in the presence of thiosulfate ions, the cupric concentration were monitored by measuring the limiting reducing current for copper(II) on a rotating platinum electrode at –150 mV Vs SHE and this measurement was found in good agreement with UV absorbance measurements. Gold leaching rates were measured using REQCM.

It is found that the steady state leaching rate is 5.6×10^{-5} mol m⁻²s⁻¹ under the following conditions: 10 mM CuSO₄, 0.4 M NH₃, 0.1 M Na₂S₂O₃, 30 °C, protected

with argon. However the diffusion limit rate of Cu(II) is calculated to be 24.6×10^{-5} mol m⁻²s⁻¹, which is substantially higher than the gold leaching rate. It is also noted that the thiosulfate concentrate is high and the flux of thiosulfate is considerably higher than that of Cu(II). The author concluded that the leaching reaction is under chemical control.

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It was also found that the Cu(II) concentration decreases continuously in the gold leaching conditions as shown in Figure 2.12.

Breuer and Jeffrey (2000 (2)) found that the gold leaching rate is not dependent on the initial Cu(II) concentration and further electrochemical studies showed copper(II)-thiosulfate reaction products hinder the gold oxidation. The reaction mechanism of Cu(II)-thiosulfate is found to be much more complicated than proposed by Breyley et al (1973).





Temperature was found to have a significant effect on the reaction rate. It is worth noting that the mixed potential of gold leaching at steady state was found to decrease with increasing temperature. The authors then suggested that the dominant effect of temperature is to enhance the gold oxidation half-cell reaction. The activation energy of the leaching reaction was 60 ± 10 kJ mol⁻¹. This result confirmed that the reaction is chemically controlled. The effect of temperature on the copper(II)-thiosulfate reaction was also presented. It was suggested that the rate of copper(II) reduction by thiosulfate increases with increasing temperature. The activation energy of the process was calculated to be 110 ± 5 kJ mol⁻¹. Thus it was concluded the temperature of the system should be minimized in order to avoid unwanted consumption of thiosulfate.

Both gold leaching rate and Cu(II) reduction rate by thiosulfate are reduced at lower thiosulfate concentrations.

As the ammonia concentration is increased, the leach rate decreases. It was also found that the mixed potential became more negative with increasing ammonia concentration concentration. These results are consistent with increasing ammonia concentration enhancing the stability of copper(II) and thus reducing the reduction potential of the cathodic half cell reaction since the $[NH_3]/[S_2O_3^{2-}]$ molar ratio are always high(from 2 ~ 6). It was found that there is a very strong relationship between the Cu(II) reduction reaction rate and ammonia concentration; a plot of $\ln(r_0)$ vs. $\ln[NH_3]$ showed the reaction order with respect to ammonia concentration was -2.5. It was concluded that ammonia is an integral part of the reaction mechanism.

The effect of ammonium concentration on the gold leaching rate and Cu(II) reduction rate was investigated. It was found that both gold leaching rate and Cu(II)-thiosulfate reduction rate are higher as ammonium concentration increases. However, since the pH changes with the change of ammonium concentration, it is not clear that this effect is due to the pH or ammonium concentration.

2.5. Summary

Thiosulfate and gold can form stable complexes $(Au(S_2O_3)_3^5)$ in aqueous solution. However thiosulfate is not thermodynamically stable and under gold leaching conditions will eventually be oxidized to sulfate in the presence of oxygen or cupric ion. The mechanisms of thiosulfate oxidation were characterized but require further study.

Gold leaching in the ammonium thiosulfate system from ore/concentrate has been intensively studied in recent years and the gold extraction rate in the presence of copper and ammonia can be compared with cyanidation in both tank and heap leaching.

The gold leaching process in ammonium thiosulfate system in the presence of copper is complicated and several contradictory mechanisms have been proposed. It is generally agreed that ammonia catalyzes the gold oxidation reaction, however the mechanism is still not clear. The Cu(II)/Cu(I) couple can facilitate the reduction of oxygen and therefore catalyze the gold leaching process. It was also reported that copper

ion may enhance the gold anodic oxidation. The selection of the $[S_2O_3^2]/[NH_3]$ ratio is apparently very critical to achieve a high gold leaching rate.

The gold leaching kinetics in the ATS system are affected by the mineralogy of the gold ore/concentrate. Therefore it is not surprising that variable results have been obtained regarding the effect of different parameters on gold leaching kinetics since most kinetics studies have been performed on ores and concentrates of variable mineralogy.

Until recently, there were few fundamental studies on the gold leaching rate in the ATS system. It is generally agreed that gold leaching in ATS system follows the electrochemical mechanism. However, no systematical fundamental study on the effect of different parameters on gold leaching rate was reported. The combination of electrochemical polarization method and direct leaching method has proved to be powerful tool to study the gold leaching kinetics in cyanide solution and has been selected in the study of the ATS system.

3. EXPERIMENTAL APPROACH

There were basically two experimental methods employed in this study, one was the electrochemical study and the other was gold disk leaching study. In both of these methods, the rotating disk electrode (RDE) technique has been applied. In this chapter, the nature of the RDE will be briefly introduced; the experimental matter of the electrochemical and gold disk leaching study will be described in detail.

3.1. Introduction to Rotating Disk Electrode

The use of rotating disk electrodes was one of the most popular methods in quantitative studies of kinetics because of its high accuracy and reproducibility. The main feature of the rotating disk electrode was that it acts as a uniformly accessible surface, which means that mass transport to the surface is uniform. The rotating disk electrode theory was studied by Levich (1962), who proposed the famous Levich equation:

$$i_L = 0.62 n F D_0^{2/3} \omega^{1/2} v^{-1/6} C_b$$

Equation 3.1

The Levich equation was based on the laminar flow condition. When the Reynolds number Re (Re = $\omega r^2/\nu$), where r was the radius of the electrode disk, exceeds a critical value (1.8 ~ 3.1 ×10⁵), the fluid flow changes qualitatively from laminar to turbulent. To avoid turbulent flow, the maximum rotating speed for 10 mm rotating disk was 17200 ~ 29600 rpm. However, when the disk vibrates axially or radially or if the

surface was uneven, turbulence occurs at lower Re values. On the other hand, when Re value approaches 10, the natural convection in the solution begins to play a role. Therefore, in order to eliminate the effect of natural convection, the rotating velocity should be much larger than 1 rpm for a radius of disk about 3 mm. For this disk size, the Levich equation can be accurately applied if the rotating velocity was in the range of $100 \sim 6000$ rpm.

3.2. Electrochemical Study

3.2.1. Equipment & Reagent

A 3 mm diameter gold rod (>99.99% pure) from Aldrich® was used as a gold rotating disk, which was tightly surrounded with a resin shield. The gold disk was soldered on to a copper base to establish electrical conductivity. A schematic diagram of the gold disk electrode was shown in Figure 3.1.

The rotating disc electrode was screwed to an EG&G® PARC Model 636 Electrode Rotator. The potentiostat was a Solartron® 1286 Electrochemical Interface, which was controlled by software CorrWare® for Windows, Electrochemistry /Corrosion Software Version 1.4. About 100 mL of the solution of the required composition was placed in an EG&G water-jacketed electrolytic cell whose temperature was controlled by a Cole-Parmer® Model 1267-62 constant temperature circulator. The counter electrode was an EG&G platinum electrode. The reference electrode was a Fisher® saturated calomel electrode (SCE) which was connected to the cell electrolyte

by an electrolyte bridge. The calomel electrode was placed in a tube containing the same electrolyte as in the cell. The schematic diagram was shown in Figure 3.2.

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Figure 3.1 Schematic diagram of gold rotating disk electrode





Doubly de-ionized water was used throughout this study. The information about reagents used in this study is listed in the following table:

Reagents	Specification	Category #	Sources
$(NH_4)_2S_2O_3$	>99%	33672-6	Aldrich Chem. Com., Inc
CuSO ₄ .5H ₂ O		C-489-500	Fisher Scientific
$Na_2S_2O_3$	>99	S-1648	Sigma chem. Co.
NaOH	5N solution	SS256B-500	Fisher Scientific
H_2SO_4	1N solution	SA212B-1	Fisher Scientific
Buffer solution	pH 4,7,10	-	Fisher Scientific
NH4OH	5N Solution, 28~30%	A-669-225	Fisher Scientific
Gold	rod, \$\$.0 mm, >99.99%	26583-7	Aldrich Chem. Com., Inc
Compress Air	-	-	Praxair Tech. Inc
Nitrogen	-	-	Praxair Tech. Inc.
Argon	98%	-	Praxair Tech. Inc.

Table 3.1 The specification and source of reagents

3.2.2. Experimental procedure & condition

The electrode surface was first ground using 1200 grit sandpaper, then polished with 2400 grit silicon carbide paper and then soft tissue paper. The above treatment alone proved to be not sufficient to ensure reproducible electrochemical measurement. The following electrochemical pretreatment (EC pretreatment) was necessary in order to get acceptable reproducibility: the polished electrode was subjected to potential cycling between -1.8 and $1.3 V_{SCE}$ in 0.1 N NaOH solution at a scan rate of 1000 mV/sec for 25 min. Finally, a stationary voltammogram was obtained and the electrode was ready for the polarization test. The solution preparation procedure was as follows:

1. Add appropriate amount of water to the vessel, which was on the top of a magnetic stirrer, and start stirrer;

2. Add certain amount of ammonium thiosulfate into vessel;

- 3. Adjust pH to desired value using NaOH solution;
- 4. Add certain amount of cupric sulfate into solution if it was required;
- 5. Adjust pH if necessary;
- 6. Transfer solution into volumetric flask and add water if necessary;

7. Fully mix the solution.

Only fresh solution was used for the polarization measurements. The scan rate was 1 mV/Sec for all the polarization measurement. The experimental procedure was as following:

1. Put about 100 mL fresh made solution into cell

2. Start circulator to keep constant temperature

3. Purge solution with appropriate gas for 15 min

4. Start experiment

For gold anodic polarization, the experiments were carried under the argon atmosphere, the sweep range was $-400 \sim 250 \text{ mV Vs SCE}$. The baseline condition of anodic polarization test was: 0.2 M (NH₄)₂S₂O₃ (0.2 M Na₂S₂O₃ and 0.4 NH₃ when the effects of ammonia and thiosulfate concentration were investigated), 25 °C, 450 rpm.

For the gold cathodic polarization experiments, the solution was saturated with air, the sweep range was from 20 mV more than open circuit potential to -600 mV Vs SCE. The baseline condition of cathodic polarization test was: 0.2 M $(NH_4)_2S_2O_3$ (0.2 M $Na_2S_2O_3$ and 0.4 NH₃ when the effects of ammonia and thiosulfate concentration were investigated),250 ppm [Cu]_T, 25 °C, 450 rpm.

The parameters investigated for the anodic and cathodic polarization were almost the same, as listed below:

- > Ammonium thiosulfate concentration, $0.1 \sim 0.8$ M
- > Ammonia concentration, $0.1 \sim 0.8$ M

> Thiosulfate concentration, $0.1 \sim 0.8$ M

- \blacktriangleright Copper concentration, 0 ~ 1500 PPM
- \blacktriangleright Tetrathionate ion concentration, 0 ~ 0.01 M

▶ pH, 8 ~ 11

 \blacktriangleright Temperature, 25 ~ 50 °C

 \blacktriangleright Rotating velocity, 100 ~ 800 rpm

3.3. The Coulometric Studies

The Coulometric test was a larger scale of polarization test (but constant potential was applied to the working electrode instead of potential sweep) so that the gold dissolution in the solution could be measured by the weight loss method. This method was applicable to anodic polarization. The purpose of this method was to investigate the gold dissolution efficiency, which was the ratio of actually dissolved gold over dissolved gold calculated from anodic current.

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In order to increase the surface area and thus enhance the sensitivity of the measurement, the working electrode was made of gold foil. The gold foil was fabricated by rolling a pure gold coin (>99.99% pure), and then the rolled gold foil was annealed at 750 °C for about 2 hours. The experimental setup in coulometric studies was almost the same as that in the polarization tests except at a larger scale, as shown in Figure 3.3.



Figure 3.3 The schematic diagram of coulometric test set up

Since the gold foil was not suitable for polishing, an alternate surface treatment method was applied. After each experiment, gold foil was soaked in 3 M HCl solution for 2 hours; and just before the experiment, gold foil was heated by a bunsen flame to remove any passivation layer. The coulometric test was one hour in duration. The gold foil was weighed before and after the test, the weight difference was the gold loss during the test, and this result was compared with that calculated from the anodic current. A solution sample was also taken and analyzed to complete the mass balance calculation for gold.

3.4. The Gold Disk Leaching Study

In the electrochemical study, gold dissolution in ammonium thiosulfate (ATS) solution was broken into separate studies of the anodic and cathodic reactions. This method offers the possibility of identifying the electrochemical mechanism by which the process of gold dissolution takes place in the ATS system. However, the gold dissolution rate predicted from this method was not necessarily correct since side reactions may occur. It was more reliable to directly leaching gold in solution and to obtain the kinetic data.

As introduced in section 3.1, the hydrodynamics of rotating disk was well defined, therefore it was decided that a rotating disk was to be used in the leaching study. The rotating disk using in this leaching study was exactly the same as the gold

electrode (see Figure 3.1) in electrochemical study, but in larger scale: the diameter of the gold disk and the resin holder were 25 and 40 mm respectively.

The rotating disc was screwed to an EG&G® PARC Model 636 Electrode Rotator. The reactor was Kontex® 500 mL water-jacketed vessel, whose temperature was controlled by a Cole-Parmer® Model 1267-62 Constant temperature circulator. The VWR® platinum redox electrode, EG&G® purge tube and Fisher® thermometer were also used in this study. In order to prevent ammonia loss, a purge line first passed through a buffer bottle containing the same solution as that in the reactor. The schematic diagram of the experimental set up is presented in Figure 3.4.





Before every test, the gold disk surface was treated as follows:

- Polish with 1200 grit abrasive paper
- Cycling 250 times between -1.3 and 1.8 V at a scan rate of 1000 mV/sec. at 0.1 N NaOH solution
- Soak the gold disk in concentrated nitric acid for 2 seconds and then wash with DI water

The solution preparation procedure was the same as that in electrochemical study.

- > Weight certain amount of fresh solution into reactor and start circulator;
- Start stirrer and sparge solution with air for half hour;
- Stop stirrer and sparge and equilibrium solution with air;
- Immerse gold disk into solution and start rotating, start timing;
- At every pre-determined interval, sample 25 mL solution and record Eh value of solution;

Experiment ends at predefined time;

Solution samples were sent for gold assay.

The baseline condition of the gold disk leaching study was: 0.2 M $(NH_4)_2S_2O_3$ (0.2 M $Na_2S_2O_3$ and 0.4 NH₃ when the effects of ammonia and thiosulfate concentration were investigated), 250 ppm $[Cu]_T$, 25 °C, 450 rpm. The parameters investigated were the same as those in the electrochemical study.

3.5. Sample Analysis

All the gold assays on solution sample were performed by International Plasma Lab in Vancouver. The gold content was determined by evaporating 25 mL solution to dryness in a lead foil boat, followed by fire assay and cupellation. The resulting bead was digested and the gold content of the resulting solution was determined by absorption spectrophotometry.

Occasionally, solution samples were analyzed for thiosulfate and tetrathionate concentration to examine thiosulfate degradation. This was done by high performance liquid chromatography (HPLC) methods right after sampling. A Dionex Series 4500I Chromatograph was used for the analysis.

4 RESULTS AND DISCUSSION

4.1 Anodic Polarization of Gold in The ATS System

The reproducibility of gold anodic polarization in the ATS system is presented in Figure 4.1 (without EC pre-treatment) and Figure 4.2 (with EC pretreatment) respectively.



Figure 4.1 The lack of reproducibility of gold anodic polarization in 1.0 M Na²S²O³ solution without EC pre-treatment (1 M NH³, pH 10, 25 °C, 600 rpm, 1mV/sec)

From Figure 4.1, it can be seen that the reproducibility is very poor without EC pretreatment: both the shape of the curve or the magnitude of the current changes substantially. This is probably due to the passivation of the gold surface by sulfur species and even polishing the surface could not totally eliminate the passivation. There was much effort put in to solve this problem and, finally, it was found that the electrochemical cleaning method can effectively eliminate the passivation, and reproducible results can be

obtained. From Figure 4.2, we can see that although the reproducibility is still not perfect, it is acceptable.



Figure 4.2 The reproducibility of the gold anodic polarization in 1.0 M Na₂S₂O₃ solution with EC pre-treatment (1 M NH₃, pH 10, 25 °C, 450 rpm, 1mV/sec).

The effects of pH (Figure 4.3), rotating velocity (Figure 4.4), $[(NH_4]_2S_2O_3]$ (Figure 4.5), $[NH_3]_T$ (Figure 4.6), $[Na_2S_2O_3]$ (Figure 4.7), $[S_4O_6^{2-}]$ (Figure 4.8), $[Cu]_T$ (Figure 4.9), and temperature (Figure 4.10) on gold anodic polarization in ATS solution are shown in the following Figures.

Figure 4.3 shows that, current densities at pH 8 and 9 are significantly higher than that at pH 10 and 11. This is inconsistent to the mechanism proposed by Jiang et al 1993(1), who suggested that the free ammonia catalyzes the anodic process. This fact is potentially important, since the buffer point of ammonium thiosulfate in aqueous solution is around pH 6, if gold leaching can be performed at pH 8 or 9 instead

of 10, less reagent(NaOH or NH₃) is needed for adjusting pH. It is also interesting that, there is a current plateau when potential is above 0.25 V_{SHE} at pH 8, which is unique among results with other pH values. This indicates that passivation may happen at pH 8. Thiosulfate becomes unstable at low pH, this result may indicate that a thiosulfate degradation product passivates the gold surface.

As shown in Figure 4.4 that, the rotating velocity has no effects on gold anodic process at experimental conditions. This result indicates that the anodic process is under surface reaction control, which is consistent with Jiang et al, 1993(1), Breuer & Jeffrey 2000 (1). Actually, we can make simple calculation to verify this result using Levich Equation as shown in Equation 4.1:

Equation 4.1

The limiting current density may be calculated by assuming values for the diffusion coefficient and kinematic viscosity of 1.0×10^{-5} cm²/sec and 0.01 cm²/sec respectively. The magnitude of calculated limiting current is around 10^{-2} A/cm² whether the limiting species is free ammonia or thiosulfate ions. The magnitude of actual current density from the experiments is around 10^{-5} A/cm², which is far below the calculated limiting current density. It is verified that the anodic process is under surface reaction control.


Figure 4.3 The effect of pH on the gold anodic polarization in 0.2 M (NH4)2S2O3 solution (25 °C, 450 rpm, 1 mV/sec)



Figure 4.4 The effect of rotating velocities on the gold anodic polarization in 0.2 M (NH4)2S2O3 solution (pH 10, 25 °C, 1 mV/sec)



Figure 4.5 The effect of concentration of ammonia thiosulfate on the gold anodic polarization (pH 10, 25 °C, 450 rpm, 1 mV/sec)







Figure 4.7 The effect of concentration of thiosulfate ion on the gold anodic polarization (0.4 M NH3, pH 10, 25 °C, 450 rpm, 1 mV/sec)



Figure 4.8 The effect of concentration of tetrathionate ion on the gold anodic polarization in 0.2 M (NH4)2S2O3 solution (pH 10, 25 °C, 450 rpm, 1 mV/sec)



Figure 4.9 The effect of copper concentration on the gold anodic polarization on 0.2 M (NH4)2S2O3 solution (pH 10, 25 °C, 450 rpm, 1 mV/sec)



Figure 4.10 The effect of temperature on the gold anodic polarization on 0.2 M (NH4)2S2O3 solution (pH 10, 450 rpm, 1 mV/sec)

; ;

Not surprisingly, as shown in Figure 4.5, with increasing of the concentration of ammonia thiosulfate, the current densities increase significantly. As it is noticed that, at 0.8 M (NH_4)₂S₂O₃, there is a clear current plateau above 0.2 V_{SHE}. This indicates that some kind of limiting process is present. However it is not due to the diffusion control. Similar to the case of pH 8, the degradation of thiosulfate may be to blame for the apparent passivation.

The introduction of ammonia in the solution increases the current densities dramatically as shown in Figure 4.6, this verifies that the ammonia plays an critical role in anodic process, which is consistent with the results of Jiang et al, 1993 (2), Zhu et al, 1996. However, further increase of ammonia has no effect on current densities beyond 0.4 M. This phenomenon is also reported by Breuer & Jeffery, 2000 (1), who suggest that the role of ammonia/ammonium is to alter the surface of gold, reducing the effect of surface passivation.

As the concentration of the thiosulfate ion increases while keeping a constant ammonia concentration (0.4 M), the current density also increases, although less significantly compared to the increasing of the concentration of ammonia thiosulfate as shown in Figure 4.7. It is very interesting to find that the current plateau is also well defined above 0.2 V_{SHE} at 0.8 M Na₂S₂O₃. This fact further indicates that there may be some sulfur species formed that blocks the gold surface.

The effect of tetrathionate on the gold anodic polarization is shown in Figure 4.8. It seems that addition of tetrathionate has a detrimental effect on gold anodic process, but the effect is marginal.

As can be seen from Figure 4.9, the introduction of copper into solution dramatically increases the current. However, Cu(II)/Cu(I) may also contribute to the anodic current as well. Therefore, it is not clear at this point that the increasing of current density is contributed by the gold oxidation or some other side reaction, such as Cu[I] oxidation.

As temperature increases, the current density also increases significantly, as shown in Figure 4.10. According to the Arrhenius equation, the relationship between activation energy (Ea), and dissolution rate (i_{corr}) can be described as follows:

Ln $i_{corr} = k \times (E/R) \times (1/T)$

Equation 4.2

The Arrhenius relations for 0.2 and 0.3 V_{SHE} are shown in Figure 4.11. The apparent activation energy is calculated from the slope of the curve as indicated in the Equation 4.2. The activation energies are 57.23 kJ/mol and 61.21 kJ/mol respectively as shown in Figure 4.11. This means that the anodic process is dramatically affected by temperature. The fact that the activation energies for both 0.2 V_{SHE} and 0.3 V_{SHE} are well above 40 kJ/mol further verifies that the anodic process is under surface reaction control.





4.2 Coulometric Tests

As was mentioned earlier, during the gold anodic polarization, the current is not necessarily 100% contributed by the gold oxidation. A number of side reactions involving Cu, $S_4O_6^{2-}$ and NH₃ may also occur at the anode in the range of anodic potential studied. The anodic polarization of gold and platinum in ammonium thiosulfate solution is compared as shown in Figure 4.12.



Figure 4.12 The comparison of anodic polarization of gold and platinum in 0.2 M (NH4)2S2O3 solution (pH 10, 450 rpm, 25°C, 1 mV/sec)

It can be seen that, the current for gold polarization is substantially higher than that for platinum in the ATS solution in the range of potential studied. Considering the reaction kinetics of electrochemical processes on platinum are generally faster than those on gold electrodes, a reasonable explanation is that gold dissolution dominates the anodic current since platinum is not dissolved in ATS solution. However, this is only indirect evidence. Coulometric tests were also performed to examine the current efficiency of the gold anodic polarization in ammonium thiosulfate solution.

Table 4.1The effect of anodic potential on the current efficiency in 0.2 M (NH4)2S2O3 solution (pH 10, 450 rpm, 1 mV/sec)

Potential	T	Electricity	Dissolved g	Current	
(V _{SHE})	(°C)	(Coul)	Calculated	Actual	efficiency(%)
0.1	18.5	0.10	0.000206	0.000214	103.80
0.2	18.5	1.58	0.0032251	0.0032	99.2
0.3	17.8	4.21	0.0086	0.0079	92.4
0.4	19.5	6.97	0.014	0.0086	60.4

From Table 4.1, It can be seen that the current efficiencies decrease constantly as anodic potential increases. The current is almost 100% due to the gold oxidation while the anodic potential is under 0.2 V_{SHE} ; above 0.3 V_{SHE} , the current efficiency decreases quickly.

From Figure 4.13, tetrathionate concentration has no significant on the gold oxidation at 0.2 V_{SHE} . However, since the surface area of the gold is not constant, the subtle effect may not be observed in the coulometric tests.

The coulometric tests verified that ammonia does have a great effect on the gold anodic oxidation (Figure 4.14). Figure 4.14 also shows that the copper ion may have an effect on the gold anodic oxidation. The dissolved gold at 0.3 V_{SHE} in the presence of copper ion is around 50 % higher than that in the absence of copper ion, This huge difference can not be explained as the surface area effect. However, the role of copper in the anodic process is not clear. Figure 4.15 shows that, the apparent current efficiency is as high as 127.53% at 0.1 V_{SHE} , which suggests that besides electrochemical oxidation, gold can also be oxidized chemically. Breuer & Jeffrey, 2000 (1) confirmed that the oxidation of gold by cupric tetramine is thermodynamically viable.











Figure 4.15 Coulometric tests: I-t curve of gold anodic oxidation in the presence of copper (pH 10)

Au + 5 S₂O₃²⁻ + Cu(NH₃)₄²⁺ \rightarrow Au(S₂O₃)₂³⁻ + Cu(S₂O₃)₃⁵⁻ + 4 NH₃

Equation 4.3

The current efficiency is 98.63% at 0.2 V_{SHE} in the presence of copper. This indicates that at ~ 0.2 V_{SHE} , the anodic oxidation of cuprous to cupric and the direct reduction of cupric to cuprous are eventually in balance.

At 0.3 V_{SHE} , the current efficiency for anodic oxidation drops far below 100%. From this result it may be concluded that, there is net oxidation of cuprous to cupric taking place at that potential. It may be further concluded that the presence of copper increases the rate of gold anodic oxidation.

4.3 Cathodic Polarization of Gold in The ATS System

The introduction of copper ion into the ammonia thiosulfate solution dramatically changes the cathodic process, as shown in Figure 4.16. In the absence of copper ion, the cathodic polarization current is very low and increases constantly as cathodic potential decreases. In the presence of copper, the zero current potential moves positively and the current increases rapidly as potential decreases and reaches the limiting current at about 0.1 V_{SHE}. It is generally agreed that the Cu(II)/Cu(I) couple facilitates the oxygen reduction. However some discrepancy exists regarding specific species involve in the cathodic process (Jiang et al, 1993(1); Li et al, 1996).



Figure 4.16 The gold cathodic process with & without copper ion addition in 0.2 M (NH₄)₂S₂O₃ solution (pH 10, 450 rpm, 25°C, 1 mV/sec)

The effect of rotating velocity on the cathodic process is shown in Figure 4.17. The limiting current increases with the increasing of rotating velocity. As shown in Figure 4.18, there exists a linear relationship between the limiting current and the square root of rotating velocity. This is in agreement with the Levich equation in Equation 4.1.

The effect of concentration of ammonia thiosulfate on gold cathodic polarization is shown in the Figure 4.19. The limiting current increases with increasing of ammonia thiosulfate concentration. According to the Levich equation, when under reactant diffusion control, the limiting current is proportional to the bulk concentration of the limiting active species, therefore the bulk concentration of limiting active species can be calculated at given limiting current, diffusion coefficient and kinematic viscosity. The active species for this cathodic process is suggested as $Cu(NH_3)_4^{2+}$ by Jiang et al, 1993(1) and Li et al ,1996. Unfortunately, the values of diffusion coefficient of $Cu(NH_3)_4^{2-}$ and the viscosity of the ammonia thiosulfate solution are not available for ammonia thiosulfate solution. However, the diffusion coefficient can be safely estimated as 1.0×10^{-5} cm²/sec, and the kinematic viscosity can be estimated as the same as that of water, which is 0.01 cm²/sec. Then the concentration of cupric ammine can be calculated from the limiting current. Since the total concentration of copper ion in the solution is known, the total concentration of copper ion in oxidation state Cu(I) can be also be obtained since Cu(NH₃)₄²⁺ predominant among the Cu(II) species. The speciation of copper under this calculation at different ammonia thiosulfate solution is shown in Figure 4.20.



Figure 4.17 The gold cathodic polarization in 0.2 M [NH4]2S2O3 solution at different rotating velocities (250 pm [Cu]T, pH 10, 25°C, 1 mV/sec)



Figure 4.18 The effect of rotating velocity on cathodic limiting current at 0.0 VSHE.



Figure 4.19 The gold cathodic polarization at different ammonia thiosulfate concentration (250 ppm [Cu]T, pH 10, 450 rpm, 25°C, 1 mV/sec)



Figure 4.20 The effect of $[(NH_4)_2S_2O_3]$ on $[Cu(NH_3)_4^{2^+}]$ and $[Cu^+]([Cu]_T = 250 \text{ ppm})$

It can be seen that, the predominant copper species in copper-ammonia-thiosulfate solution is Cu (I) instead of Cu (II). This result is consistent with experimental observation during preparing the copper-ammonia-thiosulfate solution. When copper is added as cupric sulfate into ammonium thiosulfate solution (pH 10), the solution color changes to deep blue instantaneously, which indicates that cupric tetrammine dominates in solution. However, the blue color fades over time and finally disappears, which indicates that cupric tetrammine is not stable in ammonium thiosulfate solution. The related reactions are listed below and it can be seen that the equilibrium constant of $Cu(S_2O_3)_3^{5-}$ is larger than that of $Cu(NH_3)_4^{2+}$; Cu^{2+} is thermodynamically not stable and tends to be reduced to Cu^+ in the presence of thiosulfate.

$Cu^{2+} + 4NH_3 = Cu(NH_3)_4^{2+}$	Log K = 12.6	Equation 4.4
$Cu^{+} + 3S_2O_3^{2} = Cu(S_2O_3)_3^{5}$	Log K = 13.7	Equation 4.5
$2\mathbf{C}\mathbf{u}^{2+} + 2\mathbf{S}_2\mathbf{O}_3^{2-} = 2\mathbf{C}\mathbf{u}^+ + \mathbf{S}_4\mathbf{O}_6^{2-}$	Log K = 4.9	Equation 4.6

According to Figure 4.20, with the increase of the ammonium thiosulfate concentration, the concentration of cupric tetrammine increases, leading to higher limiting cathodic current.



Figure 4.21 The gold cathodic polarization at different sodium thiosulfate concentration (250 ppm [Cu]T, 0.4 M NH3, pH 10, 450 rpm, 25°C, 1 mV/sec)



Figure 4.22 The effect of $[Na_2S_2O_3]$ on $[Cu(NH_3)_4^{2^+}]$ and $[Cu^+]([Cu]_T = 250 \text{ ppm}, 0.4 \text{ M NH}_3)$

The effect of concentration of sodium thiosulfate on limiting current is shown in Figure 4.21. The limiting current decreases with an increasing of sodium thiosulfate concentration. This result indicates that thiosulfate species are involved in the cathodic process, which is contradictory to the mechanism proposed by Jiang et al, 1993 (1), as shown in the following equation:

 $Cu(NH_3)_4^{2^+} + e \rightarrow Cu(NH_3)_2^{2^+} + 2 NH_3$ Equation 4.7 $Cu(NH_3)_2^{2^+} + 2 NH_3 + \frac{1}{4} O_2 + \frac{1}{2} H_2O \rightarrow Cu(NH_3)_4^{2^+} + OH^-$ Equation 4.8However, this result is in agreement with the mechanism that is proposed by Li & Miller,1996, in which thiosulfate ion plays a key role in the cathodic process:

$$3 S_{2}O_{3}^{2^{-}} + Cu(NH_{3})_{4}^{2^{+}} + e \rightarrow Cu(S_{2}O_{3})_{3}^{5^{-}} + 4 NH_{3}$$
Equation 4.9
Cu(S_{2}O_{3})_{3}^{5^{-}} + \frac{1}{4}O_{2} + \frac{1}{2}H_{2}O + 4 NH_{3} \rightarrow Cu(NH_{3})_{4}^{2^{+}} + 3 S_{2}O_{3}^{2^{-}} + OHEquation 4.10

Li & Miller (1996) stated that both ammonia and thiosulfate affect the cathodic reaction; excessive amounts of ammonia will hinder equation 4.9 and excessive amounts of thiosulfate will hinder equation 4.10, either of these cases will make the cathodic process less balanced and therefore decrease the cathodic reaction rate.

However, as shown in Figure 4.23, the cathodic current density increases constantly with the increasing of ammonia concentration. This may be due to the stabilization of $Cu(NH_3)_4^{2+}$ by extra ammonia. The increase of ammonia concentration helps to stabilize Cu(II) in the solution and therefore makes the $Cu(NH_3)_4^{2+}/Cu(S_2O_3)_3^{5-}$ couple more reversible and leads to high cathodic current. At 0.1 M NH₃, it appears some other reaction takes place when the potential is below 0.0 V_{SHE}.



Figure 4.23 The gold cathodic polarization at different ammonia concentration (250 ppm [Cu]T, 0.2 M NaS2O3, pH 10, 450 rpm, 25°C, 1 mV/sec)



Figure 4.24 The effect of [NH3] on $[Cu(NH3)4^{2^+}]$ and $[Cu^+]([Cu]T = 250 \text{ ppm}, 0.2 \text{ M} (NH4)2S2O3)$

Not surprisingly, as the total copper concentration increases, the cathodic current increases constantly since copper ion plays a key role in the cathodic process. It also can be seen that the Cu(I) species prevails in the range of total copper concentration range of studies.

As shown in Figure 4.27, the cathodic current increases dramatically as pH increases. This is because high pH leads to more free ammonia in solution to stabilize Cu(II) in solution and therefore enhance the cathodic process. It also can be seen that the cathodic currents keep increasing at pH 8 and 9 and do not reach a limit in the whole range of potential studied. It seems that some other cathodic maybe reaction takes place. A similar phenomenon also occurs at 0.1 M ammonia (Figure 4.23). The observation is that there is not enough free ammonia presented during these three experimental conditions.

The effect of temperature on Figure 4.29 shows that: as temperature increases from 25 to 30 $^{\circ}$ C, the current increases slightly; after 30 $^{\circ}$ C, the current decreases rapidly as temperature further increases. This result is not initially expected since high temperature generally leads to fast kinetics. A reasonable explanation is that the lower current density at high temperature results from the homogeneous reduction of Cu(II) in solution as shown in Equation 4.11.

$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \rightarrow 2Cu(S_2O_3)_3^{5-} + 8NH_3 + S_4O_6^{2-}$ Equation 4.11

The reaction rate of Equation 4.11 increases rapidly as temperature increases resulting in depleting the Cu(II) in the solution, which in turn decrease the cathodic current.



Figure 4.25 The gold cathodic polarization at different copper concentration (0.2 M (NH4)2S2O3, pH 10, 450 rpm, 25°C, 1 mV/sec)



Figure 4.26 The effect of copper concentration on $[Cu(NH_3)_4^{2^+}]$ and $[Cu^+](0.2 \text{ M} (NH_4)_2S_2O_3)$



Figure 4.27 The gold cathodic polarization at different pH value (250 ppm [Cu]T, 0.2 M (NH4)2S2O3, pH 10, 450 rpm, 25°C, 1 mV/sec)



Figure 4.28 The effect of pH on $[Cu(NH_3)_4^{2^+}]$ and $[Cu^+](250 \text{ ppm } [Cu]T, 0.2 \text{ M} (NH_4)_2S_2O_3)$



Figure 4.29 The gold cathodic polarization at different temperature (250 ppm [Cu]^T, 0.2 M (NH₄)₂S₂O₃, pH 10, 450 rpm, 1 mV/sec)

In general, ammonia, thiosulfate and copper ion all have a role in determining the rate of the cathodic process. The experimental results confirm the mechanism proposed by Li et al, 1996, which is presented in Equation 4.9 & 4.10. It also suggested that Cu(I) instead of Cu(II) dominates in the solution under the experimental conditions studied.

4.4 Evan's Diagram

In this section, the cathodic and anodic polarization curves are combined to form Evan's diagrams. It is important to mention that, the anodic polarization curves were obtained in the absence of copper ion unless otherwise noted (It was initially assumed that copper ion has no impact on the anodic process). The cathodic polarization curves were obtained in the presence of copper.

The Evan's diagrams for different rotating velocities are presented in Figure 4.30. From the intersection of corresponding anodic and cathodic polarization curves, the mixed potential and corrosion current density can be obtained. The corrosion current can be converted into corrosion rate by Faraday's Law. For example, 10^{-4} A/cm² is equivalent to corrosion rate 0.38 um/hrs as shown in Equation 4.12 The effects of different parameters on the corrosion current density and mixed potential from Evan's diagram are presented in the following section. (The complete collection of the Evan's diagrams from this study is in Appendix A).

$$r = 1 \times 10^{-4} \frac{Coul}{Sec \cdot cm^{-2}} \times \frac{cm^{-2}}{10^{-8} um^{-2}} \times \frac{60 Sec}{min} \times \frac{60 min}{hr} \times \frac{mol}{96485 Coul} \times \frac{196 \cdot 97 g}{mol} \times \frac{cm^{-3}}{19 \cdot 3 g} \times \frac{10^{-12} um^{-3}}{cm^{-3}} = 0.38 um / hr$$

Equation 4.12



Figure 4.30 The Evan's diagram of gold leaching in 0.2 M (NH4)2S2O3 solution at different rotating velocities (250 ppm [Cu]T, pH 10, 25 °C, 1 mV/sec)

As can be seen from Figure 4.34, the corrosion rate increases as rotating velocity increases, but no linear relationship can be found between the corrosion rate and the square root of rotating velocity. The rotating velocity has no impact on the anodic process (Figure 4.4), but has a dramatic impact on the cathodic process (Figure 4.17). It seems that the cathodic process controls the corrosion rate. The mixed potential increases slightly as rotating velocity increases.

Not surprisingly, the corrosion rate increases constantly as the increase of ammonium thiosulfate concentration, as shown in Figure 4.32. However, the mixed potential does not follow the pattern of corrosion rate, decreasing at first and then leveling off with increase of ammonium thiosulfate concentration.

The effect of the sodium thiosulfate concentration on the gold corrosion rate and mixed potential at fixed ammonia concentration is shown in Figure 4.33. The corrosion rate increases first as sodium thiosulfate concentration increases from 0.1 to 0.2 M Na₂S₂O₃, reaches maximum point at 0.2 M Na₂S₂O₃; further increasing of sodium thiosulfate concentration leads to lower corrosion rate. As presented in the section 4.1 and 4.2, the anodic current increases and cathodic current decreases with the increasing sodium thiosulfate concentration. The cathodic process therefore mainly controls the corrosion rate. The mixed potential drops as sodium thiosulfate concentration increases.

Since ammonia both enhances the anodic and cathodic process, it is expected that the corrosion rate increases significantly with increasing ammonia concentration at constant pH as shown in Figure 4.34. The mixed potential increases as ammonia concentration increases.



Figure 4.31 The effect of rotating velocities on gold leaching rate and mixed potential determined by Evan's diagram (0.2 M (NH4)2S2O3, 250 ppm [Cu]T, pH 10, 25 °C, 1 mV/sec)



Figure 4.32 The effect of ammonium thiosulfate concentration on gold leaching rate and mixed potential determined by Evan's diagram (450 rpm, 250 ppm [Cu]T, pH 10, 25 °C, 1 mV/sec)



Figure 4.33 The effect of sodium thiosulfate concentration on gold leaching rate and mixed potential determined by Evan's diagram (450 rpm, 0.4 M NH3, 250 ppm [Cu]T, pH 10, 25 °C, 1 mV/sec)



Figure 4.34 The effect of ammonia concentration on gold leaching rate and mixed potential determined by Evan's diagram (450 rpm, 0.2 M Na₂S₂O₃, 250 ppm [Cu]T, pH 10, 25 °C, 1 mV/sec)

The effect of total copper ion concentration on gold corrosion and mixed potential is shown in Figure 4.35. It is interesting to find that the corrosion rate decreases slightly as $[Cu]_T$ increases from 250 to 500 ppm and then increases significantly with further increase in $[Cu]_T$. The low corrosion value at 500 ppm $[Cu]_T$ may be due to the excessive consumption of thiosulfate ion since copper is added as $CuSO_4 \cdot 5H_2O$. By the same reason, the mixed potential increases as $[Cu]_T$ increases.

The effect of pH on gold corrosion rate in ammonium thiosulfate solution in the presence of copper is shown in Figure 4.36. The gold corrosion rate is negligible at pH 8 and increases rapidly from pH 9 to pH 11. Again the corrosion rate here is mainly determined by the cathodic process: in the anodic process, the corrosion currents at pH 8 and 9 are higher than those at pH 10 and pH 11(section 4.1). The mixed potential increases with the increasing of pH.



Figure 4.35 The effect of copper concentration on gold leaching rate and mixed potential determined by Evan's diagram (0.2 M (NH4)2S2O3, 450 rpm, 250 ppm [Cu]T, pH 10, 25 °C, 1mV/sec)



Figure 4.36 The effect of pH on gold leaching rate and mixed potential determined by Evan's diagram (0.2 M (NH4)2S2O3, 450 rpm, 250 ppm [Cu]^T, pH 10, 25 ^OC, 1 mV/sec)

The effect of tetrathionate addition on the gold corrosion rate is shown in Figure 4.37. It should be emphasized that no tetrathionate addition was made during the cathodic polarization study since it is assumed that the tetrathionate has no impact on cathodic process. The gold corrosion rate decreases slightly as sodium tetrathionate concentration increases. The mixed potential keeps almost constant during the sodium tetrathionate concentrations studied.

The effect of temperature on gold corrosion rate in ammonium thiosulfate solution in the presence of copper ion is shown in Figure 4.38. The corrosion rate increases slightly from 25 °C to 30 °C, then falls down significantly with further increases of temperature. Again the corrosion rate is mainly determined by the cathodic process. The mixed potential at 40 and 50 °C is significant lower that at 25 and 30 °C, which seems due to the acceleration of Cu(II) reduction at high temperature.

From the results presented above, it can be seen that, the corrosion rate is generally determined by the cathodic process if the same parameter has contradictory impact on the cathodic and anodic process. The mixed potential is generally around 0.15 V_{SHE} . If the mixed potential can be moved to $0.2 \sim 0.3 V_{SHE}$ by improving the cathodic process (since the cathodic process is the controlling factor), the gold corrosion rate can be significantly accelerated. However the corrosion rate obtained by the Evan's diagram is only an artificial prediction from the electrochemical model of the gold leaching process; the correctness of this prediction depends on the validity of the electrochemical model and assumptions made about the anodic and cathodic process (which may not be

appropriate). In the next section, the results of direct leaching of gold in ammonia thiosulfate solution in the presence of copper will be presented and compared with the results of the electrochemical studies.



Figure 4.37 The effect of sodium tetrathionate concentration on gold leaching rate and mixed potential determined by Evan's diagram (0.2 M (NH4)2S2O3, 450 rpm, 250 ppm [Cu]T, pH 10, 25 °C, 1mV/sec)



Figure 4.38 The effect of temperature on gold leaching rate and mixed potential determined by Evan's diagram (0.2 M (NH4)2S2O3, 450 rpm, 250 ppm [Cu]T, pH 10, 1mV/sec)

4.5 Direct rotating gold disk leaching studies

In this set of experiments, a gold disk was leached in ammonium thiosulfate solution at different condition and no external voltages were imposed on the disk. The effect of different parameters on the gold leaching rate were studied and compared with the results from electrochemical studies.

Since the thiosulfate species is not stable, especially in the presence of copper ion, the sulfur species were monitored in preliminary tests; the typical result is shown in the following Table 4.2. It seems that the tetrathionate forms instantaneously after the solution is made, but not significantly (< 5%). However, both thiosulfate and tetrathionate concentration are fairly constant during the gold leaching process. This result is directly contradictory to those results observed when leaching gold from ores/concentrates, where substantial amount of thiosulfate loss is generally expected.

Table	4.2	The	sulfur	speciation	in	rotating	gold	disk	leaching	test	(0.2	Μ
(NH4)2	S2O3	, 250	ppm [C	u] T , pH 10,	25 °	°C						

time	sec	0	1800	3600	5400	7200
$S_2O_3^2$	g/l	21.72	21.86	21.51	21.87	21.98
S₄O ₆ ²⁻	g/l	0.83	0.51	0.52	0.53	0.54
S _{Total}	g/l	22.55	22.37	22.03	22.40	22.52

During rotating gold disk leaching experiments, a black film can sometimes be found on the gold surface, which probably indicated that passivation took place. It is then not surprising that dissolved gold Vs time plots are not always linear as shown in Figure 4.39. Therefore, the leaching data are first fitted with 2nd order polynomial and the slopes at time zero of fitting curves were taken as gold leaching rate. The whole collection of the results of the each of these experiments can be found in Appendix B.



Figure 4.39 The variation of solution potential and dissolved gold over time at following condition: 0.2 M (NH4)2S2O3, 250 ppm [Cu]T, pH 10, 450 rpm, 25 °C

The effect of rotating velocity, ammonium thiosulfate concentration, sodium thiosulfate concentration, ammonia concentration, total copper concentration, pH, tetrathionate addition and temperature on the gold leaching rate in rotating gold disk leaching studies are presented in the following Figures. For the convenience of comparison, the effects of these parameters on corrosion rate obtained by Evan's diagram and limiting corrosion rate determined by cathodic limiting current are also imposed on the corresponding Figures. The current density (A/cm²) is converted to leaching rate by Faraday's law.

In the remaining text of this section, the "gold leaching rate" refers to the gold leaching rate from rotating gold disk leaching studies.

The effect of rotating velocity on gold leaching rate is shown in Figure 4.40. The gold leaching rate increases as rotating velocity increases as predicted by the electrochemical study. It probably indicated that the whole gold leaching process, through the range of experimental study, is under diffusion or mixed control. It is also surprising to find that the gold leaching rate obtained from the gold disk leaching studies is...substantially_higher than that_predicted_by_the_electrochemical_studies (... Evan's diagram). On the other hand, the gold leaching rate is upper bounded by limiting rate.

The effect of ammonium thiosulfate concentration on gold leaching rate is shown in Figure 4.41. As predicted by the electrochemical study, the gold leaching rate increases with increasing ammonium thiosulfate concentration. However, as was the same case with rotating velocity, gold leaching rate is significantly higher than that predicted by the electrochemical studies. The leaching rate approaches the limiting corrosion rate at low ammonium thiosulfate concentration (0.1 and 0.2 M), and the gold leaching rate is much lower than the limiting rate at higher ammonium thiosulfate concentration.

The effect of sodium thiosulfate concentration at fixed ammonia concentration is presented in Figure 4.42. The gold leaching rates are exactly the same at 0.1 and 0.2 M sodium thiosulfate concentration; and then fall down steeply from 0.2 to 0.4 M; further increasing of sodium thiosulfate has no significant influence on gold leaching rate. This trend is similar to that predicted by the electrochemical study, except that the gold leaching rate predicted by the electrochemical study reaches the







Figure 4.41 The effect of concentration of ammonium thiosulfate on gold leaching rate (450 rpm, 250 ppm, [Cu]T, pH 10, 25 °C)

maximum at 0.2 M sodium thiosulfate. The gold leaching rate from the gold disk leaching studies is again significantly higher than that from the electrochemical study. The limiting rate from cathodic polarization fall down almost linearly as sodium thiosulfate concentraion increases, whose pattern is different from those from gold disk leaching and electrochemical studies. However, the gold leaching rate from gold leaching study is clearly bounded by the limiting rate.

The effect of ammonia concentration on gold leaching rate is shown in Figure 4.43. As predicted by the electrochemcial stusies, the gold leaching rate increases as ammonia concentration increases. The gold leaching rate from the electrochemical study is again significantly lower than that from the gold disk leaching studies. The gold leaching rate approaches the limiting rate at low ammonia concentration (less then 0.4 M) and significantly lower than the limiting rate at higher concentration.

The effect of total copper concentration on gold leaching rate is shown in Figure 4.44. Due to the concern of excessive thiosulfate loss at high copper concentration, the gold disk leaching experiments were only performed at low copper concentration ($50 \sim 500$ ppm) compared to the electrochemical studies ($250 \sim 1500$ ppm). The gold leaching rate increases with increasing total copper concentration as predicted by the electrochemical studies. The gold leaching rate is again significantly higher than that from the electrochemical studies. The gold leaching rate approaches the limiting rate at 250 and 500 ppm total copper concentration.


Figure 4.42 The effect of concentration of sodium thiosulfate on gold leaching rate (0.2 M NH₃, 450 rpm, 250 ppm [Cu]^T, pH 10, 25 °C)



Figure 4.43 The effect of ammonia concentration on gold leaching rate (0.2 M Na₂S₂O₃, 450 rpm, 250 ppm [Cu]^T, pH 10, 25 °C)

The effect of pH on the gold leaching rate is shown in Figure 4.45. As predicted by the electrochemical studies, the gold leaching rates from the gold disk leaching study are almost identical at pH 8 and 9, and then increase dramatically from pH 9 to 11. The leaching rate at high pH (pH 10 and 11) is significantly higher than that from the electrochemical study at the same pH values. The limiting rate also follows the same pattern as that from gold disk leaching and electrochemical studies.

The effect of tetrathionate addition on the gold leaching rate is shown in Figure 4.46. The gold leaching rate from the gold disk leaching study decreases almost linearly with increasing of sodium tetrathionate concentration. This result verifies that tetrathionate does have a negative effect on the gold leaching rate, which is weakly suggested by the electrochemical study. The gold leaching rate from the gold disk leaching rate is again significantly higher than that from the electrochemical studies. No limiting rate is available since tetrathionate presumably has no effect on cathodic process.

The effect of temperature on gold leaching rate is shown in Figure 4.47. The gold leaching rate falls down dramatically as temperature increases from 25 to 40 °C and then levels off. This result is slightly different from the result from electrochemical study in which the leaching rate reaches the maxmium at 30 °C. The gold leaching rates are significantly higher than that from electrochemical study at low temperature (25 and 30 °C), but these two rates are almost identical at high temperature (40 and 50 °C). Except for 25 °C, the gold leaching rates from gold disk leaching are far below the limiting rate.

In general, the effect of the same parameter on the gold leaching rate from the gold leaching and electrochemical studies follows the same pattern; however, the gold leaching rate from gold disk leaching study is usually significantly greater than that predicted from the electrochemical study and is bounded by the limiting rate from the limiting cathodic current. The significant discrepancy between the gold leaching rate data from the gold disk leaching and electrochemical studies is not expected since many researchers have suggested the electrochemical nature of gold leaching in the ammonium thiosulfate in the presence of copper ions (Jiang etal, 1993(1); Li et al, 1996). However, Breuer and Jeffrey (2000) recently suggested that copper ion not only acts as an oxidant in cathodic process, but also enhances the gold anodic oxidation. This can explain the difference between gold leaching rates from the directly gold leaching study and from electrochemical study since copper ion was presumed to have no impact on the anodic process during the electrochemical study.

Experimental dissolution rates in kinetics studies usually can be correlated to the parameters affecting the rate in the form of following:

 $r=k\prod_i(p_i^{n_i})$

Equation 4.13

Where:

r: the dissolution rate, mol $m^{-2} s^{-1}$;

 κ : the rate constant;

P_i: parameter i, wiich affects the rate;

n_{it} order of dependence of the rate on the parameter i.

From Equation 4.13, it is easy to see that plot of log rate (r) versus log parameter i when all other parameters are fixed will yield a slope equal to n_i. Using the kinetics data of rotating gold disk leaching studies, the gold leaching leaching rate can be correlated to the different parameters as following:

 $r \propto [NH_3]^{1.557} \times [S_2O_3^{2^{-}}]^{-0.63} \times [OH^{-}]^{0.447} \times [Cu]_T^{0.647} \times \omega^{0.675} \times T^{-3.72}$ Equation 4.14

$$\mathbf{r} \propto [(\mathbf{NH}_4)_2 \mathbf{S}_2 \mathbf{O}_3]^{0.607} \times [\mathbf{OH}^-]^{0.447} \times [\mathbf{Cu}]_{\mathrm{T}}^{0.647} \times \omega^{0.675} \times \mathrm{T}^{-3.72}$$

Equation 4.15

Equation 4.16

 $r \propto \left[S_4 O_6^{2-}\right]^{-0.292}$

Where:

r: the dissolution rate, mol $m^{-2}s^{-1}$

 $[(NH_4)_2S_2O_3]$: ammonium thiosulfate concentration, mol/l

[OH]: hydrogen oxygen concentration, mol/l

[Cu]_T total copper species concentration, ppm

ω: rotating velocity, rpm,

T: temperature, °C

[NH₃]: ammonia concentration, mol/l

 $[S_2O_3^{2-}]$: thiosulfate ion concentration, mol/l

The Equation 4.14 is applicable when ammonia and thiosulfate are considered separately; while the Equation 4.15 is applicable when leaching reagent is ammonium thiosulfate; the Equation 4.16 correlated the gold leaching rate to the nominal tetrathionate solution. It is important to mention that these rate expression are purely empirical formula, and they are only valid in the experimental range of this rotating disk leaching study.



Figure 4.44 The effect total copper concentration on gold leaching rate (0.2 M (NH4)2S2O3, 450 rpm, pH 10, 25 °C)



Figure 4.45 The effect of pH on gold leaching rate (0.2 M (NH4)2S2O3, 450 rpm, 250 ppm [Cu] τ , 25 °C)



Figure 4.46 The effect of sodium tetrathionate concentration on gold leaching rate (0.2 M (NH4)2S2O3, 450 rpm, pH 10, 250 ppm [Cu]T, 25 °C)



Figure 4.47 The effect of temperature on gold leaching rate (0.2 M (NH4)2S2O3, 450 rpm, pH 10, 250 ppm [Cu]T)

4.6 The Mechanism

It is generally agreed that the leaching in the ATS system follows an electrochemical mechanism. However, several different mechanisms were proposed (Jiang et al, 1993(1), Zhu, 1993, Li, et al, 1996), and some controversy exists among these prior studies. According to the results of the above electrochemical study and rotating disk leaching study, gold leaching in the ATS system in the presence of copper ion is very complicated, and there are still some questions needed to be answered before a reliable mechanism can be presented.

4.6.1 Anodic process

For the anodic process, the experimental results indicate that many species are involved in the gold oxidation at the anode: NH_3/NH_4^+ , $S_2O_3^{2-}$ and Cu(II)/Cu(I). It has been suggested that the oxidation of gold occurs via an intermediate amine complex, $Au(NH_3)_2^+$, which is preferentially formed in the gold surface (Jiang, et al , 1993, 1). However, this mechanism is doubtful due to the following four reasons:

- 1. The standard reduction potential of $Au(NH_3)_2^+$ is 0.572 V (Breuer & Jeffery, 2000(1)), which is considerably more positive than the anode potentials studied.
- 2. The kinetics of gold dissolution in ammoniacal solution are very slow in the ambient condition (Meng & Han, 1993).
- 3. At pH 8 and 9, where there is less free ammonia in solution, the gold oxidation rate is higher than that at pH 10 and pH 11 (section 4.1). It is contradictory to the above

mechanism, where faster kinetics are expected at high pH due to the relatively higher free ammonia concentration.

4. As ammonia concentration is increased above 0.4 M, there is little further enhancement to the rate of gold oxidation (Section 4.1).

Pedraza et al, 1988, reported that thiosulfate ions decomposed when in contact with gold at open circuit potential, leaving a film of several sulfur-containing species. It is more likely that, as suggest by Breuer & Jeffery, 2000 (1), NH_3/NH_4^+ alter the surface of the gold surface to reduce the effect of this sulfur-containing passivation film.

The coulometric test results indicated that copper enhances the gold anodic oxidation rate, which also was observed by Breuer & Jeffery, 2000(1). The mechanism of copper enhancement effect is not clear. However, since it is evidence that, NH_3/NH_4^+ can not totally eliminate the passivation, the copper ion may somehow activate the gold surface further to accelerate the gold dissolution rate. The anodic reaction is shown in Equation 4.17.

 $Au - e + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)^{3-}$

Equation 4.17

4.6.2 Cathodic process

For the cathodic process, experimental results indicated that the cathodic process is under diffusion or mixed control. This study confirmed the mechanism proposed by Li et al, 1996, as illustrated following:

$$3 S_2O_3^{2-} + Cu(NH_3)_4^{2+} + e \rightarrow Cu(S_2O_3)_3^{5-} + 4 NH_3$$
 Equation 4.18

 $Cu(S_2O_3)_3^{5-} + \frac{1}{4}O_2 + \frac{1}{2}H_2O + 4NH_3 \rightarrow Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + OH^-$ Equation 4.19

Equation 4.18 occurs at the gold surface; Equation 4.19 occurs in the bulk solution. The schematic diagram of the gold leaching process is shown in Figure 4.48.





Figure 4.48 Proposed mechanism of gold leaching in ATS system in the presence of copper ion

4.7 Summary

The kinetics of gold leaching in ammonium thiosulfate solution in the presence of copper ion was investigated by electrochemical study and rotating gold disk leaching studies. The effects of reagent concentrations, pH, rotating velocity and temperature were studied. The tentative mechanism was also proposed.

For the electrochemical study, the gold anodic and cathodic polarization method was applied to study the kinetics of gold leaching in the ammonium thiosulfate solution in the presence of copper ion. Coulometric tests were also performed to investigate the current efficiency of gold oxidation for anodic polarization. It was found below 0.3 V_{SHE}, the anodic current was almost 100% contributed by gold oxidation in the absence of copper ion. The introduction of copper ion decreases the anodic current efficiency above 0.2 V_{SHE}. The effects of rotating velocity, pH, ammonium thiosulfate concentration. ammonia concentration, thiosulfate concentration, tetrathionate concentration (anodic polarization only), copper concentration, and temperature on the anodic and cathodic process were investigated. The anodic and cathodic polarization curves were combined in Evan's diagrams to predict kinetic data gold leaching in ammonium thiosulfate solution in the presence of copper ion. The prediction is as following:

The magnitude of gold leaching rate is around 1× 10⁻⁶ mol m⁻²s⁻¹ or 0.037 um/hr (at standard condition: 0.2 M (NH₄)₂S₂O₃, pH 10, 250 ppm Cu, 450 rpm, 25°C. the gold leaching rate is 2.73 × 10⁻⁶ mol m⁻²s⁻¹)

- The gold leaching rate increases with increasing rotating velocity
- The gold leaching rate increases with increasing pH
- The gold leaching rate increases with increasing ammonia concentration.
- The gold leaching rate increases as thiosulfate ion concentration increases from 0.1 to 0.2 M, further increases lead to lower gold leaching rates.
- As the concentration of ammonium thiosulfate increases, the gold leaching rate increases constantly.
- The introduction of tetrathionate has a mild detrimental effect on gold leaching rate.
- Gold leaching rate increases with increasing copper ion concentration.
- As temperature increases from 25 to 30 °C, gold leaching rate increases a little; further increasing of temperature decreases the gold leaching rate significantly.
- If the same parameter has contradictory effects on the anodic and cathodic process, the gold leaching rate generally follows the pattern of cathodic process.

During the rotating gold disk leaching study, the effects of the same parameters on the gold leaching rate were studied and compared with the results of the electrochemical study. In general, the effects of the same parameter on the gold leaching rate from the gold leaching and electrochemical studies follows the same pattern; however, in this study, the gold leaching rate (around 8.0×10^{-6} mol m⁻² s⁻¹ or 0.29 um/sec) from gold disk leaching study was usually greater than that from the electrochemical study but both are in the same magnitude. The discrepancy between the gold leaching rate data from the gold disk leaching and electrochemical studies is suggested due to the following reason. The anodic plolariztion study was performed in the absence of copper

ion in solution. The gold leaching rate data form the gold leaching rate is correlated with

the different parameters and presented in Equation $4.14 \sim 4.16$.

5. CONCLUSIONS & RECOMMENDATIONS

The objective of this study was to determine which factors have important effects on the gold leaching rate in ammonium thiosulfate solution in the presence of copper. The parameters considered in this study include rotating velocity, temperature, pH and the concentration of different reagents.

The conclusions of this work are listed below:

- The anodic process of gold leaching in ATS system is under surface reaction control in the range of experimental conditions of this work
- The cathodic process of gold leaching in ATS system is under diffusion or mixed kinetic control in the range of experimental conditions of this work
- The gold leaching kinetics are determined by the cathodic process and is also under diffusion or mixed kinetic control in the range of experimental conditions at this work
- The increasing of ammonia and copper species concentration can enhance the anodic and the cathodic process
- The prediction of gold leaching rate of the electrochemical study is consistent with the results of the gold leaching study
- The effects of different parameters on gold leaching rate can be correlated into a rate expression.

For the future study, the anodic oxidation of gold in the presence of copper should be studied using a rotating electrochemical quartz crystal microbalance to eliminate the side reaction effects on interpretation of the anodic current. Further study also should explore the potential to develop and implement alternative cathodic processes due to the fact the cathodic process determines the gold leaching rate. Alternative cathodic processes should seek a copper free catalyst system as an alternative to the copper-ammonia catalyst system. The potential difficulty of an environmental friendly treatment of copper – ammonia – thiosulfate solutions makes this an attractive option. A copper free cathodic process will also make the leaching system more stable.

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APPENDIX A: THE COLLECTION OF EVAN'S DIAGRAMS



A- 1The Evan's diagram at different rotating velocities



A-2 The Evan's diagram at different ammonium thiosulfate concentration



A- 3 The Evan's diagram at different sodium thiosulfate concentration



A- 4 The Evan's diagram at different ammonia concentration



A- 5 The Evan's diagram at different total copper concentration



A- 6 The Evan's diagram at different pH



A-7 The Evan's diagram at different sodium tetrathionate concentration



A-8 The Evan's diagram at different temperature

APPENDIX B: RAW DATA OF GOLD ROTATING DISK LEACHING STUDY



B-1The variation of solution potential and dissolved gold over time for the standard test: $0.2 \text{ M} (\text{NH}_4)_2\text{S}_2\text{O}_3$, 250 ppm [Cu]_T, pH 10, 450 rpm, 25°C.



B- 2 The variation of solution potential and dissolved gold over time under the following conditions: 0.2 M Na₂S₂O₃, 0.4 M NH₃, 250 ppm [Cu]_T, pH 10, 450 rpm, 25°C.



B- 3The variation of solution potential and dissolved gold over time with different rotating velocities (0.2 M (NH4)2S2O3, 250 ppm [Cu]T, pH 10, 25°C).



B- 4The variation of solution potential and dissolved gold over time with different pH (0.2 M (NH4)2S2O3, 250 ppm [Cu]T, 450 rpm, 25°C).

pH 11



B- 5The variation of solution and dissolved gold over time with different [(NH₄)₂S₂O₃] (250 ppm [Cu]_T, pH 10, 450 rpm, 25^oC).







B- 7The variation of Eh and dissolved gold over time with different [NH₃] (250 ppm [Cu]_T, pH 10, 0.2 M Na₂S₂O₃, 450 rpm, 25^oC).



B- 8The variation of Eh and dissolved gold over time with different $[Na_2S_4O_6]$ (0.2 M (NH4)₂S₂O₃, 250 ppm $[Cu]_T$,450 rpm, 25°C).



B- 9 The variation of solution potential and dissolved gold over time with different [Cu], (0.2 M (NH4)₂S₂O₃, pH 10, 25°C, 450 rpm).


B- 10 The variation of solution potential and dissolved gold over time with different temperature (0.2 M (NH4)2S2O3, 250 ppm [Cu]T, pH 10, 450 rpm).

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APPENDIX C: THE LOGARITHMIC RELATION BETWEEN GOLD LEACHING RATE AND DIFFERENT PARAMETERS



C-1 The logarithmic relationship between gold leaching rate and rotating velocity



C-2 The logarithmic relationship between gold leaching rate and concentration of ammonium thiosulfate

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C-3 The logarithmic relationship between gold leaching rate and concentration of sodium thiosulfate



C- 4 The logarithmic relationship between gold leaching rate and concentration of ammonium thiosulfate



C-5 The logarithmic relationship between gold leaching rate and concentration of total copper species



C-6 The logarithmic relationship between gold leaching rate and concentration of hydroxide ion



C- 7 The logarithmic relationship between gold leaching rate and temperature