# GOLD LEACHING IN THIOSULFATE

# SOLUTIONS CONTAINING COPPER(II)

# AND AMMONIA

*A Thesis Submitted for the Degree of*

## DOCTOR OF PHILOSOPHY

*By*

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# Contents

# *Abstract*

Due to increasing environm      ' ¬nd public concerns over the continued use of cyanide in gold recovery, rese            ¬rnative lixiviants has heightened.  Of the alternatives, thiosulfate appear     · ¦      most promising.  Considerable research conducted in the 1980's and 9·  ·    · ·     ¡at acceptable gold leach rates were only obtained in the presence of c            ¬s and ammonia.  This system though is complicated by the homogeneous . _¬¬ions involving copper(II) and thiosulfate which are poorly understood.

This study found that in the absence of oxygen, the reduction of copper(II) by thiosulfate was generally rate limited by a second order process with respect to copper(II).  Tetrathionate, the reaction product of thiosulfate oxidation by copper(II), was also found to reduce copper(II) in the presence of thiosulfate.  Other oxysulfur species such as trithionate and sulfite are shown to also reduce copper(II).  These reactions highlight the complexity of the copper(II) reduction mechanisms in thiosulfate leach solutions.

Surprisingly, the presence of oxygen does not maintain the majority of the copper in the copper(II) oxidation state with the initial rate of copper(II) reduction being significantly faster than in the absence of oxygen.  To measure thiosulfate concentration, a flow injection analysis method was developed using a 4 electrode flow through cell containing both silver and platinum working electrodes.  In the presence of oxygen an increased rate of thiosulfate oxidation occurs via a second mechanism which is consistent with oxidation by the intermediate superoxide and/or hydroxide radicals formed as a result of copper(I) oxidation by oxygen.  The thiosulfate oxidation rate was found to be largely dependent on the oxygen concentration.  The [Cu(II)]:[Cu(I)] ratio is important to the gold dissolution process as this largely governs the cathodic potential.  Surprisingly, the [Cu(II)]:[Cu(I)] ratio was almost independent of the oxygen concentration, except at very low concentrations.  Thus, thiosulfate oxidation can be minimised by utilising low oxygen concentrations with little effect on the [Cu(II)]:[Cu(I)] ratio and hence the cathodic potential.

The gold dissolution process was effectively studied for the first time using a rotating electrochemical quartz crystal microbalance, which allowed the gold oxidation reaction to be studied in actual thiosulfate leach solutions containing copper ions. The presence of copper ions was shown to significantly enhance the gold oxidation reaction. This is the reason why copper(II) is more effective than alternative oxidants in the leaching process. The gold dissolution process was shown to be largely chemically controlled. Many of the parameters that enhanced the gold oxidation reaction lowered the sustainable [Cu(II)]:[Cu(I)] ratio in the presence of oxygen.

Possibly the most significant finding in this research was the passivation of the gold dissolution process with aging of the thiosulfate leach solution. The gold oxidation reaction was shown to be hindered by an unidentified species which appears to be an intermediate oxysulfur species of thiosulfate oxidation. The passivation was also found to be dependant on the solution conditions.

Clearly, more research is required if the commercial application of this process is to be successful.

# *Statement of Authenticity*

To the best of my knowledge, this thesis contains no part previously submitted for the award of any other degree or diploma in any university or other institution, and contains no material previously published or written by another person, except where due reference is made in the text of the thesis.
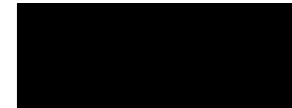
*Paul Breuer.*

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# *Publications*

Breuer, P.L. and Jeffrey, M.I. 2000, 'Thiosulfate leaching kinetics of gold in the presence of copper and ammonia', Minerals Engineering, vol. 13, no. 10-11, pp. 1071-1081.

Breuer, P.L. and Jeffrey, M.I. 2000, 'An electrochemical study of gold oxidation in solutions containing thiosulfate, ammonia and copper', in Electrochemistry in Mineral and Metal Processing V, Eds. Woods, R., Doyle, F.M. and Licht, S., The Electrochemical Society Inc., Pennington, NJ.

Breuer, P.L. and Jeffrey, M.I. 2001, 'The effect of anions on the thiosulfate leaching of gold and oxidation of thiosulfate by copper', in 6th World Congress of Chemical Engineering, Conference Media Services Australia, Doncaster, VIC.

Breuer, P.L. and Jeffrey, M.I. 2001, 'An electrochemical study of gold leaching in thiosulfate solutions containing copper and ammonia', accepted for publication in Hydrometallurgy.

Breuer, P.L. and Jeffrey, M.I. 2001, 'The reduction of copper(II) and the oxidation of thiosulfate and oxysulfur anions in gold leaching solutions', submitted to Hydrometallurgy.

Breuer, P.L., Jeffrey, M.I. and Choo, W.L. 2001, 'Fundamental aspects of the gold thiosulfate leaching process', in Cyanide: Social, industrial, and Economic Aspects, Ed. Young, C.A., Anderson, C.G. and Twidwell, L.G., New Orleans, Louisiana.

Breuer, P.L., Jeffrey, M.I., Tan, E.H.K. and Bott, A.W. 2002, 'The electrochemical quartz crystal microbalance as a sensor in the gold thiosulfate leaching process', accepted for publication in Journal of Applied Electrochemistry.

Jeffrey, M.l., Choo, W.L. and Breuer, P.L. 2000, 'The effect of additives and impurities on the cobalt electrowinning process', Minerals Engineering, vol. 13, no. 12, pp. 1231-1241.

Jeffrey, M.I. and Breuer, P.L. 2000, 'The cyanide leaching of gold in solutions containing sulfide', Minerals Engineering, vol. 13, no. 10-11, pp. 1097-1106.

Jeffrey, M.I., Breuer, P.L. and Choo, W.L. 2001, 'How rapidly do alternative lixiviants leach gold?' in Cyanide: Social, industrial, and Economic Aspects, Ed. Young, C.A., Anderson, C.G. and Twidwell, L.G., New Orleans, Louisiana.

Jeffrey, M.I., Breuer, P.L. and Choo, W.L. 2001, 'A kinetic study comparing gold leaching in the cyanide, thiosulfate and chloride systems', Metallurgical and Materials Transactions B, vol. 32B, pp. 979-986.

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# Chapter 1

# *Introduction*

## 1.1 Importance of Gold

Gold is a metal that is generally associated with wealth due to its rarity and beauty. It has found limited use other than as a monetary standard and for jewellery. Applications of gold based on its physical and chemical properties though are increasing. Gold has played a prominent role in the social and economic fabric of civilization for thousands of years and is still the only universally accepted medium of exchange. Millions of people all over the world continue to use gold as a hedge against inflation and as a basic form of savings and a reliable store of value during times of economic uncertainty or political upheaval.

Gold is used in jewellery due to its beauty, properties and rarity. Gold also offers a unique combination of properties that make it a vital material in many electronic, industrial and medical applications. These properties include resistance to corrosion, electrical conductivity, ductility, malleability, infrared (heat) reflectivity and thermal conductivity.

Gold mainly occurs in nature in the metallic form with the average concentration in the Earth's crust being approximately 4 parts per billion (Puddephatt, 1978). Concentration of gold though has occurred naturally and at parts per million is economically extracted. Native gold also contains silver in varying proportions and sometimes other metals such as platinum, palladium, mercury, copper, lead or iron (Laist, 1954). Gold was probably found on the ground and used by prehistoric man as a tool. The recovery of gold dates back at least 6000 years (Puddephatt, 1978), with the earliest mine workings of which traces remain dating back to 2900BC (Johnson and Davis, 1973). In the nineteenth century prospectors "panned" the gold containing river sands and gravels of river beds using cradles, sluices and dredges (Johnson and Davis,

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1973, Puddephatt, 1978). In the twentieth century gold production increased dramatically, the majority of which came from mines with recovery of the gold from the ore by amalgamation or the cyanide process (Puddephatt, 1978). The cyanide process is currently and has been the major recovery process utilized in the past few decades. However, the continued use of cyanide for the recovery of gold is being questioned due to a number of publicised environmental incidents and disasters in recent years.

World gold production in 2000 was 82.6 million ounces with the three largest producers, South Africa, USA and Australia generating 13.7, 10.6 and 9.5 million ounces respectively (GOLDSHEET Mining Directory). Gold is an integral part of the Australian economy worth $5.1 billion in 2000-01, representing 5% of total exports, and making gold the country's second highest export earner (Market Information and Analysis Unit, 2001). Hence research into improving the cyanide process or alternative lixiviants is important for the survival of the gold mining industry and its value to the Australian economy.

## 1.2   Chemistry of Gold

Gold is the most noble and hence the most non-reactive of all the metals (Nicol *et al.*, 1987). It has the appealing property of not undergoing corrosion in air or in the presence of strong acids or bases. The common oxidation states for gold in aqueous solutions are +1 (aurous) and +3 (auric), for which the standard reduction potentials are 1710 and 1500 mV respectively (Bard, 1973). These values are more positive than the standard reduction potential for water, 1230 mV (Bard, 1973), and thus the gold cations are thermodynamically unstable in aqueous solutions.

However, a number of ligands, such as cyanide and chloride, are known to form stable complexes with the gold cations (Marsden and House, 1992, Nicol *et al.*, 1987). The reaction between an aurous ion and a ligand, L, with a positive or negative charge, n, can be represented by Equation 1.1. The stability constant, $\beta$, for reaction 1.1 is thus given by Equation 1.2.

$$Au^+ + xL^n \leftrightarrow AuL_x^{1+nx} \qquad\qquad \textbf{1.1}$$

$$\beta = \frac{[AuL_x^{1+nx}]}{[Au^+][L^n]^x} \qquad\qquad \textbf{1.2}$$

The standard reduction potential of the gold complex, $E_C^o$, is related to the standard reduction potential of the aurous ion, $E_{Au^+/Au}^o$, and the stability constant, $\beta$, by Equation 1.3, where R is the universal gas constant (8.314 J $K^{-1}$ $mol^{-1}$), T is the absolute temperature (K), and F is the Faraday constant (96485 C $mol^{-1}$). Similarly, $\beta$ and $E_C^o$ can also be calculated for the auric ($Au^{3+}$) complexes.

$$E_C^o = E_{Au^+/Au}^o - \frac{RT}{F}\ln(\beta) \qquad\qquad \textbf{1.3}$$

Thus, for those ligands which form strong complexes with gold (ie. large $\beta$ values) the gold complex will be thermodynamically stable in aqueous solution as $E_C^o$ for the complex is more negative than 1230 mV. Hence, the aqueous chemistry of gold is limited to those gold complexes that are stable in solution. A number of ligands are known to form stable complexes with either aurous or auric cations. Those complexes that are of importance in regards the hydrometallurgical processing of gold are listed in Table 1.1. The complexes are listed in order of stability with the gold cyanide complex being the most stable (most negative $E_C^o$).

The high stability of the gold cyanide complex is the reason for its widespread use in the hydrometallurgical processing of gold bearing ores. Other ligands, such as chloride, thiosulfate and thiourea, have been investigated as alternative lixiviants but have never achieved commercial significance (Labrooy *et al.*, 1994). However, with the increase in safety and environmental concerns over the continued use of cyanide, research into alternative lixiviants has heightened in recent times. Of the alternative lixiviants, thiosulfate appears to be the most promising and is the focus of this thesis.

**Table 1.1:** Stability constants and reduction potentials for various gold complexes.

| Complex | $\beta$ | Reaction | $E_C^o$ (mV) |
|---|---|---|---|
| $Au(CN)_2^-$ | $2 \times 10^{38}$ | $Au(CN)_2^- + e^- \leftrightarrow Au + 2CN^-$ | **-570** |
| $AuS^-$ | $2 \times 10^{36}$ | $AuS^- + e^- \leftrightarrow Au + S^{2-}$ | -460 |
| $Au(HS)_2^-$ | $1.3 \times 10^{30}$ | $Au(HS)_2^- + e^- \leftrightarrow Au + 2HS^-$ | -90 |
| $Au(S_2O_3)_2^{3-}$ | $10^{26}$ | $Au(S_2O_3)_2^{3-} + e^- \leftrightarrow Au + 2S_2O_3^{2-}$ | 153 |
| $Au(thiourea)_2^+$ | $2 \times 10^{23}$ | $Au(Tu)_2^+ + e^- \leftrightarrow Au + 2Tu^+$ | 352 |
| $Au(NH_3)_2^+$ | $3 \times 10^{19}$ | $Au(NH_3)_2^+ + e^- \leftrightarrow Au + 2NH_3$ | 560 |
| $AuI_4^-$ | $5 \times 10^{47}$ | $AuI_4^- + e^- \leftrightarrow Au + 4I^-$ | 560 |
| $Au(SCN)_4^{3-}$ | $10^{42}$ | $Au(SCN)_4^{3-} + e^- \leftrightarrow Au + 4SCN^-$ | 623 |
| $AuBr_4^-$ | $10^{32}$ | $AuBr_4^- + e^- \leftrightarrow Au + 4Br^-$ | 870 |
| $AuCl_4^-$ | $10^{26}$ | $AuCl_4^- + e^- \leftrightarrow Au + 4Cl^-$ | 1002 |

(after Zhang (1997), $Au(NH_3)_2^+$ from Skibsted and Bjerrum (1974), $Au(S_2O_3)_2^{3-}$ from Pouradier (1969)).

## 1.3  Processing of Gold

Gold, which mainly occurs naturally as native or metallic gold, is found either as alluvial or reef gold (Laist, 1954). Alluvial gold, often called "free gold", is gold that occurs in sandy or gravely deposits and is not adherent to or encapsulated by the individual mineral particles. Reef gold or vein gold occurs in hard rock deposits, usually found in quartz but also not uncommonly found in a matrix of one or more base metal sulfide minerals, in which the gold is almost always very finely divided and thoroughly disseminated throughout the rock material with which it is associated.

## 1.3.1 History

The early methods of gold recovery were based on gravity concentration from alluvial deposits. Panning and sluicing are examples of early gravity methods used in which the waste material is washed away from the heavier gold by water. These methods though are not very efficient procedures for recovering gold by comparison with other recovery methods.

The hydrometallurgy of gold, or dissolution methods, are applicable to both alluvial and reef gold and involve dissolving the gold selectively from the waste material and then recovering the metal from solution. These methods require that the ore be firstly crushed and milled fine enough that the gold is liberated. Part of the gold at this point may be recovered by modern gravity concentration methods such as Knelson concentrators, jigs, spirals and tables. Dissolution methods commercially used include amalgamation, chlorination, bromination and cyanidation. Cyanidation is further described in section 1.3.2 as it is the most important process now in use.

Amalgamation provided a simple, though not very efficient, procedure in which the crushed ore was brought into contact with mercury. Gold is dissolved by the mercury to form an amalgam that the gold is subsequently recovered from by distillation. This practice however is no longer used due to the health risks associated with the use of mercury.

Chlorination involves the treatment of the gold ore with chlorine in the presence of water such that the gold is converted to the water soluble gold(III) chloride. The gold is precipitated from the recovered solution by a reducing agent such as iron, sulfur dioxide then hydrogen sulfide, copper(II) sulfide or charcoal. Gold ores are generally roasted before chlorination to convert sulfides, arsenides and antimonides to oxides as these minerals would otherwise consume chlorine. Roasting had the further advantage of breaking down the ore thereby making the gold more accessible. At one time the chlorination process was extensively used for the treatment of gold ores, but it has been superseded by the cyanidation process and is no longer used to any significant extent.

Bromination was carried out in much the same way as chlorination except bromine is used instead of chlorine. Due to the cost of bromine it was never a

competitor to the chlorination process, however it had the advantage of attacking gold more vigorously, especially telluride minerals.

Other lixiviants investigated for the hydrometallurgical recovery of gold include thiocyanate, thiosulfate, iodine and ammonia, though no commercial processes have yet evolved employing these lixiviants.

## 1.3.2 Cyanidation

The first commercial application of the cyanide process was in New Zealand in 1889, from where it spread rapidly (Laist, 1954). Cyanidation, like all hydrometallurgical operations, involves two main processes: leaching and recovery.

The first step involves leaching the high value component, in this case gold, from low value gangue material. This is achieved by leaching the crushed or milled ore with a dilute solution of sodium cyanide or an equivalent cyanide such that the gold dissolves forming the very stable gold(I) cyanide complex. The commonly accepted reaction for the dissolution of gold in a dilute cyanide solution is represented by the Elsner equation shown in Equation 1.4. This is an electrochemical reaction in which cyanide is the lixiviant and oxygen is the oxidant. Given the commercial significance of this seemingly simple electrochemical reaction, it is surprising that significant advances to the fundamental understanding of this process are still being made today (Jeffrey and Ritchie, 2000, Jeffrey, 2000, Wadsworth *et al.*, 2000, Jeffrey and Ritchie, 2001, Drok and Ritchie, 1997, Sun *et al.*, 1996, Mussatti *et al.*, 1997, Jeffrey, 1998).

$$2Au + 4CN^- + \tfrac{1}{2}O_2 + H_2O \rightarrow 2[Au(CN)_2]^- + 2OH^- \qquad 1.4$$

Cyanide is also consumed in the process due to a number of side reactions, especially with many of the sulfide minerals producing thiocyanate. Cyanide also forms strong soluble complexes with many other metal ions such as silver, copper, iron, cobalt and nickel. As some of these metal cyanide species are poorly recovered they pose an environmental threat in the tailings dams. A number of publicised accidental releases

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into the environment recently, such as the collapse of the tailings dams at Omai in Guyana and Baia Mare in Romania, have largely resulted in the growing public concerns over the continued use of cyanide in the recovery of gold.

Carbon in pulp (CIP) adsorption is the most commonly used recovery process in cyanidation, although some older plants may still utilize the Merill-Crowe process involving filtration followed by zinc cementation. The CIP process usually involves two steps, adsorption and elution. In the adsorption stage, activated carbon is agitated within the leach slurry, with the carbon transferred counter current to the pulp through a series of tanks, during which the gold cyanide complex is adsorbed onto the carbon. Loaded carbon is screened from the first CIP adsorption tank and usually washed with hydrochloric acid. The gold is then eluted from the carbon at high temperature by a solution containing sodium cyanide and sodium hydroxide. The carbon is then thermally regenerated and rejoins the CIP circuit in the last tank, while metallic gold is recovered from the eluate by electrowinning.

## 1.4   Thiosulfate Leaching of Gold

Due to the increasing environmental and public concern over the continued use of cyanide in the recovery of gold, research into alternative lixiviants has heightened in recent times. Of the alternative lixiviants, thiosulfate appears to be the most promising due to thiosulfate being non-toxic, relatively cheap compared to cyanide and generally gold recoveries are similar to those of cyanide. Leaching of gold by thiosulfate also has the benefit of decreasing the interference of some metal ions due to their lower solubility in thiosulfate compared to cyanide. However, higher reagent concentrations are required, problems of high reagent consumption and difficulties in recovery of the gold have all contributed in there being no commercial application to date. A summary of the many issues and impediments associated with thiosulfate leaching of gold ores and recovery from solution was recently published by Muir and Aylmore (2002).

## 1.4.1 History

The use of thiosulfate in the recovery of precious metals was first proposed around 100 years ago for the leaching of gold and silver ores that had been chlorine roasted (Aylmore and Muir, 2001). Silver sulfide ores were treated similarly for many years before World War II (Flett *et al.*, 1983). It was not until the 1970's that interest was again shown in thiosulfate leaching of gold. In the early 1970's, Russian researchers investigated the leaching of gold using various lixiviants, including thiosulfate (Shapiro and Shvedova, 1974, Panchenko and Lodeishchikov, 1971). In the late 1970's, Berezowsky *et al.* (1978) and Kerley (1981, 1983) separately patented atmospheric ammoniacal thiosulfate leaching processes for precious metal recovery from copper bearing metal sulfide concentrates and pressure leach residues.

In the 1980's to early 1990's much of the research work looked at applying thiosulfate leaching to ore samples (Abbruzzese *et al.*, 1995, Tozawa *et al.* 1981, Block-Bolten *et al.*, 1985, Zipperian *et al.*, 1988, Li *et al.*, 1995, Hemmati *et al.*, 1989, Gong *et al.*, 1993, Hu and Gong, 1991, Ji and Yu, 1991, Jiang *et al.*, 1993b, Langhans *et al.*, 1992, Chen *et al.*, 1996, Groudev *et al.*, 1995, Groudev *et al.*, 1996, Wan *et al.*, 1993, Wan *et al.*, 1995, Marchbank *et al.*, 1996, Cao *et al.*, 1992, Zhu *et al.*, , Wan and Brierley, 1997, Murthy, 1991, Murthy and Prasad, 1996, Hiskey and Atluri, 1988, Flett *et al.*, 1983) with only few attempts in recent times at improving the fundamental understanding of the leaching process (Barbosa-Filho *et al.*, 1994, Jiang *et al.*, 1993a, Jiang *et al.*, 1997, Muyunda, 1996, Zhu *et al.*, 1994a). The most important aspect of this work was that acceptable gold leach rates using thiosulfate are only achieved in the presence of ammonia and copper ions.

Newmont mining was the first company to attempt a pilot scale thiosulfate heap leaching process as a means of recovering gold from carbonaceous preg-robbing ores (Wan, 1997). Satisfactory test results supported continuation of process development, although the leach chemistry was found to be very complex and maintaining its stability a key factor.

## 1.4.2 Leaching

The leaching of gold in thiosulfate solutions is an electrochemical reaction, with the constituent half reactions being the oxidation of gold to gold thiosulfate, and the reduction of copper(II) ammine to copper(I) thiosulfate. These half cell reactions are shown in Equations 1.5 and 1.6 respectively.
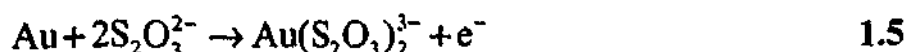
$$Au + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + e^- \qquad \text{1.5}$$

$$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- \rightarrow Cu(S_2O_3)_3^{5-} + 4NH_3 \qquad \text{1.6}$$

The thiosulfate leach system is complicated by the homogeneous reaction between copper(II) and thiosulfate according to the simplified overall reaction shown in Equation 1.7. This results in both thiosulfate loss and a decrease in the oxidant, copper(II), concentration. Limited attention has been given in the literature to the kinetics of this reaction despite its importance to the gold-thiosulfate leach system. A kinetic study and proposed mechanisms for this reaction have been published by Byerley *et al.* (1973a, 1973b and 1975). However, this study was motivated by destroying thiosulfate generated in the ammonia leaching of sulfide minerals, and hence did not focus on aspects of importance to thiosulfate leaching of gold. The major finding of this work though was that thiosulfate oxidation was significantly increased in the presence of oxygen. This has major implications for the thiosulfate leaching process as oxygen is advocated for the oxidation of copper(I) to copper(II) in order to maintain a sufficient oxidant concentration.

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \rightarrow 2Cu(S_2O_3)_3^{5-} + 8NH_3 + S_4O_6^{2-} \qquad \text{1.7}$$
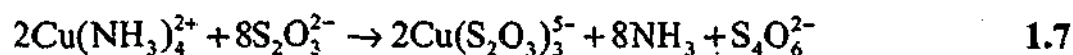
The majority of published literature on gold thiosulfate leaching is also of concern as it fails to take into account the continually changing solution conditions, especially the copper(II) and thiosulfate concentrations. Because of this very few

studies of gold leaching kinetics have been attempted (Barbosa-Filho *et al.*, 1994, Muyunda, 1996, Jeffrey, 2001).

### 1.4.3 Recovery

Very little work in comparison to leaching has been conducted on the recovery of gold from thiosulfate leach solutions. In general, consideration has been given to recovery by cementation for clarified leach solutions (Berezowsky *et al.*, 1978, Guerra and Dreisinger, 1999, Kerley, 1983, Wan *et al.*, 1993, Perez and Galaviz, 1987, Hu and Gong, 1991), whereas carbon and ion exchange resins have been investigated for adsorption from slurries (Gallagher *et al.*, 1989, Gallagher *et al.*, 1990, Thomas *et al.*, 1998, Nicol and O'Malley, 2001, Wan *et al.*, 1993). The adsorption processes have proven to be more difficult than in the case of cyanide with poor adsorption of the gold thiosulfate complex onto carbon and weak base resins. Good adsorption is obtained with the strong base resins, however stripping the gold thiosulfate complex from these resins has shown to be difficult and generally requiring several steps in order to regenerate the resin (Nicol and O'Malley, 2001). Subsequently, there has been little work carried out on the electrowinning of gold from thiosulfate solutions (Gallagher *et al.*, 1989, Abbruzzese *et al.*, 1995, Sullivan and Kohl, 1997).

## 1.5  Areas of Uncertainty in Thiosulfate Leaching

The chemistry of the thiosulfate leach solution appears to be complex and clearly remains poorly understood despite the large number of gold leaching studies that have been conducted. Obviously copper(II) is required in order to achieve acceptable gold leach rates, though copper(II) undesirably reacts with thiosulfate. The presence of oxygen has therefore been advocated to maintain the oxidant, copper(II), concentration by oxidising copper(I). However, the presence of oxygen significantly increases the rate of thiosulfate oxidation. The interaction of all these reactions has yet to be studied fundamentally in terms of the copper(II)/copper(I) redox chemistry and concentrations,

thiosulfate oxidation kinetics, recycling of the leach solution, and the effect these have on the gold leach kinetics. In order to measure the thiosulfate oxidation kinetics an analysis method for measuring the thiosulfate concentration in thiosulfate solutions containing copper ions is required.

Few fundamental studies of the gold leaching process have been attempted due to the continually changing solution chemistry making the interpretation of results difficult. Electrochemical studies (Jiang *et al.*, 1997, Jiang *et al.*, 1993a, Zhu *et al.*, 1994a) have indicated that the role of copper and ammonia in the gold leaching process are more complex than simply being the oxidant and ligand. Various solution conditions have also been identified to result in the passivation of the gold surface (Tozawa *et al.*, 1981, Jiang *et al.*, 1993a, Zhu *et al.*, 1994a, Chen *et al.*, 1996, Muyunda, 1996).

The leaching of gold in thiosulfate solutions is reviewed in detail in Chapter 2 of this thesis. Areas discussed include the chemistry of the gold thiosulfate complex, the thiosulfate solution chemistry, gold leaching kinetics and the electrochemistry of gold in thiosulfate solutions. Chapter 3 presents the results obtained from a kinetic study of copper(II) reduction by thiosulfate and other oxysulfur species in the absence of oxygen. In Chapter 4, the development of an analytical method and apparatus suitable for measuring the thiosulfate concentration of leach solutions is presented. This analysis technique is used to study the kinetics of thiosulfate oxidation in thiosulfate leach solutions in the presence of oxygen. These results are presented and discussed in Chapter 5. In Chapter 6, the results of kinetic and electrochemical studies of the gold dissolution process in thiosulfate solutions are presented and discussed. Chapter 7 then investigates the effect of thiosulfate solution aging on the gold dissolution process. Conclusions and recommendations from this research are given in Chapter 8.

# Chapter 2

# *Literature Review*

## 2.1 Gold Leaching in Thiosulfate Solutions

A review of the published literature to date relating to gold leaching in thiosulfate solutions is presented in this Chapter. Notably from the introduction presented in Chapter 1, acceptable gold leach rates using thiosulfate are only obtained in the presence of copper ions and ammonia, which is subsequently referred to in this thesis as a thiosulfate leach solution. However, the leaching of gold in these solutions is complicated by the simultaneous presence of ammonia and thiosulfate as complexing ligands, the copper(II)-copper(I) redox couple and the oxidative decomposition of thiosulfate.

### 2.1.1 Thiosulfate Ion

The thiosulfate ion, $S_2O_3^{2-}$, has tetrahedral symmetry being a structural analogue of the sulfate ion in that one of the oxygen atoms has been replaced by one sulfur atom. Calculations from binding force measurements indicate the limiting structural forms of the thiosulfate ion are:

$$
\begin{array}{cccc}
S & S & S & S^{\cdot} \\
\| & \| & \| & | \\
{}^{\cdot}O - S = O & {}^{\cdot}O - S - O^{\cdot} & O = S - O^{\cdot} & O = S = O \\
| & \| & | & | \\
O^{\cdot} & O & O^{\cdot} & O^{\cdot} \\
 & (1) & & (2)
\end{array}
$$
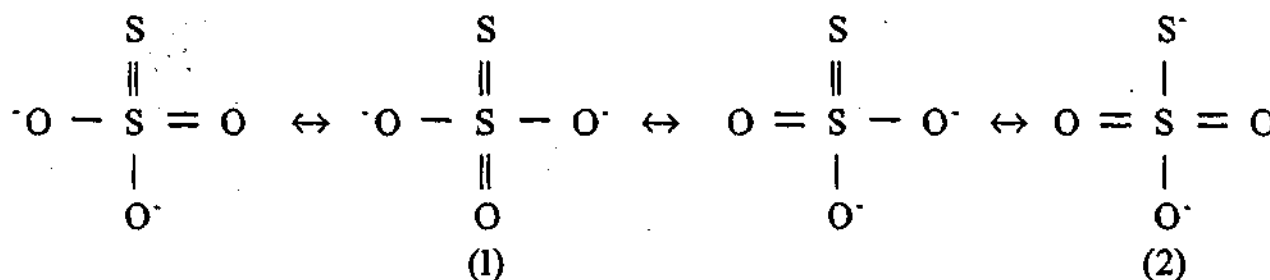
**Figure 2.1:** Limiting structural forms of thiosulfate (Kirk and Othmer, 1981).

Structure (1) explains the formation of sulfur and sulfite in the presence of acid, and (2) the formation of sulfide and sulfate in the presence of heavy metals. This sulfide-like sulfur atom (2) gives the thiosulfate ion its reducing properties and complexing abilities. Bond strengths indicate the S-S bond is more easily broken than the S-O bonds. The reaction of thiosulfate with cyanide illustrates this and is the basis for the use of thiosulfate as an antidote in cyanide poisoning (Kirk and Othmer, 1981).

$$S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^- \qquad \textbf{2.1}$$

Thus, thiosulfate ions are found to be more stable in neutral or slightly alkaline solutions containing excess base or sulfite than in acid solutions.

### 2.1.1.1  Oxidation of Thiosulfate

Electrolytic oxidation of thiosulfate solutions predominately produces tetrathionate according to Equation 2.2, with sulfite as a by-product in acid solutions and trithionate in alkaline solutions. The standard oxidation potential for this reaction is 0.08 V (Weast, 1974-75).

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \qquad \textbf{2.2}$$

The oxidation of thiosulfate in aqueous solutions by molecular oxygen is known to be very slow at room temperature and pressure (Naito *et al.*, 1970, Rolia and Chakrabarti, 1982). However, the oxidation reaction is greatly accelerated in the presence of metal ions such as copper, nickel and cobalt (Naito *et al.*, 1970, Byerley *et al.*, 1975, Byerley *et al.*, 1973b). A more detailed discussion of thiosulfate oxidation in thiosulfate leach solutions is presented in section 2.2.

Mild oxidising agents, such as hydrogen peroxide in acid solutions, oxidise thiosulfate to produce tetrathionate and trithionate while the presence of $Fe^{2+}$ promotes oxidation to sulfate. Stronger oxidizing agents such as permanganate, chromate,

chlorine, bromine, alkaline hydrogen peroxide or hypochlorite oxidise thiosulfate to sulfate. The reaction of thiosulfate with iodine in a neutral or slightly acidic solution, according to Equation 2.3, is the basis of a volumetric analytical procedure (Koh, 1990).

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \qquad\qquad \textbf{2.3}$$
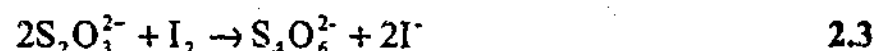
### 2.1.1.2   Reduction of Thiosulfate

Electrolytic reduction of thiosulfate with a mercury or platinum electrode produces equimolar amounts of sulfide and sulfite according to Equation 2.4 (Kirk and Othmer, 1981).

$$S_2O_3^{2-} + 2e^- \rightarrow S^{2-} + SO_3^{2-} \qquad\qquad \textbf{2.4}$$

The presence of metallic copper, zinc or aluminium can also reduce thiosulfate to form the metal sulfide and sulfite (Kirk and Othmer, 1981):

$$S_2O_3^{2-} + 2Cu \rightarrow Cu_2S + SO_3^{2-} \qquad\qquad \textbf{2.5}$$
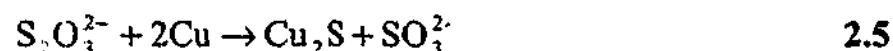
### 2.1.2   Oxidation of Gold in Thiosulfate Leach Solutions

Gold dissolves into solution in the presence of thiosulfate by the formation of a gold thiosulfate complex. The oxidation state of the gold in the gold thiosulfate complex is gold(I). Both the $Au(S_2O_3)^-$ and $Au(S_2O_3)_2^{3-}$ complexes are known with the latter being more stable (Johnson and Davis, 1973). This is evident, as shown in Table 2.1, by the much larger stability constant ($\beta$) for the $Au(S_2O_3)_2^{3-}$ complex; tabulated are a number of values published for the $Au(S_2O_3)_2^{3-}$ complex for which the source data used in calculating $\beta$ has been included where obtainable.

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**Table 2.1:**     Stability constants for gold thiosulfate and ammonia complexes.

| Complex | β | $E^o$ (mV) | $E^o$ (mV) for $Au^+/Au$ | Reference |
|---|---|---|---|---|
| $Au(S_2O_3)^-$ | $2.5 \times 10^{10}$ | NA | NA | Baranova and Ryzhenko (1981) |
| $Au(S_2O_3)_2^{3-}$ | $10^{26}$ | 153 | 1691 | Pouradier and Gadet (1969) |
| | $10^{28}$ | 153 | 1830 | Skibsted and Bjerrum (1977) |
| | $10^{28}$ | | | Sullivan and Kohl (1997) |
| | $5 \times 10^{28}$ | 150 | | Nicol *et al.* (1987) |
| | $10^{26}$ | | | Goleva *et al.* (1970), Hiskey and Atluri (1988) |
| $Au(NH_3)_2^+$ | $2 \times 10^{18}$ | 625 | 1710 | Han (2001) |
| | $10^{26}$ | 563 | 2120 | Skibsted and Bjerrum (1974) |
| | $10^{21}$ | 563 | 1830 | Skibsted and Bjerrum (1977) |
| | $3 \times 10^{19}$ | 563 | 1700 | Skibsted and Bjerrum (1974) |
| | $10^{13}$ | NA | NA | Hancock *et al.* (1974) |

NA – Not Applicable

As the thiosulfate leach solutions contain ammonia there is the possibility that gold may also be oxidised and complexed as the gold(I) ammine. Shown in Table 2.1 is a range of stability constants (β) published for the $Au(NH_3)_2^+$ complex. Many of the stability constants shown in Table 2.1 have been determined by measuring the potential of a gold electrode in solutions containing the gold complex (this is the $E^o$ value shown in Table 2.1). The stability constant was then calculated using Equation 1.3 along with the standard potential of the $Au^+/Au$ couple (also shown in Table 2.1). Although the values for the $Au(NH_3)_2^+$ reduction potential measured by Han (2001) and Skibsted and Bjerrum (1974) are similar, vastly different stability constants were estimated on the basis of using different values for the potential of the $Au^+/Au$ couple. Given that the generally accepted value for the $Au^+/Au$ couple is 1.7 V (Nicol *et al.*, 1987), the β value of $3 \times 10^{19}$ for the $Au(NH_3)_2^+$ complex is considerably lower than $10^{26}$ for the

$Au(S_2O_3)_2^{3-}$ complex. The $\beta$ value of $10^{26}$ for the $Au(NH_3)_2^+$ complex has however often been used in reference to gold leaching in solutions containing thiosulfate and ammonia. This has obviously resulted in a number of incorrect constructions of the Pourbaix diagram for the gold-thiosulfate-ammonia system and proposed gold oxidation mechanism (see section 2.4.2). An even lower $\beta$ value of $10^{13}$ for the $Au(NH_3)_2^+$ complex has been calculated from linear free energy relationships (Table 2.1). Clearly, the stability constant of the $Au(NH_3)_2^+$ complex is lower than that of the $Au(S_2O_3)_2^{3-}$ complex and hence ammonia is not likely to complex with the gold(I) in the presence of thiosulfate. This is supported by the fact that the gold rest potential changes with thiosulfate concentration rather than ammonia concentration (Wan, 1997).

### 2.1.3 Leaching of Gold in Thiosulfate leach Solutions

The leaching of gold in thiosulfate solutions is an electrochemical process in which the gold is oxidised to gold(I). The oxidation of gold in thiosulfate solutions is believed to occur according to Equation 2.6.

$$Au + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + e^- \qquad \textbf{2.6}$$
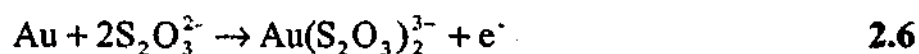
Hence, a strong enough oxidant is required in order that gold dissolves in thiosulfate solutions. Equation 2.7 shows the reduction of dissolved oxygen in alkaline solutions. The standard potential for this reaction in alkaline solutions is 0.4 V (Antelman and Harris, 1982), which is more positive than 0.153 V (Table 2.1), the standard potential for the oxidation of gold in thiosulfate solutions.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad \textbf{2.7}$$

Thus, the oxidation of gold in alkaline thiosulfate solution should occur using dissolved oxygen as the oxidant according to Equation 2.8. However, the rate of dissolution has been found to be very slow (Berezowsky *et al.*, 1978, Tozawa *et al.*,

1981), probably due to the high overpotential that is required to reduce oxygen on a gold surface (Bard, 1973).

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 4Au(S_2O_3)_2^{3-} + 4OH^- \qquad \textbf{2.8}$$
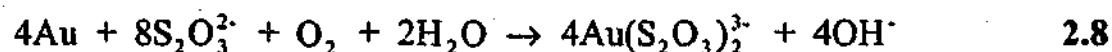
It has also been suggested that in the absence of ammonia, gold dissolution by thiosulfate is passivated by the build up of sulfur layers as a result of thiosulfate decomposition on the gold surface (Chen *et al.*, 1996, Jiang *et al.*, 1993a). The presence of ammonia is thought to prevent gold passivation by being preferentially adsorbed on the gold surface over thiosulfate, thus dissolving the gold as an ammine complex. However, gold dissolving as an ammine complex was discussed above in section 2.1.2 to be unlikely. This proposed mechanism for gold leaching in thiosulfate solutions is discussed further in section 2.4.2.

The catalytic action of copper ions was first reported in 1960 (Tyurin and Kakowski, 1960) and has been found to increase the gold dissolution rate by around 20 times (Ter-Arakelyan *et al.*, 1984). In solutions containing copper(II), ammonia and thiosulfate there is the possibility of an additional cathodic reaction: the reduction of copper(II) to copper(I), as shown in Equation 2.9. The standard potential for this reaction can be calculated using the following data, where $\beta$ is the stability constant of the respective copper complex: $E^0 (Cu^{2+}/Cu^+) = 0.15$ V (Antelman and Harris, 1982), $\log \beta(Cu(NH_3)_4^{2+}) = 12.52$ and $\log \beta(Cu(S_2O_3)_3^{5-}) = 13.77$ (Högfeldt, 1982). The $E^0$ for reaction 2.9 is calculated to be 0.22 V, and thus we can expect copper(II) tetra-ammine to oxidise gold to $Au(S_2O_3)_2^{3-}$, although the driving force for this reaction is quite low.

$$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- \rightarrow Cu(S_2O_3)_3^{5-} + 4NH_3 \qquad \textbf{2.9}$$

Gold has been found by researchers to leach for a large range of thiosulfate solution conditions, which indicates that ore-specific conditions may be required to optimise recovery. Table 2.2 shows a summary of the various thiosulfate leach conditions published within the literature. Clearly, wide ranges of conditions have been

used. The thiosulfate concentrations vary from 0.1 to 2 M, the ammonia concentrations vary from 0.1 to 6 M, while the copper concentrations vary from 0.1 to 300 mM. The more recent publications focus on lower reagent concentrations in order to minimise the rate of thiosulfate oxidation. Most researchers recognise that copper is required as the copper(II) tetra-ammine for the effective oxidation of gold in thiosulfate solutions. However, no universal agreement has been reached as to the controlling mechanism.

The alkalinity of the thiosulfate leach solutions in these studies is reflected in the pH values shown in Table 2.2. In the cases of ore leaching, the leach solution pH can change as a result of the ore being acid consuming or generating. In the thiosulfate leach system the pH is buffered by ammonia and ammonium ions according to the equilibrium shown in Equation 2.10; the pKa for ammonia is 9.25 (Weast, 1974-75). Thus, at pH values below 9.25, more ammonium ions exist than ammonia and vice versa above this pH. This has significant implications to the copper(II) ion stability as it is ammonia that forms stable complexes and not ammonium ions. With the use of ammonium thiosulfate by some researchers, the resultant solution pH (for the same ammonia concentration) is lower due to the equilibrium of Equation 2.10.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \qquad 2.10$$
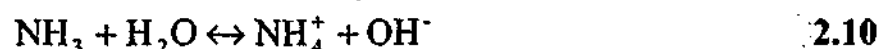
No consensus also appeared as to the preferred oxygen level or the requirement for air sparging. Oxygen though is generally recognised as being required to oxidise copper(I) to copper(II), thus maintaining some of the copper in the cupric state. An increase in temperature was generally noted to increase the gold dissolution rate but decreased recovery after a period of time due to passivation attributed to copper sulfide formation. Ammonia retention is also more difficult at elevated temperatures, and hence problems with solution stability appear to be associated with an increase in temperature. Several researchers have also advocated the addition of sulfite (Table 2.2) in an attempt to inhibit the decomposition of thiosulfate (see section 2.2). Recoveries are generally >80% from ores and comparable with recoveries using cyanide. The leach times though are relatively short, however some recent research has looked at heap leaching conditions for which the leach times are many days.

**Table 2.2:** List of the various thiosulfate leach conditions published within the literature.

| Author | Ore Type | $S_2O_3^{2-}$ (M) | $NH_3$ (M) | Cu (mM) | PH | $SO_3^{2-}$ (M) | $O_2$ Source* | Time (hr) | Temp. (°C) | % Au Recovery |
|---|---|---|---|---|---|---|---|---|---|---|
| Berezowsky et al. (1978) | CuS | 0.5-1[#] | >0.5 | 30-60 | 9-10 | | Air | | 25-50 | >90 |
| Tozawa et al. (1981) | Au plates | 0.5 | 1 | 40 | | | Oxygen | 3 | 65 | |
| Kerley (1983) | Cu-MnS | 12-25%[#] | Added | 15-60 | 7-9 | 0.1-2%[#] | | | 40-60 | >90 |
| Block-Bolten et al. (1985) | Zn-PbS | 0.1-0.5[#] | 0.75 | | | | 2 l/min | 1 | 21-50 | 90 |
| Perez and Galaviz (1987) | Mn-CuS | 5-15%[#] | Added | 15-60 | 10-11 | 0.1-2%[#] | | 1.5-2.5 | 25-40 | 95 |
| Zipperian et al. (1988) | Rhyolite, Mn | >0.1 | 0.4-4 | 200 | 10 | | Air | 1-2 | 50 | 90 |
| Hemmati et al. (1989) | Carbonaceous | 0.7 | 3 | 150 | i0.5 | 0.1-0.2 | Oxygen | 1-4 | 35 | 70 |
| Ji and Yu (1991) | Oxidised Cu | 0.1-2 | 0.8-5.2 | 8-300 | | 1% | Air | 2 | 30-65 | 94 |
| Hu and Gong (1991) | S | 1 | 2 | 16 | | | 1 l/min | 1-2 | 40 | 96 |
| Murthy (1991) | Pb-ZnS | 0.1-0.5[#] | 1 | | 6.9-8.5 | | Air | 3 | 21-70 | 95 |
| Cao et al. (1992) | S Concentrate | 0.2-0.3[#] | 2-4 | 47 | 10-10.5 | | 1 l/min | 1-2 | 60 | >95 |
| Langhans et al. (1992) | Oxidised Cu | 0.2 | 0.09 | 1 | 11 | | Air | 48 | Ambient | >83 |
| Jiang et al. (1993b) | Au | 1 | 0.5 | 10 | 10 | | | 2 | 50 | >90 |
| Gong et al. (1993) | S Concentrate | 0.7[#] | 1 | 60 | | | 0.7 l/min | 1.5-2 | 50 | 89-96 |
| Barbosa-Filho et al. (1994) | Au disc | 0.05-0.4 | 0.25-1 | 10-100 | | | | | 20-60 | |
| Wan et al. (1994) | Carbonac./S | 0.1-0.2[#] | >0.1 | 0.5 | 9-10 | | Air | 12-25[##] | Ambient | >70 |

# Ammonium salt used; * Flowrates where given are for air sparging; ## Days

Table 2.2 cont:     List of the various thiosulfate leach conditions published within the literature.

| Author | Ore Type | $S_2O_3^{2-}$ (M) | $NH_3$ (M) | Cu (mM) | PH | $SO_3^{2-}$ (mM) | $O_2$ Source* | Time (hr) | Temp. (°C) | % Au Recovery |
|---|---|---|---|---|---|---|---|---|---|---|
| Abbruzzese et al. (1995) | Au oxide | 2 | 4 | 100 | 8.5-10.5 | | Air | 3 | 25 | 80 |
| Groudev et al. (1995) | Oxide | 0.1# | Added | 8 | 8.5-9 | 6-12.5# | | 32## | Ambient | 36 |
| Song et al. (1995) | Ag-Au Conc. | 0.6-0.9# | | 100-180 | | 0.2-0.3# | | 7 | 40-50 | 92-95 |
| Groudev et al. (1996) | Fe-Cu-Pb-ZnS | 0.14# | Added | 8 | 9-10 | 6# | Air | | Ambient | 84 |
| Marchbank et al. (1996) | Carbonac. S | 0.02-0.1# | 0.12 | 1-2 | 7-8.7 | 10-50# | Air | 30-120 | 25-80 | >80 |
| Yen et al. (1996) | Au-Cu | 0.4 | 0.2 | 30 | 11 | | Air | 24 | Ambient | |
| Muyunda (1996) | Au disc | 0.4 | 0.84 | 25 | >10.5 | | Air | | 35 | |
| Wan (1997) | Carbonac. S | 0.1# | 0.1 | 0.5 | 9 | | Air | 91-116## | Ambient | 50-65 |
| Yen et al. (1998) | Au-Cu | 0.5# | 6 | 100 | 10 | | Air | 24 | Ambient | >95 |
| Thomas et al. (1998) | Oxidised S | 0.03-0.05# | 0.01-0.06 | 0.1-2 | 7-9 | 10-50# | Air | 45-55 | 80-85 | |
| Fleming (2000) | Carbonac. S | 0.05 | 0.1 | 0.5 | 7.5-8 | | | 8 | 40-60 | 80-92 |
| Balaz et al. (2000) | Sulfide Conc. | 0.5# | 0 | 62 | 6-7 | | | 2 | 70 | 54 |
| Aylmore (2001) | Au-CuS Conc. | 0.1-0.8 | 1.5-4 | 12-62 | 10.2 | | | 96 | Ambient | |
| Schmitz et al. (2001) | Carbonac. S | 0.4 | 1.9 | 16 | | 42 | | 7 | Ambient | 90-100 |
| van Z. de Jong et al. (2001) | Various | 0.25-0.5# | 1-2 | 6-12 | | | Air | 24 | 25 | 50-93 |

# Ammonium salt used; * Flowrates where given are for air sparging; ## Days

A number of gold leaching studies have also been conducted where the thiosulfate has been generated from polysulfides (Chen *et al.*, 1996), by the disproportionation of elemental sulfur with hydroxide ions (Zhu *et al.*, 1994b) or from hydrated lime solution with sulfur (Zhang *et al.*, 1992b, Zhang *et al.*, 1992a). Other methods for generating thiosulfate in-situ have been recently reviewed (Aylmore and Muir, 2001) and are not considered further due to the added complication to the solution chemistry.

### 2.1.4 Copper Speciation

Copper(II) is unstable in solutions containing thiosulfate, as a rapid reduction of copper(II) to copper(I) by thiosulfate occurs (Rabai and Epstein, 1992). However, when ammonia is also present in the solution, stable copper(II) ammine complexes form. Using the equilibrium constants for the various copper(II) ammine complexes (Högfeldt, 1982) and assuming the activity coefficients are all 1, the distribution diagram shown in Figure 2.2 was generated.
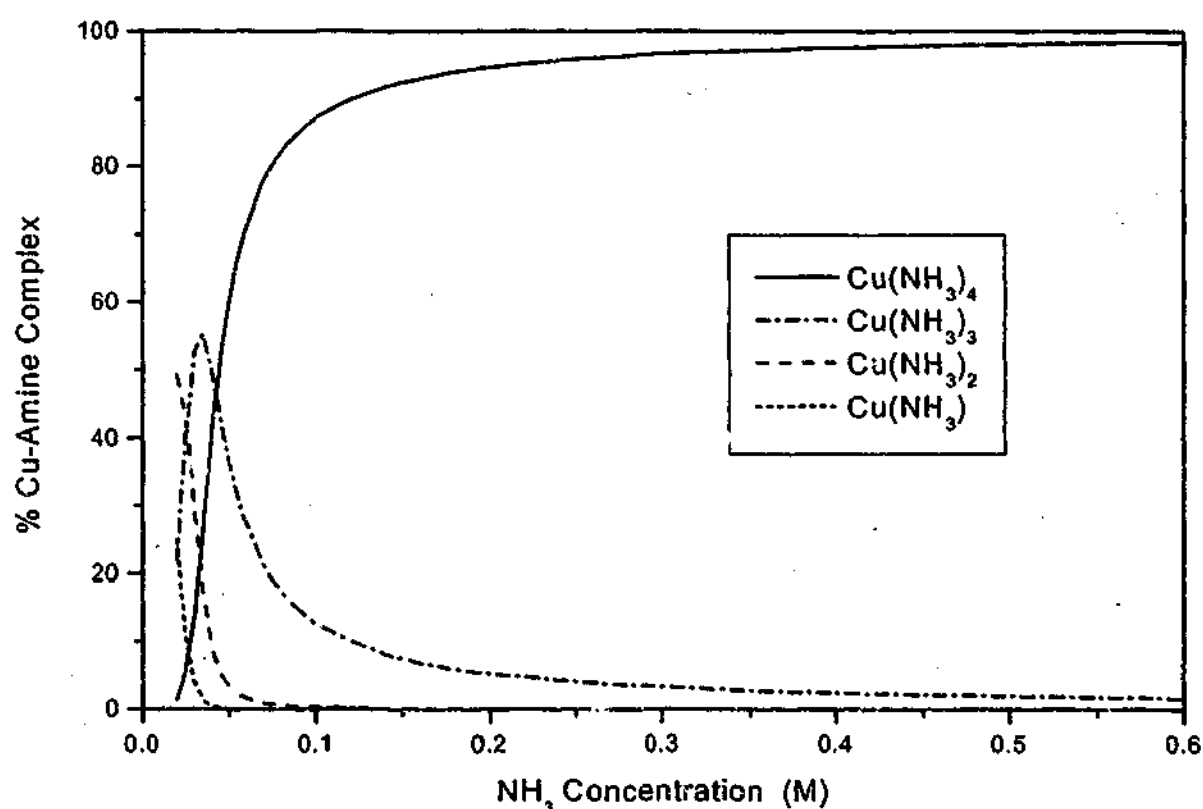


**Figure 2.2:**   Distribution of copper(II) ammine complexes as a function of ammonia concentration; 10 mM copper(II).

Thus, in thiosulfate leach solutions where the ammonia concentration is greater than 0.3 M, the dominant species formed is the copper(II) tetra-ammine complex. The coordination of the copper(II) tetra-ammine complex is square planar with the axial sites hydrated by water (Bjerrum *et al.*, 1954, Hathaway and Tomlinson, 1970). Only at ammonia concentrations greater than 3 M does the penta-ammine complex exist (Hathaway and Tomlinson, 1970); the fifth ammonia bonding at an axial site. Various anions, such as perchlorate (Hathaway and Tomlinson, 1970), thiosulfate (Byerley *et al.*, 1973a) and hydroxide ions (Reeves and Bragg, 1962), have been shown to coordinate with the copper(II) tetra-ammine by displacement of aqua ions at the axial sites.

Both ammonia and thiosulfate can potentially act as ligands for copper(I), although the published stability constants for the copper(I) ammine complexes are lower than for the copper(I) thiosulfate complexes (Smith and Martell, 1976). Using the stability constants for the copper(I) thiosulfate complexes, $\text{Log } K_1 = 10.35$, $\text{Log } K_2 = 12.27$, and $\text{Log } K_3 = 13.71$, it can estimated that for a 0.1 M thiosulfate solution containing 10 mM copper(I), 35% of the copper(I) exists as the di-thiosulfate complex, and 65% as the tri-thiosulfate complex. However, the speciation of copper(I) in solutions containing ammonia and thiosulfate is uncertain as there is no thermodynamic data available for the mixed ammonia-thiosulfate complexes of copper(I).

## 2.2   Thiosulfate Leach Solution Chemistry

Since alkaline leach solutions are used to prevent the acid decomposition of thiosulfate (Kirk and Othmer, 1981), ammonia is added to stabilise the copper as a copper(II) ammine complex; this avoids the precipitation of copper hydroxide. However, the thiosulfate leach system is complicated by the homogeneous reaction between copper(II) and thiosulfate according to the simplified reaction (copper ligands ignored) shown in Equation 2.11 (Byerley *et al.*, 1973a).

$$2Cu^{2+} + 2S_2O_3^{2-} \rightarrow 2Cu^+ + S_4O_6^{2-} \qquad \textbf{2.11}$$

In the presence of oxygen, the regeneration of copper(II) from copper(I) is known to readily occur according to the simplified reaction (copper ligands ignored) shown in Equation 2.12.
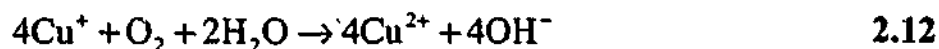
$$4Cu^+ + O_2 + 2H_2O \rightarrow 4Cu^{2+} + 4OH^-$$
**2.12**

Thus, one would anticipate that the net result of such reactions would be the continual consumption of thiosulfate, at a rate limited by either Equation 2.11 or 2.12. In addition, the copper(II) concentration will be dependant on the relative reaction rates of Equations 2.11 and 2.12; if the oxidation of copper(I) by oxygen were the fast step, then the copper would predominantly exist as copper(II). Limited attention has been given in the literature to the kinetics of reactions 2.11 and 2.12 despite their importance to the gold-thiosulfate leaching system. The only published kinetic study carried out on the oxidation of thiosulfate by copper(II) and oxygen in ammoniacal solutions was in the 1970's by Byerley *et al.* (1973a, 1973b, 1975). However, this work was motivated towards the destruction of thiosulfate generated during the ammonia leaching of sulfide minerals, and hence did not focus on aspects of importance to gold leaching.

## 2.2.1 Oxidation of Thiosulfate and Oxysulfur Anions

The oxidation of thiosulfate can occur according to Equation 2.2; the potential for this reaction is 0.08 V (Weast, 1974-75). Thus, thiosulfate ions should be oxidised by dissolved oxygen. However, Rolia and Chakrabarti (1982) found that this is a very slow process for thiosulfate solutions at pH 7 under normal pressures and temperatures with less than 10% change observed after aeration for 4 months. Hence, thiosulfate solutions prepared using double distilled water are very stable in air-tight bottles (Dhawale, 1993). At higher temperatures the final product of the oxidation of thiosulfate by dissolved oxygen in alkaline solutions was found by Rolia and Chakrabarti (1982) to be sulfate with tetrathionate undetectable. The stoichiometry for this reaction is that of Equation 2.13.

$$S_2O_3^{2-} + 2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + H_2O \qquad \qquad \textbf{2.13}$$
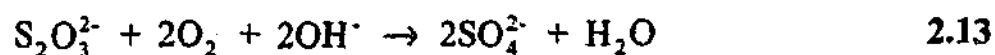
The oxidation of thiosulfate is catalysed by oxidants such as $I_2$, Fe(III) and Cu(II) (Naito *et al.*, 1970, Rabai and Epstein, 1992, Byerley *et al.*, 1973a). Rabai and Epstein (1992) showed that the kinetics of thiosulfate oxidation is extremely rapid in the presence of the copper(II) redox sensitive transition metal ion. The results of their kinetic experiments imply that only the coordinated and not the free thiosulfate is directly involved in the redox reaction.

In the presence of ammonia and absence of oxygen, Byerley *et al.* (1973a) determined the kinetics and mechanism of thiosulfate oxidation by copper(II) as shown in Equation 2.14, which is discussed in more detail in the following section. With nearly all the copper(II) complexed as the tetra-ammine, the reaction is much slower than for the aqua copper(II) ion.

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \rightarrow 2Cu(S_2O_3)_3^{5-} + 8NH_3 + S_4O_6^{2-} \qquad \qquad \textbf{2.14}$$
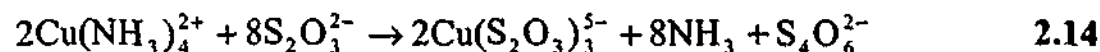
Byerley *et al.* (1973a) found from analysis of solutions sometime after completion of the reaction that trithionate was formed along with a build up of thiosulfate. The tetrathionate formed from reaction 2.14 is suggested to undergo a subsequent disproportionation with the overall reaction being that shown in Equation 2.15. The kinetics and mechanism of this reaction have been studied (Fava and Bresadola, 1955, Rolia and Chakrabarti, 1982, Naito *et al.*, 1970) with the kinetics shown to be slower than that of Equation 2.14 for the conditions investigated by Byerley *et al.* (1973a).

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad \qquad \textbf{2.15}$$
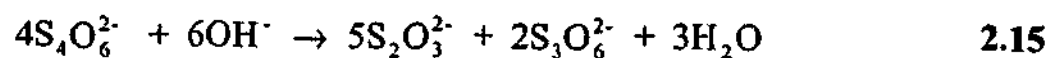
However, recent work by Zhang and Dreisinger (2002) showed that the alkaline decomposition of tetrathionate was an order of magnitude higher in the absence of oxygen, and that trithionate was either not the major reaction product or was rapidly decomposed.

Rolia and Chakrabarti (1982) also investigated the decomposition of trithionate. This was noted to be slow at room temperature with the results of experiments conducted at 80 °C indicating the stoichiometry shown in Equation 2.16. Air was not excluded from the solution, thus oxidation of thiosulfate occurred when the reaction was allowed to continue overnight.

$$S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + H_2O \qquad \textbf{2.16}$$
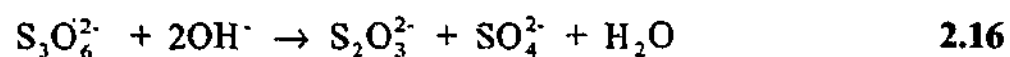
Further work published by Byerley *et al.* (1973b, 1975) found that the oxidation of thiosulfate in ammoniacal solutions in the presence of copper(II) and oxygen was significantly faster than that predicted by the rate of Equation 2.14. This indicates that thiosulfate oxidation in the presence of copper(II) and oxygen does not only occur according to the redox cycle of Equations 2.14 and 2.12. The final oxidation products were also found to be trithionate and sulfate rather than tetrathionate. From the kinetic studies different mechanisms were proposed for the generation of trithionate and sulfate. These are discussed in more detail in the following section. Despite the fact that tetrathionate and polythionates are only meta-stable, the effect any of these species or other intermediate species has on the solution chemistry and gold leaching has yet to be studied in detail. Polythionates are known to be important in the overall process, as the resin adsorption of gold thiosulfate is significantly affected by the concentration of both tetrathionate and trithionate (Nicol and O'Malley, 2001).

Subsequent to the work conducted by Byerley *et al.* (1973b, 1975), Skorobogaty and Smith (1984) have reviewed a number of published studies on the copper catalysed oxidation of thiosalts by molecular oxygen where the copper is complexed by various organic ligands. The thiosulfate oxidation products were also found to be trithionate and sulfate.

The addition of sulfite to the thiosulfate leach solution has also been advocated by a number of researchers to reduce thiosulfate oxidation (Table 2.2). Kerley (1983) claimed the addition of sulfite decreased the rate of thiosulfate oxidation and the possible loss of values due to precipitation of metal sulfides by the application of Le Chatelier's Principle to Equation 2.17. Thus, in the absence of sulfite the equilibrium would lie to the left producing sulfide that could initiate precipitation of metal sulfides, including gold sulfide. Thermodynamic data though suggests that this is unlikely to occur for the conditions used for gold leaching in thiosulfate leach solutions.

$$4SO_3^{2-} + 2S^{2-} + 3H_2O \leftrightarrow 3S_2O_3^{2-} + 6OH^- \qquad \textbf{2.17}$$
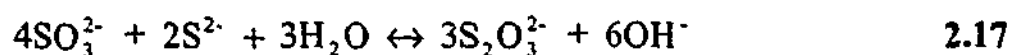
Hemmeti *et al.* (1989) reported that the addition of sulfite to thiosulfate leach solutions reduces the overall rate of thiosulfate oxidation by reducing tetrathionate back to thiosulfate according to Equations 2.18 and 216. Equation 2.18 is known to occur rapidly and quantitatively (Palmer, 1959).

$$SO_3^{2-} + S_4O_6^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-} \qquad \textbf{2.18}$$
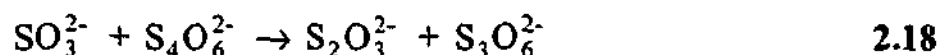
However, Wan (1997) found that the addition of sulfite in a heap leach system had no detectable benefit. Suggested also was that excess sulfite could significantly change the redox potential of the system resulting in a detrimental effect on gold extraction. In addition, dissolved oxygen and copper(II) ions in solution will decompose sulfite to sulfate (Aylmore and Muir, 2001). Hu and Gong (1991) claim that the addition of sulfite is not a practical solution as it also can be oxidised to sulfate. Thus, the loss of thiosulfate is simply being replaced by the loss of sulfite. They alternatively proposed the addition of sulfate, which was found to reduce thiosulfate oxidation. A mechanism according to Le Chatelier's Principle for the reaction shown in Equation 2.19 was proposed. As sulfate is the most stable oxysulfur species and hence Equation 2.19 is thermodynamically irreversible, this mechanism does not explain why sulfate reduces thiosulfate oxidation.

$$S_2O_3^{2-} + 2OH^- \leftrightarrow S^{2-} + SO_4^{2-} + H_2O \qquad \textbf{2.19}$$
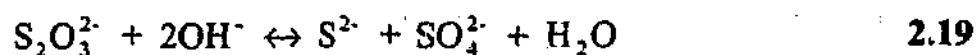
It should be noted that thiosulfate and all the other oxysulfur anions are only meta stable, with the final oxidation product being sulfate.

## 2.2.2 Kinetics and Mechanisms of Thiosulfate Oxidation

As stated above, the kinetics and mechanisms for thiosulfate oxidation in thiosulfate leach solutions applicable to gold leaching has received little attention within the published literature. A kinetic study of the reaction between copper(II) and thiosulfate (Equation 2.14) in ammoniacal solutions and in the absence of oxygen has been published by Byerley *et al.* (1973a). By continuously monitoring the copper(II) concentration they found that the reaction rate had a first order dependence on copper(II) and thiosulfate concentrations, and an inverse first order dependence on ammonia concentration. The kinetic results suggested a mechanism, shown in Equation 2.20, which involved the rate determining step of thiosulfate substitution into the copper(II) coordination sphere before electron transfer. The final reaction step is suggested to involve the generation of the singly charge anion $S_2O_3^-$, which rapidly dimerises to yield tetrathionate.

$$Cu(NH_3)_4^{2+} + H_2O \xleftrightarrow{\quad K \quad} Cu(NH_3)_3(H_2O)^{2+} + NH_3$$
$$Cu(NH_3)_3(H_2O)^{2+} + S_2O_3^{2-} \rightarrow Cu(NH_3)_3(S_2O_3) + H_2O \qquad \textbf{2.20}$$
$$Cu(NH_3)_3(S_2O_3) \rightarrow Cu(NH_3)_3^+ + 1/2S_4O_6^{2-}$$
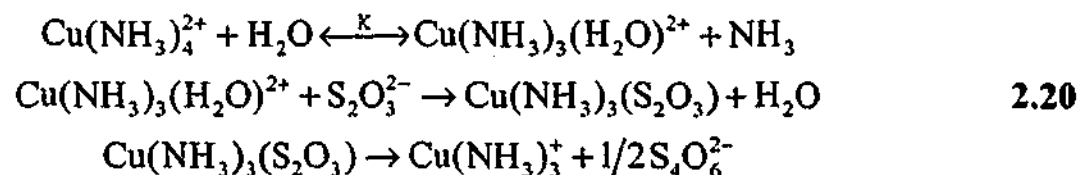
Thus, one would anticipate that in the presence of oxygen the regeneration of copper(II) from copper(I) (Equation 2.12) would result in the continual consumption of thiosulfate, at a rate limited by either Equation 2.14 or 2.12. Byerley *et al.* (1975) stated that "If a simple redox cycle, as suggested in Equations 2.14 and 2.12 is involved, a kinetic analysis, on the basis of oxygen-consumption rate measurements, should be

consistent with the kinetics obtained by following the rate of decrease of copper(II) concentration in the absence of oxygen." However, these authors (Byerley *et al.*, 1973b, Byerley *et al.*, 1975) showed that the thiosulfate oxidation rate in the presence of oxygen was more than an order of magnitude faster than that estimated from the rate of reaction between copper(II) and thiosulfate in the absence of oxygen. The other key results from their study were:

a) the final reaction products were identified as trithionate and sulfate and not tetrathionate;

b) no decrease in the copper(II) concentration was observed for solutions maintained saturated with oxygen; and

c) the oxygen consumption was found to be independent of the initial copper oxidation state, as the copper(I) was rapidly oxidised to copper(II).

Thus, the concluding statement by Byerley *et al.* (1975) was that the "Stoichiometric and kinetic results indicated, however, that such a simple sequence was definitely not the major path for thiosulfate oxidation in the presence of oxygen." The mechanisms thus proposed by Byerley *et al.* (1975) assumed that the copper(II) complexed both the oxidant (oxygen) and reductant (thiosulfate), providing a mechanism for electron transfer whereby the copper(II) itself was not reduced. The reaction sequence shown in Equations A, B and C of Scheme 1 illustrate this. The electron transfer takes place as shown in Equation C of Scheme 1 resulting in a $Cu(II) - O_2^-$ complex and releasing $S_2O_3^-$. Byerley *et al.* (1975) proposed that the $Cu(II) - O_2^-$ complex undergoes a rapid reaction with thiosulfate to provide additional $S_2O_3^-$ and a $Cu(II) - O_2^{2-}$ complex. The coordinated $O_2^{2-}$ was suggested to undergo rapid hydrolysis to form peroxide, $HO_2^-$, which is then likely to oxidise further thiosulfate. The $S_2O_3^-$ formed is assumed to rapidly dimerise to form tetrathionate. These reactions are summarised in Equations D and E of Scheme 1. The tetrathionate is assumed to undergo the thiosulfate catalysed decomposition, previously shown in Equation 2.15, to form trithionate. However, this is questionable as the earlier work by Byerley *et al.*

(1973a) indicated that this reaction was relatively slow in comparison to the trithionate formation rate observed in the presence of oxygen.

$$\left[\begin{array}{c} L \\ NH_3 \cdots Cu^{II} \cdots NH_3 \\ NH_3 \quad NH_3 \\ L \end{array}\right]^{2+} + S_2O_3^{2-} \rightarrow \left[\begin{array}{c} S_2O_3^{2-} \\ NH_3 \cdots Cu^{II} \cdots NH_3 \\ NH_3 \quad NH_3 \\ L \end{array}\right] + L \qquad \text{(A)}$$

$$\left[\begin{array}{c} S_2O_3^{2-} \\ NH_3 \cdots Cu^{II} \cdots NH_3 \\ NH_3 \quad NH_3 \\ L \end{array}\right] + O_2 \rightarrow \left[\begin{array}{c} S_2O_3^{2-} \\ NH_3 \cdots Cu^{II} \cdots NH_3 \\ NH_3 \quad NH_3 \\ O_2 \end{array}\right] + L \qquad \text{(B)}$$

$$\left[\begin{array}{c} S_2O_3^{2-} \\ NH_3 \cdots Cu^{II} \cdots NH_3 \\ NH_3 \quad NH_3 \\ O_2 \end{array}\right]^{\cdot} \rightarrow \left[\begin{array}{c} S_2O_3^{-} \\ NH_3 \cdots Cu^{II} \cdots NH_3 \\ NH_3 \quad NH_3 \\ O_2^{-} \end{array}\right] + L \rightarrow \left[\begin{array}{c} L \\ NH_3 \cdots Cu^{II} \cdots NH_3 \\ NH_3 \quad NH_3 \\ O_2^{-} \end{array}\right] + S_2O_3^{-} \qquad \text{(C)}$$

$$\left[\begin{array}{c} L \\ NH_3 \cdots Cu^{II} \cdots NH_3 \\ NH_3 \quad NH_3 \\ O_2^{-} \end{array}\right] + 3S_2O_3^{2-} + 2H_2O \rightarrow \left[\begin{array}{c} L \\ NH_3 \cdots Cu^{II} \cdots NH_3 \\ NH_3 \quad NH_3 \\ L \end{array}\right] + 3S_2O_3^{-} + 4OH^{-} \qquad \text{(D)}$$

$$2S_2O_3^{-} \xrightarrow{\text{FAST}} S_4O_6^{2-} \qquad \text{(E)}$$

**Scheme 1:** Thiosulfate oxidation mechanisms proposed by Byerley *et al.* (1975).

A second mechanism was proposed by Byerley *et al.* (1975) to explain the varying quantities of trithionate and sulfate generated for different reaction conditions. This mechanism is similar to the first except that the thiosulfate is coordinated to the copper(II)-$O_2$ at a planar site rather than an axial site. After electron transfer the $O_2^-$ is suggested to transfer to the coordinated $S_2O_3^-$ to form disulfite ($S_2O_5^{2-}$). Conceivably the formation of disulfite could also be generated from the reaction products of Equation C in Scheme 1. Quantitative oxidation of disulfite to sulfate in the presence of copper(II) and oxygen was indicated to be extremely rapid. Martell (1983) suggests a fast reaction catalysed by copper(II) occurs between disulfite and thiosulfate, which generates dithionite that is rapidly oxidised by oxygen to sulfate.

Subsequent to the work conducted by Byerley *et al.* (1973b, 1975) in the 1970's, studies into complexes formed between copper and oxygen has raised significant doubts over the existence or formation of copper(II) - oxygen complexes (Simandi, 1992). Also, catalytic oxidation processes involving copper and oxygen usually involve the autoxidation of copper(I) complexes (Simandi, 1992, Zuberbühler, 1981, Zuberbühler, 1983). Therefore, the above mechanism proposed by Byerley *et al.* (1975) for the oxidation of thiosulfate in the presence of copper(II) and oxygen would appear to be questionable.

### 2.2.3 Copper(II) Measurement

Copper(II) is an important component of the thiosulfate leach system, hence a method is required to monitor the copper(II) concentration. Analysis methods that measure total copper concentration, such as atomic adsorption spectroscopy, are useful where copper is being leached into solution from an ore. However, as both copper(II) and copper(I) exist in solution, an analysis method is required that differentiates the two oxidation states. The copper(II) ammine complexes absorb visible light, such that an ammonia solution containing copper(II) is observed to be deep blue in colour, where as solutions containing copper(I) complexes tend to be clear. The absorbance of the copper(II) ammine complexes at a wavelength of 612 nm has been used previously by Byerley *et al.* (1973a) to measure the copper(II) concentration in determining the kinetics of thiosulfate oxidation by the copper(II) ammine complexes.

The absorption spectra of the copper(II) ammine complexes has been studied in detail (Bjerrum *et al.*, 1954). The absorption and absorption wavelength of the copper(II) complexes are shown to be influenced by the coordinating ligands. Hence, changes in ammonia concentration would result in a change in the copper(II) ammine speciation and hence absorption spectra. Thiosulfate coordinated at the axial sites of the copper(II) ammine complexes has also been shown to influence the absorbance spectra such that a significant increase in absorption is observed (Byerley *et al.*, 1973a). Thus, in utilising the linear correlation of absorbance of the copper(II) ammine complexes as a means of determining the copper(II) concentration, solution conditions must remain relatively unchanged.

### 2.2.4 Thiosulfate Measurement

The standard titrimetric based approach for the determination of thiosulfate uses the oxidation of thiosulfate to tetrathionate by iodine. This is a simple method for determining thiosulfate concentration since the reaction proceeds to completion under acidic conditions and the end point can be determined visually using a starch solution (Koh, 1990). However, the likely presence of other species such as sulfite, tetrathionate and other polythionates means that one determination requires several titrations (Koh, 1990). Also, the presence of copper(II) can make the end point difficult to detect visually. Furthermore, the titration is complicated by the presence of copper(I), which is generated in the leach solutions, because it too reduces iodine. This all makes the thiosulfate determination for these leach solutions very complicated.

Ion chromatography is another alternative that enables the determination of sulfite, sulfate, thiosulfate and polythionates simultaneously. This technique can potentially provide a comprehensive solution speciation, however this method suffers from the limitation that it is relatively slow (Koh, 1990) and requires significant dilution that may result in a different solution speciation. The development time of an analysis method can also be very long; other research groups having noted difficulties in achieving this for thiosulfate leach solutions. Due to the solution chemistry continually changing, solution analysis needs to be conducted immediately. This would require a dedicated instrument and access to the current instrument was restricted. Furthermore,

the analytical equipment required is not robust enough for use in an industrial environment and expensive if only interested in measuring thiosulfate concentration.

A flow injection analysis method, which uses a standard electrochemical cell with silver working electrode and platinum counter electrode to measure thiosulfate concentration, has been developed elsewhere (Hemmati *et al.*, 1989). The method is based on measuring the current due to silver oxidation as shown in Equation 2.21, while controlling the electrode potential at 0.1 V versus the standard calomel electrode (SCE) (0.34 V versus the standard hydrogen electrode (SHE)). This potential is 0.35 V more positive than the standard potential of -0.01 V for the oxidation of silver to silver thiosulfate (Högfeldt, 1982).

$$Ag + 2S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} + e^- \qquad\qquad \textbf{2.21}$$
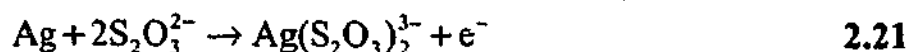
However, this technique does not consider nor corrects for the contribution to the measured current by the reduction or oxidation of other species present in gold thiosulfate leaching solutions. At a potential of 0.34 V the oxidation of copper(I) at the silver electrode will contribute to the measured current. This could be quite significant if the gold ore contains copper, as leaching of such ores usually results in a high copper concentration in the leach solution. Clearly, there is the need for a technique that is capable of easily and rapidly measuring the thiosulfate concentration in solutions used for gold leaching.

## 2.3   Kinetics of Gold Leaching in Thiosulfate Leach Solutions

A large amount of published data (Table 2.2) has looked at the leaching of gold in thiosulfate solutions containing ammonia/ammonium and copper. However, the majority of these studies measured gold recovery from ore samples, thus providing little knowledge as to the kinetics of gold leaching. The majority of published literature on gold leaching in thiosulfate leach solutions is also of concern as it fails to take into

account the changing solution conditions (as discussed in section 2.2), with most studies having been conducted with freshly prepared solutions. Because of the continually changing solution chemistry, very few fundamental studies of the kinetics of gold leaching in thiosulfate leach solutions have been attempted (Barbosa-Filho *et al.*, 1994, Muyunda, 1996, Jeffrey, 2001). These studies have focussed on the effect of various parameters on the initial gold leach kinetics in freshly prepared solutions, with little consideration given to the effect of solution aging on the kinetics of gold leaching.

## 2.3.1 Methods of Studying Kinetics

As the majority of leaching reactions are mass transport controlled (Marsden and House, 1992), the method that is used to stir the system is extremely important. Thus, reproducible mass transfer is required in order to measure the effect of varying experimental conditions on the leach kinetics. The rotating disc is the best method for measuring leach kinetics due to the laminar flow of the fluid to the disc surface giving very reproducible mass transfer. The added advantage of the rotating disc is that the flux of reactants to the disc surface can be calculated from the theoretical expression shown in Equation 2.22. This is known as the Levich equation, where $J_x$ is the flux of species X (mol m$^{-2}$ s$^{-1}$), D is the diffusion coefficient of species X in solution (m$^2$ s$^{-1}$), v is the kinematic viscosity of the solution (m$^2$ s$^{-1}$), $\omega$ is the rotation rate (s$^{-1}$) and [X] is the bulk concentration of species X (mol m$^{-3}$). If the mass transfer flux of reactants is equivalent to the leach reaction rate, then it can be concluded that the reaction is diffusion controlled for that set of experimental conditions.

$$J_x = 0.62 D_x^{2/3} v^{-1/6} \omega^{1/2} [X] \qquad\qquad \textbf{2.22}$$

The measurement of leach kinetics can be achieved either of two ways: measurement of loss of reactants or appearance of products. Each of these techniques is discussed below.

## 2.3.1.1 Appearance of Products

This approach to determining the gold leach kinetics measures the appearance of a reaction product of the leach reaction. The analysis of gold in solution is the most commonly used technique for estimating the kinetics of gold leaching. This is because the analysis for gold in solution is relatively easy with parts per billion (ppb) detection limits available using graphite AAS and ICP-MS. Also, gold thiosulfate is the only reaction product for which the concentration in solution changes only as a result of leaching; other solution reactions (section 2.2) affect the copper(I) concentration. The main disadvantage in measuring the appearance of gold in thiosulfate leach solutions is that measurable changes in the gold concentration are required. If the leach rate is low, long periods between sampling are required. As only an average rate of dissolution for the sample period is determined, little information is obtained on how the leach rate changes with time within the sample period.

## 2.3.1.2 Loss of Reactants

Alternatively to measuring leach kinetics by the rate of appearance in solution of products, one could measure the disappearance of reactants. For gold leaching in thiosulfate solutions there are three main reactants: copper(II), thiosulfate and gold. Measuring the disappearance of copper(II) or thiosulfate is not possible as these species also undergo other reactions as discussed in section 2.2. The disappearance of gold though can be measured using a rotating electrochemical quartz crystal microbalance (REQCM), which is described by Jeffrey *et al.* (2000), and can measure leach rates within seconds with a sensitivity of 1 ng. Hence, gold leach rates from a rotating electrode (Equation 2.22 applicable) can be determined at essentially constant copper(II) and thiosulfate concentrations. The electrode mass measured by the REQCM is related to the leach rate through Equation 2.23, where r is the leach rate (mol m$^{-2}$ s$^{-1}$), A is the electrode surface area (m$^2$), M is the atomic mass of the metal (g mol$^{-1}$), m is the mass of the electrode (g) and t is the time elapsed (s).

$$r = \frac{\Delta m}{A\,M\,\Delta t} \qquad\qquad \textbf{2.23}$$

## 2.3.2 Mechanistic Considerations

Having determined the kinetics of gold leaching, the mechanism by which leaching occurs can be determined. Consideration is given here also to the various methods used in evaluating the mechanism by which leaching occurs.

The dissolution reaction of metals in aqueous solutions is heterogeneous in nature for which there are usually five steps involved (Meng and Han, 1993):

1.  Mass transport of reacting species to the solid-solution interface;

2.  Mass transport of reacting species through the diffusion (Nernst) layer to the solid surface;

3.  Electrochemical/chemical reaction at the solid surface;

4.  Mass transport of soluble reaction products away from the surface through the diffusion layer;

5.  Mass transport of reaction products into the bulk solution.

The maximum rate of dissolution that can be achieved in most cases is equivalent to the rate of mass transfer of reacting species through the boundary layer (Marsden and House, 1992). Thus, in the cases where the overall reaction rate is controlled by mass transport (steps 1, 2, 4 or 5), the dissolution process is said to be diffusion controlled; simply increasing the agitation of the solution increases the dissolution rate (Marsden and House, 1992). If step 3 controls the overall reaction rate, then the dissolution process is said to be chemically controlled; the diffusion rate of all reactants is greater than the dissolution rate. In this case improvements in the leach kinetics are achieved by increasing the system temperature.

## 2.3.2.1 Mechanisms of Gold Leaching

The dissolution of gold in thiosulfate leach solutions involves two solution phase reactants, thiosulfate and copper(II). Therefore, in considering the possible mechanisms

by which the gold dissolution rate can be limited, the mass transport of both thiosulfate and copper(II) must be considered. The maximum rate of gold dissolution in thiosulfate leach solutions can be limited by the flux of either thiosulfate or copper(II), depending on which is lower. For a rotating disc the flux of reactants can be calculated from the Levich equation (Equation 2.22). Thus, for a given thiosulfate and copper(II) concentration the maximum rate of gold dissolution can be calculated.

As the concentration of copper(II) is generally an order of magnitude lower than that of thiosulfate (Table 2.2), the maximum gold dissolution rate will be limited by the flux of copper(II). According to the Levich equation, a plot of copper(II) flux, $J_{Cu(II)}$, versus copper(II) concentration, [Cu(II)], will be linear with a zero intercept. The slope is calculated from Equation 2.24, where $J_{Cu(II)}$ is the flux of copper(II) (mol m$^{-2}$ s$^{-1}$), $D_{Cu(II)}$ is the diffusion coefficient of copper(II) in solution (m$^2$ s$^{-1}$), $v$ is the kinematic viscosity of the solution (m$^2$ s$^{-1}$), $\omega$ is the rotation rate (s$^{-1}$) and [Cu(II)] is the bulk concentration of copper(II) (mol m$^{-3}$).

$$\text{Slope} = \frac{J_{Cu(II)}}{[Cu(II)]} = 0.62 D_{Cu(II)}^{2/3} v^{-1/6} \omega^{1/2} \qquad \textbf{2.24}$$

Using the published values of $0.46 \times 10^{-9}$ m$^2$ s$^{-1}$ for $D_{Cu(II)}$ (Jeffrey, 2001) and $0.89 \times 10^{-6}$ m$^2$ s$^{-1}$ for $v$ (Weast, 1974-75) at 25 $^\circ$C, the copper(II) flux can be calculated for a given rotation rate. To compare the copper(II) diffusion rate with the maximum gold dissolution rate, the reaction stoichiometry must be considered. From combining Equations 2.6 and 2.9, it can be seen that the molar ratio of gold to copper(II) is 1. Therefore, if all the copper(II) that reaches the surface is consumed, then the rate of gold dissolution will be equal to the copper(II) flux. This will be referred to as the copper(II) limiting gold dissolution rate. The copper(II) limiting gold dissolution rate as a function of copper(II) concentration at 25 $^\circ$C is shown as line (a) in Figure 2.3 for a rotation rate of 300 rpm ($\omega = 300 \times 2\pi/60$ s$^{-1}$).

By similar analysis the thiosulfate limiting gold dissolution rate can be calculated. From the stoichiometry of gold leaching in thiosulfate solutions shown in Equation 2.6, the molar ratio of gold to thiosulfate is 0.5. Thus, the thiosulfate limiting

gold dissolution rate is equal to half the thiosulfate flux. As the thiosulfate concentrations used in gold leaching studies are typically 0.1 M up to 2 M (Table 2.2), the lower thiosulfate (0.1 M) limiting gold dissolution rate was estimated to be $140 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$; in this calculation the diffusion coefficient for thiosulfate was taken to be the same as that for sulfate, $0.83 \times 10^{-9}$ m$^2$ s$^{-1}$ (Mills and Lobo, 1989). Thus, the gold dissolution rate in thiosulfate leach solutions will generally not be thiosulfate limiting. However, thiosulfate concentration can decrease due to thiosulfate oxidation as discussed in section 2.2. At low thiosulfate concentrations (say 25 mM), the thiosulfate limiting gold dissolution rate is estimated to be $39 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$. This is shown as line (b) in Figure 2.3.
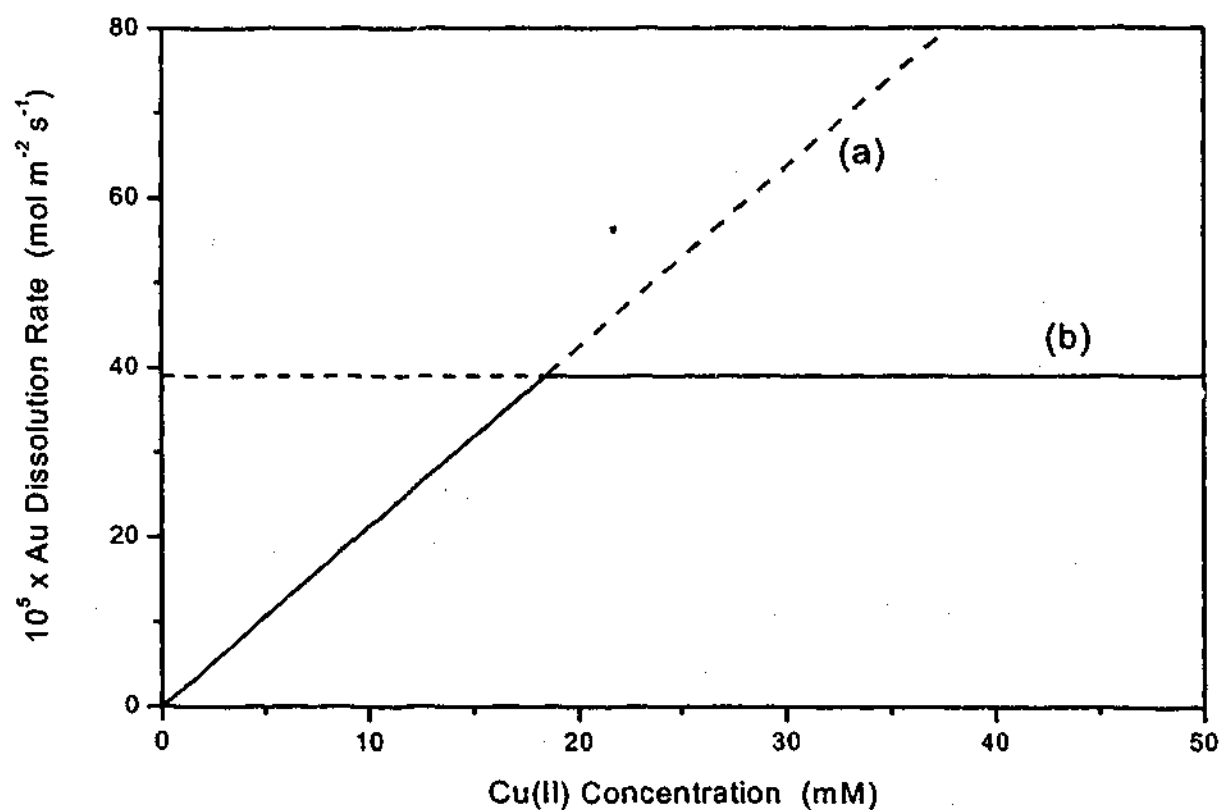


**Figure 2.3:** The copper(II) and thiosulfate limiting gold dissolution rates as a function of copper(II) concentration: 25 mM Na$_2$S$_2$O$_3$, 25 °C, 300 rpm. Lines (a) and (b) represent the copper(II) and thiosulfate limiting rates respectively. The solid lines indicate the maximum gold dissolution rate.

It is clear that at low copper(II) concentrations the copper(II) limiting rate is lower than the thiosulfate limiting rate, thus the maximum gold dissolution rate is equal

to the copper(II) limiting rate (solid part of line (a) in Figure 2.3). At high copper(II) concentrations the gold dissolution rate can become thiosulfate diffusion limited if the thiosulfate concentration becomes significantly low (solid part of line (b) in Figure 2.3). However, high copper(II) concentrations are generally avoided in order to minimise the reaction between copper(II) and thiosulfate. If measured gold dissolution rates lie on the solid lines in Figure 2.3, then the mechanism for gold dissolution is diffusion controlled. Measured gold dissolution rates that lie below these diffusion limited solid lines indicate that the gold dissolution mechanism is either chemically or mixed diffusion / chemically controlled.

### 2.3.2.2   Criteria for Determining the Controlling Mechanism

The limiting step in the gold dissolution process was discussed in the previous section to be either diffusion, chemically or mixed diffusion / chemically controlled. Detailed in this section are the criteria for diffusion and chemically controlled reactions. This involves investigating the kinetics of gold dissolution as a function of rotation rate and measuring the activation energy of the process.

### (a) Effect of Agitation

Investigating how the gold dissolution rate varies as a function of agitation will demonstrate whether the process is diffusion or chemically controlled. In the case of rotating disc experiments the Levich equation (Equation 2.22) is employed as a test to confirm whether the dissolution is diffusion controlled. If this is the case, a plot of gold dissolution rate versus $\omega^{1/2}$ will be linear passing through the origin. If the dissolution process is other than purely diffusion controlled, then the plot will either be non linear or not pass through the origin. Chemically controlled processes are independent of rotation rate.

### (b) Effect of Temperature

A more general method often used for determining the controlling mechanism of dissolution involves calculating the activation energy of the dissolution process (Power and Ritchie, 1975). The activation energy is related to the rate constant and the

temperature of the dissolution process according to Equation 2.24, known as the Arrhenius equation, where k is the rate constant (mol m$^{-2}$ s$^{-1}$), A is the frequency factor (mol m$^{-2}$ s$^{-1}$), $E_a$ is the activation energy (J mol$^{-1}$), R is the universal gas constant (8.314 J K$^{-1}$ mol$^{-1}$), and T is the absolute temperature (K).

$$k = Ae^{-E_a/RT} \hspace{3cm} \text{2.24}$$

Thus, a plot of ln(k) versus 1/T will yield a straight line of slope $-E_a$/R. According to Power and Ritchie (1975), the activation energy is a good guide to the controlling mechanism as diffusion controlled processes usually have an activation energy less than 25 kJ mol$^{-1}$, whereas chemically controlled processes have an activation energy greater than 25 kJ mol$^{-1}$.

### 2.3.3 Published Kinetic Results

A review of the published gold dissolution kinetics in thiosulfate leach solutions is presented in this section, from which it will become evident that very few fundamental studies have been attempted. As the solution chemistry is continually changing, an evaluation of the effect various parameters have on the gold leach kinetics can only be made where initial gold leach rates have been measured using freshly prepared thiosulfate leach solutions; conditions for which the solution composition is known. However, the effect of solution aging on the gold leach kinetics has received little attention, even though the gold leach kinetics are generally measured with respect to time. Also, no solution analyses have been conducted with time in order to relate changes in gold leach kinetics with changes in the solution chemistry. Despite this, the effect of various parameters on the gold leach kinetics as the solution ages gives some indications as to stability of the thiosulfate leach solution. Obviously, leaching studies conducted using ore are of little value in determining the effect of solution aging on the gold leach kinetics as the gold content diminishes with time. As evident from this review, there is a clear lack of understanding as to how the thiosulfate leach solution ages and the effect this has on gold leaching.

### 2.3.3.1 Dissolution Rates

Compiled in Table 2.3 are the initial gold leach rates determined using rotating gold discs by Barbosa-Filho *et al.* (1994), Muyunda (1996) and Jeffrey (2001). Notably the gold leach rate determined by Jeffrey (2001) is significantly higher than the gold leach rate determined by Muyunda (1996) for the same conditions. An identifiable difference between these studies was that Muyunda (1996) used polished solid pure Au (99.99%) electrodes whereas Jeffrey (2001) used electroplated gold deposits contained 5 wt% silver. The effect this may have on the measured gold leach rate are discussed further in section 2.3.3.4.

**Table 2.3:** Published gold leach rates in thiosulfate solutions.

| Reference | $[S_2O_3^{2-}]$ (M) | $[NH_3]$ (M) | [Cu] (M) | Temp. ($^\circ$C) | RPM | Au Leach Rate (mol m$^{-2}$ s$^{-1}$) |
|---|---|---|---|---|---|---|
| Barbosa-Filho *et al.* | 0.25 | 0.5 | 0.04 | 30 | 600 | $1.5 \times 10^{-5}$ |
| Muyunda | 0.4 | 0.84 | 0.025 | 30 | 350 | $4.0 \times 10^{-5}$ |
| Jeffrey | 0.4 | 0.84 | 0.025 | 30 | 300 | $9.9 \times 10^{-5}$ |

Another significant difference in the study by Jeffrey (2001) is that the gold leach kinetics was determined by the loss of gold measured using a REQCM (method discussed in section 2.3.1.2). A plot of the mass change versus time showed an induction period (approximately 120 s) that was suggested to be consistent with transient passivation. This passivation was not identified but was shown to be consistent with sulfur on the surface; sulfur had previously been suggested to complicate the leaching of gold in thiosulfate solutions (Zhu *et al.*, 1994a). The initial gold leach rate was thus taken by Jeffrey (2001) as the constant dissolution rate measured after the initial induction period. The work by Barbosa-Filho *et al.* (1994) and Muyunda (1996) on the other hand used solution analysis to determine the amount of gold leached for a given sample period and thus gold leach rates are only an average for the initial sample period. Notably, no evidence of an induction period was shown in

the data for either of these studies, even for conditions (eg. 20 °C) were the induction period for electroplated gold is greater than 10 minutes (Jeffrey, 2001).

### 2.3.3.2 Effect of Agitation

Studies of the effect agitation has on the gold dissolution rate allows the mechanisms by which gold leaching in thiosulfate solutions occurs to be investigated. The Levich plot of gold leach rate versus $\omega^{1/2}$ (rotation speed) published by Barbosa-Filho *et al.* (1994) and Jeffrey (2001) are shown in Figure 2.4. At low rotation rates the data by Jeffrey (2001) shows that the leach rate increases with rotation rate indicating the gold dissolution process is at least partially diffusion controlled. At higher rotation rates the data deviates from line (a) suggesting that the gold dissolution process is most likely mixed diffusion / chemically controlled.
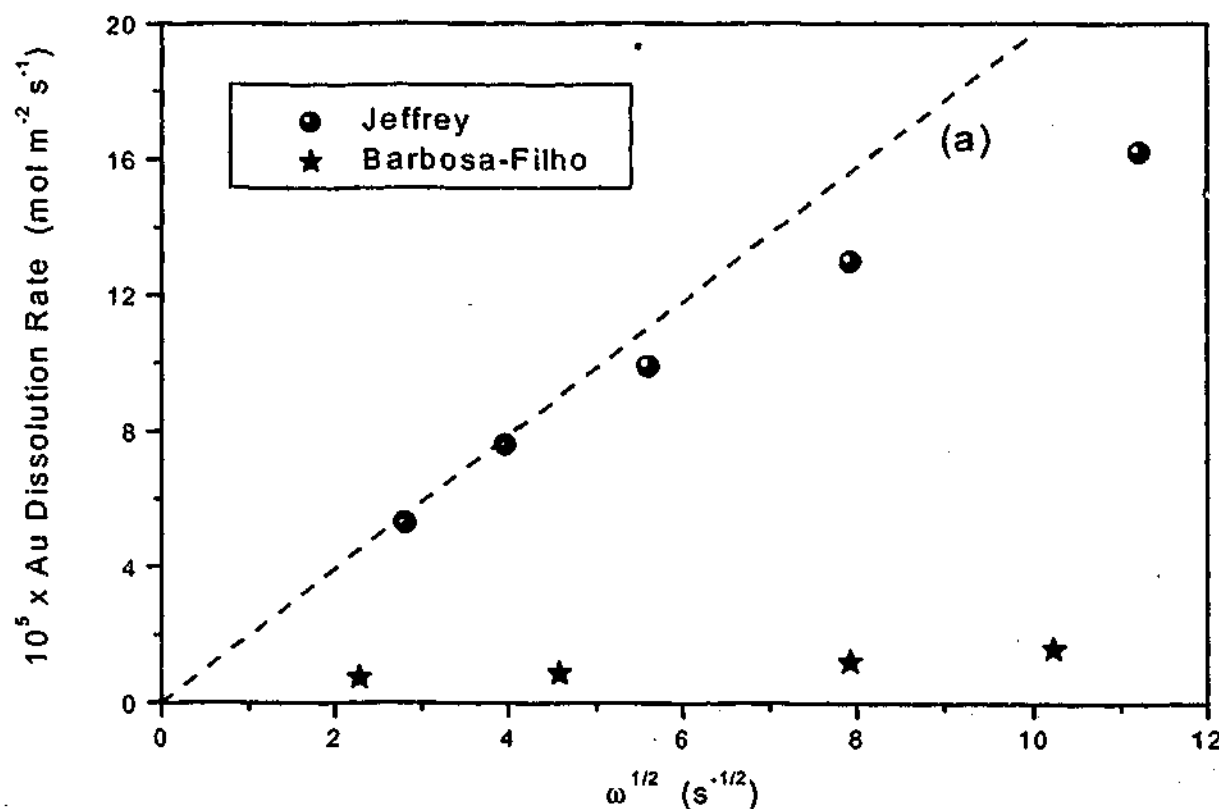


**Figure 2.4:** Levich plot for gold dissolution from data published by Barbosa-Filho *et al.* (1994) and Jeffrey (2001). Other conditions as given in Table 2.3.

However, the results of Barbosa-Filho *et al.* (1994) shown in Figure 2.4 indicate very little dependence of the gold dissolution rate on the rotation rate and are significantly lower than those measured by Jeffrey (2001). Hence, the gold dissolution process for a po' ⸳ ⸳ ⸳ d gold electrode would appear to be largely chemically controlled. The ⸳⸳⸳ runda (1996) concurred, showing that the gold dissolution rate was indepen ⸳⸳⸳ on speed. Thus, the gold dissolution process in thiosulfate solutions appears ⸳⸳ ⸳ly chemically controlled, though electroplated gold and/or the presence of si⸳ ⸳⸳ars to significantly enhance the leaching process such that it is partially diffusion controlled at low rotation rates.

### 2.3.3.3  Effect of Temperature

Chemically controlled reactions usually have a high activation energy, and thus, increasing the temperature is an easy way of enhancing the gold dissolution rate. The gold leach rate is shown by Barbosa-Filho *et al.* (1994), Muyunda (1996) and Jeffrey (2001) to increase as temperature is increased. This data is shown as an Arrhenius plot in Figure 2.5, for which the slopes give a measure of the activation energy. Clearly, Figure 2.5 shows that the activation energy of the gold dissolution process changes at approximately 30 °C. Below 30 °C the activation energy is high (106 kJ mol$^{-1}$ (Barbosa-Filho *et al.*, 1994)), indicating that the gold leaching process is most likely chemically controlled, while above 30 °C the activation energy is significantly diminished (24 kJ mol$^{-1}$ (Barbosa-Filho *et al.*, 1994)), suggesting that the process is likely to be mixed diffusion / chemically controlled. Generally, the temperature employed in gold leaching studies is in the range 30 to 60 °C in order to achieve acceptable gold leach rates, though the loss of ammonia from the leach solution increases with temperature (Muyunda, 1996). The results by Muyunda (1996) also showed that at 55 °C the gold dissolution rate was very slow after 1 hour. This is consistent with the solution composition having changed significantly and was identified as ammonia loss (only 23% remaining). Thus, the ammonia concentration needs to be controlled in order to maintain the solution stability and hence the gold leach rate.

Several gold dissolution studies conducted using ore samples also noted an initial increase in the gold dissolution rate with increasing temperature (Murthy, 1991,

Jiang *et al.*, 1993b, Zipperian *et al.*, 1988). However, it was generally observed that above 50 °C the initial gold dissolution rate decreased (Murthy, 1991, Jiang *et al.*, 1993b). Abbruzzese *et al.* (1995) however used high solution concentrations and found that increasing temperature did not have a positive effect on the initial gold dissolution rate. This was attributed to passivation by cupric sulfide and again indicates that solution instability increases with increasing temperature.
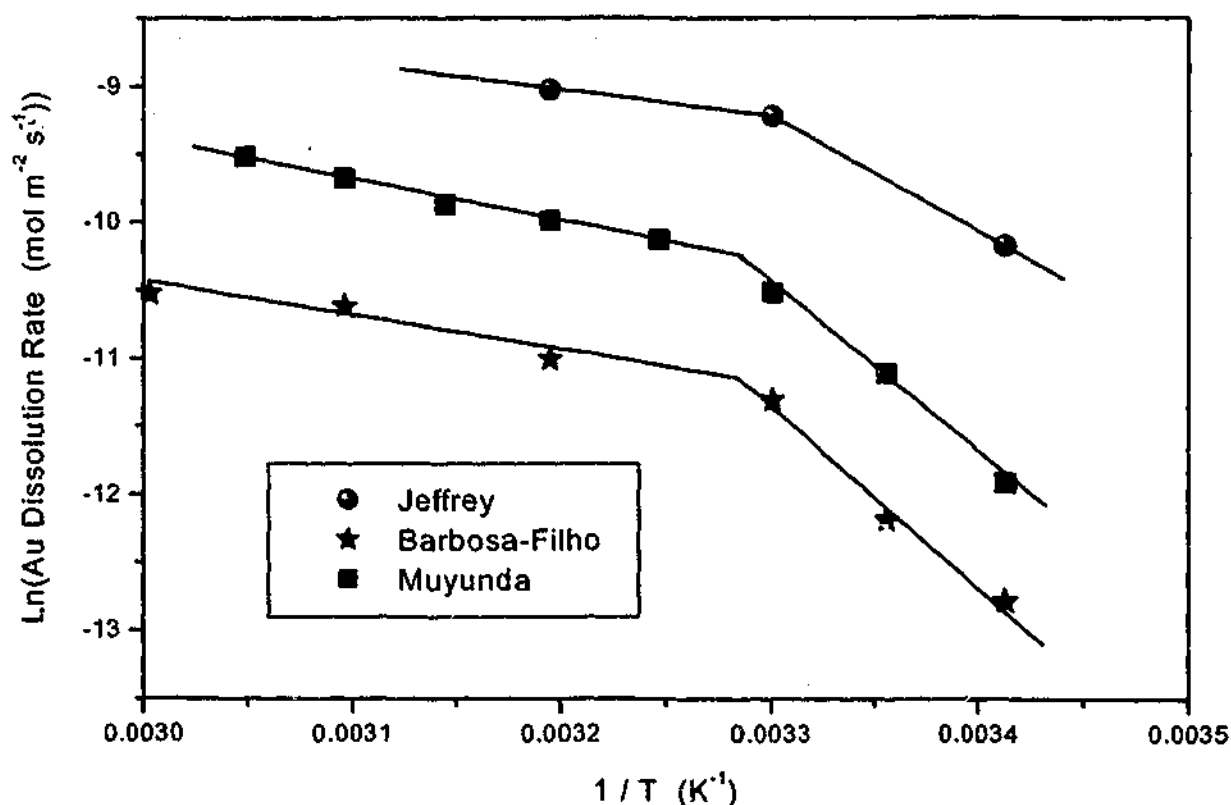
Figure 2.5: Arrhenius plot for gold dissolution from data published by Barbosa-Filho *et al.* (1994), Muyunda (1996) and Jeffrey (2001). Other conditions as given in Table 2.3.

### 2.3.3.4 Effect of Surface Finish and Gold Purity

The surface finish of an electrode is well known to affect the rate of dissolution, especially for chemically controlled reactions. The surface finish of an electroplated gold electrode would expectedly be rougher and have a greater number of surface defects than a polished solid gold electrode. For instance, Jeffrey (1998) showed that in

cyanide solutions under chemically controlled conditions the gold oxidation rate of electroplated gold is an order of magnitude greater than that of polished solid gold. Hence, the gold dissolution rate in thiosulfate solutions, which was shown above to be chemically controlled, would expectedly be higher for an electroplated gold electrode than a polished solid gold electrode. Thus, the surface finish could significantly contribute to the higher gold dissolution rates observed by Jeffrey (2001) in thiosulfate solutions.

The use of silver modified gold, subsequently referred to as gold/silver, by Jeffrey (2001) in studying the kinetics of gold leaching in thiosulfate solutions could be considered more representative of naturally occurring gold which mainly exists alloyed with some silver (Hurlbut and Klein, 1977). The gold dissolution rate in cyanide solutions has been shown to be significantly higher for gold/silver than pure gold (Jeffrey, 1998). In this case an initial increase in the rate of gold dissolution with time being consistent with a transient film forming on the gold surface that initially hinders the dissolution process. Jeffrey (2001) also made a similar observation for gold/silver dissolution in thiosulfate solutions, indicating that a surface passive film was also likely to be hindering the gold dissolution process. This study also showed that silver dissolution in thiosulfate solutions is diffusion controlled and thus is unhindered. Webster (1986) also found that the alloying of silver with gold increased the gold dissolution rate at least 6 times in thiosulfate solutions (no copper(II) or ammonia present).

## 2.3.3.5 Effect of Copper(II) Concentration

The presence of copper(II) is well recognised as being required in order to achieve acceptable gold leach rates. However, the concentration of copper(II) required and the role it plays in the dissolution process are still not clearly defined. Figure 2.6 shows the effect of copper(II) concentration on the initial gold dissolution rate published by Barbosa-Filho *et al.* (1994), Muyunda (1996) and Jeffrey (2001). The copper(II) diffusion limiting rate is indicated in figure 2.6 by line (a) which was calculated using the values of $1.01 \times 10^{-9}$ m$^2$ s$^{-1}$ for $D_{Cu(II)}$ (determined in section 6.3.1.2) and $0.80 \times 10^{-6}$ m$^2$ s$^{-1}$ for $v$ (Weast, 1974-75) at 30 °C. Notably the data by Jeffrey (2001) at low copper(II) concentrations shows a rapid increase in the gold dissolution rate with

increasing copper(II) concentration, though the rates are lower than the copper(II) diffusion limiting rates. However, at copper(II) concentrations above 5 mM the gold dissolution rate deviates significantly from the copper(II) diffusion limiting rate line indicating a change in the rate determining step of the gold dissolution process. As the gold dissolution rate becomes almost independent of copper(II) concentration at high copper(II) concentrations, this change in the rate determining step is consistent with the gold dissolution process being chemically controlled at high copper(II) concentrations. At copper(II) concentrations greater than 40 mM, the gold dissolution rates by Barbosa-Filho *et al.* (1994) are observed to decrease. This was attributed to a decrease in thiosulfate concentration due to oxidation and copper(I) complexation according to Equation 2.14. The initial leach data by Muyunda (1996) in Figure 2.6 shows that the gold dissolution rate continually increased with increasing copper(II) concentration over the range 0 to 50 mM investigated. After 1 hour though, the amount of gold leached for 50 mM copper(II) was found to be less than that for 25 mM copper(II).
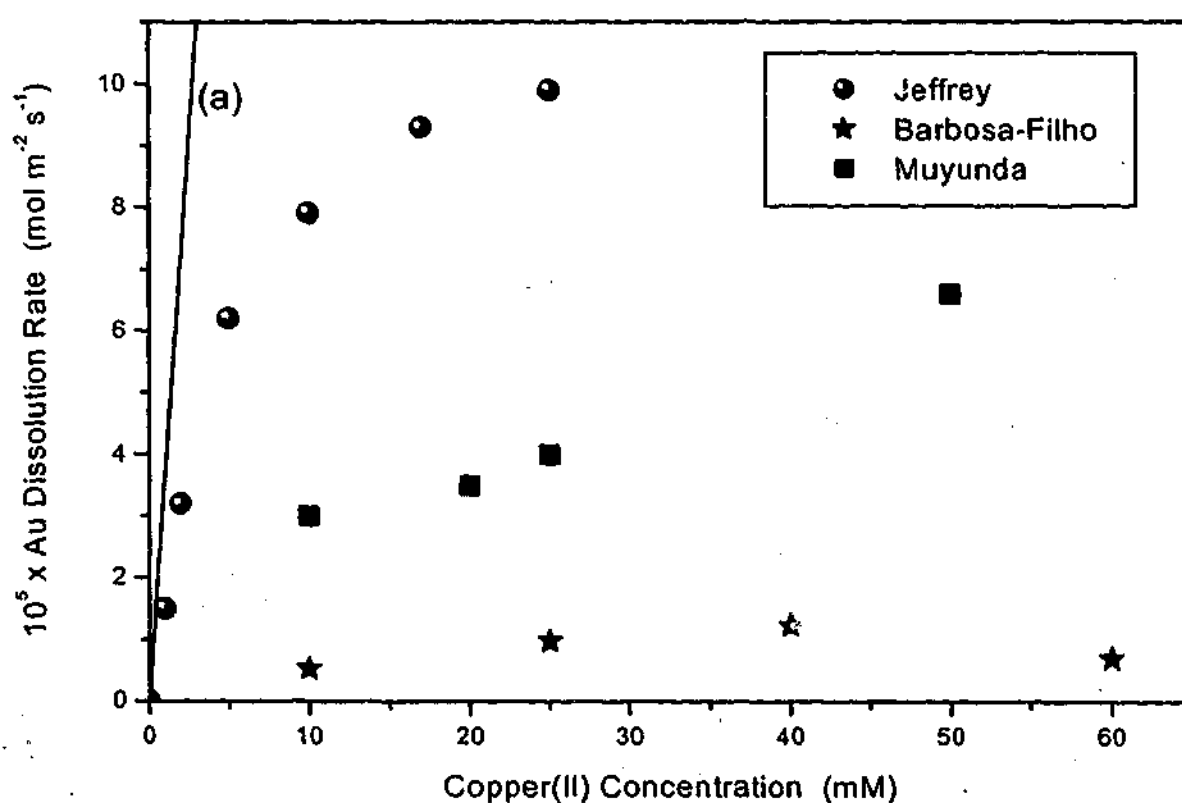


**Figure 2.6:** Effect of copper(II) concentration on the gold dissolution rate published by Barbosa-Filho *et al.* (1994), Muyunda (1996) and Jeffrey (2001). Line (a) represents the copper(II) limiting gold dissolution rate at 30 °C, 300 rpm. Other conditions as given in Table 2.3.

Many of the studies conducted using ore samples also observed an increase in the initial gold leach rate with increased copper(II) concentration (Abbruzzese *et al.*, 1995, Jiang *et al.*, 1993b). Clearly, the concentration of copper(II) in solution is an important factor, as an increase in copper(II) concentration increases the gold leach rate, especially at low concentrations. However, at higher copper(II) concentrations the gold dissolution process becomes chemically controlled, such that there is little benefit to the gold dissolution rate with further increase in the copper(II) concentration. Also, the loss of copper(II) and thiosulfate is increased via Equation 2.14, and thus high copper(II) concentrations should be avoided.

### 2.3.3.6   Effect of Thiosulfate Concentration

Thiosulfate concentration is obviously an important parameter, given the small driving force for the chemically controlled gold leaching reaction. However, excess thiosulfate was discussed in section 2.2.2 to increase the rate of copper(II) reduction. Figure 2.7 shows the effect of thiosulfate concentration on the gold leach rate published by Barbosa-Filho *et al.* (1994), Muyunda (1996) and Jeffrey (2001). Clearly, as the thiosulfate concentration is increased the gold leach rate increases. This is further evidence that the leaching process is not copper(II) diffusion controlled and is consistent with the data presented in Figure 2.6; the copper(II) concentrations in Figure 2.7 are greater than 20 mM. Such a result implies that the slowest chemical step is dependent on the thiosulfate concentration, and thus consistent with the leaching process being limited by the rate of gold oxidation. Figure 2.7 also shows that the gold leach rates determined by Muyunda (1996) decreased significantly with an increase in thiosulfate conc nuration from 0.4 to 0.6 M. This is most likely due to a rapid reduction in copper(.., concentration and hence a lower amount of gold leached at high thiosulfate concentrations in the initial sample period.

A positive effect on the gold dissolution rate of increasing the thiosulfate concentration was also observed in many of the studies conducted using ore samples (Abbruzzese *et al.*, 1995, Murthy, 1991, Jiang *et al.*, 1993b, Zipperian *et al.*, 1988). Gong *et al.* (1993) however found that the effect of thiosulfate concentration was small and hence was not involved in the rate controlling step.
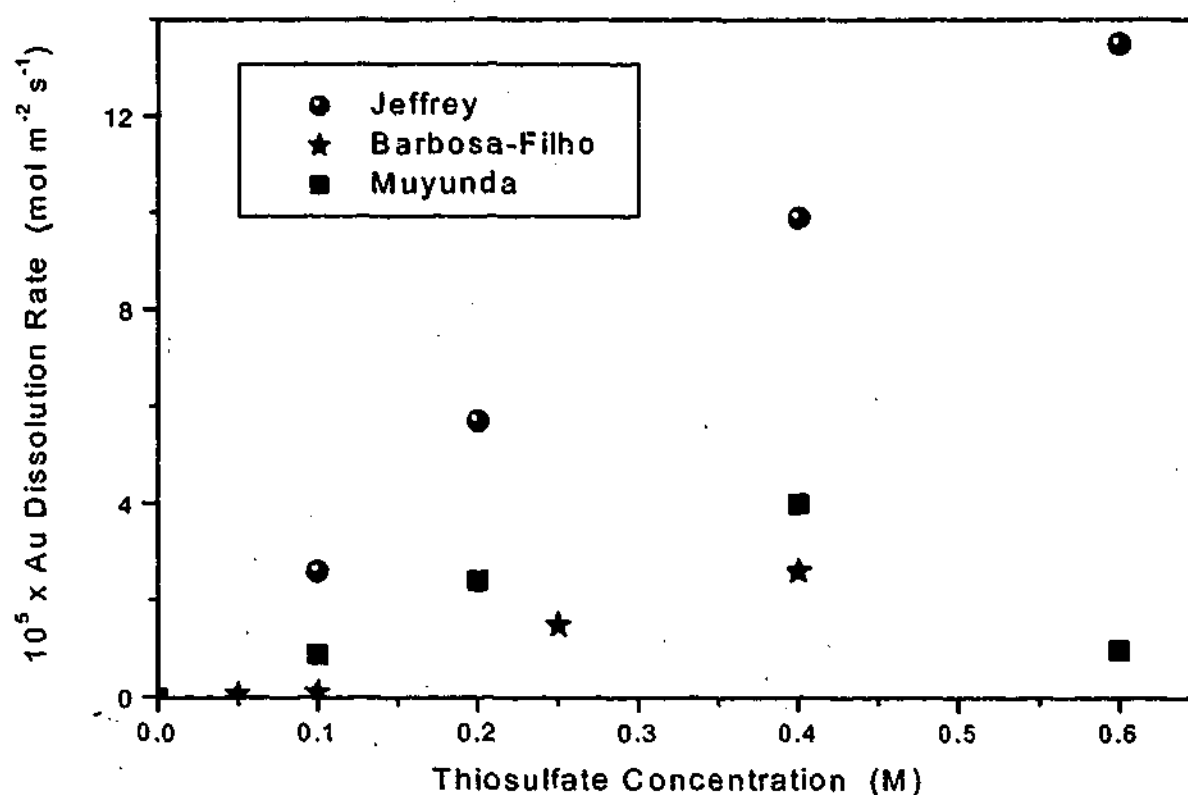
**Figure 2.7:** Effect of thiosulfate concentration on the gold dissolution rate published by Barbosa-Filho *et al.* (1994), Muyunda (1996) and Jeffrey (2001). Other conditions as given in Table 2.3.

### 2.3.3.7 Effect of Ammonia Concentration

The role of ammonia appears largely to involve the stabilisation of the copper(II) ion in solution by forming a copper(II) tetra-ammine complex. The importance of ammonia to the dissolution process is highlighted by the fact that gold leaching does not occur in the absence of ammonia (Barbosa-Filho *et al.*, 1994, Muyunda, 1996, Gong *et al.*, 1993); any added cupric is rapidly reduced to the cuprous state. Changing the ammonia concentration therefore alters the potential of the copper(II) – copper(I) couple and thus would effect both the rate of copper(II) reduction by thiosulfate and the gold leach rate. Figure 2.8 shows differences in the effect of ammonia concentration on the gold leach rate published by Muyunda (1996), Barbosa-Filho *et al.* (1994) and Jeffrey (2001). The data by Jeffrey (2001) and Barbosa-Filho *et al.* (1994) are consistent with the gold leach rate decreasing with increased ammonia concentration as a result of the decrease in copper(II) reduction potential (see section 2.4.3). However, the decrease in

gold leach rate at ammonia concentrations less than 0.4 M ammonia was attributed to the rapid reduction of copper(II) by thiosulfate; ammonia concentrations greater than 0.3 M are required such that the majority of the copper(II) is complexed as the tetra-ammine (section 2.1.4). The gold leach rates published by Muyunda (1996) however suggest that increasing the ammonia concentration increases the gold leach rate. These results are consistent with maintaining a higher copper(II) concentration over the initial sample period benefiting the average gold leach rate more than the reduction in gold leach rate due to the decrease in the copper(II) reduction potential.

Zipperian *et al.* (1988) however showed ammonia concentration had little effect on the initial gold dissolution kinetics for an ore sample. Several studies conducted using ore samples also showed an increase in the gold dissolution rate with increasing pH due to the increase in ammonia concentration (Jiang *et al.*, 1993b, Zipperian *et al.*, 1988). Gold extraction was found by Gong *et al.* (1993) to only increase slightly with increased ammonia concentration above 0.5 M.
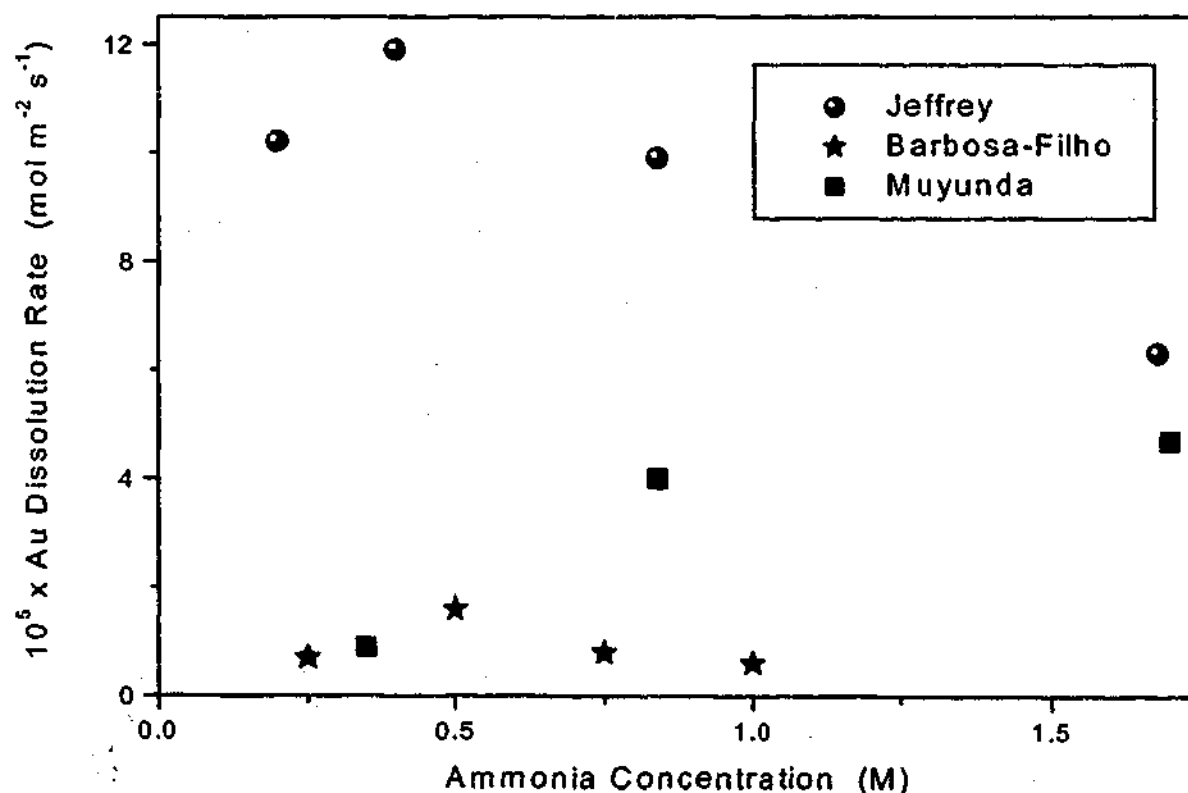


**Figure 2.8:**  Effect of ammonia concentration on the gold dissolution rate published by Barbosa-Filho *et al.* (1994), Muyunda (1996) and Jeffrey (2001). Other conditions as given in Table 2.3.

Obvious from this section and the previous two, is that in optimising the gold leach rate, the optimum copper, ammonia and thiosulfate concentrations are dependent on the leaching period of interest.

### 2.3.3.8 Effect of Oxygen

Oxygen, or some other oxidant, is required to convert copper(I) to copper(II) in order to sustain gold leaching. However, as discussed in section 2.2.2, the oxidation of thiosulfate in the presence of oxygen and copper(II) is significantly more rapid than that by copper(II) in the absence of oxygen. The precipitation of black copper sulfides often noted in the published literature is attributed to thiosulfate decomposition as a result of low solution potential, where copper(II) and oxygen are deficient, such as in stagnant solutions or solutions with high copper concentrations (Aylmore and Muir, 2001).

Very little has been published in the literature as to the effect oxygen has on the gold dissolution rate. Muyunda (1996) evaluated the effect of oxygen injection, air injection and no injection on the gold leach rate in thiosulfate solutions. The initial gold leach rates were found to be independent of oxygen injection. However, after 1 hour the gold leach rate was reduced with air injection compared to no injection, while the gold leach rate with oxygen injection was significantly reduced. Notably, the oxygen injected into the solution was rapidly consumed. The decrease in gold leach rates observed could thus be attributed to thiosulfate loss. Tozawa *et al.* (1981) also observed decreased gold dissolution with increased agitation as a result of enhanced oxygen transfer and thus thiosulfate oxidation. The amount of gold dissolved was also observed to decrease with increase oxygen partial pressure because of increase thiosulfate oxidation.

### 2.3.3.9 Effect of Other Variables

Sulfite addition was noted in section 2.2 to have been advocated by a number of researchers to stabilise the thiosulfate leach solution, thus reducing thiosulfate losses. The effect of sulfite addition on gold leach kinetics has received little attention, though the addition of sulfite has been used by a number of researchers (see Table 2.2). Work done by Michel and Frenay (1996) showed that gold leaching is effectively inhibited by

the presence of sulfite, with the gold leach rate observed to increase once the majority of the sulfite has been oxidised.

Due to the oxidation of thiosulfate in the leach solution the formation of other oxysulfur species such as tetrathionate and trithionate is expected along with a build up of sulfate (section 2.2). However, little is known about the effect these oxysulfur species may have on the gold dissolution process. Recent rotating disc work (Muir and Aylmore, 2002) suggested that the addition of up to 0.01 M trithionate or tetrathionate had little effect on the gold dissolution rate.

## 2.4   Electrochemistry

The leaching of gold in thiosulfate solutions is a corrosion process, thus electrochemical techniques should be beneficial in studying this process. Like all electrochemical processes, the leaching of gold in thiosulfate solutions occurs as a result of two half reactions, the oxidation of gold and the reduction of an oxidant. The oxidation of gold in thiosulfate solutions by oxygen is represented by the anodic and cathodic reactions shown in Equation 2.25 and 2.26 respectively.
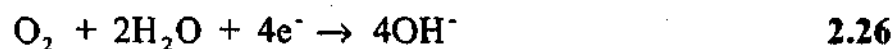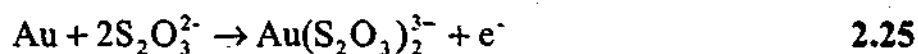
$$Au + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + e^- \qquad \textbf{2.25}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad \textbf{2.26}$$

In solutions containing copper(II), ammonia and thiosulfate, there is the possibility of an additional cathodic reaction: the reduction of copper(II) to copper(I), as shown in Equation 2.27.

$$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- \rightarrow Cu(S_2O_3)_3^{5-} + 4NH_3 \qquad \textbf{2.27}$$

To investigate an electrochemical process, each constituent half reaction can be studied independently. The following section describes how gold leaching in thiosulfate solutions can be studied electrochemically using the mixed potential theory. The subsequent sections review the published results on the gold oxidation and copper(II) reduction half reactions respectively.

## 2.4.1 Mixed Potential Theory

For every electrochemical process there are two half reactions, one involving oxidation and the other reduction. In the leaching of gold in thiosulfate solutions containing copper(II), the oxidation reaction is the oxidation of gold to gold thiosulfate, while the reduction reaction is the reduction of copper(II) to copper(I). Mixed potential theory involves studying each of the constituent half reaction independently; for example, gold oxidation must be studied in the absence of oxygen and copper(II). These are generally studied using linear sweep voltammetry (current density measured as a function of electrode potential), the resultant plot often called a polarisation curve (Power and Ritchie, 1983). Figure 2.9 shows a schematic diagram of the gold oxidation and copper(II) reduction polarisation curves determined using a rotating disc. These curves comply with the IUPAC convention in that the anodic current densities are considered positive and the cathodic current densities negative (Power and Ritchie, 1983). It is shown in Figure 2.9 that the anodic polarisation curve consists of three defined regions marked $E_R$, T and $i_L$. The potential marked $E_R$ is the rest potential of the gold electrode, and is simply the potential at which no net reaction occurs (ie. no current flows). As the potential of the gold electrode is increased in the positive direction, the current density increases exponentially. This is often referred to as the Tafel region, and marked T in Figure 2.9. The oxidation of gold in this region is usually controlled by a chemical or electrochemical reaction. At high overpotentials the current density reaches a limit, $i_L$, where the gold oxidation rate is controlled by the diffusion of thiosulfate to the gold surface; for a rotating disc the flux can be calculated from the Levich equation (Equation 2.22). Hence, further increases in potential do not increase the current density.

$$Au + 2S_2O_3^{2-} > Au(S_2O_3)_2^{3-} + e^-$$

Anodic

$$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- > Cu(S_2O_3)^{5-} + 4NH_3$$
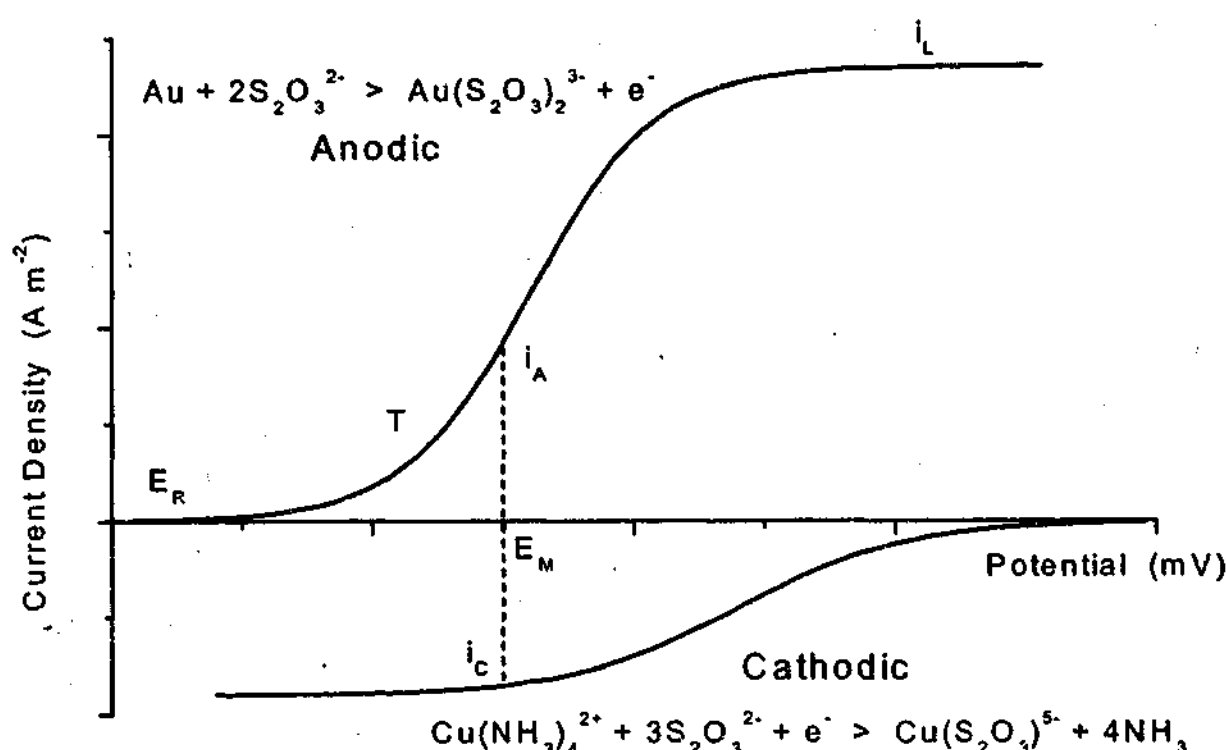
**Figure 2.9:** Schematic diagram showing the polarisation curves for the oxidation of gold and reduction of copper(II). The rest potential is labelled $E_R$, the Tafel region T, and the diffusion limiting current density $i_L$. Combining the anodic and cathodic curves, the mixed potential, $E_M$ and the corrosion current density, $i_A = i_C$ can be estimated.

Having measured and superimposed the anodic and cathodic polarisation curves, as shown in Figure 2.9, the potential and corrosion rate can be estimated. For a corrosion reaction the anodic and cathodic currents must always be equal, $i_A = i_C$. This current is often referred to as the corrosion current, which is equivalent to the corros. rate. The potential at which the anodic and cathodic currents are equal is called the mixed potential, $E_M$, or the corrosion potential. This is the basis of mixed potential theory, which can also be used to determine the rate determining step for the process (Power and Ritchie, 1983). The schematic shown in Figure 2.9 indicates that the reaction rate is controlled by the diffusion of the oxidant to the electrode surface.

The use of mixed potential theory in studying the dissolution of gold in thiosulfate solutions has not been attempted in the published literature. Several attempts though have been made to study this process using electrochemical techniques as

discussed in the following two sections. Surprisingly however, no electrochemical studies using rotating disc electrodes have been published for either the anodic or cathodic reactions; the use of a rotating disc, as described in section 2.3.2.1, gives well defined mass transport of reactants to the electrode surface. Hence, only qualitative information can be drawn from the published electrochemical studies. Thus, one of the major aims of this research was to study individually the anodic and cathodic reactions using rotating disc electrodes and to couple these with mixed potential theory to gain a better understand of the gold dissolution process in thiosulfate solutions.

### 2.4.2 Gold Oxidation Half Reaction

Very few attempts at studying the oxidation of gold in thiosulfate solutions (anodic half reaction) using electrochemical techniques have been published (Zhu *et al.*, 1994a, Jiang *et al.*, 1993a, Wang, 1992). In all these studies the gold electrode was stationary and hence the mass transport of reactants to the surface is not well defined. Linear sweep voltammetry was used in each of these studies, with impedance spectroscopy also being utilised by Zhu *et al.* (1994a).

As shown in Figure 2.10, Zhu *et al.* (1994a) observed no anodic peak for the oxidation of gold in a 0.1 M thiosulfate solution; the rise in current observed above 300 mV was attributed to the onset of thiosulfate oxidation. However, shown also in Figure 2.10, is that at higher thiosulfate concentrations, the presence of an anodic peak for gold oxidation is observed at approximately 250 mV (Zhu *et al.*, 1994a, Jiang *et al.*, 1993a, Wang, 1992).

The presence of ammonia has also been shown to increase the measured current in the potential region of gold oxidation (Zhu *et al.*, 1994a, Jiang *et al.*, 1993a, Wang, 1992). Figure 2.11 shows the linear sweep voltammograms measured by Zhu *et al.* (1994a) in the absence and presence of ammonia. Interpretation of these results is difficult, as the thiosulfate oxidation peak largely masks the gold oxidation peak. Wang (1992) suggested the presence of ammonia suppresses the oxidation of thiosulfate and thereby increases the dissolution of gold. Jiang *et al.* (1993a) however suggested that the presence of ammonia both improves the gold dissolution rate and reduces the passivation.
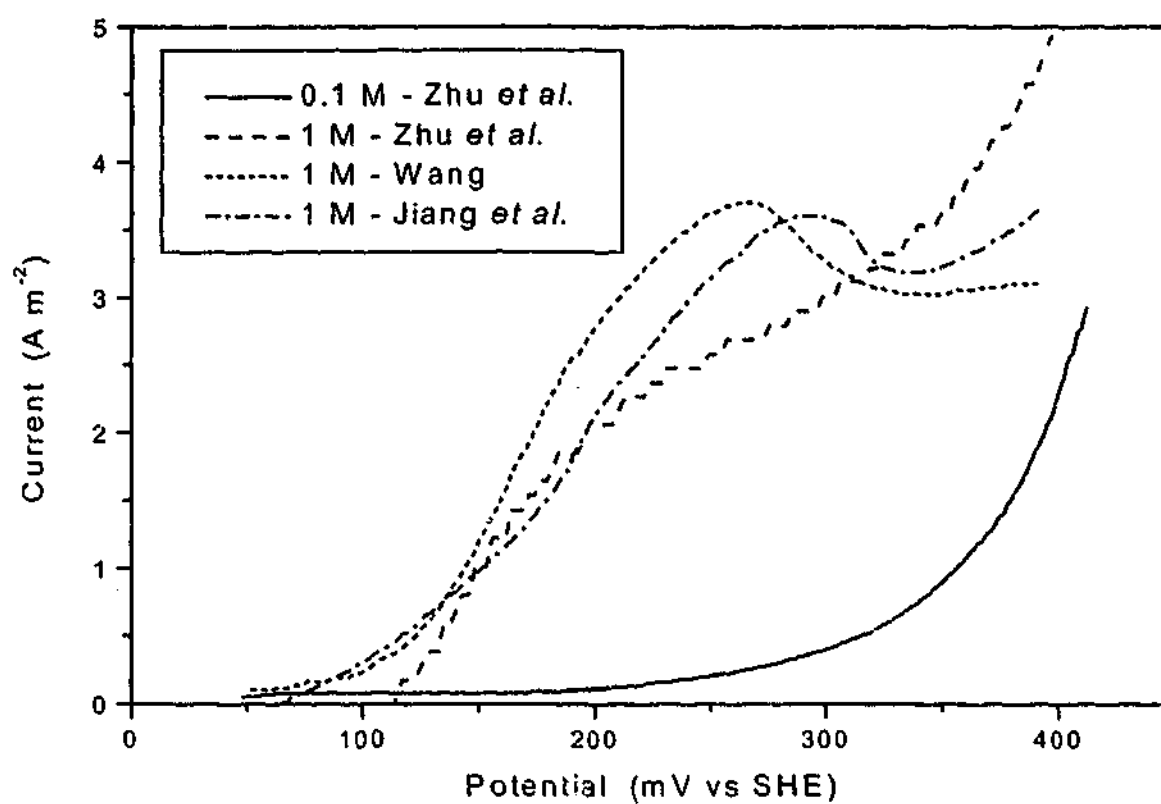
**Figure 2.10:** Voltammograms for a gold electrode in thiosulfate solutions (Zhu *et al.*, 1994a, Jiang *et al.*, 1993a, Wang, 1992).
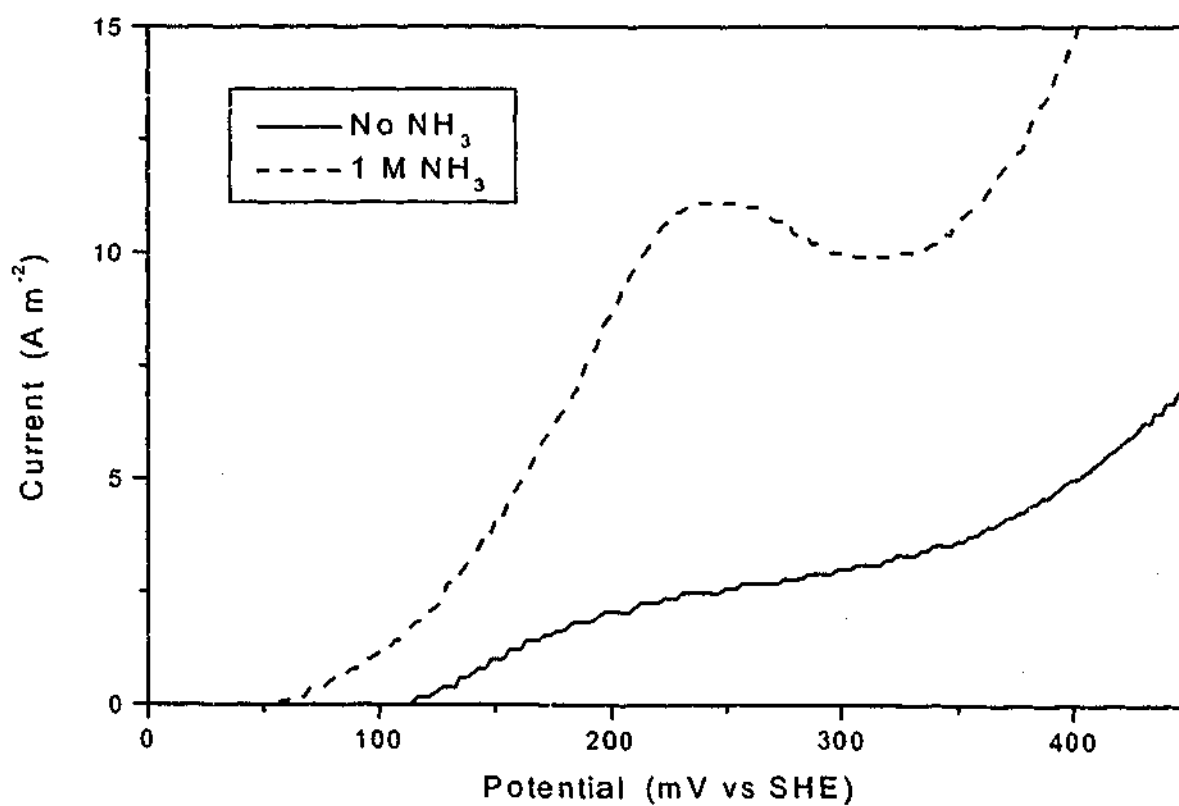


**Figure 2.11:** Effect of ammonia on the gold voltammogram in thiosulfate solutions (Zhu *et al.*, 1994a).

Two possible mechanisms considered by Jiang *et al.* (1993a) to explain the effect of ammonia were the adsorption of ammonia on the surface reducing passivation and ammonia taking part in the anodic reaction. A current step technique was used to exclude the adsorption mechanism. Hence, Jiang *et al.* (1993a) proposed that gold oxidation in thiosulfate leach solutions occurs via an intermediate ammine complex according to Equation 2.28. However, as the standard reduction potential of the $Au(NH_3)_2^+$ complex is around 600 mV (see Table 2.1), this mechanism is unlikely.

$$Au \rightarrow Au^+ + e^-$$
$$Au^+ + 2NH_3 \rightarrow Au(NH_3)_2^+ \qquad \textbf{2.28}$$
$$Au(NH_3)_2^+ + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + 2NH_3$$
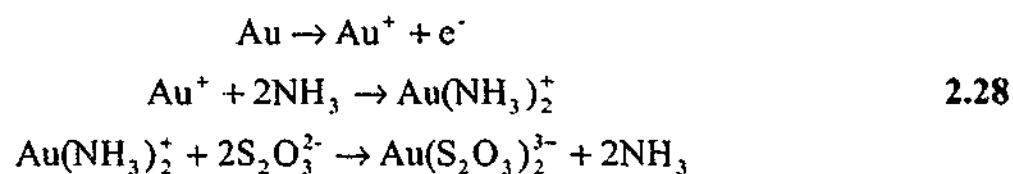
Clearly, to establish the anodic polarisation curve for gold oxidation in thiosulfate solutions and to better understand the effect of ammonia, differentiation of the gold oxidation reaction from thiosulfate oxidation is required. An instrument that has this ability is the rotating electrochemical quartz crystal microbalance (REQCM), which is described by Jeffrey *et al.* (2000). When conducting electrochemical experiments with the REQCM, the additional information obtained is the changes in electrode mass. As the oxidation of gold is the only reaction involving a mass change, the current due to gold oxidation can be calculated using Faraday's law as shown in Equation 2.29, where n is the number of electrons transferred per mole of gold reacted, F is Faraday's constant (96485 $C$ $mol^{-1}$) and r is the rate of gold oxidation ($mol$ $m^{-2}$ $s^{-1}$), calculated from the mass changes using Equation 2.23.

$$i_{calc} = nFr \qquad \textbf{2.29}$$

## 2.4.3 Copper(II) Reduction Half Reaction

Given that the study of copper(II) reduction in thiosulfate leach solutions (cathodic half reaction) should be relatively straight forward using an inert electrode, it is surprising that only two publications have attempted to study this reaction (Michel and Frenay, 1996, Jiang *et al.*, 1993a). Again, these studies are of limited value as stationary gold electrodes were used. Thus, the cathodic voltammograms obtained with a gold electrode are affected by gold oxidation that also occurs in the potential region of interest. The potential scale of the voltammograms published by Jiang *et al.* (1993a) is also questionable as copper(II) reduction is shown to only occur at potentials less than 0 mV versus SHE, which is below the potential region observed for gold oxidation. The study by Michel and Frenay (1996) indicates that copper(II) reduction can occur at potentials up to 300 mV.

Despite the limited value of these studies, some information regarding the cathodic reaction can be drawn from the results published by Michel and Frenay (1996). A schematic representation of the polarisation curve for a thiosulfate leach solution measured using an inert electrode is shown in Figure 2.12 for a solution in which a portion of the copper(II) has been reduced to copper(I); the reduction of copper(II) by thiosulfate was discussed previously in section 2.2. The cathodic reaction is a reversible process (Michel and Frenay, 1996) with copper(I) oxidation observed at potentials greater than the solution potential ($E_h$); a diffusion limiting current density for copper(I) oxidation, $i_L(1)$, may not be observed due to thiosulfate oxidation. At potentials less than $E_h$, the cathodic polarisation curve due to copper(II) reduction (Equation 2.27) is observed; at lower potentials the current density, $i_L(2)$, is copper(II) diffusion limited.

The investigation conducted by Michel and Frenay (1996) established a clear dependence of the copper(II) and copper(I) polarisation curve potentials with respect to thiosulfate and ammonia concentrations. A mean negative shift of 25 mV when ammonia concentration is doubled and a mean positive shift of 17 mV when thiosulfate concentration is doubled were determined. Thus, the thiosulfate leach solution composition affects the copper(II) reduction potential as indicated by the arrow labelled A in Figure 2.12.
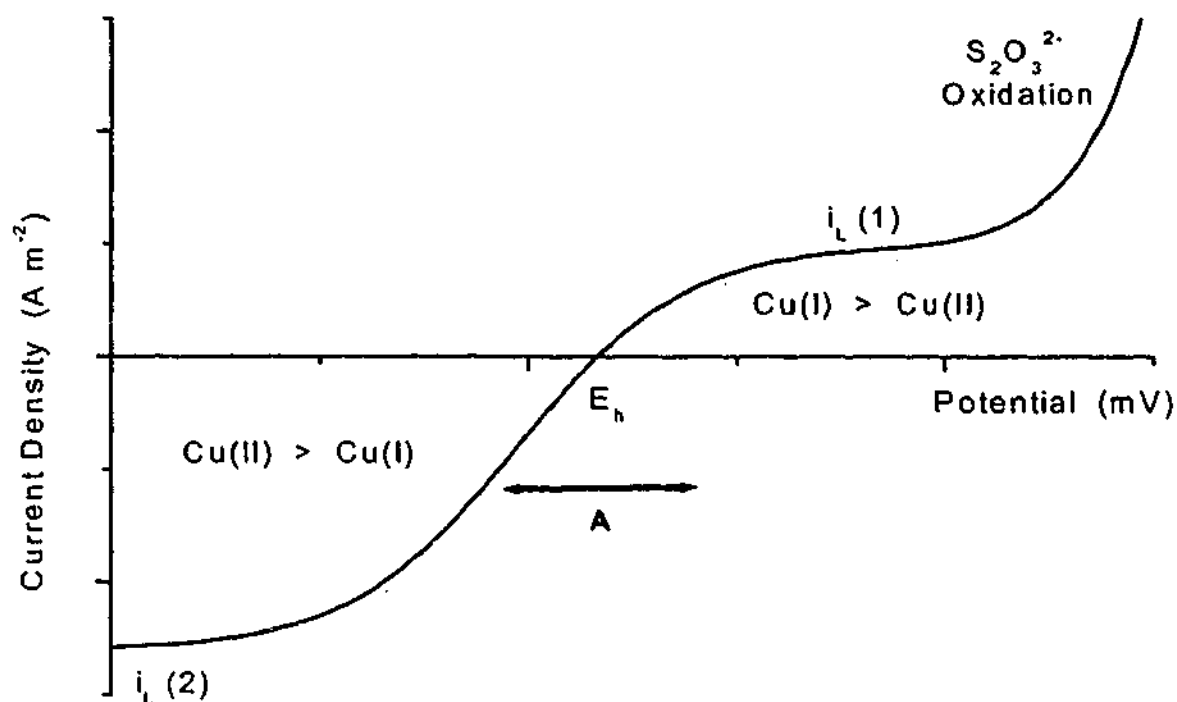
**Figure 2.12:** Schematic diagram showing the voltammogram for a thiosulfate leach solution measured using an inert electrode. Solution potential is labelled $E_h$, and $i_L(1)$ and $i_L(2)$ are the diffusion limiting current densities for Cu(I) oxidation and Cu(II) reduction respectively.

## Chapter 3

# *Copper(II) Reduction by Thiosulfate and Oxysulfur Species*

## 3.1 Introduction

The kinetics of gold leaching was shown in section 2.3.3.5 of the review to be dependent on copper(II) concentration. Just as importantly, the kinetics of gold leaching is also dependent on the [Cu(II)]:[Cu(I)] ratio which determines the potential of the cathodic half reaction (see section 7.3.1). It was clearly identified in section 2.2 of the review that the thiosulfate leach solution chemistry continually changes and is very complex due to the presence of copper(II), thiosulfate and oxygen. Hence, given the importance of both copper(II) concentration, the [Cu(II)]:[Cu(I)] ratio and thiosulfate loss to the thiosulfate leach system, it is surprising that there has been little fundamental research conducted into the solution chemistry.

In the absence of oxygen, the undesirable reduction of copper(II) by thiosulfate occurs according to the simplified overall reaction shown in Equation 3.1 (Byerley *et al.*, 1973a); for simplicity the ligands complexed with copper have been ignored.

$$2Cu^{2+} + 2S_2O_3^{2-} \rightarrow 2Cu^+ + S_4O_6^{2-} \qquad \textbf{3.1}$$

Under aerated conditions (see Chapter 5), the presence of oxygen increases the rate of copper(II) reduction and thiosulfate oxidation, though copper(II) is maintained in solution due to copper(I) oxidation. Studying the kinetics of gold leaching under anaerobic conditions allows the effect of decreasing copper(II) concentration, and hence the [Cu(II)]:[Cu(I)] ratio, to be investigated with minimal decrease in the thiosulfate

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concentration (see Chapter 7). The objective of the work presented in this chapter was to conduct a study into the rate of copper(II) reduction by thiosulfate in the absence of oxygen for solutions applicable to gold leaching. This was achieved by measuring the copper(II) concentration using UV-Vis spectrophotometry. As the kinetics of this reaction are shown to be complicated, further studies were undertaken into the reduction of copper(II) by other oxysulfur species.

## 3.2    Experimental

All experiments were carried out using solutions prepared from analytical grade reagents and distilled water. Trithionate was prepared by the equimolar addition of sulfite to tetrathionate; the formation of trithionate and thiosulfate as reaction products is known to be quantitative (Palmer, 1959).

### 3.2.1  Copper(II) Measurement

The copper(II) reduction kinetics were measured by monitoring the concentration of the copper(II) ammine complexes using UV-Vis spectrophotometry. As discussed in the review, this technique has been used previously to measure the kinetics of copper(II) reduction by thiosulfate. However, it was considered prudent to confirm this analytical technique was applicable for the system being studied. The absorbances as a function of wavelength for several solutions in a 1 cm path length cell are shown in Figure 3.1. Clearly shown is the very broad absorbance peak of the copper(II) ammine complexes at 605 nm. From the other absorbance profiles shown in Figure 3.1 it can be seen that ammonia, ammonium, sulfate, thiosulfate and copper(I) ions all have negligible absorbance at this wavelength. Tetrathionate and other oxysulfur species used in this study (not shown in Figure 3.1) were also found to give negligible absorbance at this wavelength. Thus, monitoring the height of the absorbance peak at 605 nm should give a simple measure of the copper(II) concentration in solution with no interference from other species present.
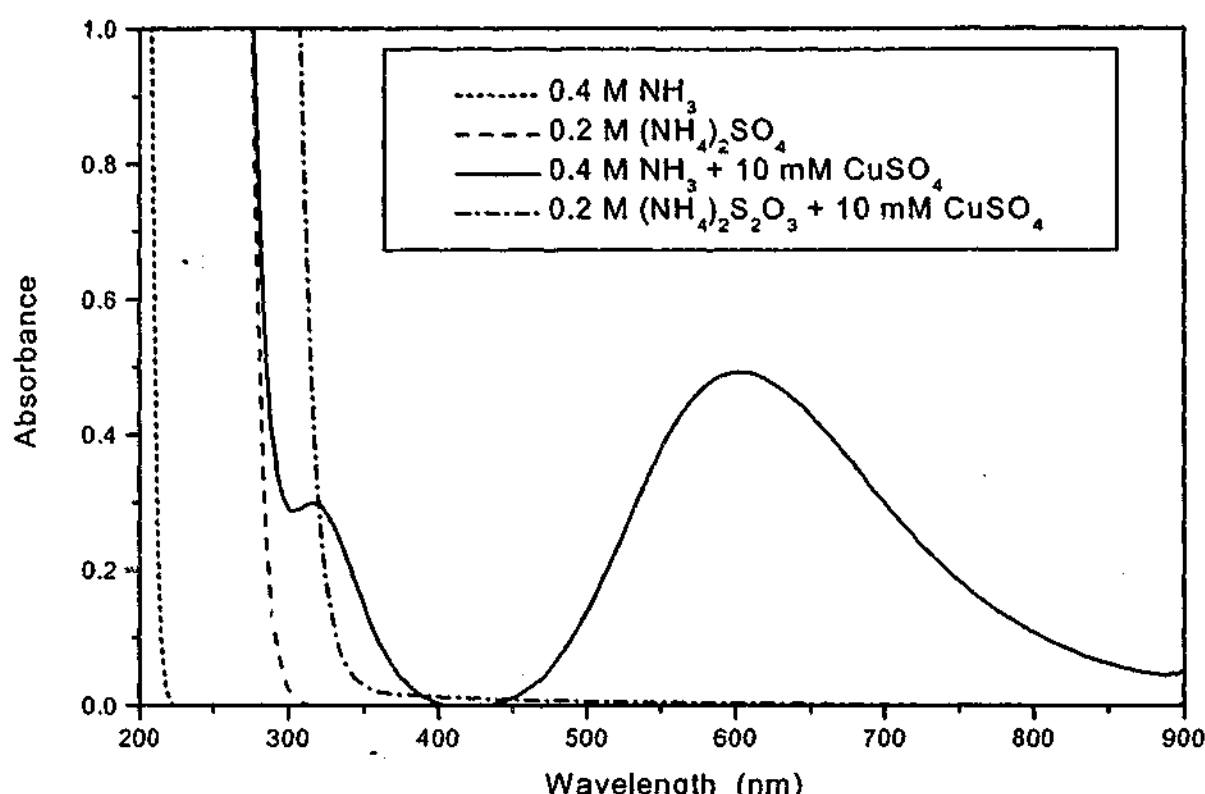
**Figure 3.1:** Wavelength scan of absorbance for various solutions using UV-Vis spectrophotometry; the addition of copper sulfate to thiosulfate in the absence of ammonia rapidly forms copper(I).

However, as noted in the review, ammonia concentration and the presence of other solution species influence the copper(II) ammine absorbance peak (Hathaway and Tomlinson, 1970, Byerley *et al.*, 1973a). Figure 3.2 shows the effect sulfate and thiosulfate each have on the absorbance peak. The increase in the absorbance of the copper(II) ammine complexes in the presence of thiosulfate was observed previously (Byerley *et al.*, 1973a) and is attributed to thiosulfate ion association at the axial sites of the copper(II) ammine complexes. Given that the solution composition influences the copper(II) absorbance peak height, changes in the solution composition could therefore influence the copper(II) measurement. This effect will be constant for experiments conducted in the absence of oxygen, as only a small decrease in thiosulfate concentration occurs. Thus, the peak height is directly proportional to copper(II) concentration during these experiments. To check this, the copper(II) concentration was also measured by the diffusion limiting reduction current for copper(II) on a rotating platinum electrode at -150 mV versus SHE as the reduction of copper(II) by thiosulfate

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proceeded in the absence of oxygen. Good agreement between the copper(II)-time profiles measured by the diffusion limiting current and the absorbance measurements were observed and confirmed that the relationship between absorbance and copper(II) concentration is linear. As the solution composition remains relatively constant throughout experiments, the absorbance readings are converted to a copper(II) concentration using a linear correlation for which the parameters are determined by extrapolating the kinetics data back to the time of copper(II) addition, at which point the copper(II) concentration is known.
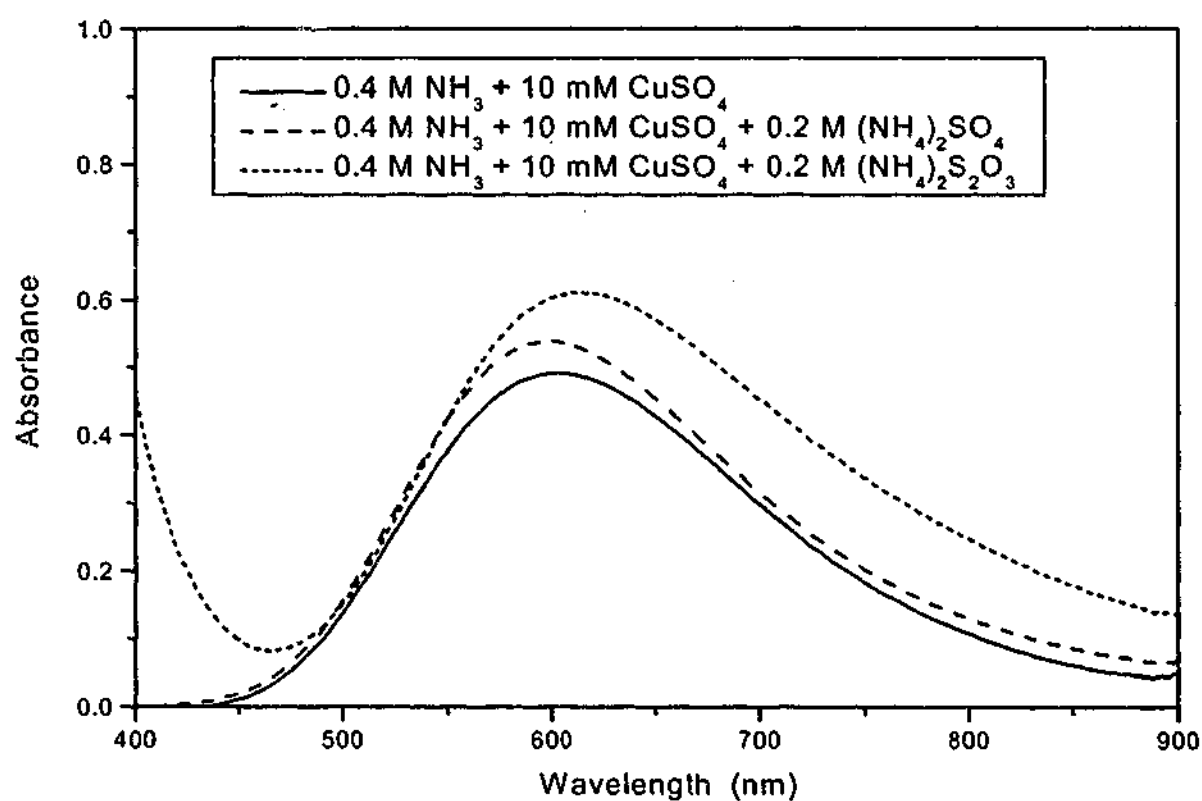


**Figure 3.2:** Wavelength scan of absorbance for copper(II) containing solutions using UV-Vis spectrophotometry.

## 3.2.2 Experimental Procedures

Measurements of the copper(II) reduction rate in thiosulfate solutions in the absence of oxygen were conducted using a sealed UV cell. Firstly, a solution was prepared containing all components other than copper(II) and ammonia. This solution

was stirred within a sealed jacketed vessel (100 ml) maintained at a constant temperature ±0.1 °C and purged using argon before commencing experiments. A concentrated copper(II)-ammonia solution was injected into the vessel and after a short mixing time, a sample was withdrawn and sealed within a UV cell (at all times excluding contact of the solution with air). The UV cell was then placed in a temperature controlled jacketed cell holder within a GBC UV-Vis spectrophotometer. The solution absorbance at 605 nm was recorded at regular time intervals via a computer. Unless stated otherwise experiments were conducted at 30 °C and all solutions contained 0.1 M sodium thiosulfate, 0.4 M ammonia and 10 mM copper sulphate.

## 3.3 Copper(II) Reduction in Thiosulfate Solutions

As the copper(II) concentration has a significant effect on the gold leach rate (section 2.3.3.5), experiments were conducted in the absence of oxygen in order to measure the copper(II)-time profiles as a result of the copper(II) reduction by thiosulfate. From the large number of gold leaching studies published using thiosulfate in the past three decades and some preliminary experiments conducted, a solution containing 0.1 M sodium thiosulfate, 0.4 M ammonia and 10 mM copper sulfate at 30 °C was chosen as the standard conditions. The measured absorbance-time profile for this solution is shown in Figure 3.3. It can be seen that the absorbance decreases due to a decrease in the copper(II) concentration as a result of its reaction with thiosulfate. Also shown on the second y axis in Figure 3.3 is the copper(II) concentration which was calculated from the extrapolated absorbance at the time of copper and ammonia addition; the only point at which the copper(II) concentration was known.

It has been suggested previously (Byerley *et al.*, 1973a) that the kinetics of copper(II) reduction in ammoniacal thiosulfate solutions under argon are pseudo-first order with respect to copper(II) concentration (thiosulfate is in excess and hence remains relatively constant). Pseudo-first order kinetics are simply shown by a linear plot of Log([Cu(II)]) versus time. Figure 3.4 is such a plot for the data shown in

Figure 3.3. Clearly, the plot is not linear and hence the kinetics are obviously not pseudo-first order with respect to copper(II) concentration for the conditions used in this experiment.
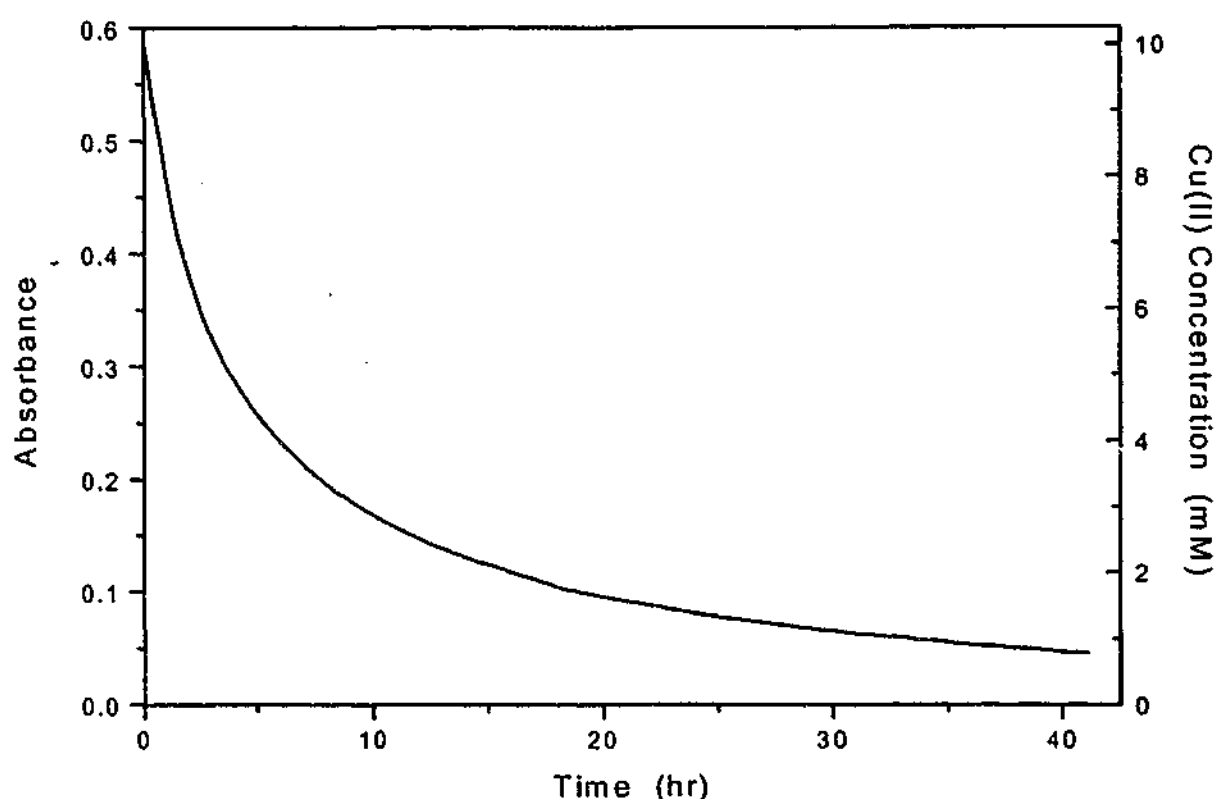


**Figure 3.3:** Absorbance / copper(II) concentration versus time plot for standard solution conditions of 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

Fitting kinetic equations to the data in Figure 3.3 suggested that the copper(II) reduction kinetics were more consistent with the rate limiting reaction step being a second order process. For such a process, a plot of the inverse of copper(II) concentration versus time will have a linear relationship. Figure 3.4 also shows such a plot for which it is clear that the kinetics are more consistent with a rate limiting second order process with respect to copper(II) concentration than a first order process. The deviation from the initial linearity in the second order plot with time is attributed to further copper(II) reduction by tetrathionate (section 3.3.4). This indicates that the reaction mechanisms of copper(II) reduction in thiosulfate solutions are more complex than those proposed by Byerley *et al.* (1973a) shown in Equation 2.20 of the review.
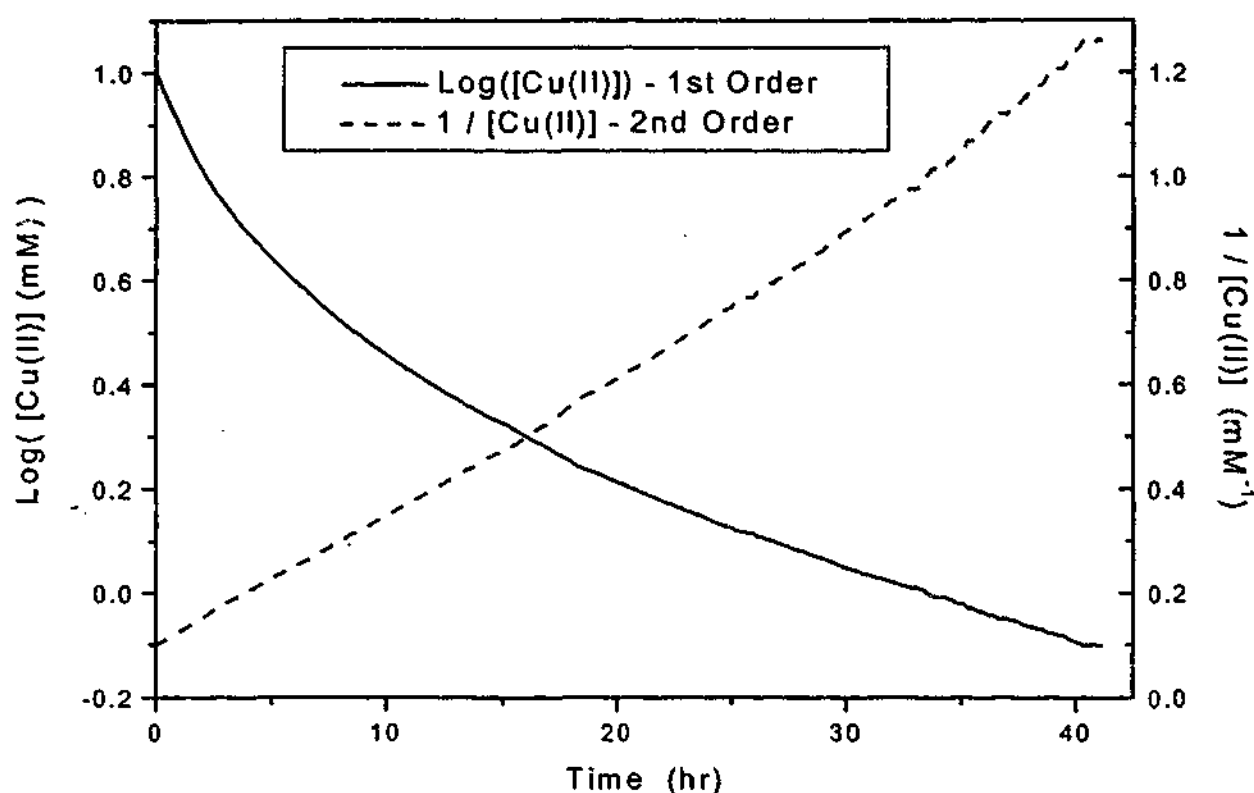
**Figure 3.4:** $1^{st}$ and $2^{nd}$ order plots of the copper(II) reduction kinetics shown in Figure 3.3 for the standard solution conditions of 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

## 3.3.1 Effect of Trace Amounts of Oxygen

The effect of oxygen on the chemistry of thiosulfate leaching solutions was indicated in the review to be complex and hence is considered in detail in Chapter 5. In order to measure the rate of copper(II) reduction by measuring the change in copper(II) concentration, the exclusion of oxygen is paramount. To illustrate this, Figure 3.5 shows the very reproducible (±2%) copper(II)-time profile recorded for the standard solution conditions whereby the solution was prepared under argon from which a sample was taken and sealed within a UV cell. The other copper(II)-time profile shown in Figure 3.5 was obtained by pumping continuously solution through a UV cell from a standard solution prepared and maintained under a positive pressure atmosphere of argon. Clearly, there is an observed difference in the two profiles. The presence of oxygen is shown in Chapter 5 to result in the copper(II) concentration initially

decreasing faster and an equilibrium copper(II) concentration is established due to copper(I) oxidation. Thus, the observed difference in Figure 3.5 is consistent with the very low diffusion of oxygen in the case where the solution was pumped through the UV cell. Thus, sealing the solution in the UV cell was found to be the only way to exclude oxygen from the solution in order to investigate the rate of copper(II) reduction in thiosulfate solutions.
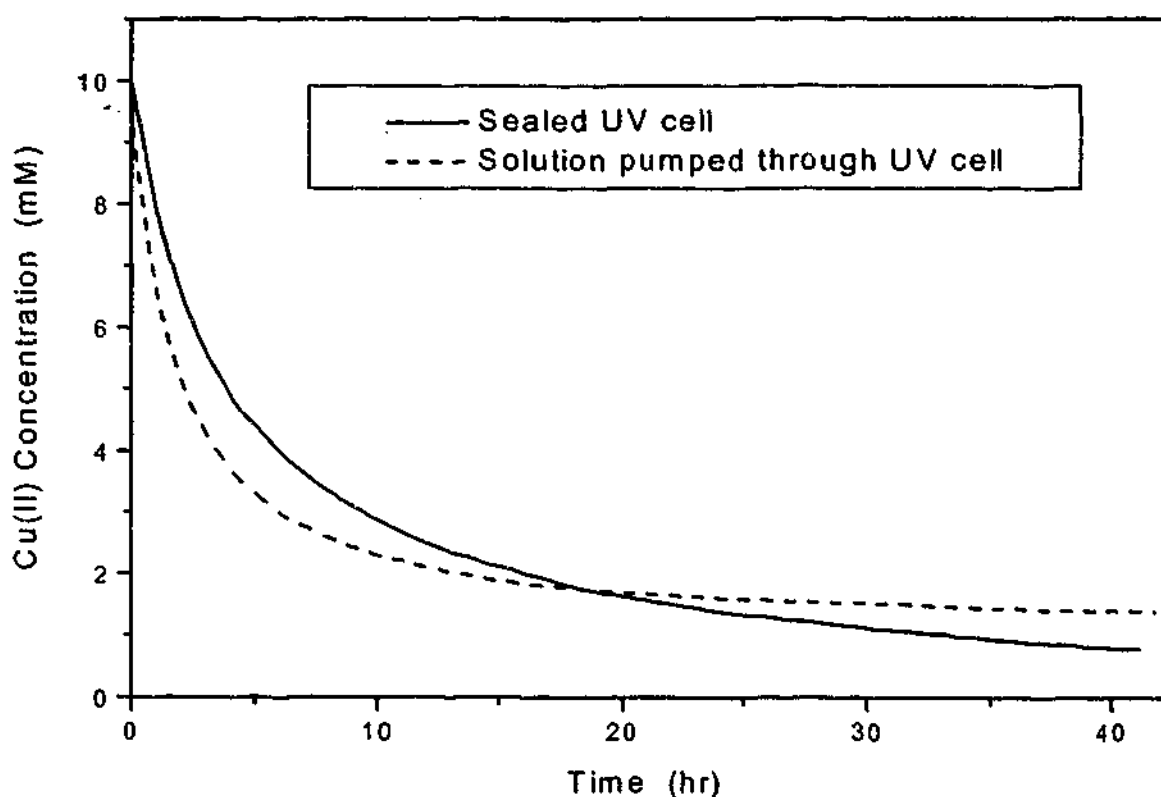


**Figure 3.5:** Effect of trace amounts of oxygen on the rate of copper(II) reduction: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

## 3.3.2 Effect of Electrolyte

In the work conducted in the absence of oxygen by Byerley *et al.* (1973a), it was noted that when the ionic strength of the reaction solution was increased by the addition of sodium sulfate, slightly lower rates of copper(II) reduction were observed. This effect was not further quantified or explained in terms of their proposed reaction mechanism, probably because the studies were aimed at increasing the rate of thiosulfate oxidation. Hu and Gong (1991) have also shown that the addition of sulfate

inhibits the decomposition of thiosulfate during gold leaching. They attributed this effect to thiosulfate and sulfate being in equilibrium according to Equation 2.19 of the review; the addition of sulfate was thought to shift the equilibrium towards thiosulfate. Given the formation of sulfate is irreversible this explanation is unlikely. In light of these observations, the effect of several electrolytes and their concentration on the rate of copper(II) reduction was investigated.

### 3.3.2.1 Effect of Sulfate Ions

During the thiosulfate leaching of gold, the continual recycling of the thiosulfate leach solution will increase the concentration of sulfate due to the continual oxidation of thiosulfate. Thus it was decided to perform a more thorough study on the effect of sulfate on copper(II) reduction by thiosulfate. Clearly shown in Figure 3.6 is that the rate of copper(II) reduction is significantly reduced with increasing sulfate concentration. For instance, the initial reaction rate for solutions in the absence of sulfate is 2.3 times higher than the initial rate for solutions containing 0.1 M sulfate.
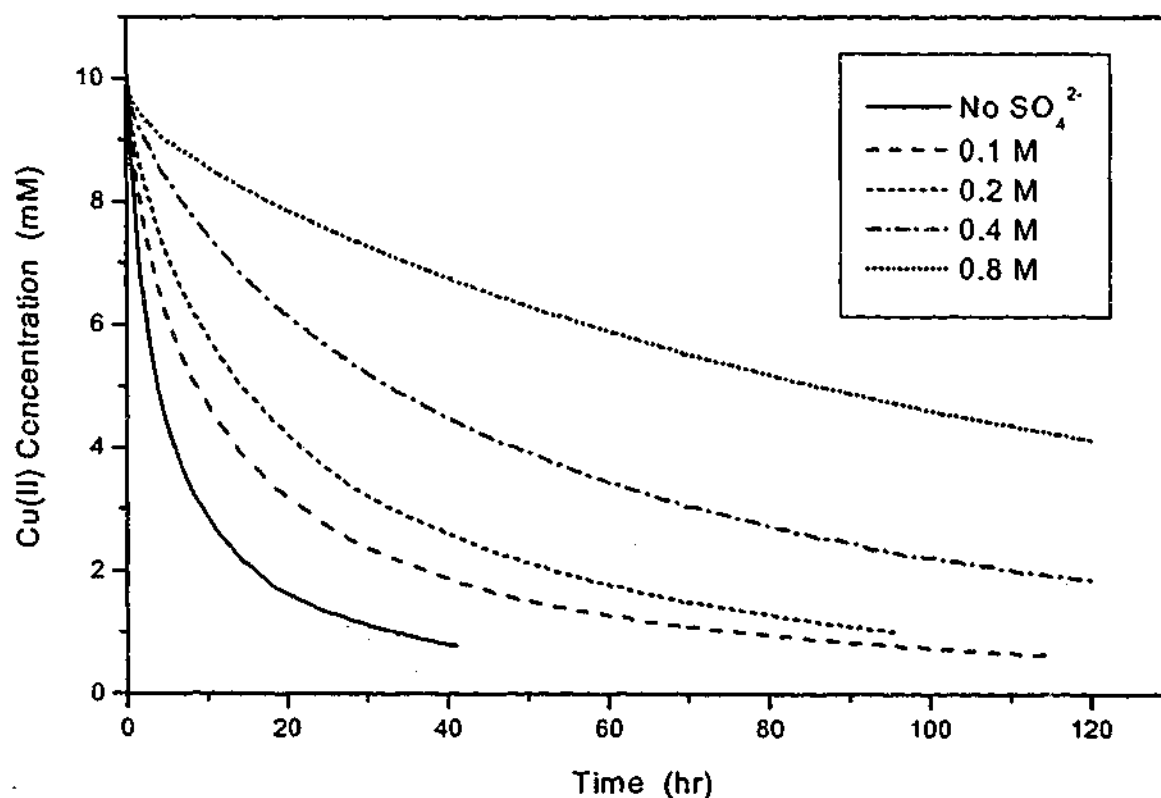


**Figure 3.6:** Effect of sulfate addition ($Na_2SO_4$) on the rate of copper(II) reduction: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

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However, it can be seen from Figure 3.6 that for solutions containing 0.8 M sulfate, the copper(II) reduction rate is significantly reduced with 5 days required for the copper(II) concentration to decrease from 10 to 4.1 mM; in comparison the copper(II) concentration is reduced to 5 mM in 4 hours in a solution without added sulfate.

Useful information concerning the effect of sulfate on the rate of copper(II) reduction can be obtained by plotting the log of initial reaction rate against the log of sulfate concentration. The slope of such a plot is simply the reaction order with respect to sulfate. However, as shown in Figure 3.7, it can be seen that the data does not exhibit a simple linear relationship. Instead, at low sulfate concentrations, there is only a weak dependence of reaction rate on sulfate concentration; the initial reaction rate at 0.01 M sulfate being very close to that measured in the absence of sulfate. However, the dependence approaches an inverse first order with respect to sulfate at high concentrations. The reason for this behaviour can be partially attributed to the presence of hydroxide, and is discussed below in section 3.3.3.
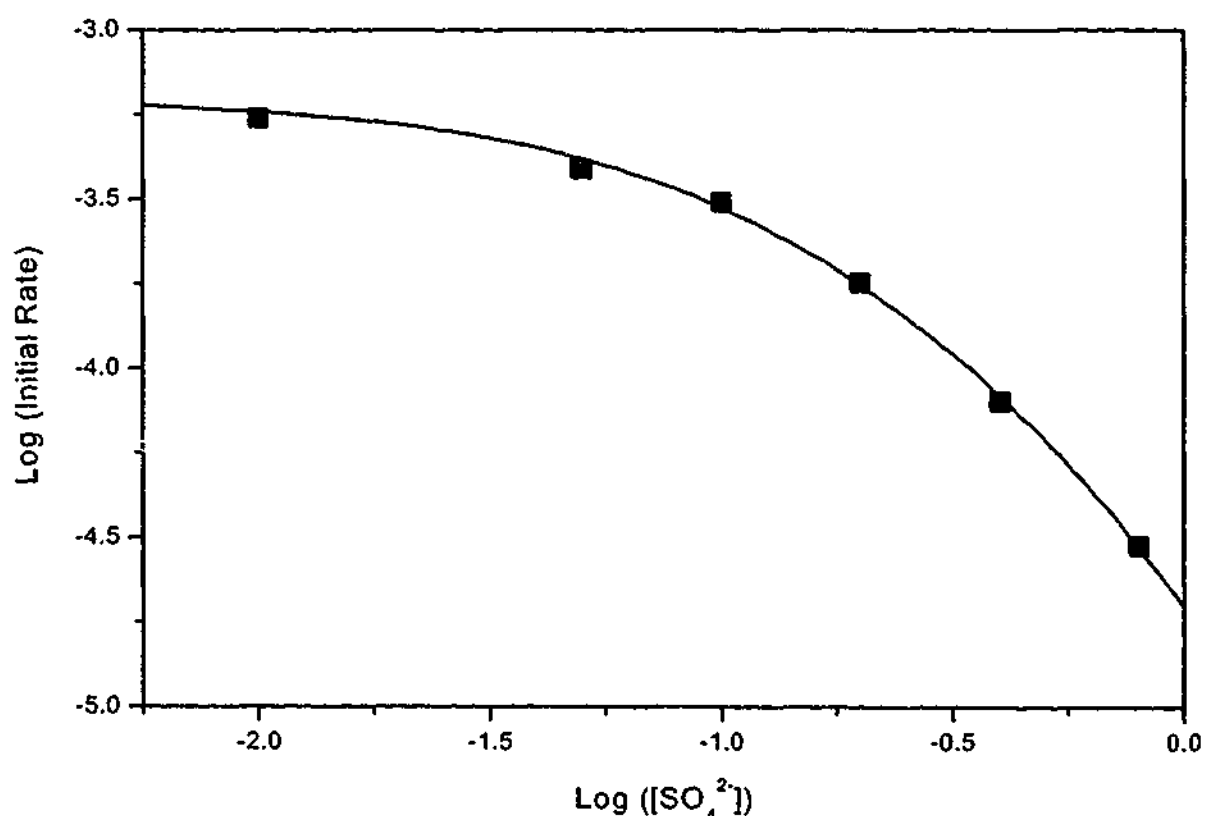


**Figure 3.7:** Initial rate dependence of copper(II) reduction on sulfate concentration: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

### 3.3.2.2 Mechanism for the Action of Sulfate Ions

To help elucidate the mechanism for the effect of sulfate on the rate of copper(II) reduction by thiosulfate, an experiment was carried out whereby thiosulfate was injected into a solution containing copper, ammonia and sulfate, instead of the standard procedure of injecting copper(II) with ammonia into a thiosulfate solution containing sulfate. Prior to injection of thiosulfate, the copper(II) was allowed to equilibrate with the ammonia and sulfate for 15 minutes. Figure 3.8 shows that the initial reaction rate in this instance was observed to involve a measurable induction period. The reaction rate then increased, reaching a maximum such that a similar profile is observed to that where the copper and ammonia were added last, except shifted by the induction time. In view of these findings, a likely explanation for the effect sulfate has on the rate of copper(II) reduction by thiosulfate is based on the following discussion.
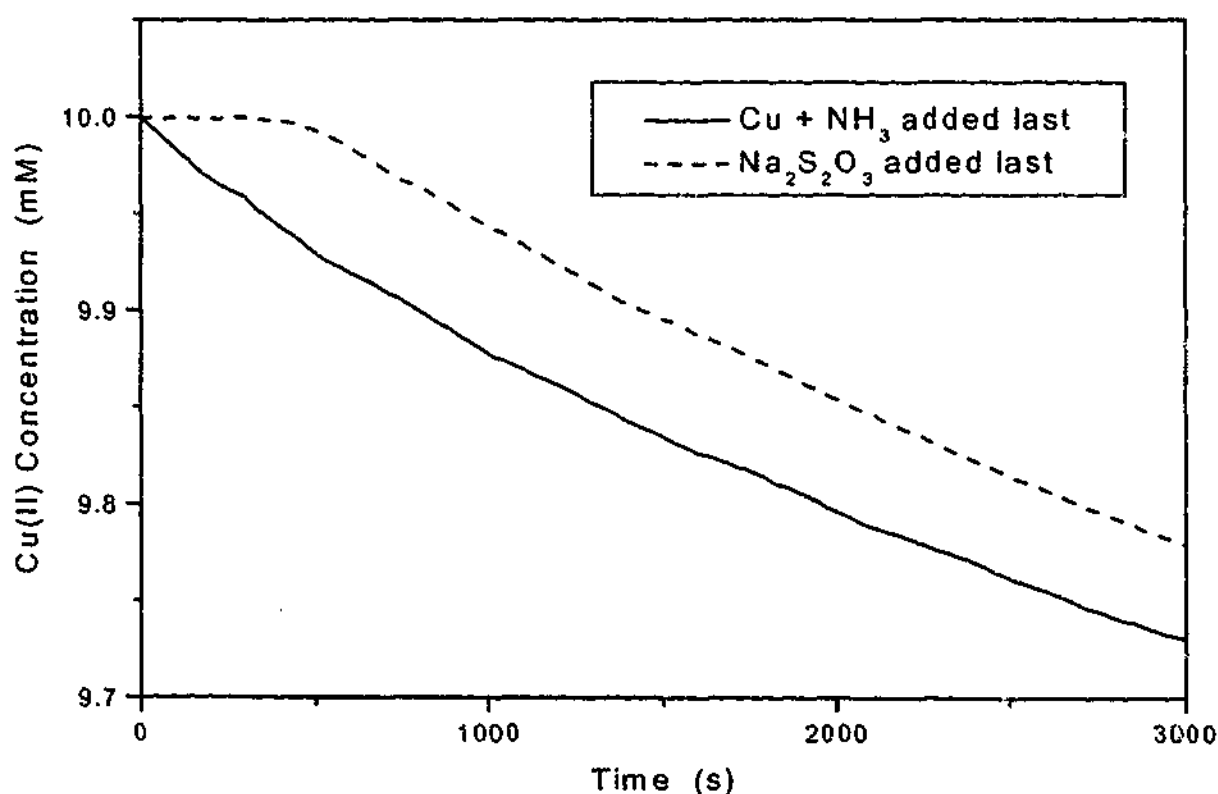


**Figure 3.8:** Dependence of the initial copper(II) reduction rate on the way the solution is mixed: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 0.8 M $Na_2SO_4$, 10 mM $CuSO_4$, 30 °C.

For solutions containing 10 mM copper(II) and 0.4 M ammonia, the copper(II) is predominantly complexed as the copper(II) tetra-ammine species with the two axial coordinate sites remaining unoccupied by ammonia; ammonia concentrations greater than 3 M are required before the copper(II) penta-ammine becomes the dominant species (Hathaway and Tomlinson, 1970). As noted previously (Byerley *et al.*, 1973a) and also seen in this study, the absorbance of the copper(II)-ammonia solution increases (~15%) upon the addition of thiosulfate. This increase in absorbance is attributed to thiosulfate displacing water from a copper(II) axial site, as shown in Equation 3.2.

$$
\begin{bmatrix} H_2O \\ NH_3 \diagdown \quad \diagup NH_3 \\ Cu \\ NH_3 \diagup \quad \diagdown NH_3 \\ H_2O \end{bmatrix}^{2+} + S_2O_3^{2-} \rightarrow \begin{bmatrix} S_2O_3 \\ NH_3 \diagdown \quad \diagup NH_3 \\ Cu \\ NH_3 \diagup \quad \diagdown NH_3 \\ H_2O \end{bmatrix} + H_2O \qquad \textbf{3.2}
$$
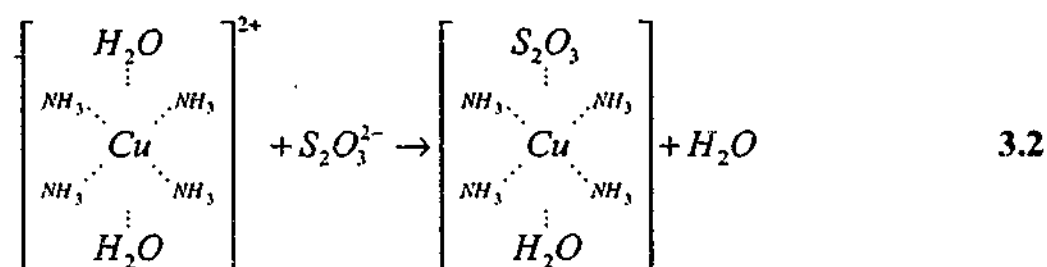
It is believed that the reaction between copper(II) and thiosulfate almost certainly occurs via a complexation first of the thiosulfate to the copper(II) at an axial coordination site. This is known as an inner sphere reaction. However, the presence of sulfate in solution increases the competition with the thiosulfate anions to complex with the copper(II) at the axial coordinate sites. The initial copper(II) absorbance was observed to decrease as the concentration of sulfate in solution increased which is consistent with this mechanism. In the instance where the experiment was performed by adding the thiosulfate to the copper(II)/ammonia/sulfate solution, the sulfate was able to substitute into the inner coordination sphere of copper(II) prior to the addition of thiosulfate. This results in a very low initial rate of reaction between the copper(II) and thiosulfate, as the thiosulfate must displace the sulfate before the reaction can occur. A similar dependence of reaction rate on the way solutions are mixed has been reported for the chloride substitution in the inner sphere reaction between $Fe^{3+}$ and $Cr^{2+}$ (Dulz and Sutin, 1964).

### 3.3.2.3  Other Anions

It has been observed that the addition of other anions also decreases the rate of copper(II) reduction by thiosulfate. The results from these experiments are shown in Figure 3.9. It can be seen that the addition of 0.1 M chloride reduces the rate of copper(II) reduction, however the effect is not as dramatic as it was for 0.1 M sulfate. The initial reaction rate in the presence of chloride is 0.65 times lower than in the absence of chloride, although it is 1.5 times higher than in the presence of 0.1 M sulfate. The addition of 0.1 M nitrate is observed to have a similar effect on the rate of copper(II) reduction to that of chloride. Figure 3.9 also shows that the addition of 0.1 M sodium phosphate to a thiosulfate leach solution almost stops the reduction of copper(II) by thiosulfate; only half the copper(II) being reduced after 4 days.
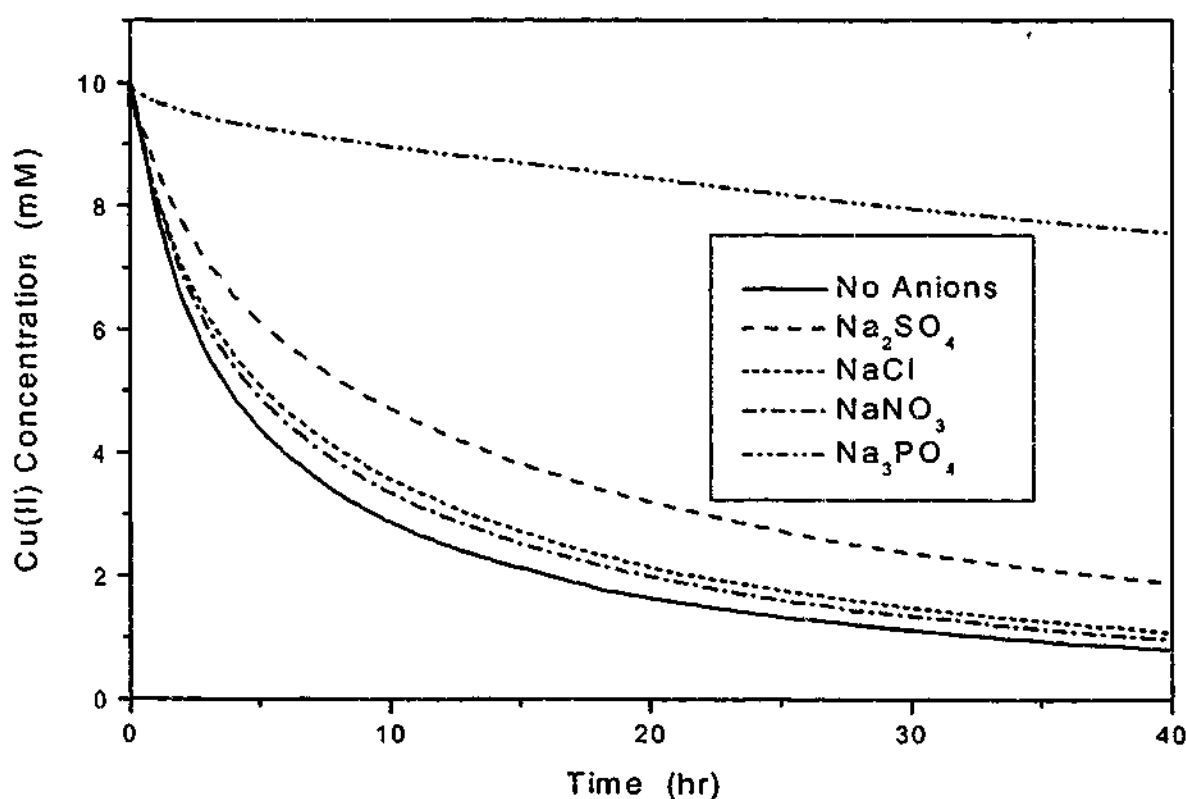


**Figure 3.9:**  Comparison of the effect 0.1 M of sulfate, chloride, nitrate and phosphate ions have on the rate of copper(II) reduction: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

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The rate of copper(II) reduction in the presence of 0.01 M phosphate (not shown in Figure 3.9) was also found to be lower than for 0.1 M sulfate, even though the concentration is an order of magnitude lower. Obviously phosphate readily complexes with the copper(II) and prevents the substitution of thiosulfate into the copper(II) inner coordination sphere. This could be partially due to the negative overall charge the copper(II) complex takes on once complexed with a phosphate ion, thus resulting in the repulsion towards other anions such as thiosulfate. Clearly, the presence of anions, and especially phosphate, stabilise the copper(II) against reduction by thiosulfate.

### 3.3.3 Solution pH

Many of the gold leaching studies have been conducted using ammonium thiosulfate (see Table 2.2). In substituting ammonium ions for sodium ions in the thiosulfate salt used, the solution pH changes according to the equilibrium shown in Equation 3.3; the pKa of ammonia is 9.25 (Weast, 1974-75).

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \qquad\qquad 3.3$$
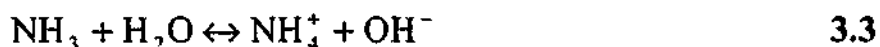
Clearly, the concentrations of ammonia and ammonium ions in solution influences the hydroxide ion concentration and hence the solution pH; the addition of ammonium ions will reduce the hydroxide ion concentration and hence pH. In solutions prepared using 0.4 M ammonia and 0.1 M sodium thiosulfate, the pH is 11.4 (the free $[OH^-]$ = 2.5 mM). The use of 0.1 M ammonium thiosulfate introduces 0.2 M of ammonium ions, which influences the equilibrium of Equation 3.3 such that a pH of 9.8 is observed.

### 3.3.3.1 Effect of Hydroxide Ions

The effect of using ammonium thiosulfate instead of sodium thiosulfate, and hence reducing the solution pH, is clearly shown in Figure 3.10 to enhance the rate of copper(II) reduction; ammonia concentration and solution ionic strength are the same

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for these solutions. Besides the substitution of ammonium ions for sodium, which is likely to have little to no effect on the solution chemistry, the hydroxide ion concentration decreases as reflected in the measured solution pH. Also shown in Figure 3.10 is that the addition of sodium hydroxide, which increases pH, reduces the rate of copper(II) reduction. These results are consistent with the copper(II) tetra-ammine being stabilised by hydroxide ions, and thus at low pH, copper(II) is more easily reduced.
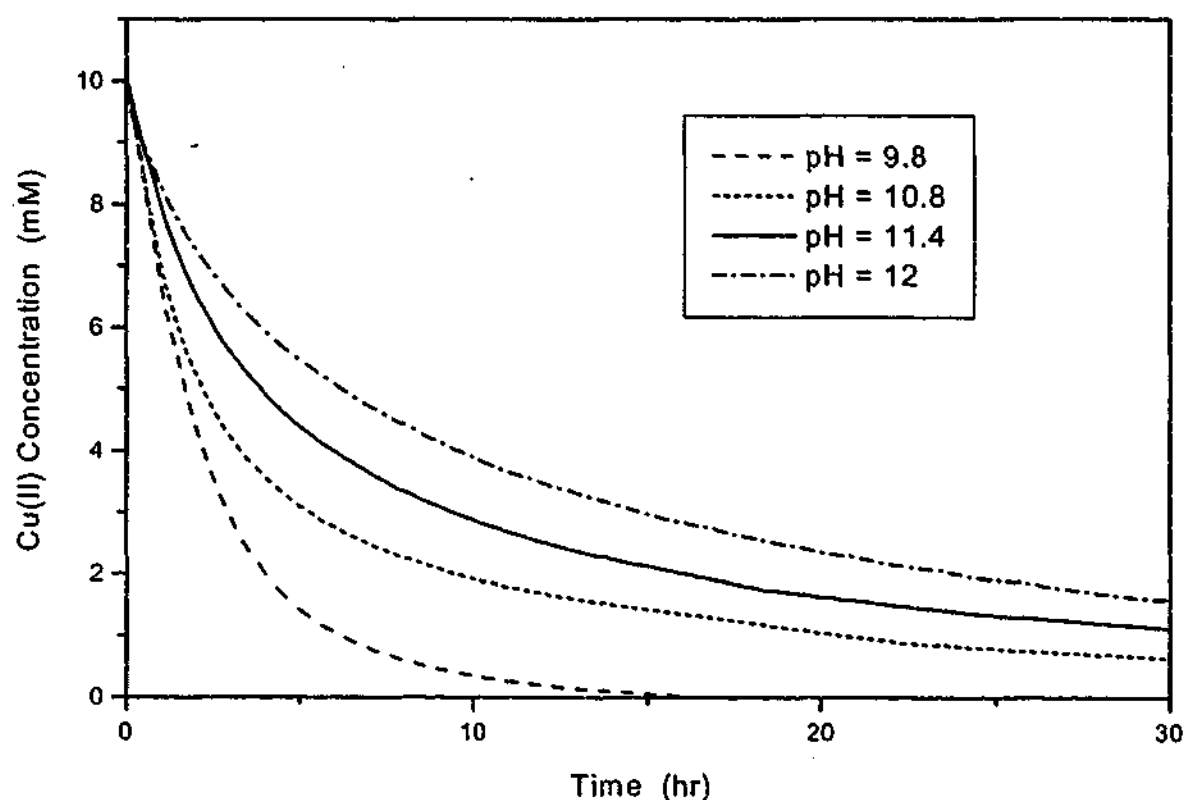


**Figure 3.10:** Effect of solution pH, adjusted by substituting $(NH_4)_2S_2O_3$ for $Na_2S_2O_3$ or the addition of NaOH, on the rate of copper(II) reduction (pH = 9.8 – 0.1 M $(NH_4)_2S_2O_3$, pH = 10.8 – 0.02 M $(NH_4)_2S_2O_3$, pH = 12 – 0.01 M NaOH): 0.1 M $S_2O_3^{2-}$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

The complexation of hydroxide ions with copper(II) in ammonia solutions has been studied previously, and it was shown that the number of hydroxide ions complexing with the copper(II) at the axial sites increased with increasing hydroxide ion concentration (Reeves and Bragg, 1962). It was also shown that at pH > 12, the copper(II) became unstable due to polymerisation, resulting in the precipitation of copper(II) from solution. Obviously hydroxide ions readily complex with copper(II)

and hence compete with the thiosulfate anions in complexing with the copper(II) at the axial coordinate sites. Thus, it is likely that in all the experiments conducted, hydroxide plays some role in reducing the rate of copper(II) reduction by thiosulfate. This is most likely why the addition of low concentrations of sulfate (0.01 M) were found in section 3.3.2.1 to have little impact on the rate of copper(II) reduction; under these conditions the copper(II) is primarily stabilised by hydroxide ions.

### 3.3.3.2 Reaction Order

An interesting aspect to the data shown in Figure 3.10 is that at the lower pH values the kinetics of copper(II) reduction deviate from second order. Figure 3.11 shows that the kinetics of copper(II) reduction at pH 9.8 are clearly no longer second order as the plot of 1/[Cu] versus time is non linear. However, the plot of log([Cu]) versus time also shown in Figure 3.11 is approximately linear, suggesting that the kinetics of copper(II) reduction at lower pH values are more consistent with a rate limiting first order reaction step.
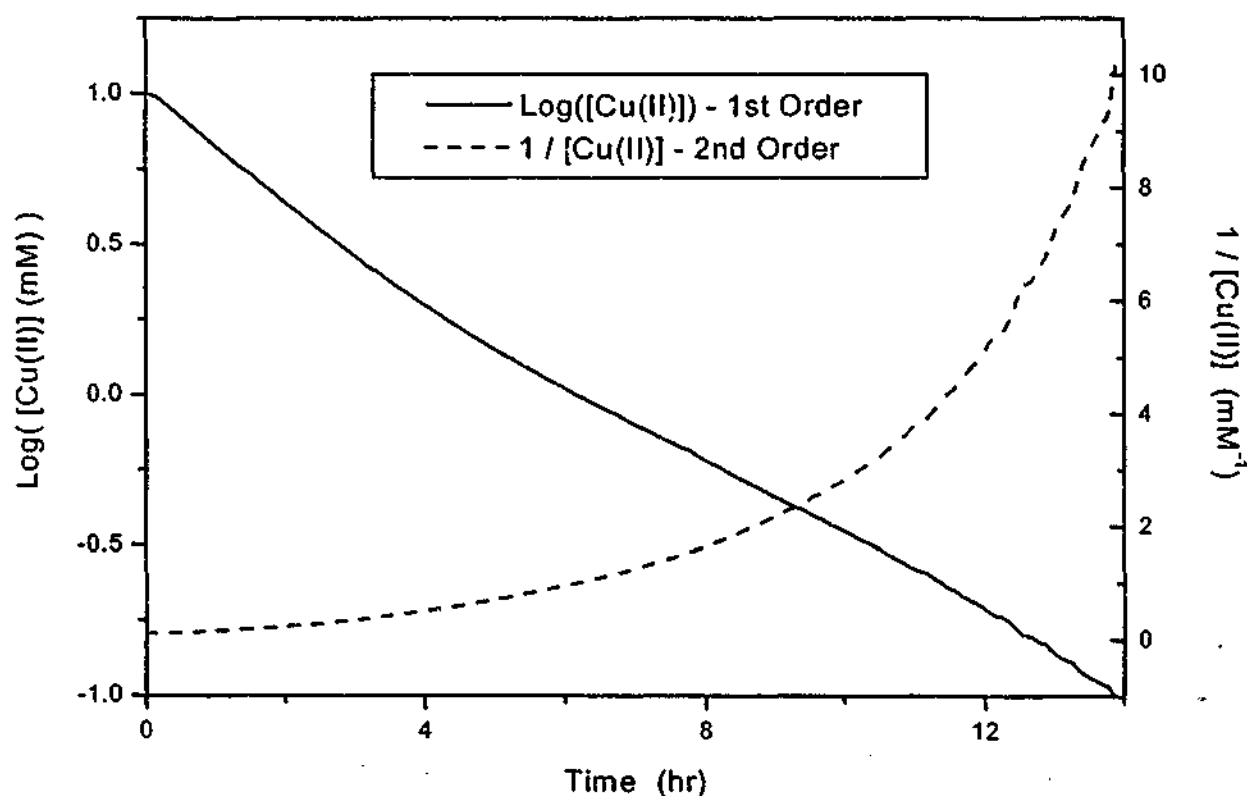


**Figure 3.11:** 1st and 2nd order plots of the copper(II) reduction kinetics at pH = 9.8: 0.1 M $(NH_4)_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

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The rate of copper(II) reduction for solutions prepared using ammonium thiosulfate rather than sodium thiosulfate were also found to compare closely with those published by Byerley *et al.* (1973a). Byerley *et al.* (1973a) also observed a similar slight S shape in the log([Cu]) versus time plot as shown in Figure 3.11. Such observations are consistent with the published kinetics by Byerley *et al.* (1973a) having been conducted using ammonium thiosulfate or that the pH was reduced below 10.

The change in reaction order of copper(II) reduction with a decrease in solution pH and hence hydroxide concentration, could be attributed to the lack of anions in solution to compete with thiosulfate for complexation at the axial coordinate sites. Expectedly, the addition of 0.4 M sodium sulfate to an ammonium thiosulfate solution, decreased the rate of copper(II) reduction. The kinetics of copper(II) reduction in this case are clearly shown in Figure 3.12 to be more consistent with a rate limiting second order reaction step.
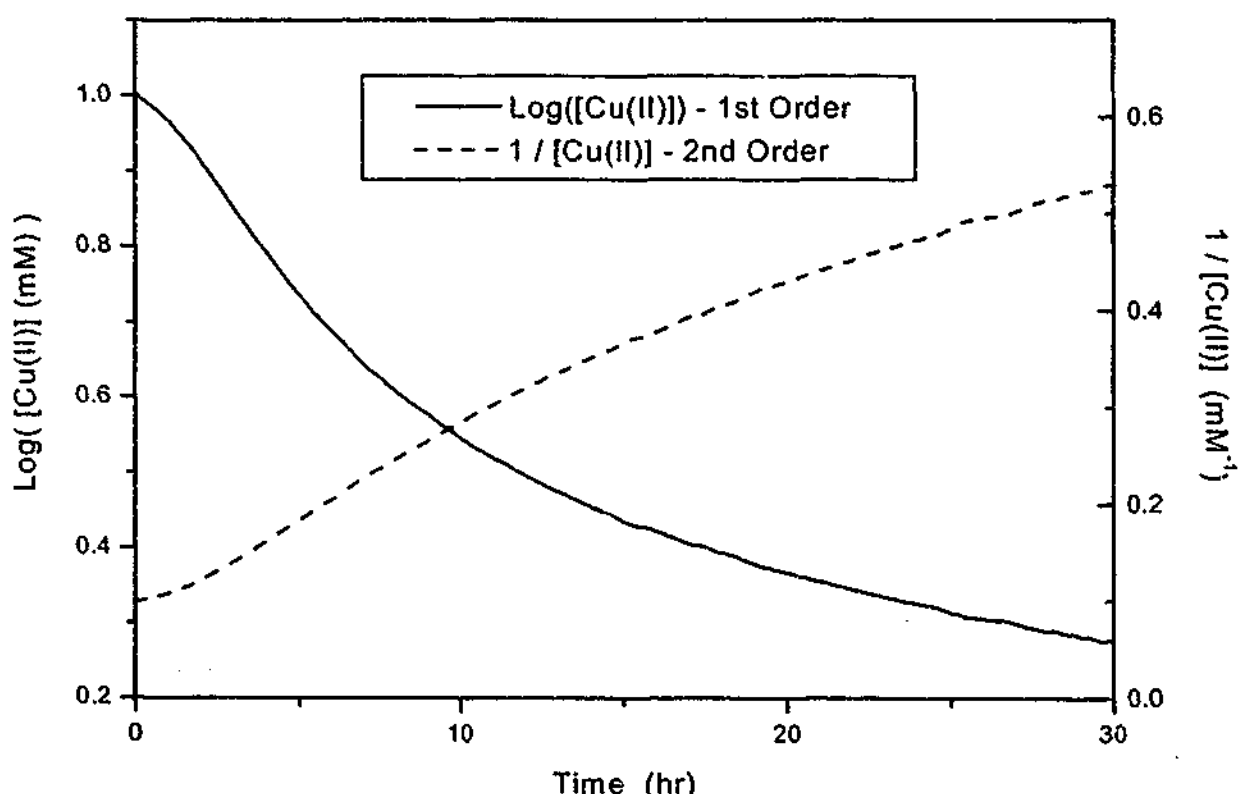


**Figure 3.12:** $1^{st}$ and $2^{nd}$ order plots of the copper(II) reduction kinetics at pH = 9.8 with the addition of sulfate: 0.1 M $(NH_4)_2S_2O_3$, 0.4 M $Na_2SO_4$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

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Thus, at low anion concentrations conceivably both of the copper(II) axial sites may be complexed by thiosulfate ions which could facilitate a more rapid copper(II) reduction to copper(I) whereby the rate limiting reaction step is shown to be a first order process. The kinetics of copper(II) reduction by thiosulfate though would appear to be rate limited by a second order reaction step unless the anion concentration is very low; a condition that will not exist in practice.

### 3.3.4  Effect of Tetrathionate

It is well recognised that tetrathionate is a product of copper(II) reduction by thiosulfate in the absence of oxygen (Byerley *et al.*, 1973a). However, the effect of tetrathionate on the rate of copper(II) reduction has not previously been considered or investigated. Thus, experiments were carried out where tetrathionate was added to the thiosulfate solution, and the results are shown in Figure 3.13. It should be clear that the addition of 10 mM tetrathionate results in copper(II) being reduced more rapidly than in the absence of added tetrathionate. This result implies that tetrathionate can also be oxidised by copper(II); the product of this reaction is possibly trithionate (Tan and Rolia, 1985). The addition of 2 mM tetrathionate is also shown in Figure 3.13 to increase the initial rate of copper(II) reduction.

### 3.3.4.1  Copper(II) Reduction by Tetrathionate

A better interpretation of the results can be made by plotting the rate of copper(II) reduction (slope of the copper(II)-time profiles in Figure 3.13) versus the copper(II) concentration as shown in Figure 3.14. Clearly, the addition of 10 mM tetrathionate results in the rate of copper(II) reduction being significantly greater than that observed in the absence of added tetrathionate. Hence, tetrathionate is also being oxidised by copper(II). However, the copper(II) reduction rate for the addition of 2 mM tetrathionate is observed to match that obtained in the absence of added tetrathionate once the copper(II) concentration had reduced below 4 mM.
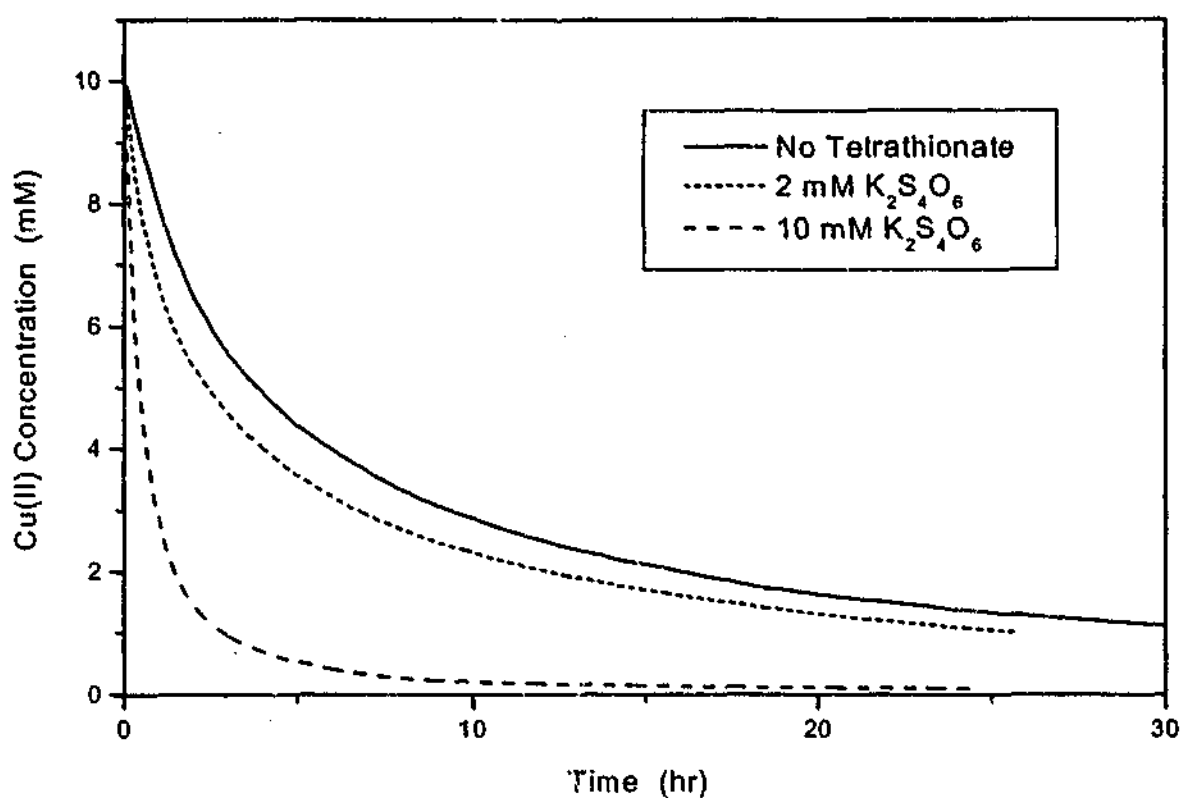
**Figure 3.13:** Effect of added tetrathionate ($K_2S_4O_6$) on the rate of copper(II) reduction by thiosulfate: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.
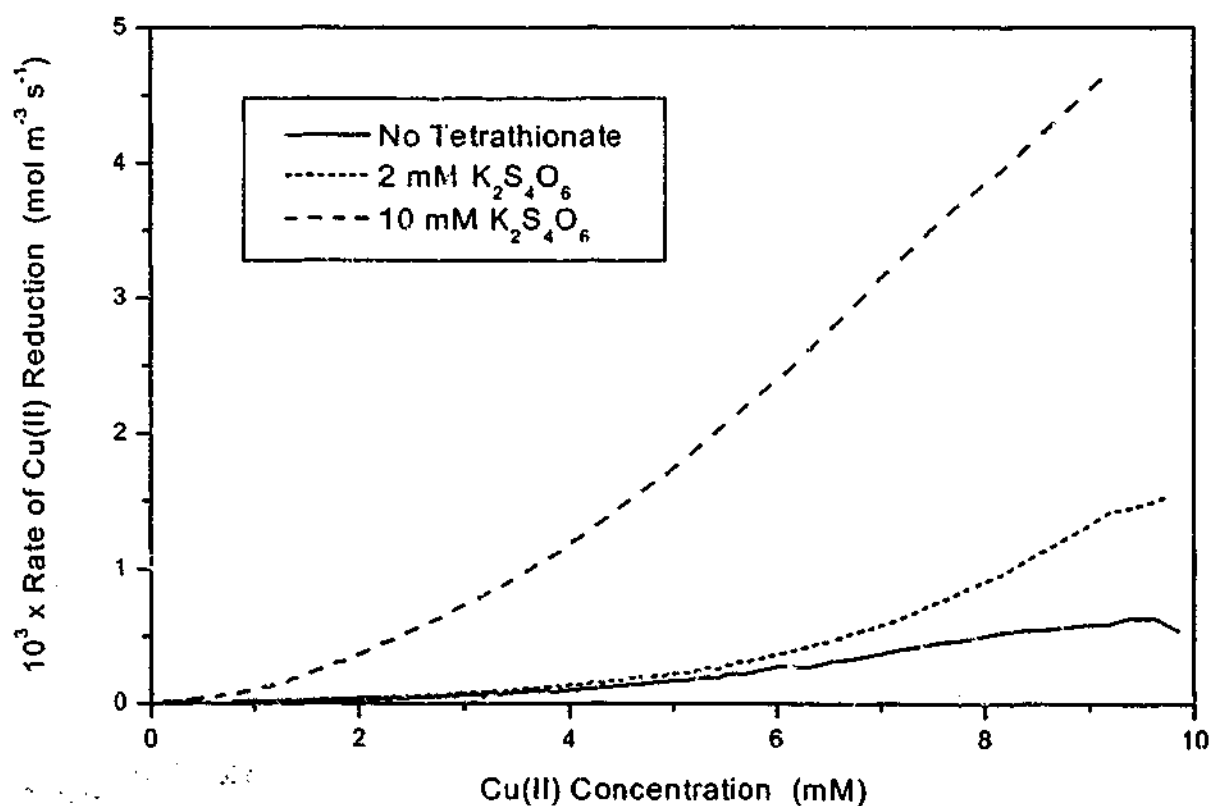


**Figure 3.14:** Rate of copper(II) reduction by thiosulfate in the presence and absence of added tetrathionate: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

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Interpretation of the results shown in Figure 3.14 is complicated by the fact that tetrathionate is a product from the oxidation of thiosulfate, as well as being capable of reducing copper(II), as indicated by Equations 3.4 and 3.5, where X is a higher oxidation state oxysulfur species, possibly trithionate (Tan and Rolia, 1985).

$$2Cu^{2+} + 2S_2O_3^{2-} \rightarrow 2Cu^+ + S_4O_6^{2-} \qquad \textbf{3.4}$$

$$Cu^{2+} + S_4O_6^{2-} \rightarrow Cu^+ + X \qquad \textbf{3.5}$$
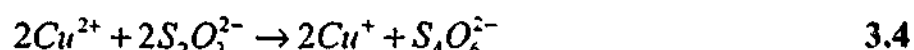
In the absence of added tetrathionate, the concentration of tetrathionate will slowly increase due to the reaction of thiosulfate with copper(II). Whilst this is occurring, the reaction rate between tetrathionate and copper(II) is also increasing due to the increase in tetrathionate concentration. It can be readily demonstrated that for the reaction sequence shown in Equations 3.4 and 3.5, since thiosulfate is in large excess, the tetrathionate concentration will reach a 'steady state' value at which the rate of tetrathionate formation equals the rate of tetrathionate oxidation. This is shown schematically in Figure 3.15 where copper(II) reduction has been modelled by Equations 3.4 and 3.5 in the absence and presence of added tetrathionate. In the instance where tetrathionate was added to the thiosulfate leach solution, both reactions 3.4 and 3.5 are able to occur initially. Since the reaction between tetrathionate and copper(II) is relatively fast, the rate of formation of tetrathionate is slower than the rate of tetrathionate oxidation. Thus, the tetrathionate concentration will decrease. It is a simple matter to demonstrate, as shown Figure 3.15 by modelling Equations 3.4 and 3.5, that the concentration of tetrathionate will become independent of the initial tetrathionate concentration, provided that there is enough copper(II) in order for this 'steady state' to be reached. The data shown in Figure 3.14 for 2 mM added tetrathionate suggests that such a 'steady state' is achieved at 4 mM copper(II), since this is the concentration at which the copper(II) reduction rate equals the rate in the absence of added tetrathionate. In the case where 10 mM tetrathionate is added, the 'steady state' is not obtained before all the copper(II) has been reduced.
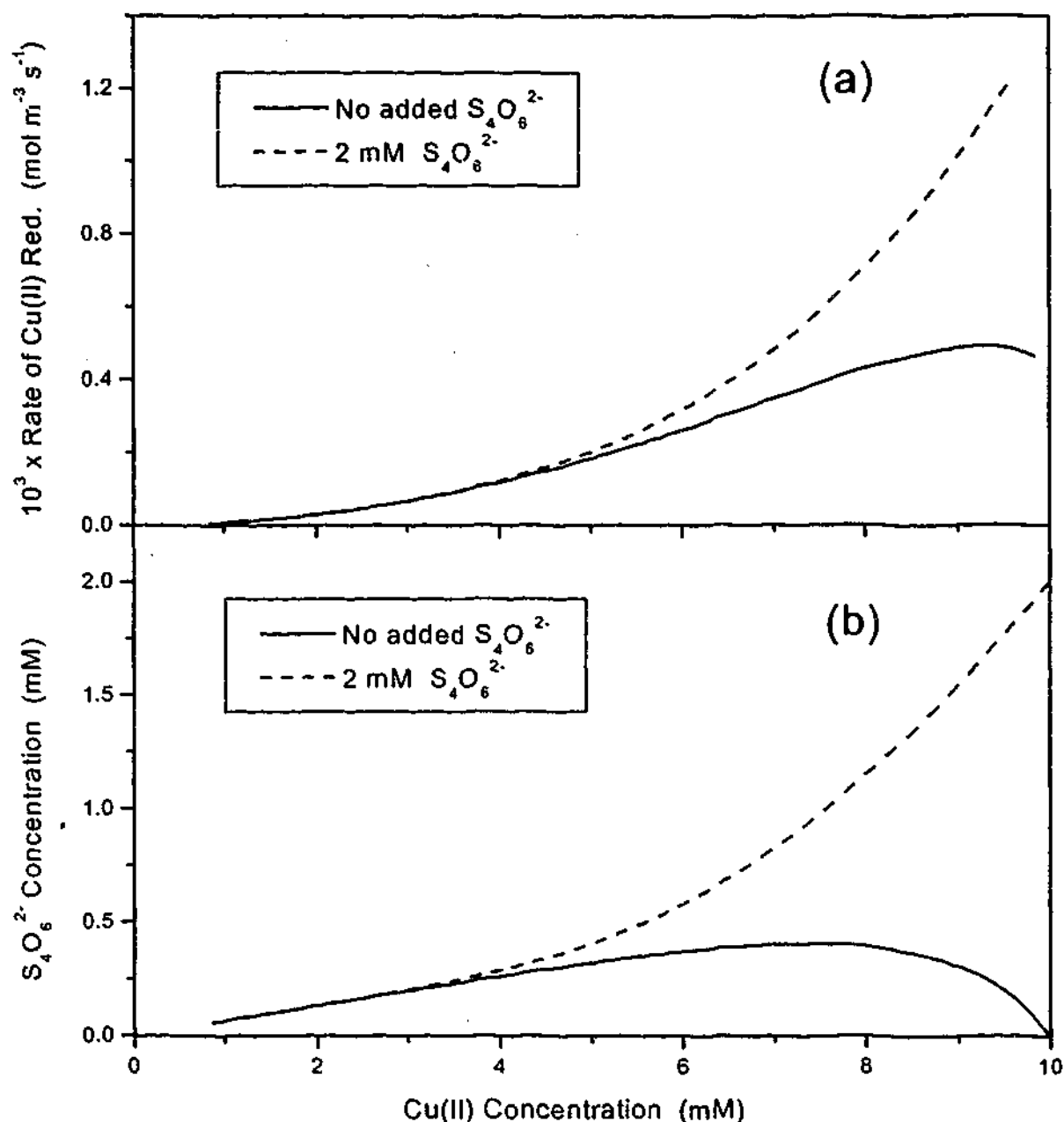
**Figure 3.15:** Model prediction of the rate of copper(II) reduction (a) and tetrathionate concentration (b) in the presence and absence of added tetrathionate: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

### 3.3.4.2 Effect of Sulfate

The effect of sulfate on the rate of copper(II) reduction by tetrathionate in the presence of thiosulfate has also been studied. Shown in Figure 3.16 is the effect of 0.4 M sulfate on the copper(II) reduction rate in the presence of thiosulfate and 10 mM tetrathionate. It should be clear that sulfate addition has little effect on the initial copper(II) reduction rate. These results are consistent with the reduction of copper(II)

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by tetrathionate occurring via an outer sphere mechanism since sulfate ions hinder the inner sphere by complexing with copper(II) at the axial sites. Hence, the tetrathionate does not need to complex with the copper(II) in order for the reaction to occur.
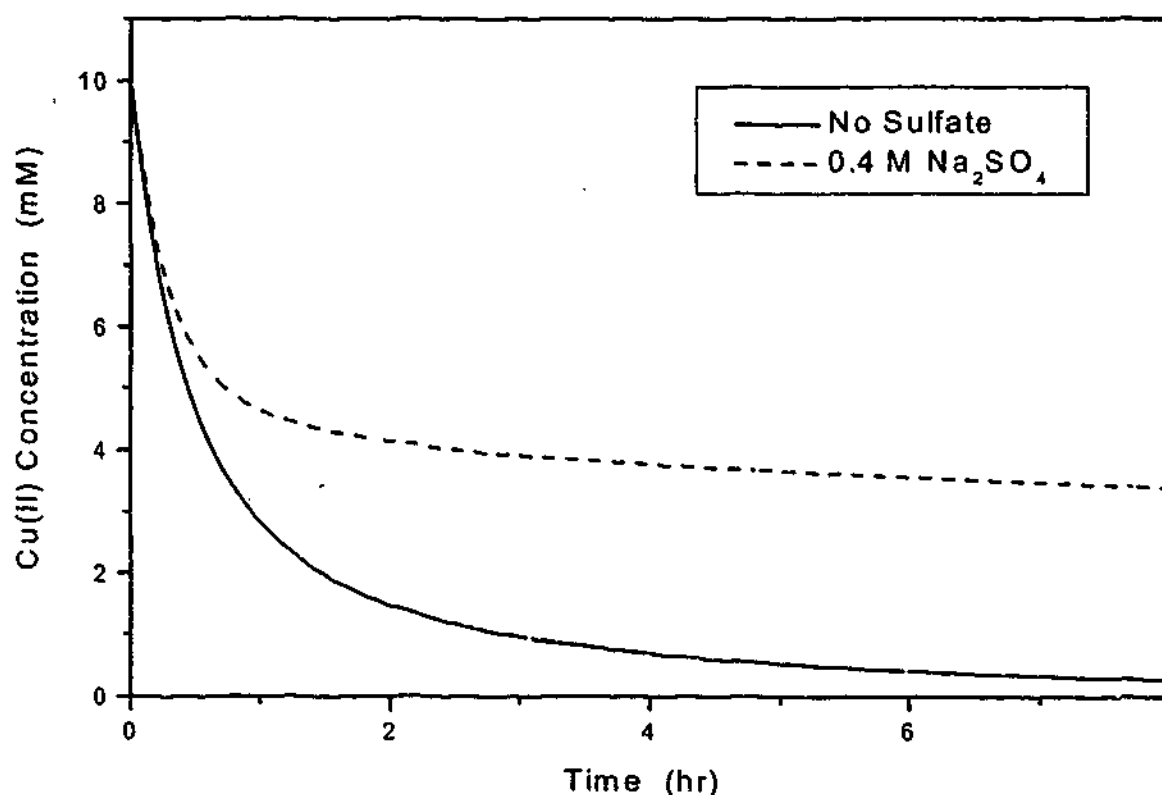


**Figure 3.16:** Effect of sulfate on the rate of copper(II) reduction by tetrathionate in thiosulfate solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 10 mM $K_2S_4O_6$, 30 °C.

These findings are important in terms of the concentration of tetrathionate that could be expected in solution in the absence of oxygen. When sulfate is added to solution, the reaction between thiosulfate and copper(II) is slowed, whilst the reaction between tetrathionate and copper(II) is relatively unaffected. Since the steady state tetrathionate concentration is achieved when the rates of these reactions are equal, it should be clear that the tetrathionate concentration at steady state would be significantly lower in the presence of sulfate. In a similar manner, if the reaction between copper(II) and thiosulfate is accelerated by adding ammonium ions, the tetrathionate concentration at steady state will be significantly higher. This will have significant ramifications for the resin recovery of gold from thiosulfate solutions, since it is known that tetrathionate decreases the gold loading (Nicol and O'Malley, 2001).

Another interesting aspect of the data shown in Figure 3.16 is that in the presence of sulfate, the rate of copper(II) reduction becomes very slow at around 4 mM copper(II). In fact, by comparing Figures 3.16 and 3.6, it can be seen that the rate is only slightly higher than that for 0.4 M sulfate in the absence of any added tetrathionate below 4 mM copper(II). Such a result suggests that almost all of the tetrathionate (10 mM) has been consumed, even though the copper(II) concentration has only decreased by 6 mM. Since it is likely that the stoichiometry of the reaction between copper(II) and tetrathionate will be 1:1, the results shown in Figure 3.16 are consistent with another reaction consuming tetrathionate. A reaction sequence that could account for this result is described below.

As discussed in the section 2.2.1 of the review, tetrathionate is a meta-stable species that undergoes decomposition in alkaline solutions (Zhang and Dreisinger, 2002, Naito *et al.*, 1970, Rolia and Chakrabarti, 1982). Since the reaction between tetrathionate and hydroxide ions involves ions of like charge, the reaction rate is likely to increase with increased ionic strength (Laidler, 1963). So when the solution contains 0.4 M sulfate, some of the tetrathionate reacts with copper(II), whilst some is decomposed to form trithionate and other oxysulfur species. Even if the trithionate reacts with copper(II), as is shown in section 3.3.5 below, less than 10 mM copper(II) will be consumed as only 1 trithionate is formed per 2 tetrathionate reacted according to Equation 2.15. The decomposition of some tetrathionate to form trithionate though would account for the slightly higher copper(II) reduction rate below 4 mM copper(II), as more trithionate is generated than in the absence of added tetrathionate. In the absence of sulfate, the reaction between tetrathionate and hydroxide will occur more slowly, and hence more copper(II) is reduced by tetrathionate.

## 3.3.5 Effect of Trithionate

As discussed in the review, trithionate is likely to be formed in thiosulfate leach solutions. Trithionate has been found to decompose slowly at room temperature in alkaline solutions (Rolia and Chakrabarti, 1982) and hence is considered to be relatively stable in alkaline thiosulfate solutions (Fleming, 2000, Byerley *et al.*, 1973a). However, it is only meta-stable and may be oxidised by copper(II).

### 3.3.5.1 Copper(II) Reduction by Trithionate

An experiment where 10 mM trithionate was added to the thiosulfate leach solution was performed, the result of which is shown in Figure 3.17. Clearly, the rate of copper(II) reduction is increased in the presence of trithionate indicating that trithionate is oxidised by copper(II) in thiosulfate solutions. Figure 3.17 also shows the effect of sulfate addition on the rate of copper(II) reduction in solutions containing thiosulfate and trithionate. In this case the rate of reaction in the presence of trithionate is greatly reduced by the addition of sulfate. A similar result was observed for the reaction between copper(II) and thiosulfate. These results are consistent with the oxidation of trithionate by copper(II) also being an inner sphere reaction. Since it is known that trithionate also decreases the gold loading on resins (Nicol and O'Malley, 2001), further research is required to establish the long term effect of the solution conditions on the trithionate concentration, especially in the presence of oxygen. However, this is beyond the focus of the research presented in this thesis.
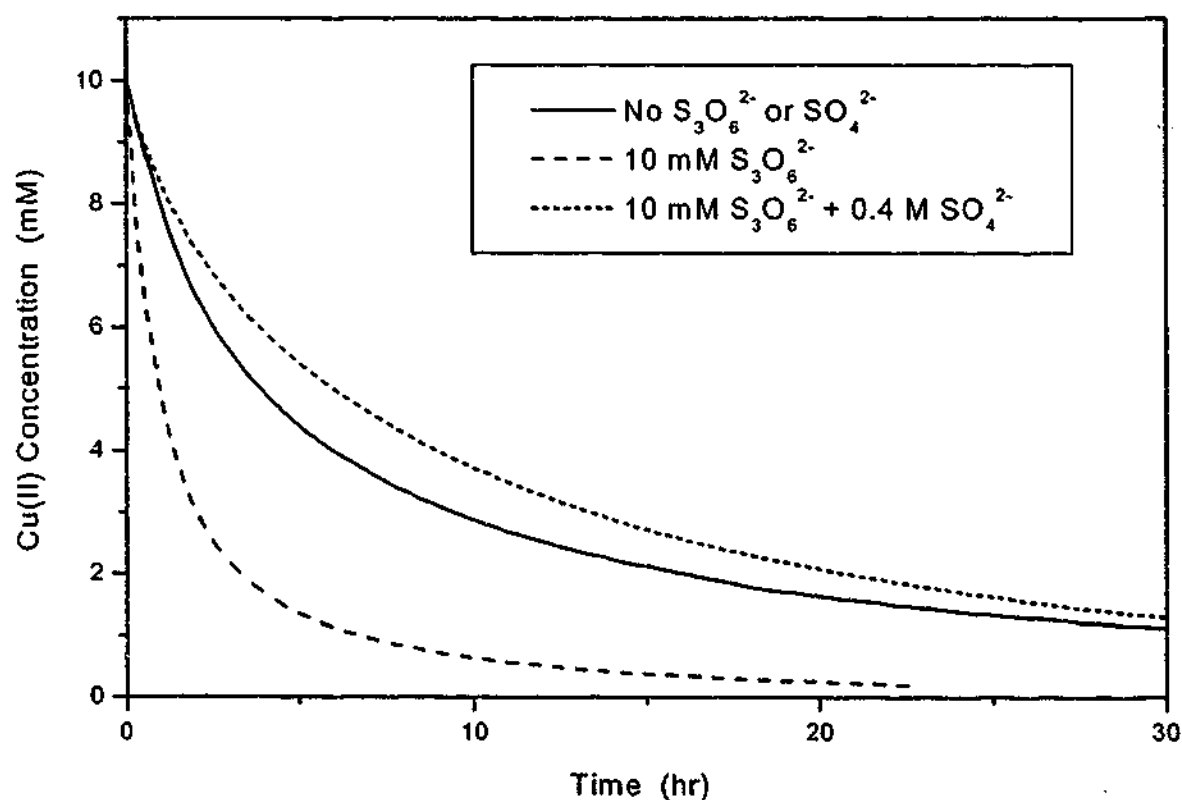


**Figure 3.17:** Effect of added trithionate and trithionate plus sulfate on the rate of copper(II) reduction in thiosulfate solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

### 3.3.6 Effect of Sulfite

A number of researchers have advocated the use of sulfite as an additive either to minimise thiosulfate oxidation (Hemmati *et al.*, 1989, Marchbank *et al.*, 1996), or to inhibit the decomposition of thiosulfate to form sulfide (Kerley, 1983). As copper(II) is the oxidant within the leach system, the effect that the addition of sulfite (a reductant) has on the chemistry of thiosulfate leach solutions was studied.

### 3.3.6.1  Copper(II) Reduction by Sulfite

The reaction between copper(II) and sulfite was studied in the presence of thiosulfate, and the results from these experiments are shown in Figure 3.18. Clearly, the presence of sulfite dramatically increases the rate of copper(II) reduction in thiosulfate solutions. At sulfite concentrations equal to the initial copper(II) concentration (10 mM), the copper(II) reduction rate is substantially faster than for the same solution without sulfite; the initial copper(II) reduction rate is 15 times higher than in the absence of sulfite. Such a result implies that sulfite is being rapidly oxidised by copper(II); sulfite like thiosulfate is only meta-stable. Thus, any addition of sulfite to the leach solution will only result in the rapid reduction in copper(II) concentration and hence reduce the gold leach rate (see Chapter 6). The kinetic plot for a solution containing 2 mM sulfite (20% of the copper(II) concentration) is also shown in Figure 3.18. Clearly the initial rate of copper(II) reduction is also rapid as observed for 10 mM added sulfite. However the rate of copper(II) reduction decreases rapidly at 7 mM copper(II) and the reaction rate as a function of copper(II) concentration (graph not shown) approaches that observed for the same solution without added sulfite. Below 7 mM copper(II), the copper(II) reduction rate overlays that obtained in the absence of sulfite. Such a result indicates that copper(II) is reduced rapidly by sulfite, but once all the sulfite has been consumed the copper(II) reduction rate returns to that observed in the absence of sulfite.

Another important finding that can be inferred from the results for the solution containing 2 mM sulfite is the stoichiometry of the reaction between sulfite and copper(II). The oxidation of sulfite is known to produce either sulfate or dithionate

$(S_2O_6^{2-})$ as the reaction product (Lappin, 1994), as shown in the simplified Equations 3.6 and 3.7 respectively (copper ligands ignored).

$$2Cu^{2+} + SO_3^{2-} + 2OH^- \rightarrow 2Cu^+ + SO_4^{2-} + H_2O \qquad\qquad \textbf{3.6}$$

$$Cu^{2+} + SO_3^{2-} \rightarrow Cu^+ + 0.5S_2O_6^{2-} \qquad\qquad \textbf{3.7}$$
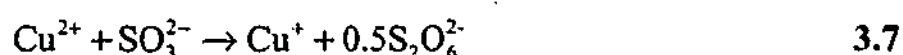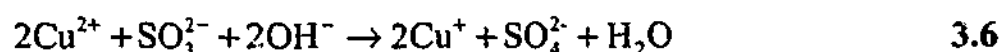
The results shown in Figure 3.18 suggest that in oxidising 2 mM sulfite, about 3 moles of copper(II) were reduced. Considering that some of the copper(II) reduction will be as a result of its reaction with thiosulfate and the generated tetrathionate from this reaction, it could be argued that the stoichiometry of sulfite oxidation is 1 sulfite per 1 copper(II). Such a result implies that dithionate is the main reaction product from the oxidation of sulfite by copper(II).
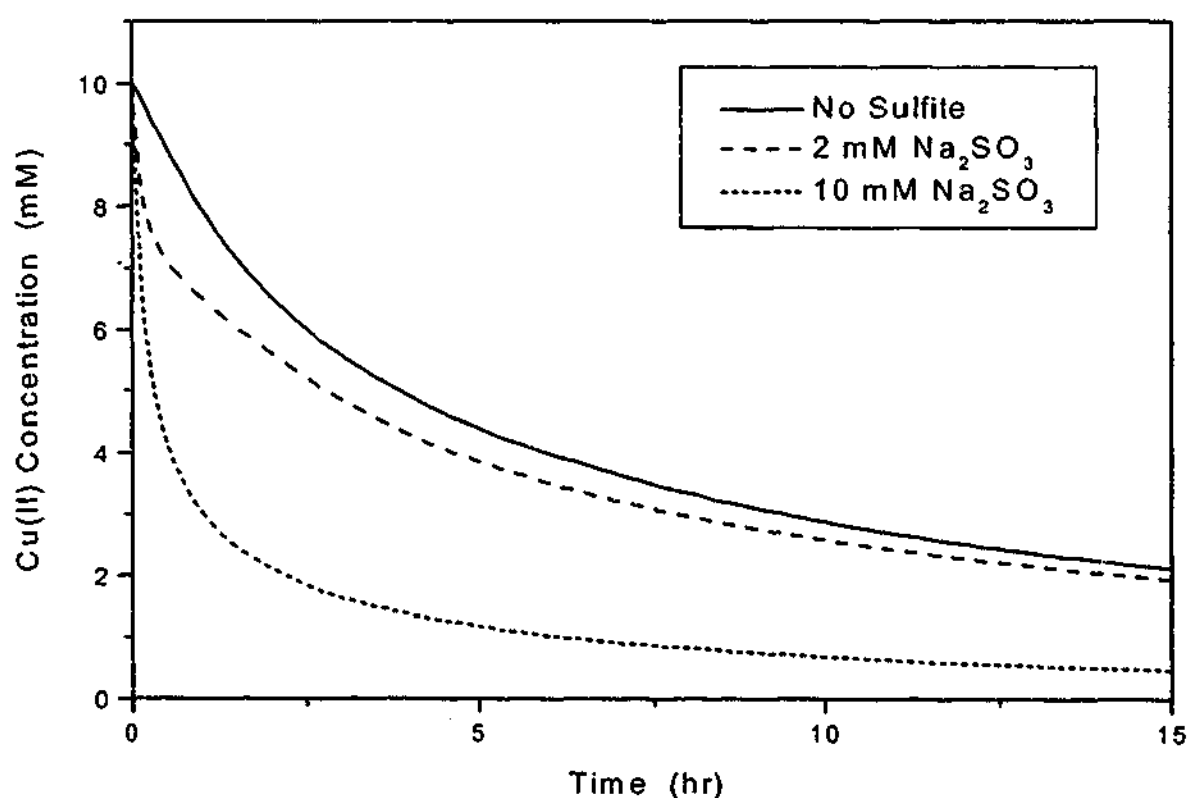


**Figure 3.18:** Effect of sulfite on the rate of copper(II) reduction in thiosulfate solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C.

### 3.3.6.2 Effect of Sulfate

The oxidation of sulfite by copper(II) in the presence of sulfate was also investigated, and the results are shown in Figure 3.19. It can be seen that the rate of copper(II) reduction in the presence of sulfite is greatly reduced by the addition of sulfate. This result is similar to that observed for the reduction of copper(II) by thiosulfate and trithionate. Such a result suggests that the oxidation of sulfite by copper(II) is also an inner sphere reaction, and the role of sulfate addition is to hinder the incorporation of sulfite into the copper(II) coordination sphere. It has been previously published that the oxidation of sulfite by metal ions is dependant on the metal ion lability (Lappin, 1994). For outer sphere reactions, sulfate is the dominant product with a reaction stoichiometry of 1:2 sulfite to metal ion. For labile metal ions, inner sphere reactions produce dithionate as the major reaction product with a stoichiometry of 1:1. The results presented here are consistent with an inner sphere reaction with dithionate as the reaction product.
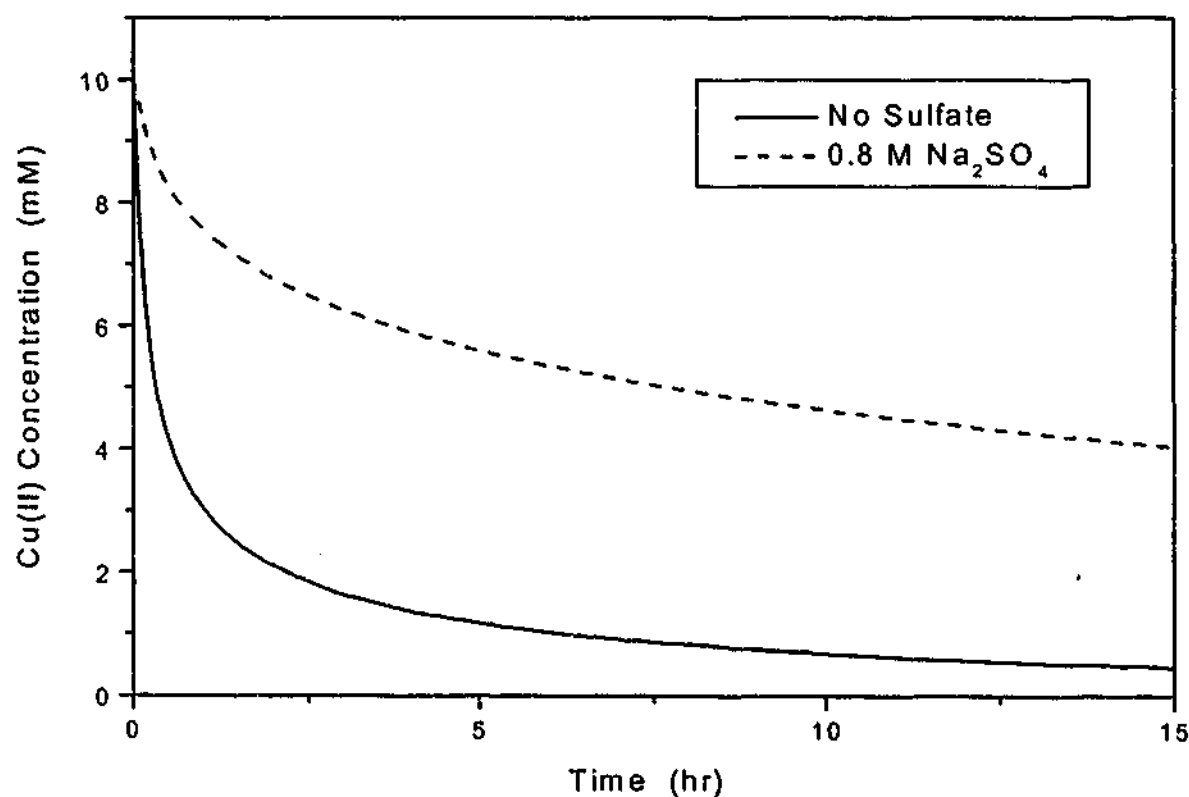


**Figure 3.19:** Effect of sulfate on the rate of copper (II) reduction by sulfite in thiosulfate solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 10 mM $Na_2SO_3$, 30 °C.

### 3.3.7 Effect of Experimental Variables

In light of the results presented in the previous sections indicating that the reduction of copper(II) in thiosulfate solutions in the absence of oxygen is complex, the effect each of the experimental variables has on the rate of copper(II) reduction was further studied. The objective was thus to gain insight as to the effect of experimental variables on the copper(II)-time profile for solutions applicable to gold leaching in the absence of oxygen.

### 3.3.7.1 Copper(II) Concentration

The effect of varying the initial copper(II) concentration on the kinetics of the copper(II) reduction was investigated. Interpretation of this data is best shown by a plot of copper(II) reduction rate versus copper(II) concentration as shown in Figure 3.20. Clearly, the initial rate of copper(II) reduction is dependent of the initial copper concentration, though the rates are similar at the same copper(II) concentration.
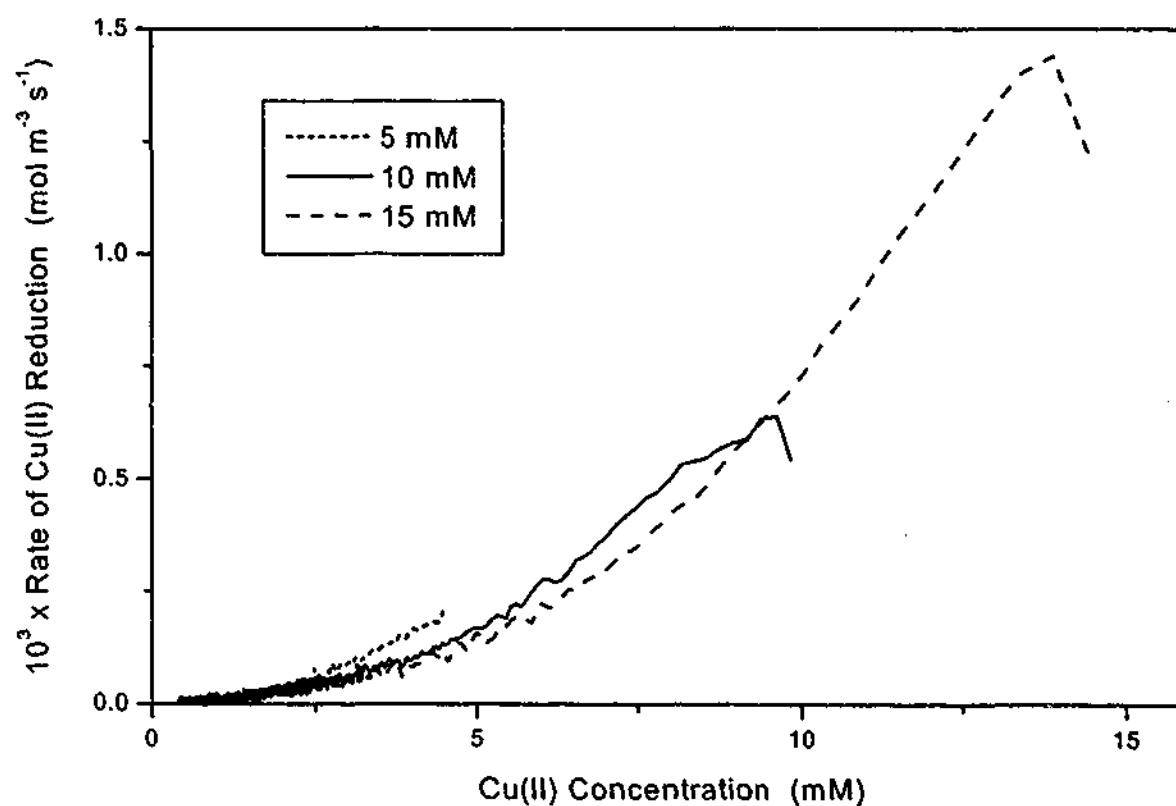


**Figure 3.20:** Effect of copper(II) concentration on the rate of copper(II) reduction as a function of copper(II) concentration: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 30 °C.

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An exact overlay of the curves shown in Figure 3.20 is not seen due to the small reduction in thiosulfate concentration according to the reaction shown in Equation 3.1. This result indicates that copper(I) has no effect on the reaction rate and hence the reduction of copper(II) is irreversible. Such a result is hardly surprising.

### 3.3.7.2  Thiosulfate Concentration

The effect of thiosulfate concentration on the kinetics of copper(II) reduction is shown in Figure 3.21. Not surprisingly, the rate of copper(II) reduction by thiosulfate is reduced at lower thiosulfate concentrations and the profiles are similar. The reaction order with respect to thiosulfate concentration can be calculated using the initial rate at time zero (the only point for which the thiosulfate concentration is truly known), and plotting $\ln(r_0)$ vs. $\ln[S_2O_3{}^{2-}]$. From this graph, it was found that the reaction order is 1.1.
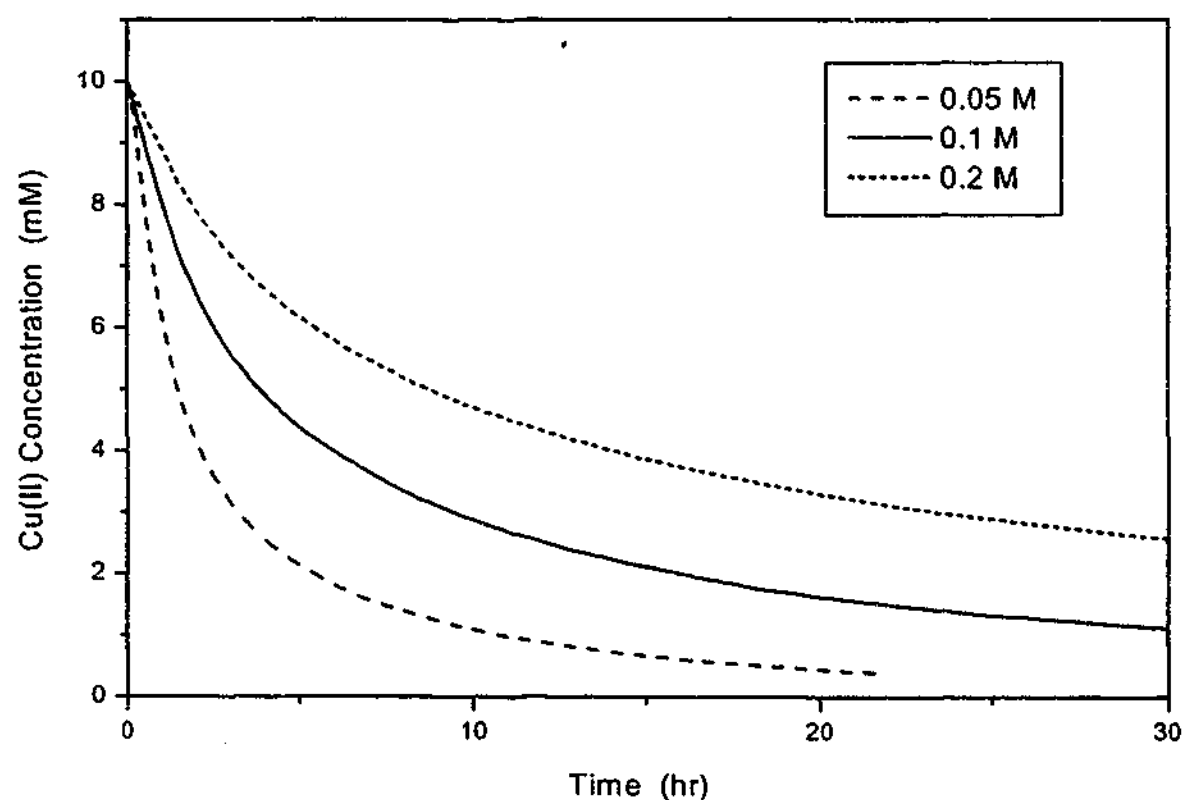


**Figure 3.21:**  Effect of thiosulfate concentration on the rate of copper(II) reduction in thiosulfate solutions: 0.4 M NH$_3$, 10 mM CuSO$_4$, 30 °C.

### 3.3.7.3 Ammonia Concentration

Figure 3.22 shows the effect of ammonia concentration on the rate of copper(II) reduction in thiosulfate solutions. It can be seen that there is a very strong inverse relationship between the rate of copper(II) reduction 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. Obviously, ammonia is an integral part of the reaction mechanism. It has been suggested that the copper(II) tetra-ammine is in equilibrium with the copper(II) tri-ammine complex, and it is the tri-ammine complex which reacts with thiosulfate (Byerley *et al.*, 1973a). This mechanism is shown in Equation 2.20. However, this mechanism only predicts an order of -1 with respect to ammonia concentration. Clearly, the reaction is more complicated than previously thought. Maintaining sufficient ammonia in solution is thus vital to minimising the rate of copper(II) reduction in thiosulfate leach solutions.
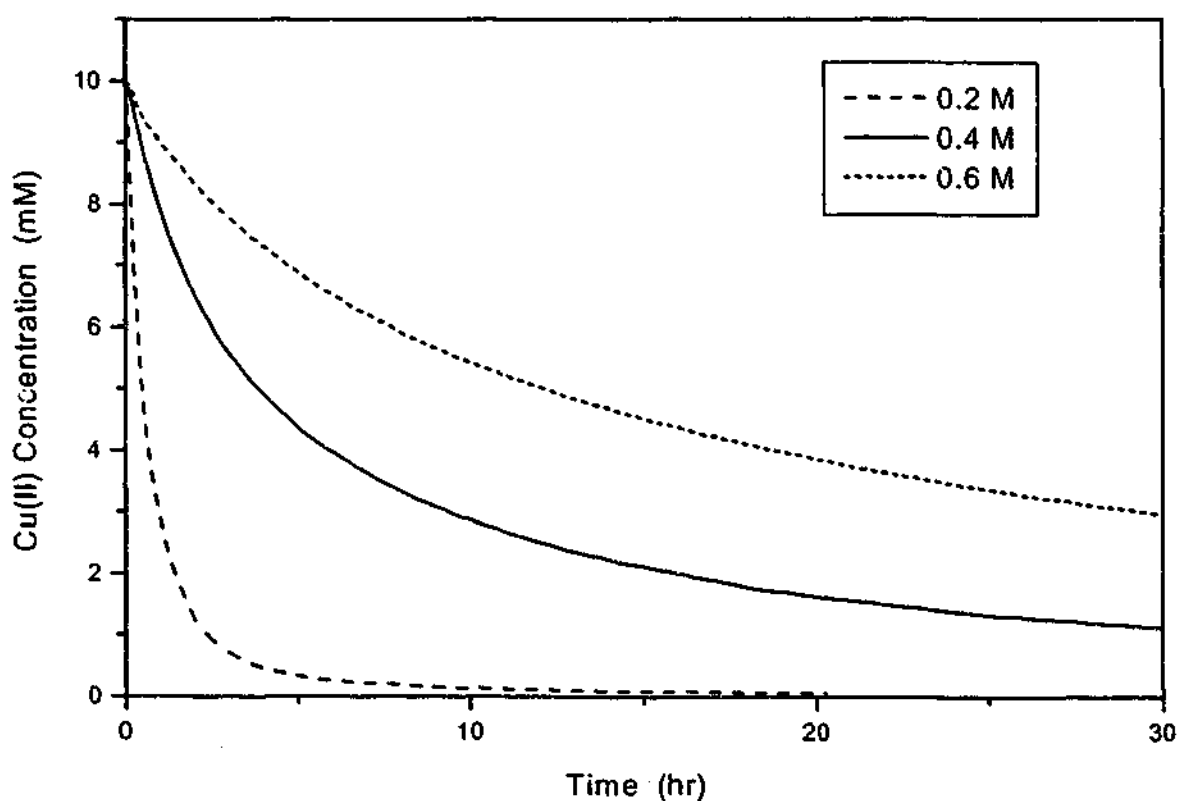


**Figure 3.22:** Effect of ammonia concentration on the rate of copper(II) reduction in thiosulfate solutions: 0.1 M $Na_2S_2O_3$, 10 mM $CuSO_4$, 30 °C.

### 3.3.7.4 Temperature

The effect of temperature on the rate of copper(II) reduction was studied, and Figure 3.23 shows the results obtained. As expected the rate of copper(II) reduction increases with increasing temperature. The activation energy of the process was calculated using an Arrhenius plot of ln(rate) vs. 1/T to be $110 \pm 5$ kJ mol$^{-1}$. Clearly, increasing the temperature to enhance the gold dissolution kinetics would have to be carefully evaluated against the increased rate of copper(II) reduction.
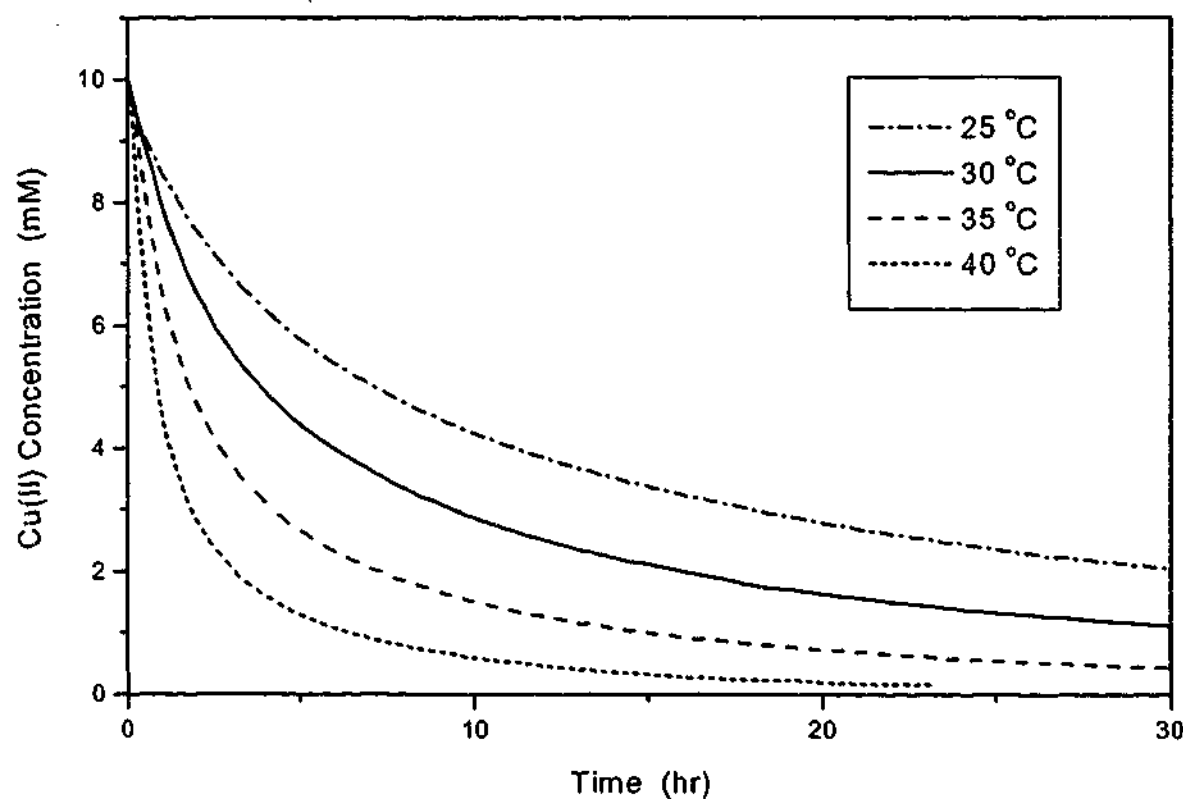


**Figure 3.23:** Effect of temperature on the rate of copper(II) reduction in thiosulfate solutions: 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$, 10 mM CuSO$_4$.

## 3.4  Summary

The reduction of copper(II) in thiosulfate solutions was shown to be very complex. Not only was copper(II) reduced by thiosulfate, but tetrathionate and other oxysulfur reaction products were also found to reduce copper(II).

The reduction of copper(II) by thiosulfate was shown to be rate limited by a second order reaction step in the presence of anions. Evidence was presented that the presence of anions compete with thiosulfate in complexing to copper(II) at the axial sites, thus reducing the rate of copper(II) reduction by thiosulfate. This is consistent with the mechanism for copper(II) reduction by thiosulfate being an inner sphere reaction. Phosphate was shown to be a very effective anion in that the rate of copper(II) reduction almost ceased with the addition of 0.1 M phosphate.

The results presented for copper(II) reduction by tetrathionate and trithionate indicated outer sphere and inner sphere reaction mechanisms respectively. As these oxysulfur species reduce the gold loading onto resins, the formation and disappearance of these species require further investigation, especially for conditions where the copper(II) concentration is maintained by the presence of oxygen. The addition of sulfite was also shown to rapidly reduce copper(II) via an inner sphere reaction mechanism. Obviously, the addition of sulfite reduces the rate of thiosulfate oxidation as copper(II) is reduced by sulfite rather than thiosulfate. The subsequently lower copper(II) concentration further reduces the rate of thiosulfate oxidation. This however results in poor gold leach kinetics (see Chapter 6).

As the copper(II) coordination sphere is stabilised by the presence of anions such as sulfate or phosphate, then the oxidation of thiosulfate and trithionate will be slowed. However, the rate of tetrathionate oxidation still proceeds rapidly. Hence, in the absence of oxygen the leach solutions are more likely to accumulate trithionate rather than tetrathionate. With time, all of the oxysulfur species will be oxidised to sulfate, as long as copper(II) remains present in the solution.

Increasing the ammonia concentration was also shown to have a very positive impact in reducing the rate of copper(II) reduction. The importance of maintaining a sufficient ammonia concentration was clearly highlighted by the estimated reaction order with respect to ammonia concentration of -2.5. This again highlights the complexity of the copper(II) reduction mechanisms.

# Chapter 4

# *Development of an Analytical Method for*

# *Thiosulfate Measurement*

## ·4.1   Introduction

As the rate of thiosulfate oxidation in leach solutions containing copper in the presence of oxygen is important to the gold thiosulfate leaching process, a method for measuring the thiosulfate concentration in thiosulfate leach solutions was required. As discussed in section 2.2.4 of the review, there are a number of limitations to the analytical techniques available. Hence, a new technique was needed that is capable of easily and rapidly measuring thiosulfate concentration in solutions applicable to gold leaching. A simple analysis technique was developed using a rotating electrochemical quartz crystal microbalance (REQCM) which is based on measuring the leach (oxidation) rate of silver in thiosulfate solutions. Due to a number of metal ions forming complexes with thiosulfate, consideration was also required as to whether the measured thiosulfate concentration was a total or, more applicably, an available thiosulfate concentration for gold leaching.

## 4.2   Experimental

All experiments were carried out using solutions prepared from analytical grade . reagents and distilled water. Unless specified otherwise solutions contained 0.1 M sodium sulfate and 0.1 M ammonia, and all REQCM experiments were conducted using a rotation rate of 300 rpm and at a temperature of 30 °C. Potential scans were

conducted at 1 mV s$^{-1}$. The Radiometer PGP201 potentiostat was computer controlled and data was logged via the computer.

The REQCM (see section 4.2.1 below) was used in the development of the analysis technique. Rotating disc electrodes were prepared by mounting 10 MHz AT cut quartz crystals onto holders (PVC cylinders) as shown in Figure 4.1. Platinum was first sputtered onto each side of the quartz electrodes in the shape of a disc with a small flag using a Balzers SCD-050 sputter coating system. Wires were connected to the flags each side of the quartz crystal using silver loaded epoxy resin and the crystals were mounted in the PVC holders using silicon. The flag of the crystal was covered with varnish to leave a platinum disc. Prior to each experiment conducted requiring a silver electrode, the platinum electrode was electroplated with silver from a solution containing 0.025 M silver cyanide, 0.23 M potassium cyanide and 0.11 M potassium carbonate at 50 A m$^{-2}$. To prepare a copper electrode, the platinum electrode was electroplated at 150 A m$^{-2}$ from a solution containing 0.75 M copper sulfate and 0.25 M sulfuric acid.
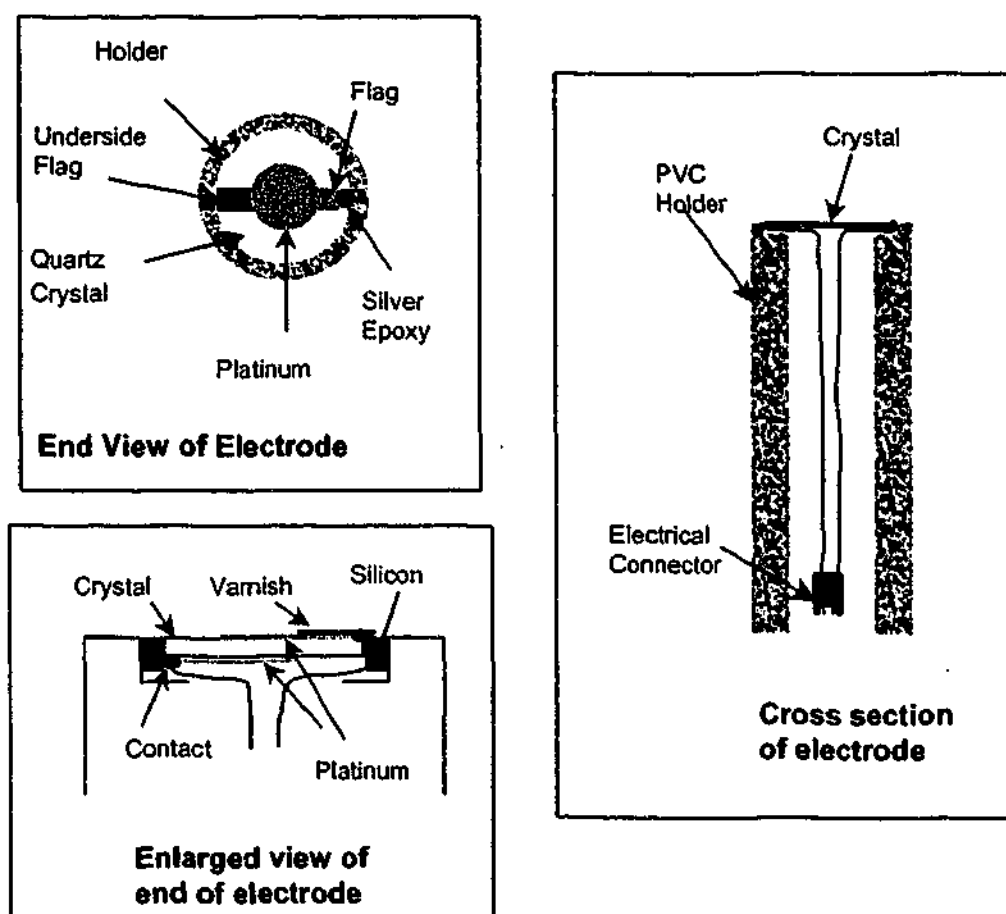


**Figure 4.1:** Illustration showing the construction of the REQCM electrodes.

## 4.2.1 The REQCM

The REQCM is simply a rotating form of the EQCM, which are commercially available and have been used in the study of many deposition and adsorption processes (Ward, 1995). The first application of the REQCM was by Ritchie *et al.* (1994), who measured the deposition of copper from copper cyanide solutions. Jeffrey (1998) described an improvement to the stability of this early version, in which the entire EQCM circuit was contained within the rotating shaft as shown in Figure 4.2.
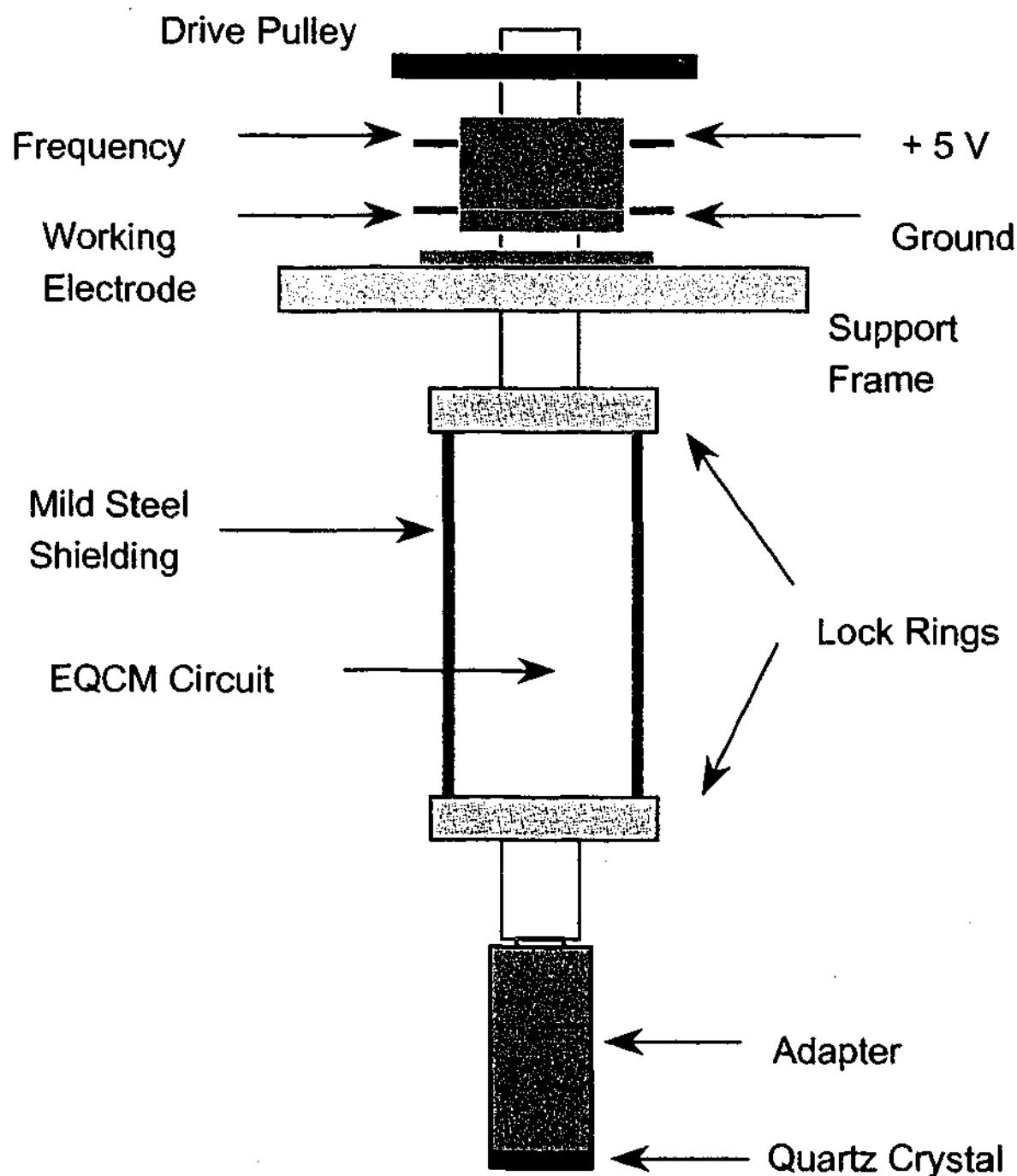
**Figure 4.2**    Illustration showing the design of the REQCM.

The QCM gets its name from the use of a quartz crystal to measure mass changes. When a stress is applied to a quartz crystal, an electric potential is created across the crystal, the magnitude of which is proportional to the applied stress (Ward, 1995). This is known as the piezoelectric effect. The basis of the QCM is the converse piezoelectric effect in that a potential is applied across the quartz crystal which results in a mechanical strain. Reversing the potential, induces an equal strain but in the opposite direction. Thus, when an alternating potential is applied across the quartz crystal using a thin metal coating each side of the quartz crystal as shown in Figure 4.1, mechanical oscillation occurs with its amplitude parallel to the surface of the crystal. The frequency of the oscillation is determined by Equation 4.1, where $f_o$ is the fundamental frequency of oscillation, $v_t$ is the transverse velocity of sound in quartz ($3.34 \times 10^4$ m s$^{-1}$), and $t_Q$ is the thickness of the quartz (Ward, 1995).

$$f_o = \frac{v_t}{2t_Q}$$

4.1

Equation 4.1 assumes that the velocity of sound is the same in the electrode material as that in quartz. This is likely to be valid as the thickness of the electrode material is small relative to the quartz. If it is further assumed that the density of the electrode material is the same as the quartz, then the frequency change of the quartz crystal, $\Delta f$, during deposition or leaching can be equated to the mass change by the Sauerbrey equation. This is shown in Equation 4.2 where $\Delta m$ is the mass change, A is the area of the piezoelectrically active area, $\rho_q$ is the density of the quartz crystal and $\mu_q$ is the shear modulus of the AT cut quartz crystal ($2.947 \times 10^{11}$ dyn cm$^{-2}$) (Ward, 1995).

$$\Delta f = \frac{-2f_o^2 \Delta m}{A\sqrt{\mu_q \rho_q}}$$

4.2

Equation 4.2 is valid if the electrode thickness is less than 2% of the quartz thickness, which is usually the case for EQCM applications. Thus, to measure the mass

change of chemical or electrochemical processes, all that is required is to apply an AC potential to the quartz crystal, and a frequency counter to measure the resultant frequency of oscillation. Transformers are used to isolate the potentiostat from the QCM circuit, a critical feature when using a potentiostat with the working electrode at virtual ground (as in most commercial potentiostats) to conduct electrochemical experiments (Ward, 1995). The frequency of the crystal oscillation was measured with an Optoelectronics model 3000A hand held frequency counter, accurate to 1Hz. The frequency counter and potentiostat were interfaced with an IBM compatible PC to accommodate data acquisition and analysis using software that was written in Q-Basic.

## 4.3   Development of an Analytical Method

The aim was to develop an analytical method that measures thiosulfate concentration in thiosulfate leach solutions via the leach (oxidation) rate of a particular metal. In order to measure thiosulfate concentration via the oxidation rate of a metal, some preliminary work was conducted to establish a possible metal candidate. Based on the work previously conducted by Hemmati *et al.* (1989), silver was an obvious starting choice.

### 4.3.1  Use of REQCM to Measure Oxidation Rates

Development of the analysis technique was conducted using a rotating electrochemical quartz crystal microbalance (REQCM), which was described above in section 4.2.1. The change in electrode mass measured by the REQCM, $\Delta m$ (g), was used to calculate the rate of metal oxidation, r (mol m$^{-2}$ s$^{-1}$), according to Equation 4.3, where A is the electrode surface area (m$^2$), M is the atomic mass of the metal (g mol$^{-1}$) and t is the time elapsed (s).

$$r = \frac{\Delta m}{A \, M \, \Delta t} \qquad\qquad 4.3$$

### 4.3.1.1 Silver Leach (Oxidation) Rate in Thiosulfate Leach Solutions

The REQCM was used to measure mass changes of a silver electrode, whilst the applied potential was scanned, in solutions of various thiosulfate concentrations. The change in electrode mass with time was then converted to a silver oxidation rate using Equation 4.3. Figure 4.3 illustrates both the mass change and calculated silver oxidation rate versus applied potential for a silver electrode in a 0.12 M thiosulfate solution. As the electrode potential is increased the typical exponential growth in silver oxidation rate is observed. A thiosulfate diffusion limiting silver oxidation rate was not obtained as this occurs at higher potentials, for which the rate is extremely fast due to the very high concentration of thiosulfate.

One factor that must be considered when analysing the frequency response of the EQCM is the surface roughness of the film of interest. For example, Zhang *et al.* (1998) have shown that surface roughness changes may induce frequency shifts of 100 ppm (1000 Hz for a 10 MHz crystal). Since the silver surface is being oxidised, there may be a change in the surface morphology during the experiment. To assess the effect of changes in surface roughness, the current measured during silver oxidation is also shown in Figure 4.3. As the oxidation of silver is the only reaction occurring at the electrode surface in this potential region, the rate of silver oxidation, r, is directly related to the measured current, i, by Faraday's law as shown in Equation 4.4, where n is the number of electrons transferred per mole of metal reacted and F is Faraday's constant (96485 C mol$^{-1}$). Thus, in Figure 4.3 the current density axis scale has been set equal to the oxidation rate scale multiplied by the Faraday constant. It can be seen that the measured current density response directly matches the silver oxidation response at all potentials. Such a result implies that the EQCM is mainly measuring frequency changes that result from changes in mass of the silver electrode. Thus, changes in surface roughness are not a major contributor to the measured frequency change.

$$i = nFr \hspace{4cm} \textbf{4.4}$$
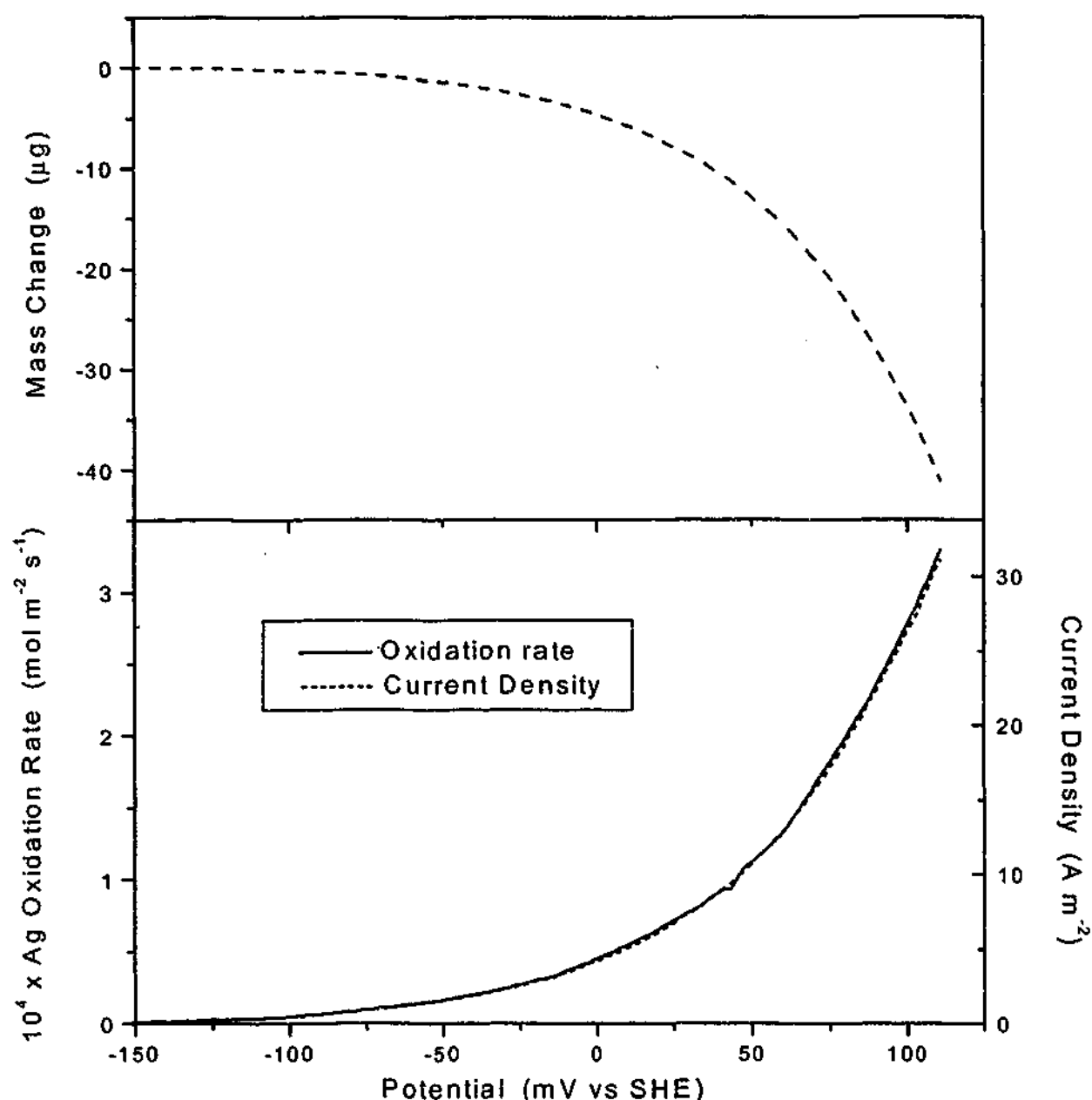
**Figure 4.3:** Mass change of silver electrode versus potential in 0.12 M thiosulfate solution: 300 rpm, 30 °C. The lower part of this figure shows the calculated silver oxidation rate and the measured current.

An important consideration for thiosulfate analysis in solutions containing ammonia is that depending on the potential applied to the silver electrode and the ammonia concentration of the thiosulfate leach solution, silver can also be oxidised to form the ammine complex, as shown in Equation 4.5. The standard electrode potential for this reaction is 0.372 V (Högfeldt, 1982), which is significantly higher than $-0.01$ V for the formation of the silver thiosulfate complex (Equation 2.12).
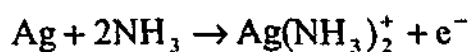
$$Ag + 2NH_3 \rightarrow Ag(NH_3)_2^+ + e^- \qquad\qquad \textbf{4.5}$$

Figure 4.4 shows a comparison between the oxidation of silver in a 0.12 M thiosulfate solution and a 0.4 M ammonia solution. These concentrations were chosen as they represent the typical composition of a thiosulfate leach solution. It can be seen from Figure 4.4 that the oxidation of silver in thiosulfate solutions occurs much more readily than in the ammonia solution; there is a good separation of around 200 mV between the oxidation curves. If an applied potential of 100 mV or less is utilised, then the oxidation of silver could be expected to be limited to the formation of the thiosulfate complex. Also shown in Figure 4.4 is the oxidation rate versus applied potential for copper in either 0.12 M thiosulfate or 0.4 M ammonia solutions. In this case, it is clear that the formation of the ammine complex occurs at a very similar potential to the thiosulfate complex. Hence, silver is clearly a better choice than copper for measuring the thiosulfate concentration in thiosulfate leach solutions that contain ammonia.
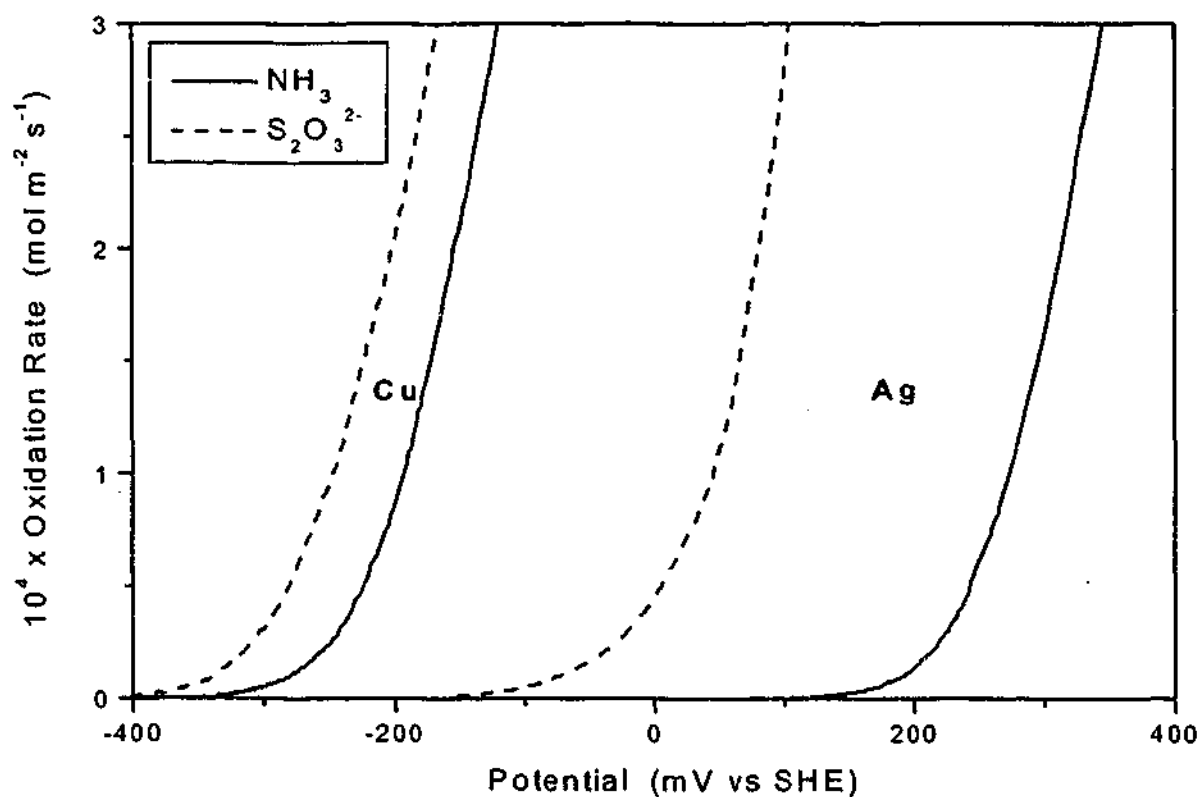


**Figure 4.4:** Copper and silver oxidation rates versus potential in separate solutions of 0.12 M thiosulfate and 0.4 M ammonia: 300 rpm, 30 °C.

From Figure 4.4 it is also evident that the silver oxidation rate increases rapidly in the potential region from −100 to 50 mV. Since the oxidation reaction is chemically controlled in this potential region, it is likely that the silver oxidation rate will be sensitive to changes in temperature and the electrode surface. At potentials greater than 50 mV, the silver oxidation rate is too high for practical use, as a significant quantity of silver is consumed in every measurement.

## 4.3.1.2   Effect of Dilution

In order to improve the technique for the determination of thiosulfate concentration, it was decided that the thiosulfate leach solution should be diluted. This would result in the silver oxidation rate being lower. The most important consideration in dilution is to maintain the solution chemistry; otherwise the concentration of thiosulfate measured in the diluted sample may not be representative of the thiosulfate concentration in the actual leach solution. There are two possible reasons why the solution chemistry could be different due to dilution. The first possibility is that the dilution could result in a significant increase in the reaction rate between copper(II) and thiosulfate. This would result in a lower value of thiosulfate concentration. The second possibility is that the dilution could change the copper(I) complex speciation. As will be shown in section 4.3.1.3, the thiosulfate which is complexed with copper(I) is not measured using this technique. Thus, if the amount of thiosulfate complexed to copper(I) is varied, the free thiosulfate in the diluted solution would change. The methods used to minimise these problems are outlined below.

A number of experiments were conducted to establish what effect dilution had on the reaction between copper(II) and thiosulfate. Dilution into a 0.1 M sodium sulfate solution was firstly considered. However, upon dilution of a leach solution by a factor of 10 with 0.1 M sodium sulfate, the copper was observed to precipitate. This is obviously undesirable for an analytical method. Therefore, dilution into an electrolyte solution containing ammonia is required. It was found that 0.1 M ammonia was required in order to stabilise the copper(II). Even though the reaction order with respect to ammonia was shown to be −2.5 (section 3.3.7.3), the reaction between thiosulfate and copper(II) is very slow as a result of dilution. With 0.4 M ammonia in the diluent the copper(II)-thiosulfate reaction rate is observed to almost completely cease.

Another important consideration with dilution into ammonia is the relative potentials for the oxidation of silver as the silver ammine and silver thiosulfate complexes. The silver oxidation rate as a function of potential for an experiment conducted with a solution containing 6 mM thiosulfate (1 in 20 dilution) and 0.1 M ammonia is shown in Figure 4.5. It can be seen that the curve is nowhere near as steep as that observed for the undiluted solution. This is advantageous for an analytical technique. In comparison, the oxidation curve for silver in a 0.1 M ammonia solution in the absence of thiosulfate is also shown in Figure 4.5. It is clear that in these solutions, the oxidation of silver as the silver ammine does not occur at potentials more negative than 200 mV. In contrast, in solutions containing 0.4 M ammonia, Figure 4.5 shows that the oxidation of silver occurs at potentials more positive than 130 mV. Thus, the potential applied to the silver electrode for a diluted solution contained 0.4 M ammonia would need to be less than 130 mV to avoid the oxidation of silver as the silver ammine. If the diluted solution contains 0.1 M ammonia, then a potential of 200 mV could be used.
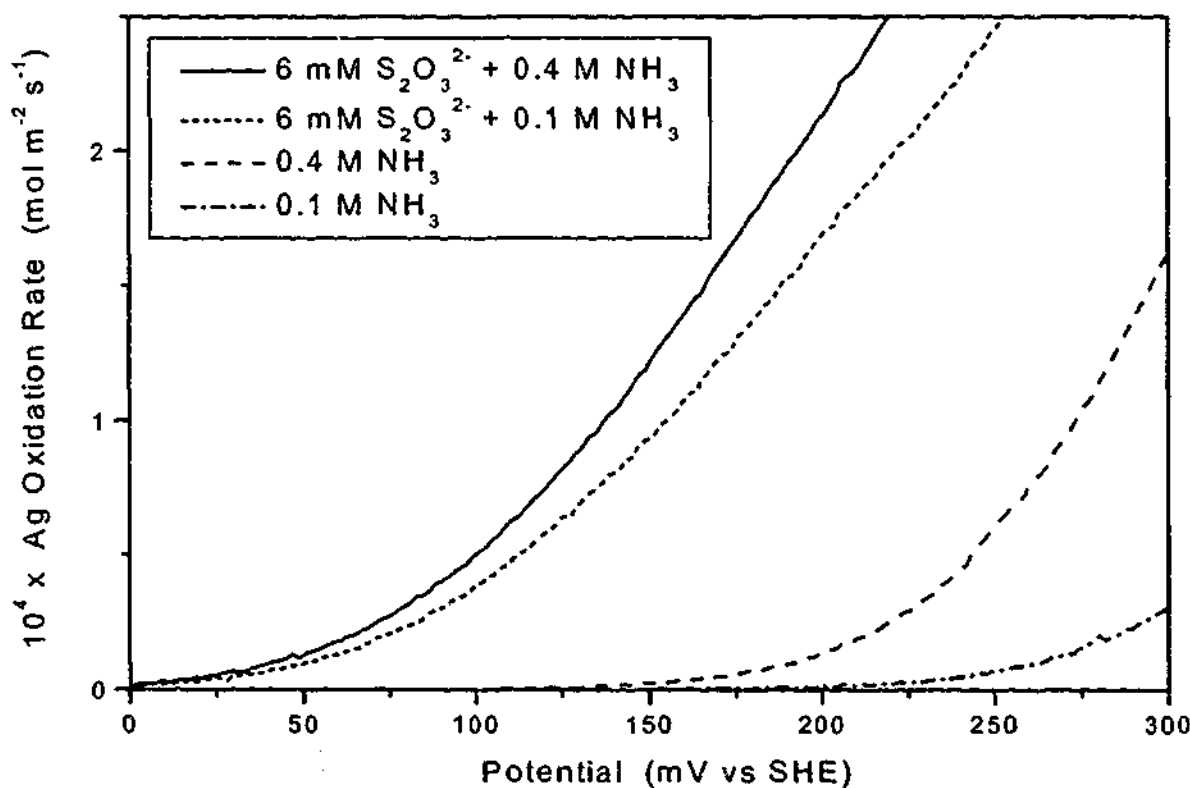


**Figure 4.5:** Effect of ammonia on the silver oxidation rate in thiosulfate solutions: 0.1 M $Na_2SO_4$, 300 rpm, 30 °C.

It is often beneficial to impose a higher overpotential to the silver electrode, as the reaction is likely to be less sensitive to changes in the surface state of the silver. Hence it was decided that the diluted solution should contain 0.1 M ammonia, and a potential of 200 mV was chosen.

Another important variable that must be considered is changes in the ammonia concentration of the thiosulfate leach solution. Figure 4.5 also shows a comparison between the oxidation of silver in 6 mM thiosulfate and either 0.1 or 0.4 M ammonia. It is clear that the silver oxidation curves differ, even at low overpotentials where the formation of the silver ammine complex does not occur. These results are similar to the oxidation of copper in thiosulfate solutions, where the addition of ammonia results in oxidation at more negative potentials (Choo and Jeffrey, 2001). One possible explanation for this phenomena is that silver is capable of forming a mixed thiosulfate/ammonia complex. Unfortunately thermodynamic data on such species are not available. From a practical point of view, the results shown in Figure 4.5 indicate that careful control of the ammonia concentration is required. Consequently a 1 in 20 dilution was chosen so that if the ammonia concentration of the leach solution did vary, then the concentration of ammonia after dilution remains relatively constant.

### 4.3.1.3 Thiosulfate Measurement using a REQCM

Once all of the parameters for the thiosulfate analysis had been chosen, the next task was to perform a calibration. Figure 4.6 shows the calibration curve for silver oxidation rate (determined by applying a constant potential of 200 mV versus SHE to the electrode) versus thiosulfate concentration in solutions containing 0.1 M ammonia and 0.1 M sodium sulfate. Clearly, under these conditions the silver oxidation rate varies linearly with thiosulfate concentration; the linear correlation has an R value of 0.999. This is very useful in any analytical technique, as elaborate curve fitting of the standards is not required. In addition, any change in the system variables, such as electrode surface area, can be adjusted for by using a single point reslope.

For this technique to be useful it is important that other species in the thiosulfate leach solution have no effect on the silver oxidation rate. It is shown in Chapter 6 that the gold oxidation process is catalysed by the presence of copper(II).
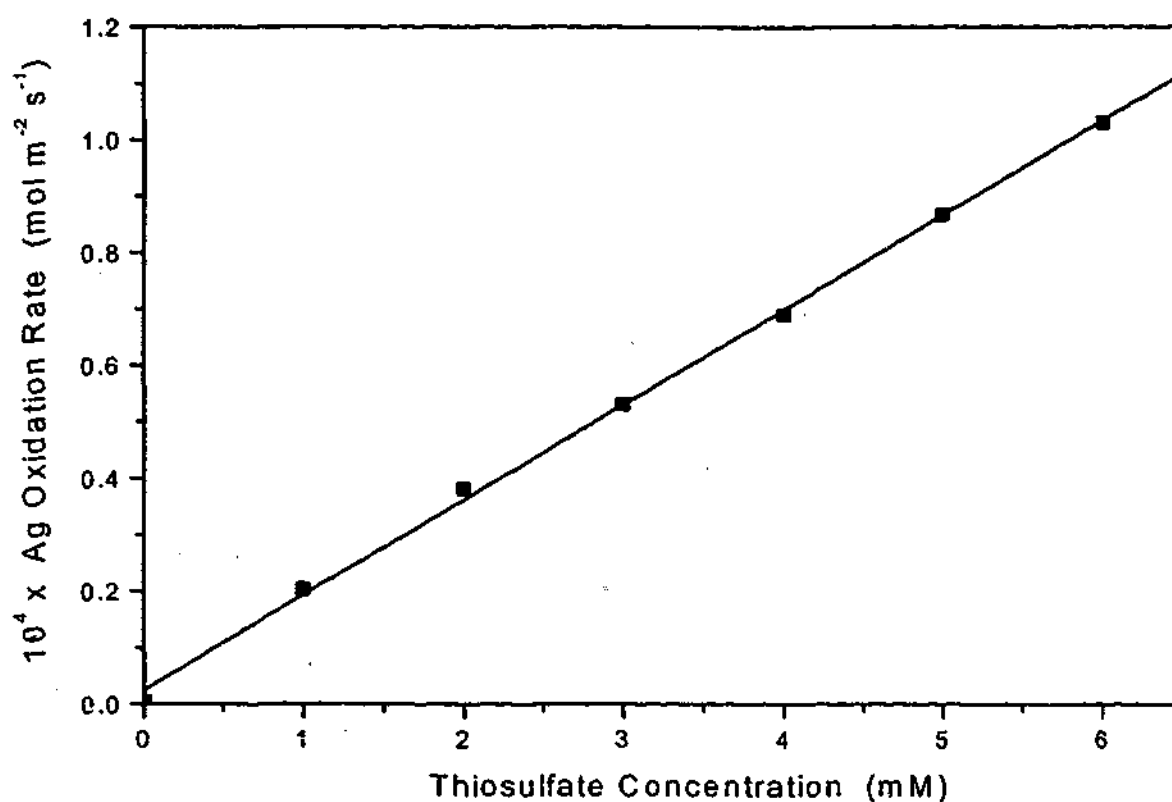
**Figure 4.6:** Calibration curve of silver oxidation rate (200 mV vs. SHE) versus thiosulfate concentration for the REQCM: 0.1 M $NH_3$, 0.1 M $Na_2SO_4$, 300 rpm, 30 °C.

The effect of copper(II) on the silver oxidation rate was investigated by measuring the silver oxidation rate just after copper(II) + ammonia was added to a thiosulfate solution, so that very little reaction between thiosulfate and copper(II) had occurred. The silver oxidation curve is shown in Figure 4.7a; it is clear that the silver oxidation rate in a thiosulfate solution is unaffected by the presence of copper(II). An experiment was also performed where tetrathionate was added to the thio ..fate leach solution. The data shown in Figure 4.7a indicates that the presence of tetrathi .te also has no effect on the silver oxidation rate in thiosulfate solutions. Such a result is not surprising, as silver does not form complexes with tetrathionate or other polythionates. During the experiments where the mass change was measured with the REQCM, the electrode current was also measured. Figure 4.7b shows the current that is measured at the silver electrode in the solution containing thiosulfate and ammonia. In a similar manner to Figure 4.3, the current density response is the same as the silver oxidation response calculated from the mass changes. This is because under these conditions, the

oxidation of silver is the only electrochemical reaction that occurs, and hence the current directly relates to the rate of mass change. However, Figure 4.7b shows that in the presence of copper(II), the measured current is lower at potentials less than 180 mV due to the reduction of copper(II) at the electrode surface contributing to the measured current. At potentials above 180 mV the oxidation of copper(I) to copper(II) contributes to the measured current. This highlights the limitation to the method proposed by Hemmati *et al.* (1989). Tetrathionate is shown in Figure 4.7b to have no effect on the measured current as tetrathionate is neither oxidised nor reduced in this potential region.
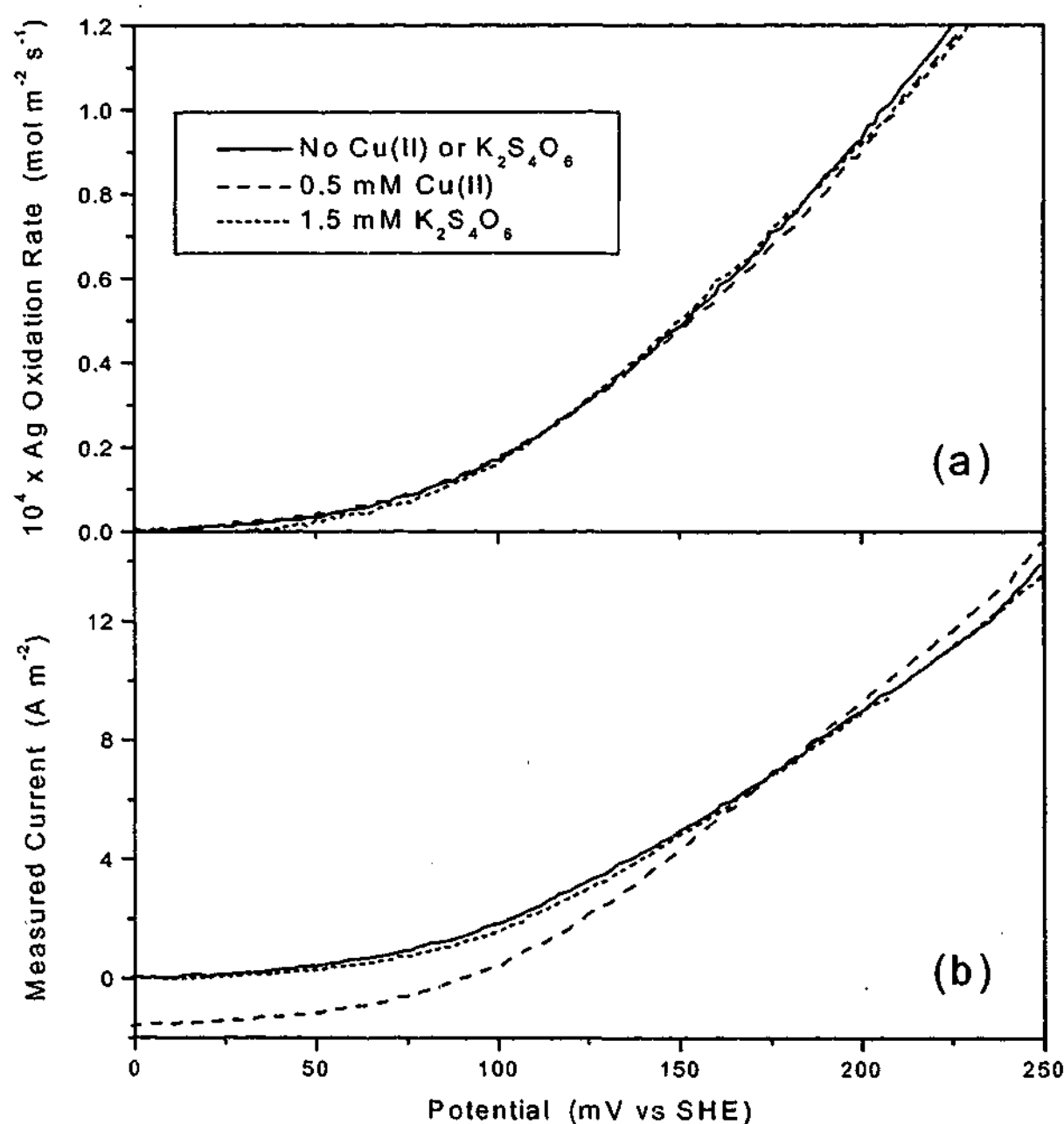


**Figure 4.7:** Effect of copper(II) and tetrathionate on the silver oxidation rate (a) and the measured electrode current (b): 6 mM $Na_2S_2O_3$, 0.1 M $Na_2SO_4$, 0.1 M $NH_3$, 300 rpm, 30 °C.

During gold leaching in thiosulfate leach solutions, a proportion of the copper is always present as copper(I) due to copper(II) reduction (see Chapters 3 and 5). Hence the effect of copper(I) on the silver oxidation rate was also studied. This is more complex than the addition of copper(II), as both thiosulfate and ammonia can complex with copper(I). Shown in Figure 4.8 is the silver oxidation curve for a solution containing 6 mM thiosulfate and 0.1 M ammonia to which 1.5 mM copper(I) thiocyanate was added (a stable source of copper(I) – the addition of 1.5 mM potassium thiocyanate had no effect on the measured silver oxidation rate at these potentials). The silver oxidation rate curve in the absence of added copper(I) is also shown in Figure 4.8 for comparison. It can be seen that the measured silver oxidation rate is much lower in the instance where 1 mole of copper(I) has been added for each 4 moles of thiosulfate.
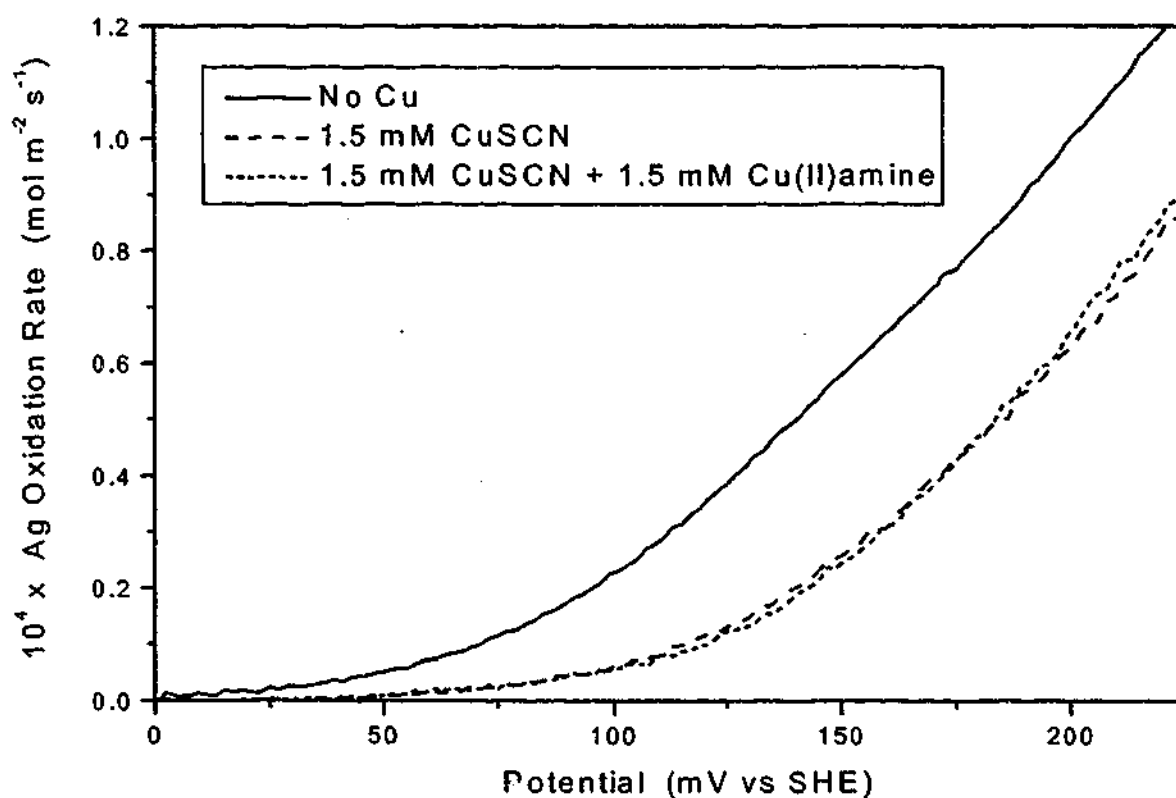


**Figure 4.8:** Effect of copper(I) on the silver oxidation rate: 6 mM $Na_2S_2O_3$, 0.1 M $NH_3$, 0.1 M $Na_2SO_4$, 300 rpm, 30 °C.

At 200 mV in Figure 4.8, the measured silver oxidation rate in the presence of copper(I) is 64% of that measured in the absence of added copper(I) thiocyanate. Such a result is consistent with a proportion of the thiosulfate forming a complex with copper(I), and then this thiosulfate not being available for the oxidation of silver. In this solution it would appear that on average approximately 1.5 moles of thiosulfate are complexed with each mole of copper(I). It is possible that some of the copper is also complexed as the copper(I) ammine or as a mixed copper(I) ammine-thiosulfate complex. However the speciation of copper(I) in solutions containing ammonia and thiosulfate is uncertain as there is no thermodynamic data available for the mixed ammonia-thiosulfate complexes of copper(I).

An experiment was also conducted for a solution containing 1.5 mM copper(I) and 1.5 mM copper(II). As can be seen from Figure 4.8, for solutions containing copper(I), there is no difference in the silver oxidation rate in the presence or absence of copper(II). These results are consistent with the results shown in Figure 4.7 for copper(II) addition in the absence of copper(I).

Another consideration with the presence of copper(I) is the possibility that the amount of thiosulfate complexed by the copper(I) changes when the solution is diluted into 0.1 M ammonia. In order to confirm that under these conditions, this effect is minimal, an experiment was conducted where the silver oxidation rate was also measured in undiluted leach solutions at a rotation rate of 60 rpm and an applied potential of 200 mV. It was found that when 25 mM copper(I) is added to 100 mM thiosulfate, (the same ratio as used in the diluted solution presented in Figure 4.8), the silver oxidation rate decreased by 64%. This decrease is identical to that measured for the diluted solution. Hence it can be concluded that the conditions selected for the analysis of thiosulfate concentration are very good, with the measured silver oxidation rate being directly proportional to the thiosulfate concentration and unaffected by the presence of copper(II) and tetrathionate. In addition, in the presence of copper(I), the silver oxidation rate measured reflects the free thiosulfate which is available to leach gold; i.e. not including the thiosulfate which is complexed with copper(I).

## 4.3.2 Flow Injection Analysis System

Whilst the REQCM is capable of determining thiosulfate concentration by measuring the silver leach rate of a diluted sample, this instrument is not commercially available and the procedure is time consuming in terms of individual solution preparation and cleanup for each sample. Thus, a flow injection analysis (FIA) method utilising an EQCM cell was investigated as a means of simply and rapidly measuring the thiosulfate concentration of thiosulfate leach solutions. The application of QCM (Muratsugu *et al.*, 1993) and EQCM (Briseno *et al.*, 2001, Gering and Rosentreter, 2001, O'Sullivan and Guilbault, 1999) in flow cells is not new; this method has been used in a number of analytical techniques in the past few years.

The FIA system that was used in these studies is shown in Figure 4.9. A sample is firstly charged into the injection loop of the injection valve and then is switched such that the sample is flushed into the system with carrier solution. The sample is then diluted with a separate carrier solution stream in a mixing tee before passing through the EQCM cell. The carrier solution contained 0.1 M sodium sulfate and 84 mM ammonia; under these conditions, when a sample containing 0.4 M ammonia is diluted 1 in 20, the mixed solution entering the EQCM cell contained 0.1 M ammonia. The constant temperature bath was held at 30 °C.
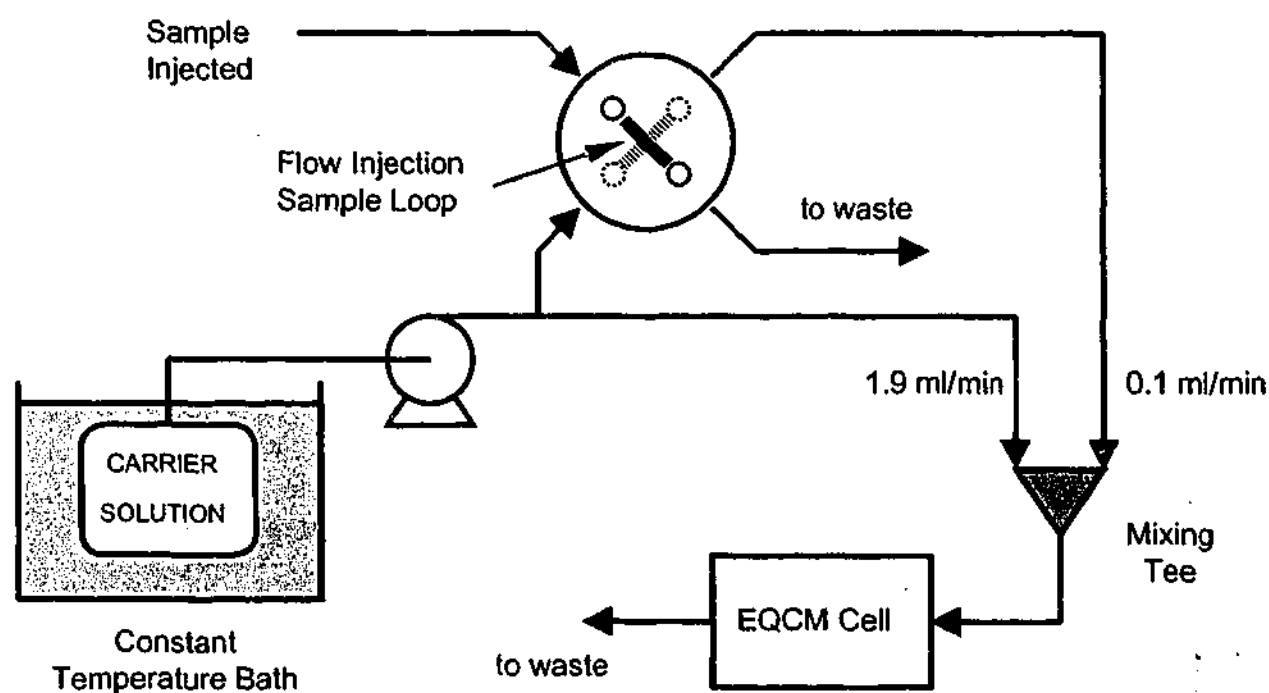


**Figure 4.9:** Flow diagram of FIA system using an EQCM cell.

### 4.3.2.1 EQCM Flow-through Cell Design

The EQCM cell used in these studies is shown in Figure 4.10 and was purpose built to utilise the same electrodes as the REQCM. This had the advantages of simple replacement and simplicity to electroplate silver onto the electrode using the REQCM. The electrode can be electroplated with silver within the cell by pumping the same plating solution through the cell and applying a constant current. This requires either changing the carrier solution to the plating solution, or utilising an additional pump and a bypass for the plating solution. Pump selection was also very important as unsteady solution flow was found to have a large effect on the EQCM cell response. For the EQCM cell, the electrode is stationary and it is the solution flow which results in mass transfer of the thiosulfate to the silver surface. Unlike the REQCM, the mass transfer under these conditions is not well defined. Since the mass sensitivity varies spatially across the crystal surface, it is important that the concentration of thiosulfate across the silver electrode is as uniform as possible. Hence the flow channel was designed with a 7 mm width, and the silver surface of the crystal was placed centrally in the flow channel. This minimises edge effects on the flow of solution over the silver surface.
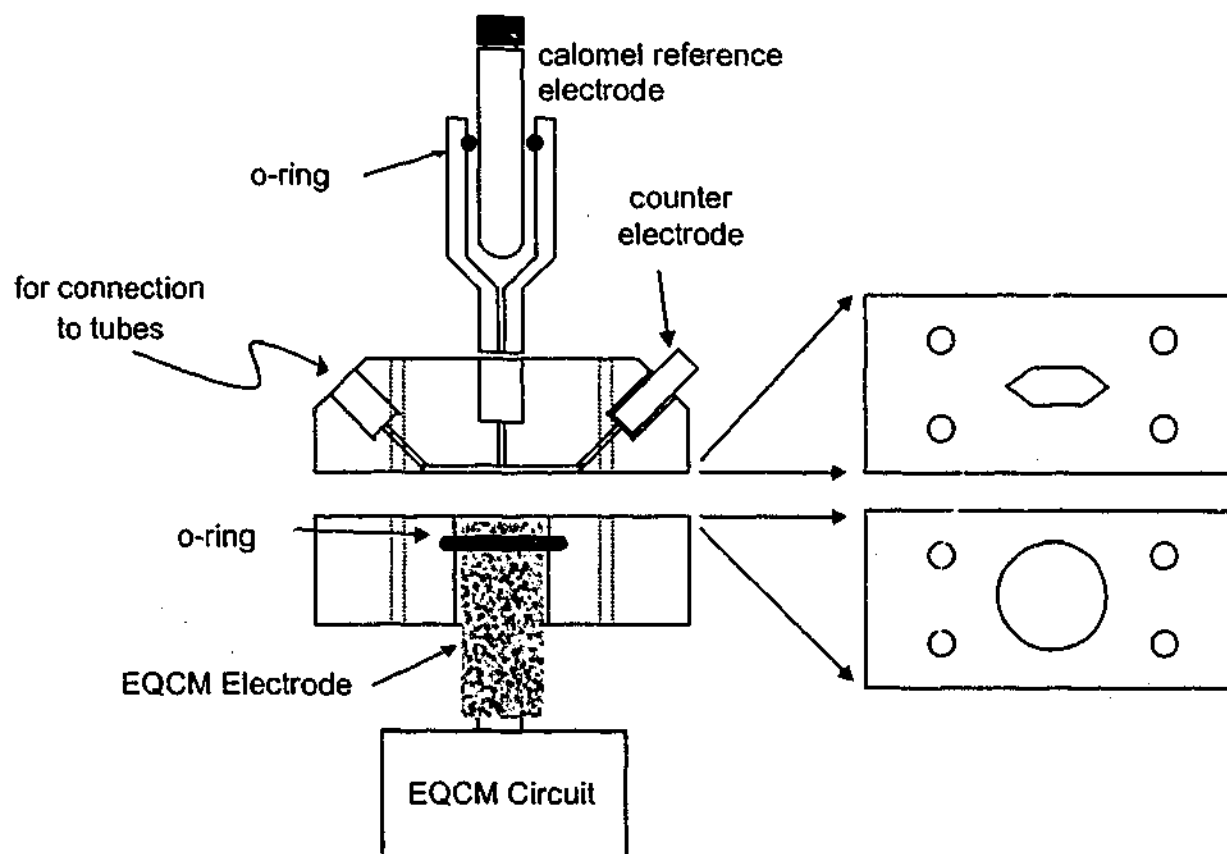


**Figure 4.10:** Diagram of the EQCM cell used in the FIA system.

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**4.3.2.2   Response and Calibration of EQCM Flow-through Cell**

Recording of the electrode mass change began at the time of sample injection and continued until the effect of the injected sample ceased.  Figure 4.11 shows the recorded mass change for the EQCM during an injection of a solution containing 0.1 M sodium thiosulfate and 0.4 M ammonia.  Clearly, the mass of the silver electrode is unchanged initially.  Once the injected sample reaches the cell the measured mass of the silver electrode begins to decrease, reaching a maximum rate approximately 60 seconds after the sample was injected.  The mass change then decays away as the injected sample is flushed out of the cell.  The rate of silver oxidation can again be calculated using Equation 4.1 and is also shown in Figure 4.11.  This bell shape curve is typical of flow injection analysis measurements.

To test that the EQCM response in the flow through cell also conformed to the Sauerbrey equation, the current was measured during the injection of the thiosulfate sample, and the response has been overlayed in Figure 4.11.  In a similar manner to Figure 4.3, the current density axis scale is equal to the oxidation rate scale multiplied by the Faraday constant.  It should be clear that the oxidation rate curve calculated using the Sauerbrey equation is very similar to the current density curve.  Such a result indicates that the response of the EQCM cell is close to ideal, and that there is very little spatial variation in the silver oxidation rate.

Having established that the FIA-EQCM technique gave a measurable response to the presence of thiosulfate in leach solutions, the reproducibility and relationship between mass change and thiosulfate concentration were investigated.  Figure 4.12 shows a calibration curve for measurements of mass change versus thiosulfate concentration.  Not surprisingly, this relationship was found to be linear ($R = 0.995$).  Thus, the FIA-EQCM gives a simple and rapid analysis technique for measuring the available thiosulfate concentration in thiosulfate leach solutions.
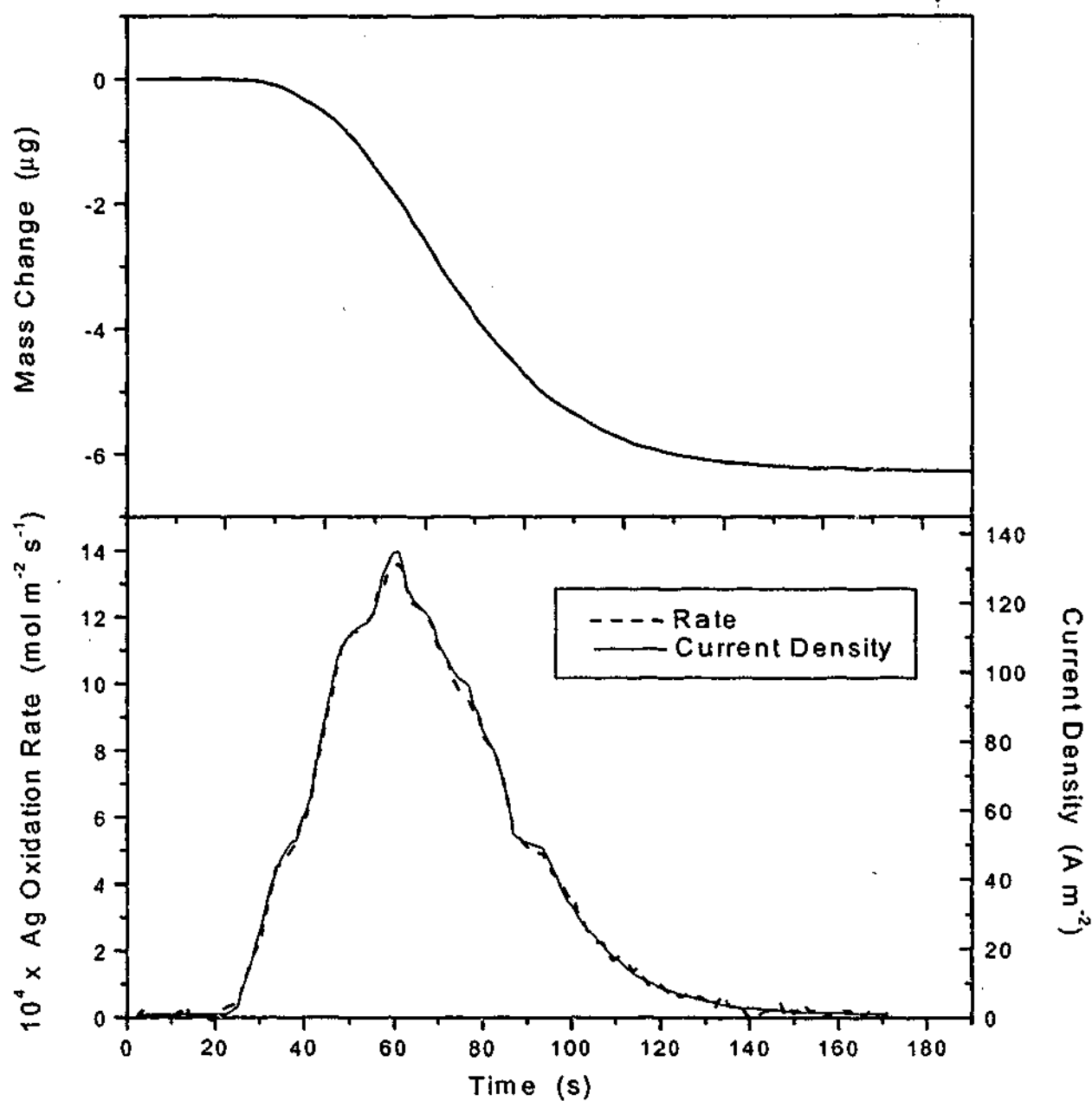
**Figure 4.11:** Recorded mass change for the EQCM cell (applied potential of 200 mV versus SHE) during injection of a solution containing 0.1 M $Na_2S_2O_3$ and 0.4 M $NH_3$. The lower part of this figure shows the silver oxidation rate (differentiation of the mass change) and the measured current.
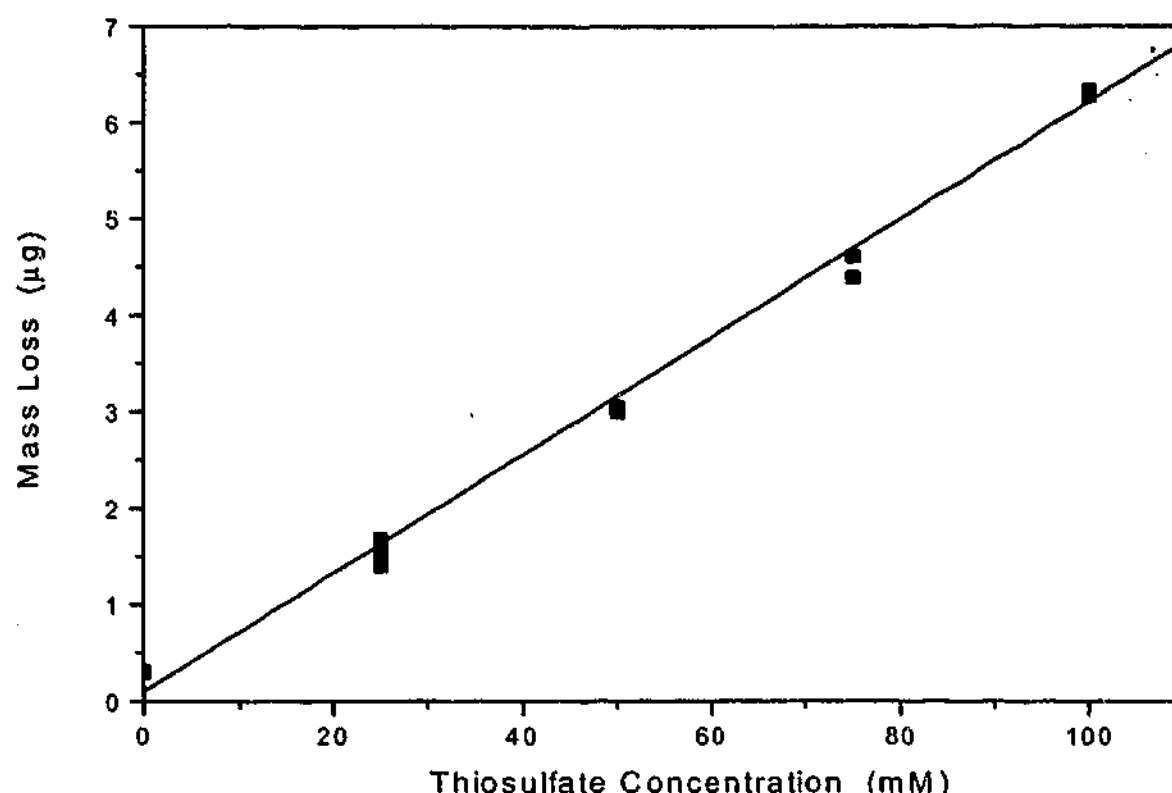
**Figure 4.12:** Calibration curve of silver mass loss versus thiosulfate concentration for the EQCM cell: electrode held at 200 mV versus SHE and the injected solution contained 0.4 M $NH_3$ and $Na_2S_2O_3$.

### 4.3.3  Development of a 4 Electrode Electrochemical Cell

Whilst the FIA system with an EQCM cell provided a means of simply and rapidly measuring thiosulfate concentration in thiosulfate leach solutions applicable to gold leaching within the laboratory, it was not robust in the requirement of a quartz crystal and the need to regularly replenish the electrode surface with silver. Hence, the possibility of estimating the silver oxidation rate from the measured current of a solid silver electrode was investigated. The evaluation and development of an analysis technique based on this approach is described below.

### 4.3.3.1 Measured Current versus Silver Oxidation Rate

The current due to silver oxidation, $i_{calc}$ (A m$^{-2}$), can be calculated from the rate of silver oxidation, r (mol m$^{-2}$ s$^{-1}$), by Faraday's law shown previously in Equation 4.4. Thus, the current associated with measured mass changes of a REQCM electrode can be calculated. Figure 4.13 shows the current due to silver oxidation calculated from the mass changes of a silver electrode measured using a REQCM as the electrode potential was scanned in a solution containing 6 mM thiosulfate, 0.1 M ammonia and 0.1 M sulfate. Also shown in Figure 4.13 is the measured current of the silver electrode versus the scanned potential. The measured current closely matches the calculated current for silver oxidation, as previously indicated by the data shown in Figure 4.3. This is not surprising as the only reaction occurring at the electrode surface under these conditions is silver oxidation.
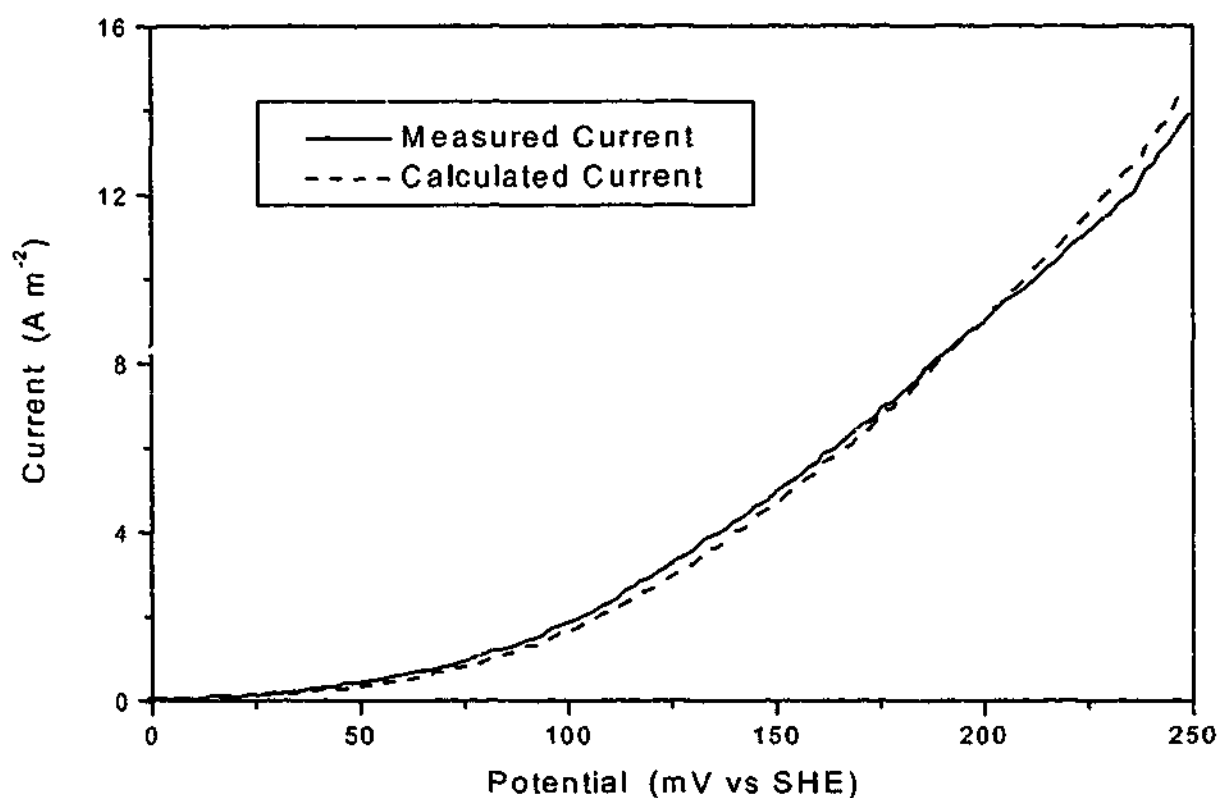


**Figure 4.13:** Potential scan of a silver electrode in a thiosulfate solution showing the measured current of the silver electrode and the calculated current for silver oxidation (determined from the measured mass change): 6 mM Na$_2$S$_2$O$_3$, 0.1 M NH$_3$, 0.1 M Na$_2$SO$_4$, 300 rpm, 30 °C.

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Clearly, under conditions where silver oxidation is the only reaction occurring at the electrode surface, the method for measuring thiosulfate concentration developed by Hemmati *et al.* (1989) is valid, as the measured current is directly related to the silver oxidation rate. However, as discussed in the review, thiosulfate leach solutions contain copper(II) as the oxidant for gold leaching. This results in the presence also of copper(I) due to the reaction between copper(II) and thiosulfate. Figure 4.14 shows the comparison between the measured current of the silver electrode and that calculated from the measured mass change of a silver electrode in a solution containing 6 mM thiosulfate, 0.1 M ammonia, 0.1 M sulfate, 1 mM copper(II) and 1 mM copper(I). Clearly, under these conditions the measured current fails to agree with the calculated current for silver oxidation over the entire potential region other than at the potential where copper(I) oxidation is matched by copper(II) reduction at the electrode surface (170 mV). Below 170 mV the measured current is lower than the calculated current for silver oxidation due to copper(II) reduction at the electrode surface, whilst at potentials higher than 170 mV the measured current is higher due to copper(I) oxidation.
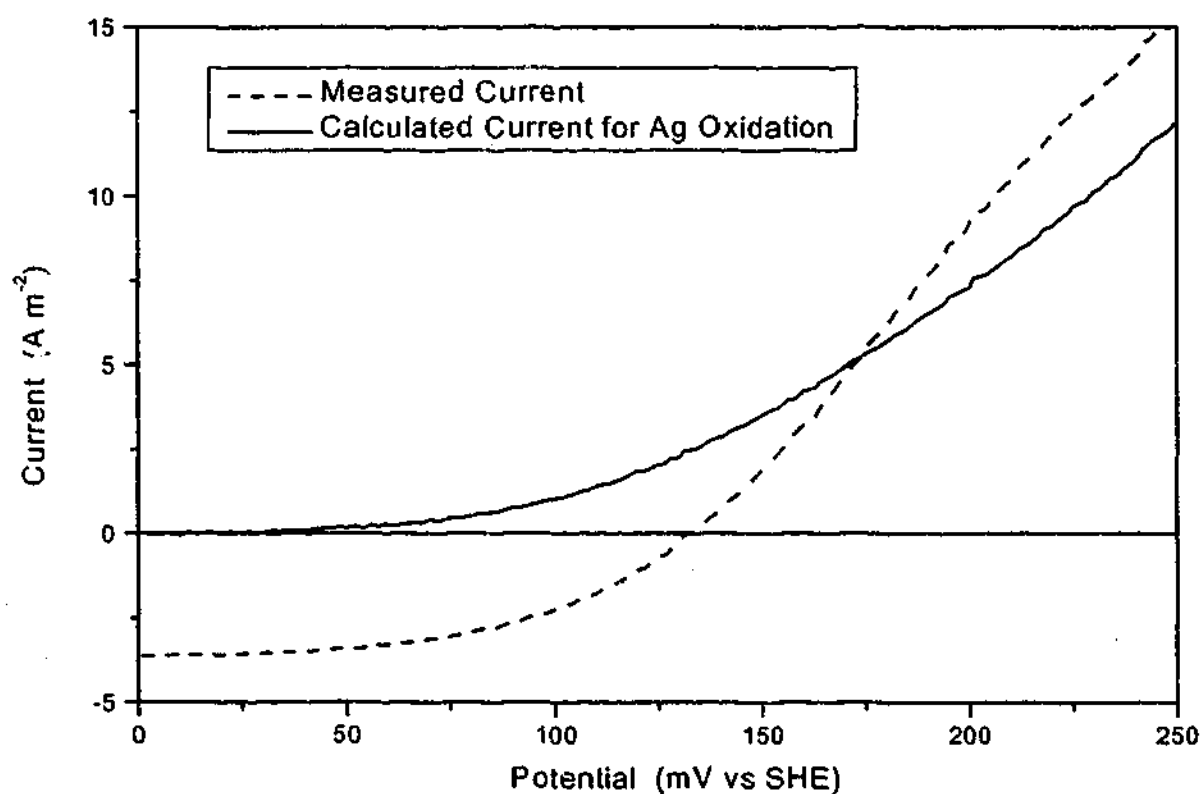


**Figure 4.14:** Measured current of a silver electrode and the calculated current for silver oxidation in a thiosulfate solution containing 1 mM Cu(II) and 1 mM Cu(I): 6 mM $Na_2S_2O_3$, 0.1 M $NH_3$, 0.1 M $Na_2SO_4$, 300 rpm, 30 °C.

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As the concentrations of copper(II) and copper(I) vary, the potential at which the measured and calculated currents match will also vary. This clearly highlights the limitations in using the measured current of a silver electrode at constant potential as a means of determining thiosulfate concentration, especially for thiosulfate leach solutions.

### 4.3.3.2 Adjusted Current versus Silver Oxidation Rate

To overcome these limitations in using the measured current of a solid silver electrode to determine thiosulfate concentration, the measured current of an inert electrode was proposed as a means of estimating the proportion of the measured current of the silver electrode that is due to reactions other than silver oxidation. Figure 4.15 shows the measured current obtained for a platinum electrode in the same solution used in Figure 4.14. The current measured on the platinum electrode is the reduction of copper(II) at potentials less than 170 mV and the oxidation of copper(I) at higher potentials. Also shown in Figure 4.15 is the difference ($i_{Ag} - i_{calc}$) between the measured current for the silver electrode and the calculated current for silver oxidation determined from the measured mass change. This is a calculation of the current measured for the silver electrode that is due to reactions other than silver oxidation. Clearly, this calculated current due to reactions other than silver oxidation closely matches the profile of the current measured on the platinum electrode. However, it can be seen that the current measured on the platinum electrode is lower than the calculated current due to reactions other than silver oxidation occurring at the silver electrode surface. This indicates that copper(II) reduction and copper(I) oxidation occur more readily on a silver surface than a platinum surface in this chemically controlled potential region. However, the limiting currents (not shown) due to either copper(II) reduction or copper(I) oxidation were found to be the same on both electrodes.
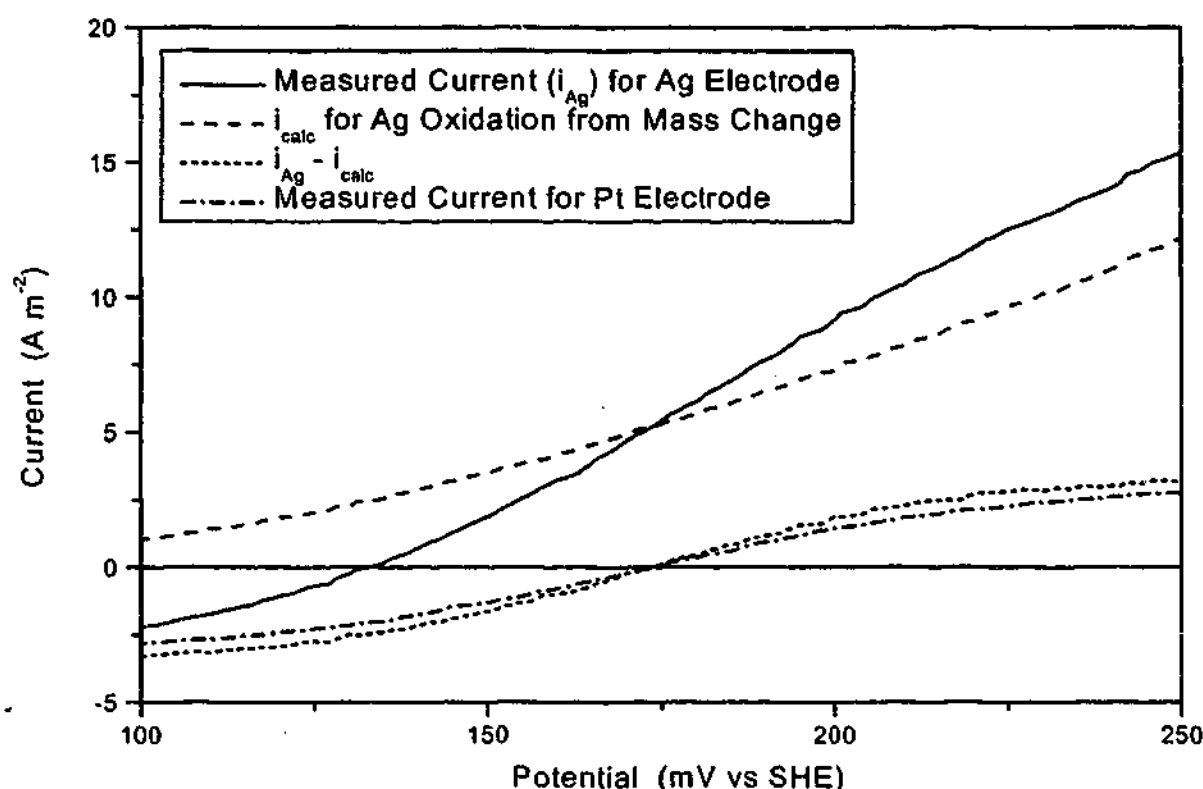
**Figure 4.15:** The difference in the measured current for a silver electrode and the current due to silver oxidation is shown compared to the current measured for a platinum electrode: 6 mM $Na_2S_2O_3$, 0.1 M $NH_3$, 0.1 M $Na_2SO_4$, 1 mM $CuSO_4$, 1 mM CuSCN, 300 rpm, 30 °C.

Obviously, the platinum electrode does not give an exact measure for the portion of the measured silver electrode current due to reactions other than silver oxidation ($i_{Ag}$ - $i_{calc}$) in the potential region of interest. However, a correction of 25% to the measure current of the platinum electrode gives a good estimate of $i_{Ag}$ - $i_{calc}$ in this potential region. Thus, an estimate of the current due to silver oxidation can be calculated from the measured silver and platinum electrode currents ($i_{Ag}$ – 1.25 x $i_{Pt}$). This estimated current due to silver oxidation is shown in Figure 4.16 to closely match the calculated current for silver oxidation from the measured mass change. Given that this analytical approach to measuring thiosulfate concentration in thiosulfate leach solutions corrects for the additional current measured on the silver electrode, errors in this approach are minimised by carefully choosing the potential. As shown in Figure 4.16 the correction would be small at the solution potential ($E_h$) of 170 mV. The $E_h$ values generally observed for thiosulfate leach solutions (not fresh solutions) range

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from 150 to 200 mV. Dilution, as proposed in section 4.3.1.2, has only a small effect on the solution $E_h$, thus 170 mV was chosen in order to minimise the correction for reactions other than silver oxidation occurring at the silver electrode.
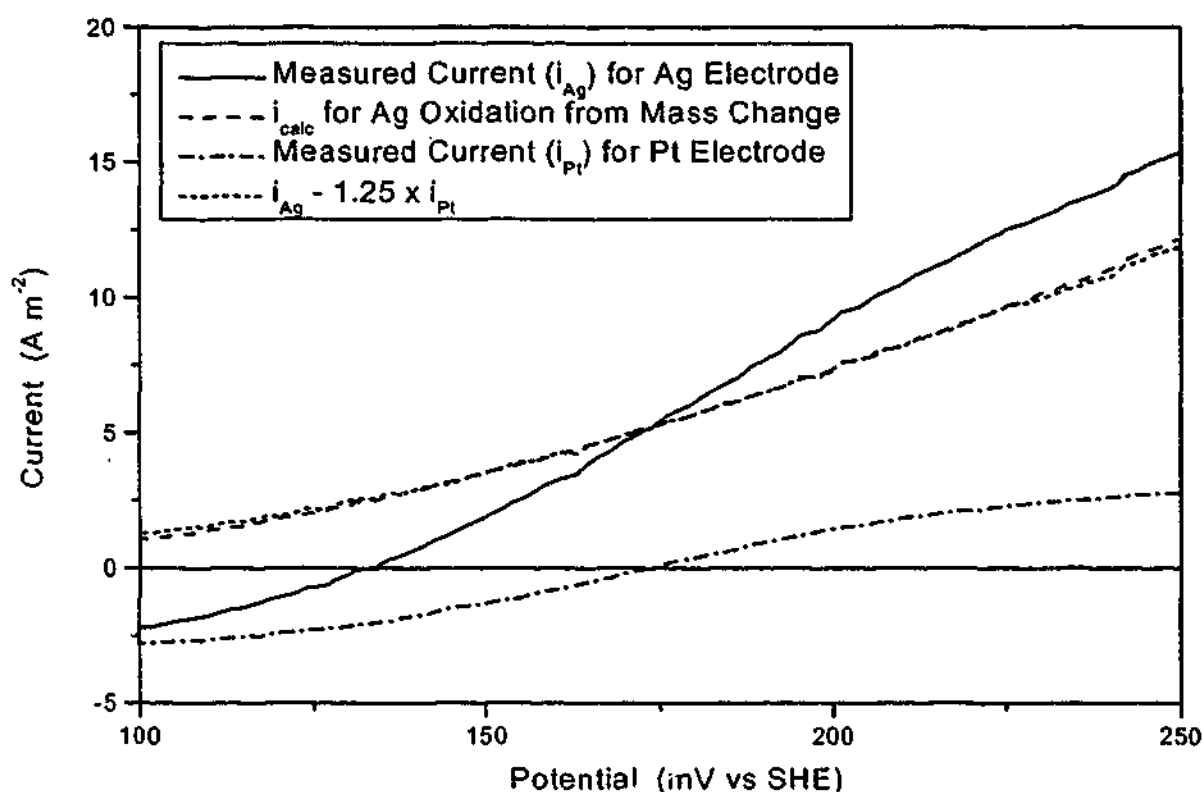


**Figure 4.16:** The measured current for a silver electrode adjusted by the current measured for a platinum electrode ($i_{Ag} - 1.25$ x $i_{Pt}$) is shown compared to the calculated current due to silver oxidation: 6 mM $Na_2S_2O_3$, 0.1 M $NH_3$, 0.1 M $Na_2SO_4$, 1 mM $CuSO_4$, 1 mM CuSCN, 300 rpm, 30 °C.

### 4.3.3.3   Design of 4 Electrode Flow-through Cell

In order to use the analytical method developed above in a FIA system, a purpose built 4 electrode flow-through cell as shown in Figure 4.17 was constructed. This incorporates two working electrodes, one being silver and the other platinum, a reference electrode and a counter electrode. The two working electrodes are the exposed ends of embedded wire of the same diameter where the measured current càn be corrected for a difference in the cross-sectional area if required. The cell utilises a

0.2 mm thick membrane to provide a flow channel for the solution over the electrode surfaces. With two working electrodes a bipotentiostat can be used to measure the current of the two working electrodes while controlling the potential. Alternatively, a simple operational amplifier circuit could be utilised, as the potential applied to the two working electrodes is the same (Bard and Faulkner, 1980).
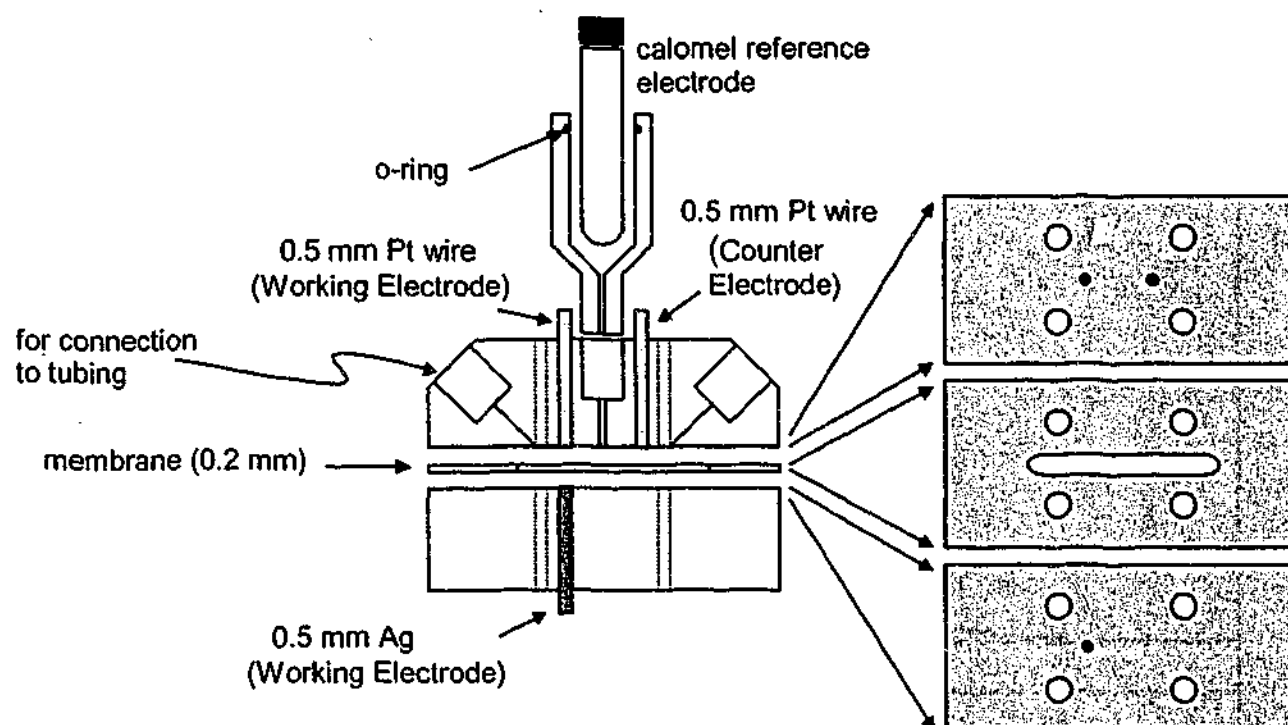


**Figure 4.17:** Diagram of the 4 electrode cell used for FIA measurement of thiosulfate concentration.

### 4.3.3.4 Response and Calibration of 4 Electrode Flow-through Cell

The 4 electrode flow-through cell was incorporated into the FIA system shown in Figure 4.9 in place of the EQCM cell. The response of this cell to injection of a solution containing 0.1 M thiosulfate and 0.4 M ammonia is shown in Figure 4.18. Recording of the working electrode currents commenced at the time of sample injection. Initially the measured current on both of the working electrodes is very small. The slight measurable current for the silver electrode is possible due to a small amount of silver oxidation to silver ammine, as shown in Figure 4.5 for 0.1 M ammonia. Once the

injected sample reaches the cell the measured current for the silver electrode increases, reaching a maximum approximately 30 seconds after sample injection, and then decays as the sample is flushed from the cell. The measured current of the platinum electrode is observed to remain relatively unchanged, as no solution species are present in this sample that are either oxidised or reduced at 170 mV.
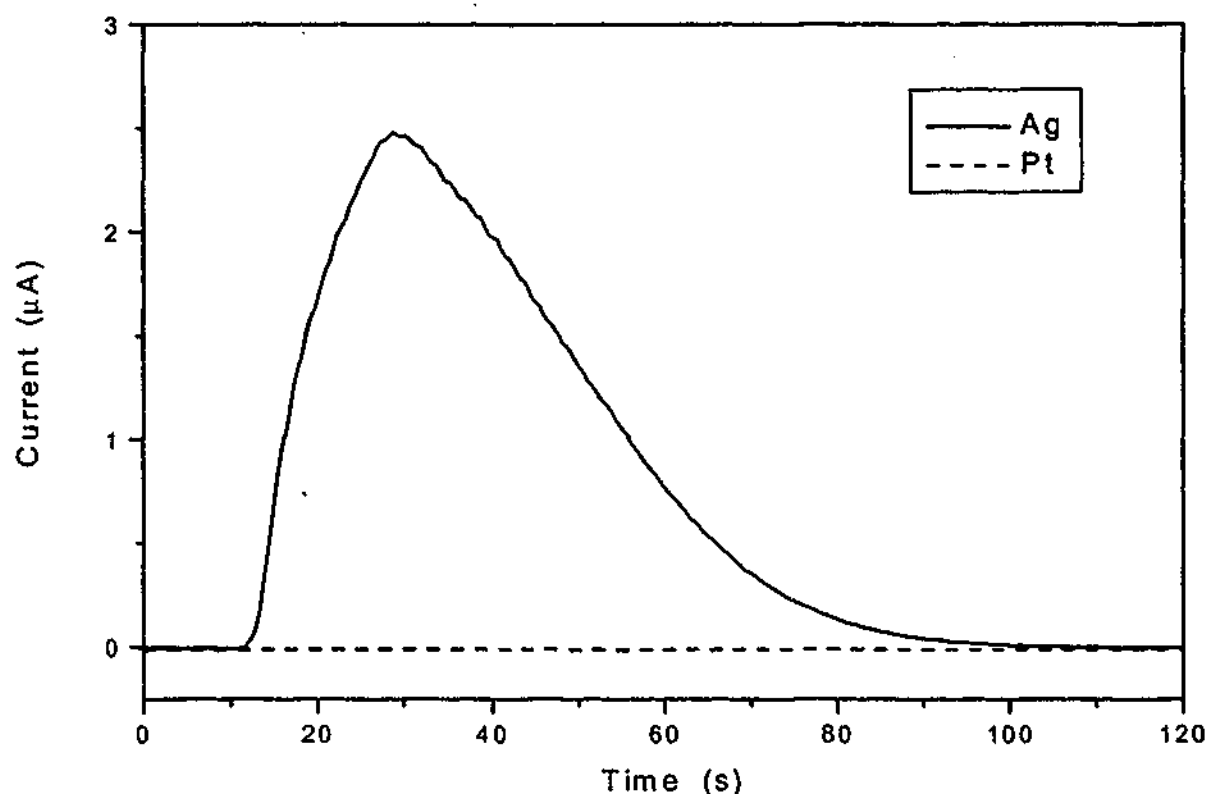


**Figure 4.18:** Response of the 4 electrode cell: Injected solution contained 0.4 M $NH_3$ and 0.1 M $Na_2S_2O_3$, 170mV.

The measured currents shown in Figure 4.18 are used in the following way to obtain a measure of the silver oxidation rate and hence the quantity of silver oxidised, which was shown in section 4.3.1.3 to be directly related to thiosulfate concentration. The difference in the measured currents is firstly calculated according to Equation 4.6. For the case where silver oxidation is the only reaction occurring at the electrode surface, as shown in Figure 4.18, $\Delta i = i_{Ag}$.

$$\Delta i = i_{Ag} - 1.25 \times i_{Pt} \qquad \qquad \textbf{4.6}$$

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This Δi is then adjusted to account for the baseline currents by subtracting the average measured Δi for the first 10 seconds. This correction is clearly small as only very small currents are measured on either working electrode for the carrier solution. The current due to silver oxidation is related to the silver oxidation rate by Faraday's law (Equation 4.4), hence, the mass change of the silver electrode is directly proportional to the integration of Δi (charge) with respect to time. Thus, the measured charge given by the area under the adjusted Δi curve is directly related to the mass change of the silver electrode and hence is directly related to thiosulfate concentration.

This calculation is best illustrated by considering the cell responses for thiosulfate solutions containing also copper(II) and copper(I). To check that the 4 electrode cell was correctly accounting for addition current due to reactions other than silver oxidation occurring at the silver electrode surface, a sample containing 0.1 M thiosulfate, 0.4 M ammonia and 10 mM copper(II) was injected directly after the concentrated copper + ammonia was mixed with the thiosulfate solution. Figure 4.19 shows the measured currents for the silver and platinum electrodes along with the adjusted Δi. Clearly, negative currents are measured on the platinum electrode as a result of copper(II) reduction on the electrode surface. For comparison the adjusted Δi calculated for the same solution in the absence of copper(II) is also shown in Figure 4.19. Calculation of charge from the adjusted Δi profiles gives expectedly the same measure of charge, though a slight difference in the profiles is observed.

Similarly, a sample containing 0.1 M thiosulfate, 0.4 M ammonia, 5 mM copper(II) and 5 mM copper(I) was injected, the response curves for which are shown in Figure 4.20. In this case a small positive current is observed on the platinum electrode due to copper(I) oxidation at the electrode surface. This indicates that the diluted solution $E_h$ is slightly less than 170 mV. Shown also in Figure 4.20 is the adjusted Δi for this solution and Δi for the same solution without added copper. The calculated charge for the solution with added copper was 92% of the charge calculated for the same solution without added copper. As the thiosulfate complexed with copper(I) does not contribute to the oxidation of silver (section 4.3.1.2), a measured charge of 92.5% was expected. Hence, this approach gives a very good measure of the available thiosulfate for leaching.
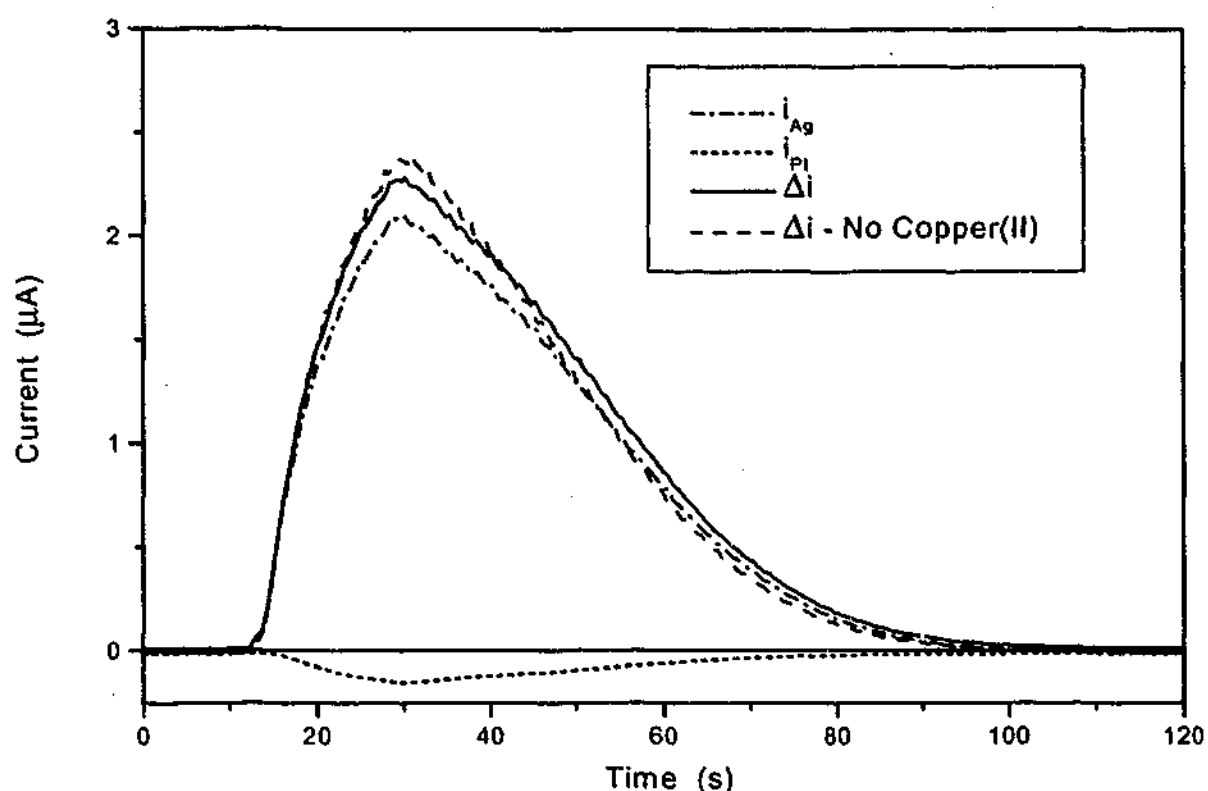
**Figure 4.19:** Measured currents and adjusted $\Delta i$ for a sample containing 0.4 M NH$_3$, 0.1 M Na$_2$S$_2$O$_3$, 10 mM CuSO$_4$: 170 mV.
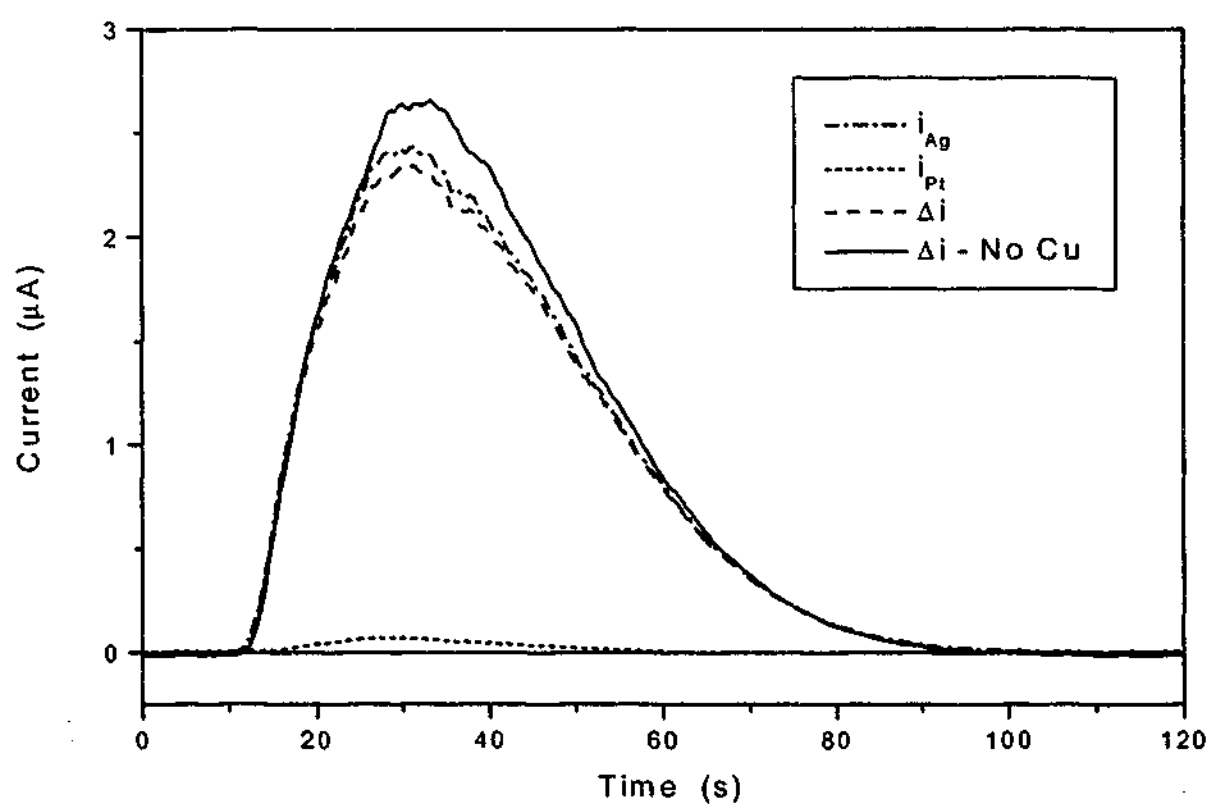


**Figure 4.20:** Measured currents and adjusted $\Delta i$ for a sample containing 0.4 M NH$_3$, 0.1 M Na$_2$S$_2$O$_3$, 5 mM CuSO$_4$ and 5 mM CuSCN: 170 mV.

The relationship between measured charge (area under the $\Delta i$ response curve) and thiosulfate concentration was subsequently determined for the 4 electrode flow-through cell. Figure 4.21 shows expectedly that the calibration curve for measured charge versus thiosulfate concentration is linear, with little scatter in the data (R=0.999).
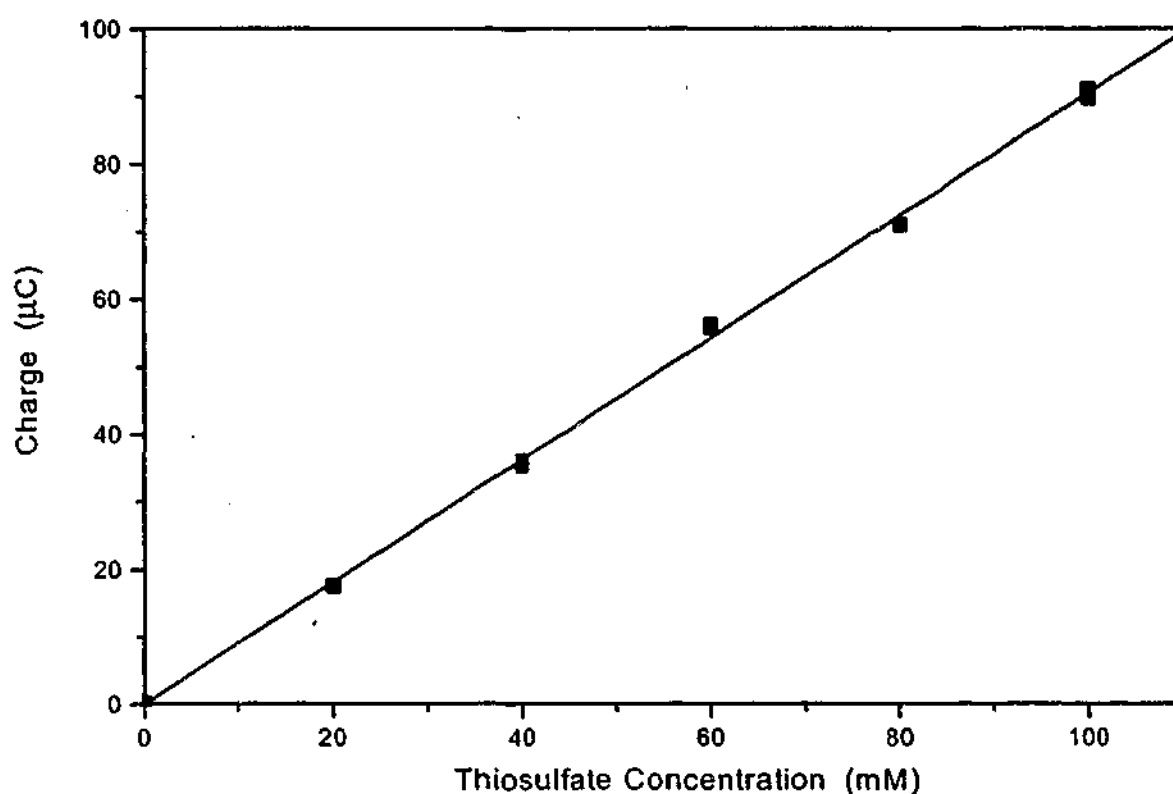


**Figure 4.21:** Calibration curve of measured charge versus thiosulfate concentration at an applied potential of 170 mV for FIA using the 4 electrode cell.

Variations in the measured current response curves due to solution composition were generally found to have minimal effect (less than 5%) on the measured charge. This error though was eliminated by utilising standards with the same composition as the solution being analysed. Thus, a simple FIA technique has been developed that was subsequently used (Chapter 5) in determining the rates of thiosulfate oxidation in the presence of oxygen for thiosulfate leach solutions applicable to gold leaching.

## 4.4 Summary

Development of an analytical method to measure the thiosulfate concentration in thiosulfate leach solutions applicable to gold leaching was successfully carried out with the use of a REQCM. The silver oxidation rate (measured by the rate of mass loss) was shown to be dependent on thiosulfate concentration, with dilution of the leach solution required to reduce the rate of silver oxidation. The thiosulfate concentration measured by this technique was also shown to be that of the free thiosulfate available for leaching, hence does not measure the thiosulfate complexed with copper(I).

A FIA method was developed utilising a purpose built EQCM cell to measure mass loss as a function of thiosulfate concentration. The requirement of a quartz crystal and the need to regularly replenish silver on the electrode surface, resulted in the development of an alternative method which utilises a more robust analysis cell. This alternative method involved using the measured current of a solid platinum electrode to estimate the proportion of the current measured for a solid silver electrode that is due to reactions other than silver oxidation. Thus, the difference in these measured currents is an estimate of the current measured on the silver electrode due to silver oxidation. The REQCM was used to verify that this approach gives a much better estimate of the thiosulfate concentration than measuring the current of a solid silver electrode alone, as previously advocated by Hemmati *et al.* (1989).

A purpose built 4 electrode flow through cell, containing both silver and platinum working electrodes, was incorporated into a FIA system. The integration of the difference between the measured currents of the two working electrodes during the sample injection period gives a measure of charge due to silver oxidation. This charge was shown to be linearly related to the thiosulfate concentration of the injected sample. Thus, a FIA method utilising a 4 electrode flow through cell was successfully developed giving a very simple, rapid and robust technique for measuring the thiosulfate concentration in thiosulfate leach solutions applicable to gold leaching.

# Chapter 5

# *Effect of Oxygen on the Thiosulfate Leach*

# *Solution Chemistry*

## 5.1  Introduction

The oxidation of thiosulfate by oxygen was described in the review to be very slow for a thiosulfate solution prepared using double distilled water. In the presence of copper(II) and ammonia the oxidation of thiosulfate occurs according to Equation 5.1 (Byerley *et al.*, 1973a), which was studied in detail in Chapter 3. In the presence of oxygen, the regeneration of copper(II) from copper(I) is known to occur readily according to the simplified reaction (copper ligands ignored) shown in Equation 5.2.
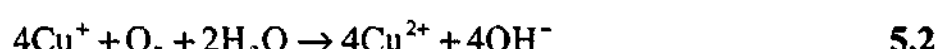
$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \rightarrow 2Cu(S_2O_3)_3^{5-} + 8NH_3 + S_4O_6^{2-} \qquad \textbf{5.1}$$

$$4Cu^+ + O_2 + 2H_2O \rightarrow 4Cu^{2+} + 4OH^- \qquad \textbf{5.2}$$

Thus, one would anticipate that the net result of such reactions would be the continual consumption of thiosulfate, at a rate limited by either Equation 5.1 or 5.2. However, in the presence of oxygen the rate of thiosulfate oxidation in ammoniacal solutions containing copper(II) is more than an order of magnitude faster than that predicted by the rate of Equation 5.1 (Byerley *et al.*, 1973b, Byerley *et al.*, 1975). Clearly, the thiosulfate leach solution chemistry is significantly more complex in the presence of oxygen; oxygen appears to play another role apart from oxidising copper(I) to copper(II) according to Equation 5.2.

The objective of the work in this chapter was to study in detail the kinetics of thiosulfate oxidation in the presence of oxygen for thiosulfate leach solutions applicable to gold leaching. This was achieved using the thiosulfate analysis technique developed in Chapter 4, and thus is not inferred from oxygen consumption measurements as used previously (Byerley *et al.*, 1973b, Byerley *et al.*, 1975); oxygen consumption may not be directly related to thiosulfate oxidation due to the differing oxidation rates of the intermediate oxysulfur species formed during the oxidation of thiosulfate through to trithionate and sulfate. An important consideration in this work was the effect of oxygen on the copper(II) concentration as the presence of oxygen does not maintain the copper in the copper(II) oxidation state as previously suggested (Byerley *et al.*, 1975). Optimum conditions were also investigated in order to minimise the rate of thiosulfate oxidation whilst maintaining an acceptable copper(II) concentration for gold leaching.

## 5.2   Experimental

All experiments were carried out using solutions prepared from analytical grade reagents and distilled water. The concentration of the copper(II) ammine complexes were monitored using UV-Vis spectrophotometry as outlined in section 3.2.1. The solution was stirred within a jacketed vessel (100 ml) maintained at a constant temperature ±0.1 °C and purged with gas of known oxygen concentration before commencing experiments. Evaporation and volatilisation losses of ammonia were minimised by first equilibrating the sparged gas with a solution at the same temperature and having the same ammonia concentration as the experiment being conducted. A concentrated copper(II)-ammonia solution was injected into the vessel and after a short mixing time the solution was continually pumped through a UV cell. The UV cell was housed in a temperature controlled jacketed cell holder within a GBC UV-Vis spectrophotometer. The solution absorbance at 605 nm was recorded at regular time intervals via a computer. Other solution species gave zero absorbance at this wavelength. In order to convert absorbance readings to a copper(II) concentration the kinetics data was extrapolated back to zero time at which point the copper(II) concentration is known. The variation in the copper(II) absorbance with thiosulfate

concentration was also corrected for using a linear correction between the extrapolated initial absorbance and the final absorbance. The thiosulfate concentration was monitored by withdrawing a sample at regular time intervals for analysis using the method developed in Chapter 4. Unless otherwise specified, these experiments were conducted at 30 °C, air sparged at 1000 $cm^3\ min^{-1}$ and the solutions initially contained 0.4 M ammonia, 0.1 M sodium thiosulfate, and 10 mM copper sulfate.

For experiments in which the copper was initially present as copper(I), a concentrated ammonia solution was injected into the vessel containing a solution of thiosulfate and copper(I). Unless otherwise specified, the solutions used in each of these experiments initially contained 0.4 M ammonia, 0.1 M sodium thiosulfate, and 10 mM copper(I) thiocyanate. In order to convert absorbance data to copper(II) concentrations the zero time absorbance for the same solution initially containing copper(II) instead of copper(I) was used.

## 5.3 Effect of Oxygen on the Solution Chemistry

For gold leaching in thiosulfate leach solutions, the copper(II) and thiosulfate concentrations are important (Chapter 2). Therefore, knowing the effect oxygen has on the copper(II) concentration and the rate of thiosulfate oxidation is vital in the continued use and recycle of thiosulfate leach solutions. The effect of various parameters on the copper(II) concentration and the thiosulfate oxidation rate were investigated. It should be noted that a mechanistic study of the solution chemistry was not an objective in this research. However, the results presented within this chapter do give some insight into the reactions and mechanisms possibly involved.

### 5.3.1 Copper(II) Concentration and Thiosulfate Oxidation

From the review presented in Chapter 2, it was expected that the presence of oxygen would maintain the copper in the copper(II) oxidation state, though the rate of thiosulfate oxidation was expected to be higher than in the absence of oxygen.

However, initial experiments showed that the copper was not maintained in the copper(II) oxidation state by the presence of oxygen.

### 5.3.1.1 Copper(II) Concentration

An initial experiment was conducted using a freshly prepared thiosulfate leach solution initially containing copper(II) in order to investigate the effect of oxygen on the copper(II) concentration in solution. Figure 5.1 shows the measured copper(II) concentration for a thiosulfate leach solution which had been continuously sparged with air. Also shown in Figure 5.1 for comparison is the measured copper(II) concentration for the same solution in the absence of oxygen (Argon). In this instance, the copper(II) concentration decreases due to its reaction with thiosulfate (Equation 5.1). After 1 hour, around 2 mM of copper(II) had reacted with thiosulfate (obviously under these conditions, this reaction is slow). It should be clear for Figure 5.1 that initially the copper(II) concentration in the thiosulfate solution decreases more rapidly in the presence of oxygen. Such a result is surprising given that copper(I) can be readily oxidised in the presence of oxygen to produce copper(II).

It can also be seen from Figure 5.1 that the copper(II) concentration decreases to a minimum value at which point the rate of copper(II) reduction is matched by the rate of copper(I) oxidation. The copper(II) concentration then increases, such that after 1 hour, all the copper is again present as copper(II). This is shown in Figure 5.2 to correspond with all the thiosulfate having been oxidised. The increase in the copper(II) concentration from the minimum is attributed to the decrease in thiosulfate concentration (see section 5.3.3.2). In a separate experiment shown in Figure 5.1, the air sparging was stopped after 0.5 hours At this point copper(I) is no longer being oxidised to copper(II) and the copper(II) concentration is observed to decrease rapidly. This indicates that the rate of copper(II) reduction occurs at a much higher rate in an air sparged thiosulfate solution than in the absence of oxygen. Obviously, the rate of copper(I) oxidation must also be rapid in order to maintain the copper(II) concentration above 5 mM.
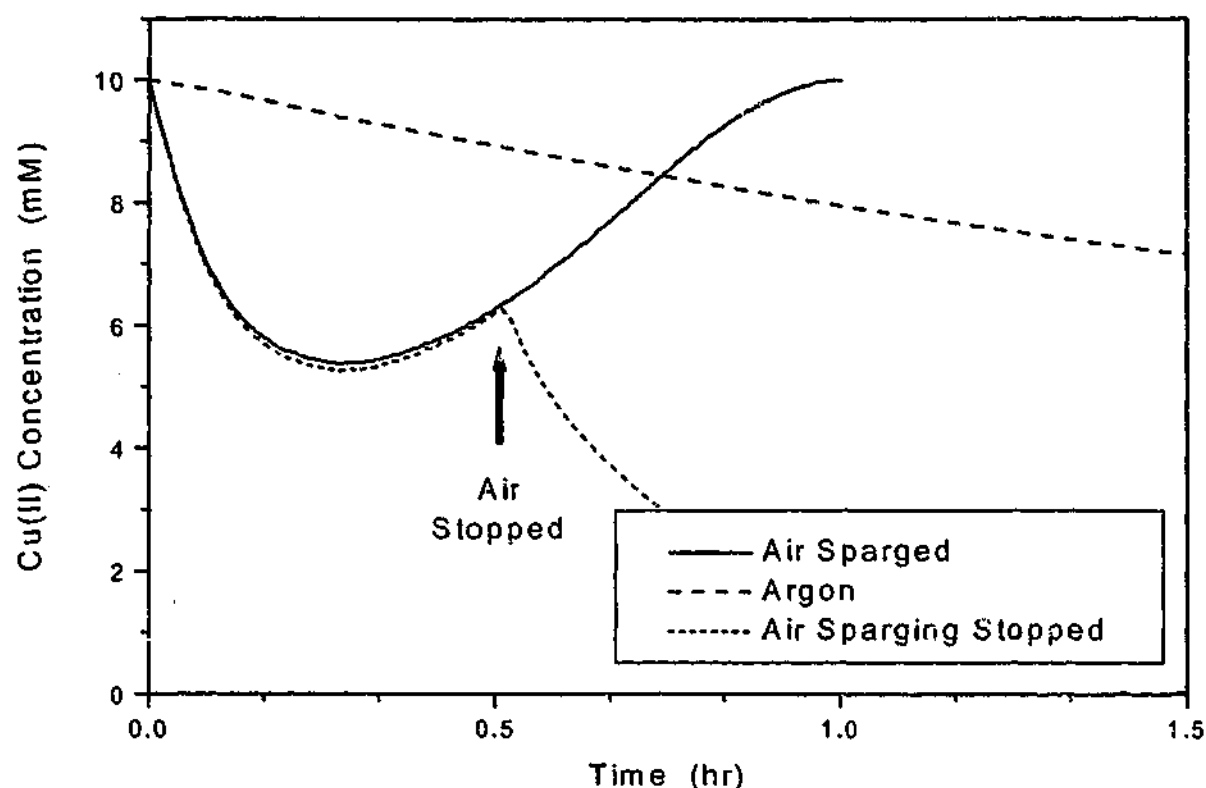
**Figure 5.1:** Effect of oxygen (air sparging) on the copper(II) concentration in a typical thiosulfate leach solution: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C, air sparged at 1000 $cm^3$ $min^{-1}$.

One of the most important aspects of the data shown in Figure 5.1 is that during the oxidation of thiosulfate, copper exists as both copper(I) and copper(II). In the work conducted by Byerley *et al.* (1975), the authors claimed that no decrease in the copper(II) concentration occurred. In addition, the mechanisms proposed by these authors (see section 2.2.2) do not account for the formation of copper(I) in solution. Another important point regarding the mechanisms involved in copper(II) reduction is that no induction period is observed for copper(II) reduction in the presence of oxygen. Hence, a mechanism that is consistent with oxygen increasing the rate of copper(II) reduction by thiosulfate to copper(I) is required. In Chapter 3 it was shown that the copper(II) reduction by thiosulfate was generally second order with respect to copper(II), indicating that the slow step in the mechanism was two $Cu(II)-S_2O_3^{2-}$ complexes reacting to give copper(I) and tetrathionate. As the formation of $Cu(II)-O_2$ complexes is considered highly unlikely (Simandi, 1992), it would appear that the presence of oxygen provides an alternative mechanism to this slow step.

The copper(II) concentration and the [Cu(II)]:[Cu(I)] ratio in thiosulfate leach solutions are very important to the gold dissolution process (Chapters 6 and 7); the latter essentially determines the potential at which gold leaching occurs. The effect of various parameters on the copper(II) concentration and the [Cu(II)]:[Cu(I)] ratio is thus an important aspect investigated in this chapter.

### 5.3.1.2    Thiosulfate Oxidation Rate

The rate of thiosulfate oxidation was determined using the procedure developed in Chapter 4. Figure 5.2 shows the measured thiosulfate concentrations as a function of time for a 0.1 M thiosulfate leach solution sparged with air or maintained under argon. Clearly, the rate of thiosulfate consumption is very rapid in the presence of oxygen (air); all of the thiosulfate is oxidised in 1 hour. In comparison less than 5% of the thiosulfate was oxidised under argon for the same time period. Based on the initial copper(II) reduction rate under argon (0.58 mmol $s^{-1}$), it can be estimated that it would take at least 2 days to consume all the thiosulfate on the basis of the simple copper(II)/copper(I) redox cycle of Equations 5.1 and 5.2. A similar observation by Byerley *et al.* (1975) led to the conclusion that a simple copper(II)/copper(I) redox cycle as presented in Equations 5.1 and 5.2 was not the dominant cause of thiosulfate oxidation.

However, the initial rate of copper(II) reduction in the presence of oxygen is significantly faster than that observed in the absence of oxygen (Figure 5.1). Based on this initial rate in the presence of oxygen, it can be estimated that all the thiosulfate will be oxidised in 2.3 hours. Thus, it is conceivable that a redox cycle with an enhanced rate of copper(II) reduction plays an important role in the oxidation of thiosulfate in the presence of oxygen. The results presented in Figures 5.1 and 5.2 clearly indicate that the presence of oxygen increases both the rate of thiosulfate oxidation and the rate of copper(II) reduction to copper(I). Thus, mechanisms other than those proposed by Byerley *et al.* (1975) are needed which explain both of these observations. This is currently the focus of further research in this area being conducted at Murdoch University.
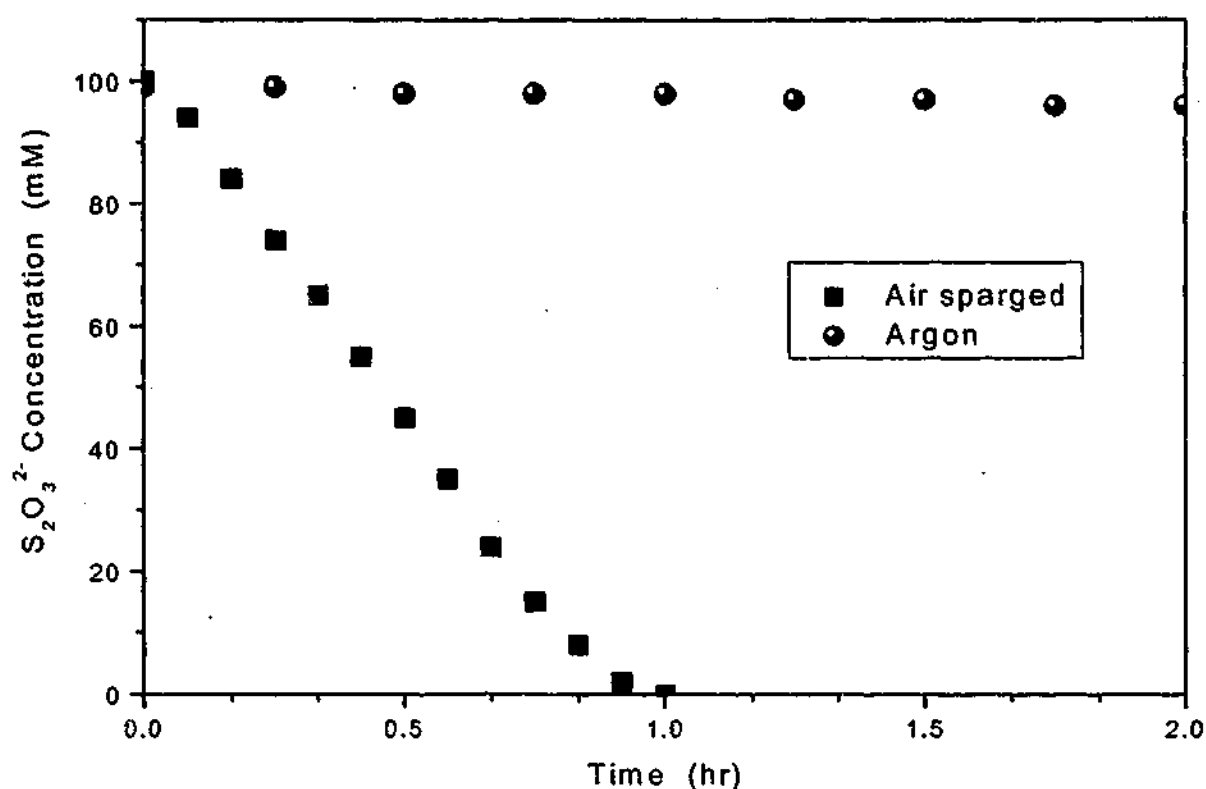
**Figure 5.2:** Effect of oxygen (air sparging) on the rate of thiosulfate oxidation in a typical thiosulfate leach solution: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C, air sparged at 1000 $cm^3$ $min^{-1}$.

## 5.3.1.3  Effect of Anions

The presence of anions was shown in Chapter 3 to significantly reduce the rate of copper(II) reduction by thiosulfate. Figure 5.3 shows the effect of 0.1 M sodium phosphate on the copper(II) concentration profile and the rate of thiosulfate oxidation. Clearly, the presence of phosphate dramatically reduces the initial rates of copper(II) reduction and thiosulfate oxidation. As the copper(II) concentration is shown to remain above 8.5 mM in the presence of 0.1 M phosphate, the rate of copper(II) reduction in the presence of anions is obviously much slower (initial rate approximately an order of magnitude slower). This is consistent with anions competing for coordination at the copper(II) axial sites as discussed in section 3.3.2.2 and thus reducing the rate of . copper(II) reduction by thiosulfate involving oxygen.

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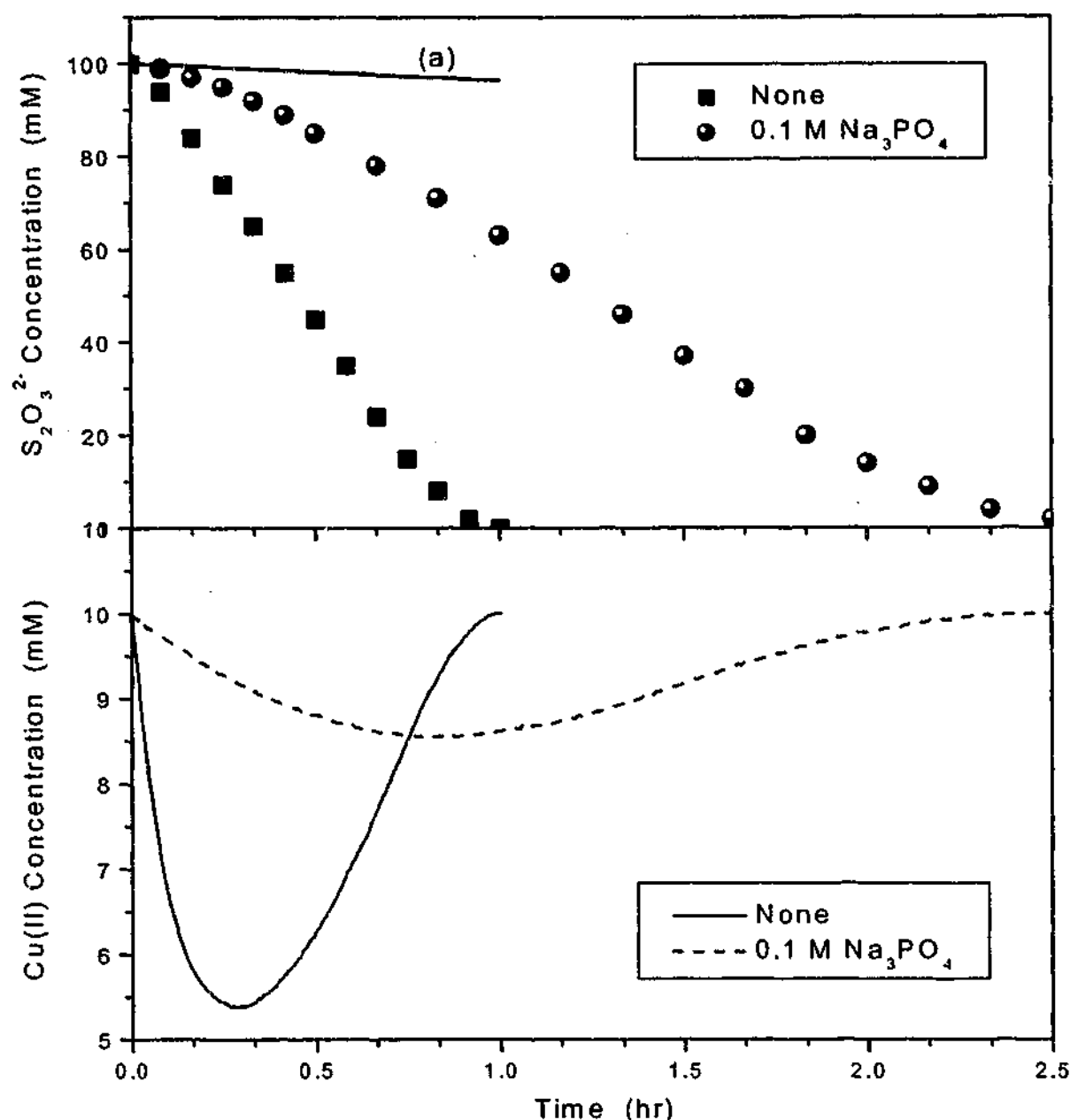
**Figure 5.3:** Effect of phosphate ions on the rate of thiosulfate oxidation and the copper(II) concentration profile: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C, air sparged at 1000 $cm^3$ $min^{-1}$.

The effect of anions on the initial rate of thiosulfate oxidation is also shown in Figure 5.3 to be significant. Based on the initial rate of copper(II) reduction in the presence of 0.1 M sodium phosphate, the maximum rate of thiosulfate oxidation as a result of copper(II) reduction can be estimated (ignoring the thiosulfate complexed with copper(I) as this is small) and is indicated by line (a) in Figure 5.3. The initial thiosulfate oxidation rate is similar to this line and thus is conceivably due to the rate of copper(II) reduction by thiosulfate in the presence of oxygen. However, the rate of

thiosulfate oxidation increases significantly as evident by the deviation in the thiosulfate concentration from line (a) in Figure 5.3. As a result of the increased rate of thiosulfate oxidation, the time taken for all the thiosulfate to be oxidised in the presence of 0.1 M phosphate is only 2.5 times longer than the time taken in the absence of added phosphate. This clearly indicates that at least one other mechanism is involved in the oxidation of thiosulfate, via which the majority of the thiosulfate is oxidised.

### 5.3.1.4   Effect of Initial Copper Oxidation State

The effect of the initial copper oxidation state on the rate of thiosulfate oxidation by oxygen was also investigated. Figure 5.4 shows a comparison of the copper(II) concentration measured for identical solutions with the exception that the copper was initially present as either copper(II) or copper(I). It should be clear from Figure 5.4 that for the solution initially containing only copper(I), the copper(II) concentration increases rapidly due to the oxidation of copper(I) by oxygen. This clearly shows that the rate of copper(I) oxidation by oxygen to copper(II) is very fast for these conditions. Notably, the copper(II) concentration increases to a maximum value, before decreasing slightly to a minima. Such a result is consistent with an increase in the relative rate of copper(II) reduction to copper(I) oxidation during this time. It is worth noting that intermediate oxysulfur species formed during thiosulfate oxidation are likely to be reactive towards copper(II). Hence, it is possible that the decrease in the copper(II) concentration observed when starting with copper(I) is due to the increase in copper(II) reduction rate as a result of the increase in the concentration of the intermediate oxysulfur species.

The thiosulfate concentration profiles in Figure 5.4 also indicate that the oxidation of thiosulfate is slightly faster when the solution initially contains copper(I). In this instance, a faster initial increase in the concentrations of the reaction products from the oxidation of copper(I) by oxygen occurs. Such a result suggests that the reaction products of copper(I) oxidation by oxygen may be involved in the oxidation of thiosulfate. This is also consistent with the results shown in Figure 5.3 for solutions containing phosphate, which suggests that another mechanism is responsible for most of the thiosulfate oxidation. Clearly, details regarding the mechanisms of copper(I) oxidation by oxygen need to be considered.
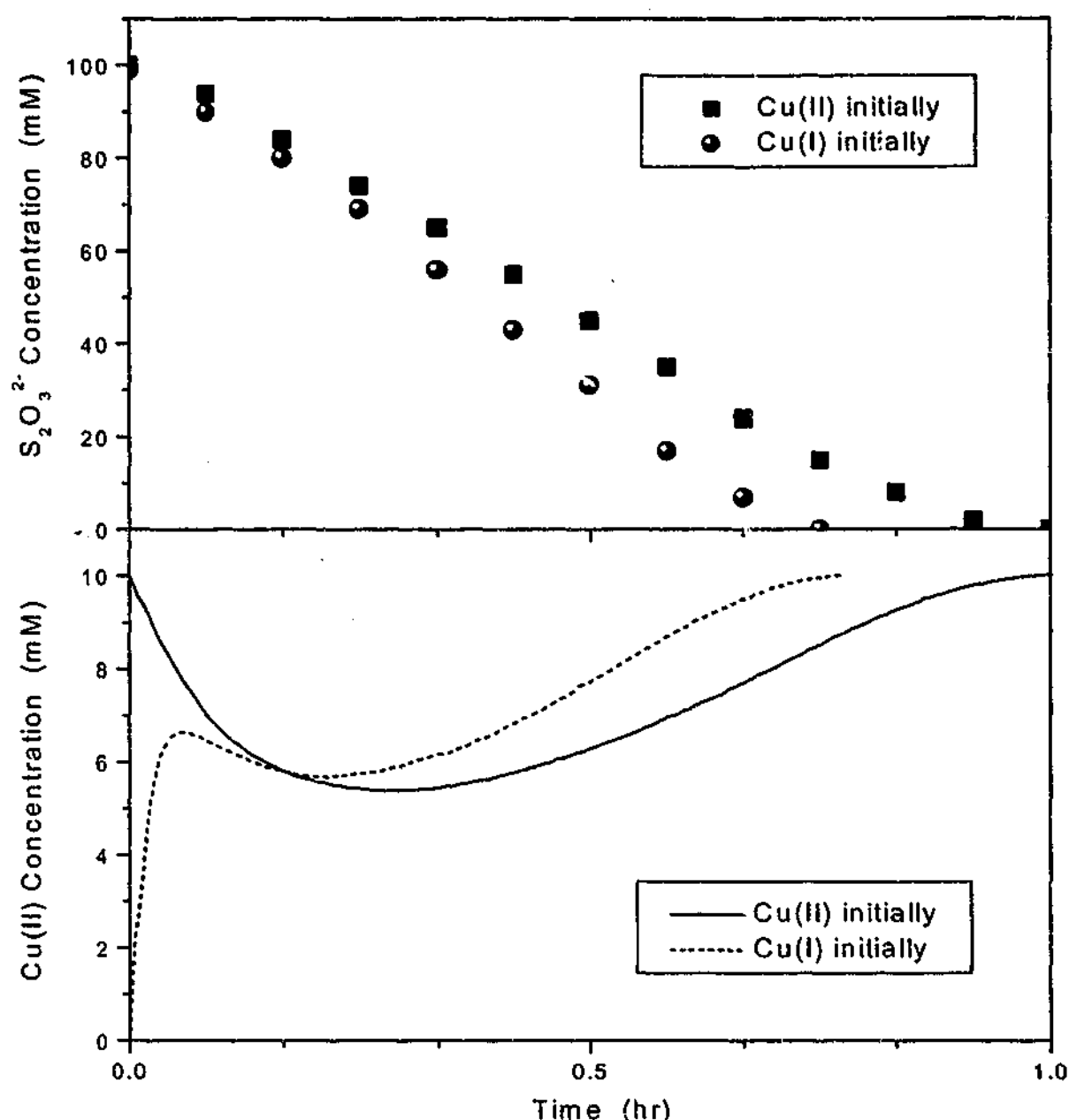
**Figure 5.4:** Effect of initial copper oxidation state on the rate of thiosulfate oxidation and the copper(II) concentration profile: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM Cu, 30 °C, air sparged at 1000 $cm^3$ $min^{-1}$.

### 5.3.1.5 Copper(I) Oxidation by Oxygen

The oxidation of copper(I) complexes by oxygen has been studied extensively (Zuberbühler (1983, 1981) and Simandi (1992) and references within), especially in relation to biological systems. The second order rate constants for the autoxidation of copper(I) complexes with ammonia are roughly 1 to 20 $M^{-1}$ $s^{-1}$ (Zuberbühler, 1983)

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indicating that the reactions involved are rapid. However, the rate of oxidation can be significantly lowered if the corresponding copper(I) and copper(II) complexes have significantly different structures whereby extensive rearrangement of the coordination sphere is necessary before electron transfer can take place (Zuberbühler, 1983). It is well established that the first steps involved in the oxidation of copper(I) by oxygen (Equation 5.2) results in the formation of copper(II) and peroxide according to Equation 5.3 (Zuberbühler, 1983).

$$2Cu^+ + O_2 \xrightarrow{\ H_2O\ } 2Cu^{2+} + HO_2^- + OH^- \qquad\qquad 5.3$$
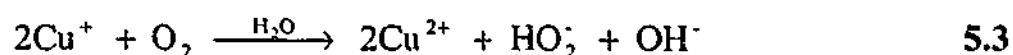
The mechanisms for reaction 5.3 however are not clear. Based on kinetic results it is firmly established that the autoxidation of copper(I) complexes occurs via inner sphere mechanisms involving dioxygen adducts formed according to Equation 5.4; this is believed to be common to the autoxidation of most if not all copper(I) complexes (Zuberbühler, 1983).

$$Cu^+ + O_2 \longleftrightarrow Cu^+O_2 \qquad\qquad 5.4$$

The $Cu^+O_2$ adduct may equally be viewed as a copper(II) superoxide complex, $Cu^{2+}O_2^-$ (Zuberbühler, 1983). However, superoxide has not been identified chemically or spectrophotometrically in its free or complexed form during copper(I) autoxidation (Zuberbühler, 1983). This is not surprising given that the superoxide reactivity (of the order $10^9\ M^{-1}\ s^{-1}$) is close to diffusion rates (Zuberbühler, 1983).

It has been known for about a century that the decomposition of hydrogen peroxide to oxygen and water is dramatically accelerated by the presence of metal ions, with the decomposition being the order of seconds in the presence of copper(II) (Luo *et al.*, 1988). Byerley *et al.* (1975) however suggested that any peroxide formed in oxygenated thiosulfate solutions containing copper(II) and ammonia results directly in further thiosulfate oxidation. A series of experiments were therefore conducted in order to ascertain the effect of peroxide on the thiosulfate leach solution chemistry.

The addition of 50 mM hydrogen peroxide to a 0.1 M thiosulfate and 0.4 M ammonia solution (no copper) was found to result in less than 30% oxidation of thiosulfate after 1 hour. Obviously this reaction does not occur at an appreciable rate. However, in the presence of copper(II) a very fast reaction occurs on the addition of peroxide. This is shown in Figure 5.5, where the copper(II) concentration is observed to decrease rapidly on the addition of 5 mM hydrogen peroxide. A very rapid reaction was also observed on the addition of hydrogen peroxide to a thiosulfate leach solution containing copper only in the copper(I) oxidation state (not shown). These results show that the decomposition of peroxide in thiosulfate leach solutions is catalysed by the presence of copper and was found to be very rapid; being significantly faster than the oxidation of thiosulfate by peroxide. The addition of hydrogen peroxide to a thiosulfate leach solution was also found to result in a rapid decrease in the thiosulfate concentration. Such a result implies that the intermediates of peroxide decomposition oxidise thiosulfate and not peroxide directly as suggested by Byerley *et al.* (1975).
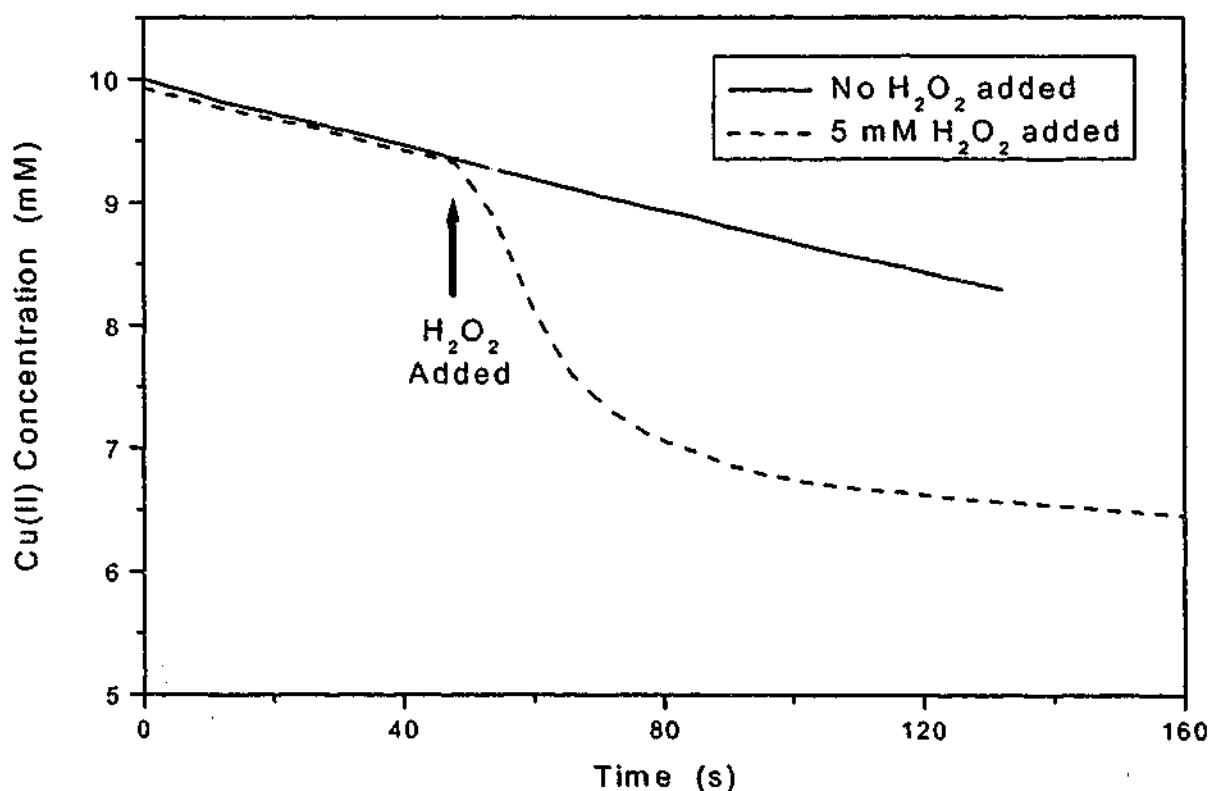


**Figure 5.5:**   Decomposition of hydrogen peroxide in thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C, air sparged at 1000 $cm^3$ $min^{-1}$.

Reaction mechanisms consistent with the results presented in this chapter for thiosulfate oxidation, copper(II) reduction and copper(I) oxidation in thiosulfate leach solutions are shown in Scheme 2. Reactions B to G of Scheme 2 describe the copper catalysed decomposition of peroxide, which are obviously an integral part of the thiosulfate leach solution chemistry once copper(I) is formed in the presence of oxygen. The two paths for thiosulfate oxidation as predicted by the results of Figure 5.3 are ascribed to Equations A and H of Scheme 2. Equation A is the copper(II)-thiosulfate reaction that is catalysed by oxygen as evident in Figure 5.1 by the higher initial rate of copper(II) reduction. Equation H is the oxidation of thiosulfate by superoxide or hydroxide radicals as a result of copper(I) oxidation. Obviously a series of complex reactions are involved in copper(II) reduction and copper(I) oxidation (Equations A, B, D, E and F of Scheme 2).

$$Cu^{2+} + S_2O_3^{2-} \xrightarrow{O_2} Cu^+ + X \qquad \text{A}$$

$$Cu^+ + O_2 \longleftrightarrow Cu^{2+} + O_2^- \qquad \text{B}$$

$$2O_2^- \xrightarrow{H_2O} O_2 + HO_2^- + OH^- \qquad \text{C}$$

$$Cu^{2+} + HO_2^- + OH^- \longleftrightarrow Cu^+ + O_2^- + H_2O \qquad \text{D}$$

$$Cu^+ + HO_2^- \xleftarrow{H_2O} Cu^{2+} + OH + 2OH^- \qquad \text{E}$$

$$Cu^+ + OH \longrightarrow Cu^{2+} + OH^- \qquad \text{F}$$

$$OH + HO_2^- \longrightarrow H_2O + O_2^- \qquad \text{G}$$

$$R + S_2O_3^{2-} \longrightarrow P \quad (R = O_2^- \text{ or } OH) \qquad \text{H}$$
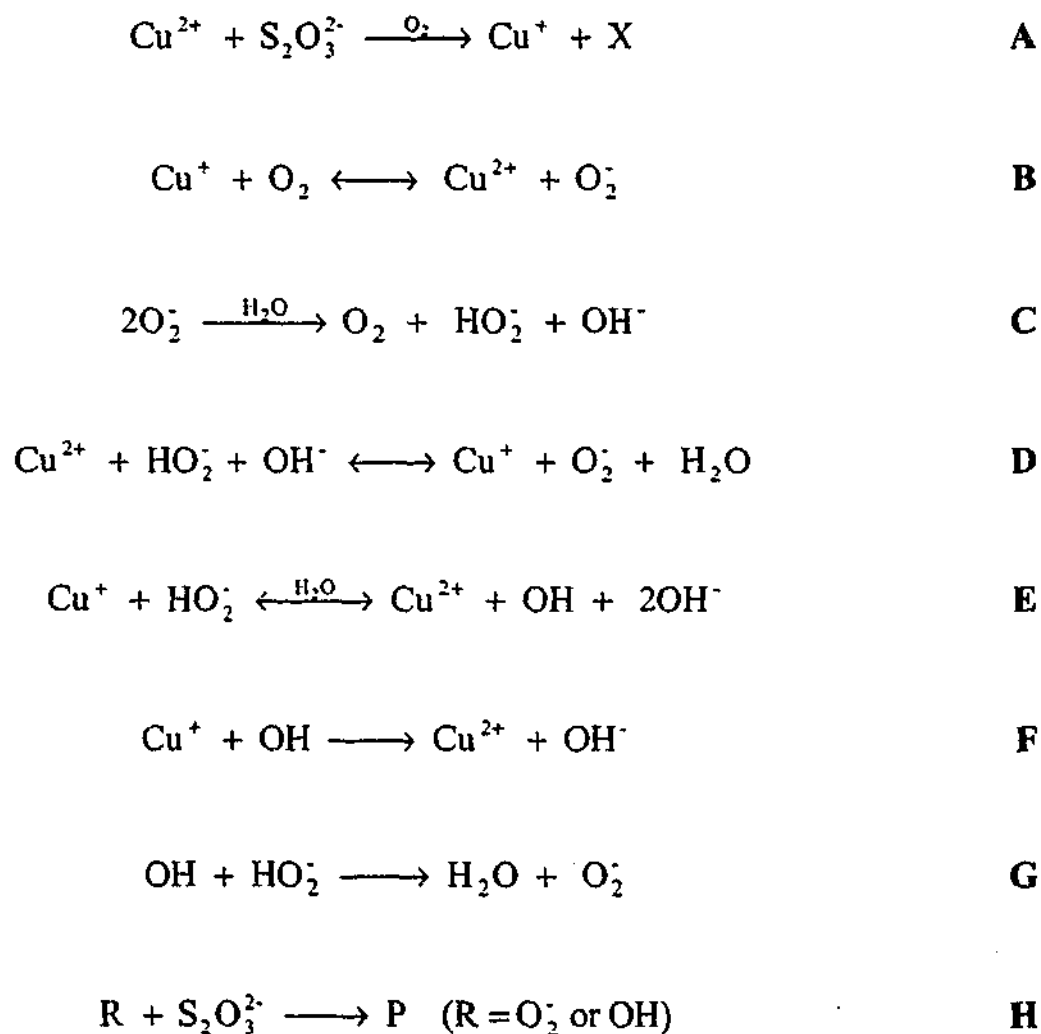
**Scheme 2:**   Proposed mechanisms for thiosulfate oxidation.

Even though it is shown in Figure 5.2 that all the thiosulfate has been oxidised in 1 hour, the oxidation of the other intermediate oxysulfur species, such as tetrathionate, may still be occurring. This has been shown to be the case in several of the references cited by Skorobogaty and Smith (1984). While these oxysulfur species may undergo further copper(II) catalysed oxidation involving similar mechanisms to those presented in Scheme 2 for the oxidation of thiosulfate (Equations A and H), this is beyond the focus of this thesis.

A detailed study of the individual reactions involved in thiosulfate leach solutions in the presence of oxygen is beyond the focus of this thesis. However, there are three main reactions taking place that are of interest to the gold thiosulfate leaching process. These are the oxidation of thiosulfate, the reduction of copper(II) and the oxidation of copper(I); the latter 2 determine the [Cu(II)]:[Cu(I)] ratio. Before attempting to study the effect of various parameters on the kinetics of thiosulfate oxidation and the [Cu(II)]:[Cu(I)] ratio, it was important to establish some fundamental understanding of the copper(I) oxidation kinetics in thiosulfate leach solutions. Thus, the effect of various parameters on the copper(II) reduction rate can then be inferred from the copper(II) concentration profiles.

### 5.3.2  Effect of Parameters on Copper(I) Oxidation by Oxygen

A detailed study of the oxidation of copper(I) by oxygen to copper(II) was effectively achieved by measuring the initial rate of copper(II) formation in solutions initially containing only copper(I).

### 5.3.2.1  Oxygen Concentration

Figure 5.6 shows the measured copper(II) concentration with time for a thiosulfate solution initially containing 10 mM copper(I) which had been continuously sparged with gas of different oxygen concentrations. It should be clear that when the solution is sparged with pure oxygen, the rate of oxidation of copper(I) to copper(II) is very rapid; more than half the copper(I) is oxidised to copper(II) by the time the first measurement of copper(II) concentration was made just 30 seconds after ammonia

addition. However, the copper(II) concentration profile does not approach 10 mM due to copper(II) reduction also taking place. When a gas containing 1.9% oxygen and 98.1% nitrogen is sparged through the same solution, the rate of copper(I) oxidation is substantially slower. In 5 minutes, only 2 mM of copper(I) had been oxidised to copper(II), as compared to 7 mM in 1 minute for pure oxygen. Such a result is hardly surprising, as the dissolved oxygen concentration is a function of the partial pressure of oxygen in the gas phase.
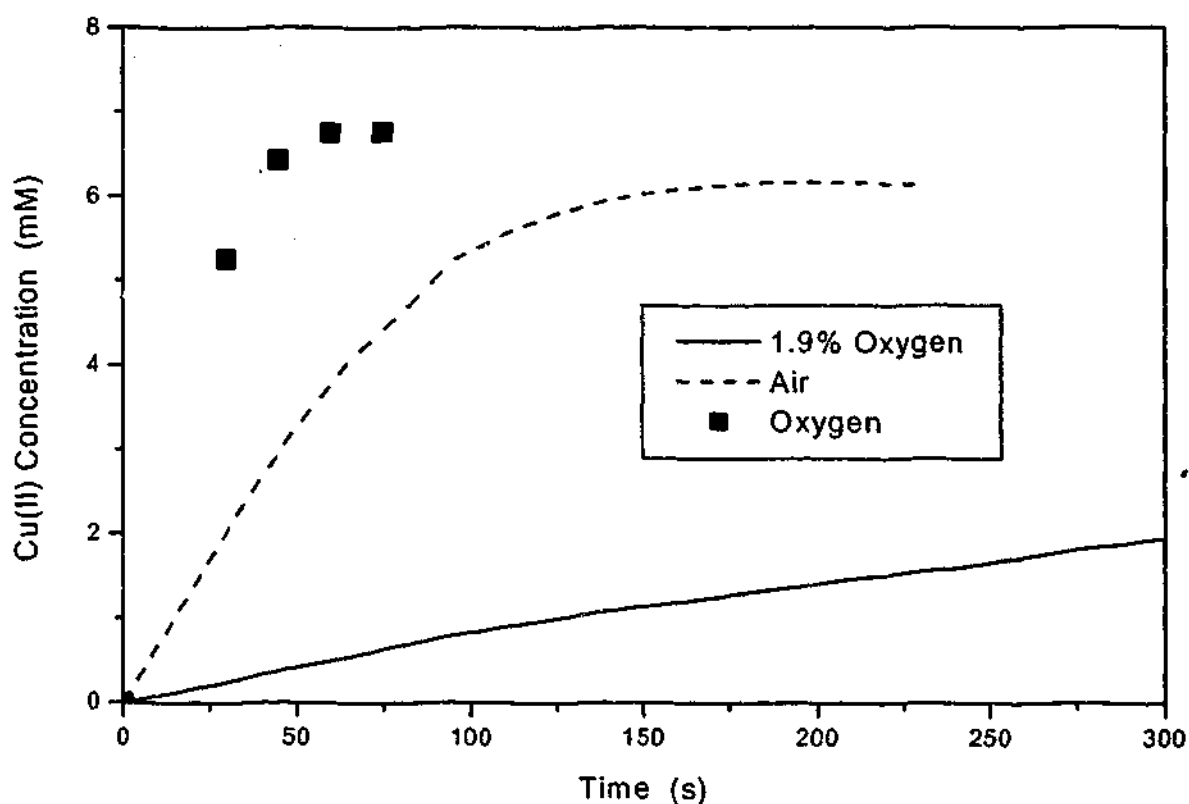


**Figure 5.6:** Effect of oxygen concentration on the rate of copper(I) oxidation: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM CuSCN, 30 °C, gas sparged at 1000 $cm^3$ $min^{-1}$.

Given that the rate of copper(I) oxidation is fast and highly dependent on oxygen concentration, it is likely that the mass transfer rate of oxygen into solution will be important. This was investigated by varying the flow rate of air sparged through a solution that initially contained only copper(I). Figure 5.7 clearly shows that the rate of copper(I) oxidation is highly dependant on the mass transfer rate of oxygen from the sparged air into solution. When the air flow rate is 10 $cm^3$ $min^{-1}$, it can be seen from

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Figure 5.7 that the copper(II) concentration initially jumps to around 0.3 mM. Such a result is consistent with the copper(I) rapidly consuming the majority of dissolved oxygen in solution. As the initial oxygen in solution is consumed the rate of copper(I) oxidation decreases due to the decreasing oxygen concentration to the point where the copper(I) oxidation rate is matched by the mass transfer rate of oxygen into solution. This results in a lower "equilibrium" oxygen concentration in solution, and hence a low overall rate of copper(I) oxidation. When the solution is heavily sparged $(1000 \text{ cm}^3 \text{ min}^{-1})$ with air, the rate of oxygen mass transfer maintains the solution oxygen concentration close to the initial equilibrium oxygen concentration.
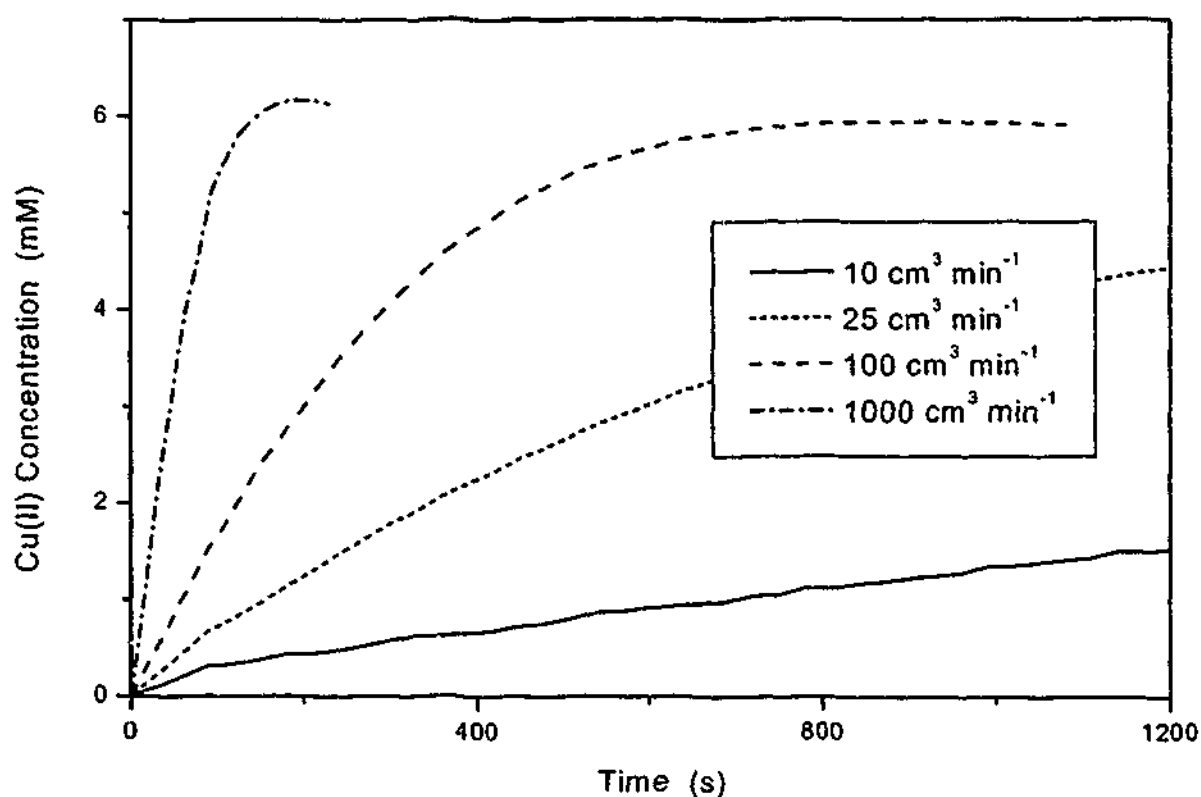


**Figure 5.7:** Effect of air sparge rate on the rate of copper(I) oxidation: 0.4 M NH$_3$, 0.1 M Na$_2$S$_2$O$_3$, 10 mM CuSCN, 30 °C, air sparged.

### 5.3.2.2 Copper(I) Concentration

Figure 5.8 expectedly shows that the rate of copper(I) oxidation is dependant on the copper(I) concentration. Estimates of the initial rate indicate the reaction order with respect to copper(I) is first order; accurate initial rates of copper(I) oxidation were not

measurable with the experimental set up used. For the solution initially containing only 2 mM copper(I), an equilibrium between the copper(I) oxidation and copper(II) reduction rates had been reached by the time the first measurement of copper(II) concentration was made just 35 seconds after commencing the experiment.
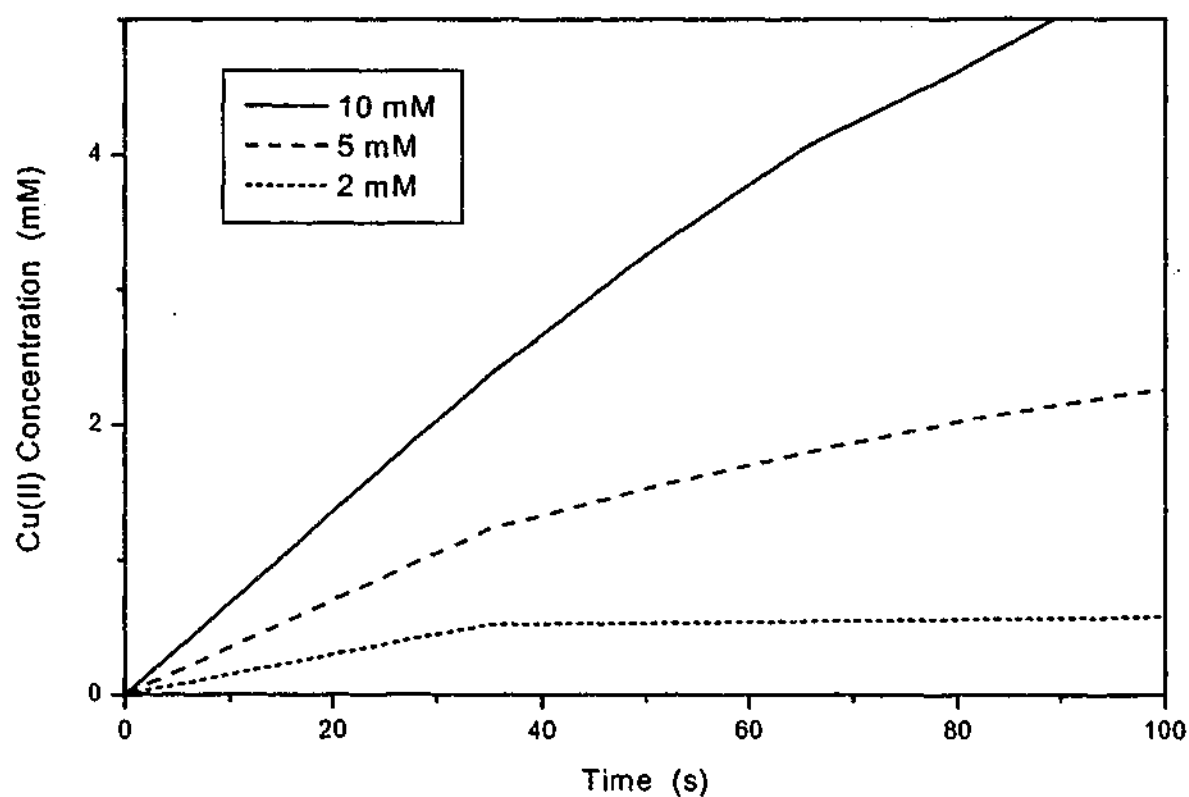


**Figure 5.8:** Effect of copper(I) concentration on the rate of copper(I) oxidation: 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$, 30 °C, gas sparged at 1000 cm$^3$ min$^{-1}$.

### 5.3.2.3 Ammonia and Thiosulfate Concentration

Both ammonia and thiosulfate can potentially act as ligands for copper(I), although the published stability constants for the copper(I) ammine complexes are lower than for the copper(I) thiosulfate complexes (Smith and Martell, 1976). Using the stability constants for the copper(I) thiosulfate complexes, Log K$_1$ = 10.35, Log K$_2$ = 12.27, and Log K$_3$ = 13.71, it can be estimated that for a 0.1 M thiosulfate solution, 35% of the copper(I) exists as the di-thiosulfate complex and 65% as the tri-thiosulfate complex. However, the speciation of copper(I) in solutions containing ammonia and thiosulfate is uncertain as there is no thermodynamic data available for the mixed

ammonia-thiosulfate complexes of copper(I). Recently it has been shown that the potential required to oxidise copper metal to copper(I) in ammonia-thiosulfate solutions is significantly more negative than for the corresponding thiosulfate or ammonia solutions (Choo and Jeffrey, 2001). Thus, it is conceivable that a number of mixed ligand complexes of copper(I) are present in solutions containing thiosulfate and ammonia; the formation of the possible complexes is shown in Equation 5.5.

$$[Cu(S_2O_3)_3]^{5-}$$

$$\updownarrow \pm S_2O_3^{2-}$$

$$[Cu(S_2O_3)_2]^{3-} \xleftrightarrow{\pm NH_3} [Cu(S_2O_3)_2NH_3]^{3-} \qquad \textbf{5.5}$$

$$\updownarrow \pm S_2O_3^{2-}$$

$$[Cu(S_2O_3)NH_3]^- \xleftrightarrow{\pm NH_3} [Cu(S_2O_3)(NH_3)_2]^-$$
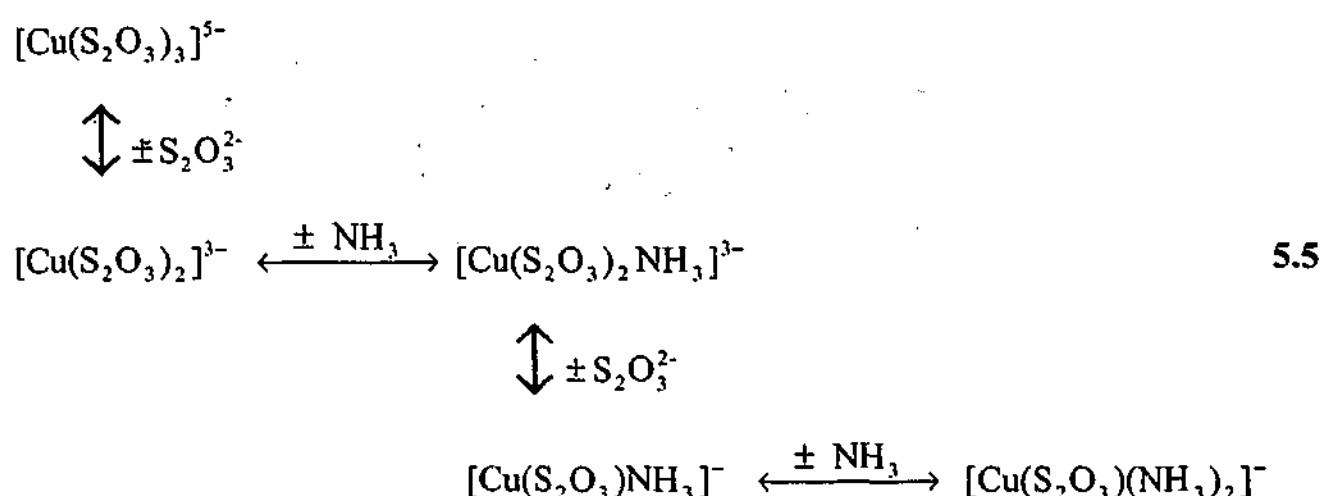
When copper(I) is oxidised to copper(II), the dominant species formed is the copper(II) tetra-ammine complex. It should be clear that for any of the species shown in Equation 5.5, ligand exchange or addition and coordination rearrangement is required in order for copper(I) oxidation to occur. The interaction of copper(I) complexes with dioxygen in ammonia solutions has been studied in some detail (Zuberbühler, 1981, Zuberbühler, 1983). In a solution containing ammonia the electron transfer takes place within a species $[Cu(NH_3)_3O_2]^+$, which can be looked at as a typical cupric complex with $O_2^-$ as the fourth ligand (Zuberbühler, 1981). A similar mechanism can be envisioned for solutions containing ammonia and thiosulfate. It is likely that the oxidation of copper(I) proceeds more rapidly via the $[Cu(S_2O_3)(NH_3)_2]^-$ complex than the other complexes shown in Equation 5.5. In this instance, a possible pathway for the oxidation reaction is shown in Equation 5.6. Based on such a pathway, it is likely that the concentration of both thiosulfate and ammonia would have a significant effect on the rate of copper(I) oxidation, since the speciation of copper(I) will be highly dependent on the relative concentrations of these ligands.

$$[Cu^I(S_2O_3)(NH_3)_2]^- + O_2 \rightarrow [Cu^I(S_2O_3)(NH_3)_2O_2]^-$$

$$[Cu^I(S_2O_3)(NH_3)_2O_2]^- + NH_3 \rightarrow [Cu^{II}(NH_3)_3O_2]^+ + S_2O_3^{2-} \qquad \textbf{5.6}$$

$$[Cu^{II}(NH_3)_3O_2]^+ + NH_3 \rightarrow [Cu^{II}(NH_3)_4]^{2+} + O_2^-$$
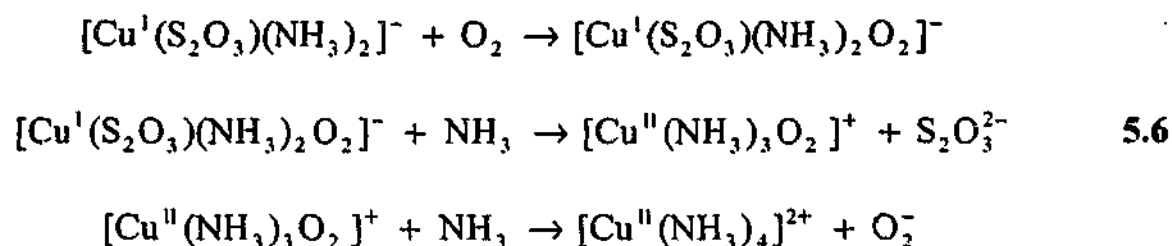
Figure 5.9 shows the effect of ammonia concentration on the rate of copper(I) oxidation. It can be seen that there is a significant increase in the rate of copper(I) oxidation as the ammonia concentration increases. This is not surprising since ammonia forms a strong complex with copper(II); ammonia must be added to the copper(I) coordination sphere in order to form the stable copper(II) tetra-ammine species.
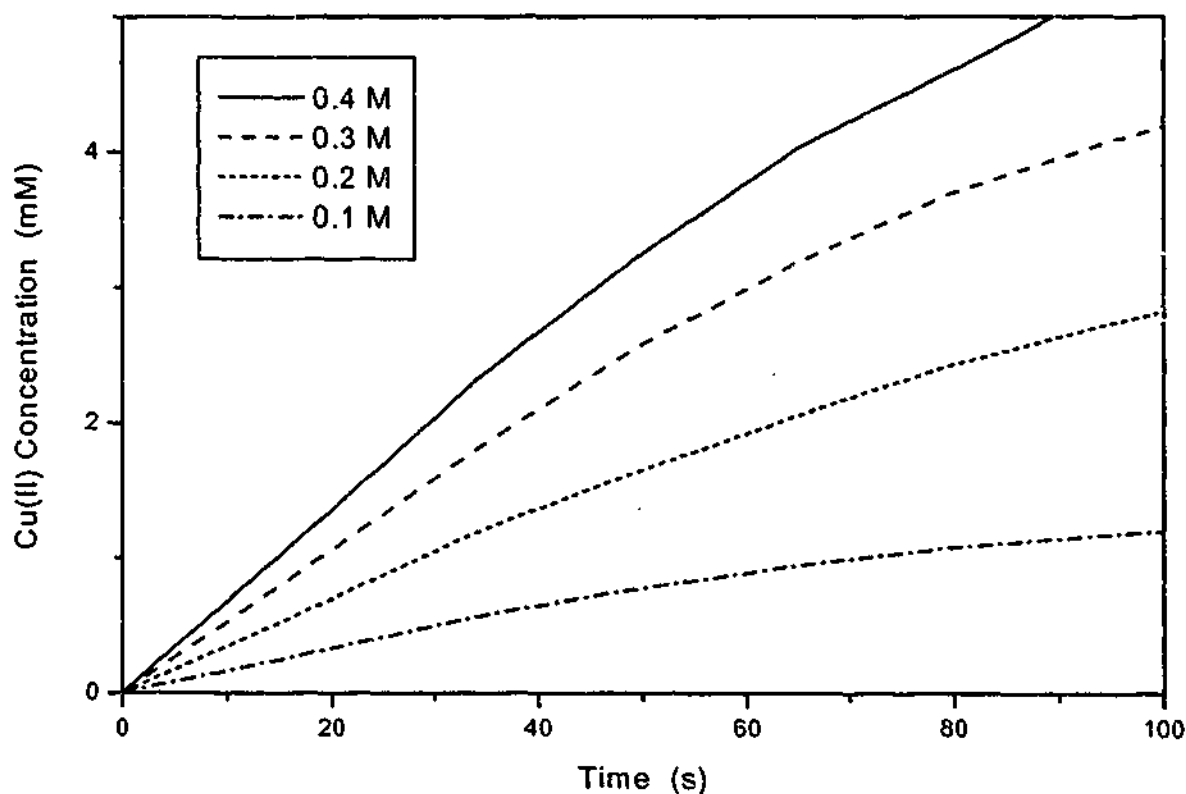


**Figure 5.9:** Effect of ammonia concentration on the rate of copper(I) oxidation: 0.1 M Na$_2$S$_2$O$_3$, 10 mM CuSCN, 30 °C, air sparged at 1000 cm$^3$ min$^{-1}$.

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Figure 5.10 shows the effect of thiosulfate concentration on the rate of copper(I) oxidation. At thiosulfate concentrations greater than 0.1 M, additional thiosulfate is seen to have a negative impact on the initial rate of copper(I) oxidation, whereas for thiosulfate concentrations lower than 0.1 M it would appear that the initial rate of copper(I) oxidation is almost independent of thiosulfate concentration. This indicates that when the thiosulfate concentration is greater than 0.1 M (for 0.4 M ammonia), the copper(I) is stabilised in such a way that the rate of ligand exchange or addition of ammonia and oxygen is slower. These results are consistent with the reactions shown in Equations 5.5 and 5.6.
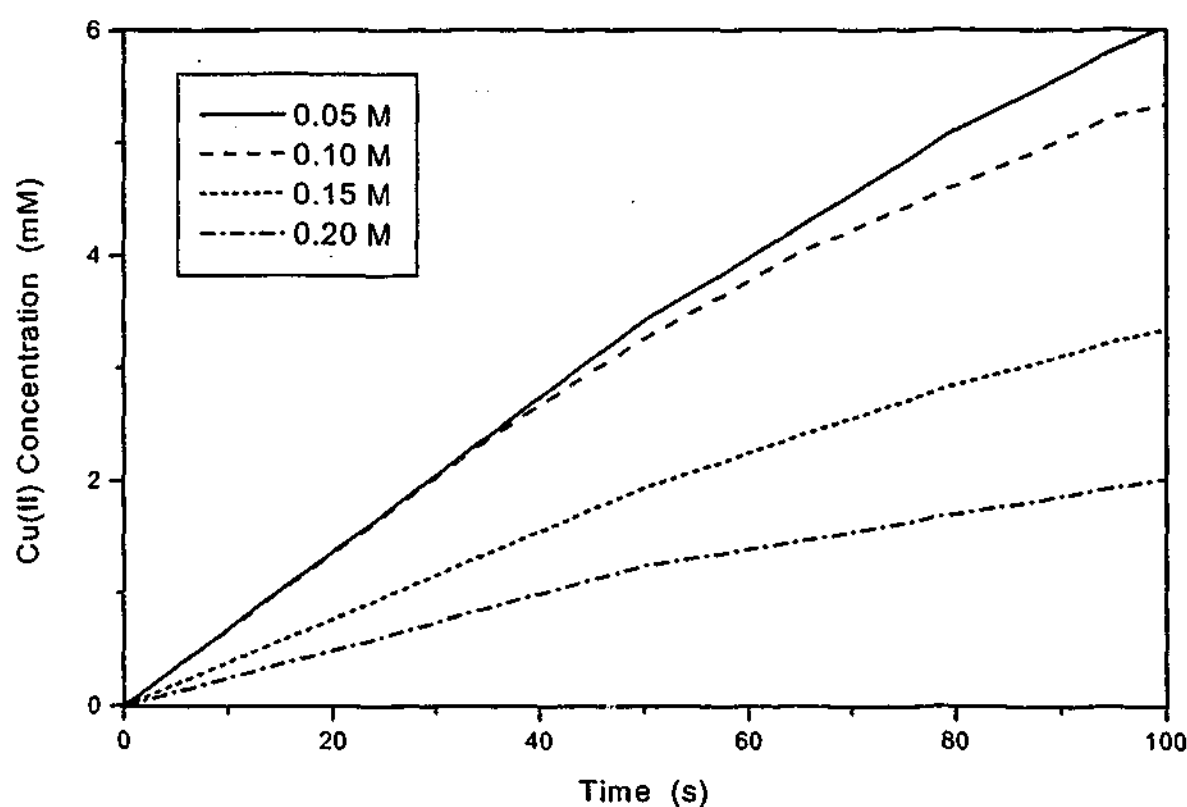


**Figure 5.10:** Effect of thiosulfate concentration on the rate of copper(I) oxidation: 0.4 M NH$_3$, 10 mM CuSCN, 30 °C, air sparged at 1000 cm$^3$ min$^{-1}$.

### 5.3.2.4 Anions

Figure 5.11 clearly shows that anions have little effect on the rate of copper(I) oxidation. The addition of anions to the thiosulfate leach solution though was shown in Figure 5.3 to greatly reduce the rate of copper(II) reduction. Thus, the presence of

anions has a positive effect on the copper(II) concentration by reducing the rate of copper(II) reduction while having very little effect on the rate of copper(I) oxidation.
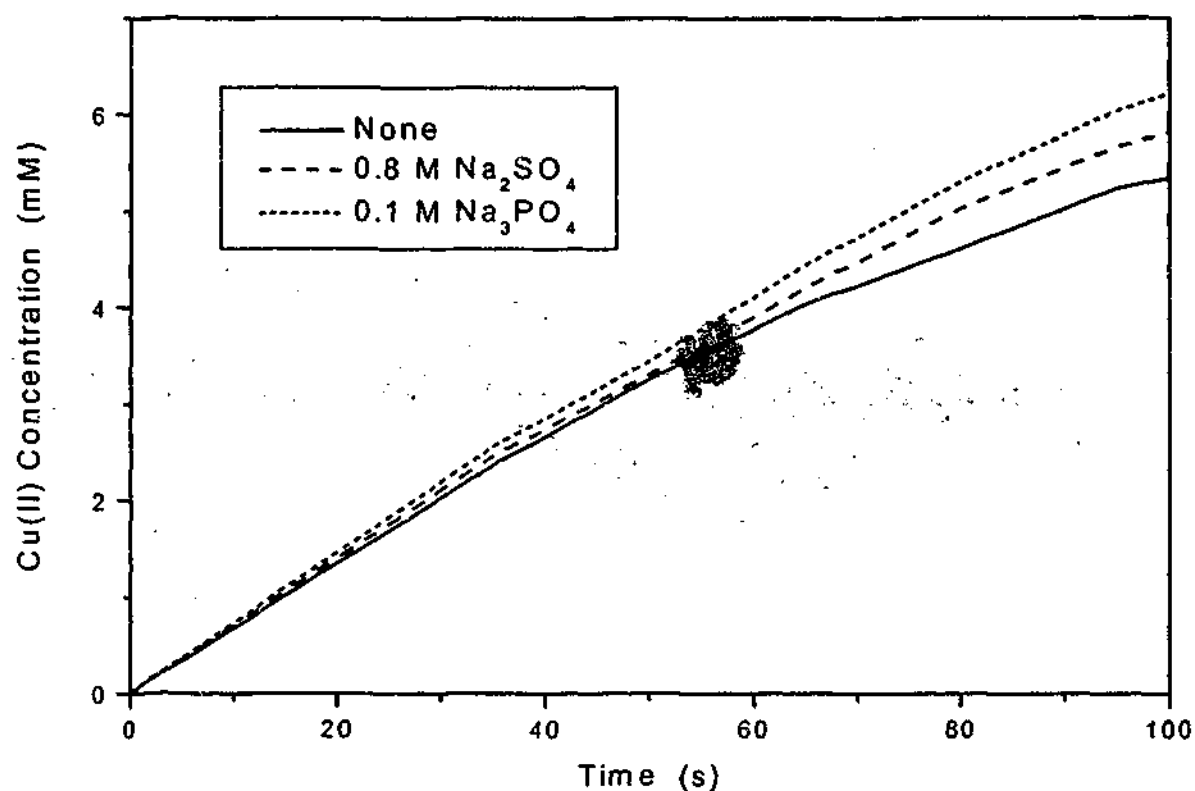


**Figure 5.11:** Effect of anions on the rate of copper(I) oxidation: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM CuSCN, 30 °C, air sparged at 1000 $cm^3 min^{-1}$.

### 5.3.2.5 pH

The effect of solution pH on the rate of copper(II) reduction by thiosulfate in the absence of oxygen was previously shown to be an anion effect as a result of the change in hydroxide concentration (section 3.3.2.3). For copper(I) oxidation, the solution pH (adjusted by substituting ammonium thiosulfate for sodium thiosulfate) is shown in Figure 5.12 to have little effect on the initial rate of copper(I) oxidation which is consistent with the results shown in Figure 5.11 for anions. However, pH obviously has a significant effect on the rate of copper(II) reduction since the copper(II) concentration is observed in Figure 5.12 to be relatively constant after the first measurement at 20 seconds. This is investigated further in section 5.3.3.5.
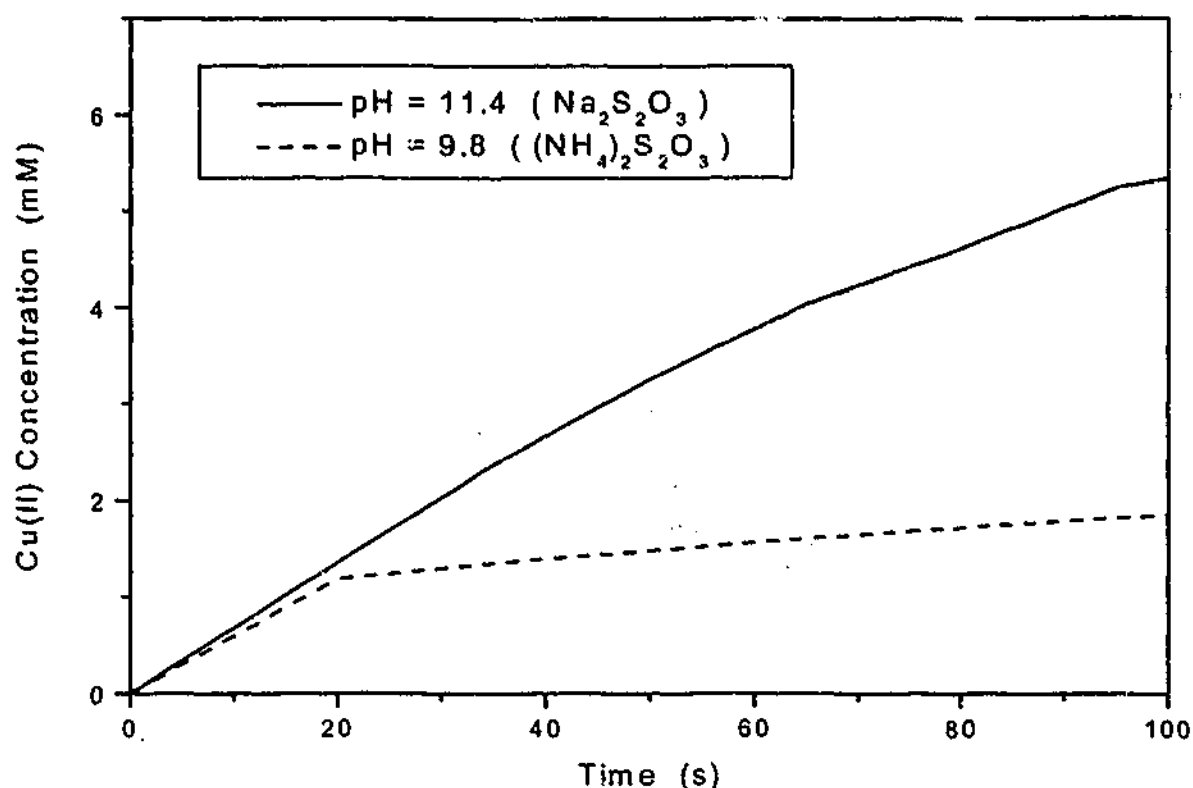
**Figure 5.12:** Effect of pH on the rate of copper(I) oxidation: 0.1 M $S_2O_3^{2-}$, 0.4 M $NH_3$, 10 mM CuSCN, 30 °C, air sparged at 1000 $cm^3$ $min^{-1}$.

### 5.3.3 Effect of Parameters on the [Cu(II)] and Thiosulfate Oxidation Rate

The copper(II) concentration and the rate of thiosulfate oxidation are of vital importance to the gold thiosulfate leaching process. The [Cu(II)]:[Cu(I)] ratio is also important as this essentially determines the potential at which gold leaching occurs (Chapter 7). Hence, understanding the effect each of the various parameters have on the copper(II) concentration, [Cu(II)]:[Cu(I)] ratio and the rate of thiosulfate oxidation allows the conditions for gold leaching to be optimised. Having gained some fundamental understanding of copper(I) oxidation by oxygen above in section 5.3.2, it is also possible to extract from the copper(II) concentration profiles the effect of various parameters on the rate of copper(II) reduction.

### 5.3.3.1   Oxygen Concentration

Figure 5.13 shows the effect of oxygen concentration on the rate of thiosulfate oxidation and the copper(II) concentration. Clearly, the rate of thiosulfate oxidation is very rapid when the solution is sparged with pure oxygen; all the thiosulfate is consumed in less than 25 minutes, compared to 1 hour for air. Also shown in Figure 5.13 is the change in thiosulfate concentration when the solution is sparged using a gas composed of 1.9% oxygen in nitrogen. In this instance, the thiosulfate oxidation rate is significantly reduced, and after 2 hours only 10% of the thiosulfate has been destroyed.

It is well known that the gold leach rate in thiosulfate solutions is highly dependant on the copper(II) concentration (section 2.3.3.5 of the review). It is evident from Figure 5.13 that the copper(II) concentration is maintained above 5 mM for each of the three sparged gases used in the present study. As the sustainable copper(II) concentrations are similar, the effect of the oxygen concentration on the rate of copper(II) reduction must be very similar to the effect on the copper(I) oxidation rate previously shown in Figure 5.6. These results clearly show that increasing the oxygen concentration increases the copper(I) oxidation rate and associated reactions of scheme 2, which increases the rate of thiosulfate oxidation. Thus, from an economic point of view, solutions sparged with low concentrations of oxygen are desirable, as the thiosulfate consumption rate will be low with little to no effect on the copper(II) concentration and hence the [Cu(II)]:[Cu(I)] ratio.

Shown in Figure 5.14 is the effect of air sparge rate on the thiosulfate oxidation rate and the copper(II) concentration. Clearly, the rate of thiosulfate oxidation decreases with decreasing sparge rate; such a result is hardly surprising, as when the sparge rate is low the oxygen in solution is consumed faster than it is replenished leading to a lower "equilibrium" concentration of oxygen in solution. Therefore, reducing the mass transfer rate of oxygen into solution significantly reduces the rate of thiosulfate consumption. The copper(II) concentrations are observed in Figure 5.14 to decrease to a minimum value of around 5 mM before increasing again. These results are consistent with those presented in Figure 5.13 and again indicate that decreasing the solution oxygen concentration decreases both the rate of copper(I) oxidation and copper(II) reduction. The net effect being almost no change in the copper(II)

concentration and hence the [Cu(II)]:[Cu(I)] ratio. However, at very low oxygen concentrations in solution (low gas phase oxygen concentration or sparge rate) the maintainable copper(II) concentration will be lower (see Chapter 7) as the rate of copper(II) reduction by thiosulfate and other oxysulfur species (Chapter 3) becomes significant in relation to the rates of the reactions shown in Scheme 2.
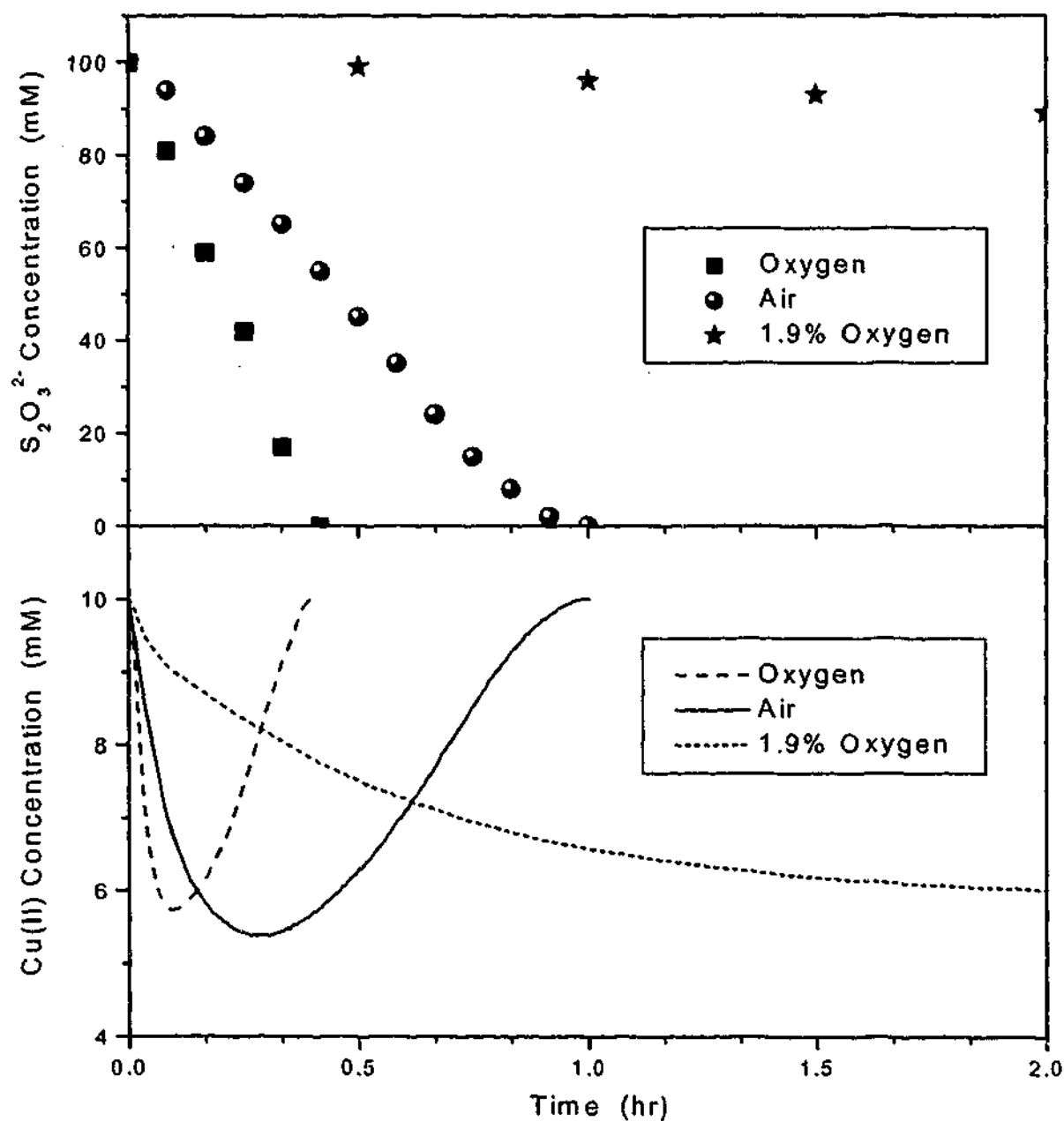


**Figure 5.13:** Effect of oxygen concentration on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C, gas sparged at 1000 $cm^3$ $min^{-1}$.
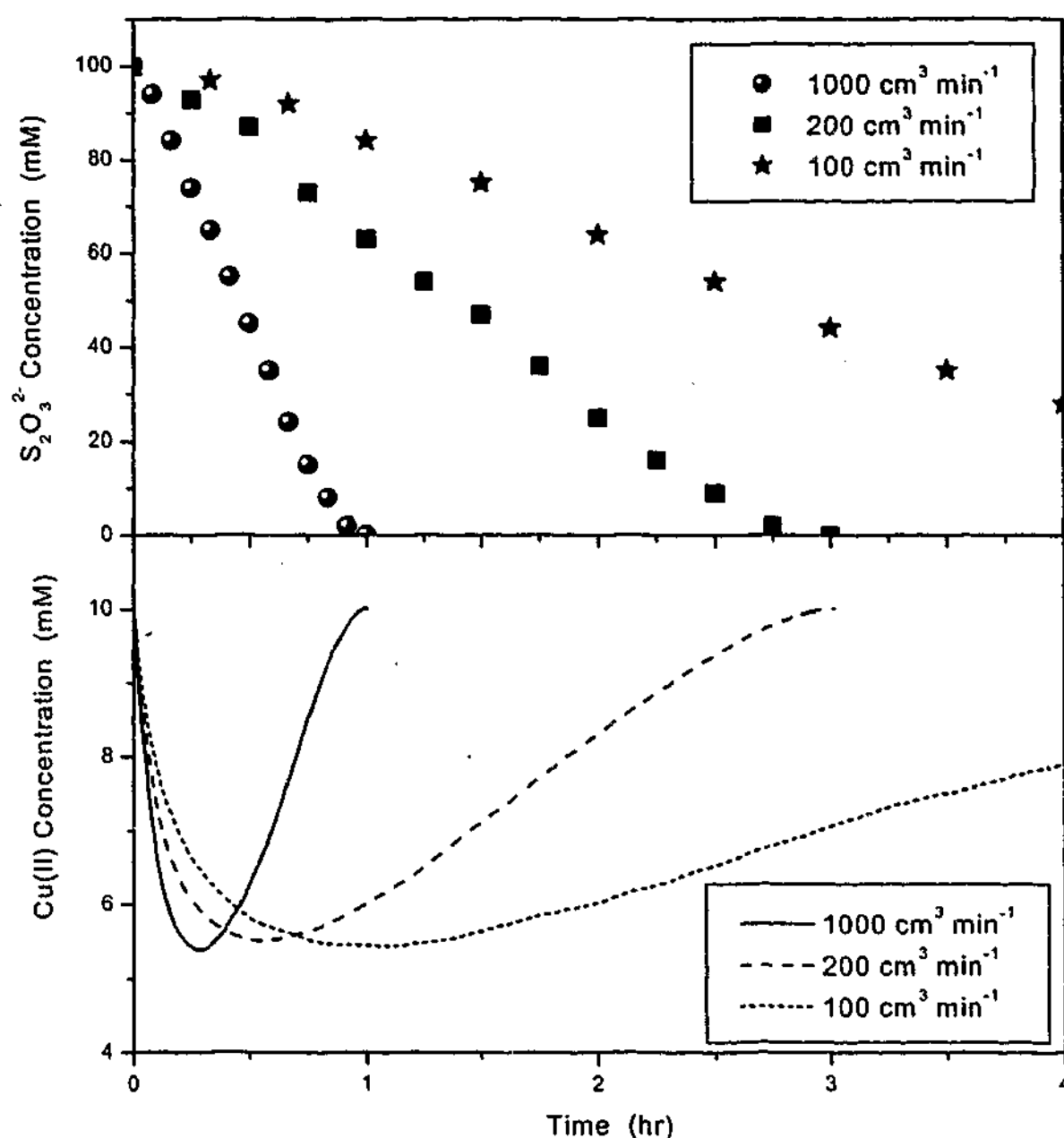
**Figure 5.14:** Effect of air sparge rate on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 30 °C, air sparged.

### 5.3.3.2  Thiosulfate Concentration

Presented in Figure 5.15 is the effect of thiosulfate concentration on the rate of thiosulfate oxidation and the copper(II) concentration. From this data, it can be seen that all the thiosulfate profiles show an induction period and have similar maximum thiosulfate oxidation rates. Hence, it would appear that the rate of thiosulfate oxidation is almost independent of thiosulfate concentration. However, the copper(II)

concentration profiles in Figure 5.15 indicate that increasing the thiosulfate concentration increases the rate of copper(II) reduction and reduces the sustainable copper(II) concentration and hence the [Cu(II)]:[Cu(I)] ratio; the thiosulfate concentration having little effect on the copper(I) oxidation rate (Figure 5.10) at thiosulfate concentrations less than 0.1 M. At higher thiosulfate concentrations the copper(I) oxidation rate decreases and thus would contribute to the lower sustainable copper(II) concentrations observed for 0.15 M thiosulfate.
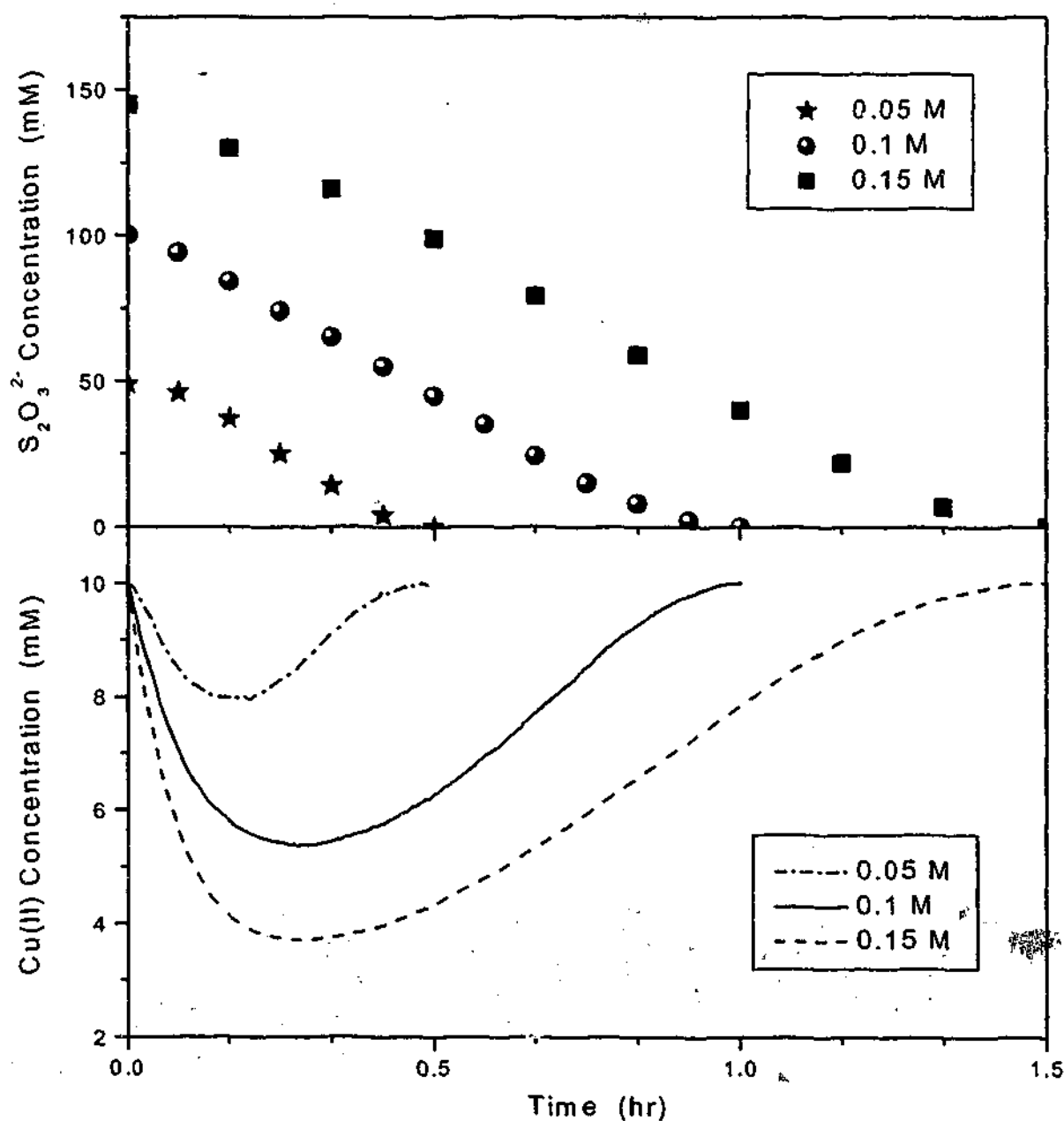


**Figure 5.15:** Effect of thiosulfate concentration on the rate of thiosulfate oxidation and the copper(II) concentration: 0.4 M NH$_3$, 10 mM CuSO$_4$, 30 °C, air sparged at 1000 cm$^3$ min$^{-1}$.

Obviously, in oxygenated solutions, the benefit of increasing the thiosulfate concentration on the gold dissolution process (section 6.3.5) needs to be optimised against the decrease in copper(II) concentration and the [Cu(II)]:[Cu(I)] ratio.

### 5.3.3.3 Copper Concentration

The effect of copper concentration on the rate of thiosulfate oxidation and the copper(II) concentration is shown in Figure 5.16. It can be seen that a decrease in the copper concentration by a factor of 5 only decreases the rate of thiosulfate oxidation by a factor of 2. Figure 5.16 also shows that the copper concentration has a significant effect on the observed sustainable copper(II) concentration and the [Cu(II)]:Cu(I)] ratio. As the copper concentration decreases, the [Cu(II)]:Cu(I)] ratio and hence the cathodic potential for gold leaching (Chapter 7) decrease significantly. Clearly, increasing the copper concentration, which benefits the cathodic potential, must be optimised against increased thiosulfate oxidation rates.

### 5.3.3.4 Ammonia Concentration

Figure 5.17 shows the effect of ammonia concentration on the rate of thiosulfate oxidation and the copper(II) concentration. It can be seen that the rate of thiosulfate oxidation for a solution containing 0.2 M ammonia is similar to that for a solution containing 0.4 M ammonia. Not surprisingly, the copper(II) concentration profile shows that the initial rate of copper(II) reduction increases with decreasing ammonia concentration and thus results in a lower sustainable copper(II) concentration. The copper(I) oxidation rate was shown in Figure 5.9 to decrease with decreasing ammonia concentration and thus would also contribute to the lower copper(II) concentration. Thus, increasing the ammonia concentration has little effect on the thiosulfate oxidation rate, but increases the sustainable copper(II) concentration and hence the [Cu(II)]:[Cu(I)] ratio which benefits the cathodic reduction potential for gold leaching.
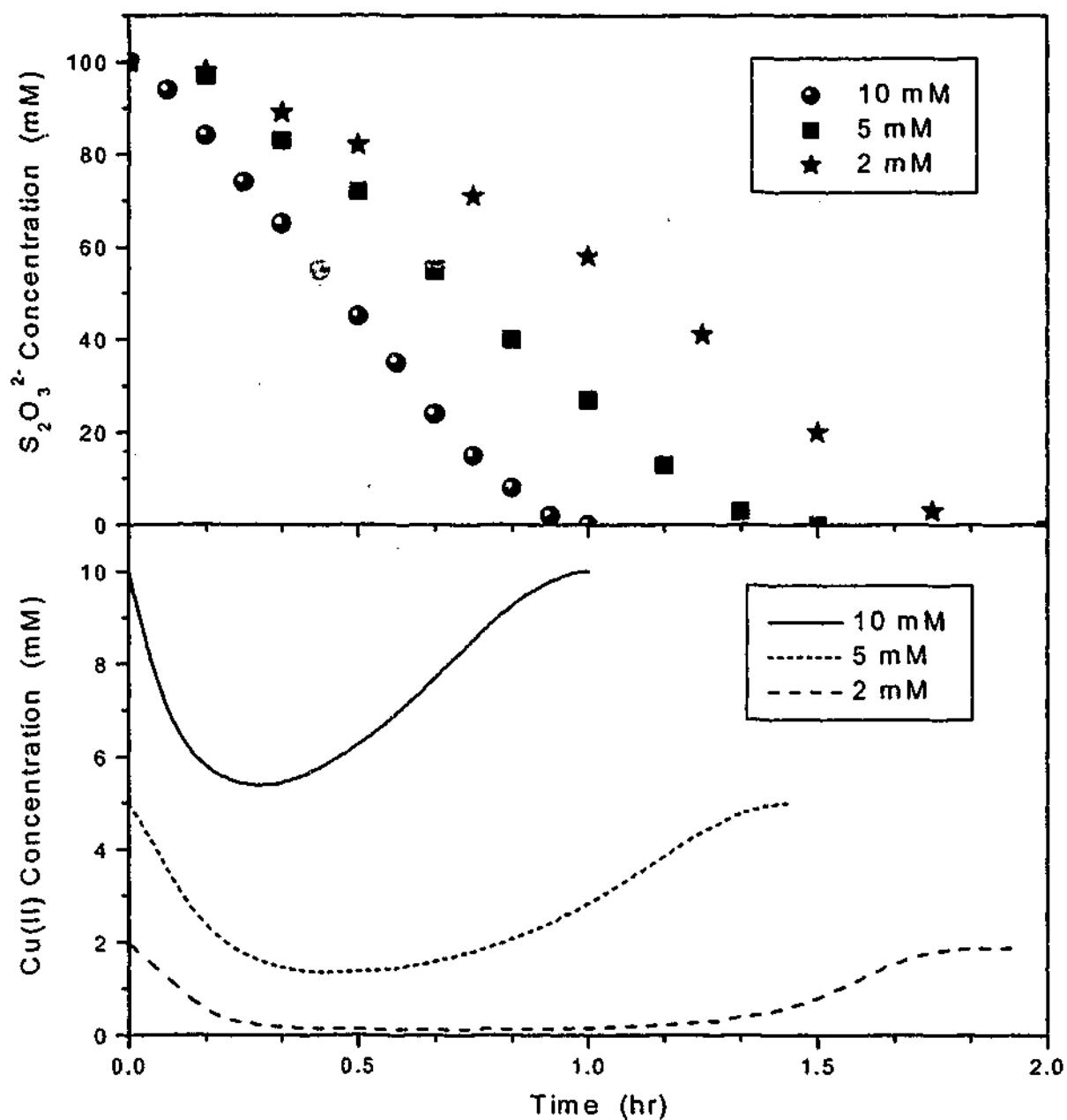
**Figure 5.16:** Effect of copper concentration on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 30 °C, air sparged at 1000 $cm^3$ $min^{-1}$.
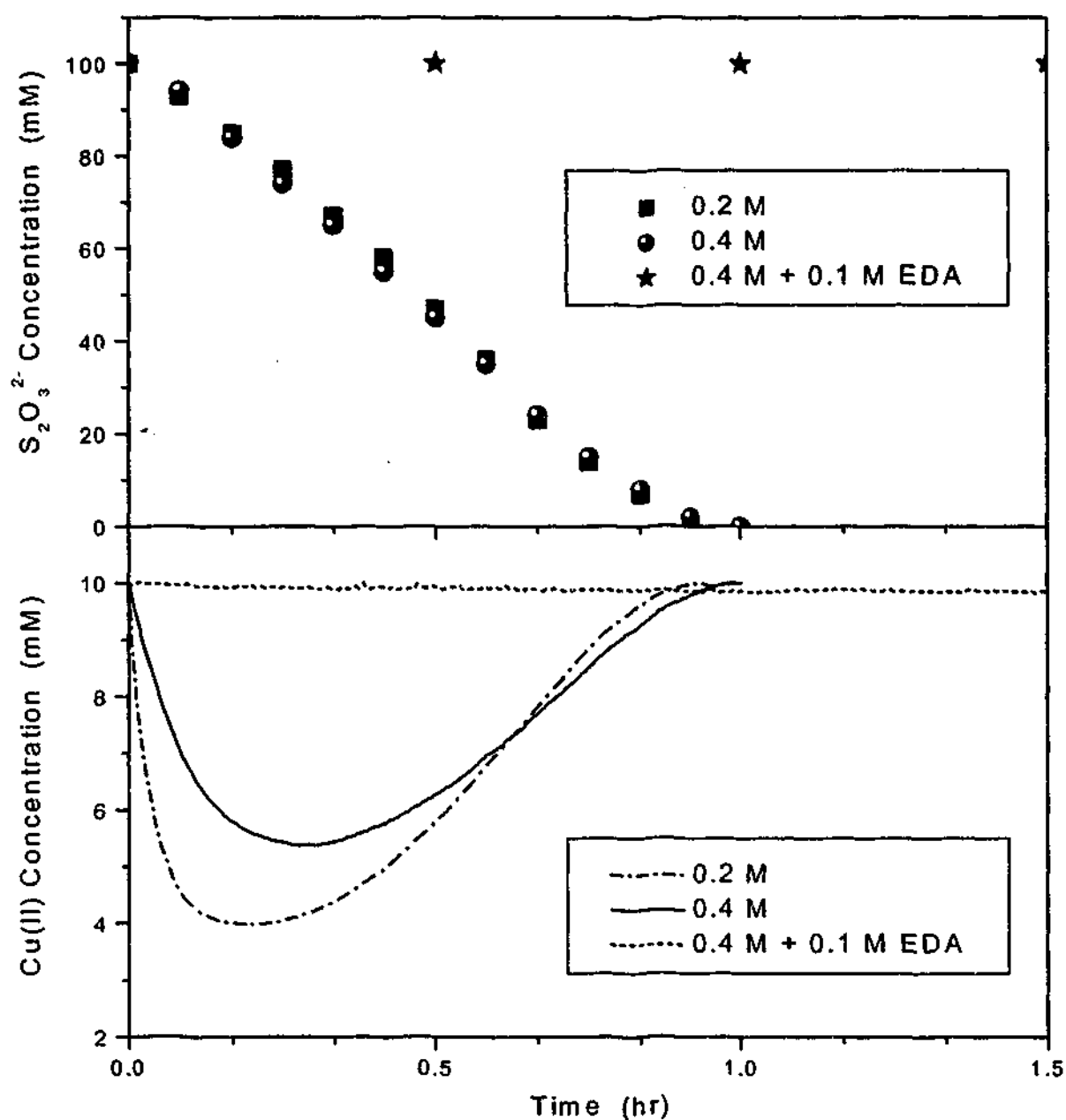
**Figure 5.17:** Effect of ammonia concentration on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M $Na_2S_2O_3$, 10 mM $CuSO_4$, 30 °C, air sparged at 1000 $cm^3$ $min^{-1}$ (EDA = ethylenediamine).

Also shown in Figure 5.17 is the thiosulfate and copper(II) concentrations for a solution containing 0.4 M ammonia and 0.1 M ethylenediamine. It should be clear that for this solution, no decrease in either copper(II) or thiosulfate concentrations is observed. Such a result suggests that ethylenediamine forms a very strong complex with copper(II) which stops any copper(II) reduction and hence thiosulfate oxidation from occurring. According to the thermodynamic data (Smith and Martell, 1976, Smith and Martell, 1975), the copper(II) ethylenediamine complex is significantly more stable

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than the copper(II) ammine complexes. The copper(II) is complexed by two ethylenediamine molecules at the four planar sites, with the axial sites available for possible thiosulfate complexation (Hathaway and Tomlinson, 1970). In studies previously published using various organic ligands for the copper(II) catalysed oxidation of thiosalts by molecular oxygen (Skorobogaty and Smith, 1984), the oxidation was only observed to occur at low ligand to copper(II) ratios. This suggests that only the two and three coordinated complexes were catalytically active and that the copper(II) complex must be able to be reduced in order for thiosulfate oxidation to occur. The addition of 50 mM hydrogen peroxide to a fresh thiosulfate leach solution containing ethylenediamine resulted in a 25% reduction in the thiosulfate concentration in less than 10 minutes. This is further evidence that the radicals involved in peroxide decomposition oxidise thiosulfate and hence supports the notion that thiosulfate oxidation results from the products of copper(I) oxidation. Obviously peroxide is strong enough to reduce copper(II) in the presence of ethylenediamine whereas thiosulfate with or without oxygen is not.

### 5.3.3.5 pH

The common use of ammonium thiosulfate in leaching studies was discussed in section 2.1.3 where it was shown to lower the solution pH. Figure 5.18 shows the effect of pH on the copper(II) concentration and the thiosulfate oxidation rate. Not surprisingly, the sustainable copper(II) concentration is observed to be lower as a result of an increase in the copper(II) reduction rate; the copper(I) oxidation rate is unaffected by pH (section 5.3.2.5). The thiosulfate oxidation rate is also shown in Figure 5.18 to be faster at lower pH.
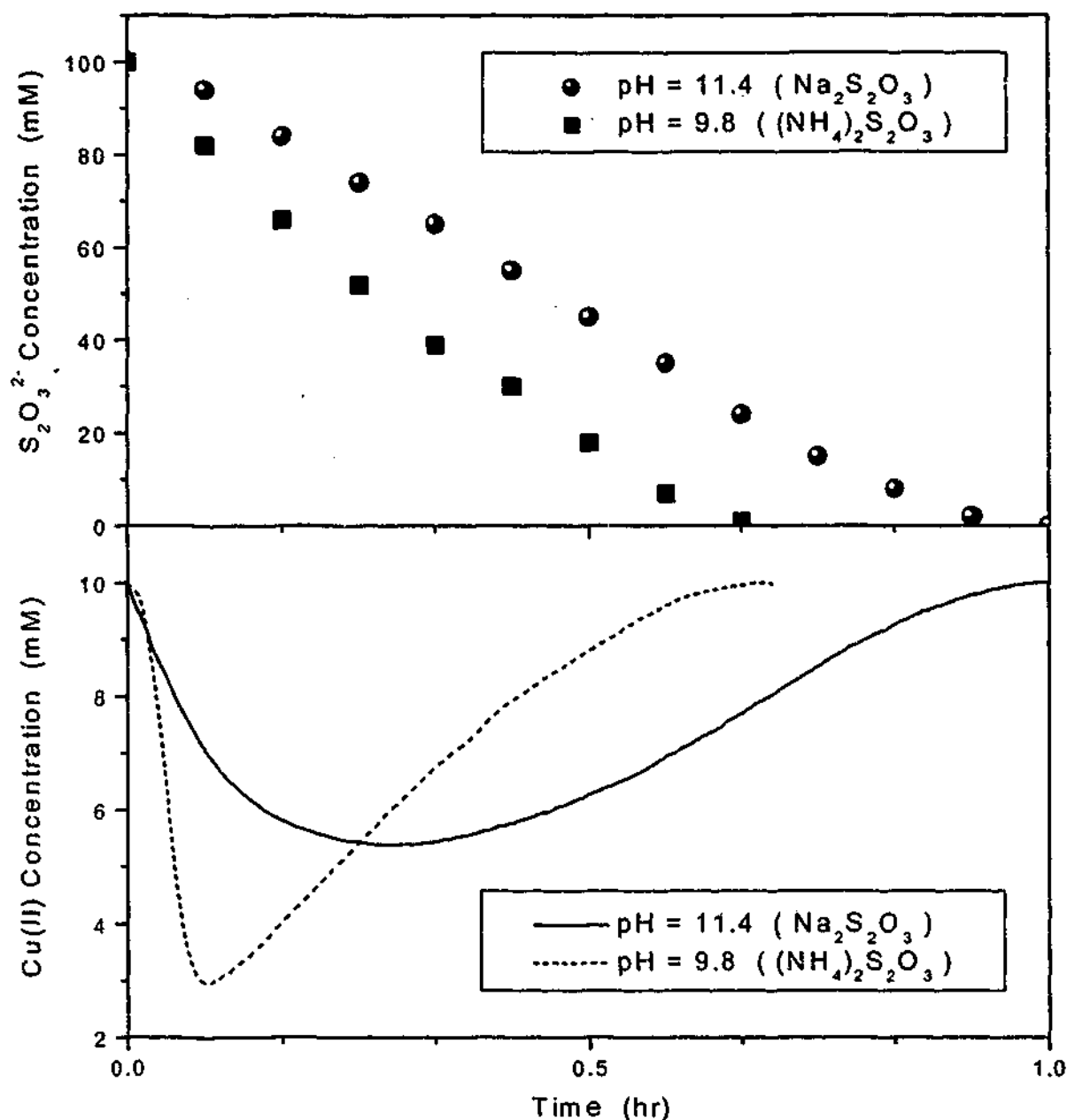
**Figure 5.18:** Effect of pH on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$, 10 mM CuSO$_4$, 30 $^o$C, air sparged at 1000 cm$^3$ min$^{-1}$.

## 5.4   Summary

Clearly, the results presented in this chapter highlight the complexity of the thiosulfate leach solution chemistry, especially in the presence of oxygen. The rate of thiosulfate oxidation and copper(II) reduction were found to be significantly faster in

the presence of oxygen. The initial rate of copper(II) reduction was higher in the presence of oxygen indicating that oxygen increases the rate of copper(II) reduction by thiosulfate to copper(I), though the mechanism for this remains unclear. The rates of thiosulfate oxidation and copper(II) reduction were a͏ͬ ͏ ͺͻ ʹo be affected differently by the presence of anions. This indicated that thio͏ ͘ ͏ ͺ ion may occur via two mechanisms. The main mechanism for thiosulfate o͏ ͘ ͺ ͘ shown to be consistent with thiosulfate oxidation by the intermediate superc͏ ͺ ͘ ͹roxide radicals formed as a result of copper(I) oxidation. A reaction sc͏ ͺ ͻ ͺs also presented that is consistent with these results.

Three main overall reaction rates of importance to the leaching of gold in thiosulfate solutions were further investigated. These were the rate of thiosulfate oxidation, the rate of copper(I) oxidation and the rate of copper(II) reduction; the latter 2 determine the $[Cu(II)]:[Cu(I)]$ ratio and hence the cathodic reduction potential. The copper(I) oxidation rate was shown to be largely dependent on the oxygen concentration and was influenced by the ammonia and thiosulfate concentrations. Anions were found to have little effect on the copper(I) oxidation rate.

The thiosulfate oxidation rate was shown to be largely dependent on the oxygen concentration in solution (this being related to the oxygen mass transfer rate). The ammonia and thiosulfate concentrations though were found to have little effect on the thiosulfate oxidation rate. Surprisingly, the presence of anions only had a small effect on the overall rate of thiosulfate oxidation compared to the significant decrease observed in the copper(II) reduction rate.

A high $[Cu(II)]:[Cu(I)]$ ratio is desirable for gold leaching. Thus, a possible advantage the presence of anions offer is the higher sustainable copper(II) concentration and hence a higher $[Cu(II)]:[Cu(I)]$ ratio. The sustainable copper(II) concentration and thus the $[Cu(II)]:[Cu(I)]$ ratio was also increased by increasing the ammonia concentration but decreased with increasing thiosulfate concentration. Surprisingly, the $[Cu(II)]:[Cu(I)]$ ratio was found to increase with increasing total copper concentration, though the rate of thiosulfate oxidation also increases.

# Dissolution of Gold in Thiosulfate Leach Solutions

## 6.1 Introduction

The dissolution of gold in thiosulfate solutions containing copper(II) and ammonia is an electrochemical process, with the constituent half reactions believed to be the oxidation of gold to gold thiosulfate according to Equation 6.1, and the reduction of copper(II) ammine to copper(I) thiosulfate according to Equation 6.2.

$$Au + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + e^- \qquad \textbf{6.1}$$

$$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- \rightarrow Cu(S_2O_3)_3^{5-} + 4NH_3 \qquad \textbf{6.2}$$
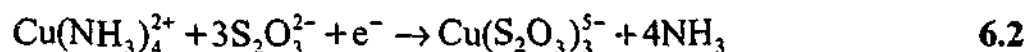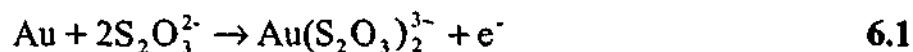
Though attempts have been made to study the mechanisms of this process and the role of copper in the dissolution process, these remain unclear. The dissolution process is also complicated by the fact that the solution chemistry is continually changing (Chapters 3 and 5). Obviously, the effect this has on the dissolution process is also of considerable importance and is addressed in Chapter 7.

The focus of this chapter is on the mechanisms of the gold dissolution process. Problems associated with the conventional methods used previously for studying this process are also highlighted. The rotating electrochemical quartz microbalance (REQCM) is utilised to measure both gold leach rates and conduct electrochemical experiments in order to establish the role of copper(II) in the gold dissolution process. The mechanism and the effect of various parameters on the gold dissolution process are also investigated for freshly prepared thiosulfate leach solutions.

## 6.2  Experimental

All experiments were carried out using solutions prepared from analytical grade reagents and distilled water.  Unless otherwise specified, all experiments were performed at 30 °C, at a rotation rate of 300 rpm, and the solutions contained 0.1 M sodium thiosulfate, 0.4 M ammonia, and 10 mM copper sulfate; a concentrated copper(II) ammonia solution being injected just prior to conducting gold leaching or electrochemistry experiments.  Solutions were degassed with argon in order to minimise the change in the solution chemistry with time.  Solutions initially containing copper(I) were prepared by degassing a solution containing copper thiocyanate and thiosulfate to which the ammonia solution was then injected just prior to commencing the experiment.

Kinetics measurements were performed with a rotating electrochemical quartz crystal microbalance (REQCM), previously described in section 4.2.1.  This technique is the most accurate means of measuring metal leach rates; it measures gold leach rates in real time with a sensitivity of 1 ng (Jeffrey, 1998).  The REQCM was interfaced with a potentiostat to enable the measurement of mixed potential and to conduct electrochemical experiments.  Linear sweep voltammetry was carried out at a scan rate of 1 mV s$^{-1}$ using a Radiometer PGP201 potentiostat.  The frequency of the quartz crystal oscillations were measured with an Optoelectrics model 3000A hand held frequency counter, which was interfaced along with the potentiostat to an IBM compatible computer for data acquisition.  All potentials were measured relative to the saturated calomel electrode (+0.242 V vs. SHE), but are reported relative to the SHE.  A platinum wire was used as the counter electrode.  Mass changes were measured simultaneously with current using the REQCM.  Prior to each experiment, gold was electroplated onto the platinum coated quartz electrode at 25 A m$^{-2}$ from a solution containing 0.02 M potassium dicyanoaurate, 0.23 M potassium cyanide, 0.086 M potassium carbonate.  The gold was plated for approximately 5 minutes such that 250 μg of gold was deposited.

## 6.3    Dissolution of Gold in Thiosulfate Leach Solutions

The dissolution of gold in thiosulfate solutions was highlighted in the review to be slow in the absence of copper(II). Thus, in order to study the dissolution of gold in thiosulfate solutions containing copper(II) and ammonia, the role of copper(II) in the dissolution process needs to be clearly identified.

### 6.3.1    Role of Copper(II)

#### 6.3.1.1    Kinetics of Gold Leaching

As discussed in the review, the oxidation of gold in thiosulfate solutions by oxygen is believed to occur according to Equation 2.8, though at a very slow rate. Leaching experiments were performed using a rotating electrochemical quartz crystal microbalance (REQCM), and a kinetic plot of mass versus time for a gold electrode in an air saturated solution containing only thiosulfate is shown in Figure 6.1. It should be clear from this data that the gold leach reaction proceeds very slowly; only a 140 ng decrease in the electrode mass being recorded after 6 minutes. The mixed potential is also shown in Figure 6.1 to be 110 mV, which indicates that a high overpotential is required to reduce oxygen on the gold surface; the standard oxygen reduction potential in alkaline solutions is 0.4 V (Antelman and Harris, 1982).

In solutions containing copper(II), ammonia and thiosulfate (referred to as thiosulfate leach solutions) there is the possibility of an additional cathodic reaction: the reduction of copper(II) to copper(I), as shown in Equation 6.2. Figure 6.1 also shows the kinetic plot for gold dissolution in a thiosulfate leach solution. Initially a very slow rate of gold leaching is indicated by very little change in the electrode mass. This induction period indicates that the gold leaching process is hindered initially in some way. This was previously identified by Jeffrey (2001) who found this was consistent with sulfur on the gold surface (see section 2.3.3.1). The initial hindrance to leaching is slowly overcome with the mass of the electrode decreasing as the gold begins to leach. The gold leach rate is observed to increase until a constant rate is attained some minutes

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after placing the electrode in solution. This is consistent with the negative shift observed in the measured mixed potential. Clearly leaching in this instance is substantially more rapid. It is also worth noting that the mixed potential (238 mV) is more positive than for the solution in the absence of copper(II) (110 mV). This result confirms that copper(II) is acting as the oxidant.
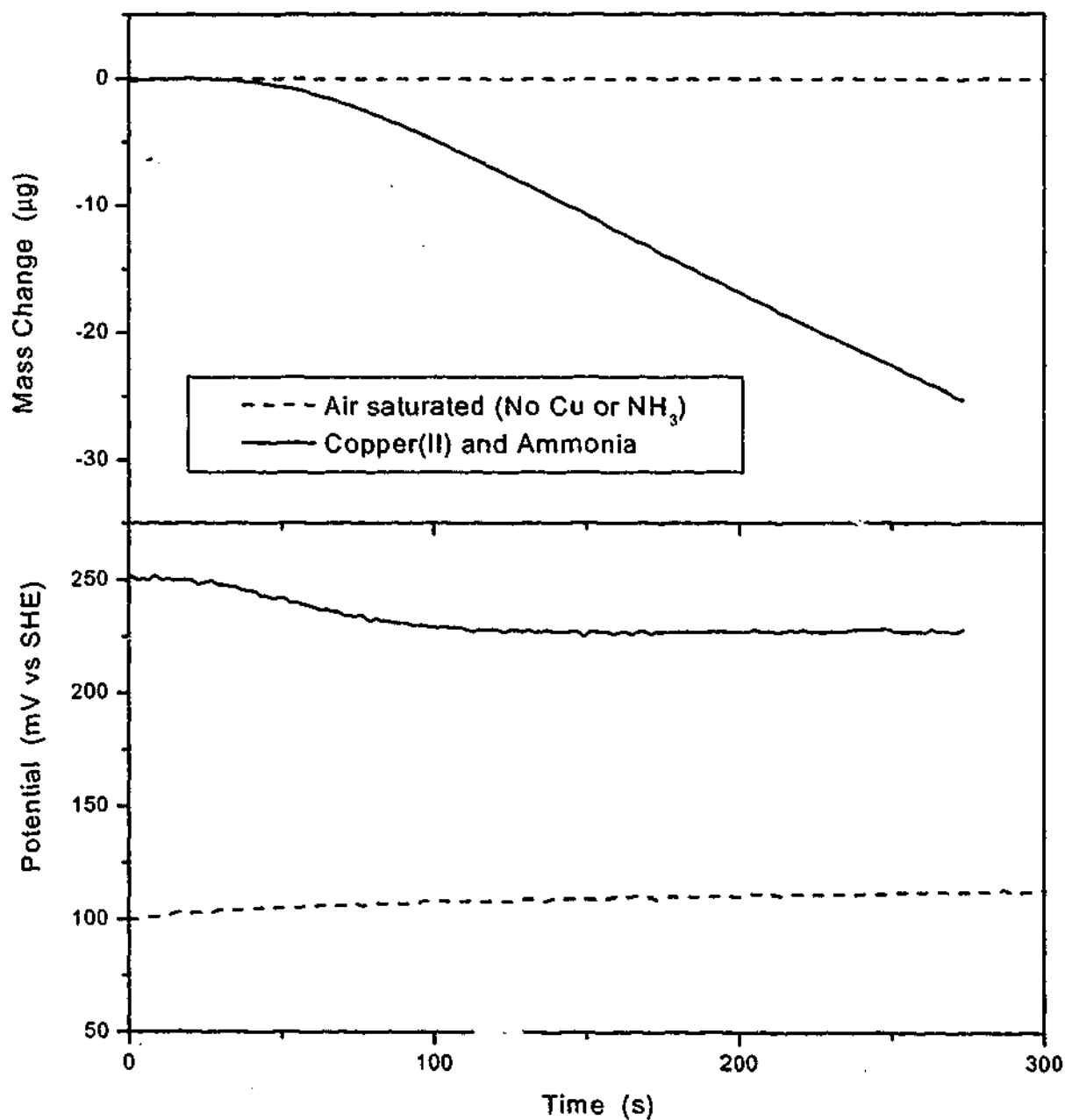


**Figure 6.1:** Kinetic plot showing the change in mass versus time for gold in an air saturated thiosulfate solution (no copper or ammonia) and in a separate thiosulfate solution containing copper(II) and ammonia. The lower part of this figure shows the mixed potential measured for each system: 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$, 10 mM CuSO$_4$, 300 rpm, 30 °C.

### 6.3.1.2  Cathodic Reactions: Reduction of Copper(II) and Oxygen

The first objective in studying the cathodic reactions was to establish the potential region in which these reactions occur. This is obviously important, as there is little point discussing the anodic reaction in the potential region where leaching does not occur. The study of the cathodic reaction is simply achieved by replacing the gold electrode with an inert platinum electrode. The resultant voltammograms for three systems are shown in Figure 6.2; each of these systems are discussed below.
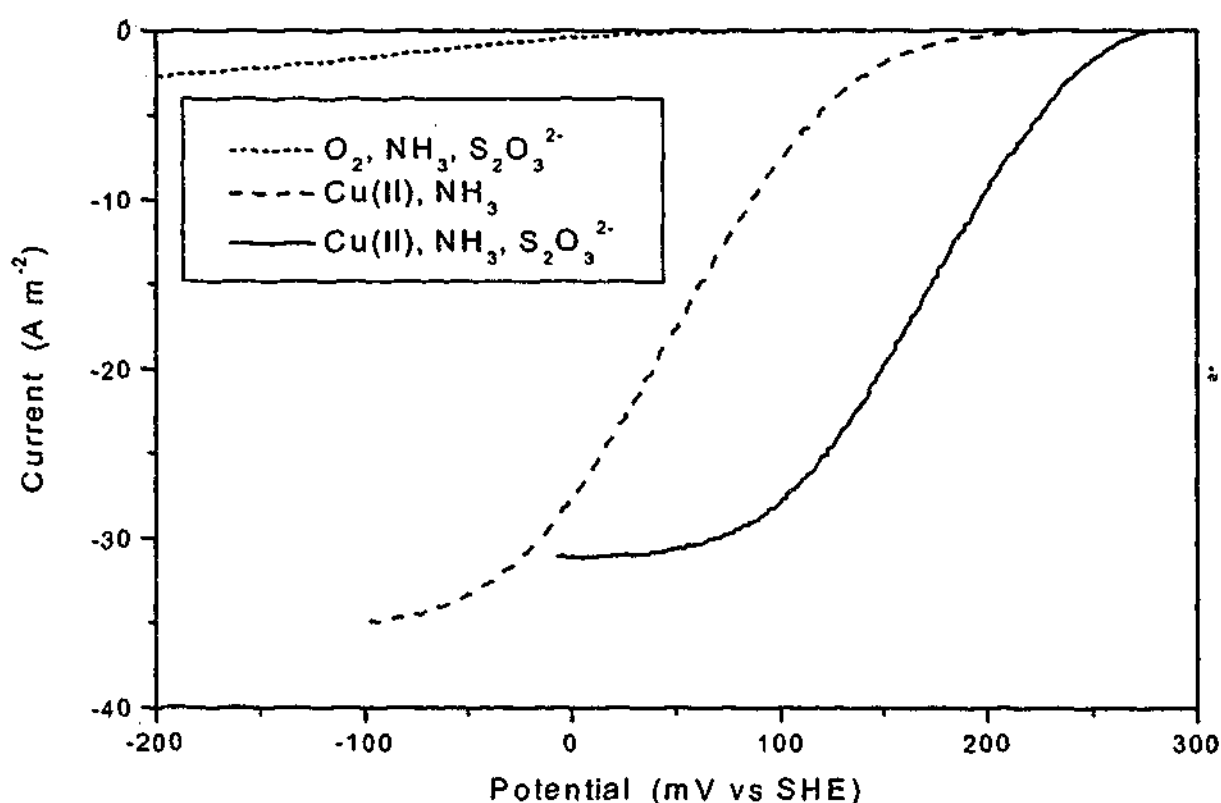


**Figure 6.2:** Linear sweep voltammograms for the reduction of oxygen (air saturated) in an ammonia/thiosulfate solution, and for the reduction of copper(II) in separate ammonia and ammonia/thiosulfate solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

**Ammonia/thiosulfate.** In solutions containing ammonia and thiosulfate alone, there are two possible reactions; the reduction of dissolved oxygen, and the reduction of thiosulfate. In the voltammogram shown in Figure 6.2, it is clear that oxygen reduction occurs at potentials more negative than 100 mV. Thiosulfate reduction does not occur until the potential is more negative than −500 mV (not shown in Figure 6.2).

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**Copper/ammonia.** For this solution, which contains copper(II) ammine complexes, there is the possibility of reducing copper(II) to copper(I), as the copper(I) ammine complexes are also stable in alkaline solutions. It can be seen from Figure 6.2 that this reaction occurs at potentials more negative than 225 mV. The current density reaches a limiting plateau at −150 mV; at these potentials the reduction of copper(II) is limited by the mass transfer of copper(II) to the platinum surface. The diffusion coefficient for copper(II) under these conditions was calculated from the limiting current using the Levich equation (Equation 2.22) to be $1.01 \times 10^{-9}$ m$^2$ s$^{-1}$.

**Copper/ammonia/thiosulfate.** It should be immediately clear from Figure 6.2 that the voltammogram for this system is not just a combination of the other two systems. The most obvious change is the difference in the copper(II) reduction potential in the presence and absence of thiosulfate. The more positive value for solutions containing thiosulfate indicates that thiosulfate is complexed to copper(I) and thus is more stable than the copper(I) ammine complexes; this result is consistent with the published stability constants for the copper(I) di-ammine and copper(I) trithiosulfate complexes (log $\beta$ = 10.13 and 13.77 respectively (Högfeldt, 1982)). It was also indicated in Chapters 4 and 5 that copper(I) may be present as a mixed ammine/ thiosulfate complex. Thus, the cathodic reaction for gold dissolution in thiosulfate leach solutions may be represented by Equation 6.3 ($1 \leq y \leq 3$, $x \leq 2$, $2 \leq x + y \leq 3$), the reduction of copper(II), predominantly present as the tetra-ammine complex for ammonia concentrations greater than 0.3 M, to a copper(I) mixed ammine/thiosulfate complex, which is dependant on the ligand concentrations.

$$[Cu(NH_3)_4]^{2+} + yS_2O_3^{2-} + e^- \rightarrow [Cu(NH_3)_x(S_2O_3)_y]^{1-2y} + (4-x)NH_3 \qquad 6.3$$

### 6.3.1.3 Anodic Reaction: Oxidation of Gold

In a similar manner to the cathodic reactions, the oxidation of gold in thiosulfate solutions (anodic reaction) can be studied using traditional electrochemical techniques. The polarisation curve recorded for a gold electrode in a solution containing 0.1 M thiosulfate and 0.4 M ammonia is shown in Figure 6.3 (as the solid line). It can be seen

that in the potential region 150 to 300 mV, there is an oxidation reaction occurring, although at a low rate. At potentials more positive than 300 mV, the current density increases rapidly. This is consistent with the polarisation curve published by Zhu *et al.* (1994a) for 0.1 M thiosulfate shown in Figure 2.10 of the review. For a gold electrode in a solution containing thiosulfate and ammonia at such potentials, there are two possible oxidation half reactions: gold oxidation to gold thiosulfate ($E^0 = 0.15$ V (Pouradier and Gadet, 1969)), and thiosulfate oxidation ($E^0 = 0.08$ V (Weast, 1974-75)). Thus, conventional electrochemical techniques are of limited value as the measured current ($i_{measured}$) is a sum of all the reactions occurring at the electrode interface. However, as gold oxidation is the only reaction which involves mass changes, this process can effectively be studied using a REQCM. Figure 6.3 also shows the electrode mass that 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 oxidised to soluble gold thiosulfate. These mass changes are converted to a calculated equivalent current density for gold oxidation ($i_{calculated}$) using Faraday's Law shown in Equation 6.4, where n is the number of electrons transferred per atom of gold oxidised, F is the Faraday constant (96485 C mol$^{-1}$), A is the surface area of the electrode (m$^2$), M is the atomic mass of gold (196.97 g mol$^{-1}$), m is the measured mass of the electrode (g), and t is the elapsed time of the experiment (s).

$$i_{calculated} = \frac{n\,F}{A\,M} \times \frac{\Delta m}{\Delta t} \qquad\qquad \textbf{6.4}$$

The calculated current density is also shown in Figure 6.3 as a dashed line. It is clear that at potentials negative of 200 mV, the calculated current density matches the measured current density; such a result implies that in this potential region thiosulfate oxidation does not occur. However, the gold oxidation process is obviously hindered. At potentials more positive than 200 mV, it can be seen from Figure 6.3 that the calculated current density deviates from the measured current density; this implies that thiosulfate oxidation has commenced and sharply increases above 300 mV.
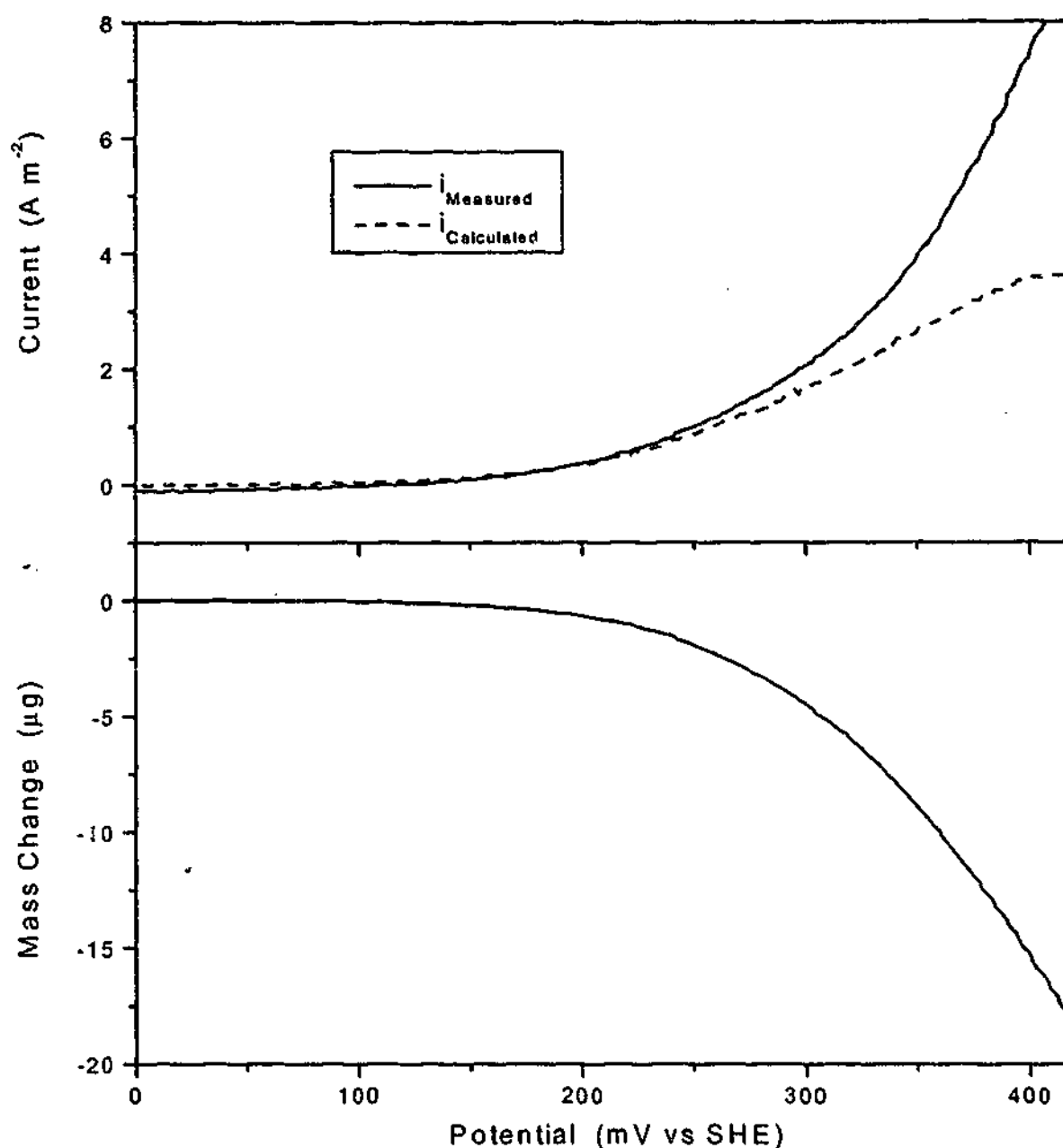
**Figure 6.3:** Linear sweep voltammogram showing the oxidation of gold to gold thiosulfate: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 300 rpm, 30 °C. Also shown is the mass change measured using the REQCM, and the partial current density ($i_{calculated}$) derived from this.

For the thiosulfate leach system, ammonia is required in order to stabilise the copper in the copper(II) oxidation state since leaching is performed at pH > 8. The effect of ammonia on the gold oxidation process was studied and Figure 6.4 shows the calculated current densities for gold oxidation at various ammonia concentrations. It is clear that in the absence of ammonia, the gold oxidation process is greatly hindered in the potential range 100 to 300 mV. However, in solutions containing high

concentrations of ammonia, gold oxidation occurs quite readily. It has been suggested that the oxidation of gold in thiosulfate solutions containing ammonia occurs via an intermediate ammine complex (Jiang *et al.*, 1993a), as shown in Equation 6.5. However, if this were true, then the first two steps of this reaction would still occur in the absence of thiosulfate. This would result in a measurable current in the potential region of interest in solutions solely containing ammonia, a feature that was not observed in this study. It seems more likely that the action of ammonia is to either form a mixed gold-ammine-thiosulfate complex, or its role is to affect the surface of the gold electrode in some way that allows the gold oxidation reaction to occur more readily. At this stage, the reason for the effect of ammonia is uncertain.

$$Au \rightarrow Au^+ + e^-$$
$$Au^+ + 2NH_3 \rightarrow Au(NH_3)_2^+$$
$$Au(NH_3)_2^+ + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + 2NH_3$$

6.5
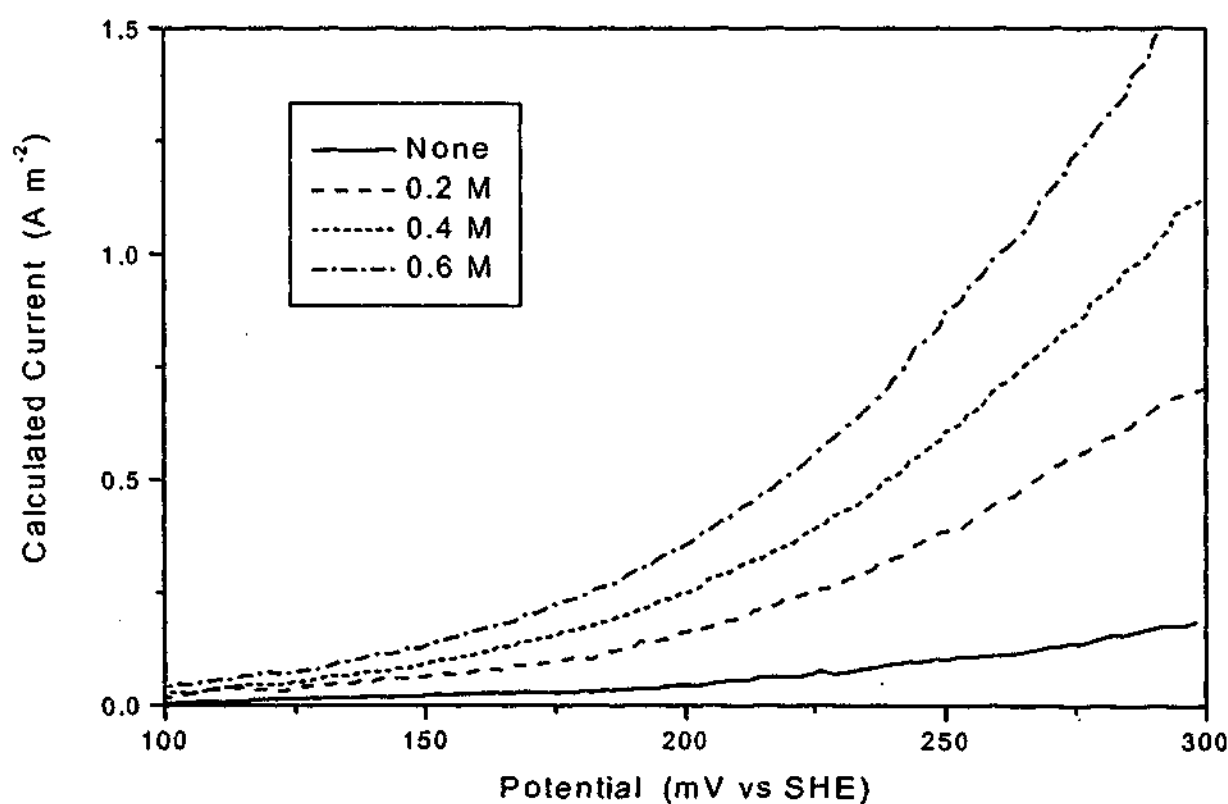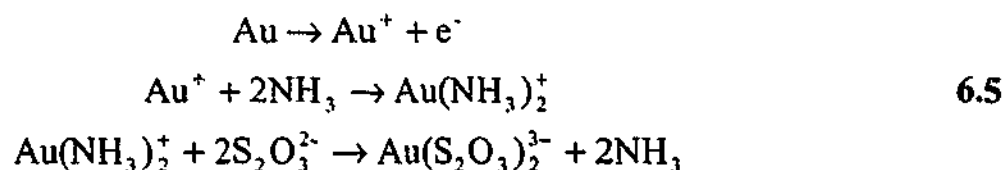


**Figure 6.4:** Effect of ammonia concentration on the voltammograms for gold oxidation in thiosulfate solutions: 0.1 M Na$_2$S$_2$O$_3$, 300 rpm, 30 °C.

### 6.3.1.4 Combination of Anodic and Cathodic Polarisation Curves

In a traditional Evans' type diagram, the anodic and cathodic polarisation curves are plotted as E versus ln(|i|), and the intersection point of these curves is used to determine the mixed potential and corrosion current density (reaction rate). However, to maintain uniformity with the oxidation polarisation curves presented in Figures 6.2 and 6.4, it was decided to plot the data as |i| versus E throughout this thesis; these graphs will be referred to as Evans' type diagrams as they convey similar information to the tradition diagrams presented as E versus ln(|i|). The Evans' type diagram shown in Figure 6.5 shows the anodic (oxidation of gold) and cathodic (reduction of copper(II)) polarisation curves for the gold dissolution process.
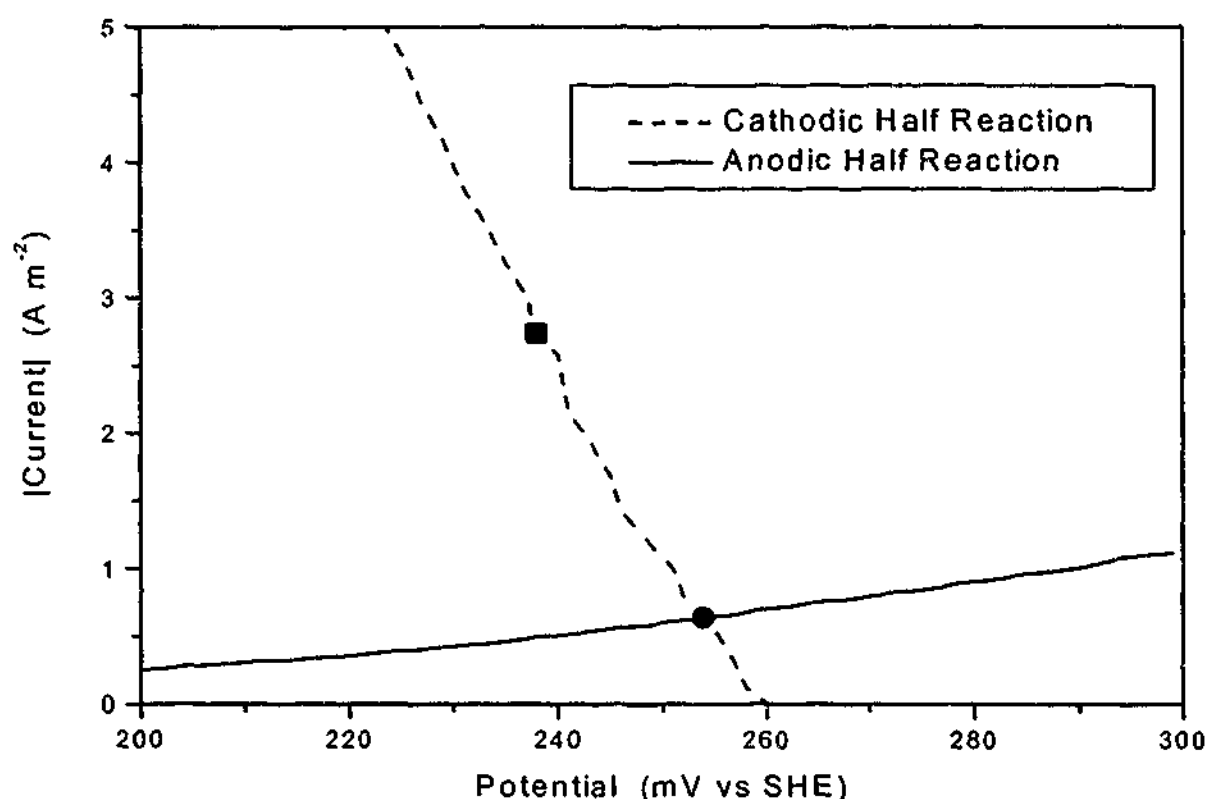


**Figure 6.5:** Evans' type diagram showing the oxidation of gold, and the reduction of copper(II) on platinum in an ammonia/thiosulfate solution: 0.4 M $NH_3$, 0.1 M $Na_2S_2O_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C. Also shown, as a square symbol, is the measured mixed potential and reaction rate (as current density) during gold leaching.

From an Evans' diagram, the rate of reaction can be estimated from the current density at the intersection point of the anodic and cathodic polarisation curves. The oxidation current density (i) at this intersection point is related to the rate of dissolution (r) according to Faraday's law shown in Equation 6.6, where n is the number of electrons involved in the oxidation of a single gold atom and F is the Faraday constant ($96485 \ C \ mol^{-1}$).

$$r = \frac{i}{nF} \qquad\qquad 6.6$$

From the point of intersection in Figure 6.5 (highlighted by a dot) it can be estimated that the mixed potential of leaching would be 263 mV, and the corresponding leach rate would be $0.75 \times 10^{-5} \ mol \ m^{-2} \ s^{-1}$ ($0.72 \ A \ m^{-2}$). Leaching experiments were also carried out using the REQCM, and the actual mixed potential and reaction rate at steady state were 238 mV and $2.8 \times 10^{-5} \ mol \ m^{-2} \ s^{-1}$ ($2.7 \ A \ m^{-2}$) respectively (square symbol in Figure 6.1). Obviously, the Evans' type diagram does not accurately predict what occurs during gold dissolution in thiosulfate leach solutions. It should be obvious that the measured reaction rate corresponds very well with the current density measured for the cathodic reaction at the actual mixed potential of 238 mV (the square symbol is close to the cathodic polarisation curve). Such a result implies it is the anodic curve that is incorrect; at the measured mixed potential of 238 mV the gold oxidation rate is substantially lower than the measured gold leach rate. Such a result is very unusual as it is usually the cathodic reaction that is difficult to study as an inert electrode, such as platinum, is used instead of gold. Now the question that must be answered is "Why doesn't the polarisation curve for gold in a solution containing thiosulfate and ammonia represent what actually occurs during leaching?" As will be shown in the following discussion, the reason is that copper(II) has been omitted from the solution used in determining the polarisation curve for gold oxidation.

### 6.3.1.5 Oxidation of Gold in the Presence of Copper.

It is very difficult to study the oxidation of gold to gold thiosulfate in solutions containing copper ions using standard electrochemical techniques as the measured current is a sum of all the electrochemical reactions occurring at the electrode-solution interface. At potentials greater than 200 mV the measured current was shown in Figure 6.3 to be the sum of the currents due to gold oxidation and thiosulfate oxidation. For a thiosulfate leach solution the reduction of copper(II) to copper(I) also contributes to the measured current. To differentiate between these reactions, the REQCM was used to determine the partial current density due to gold oxidation ($i_{calculated}$) from the measured mass changes using Equation 6.4.

Initially the REQCM was used to study the leaching of gold at a fixed potential of 238 mV. This is the mixed potential observed for the gold leaching experiment shown in Figure 6.1. A plot of mass versus time at steady state oxidation is shown in Figure 6.6 for solutions containing thiosulfate alone, thiosulfate + ammonia, and thiosulfate + ammonia + copper(II). Not surprisingly, in solutions containing solely thiosulfate, very little mass change is observed during the experiment. This is what is predicted from the gold oxidation voltammograms shown in Figure 6.4. In comparison, when ammonia is added to the solution, the gold leaches more readily, although the reaction rate is substantially lower than the measured gold leach rate in a thiosulfate/ammonia/copper(II) solution. This result is predicted in Figure 6.5. The most important result shown in Figure 6.6 is the kinetic plot for gold dissolution in a solution containing thiosulfate, ammonia and copper(II). It is clear that for this solution the gold leaches much more rapidly than it does in the absence of copper(II). In fact, the gold leach rate measured at 238 mV from Figure 6.6 ($2.8 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$) is identical to the rate obtained during gold dissolution in the absence of potentiostatic control (in that instance the mixed potential, 238 mV, was set up by the oxidant, copper(II)). It would thus appear that the presence of copper(II) in the thiosulfate leach solution results in a significant enhancement to the gold oxidation half reaction. If the presence of copper(II) was solely to provide a strong enough oxidant for the system, then the reaction rate at a fixed potential would be the same for the thiosulfate/ammonia solution as it is for the thiosulfate/ammonia/copper(II) solution. This is the basis of mixed potential theory.
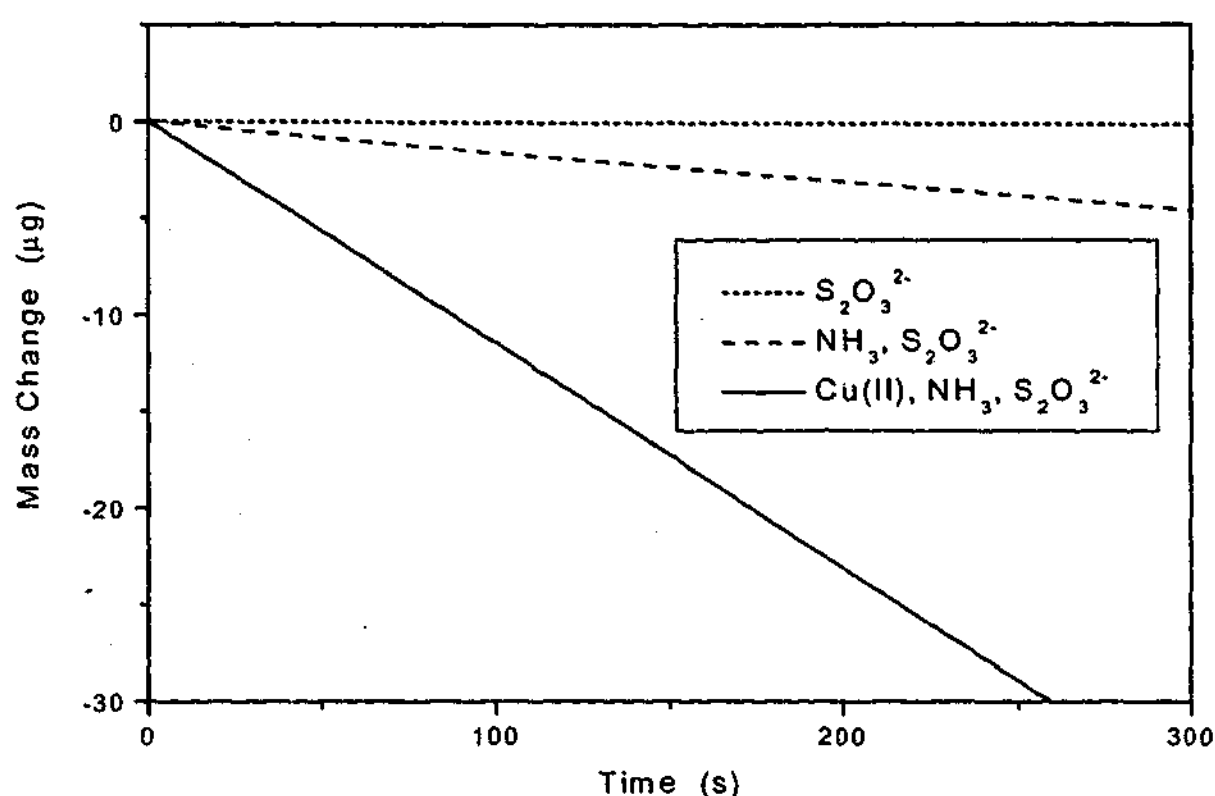
**Figure 6.6:**   Kinetic plot showing the leaching of gold at a fixed potential of 238 mV in solutions containing either thiosulfate, thiosulfate and ammonia, or thiosulfate, ammonia and copper: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

The enhancement of the gold oxidation reaction by copper(II) can be further demonstrated by measuring the gold leach rate obtained in thiosulfate/ammonia solutions containing different oxidants. The results of these experiments are shown in Figure 6.7. In each of the experiments, the oxidant addition was performed such that the mixed potential obtained during leaching was identical for each of the solutions. According to mixed potential theory, since the mixed potential is the same for each of the oxidants, the leach rate should be identical. The first oxidant studied was oxygen, as this is the most difficult oxidant to 'set' the potential for, since the concentration of the oxidant is limited by its solubility. To obtain a positive enough potential, the pH of the solution was reduced to 9.4 by decreasing the ammonia concentration to 0.2 M, and substituting sodium thiosulfate with ammonium thiosulfate. Using a partial pressure of oxygen of 1 atm under these conditions, the mixed potential was found to be 175 mV. As shown in Figure 6.7, using oxygen as an oxidant at this potential does not leach gold

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at a significant rate. The potentiostat is also a very useful 'oxidant', as the mixed potential is simply applied under feedback control. However, at a potential of 175 mV, leaching is also very slow. The third oxidant investigated was cobalt(III) hexa-ammine (solution contained 1 mM Co(III) and enough Co(II) was added to reduce the mixed potential to 175 mV). Like the other oxidants, leaching in this instance is very slow. When a mixture of copper(II) and copper(I) is added to the solution, it is clear from Figure 6.7 that leaching is very rapid, even though the mixed potential is identical to that obtained using the other oxidants. The inescapable conclusion that can be drawn from these results, as well as the results shown in Figure 6.6, is that the gold oxidation reaction is enhanced once copper(II) is added to solution. Thus, gold oxidation (Equation 6.1) is catalysed by the presence of copper(II) and hence copper(II) does not solely act as the oxidant in the thiosulfate leach system.
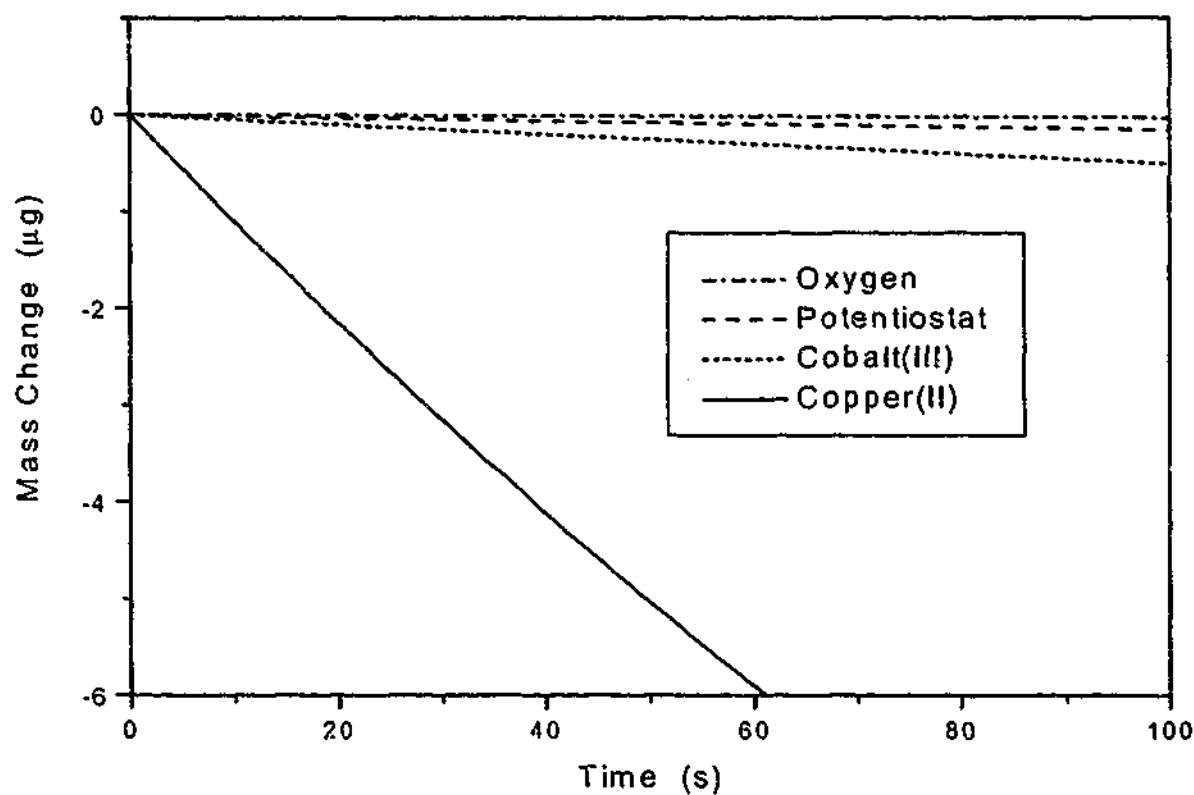


**Figure 6.7:** Kinetic plot showing the leaching of gold in 0.1 M ammonium thiosulfate and 0.2 M ammonia with different oxidants: 300 rpm, 30 °C. The ratio of the oxidised to reduced form of the oxidant was adjusted so that the mixed potential was 175 mV for all experiments.

So what does the voltammogram for gold oxidation in the presence of copper(II) actually look like? Using the REQCM, the partial current density for gold oxidation ($i_{calculated}$) can be plotted as a function of potential, since the mass change can be measured in-situ and in real time. Shown in Figure 6.8 is a voltammogram (solid line) showing the total current density measured for a gold electrode in a thiosulfate leach solution. It should be clear that this curve tells us little about the gold oxidation process; perhaps the only useful information that can be gained is the mixed potential ($E_m$) for the system (E at which i=0). From the mass change measured as a function of potential the partial current density for gold oxidation in thiosulfate leach solutions can be calculated; the resultant voltammogram has been overlaid in Figure 6.8 as a dashed line.
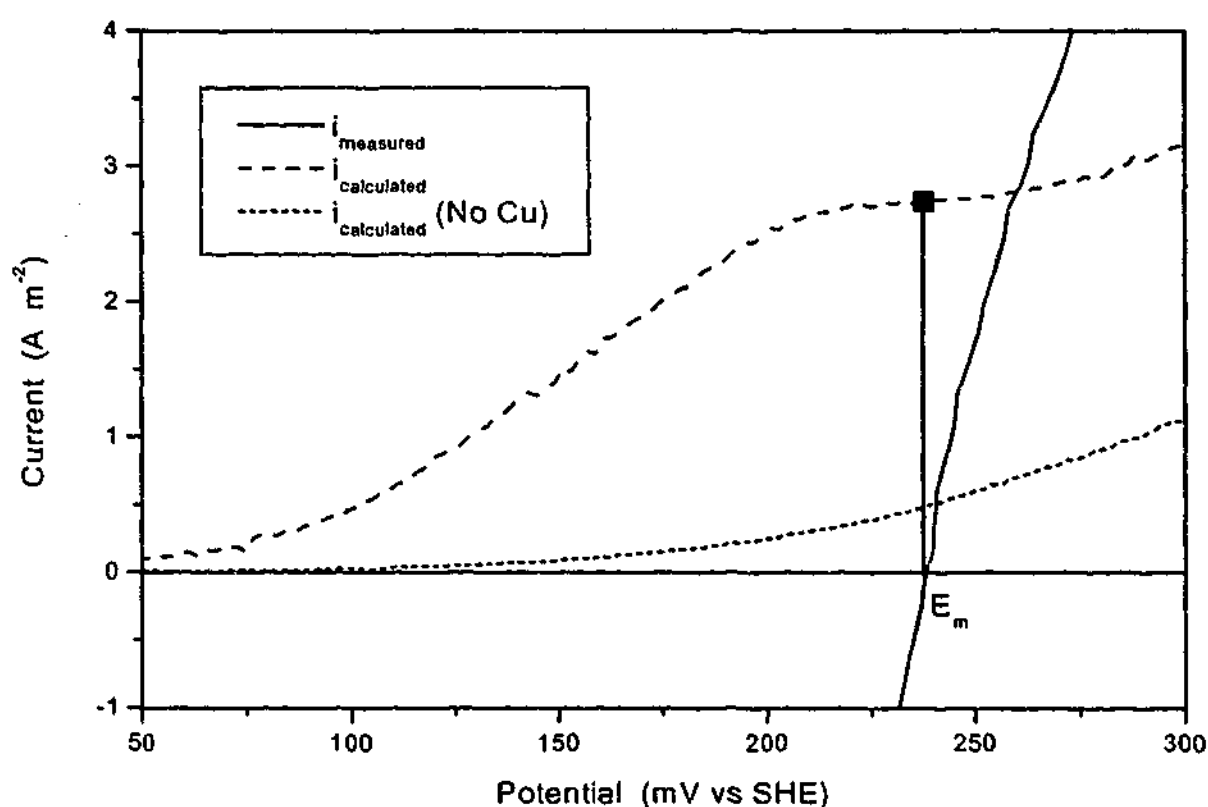


**Figure 6.8:** Linear sweep voltammogram for a gold electrode in a thiosulfate leach solution (solid line): 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C. Also shown is the calculated current for gold oxidation (dashed line) derived from the mass change measured using the REQCM. The calculated current in the absence of copper is also shown for comparison. The square symbol marks the mixed potential and reaction rate (as current density) measured during leaching.

It is clear from Figure 6.8 that in the presence of copper(II) the gold oxidation reaction is rapid and occurs at low overpotentials. The partial current density for gold oxidation in ammonia/thiosulfate solutions in the absence of copper(II) has been overlaid in Figure 6.8 for comparison. The measured gold leach rate and mixed potential is also marked in Figure 6.8 as a square. Clearly, this point is much closer to the voltammogram obtained in the presence of copper(II) than that obtained in the absence of copper(II). Such a result implies that the voltammogram obtained in the presence of copper(II) is a much better representation of the gold oxidation half reaction during leaching in thiosulfate leach solutions.

So how much copper(II) is required to promote the gold oxidation half reaction? This was investigated by measuring the gold oxidation rate as a function of copper(II) concentration. Figure 6.9 shows that at any potential, the gold oxidation half reaction is enhanced significant at low copper(II) concentrations. However, this effect becomes steady at high copper(II) concentrations. Thus maintaining the copper(II) concentration above 2 mM is recommended in order to achieve appreciable gold oxidation rates.
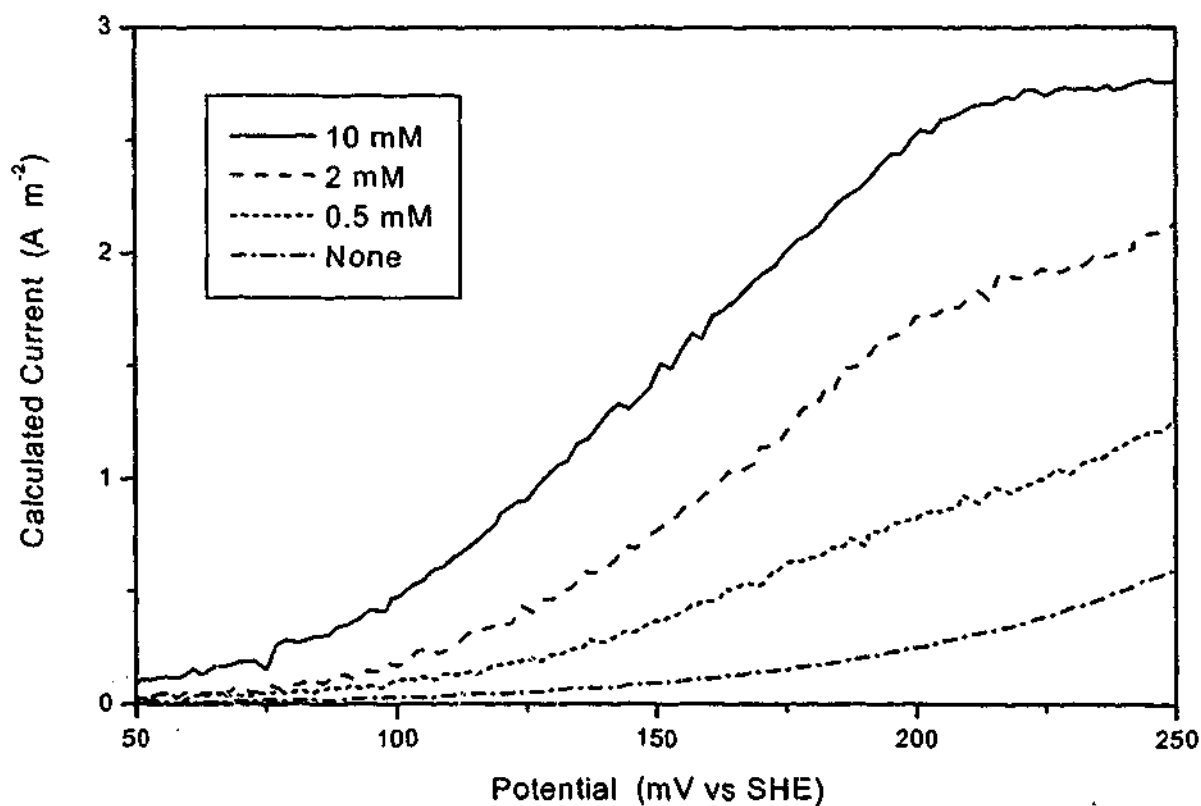


**Figure 6.9:** Linear sweep voltammograms showing the effect of copper(II) concentration on the calculated current for gold oxidation: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 300 rpm, 30 °C.

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It was shown in Chapters 3 and 5 that when fresh thiosulfate leach solutions are prepared initially containing copper(II), the copper(II) commences reacting immediately with thiosulfate generating copper(I) and tetrathionate. This means that the effect of copper(II) on the gold oxidation half reaction could be attributed to one or more of three factors: 1) the presence of copper(II); 2) the formation of tetrathionate; or 3) the formation of copper(I). During the time taken to record the voltammograms shown in Figure 6.8, the copper(II) concentration had decreased (estimated from Figure 3.3) to 9.5 mM, resulting in the formation of 0.25 mM tetrathionate and 0.5 mM copper(I). Thus, experiments were performed to determine which of these effects is dominant.

In the first of these experiments, 0.5 mM copper(II) sulfate was added to a de-oxygenated solution containing thiosulfate. This allows the reaction between copper(II) and thiosulfate to occur very rapidly, generating 0.5 mM copper(I) and 0.25 mM tetrathionate. Ammonia was then added whilst maintaining the solution under an inert atmosphere. Figure 6.10 shows the calculated current for gold oxidation as a function of potential for this solution. Shown also in Figure 6.10 for comparison is the gold oxidation voltammogram measured in the absence of copper. Clearly, the gold oxidation reaction is enhanced by the presence of copper(I) and/or tetrathionate. However, in comparison to the voltammogram shown in Figure 6.10 for the solution initially prepared with 10 mM copper(II), which contained 9.5 mM copper(II), 0.5 mM copper(I) and 0.25 mM tetrathionate when the voltammogram was measured, the gold oxidation rate is significantly lower. Hence, the enhancement to the gold oxidation reaction observed in Figure 6.8 is largely due to the presence of copper(II).

As the gold oxidation reaction was found to be enhanced in the presence of copper(I) and tetrathionate, a further experiment was conducted to establish whether this was due to the copper(I) and/or the tetrathionate. In this experiment, 0.5 mM cuprous chloride was added to a de-oxygenated solution containing thiosulfate and ammonia. The resultant voltammogram for gold oxidation in this instance is shown in Figure 6.10 to closely overlay that obtained for the solution containing both copper(I) and tetrathionate. Obviously, tetrathionate has no effect on the gold oxidation half reaction and that the presence of copper(I) enhances gold oxidation. It can also be seen by comparing Figures 6.9 and 6.10 that the gold oxidation voltammograms obtained in the presence of 0.5 mM copper(II) or 0.5 mM copper(I) compare very closely. This

suggests that the gold oxidation reaction is enhanced by copper, regardless of the oxidation state. However, to achieve acceptable gold leach rates, copper(II) is required as the oxidant in the thiosulfate leach system.
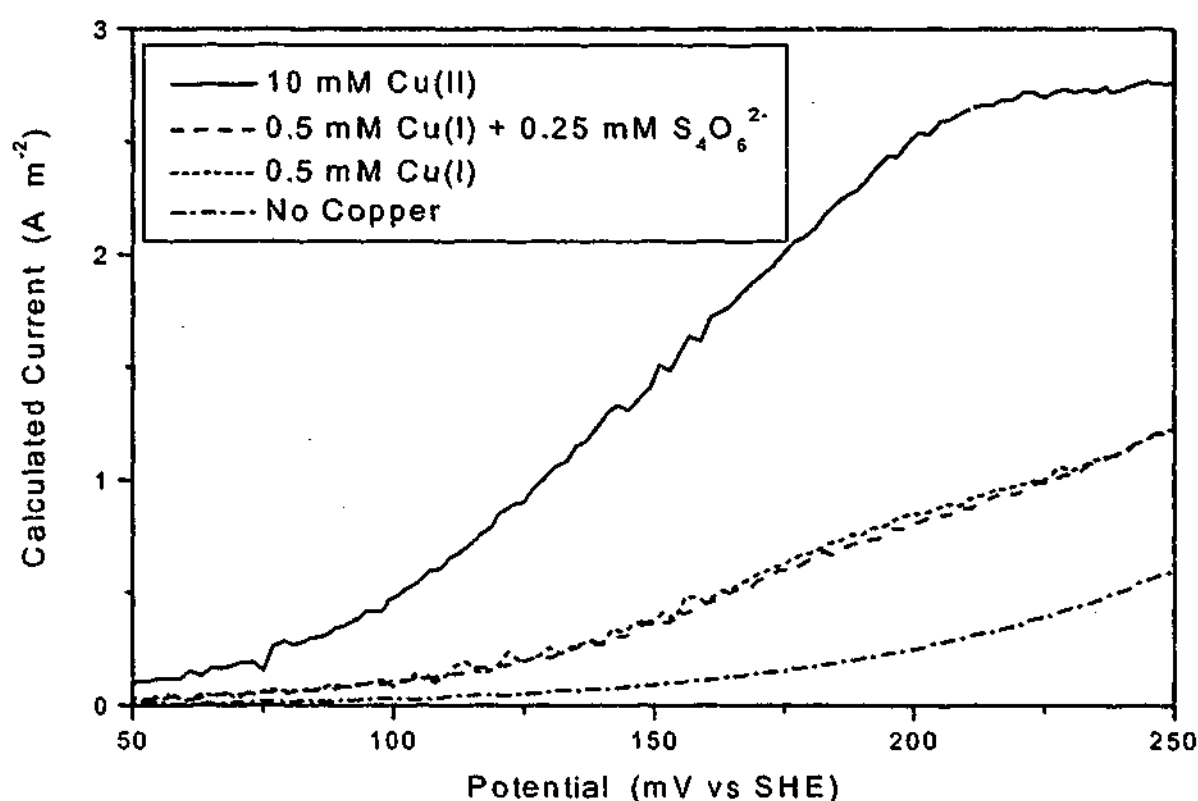


**Figure 6.10:** Linear sweep voltammograms showing the calculated current for gold oxidation in thiosulfate plus ammonia solutions containing also copper(I) and copper(I) plus tetrathionate. Also shown are the voltammograms for gold oxidation in the absence of copper, and with 10 mM copper(II): 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 300 rpm, 30 °C.

## 6.3.2 Effect of Gold Form and Purity

As discussed in the review, naturally occurring gold generally exists as a gold/ silver alloy (Hurlbut and Klein, 1977). Despite this, the effect small amounts of silver alloyed with gold have on the gold leach rate in thiosulfate leach solutions has received little attention. In addition, gold leach studies can also be conducted using gold discs of different forms. That is, the gold disc may be formed by a number of methods such as casting, sputter coating or by electrodepositing gold onto a disc surface.

## 6.3.2.1  Electrodeposited Gold

As noted in section 6.2, this study utilised electrodeposited gold electrodes for use with the REQCM. It was found in this study that the gold dissolution rate in thiosulfate leach solutions was dependant on the age of the plating solution. Table 6.1 presents the gold leach rates measured in a freshly prepared thiosulfate leach solution with aging of the plating solution. Clearly, the gold leach rate decreases as the plating solution ages with use, and more so (15%) after the first several uses (1 day). The decrease over 3 weeks of continual use after this initial period is noted in Table 6.1 to be much smaller (4%). To minimise this effect only aged plating solutions were used throughout this study and experimental results were compared against the standard conditions on a regular basis. As most of the variables studied have a significant effect on the gold leach rate, the relativities observed are generally much greater than variations due to the plating solution age.

**Table 6.1:**  Gold leach rates measured as the electroplating solution aged: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

| Age of Plating Solution | $10^5$ x Gold Leach Rate (mol m$^{-2}$ s$^{-1}$) |
|---|---|
| Fresh | 3.3 |
| 1 Day | 2.8 |
| 3 Weeks | 2.7 |

## 6.3.2.2  Surface Finish

As noted in the review, both electroplated gold and solid gold electrodes have been used previously to study the kinetics of gold leaching in thiosulfate leach solutions. As the surface finish is well known to affect the rate of dissolution, especially for chemically controlled reactions, the effect of surface finish on the gold leach rate was investigated. For the REQCM electrodes used in this study it was also possible to sputter coat a gold disc onto the quartz rather than electroplating gold onto the platinum.

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The leach rate of gold in this form was found to be $3.2 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$ in a freshly prepared thiosulfate leach solution. This compares closely with that shown in Table 6.1 for electrodeposited gold from a fresh electroplating solution. Thus, the surface finish (roughness) would appear to be similar for these two forms of gold. This is not surprising as the surface finish of the quartz will largely govern the surface finish of the sputter coated or electroplated gold and hence the gold leach rate. It should be noted though, it is the relative gold leach rates that are important in the quest to better understand the fundamentals of the gold dissolution process and not the absolute rates; the later not being an objective of the current study. Hence, comparative experiments were conducted with the same electrode to minimise the difference in surface roughness between experiments.

The surface finish of a polished solid gold electrode though would expectedly be much smoother and have fewer defects than electroplated gold. Rotating disc studies conducted by Barbosa-Filho *et al.* (1994) and Muyunda (1996) using polished solid gold electrodes, measured gold leach rates around $0.5 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$ for the standard thiosulfate leach solution conditions used in this study (0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C). This is much lower than the gold leach rates around $2.8 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$ measured in this study for the standard thiosulfate leach solution conditions. In order to check the relativity of these gold leach rates for different surface finishes, experiments were conducted using both electroplated and solid gold electrodes. To achieve this, the gold oxidation rate at 250 mV was determined for both electroplated gold and solid gold in a solution containing 0.4 M ammonia and 0.3 M thiosulfate at 40 °C without copper(II); the current measured at this potential is a result of gold oxidation only (Figure 6.3). Figure 6.11 shows the measured transient current densities for the electroplated and solid gold electrodes submerged into this solution whilst holding the electrode potential at 250 mV. Clearly, the measured current densities on the electroplated gold electrode after 400 s are almost an order of magnitude higher than that measured on the solid gold electrode. This confirms that the surface finish has a significant effect on the gold oxidation rate. A similar effect has also been observed during cyanidation studies for conditions where the gold dissolution process is chemically controlled (Jeffrey, 1998).

The transient responses shown in Figure 6.11 are also very interesting. The response for the electroplated gold electrode is consistent with an induction period as observed previously in Figure 6.1. However, the response of the solid gold electrode shows little evidence of an induction period. This is consistent with all the published kinetic data for solid gold electrodes that showed no evidence of an induction period, especially at lower temperatures where the sample period was shorter than the induction period for electroplated gold. The reason for no induction period being detected for solid gold electrodes is unclear, though it is likely to be related to the surface finish and the effect this has on the surface passivation.
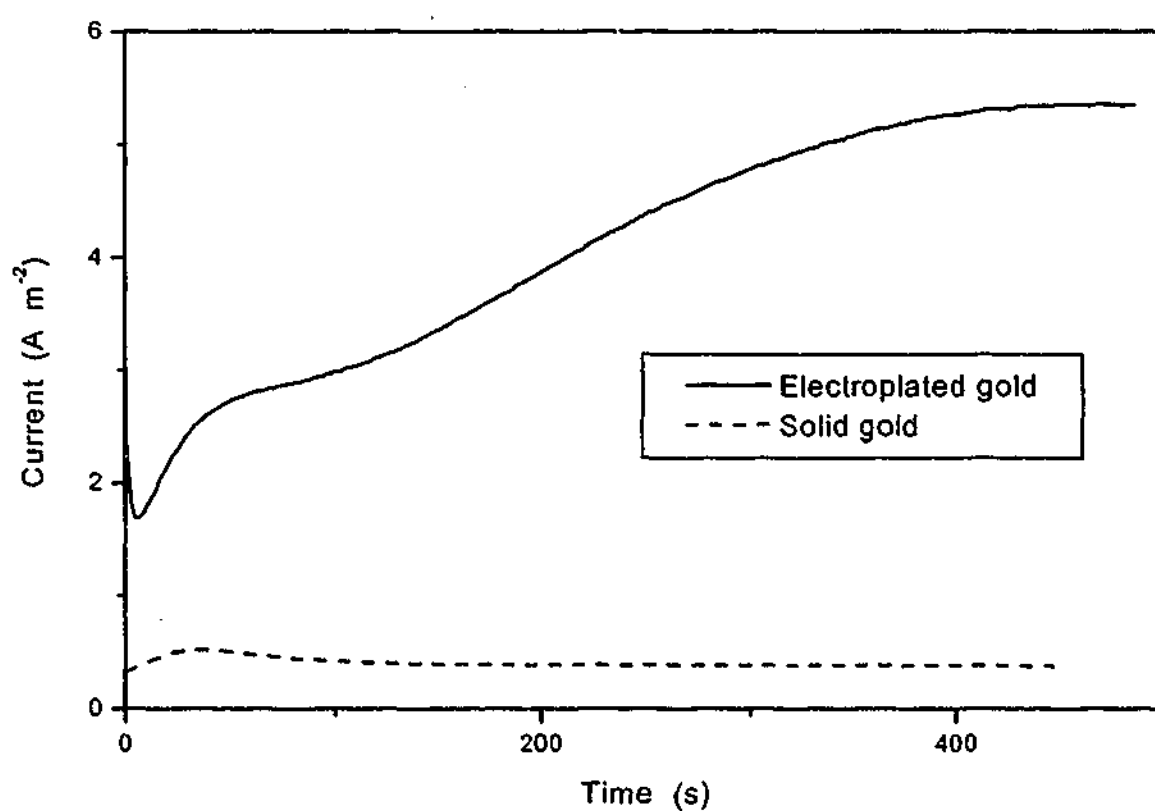


**Figure 6.11:** Initial transient current measured for electroplated and solid gold electrodes at 250 mV in a thiosulfate leach solution: 0.3 M $Na_2S_2O_3$, 0.4 M $NH_3$, 300 rpm, 40 °C.

### 6.3.2.3 Gold Purity

Naturally occurring gold mainly exists alloyed with some silver (Hurlbut and Klein, 1977). Thus, the leach study conducted by Jeffrey (2001), using electroplated silver modified gold could be considered more representative of naturally occurring gold. However, the effect of small quantities of silver alloyed with gold, subsequently referred to as gold/silver, has not been investigated. Electroplated gold/silver was achieved by the addition of 0.2 mM silver nitrate to the gold plating solution, which gave a resultant deposit containing 2 wt% silver. The gold leach rate for freshly electroplated gold/silver in a fresh thiosulfate leach solution was found to be more than double the rate observed for electroplated pure gold. However, the measured gold leach rate was found to decrease the longer the electrode was left standing after electroplating. No further decrease in the measured gold leach rate though was found after allowing the electroplated electrode to stand overnight. A similar reduction in gold leach rate was also observed by placing the electroplated gold/silver electrode in an oven at 60°C for an hour.

To quantify this effect, experiments were conducted for the conditions used in Figure 6.11 using electroplated gold/silver. The measured transient current densities for electroplated gold/silver are shown in Figure 6.12 compared to that of electroplated gold. Clearly, for freshly electroplated gold/silver the induction period is relatively short and the gold oxidation rate is more than 3 times that of electroplated gold. Allowing the gold/silver electrode to stand overnight after electroplating is shown in Figure 6.12 to increase the induction period and significantly decrease the gold oxidation rate; though the gold/silver oxidation rate is still 50% higher than the electroplated gold oxidation rate. The reason for the much higher leach rates observed for freshly electroplated gold/silver was not resolved. An almost identical difference (gold versus gold/silver after standing) was also observed in the measured current densities for solid gold and gold/silver (2 wt% silver) electrodes (not shown in Figure 6.12). Subsequently, any experiments conducted with electroplated gold/silver, the electroplated electrode was allowed to stand overnight or placed in an oven at 60 °C for an hour before using.
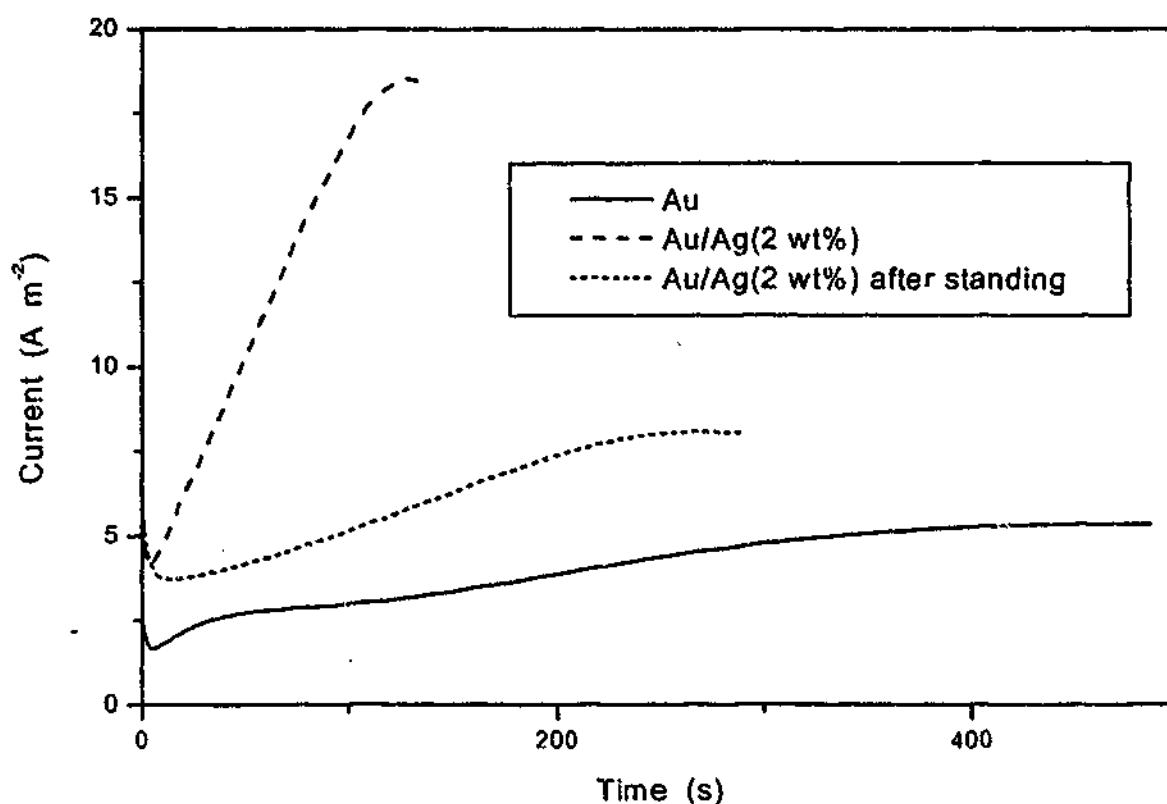
**Figure 6.12:** Initial transient current measured for electroplated gold and gold/silver electrodes at 250 mV in a thiosulfate leach solution: 0.3 M $Na_2S_2O_3$, 0.4 M $NH_3$, 300 rpm, 40 °C.

## 6.3.3 Effect of Copper Concentration

The presence of copper was clearly shown in section 6.3.1. to not solely act as the oxidant in the thiosulfate leaching process, but also enhanced the gold oxidation process resulting in significantly higher gold dissolution rates. The concentration of copper(II) was also shown in Chapters 3 and 5 to have a significant effect on the rate of thiosulfate oxidation. Thus, the concentration of copper(II) in solution is clearly an important factor and the effect this has on the dissolution kinetics required further investigation.

### 6.3.3.1 Kinetics

The kinetics of gold dissolution in freshly prepared thiosulfate leach solutions containing different quantities of copper(II) were investigated using the REQCM. Figure 6.13 shows the effect of copper(II) concentration on the gold leach kinetics. The data is initially presented in this form as it shows both the effect of copper(II) on the initial induction period and the steady state gold leach rate. Clearly, the steady state gold leach rate is observed to decrease as the copper(II) concentration decreases, however, the time taken to reach the steady leach rate increases with decreasing copper(II) concentration.
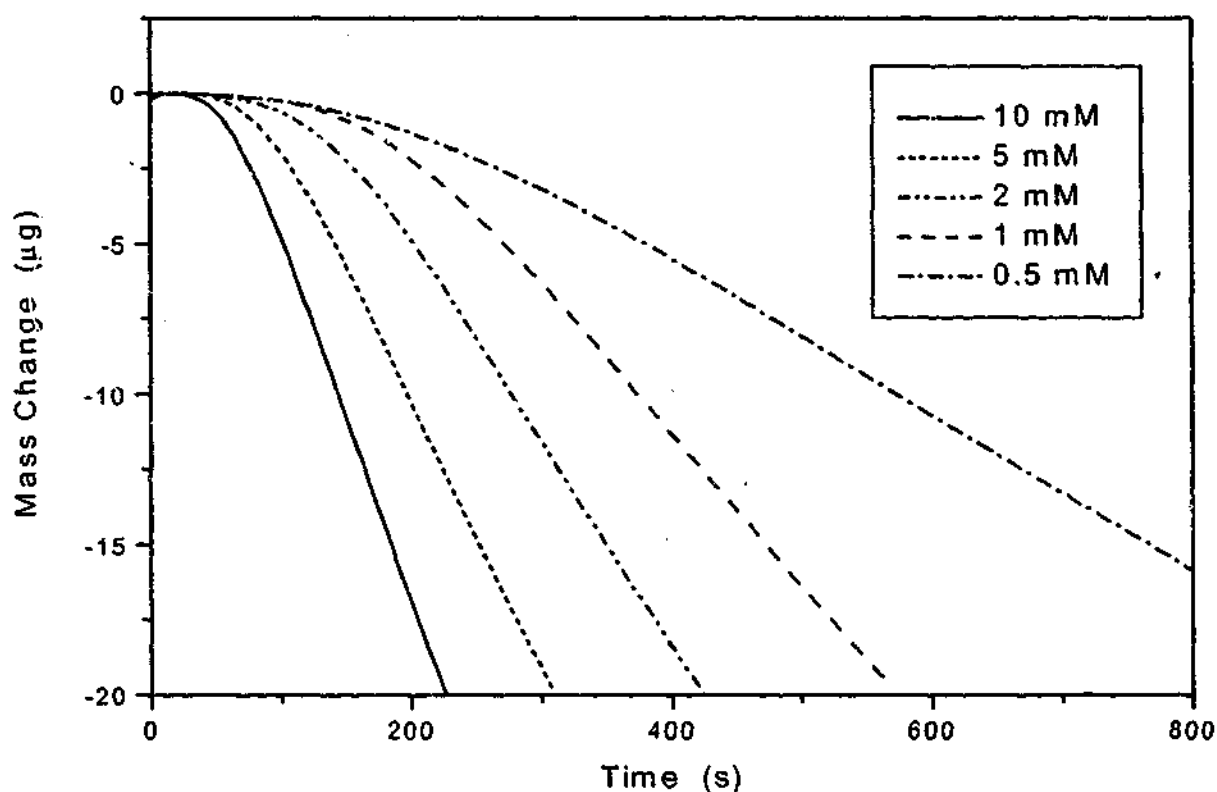


**Figure 6.13:** Kinetic plot showing the effect of copper(II) concentration on the leaching of gold in fresh thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

The effect of copper(II) concentration on the steady state gold leach rate in fresh thiosulfate leach solutions is best represented as shown in Figure 6.14. Clearly, the gold leach rate does not increase linearly with increasing copper(II) concentration. At low

copper(II) concentrations the gold leach rate increases significantly with increasing copper(II) concentration. At copper(II) concentrations above 2 mM the observed increase in gold leach rate with increasing copper(II) concentration is diminished; only a 60% increase in gold leach rate observed for an increase from 2 mM to 10 mM in copper(II) concentration.
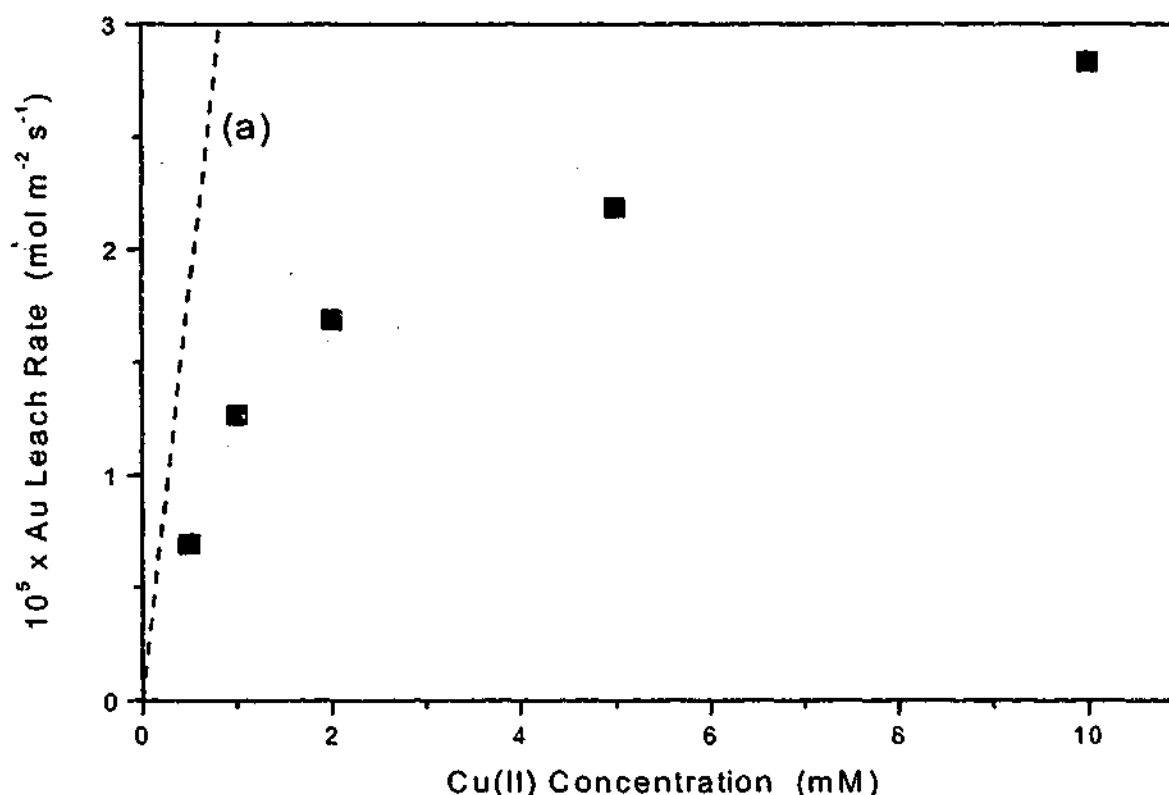


**Figure 6.14:** The effect of copper(II) concentration on the steady state gold leach rate in fresh thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C. Line (a) is the diffusion limiting gold leach rate calculated using the Levich equation.

The advantage of having conducted experiments using a rotating gold disc is that the measured rate of gold dissolution can be compared to the rate of mass transfer of reactants to the disc surface. As thiosulfate is in excess, the gold dissolution process is ultimately limited by the flux of copper(II) to the electrode surface-solution interface. This is calculated using the Levich equation (Equation 2.22), for which the copper(II) diffusion coefficient is taken to be $1.01 \times 10^{-9}$ $m^2$ $s^{-1}$ (calculated in section 6.3.1.2) and the kinematic viscosity of the solution as $0.80 \times 10^{-9}$ $m^2$ $s^{-1}$ (Weast, 1974-75) at 30 °C.

Shown in Figure 6.14 as a dashed line labelled (a) is the calculated diffusion limiting gold leach rate based on the diffusion limiting flux of copper(II) to the disc surface. Obviously at low copper(II) concentrations the gold leach rate is partially diffusion controlled. However, at copper(II) concentrations greater than 2 mM the gold leach rate is significantly lower than the copper(II) diffusion limited gold leach rate and is almost independent of the copper(II) concentration. This indicates that the leaching of gold is mainly chemically controlled at copper(II) concentrations greater than 2 mM. This was confirmed by experiments conducted with 10 mM copper(II) in which the gold leach rate was found to be almost independent of rotation rate.

## 6.3.3.2 Electrochemistry

In section 6.3.1 it was shown that in the presence of thiosulfate the cathodic half reaction (copper(II) reduction) occurs at more positive potentials. The cathodic half reaction potential is also shown in section 7.3.1 to be largely dependant on the concentrations of copper(II) and copper(I). Figure 6.15 shows the voltammograms measured using a platinum electrode for fresh thiosulfate leach solutions of different copper(II) concentrations. Clearly, the current due to copper(II) reduction decreases with decreasing copper(II) concentration. Hence, mixed potential theory indicates that gold leaching will occur at lower potentials with decreasing copper(II) concentration. It should be noted that the small positive currents measured for these solutions is due to copper(I) oxidation. This is a result of the homogeneous reduction of copper(II) by thiosulfate as detailed in Chapter 3 during measurement of the gold leach rate and then the anodic and cathodic voltammograms.
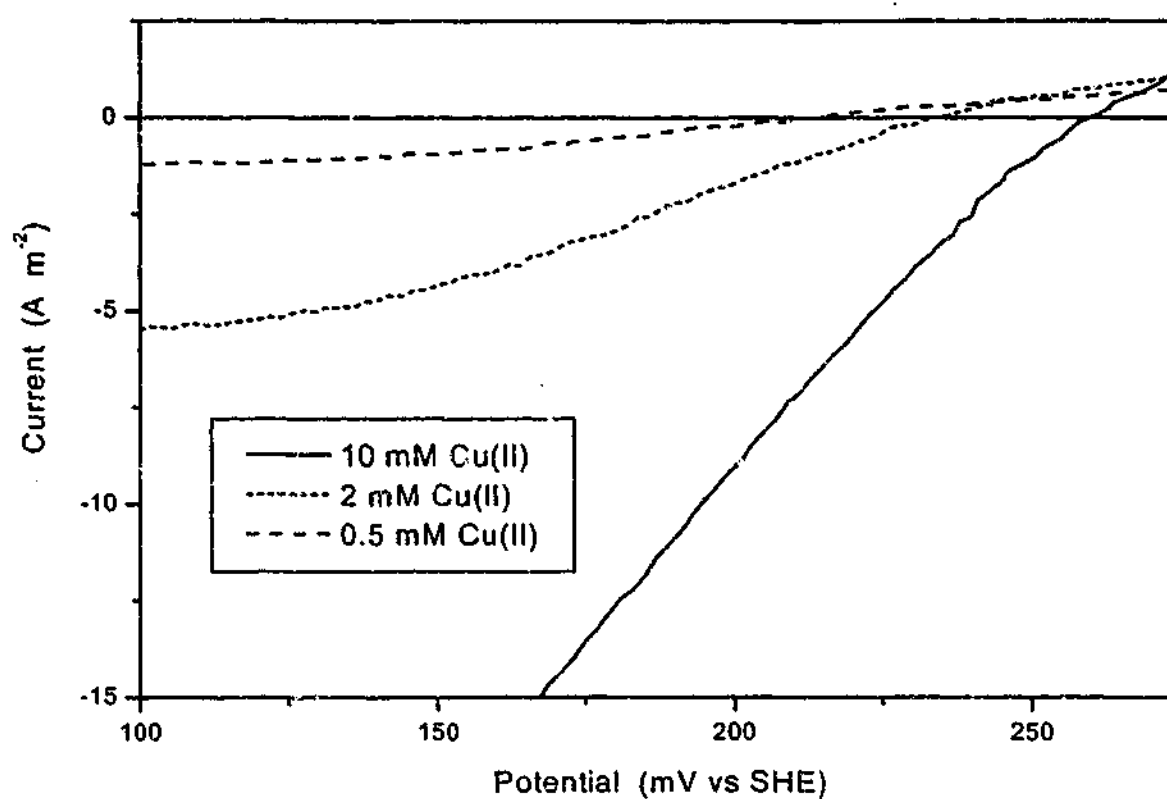
**Figure 6.15:** Linear sweep voltammograms for the reduction of copper(II) in fresh thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 300 rpm, 30 °C. A platinum electrode was used in these experiments.

The voltammograms for gold oxidation were shown previously in Figure 6.9, where the anodic reaction (gold oxidation) was observed to decrease with decreasing copper(II) concentration. Shown in Figure 6.16 as an Evan's type diagram are the cathodic and anodic curves measured using the REQCM for solutions containing 10, 2 and 0.5 mM copper(II), presented previously in Figures 6.15 and 6.9 respectively. These curves predict a decrease in gold leach rate (current) and mixed potential with a decrease in copper(II) concentration as both the anodic and cathodic curves decrease with decreasing copper(II) concentration. Overlaying this data, as square symbols, are the gold leach rates (as a calculated current) from Figure 6.14 plotted against the measured mixed potential. Clearly, the measured gold leach rates and mixed potentials closely match those predicted by mixed potential theory. Thus, the effect of copper(II) concentration on gold leach rate is accounted for by the effect of copper(II) on the individual anodic and cathodic reactions.
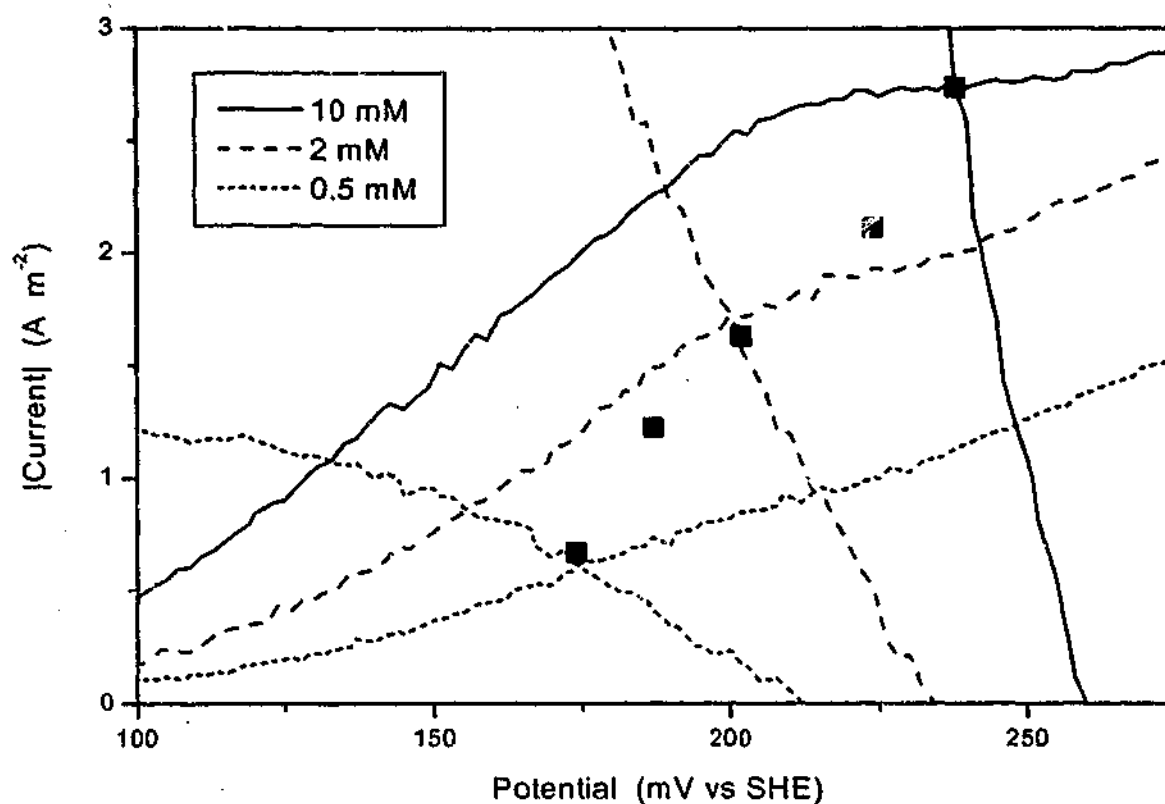
**Figure 6.16:** Evans' type diagram showing the anodic and cathodic curves for fresh thiosulfate leach solution containing 10, 2 and 0.5 mM copper(II): 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 300 rpm, 30 °C. Also shown, as square symbols, are the measured reaction rates (as current density) and mixed potentials for the gold leach rates shown in Figure 6.14.

## 6.3.4 Effect of Temperature

It is well known that the reaction rates of an electrochemical process are affected by temperature, especially if chemically controlled. According to the Arrhenius equation shown in Equation 6.7, the rate constant is exponentially related to $1/T$; $k$ is the rate constant (mol m$^{-2}$ s$^{-1}$), A is the frequency factor (mol m$^{-2}$ s$^{-1}$), $E_a$ is the activation energy (J mol$^{-1}$), R is the universal gas constant (8.314 J K$^{-1}$ mol$^{-1}$), and T is the absolute temperature (K).

$$k = Ae^{-E_a/RT} \qquad\qquad 6.7$$

Thus, a plot of ln(k) versus 1/T should be a straight line of slope $-E_a/R$. If the concentration of reactants is constant, either the dissolution rate or the current density can be substituted for the rate constant to enable the calculation of the activation energy for the dissolution or oxidation of gold respectively.

### 6.3.4.1 Kinetics

The gold leach rate as a function of temperature was measured using the REQCM to determine the activation energy for gold dissolution. Figure 6.17 shows the effect of temperature on the kinetics of gold leaching. Clearly, the steady state gold leach rate is observed to increase dramatically as the temperature increases. Notable also is the significant reduction in the induction period to gold dissolution with increasing temperature.
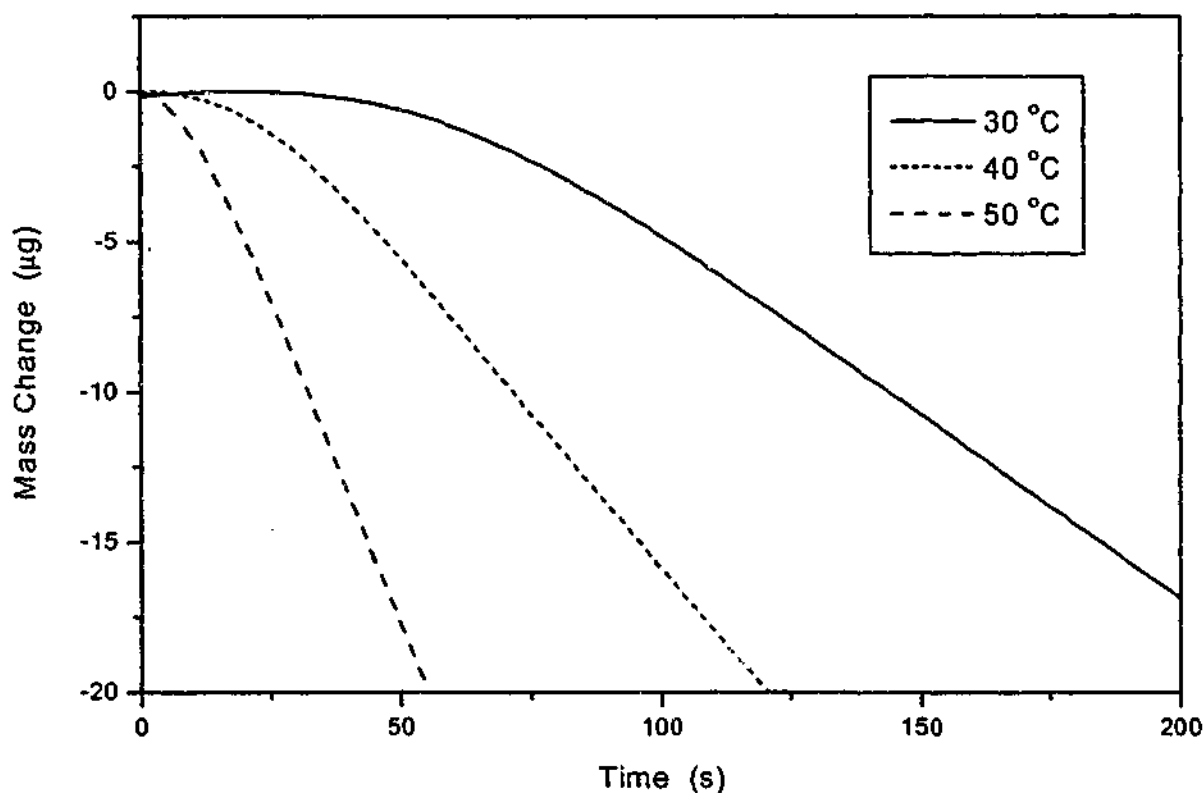


**Figure 6.17:** Kinetic plot showing the effect of temperature on the leaching of gold in fresh thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm.

The activation energy for the gold dissolution process can be calculated from an Arrhenius plot of ln(r) versus 1/T, as shown in Figure 6.18. The Arrhenius plot for the temperature range investigated was found to be linear and the activation energy was calculated to be $53 \pm 3$ kJ mol$^{-1}$. The activation energy is generally recognised as being a good guide as to whether the process is diffusion or chemically controlled. According to Power and Ritchie (1975), diffusion controlled processes usually have an activation energy less than 25 kJ mol$^{-1}$, whereas chemically controlled processes have an activation energy greater than 25 kJ mol$^{-1}$. Therefore, the observed activation energy of 53 kJ mol$^{-1}$ is further evidence that the gold dissolution process in thiosulfate leach solutions is chemically controlled.
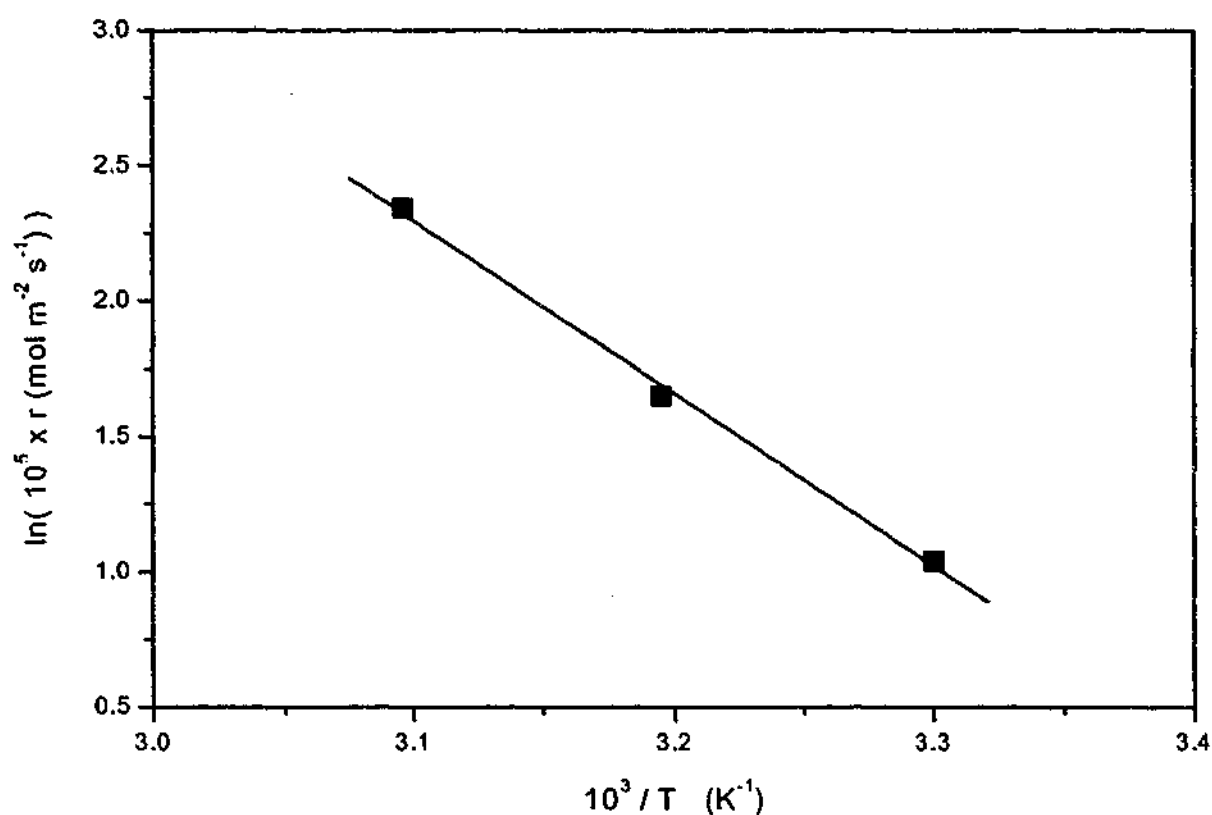


**Figure 6.18:** Arrhenius plot for the rate of gold dissolution as a function of 1/T: 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$, 10 mM CuSO$_4$, 300 rpm.

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As discussed in section 2.3.3.3, lower activation energies of around 25 kJ mol$^{-1}$ (Barbosa-Filho *et al.*, 1994, Muyunda, 1996) have been previous published for temperatures above 30 °C, suggesting the process is likely to be mixed diffusion/ chemically controlled. These lower published activation energies by these researchers could be attributed to the gold leach rates being an average gold leach rate for the initial sample period; the solution chemistry changes more rapidly as the temperature increases, and hence the gold leach rate decreases faster (section 7.3.3.4). Clearly, increasing temperature significantly increases the gold leach kinetics, however this also increases the rates of copper(II) reduction and thiosulfate oxidation (Chapters 3 and 5).

### 6.3.4.2  Electrochemistry

Figure 6.19 shows the Evans' type diagram for the cathodic and anodic curves measured using the REQCM for fresh thiosulfate leach solutions at various temperatures. The copper(II) reduction potential (cathodic curves) is shown to be almost independent of temperature, though, typical of electrochemical processes the measured current increases with increasing temperature. However, temperature is shown to have a dramatic effect on the gold oxidation reaction (anodic curves). From the leaching experiments shown in Figure 6.17, the actual mixed potentials and reaction rates at steady state are shown in Figure 6.19, marked as squares, to closely correspond to the points of intersection of the respective cathodic and anodic curves. Clearly, the large increase in gold leach rate with increasing temperature is a result of the significant increase in the anodic reaction.
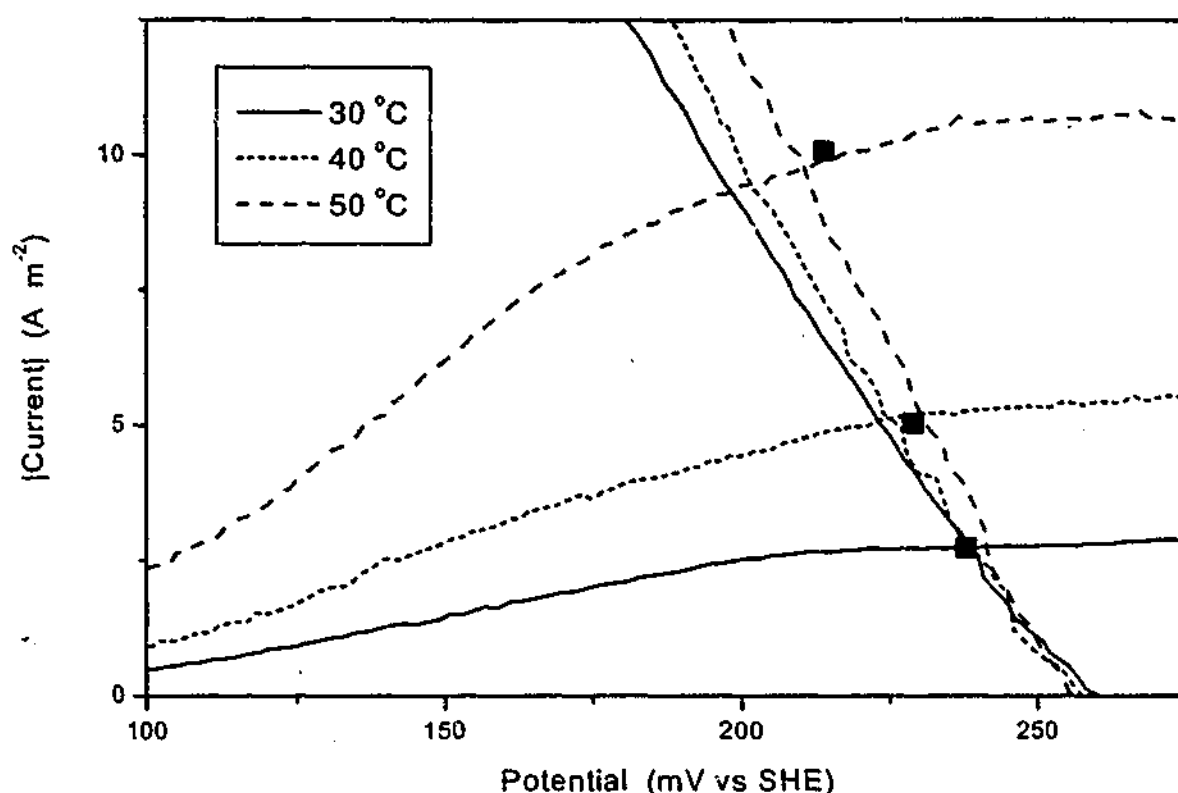
**Figure 6.19:** Evans' type diagram showing the anodic and cathodic curves for fresh thiosulfate leach solutions at various temperatures: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm. Also shown as square symbols, are the measured reaction rates (as current density) and mixed potentials for the gold leach rates shown in Figure 6.17.

## 6.3.5 Effect of Thiosulfate Concentration

The thiosulfate concentration continually decreases due to its oxidation and hence requires replenishment for reuse. Thus, understanding the effect of thiosulfate concentration on the gold dissolution process is important. The cathodic reaction (copper(II) reduction) was discussed in section 2.4.3 of the review to occur at higher potentials with increased thiosulfate concentration. The anodic reaction (gold oxidation) should also increase with increasing thiosulfate concentration since thiosulfate partakes in the gold oxidation reaction (Equation 6.1).

## 6.3.5.1 Kinetics

Expectedly, no measurable gold leaching was found to occur in solutions containing no thiosulfate. Figure 6.20 shows the effect of thiosulfate concentration on the kinetics of gold leaching. Notably, the gold dissolution rate increases as the thiosulfate concentration increases. This is consistent with the controlling reaction step involving thiosulfate. However, the effect of thiosulfate concentration on the initial induction period is small, with the time taken to reach steady state leaching increasing slightly with decreasing thiosulfate concentration.
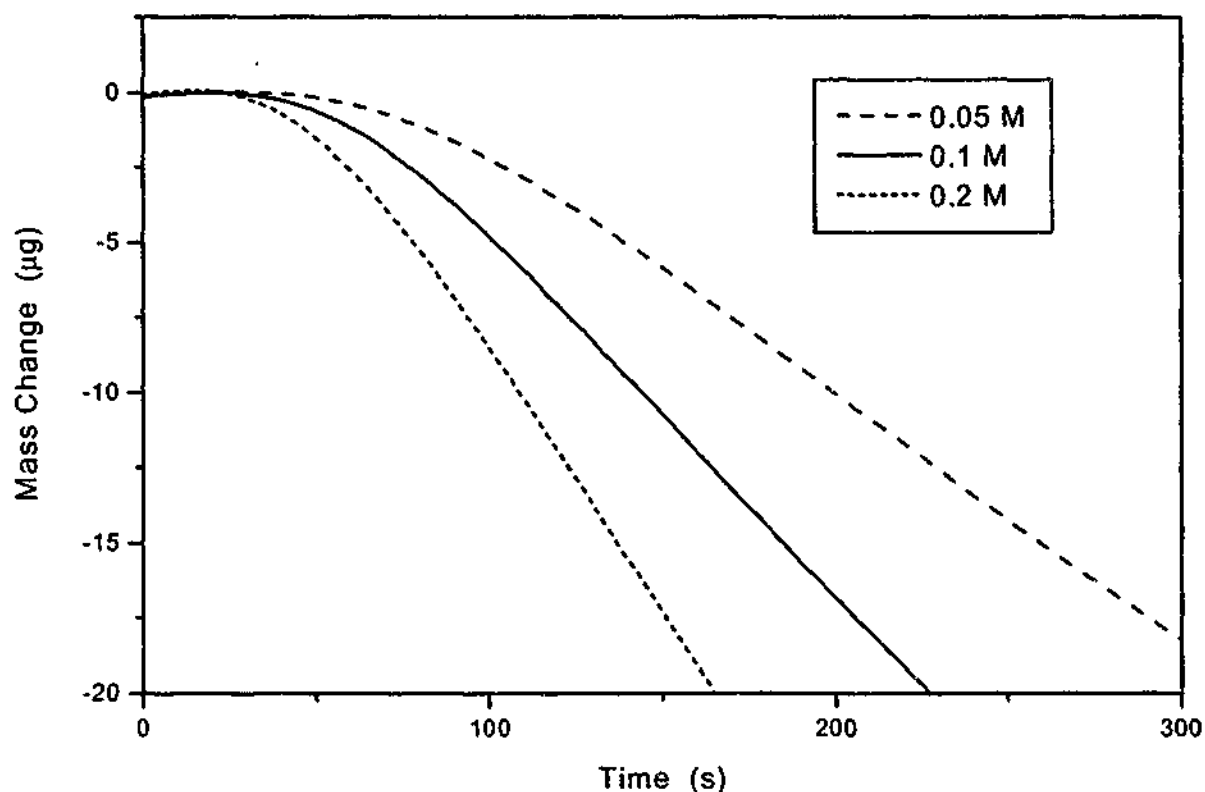


**Figure 6.20:** Kinetic plot showing the effect of thiosulfate concentration on the leaching of gold in fresh thiosulfate leach solutions: 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

The effect of thiosulfate concentration on the gold leach rate in fresh thiosulfate leach solutions is shown more clearly in Figure 6.21. Obviously, at very low thiosulfate concentrations, the gold leach rate increases more rapidly with increasing thiosulfate concentration than at higher thiosulfate concentrations. Thus, increasing thiosulfate concentration increases the gold dissolution rate, though the rate of copper(II) reduction

(section 3.3.7.2) increases or the sustainable copper(II) concentration in the presence of oxygen decreases (section 5.5.2). The effect these have on the gold leach rate as the solution ages is addressed further in Chapter 7.
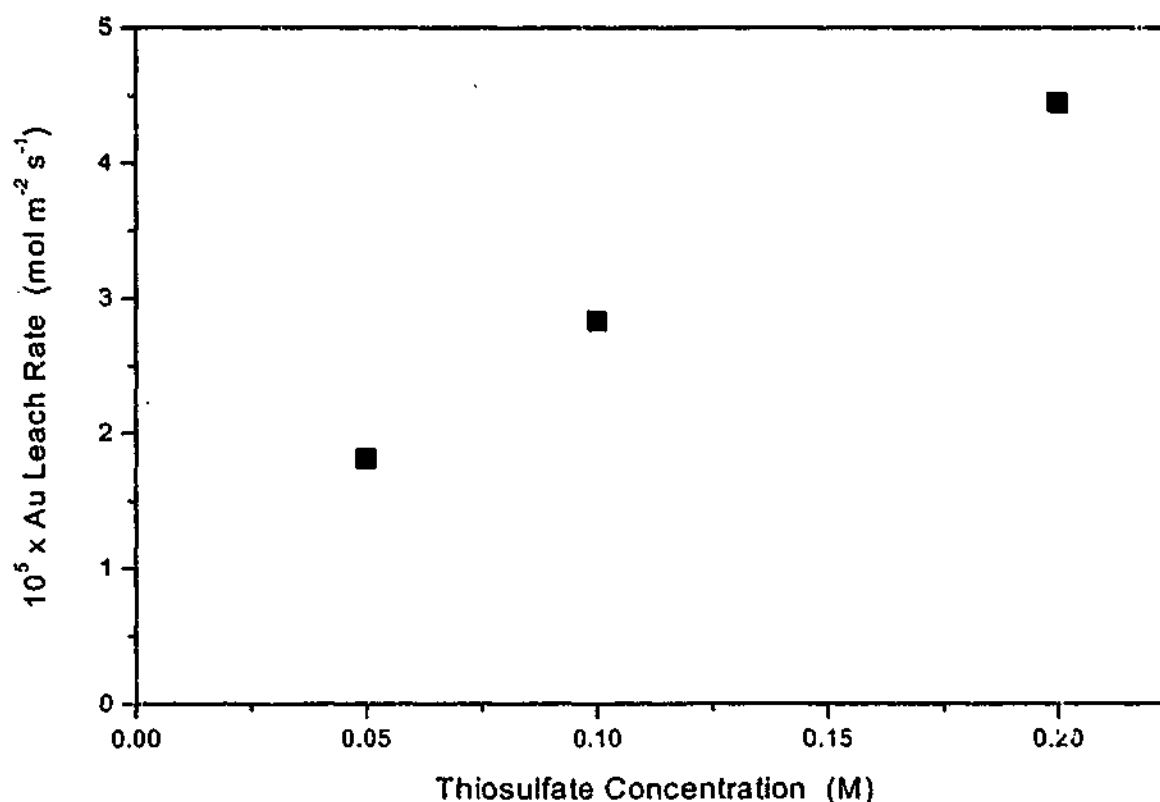


**Figure 6.21:** The effect of thiosulfate concentration on the gold leach rate in fresh thiosulfate leach solutions: 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

### 6.3.5.2 Electrochemistry

Figure 6.22 shows, as an Evans' type diagram, the cathodic and anodic curves measured using the REQCM for fresh thiosulfate leach solutions of various thiosulfate concentrations. As identified previously by Michel and Frenay (1996) the copper(II) reduction potential (cathodic curves) increase with increasing thiosulfate concentration, though this effect appears to diminish above 0.1 M thiosulfate. The significant effect of thiosulfate concentration though is on the gold oxidation reaction (anodic curves). From the leaching experiments shown in Figure 6.21, the reaction rates (calculated current) and actual mixed potentials at steady state are shown in Figure 6.22, marked as squares, to closely correspond with the points of intersection of the respective cathodic

and anodic curves. Clearly, the increase in gold leach rate with increasing thiosulfate concentration is a result of the increase in the anodic reaction, and that thiosulfate concentrations of 0.1 M or greater maximises the copper(II) reduction potential.
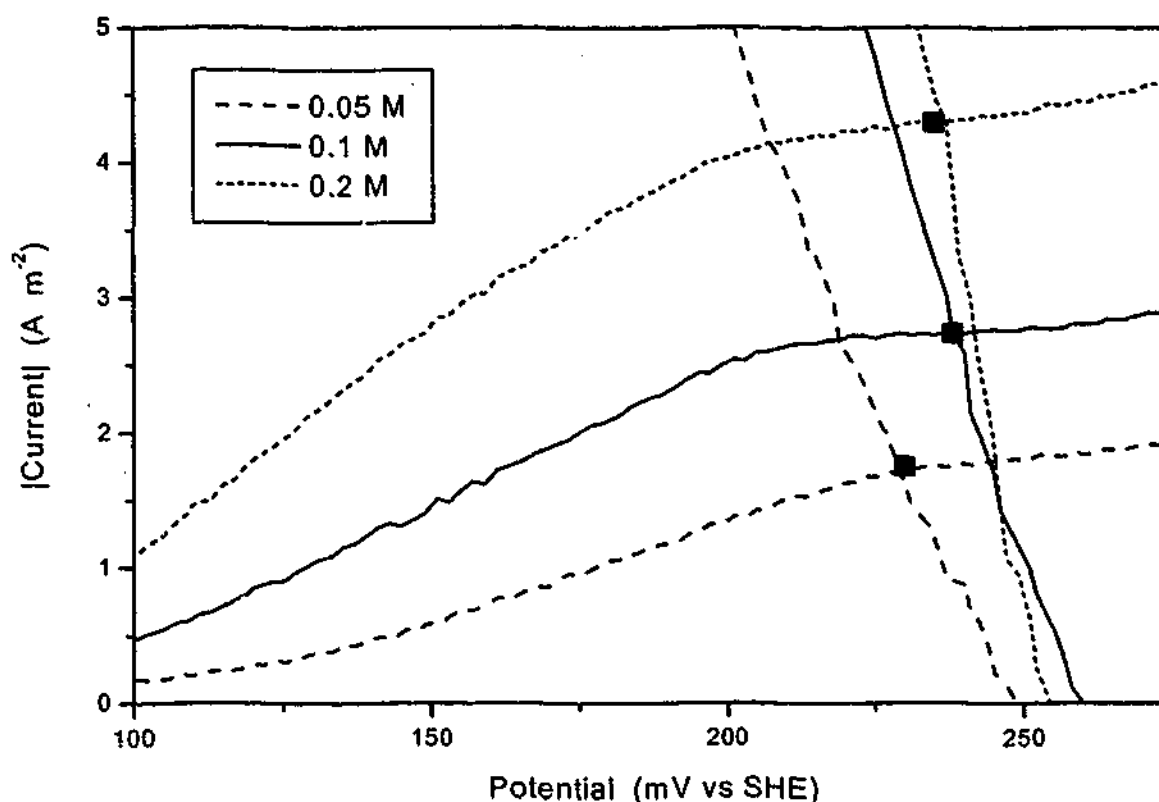


**Figure 6.22:** Evans' type diagram showing the anodic and cathodic curves for fresh thiosulfate leach solutions of various thiosulfate concentrations: 0.4 M NH$_3$, 10 mM CuSO$_4$, 300 rpm, 30 °C. Also shown as square symbols, are the measured reaction rates (as current density) and mixed potentials for the gold leach rates shown in Figure 6.21.

## 6.3.6 Effect of Ammonia Concentration

Ammonia was shown in Chapters 3 and 5 to be a vital requirement in the stabilisation of the copper(II) species in thiosulfate leach solutions. Though a positive effect of ammonia on the gold oxidation reaction in the absence of copper(II) was highlighted in Figure 6.4, the effect of ammonia on the gold dissolution process in the presence of copper(II) was not clear from the published literature (section 2.3.3.7).

### 6.3.6.1 Kinetics

No measurable gold leaching was found to occur in solutions containing no ammonia, as all copper(II) is rapidly reduced to copper(I). The effect of ammonia concentration on the kinetics of gold leaching is shown in Figure 6.23. Notably, the gold leach rates are similar, though the measured mixed potentials (see Figure 6.25) are quite different. The initial induction period to gold dissolution is also shown to increase the time taken to reach a steady state leach rate with increasing ammonia concentration.
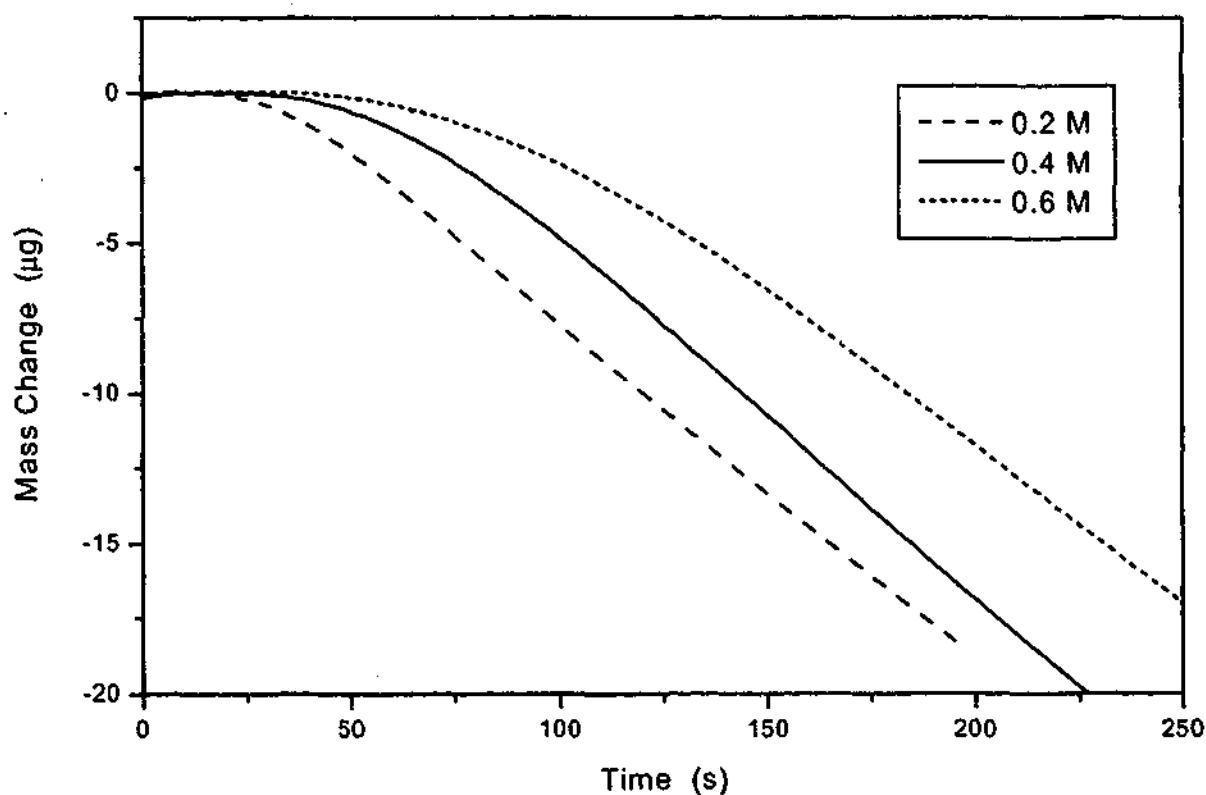
**Figure 6.23:** Kinetic plot showing the effect of ammonia concentration on the leaching of gold in fresh thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

The effect of ammonia concentration on the steady state gold leach rate in fresh thiosulfate leach solutions is shown more clearly in Figure 6.24. As the gold dissolution rate for 0.2 M and 0.4 M ammonia are similar, ammonia concentrations of at least 0.4 M are recommended due to the positive effect ammonia has on reducing the copper(II) reduction rate (sections 3.3.7.3 and 5.3.3.4). However, above 0.4 M ammonia the gold leach rate in observed in Figure 6.24 to decrease with further increases in ammonia

concentration. These results are also consistent with those previously published by Barbosa-Filho *et al.* (1994) and Jeffrey (2001), where the optimum ammonia concentration was 0.5 M (Figure 2.8), above which the gold leach rate decreased.
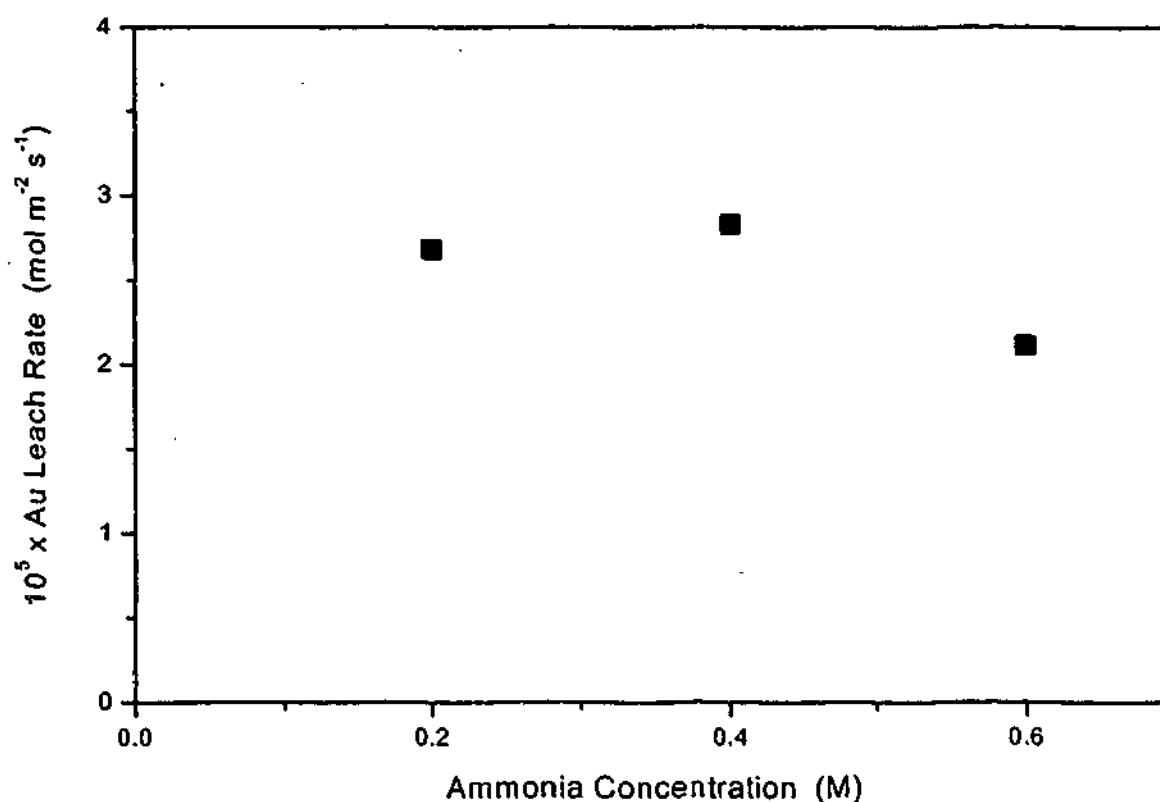


**Figure 6.24:** The effect of ammonia concentration on the gold leach rate in fresh thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

### 6.3.6.2  Electrochemistry

Shown in Figure 6.25, as an Evans' type diagram, is the cathodic and anodic curves measured using the REQCM for fresh thiosulfate leach solutions of various ammonia concentrations. As discussed in the review (section 2.4.3) the copper(II) reduction potential (cathodic curves) are observed in Figure 6.25 to decrease with increasing ammonia concentration due to the increased stability of copper(II). The effect of ammonia concentration on the anodic reaction though is interesting. The results shown in Figure 6.25 indicate that in the presence of copper(II), the gold oxidation reaction is enhanced by increasing the ammonia concentration up to around 0.4 M ammonia, above which it is hindered by the further addition of ammonia.

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However, it was shown in Figure 6.4 that increasing the ammonia concentration above 0.4 M in the absence of copper(II) further enhances the gold oxidation reaction. The reason for this is unclear. Overlaying this data, marked as squares, are the reaction rates (calculated current) and actual mixed potentials at steady state from the leaching experiments shown in Figure 6.24. Clearly, the leach rates and mixed potentials closely correspond to those predicted by mixed potential theory (the points of intersection of the respective cathodic and anodic curves). As the anodic reaction is only slightly affected by changing the ammonia concentration and that the gold oxidation curves are nearly flat in the potential region in which leaching occurs, the gold leach rates are somewhat similar. The effect of ammonia on the cathodic reaction though accounts for the observed differences in mixed potential measured during leaching; ammonia stabilises the copper(II) thus resulting in a lower copper(II) reduction potential with increasing ammonia concentration.
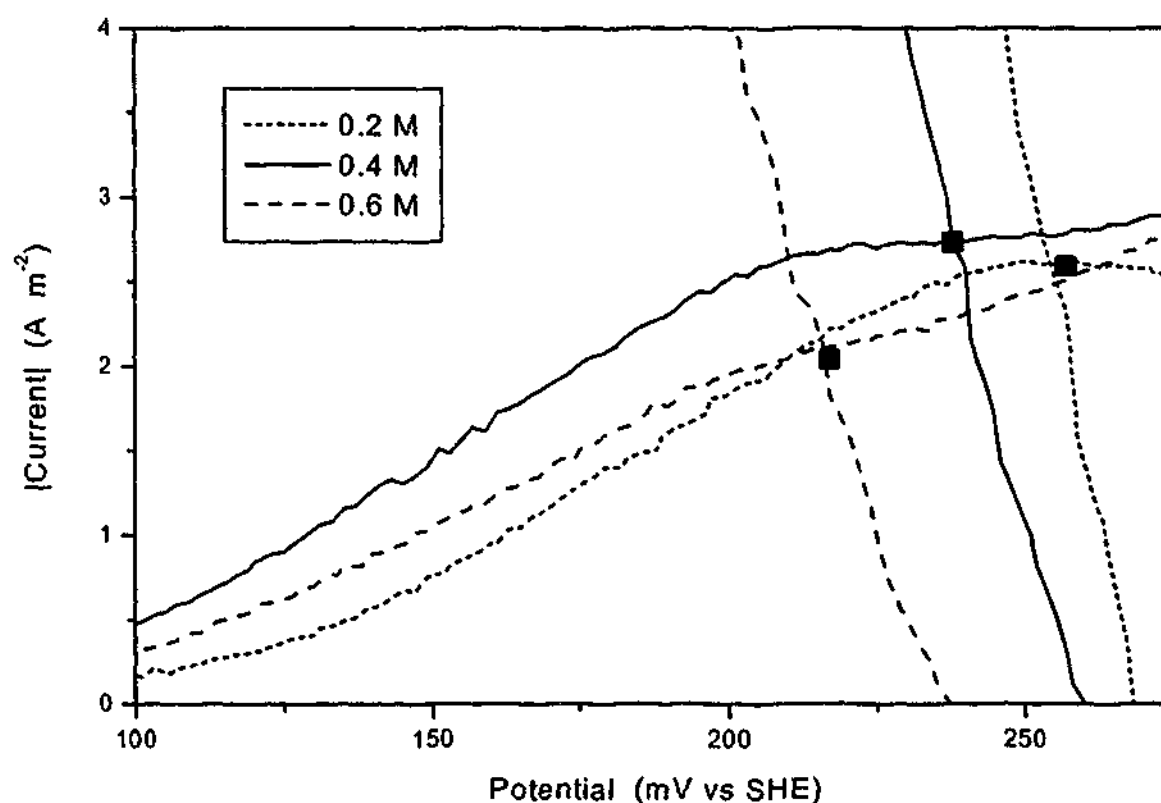


**Figure 6.25:** Evans' type diagram showing the anodic and cathodic curves for fresh thiosulfate leach solutions containing various concentrations of ammonia: 0.1 M $Na_2S_2O_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C. Also shown as square symbols, are the measured reaction rates (as current density) and mixed potentials for the gold leach rates shown in Figure 6.24.

### 6.3.7 Effect of Sulfate

A very positive effect of anions such as sulfate and phosphate were observed in decreasing the rate of copper(II) reduction by thiosulfate in the absence of oxygen (section 3.3.2). Higher copper(II) concentrations were also maintained for thiosulfate leach solutions containing phosphate in the presence of oxygen (section 5.3.1.3). As anions stabilise the copper(II) against reduction they could decrease the cathodic reaction potential. However, the effect of anions on the gold oxidation reaction and thus the overall dissolution process has not been determined.

### 6.3.7.1 Kinetics

The effect of sulfate is shown in Figure 6.26 to reduce the kinetics of gold leaching; the mixed potential being expectedly lower in the presence of anions (shown in Figure 6.27). The initial induction period to gold dissolution is also observed to take longer to overcome in the presence of sulfate.
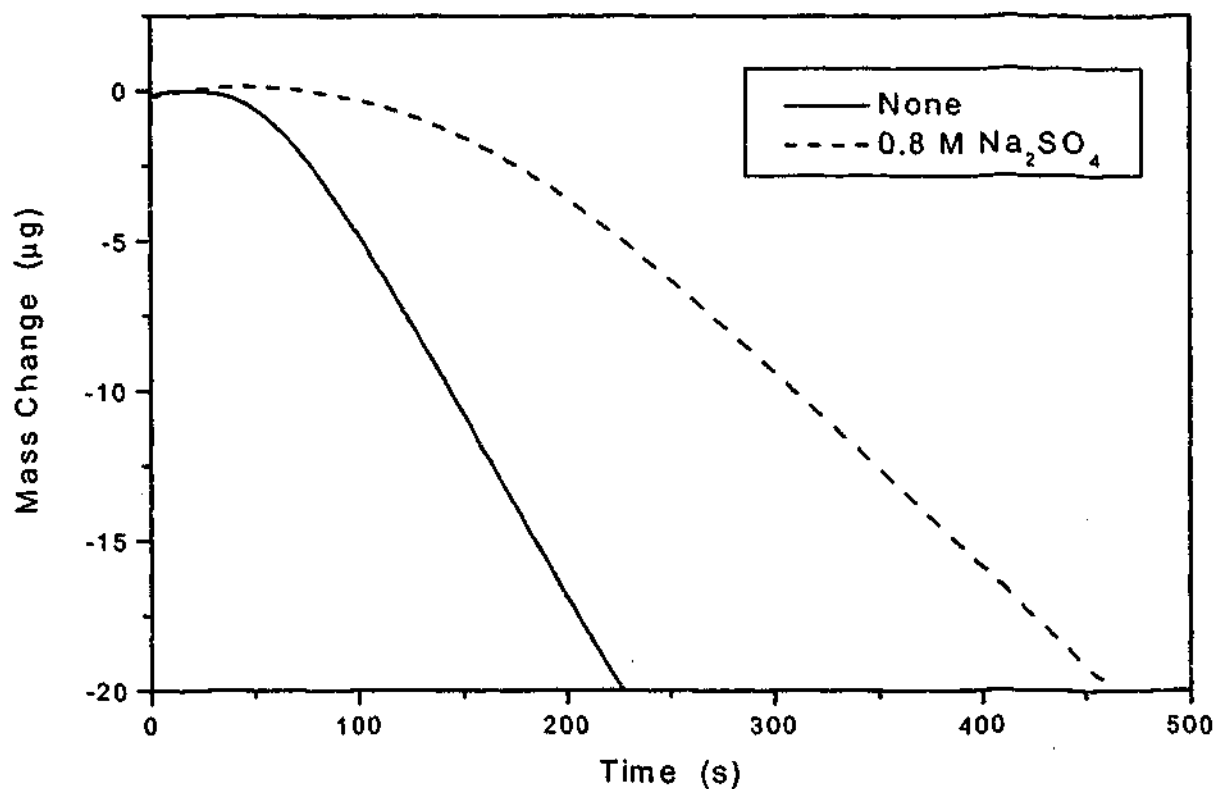


**Figure 6.26:** Kinetic plot showing the effect of anions (sulfate) on the leaching of gold in fresh thiosulfate leach solutions: $0.1$ M $Na_2S_2O_3$, $0.4$ M $NH_3$, $10$ mM $CuSO_4$, $300$ rpm, $30\ ^{\circ}C$.

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### 6.3.7.2 Electrochemistry

Figure 6.27 shows, as an Evans' type diagram, the cathodic and anodic curves measured using the REQCM for fresh thiosulfate leach solutions with and without the addition of sulfate. Clearly, the cathodic reaction potential decreases due to copper(II) stabilisation with the addition of anions. The presence of anions is also shown in Figure 6.27 to reduce the anodic reaction. The reason for this is unclear. Marked as squares, are the reaction rates (calculated current) and actual mixed potentials at steady state from the leaching experiments shown in Figure 6.26, which are closely predicted by mixed potential theory (the points of intersection of the respective cathodic and anodic curves). Thus, the presence of anions stabilises copper(II) such that the gold leach kinetics are reduced. The effect anions have on the gold leach rate as the leach solution ages is further evaluated in Chapter 7.
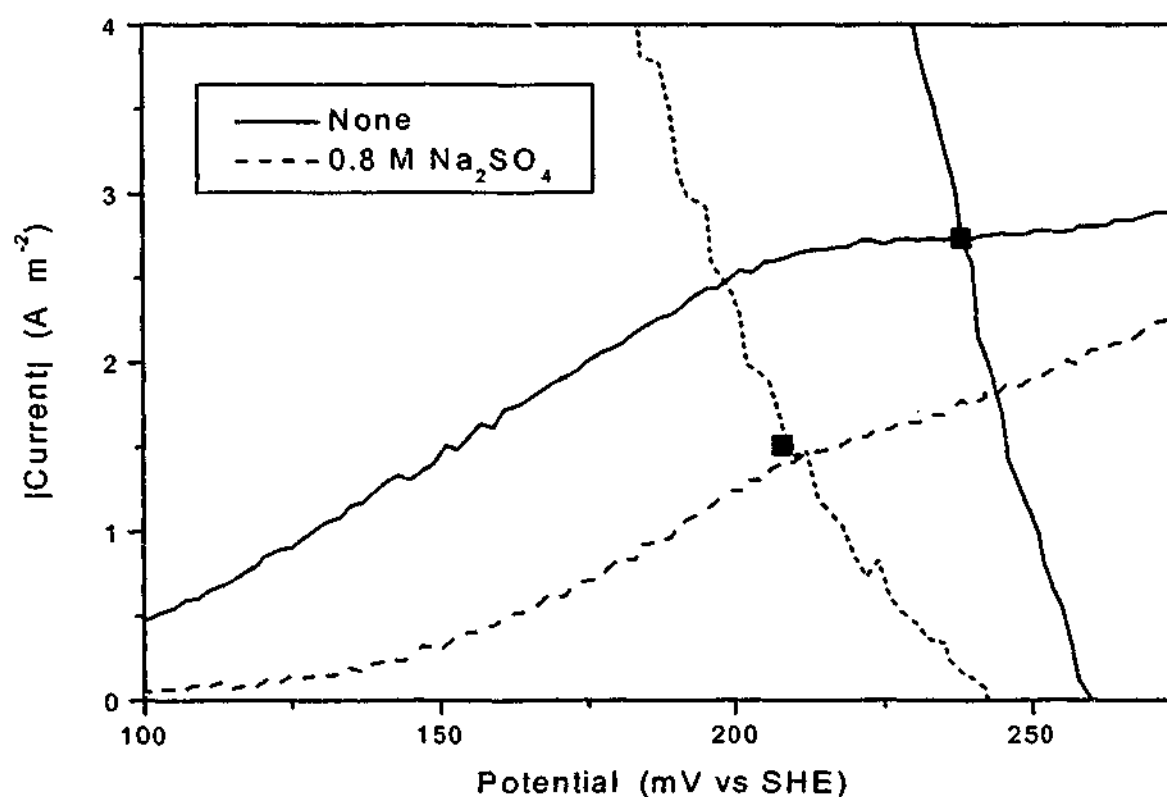


**Figure 6.27:** Evans' type diagram showing the effect of sulfate on the anodic and cathodic curves for fresh thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 0.8 M $Na_2SO_4$, 10 mM $CuSO_4$, 300 rpm, 30 °C. Also shown as square symbols are the measured reaction rates (as current density) and mixed potentials for the gold leach rates shown in Figure 6.26.

## 6.3.8 Effect of pH

The effect of using ammonium thiosulfate instead of sodium thiosulfate was shown in section 3.3.3 to result in a lower thiosulfate leach solution pH because of the equilibrium shown in Equation 3.3. This ultimately resulted in unfavourable changes in the solution chemistry (sections 3.3.3.1 and 5.3.3.5).

### 6.3.8.1 Kinetics

The effect of pH on the kinetics of gold leaching in fresh thiosulfate leach solutions is shown in Figure 6.28, where a pH of 11.4 is for sodium thiosulfate and a pH of 9.8 is for ammonium thiosulfate. Clearly, pH has little effect on the gold dissolution process with only a slightly faster gold leach rate observed at lower pH.
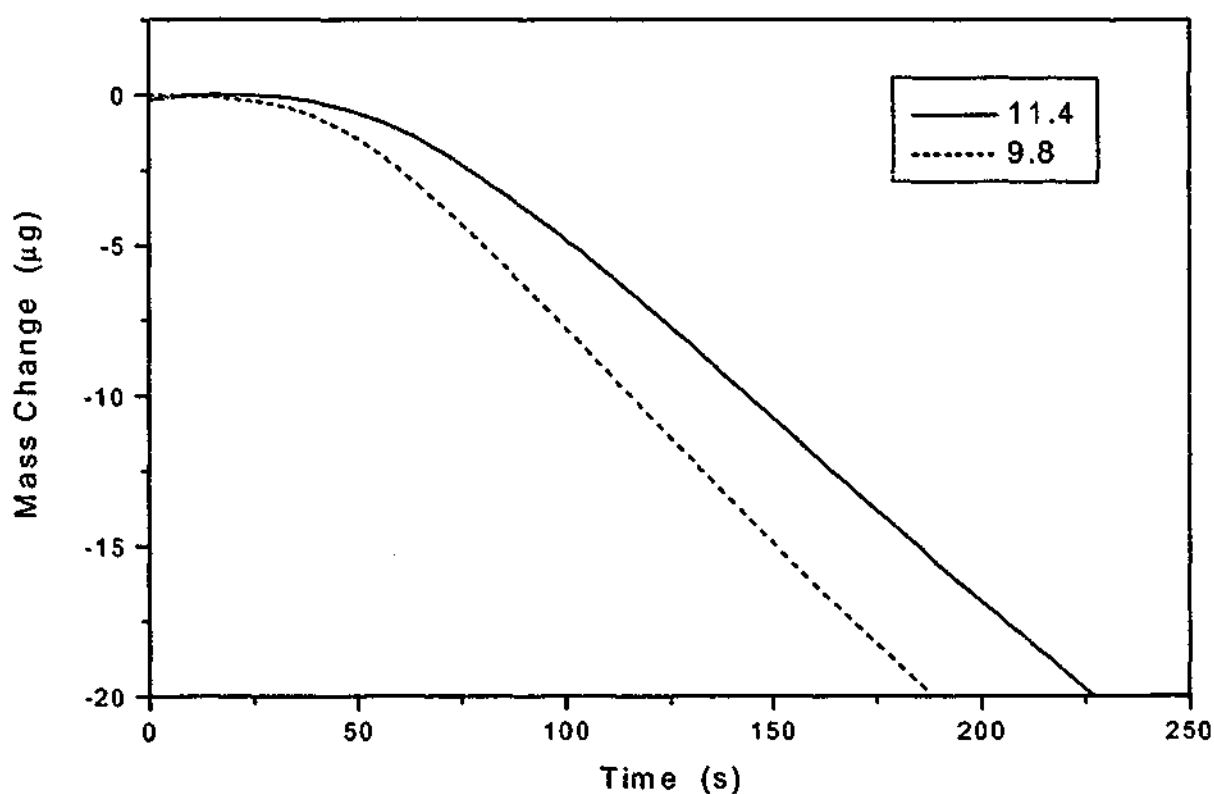


**Figure 6.28:** Kinetic plot showing the effect of pH on the leaching of gold in fresh thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

An electrochemical study (results not shown) confirmed that both the cathodic and anodic reactions were marginally increased at lower pH, such that the mixed potential was relatively unchanged. A comparison of the kinetic plots shown in Figure 6.28 also reveals that lower pH reduces slightly the initial induction period for gold leaching. Obviously, there is little benefit to the gold leach rate in using ammonium thiosulfate, as the resultant lower pH increases the rate of copper(II) reduction in the absence of oxygen (section 3.3.3) and results in the sustainable copper(II) concentration being lower and the rate of thiosulfate oxidation increasing in the presence of oxygen (section 5.3.3.5).

## 6.4 Summary

It has been shown that the electrochemistry of the gold dissolution process in thiosulfate solutions containing copper(II) and ammonia is very complex. However, with the advent of the REQCM the gold dissolution process could successfully be studied. The dominant cathodic reaction appears to be the reduction of copper(II) tetra-ammine to a copper(I) mixed ammonia/thiosulfate complex; this reaction proceeds quite rapidly. However, the anodic reaction, the oxidation of gold, was found to be very passive, with ammonia being required in order for the reaction to occur at an appreciable rate. It has also been shown that the presence of copper in solution significantly enhances the gold oxidation reaction; this is the reason why copper(II) is more effective than alternative oxidants in the leaching process. Copper(II) concentrations greater than 2 mM are recommended in order to achieve appreciable gold oxidation rates. Thus, from Chapter 5, higher total copper concentrations (>5 mM) are required in order to maintain at least 2 mM copper(II) in the presence of oxygen.

The results presented in this chapter indicate that the gold oxidation reaction is passive (not diffusion controlled) and an induction period is observed for electroplated gold. This was not detectable for solid gold electrodes for which the gold oxidation rates were found to be significantly lower due to the smoother surface finish. The reason for the initial induction period was not identified by this study; however, the time

of this induction period was found to be related to the copper(II) stability. The presence of 2 wt% silver alloyed with the gold was also found to result in higher gold oxidation rates.

The effects of several parameters on the gold dissolution process were also investigated in this chapter. These results showed that the anodic reaction (gold oxidation) increased with increasing thiosulfate and copper(II) concentrations, and temperature but decreased on the addition of anions, such as sulfate, or higher ammonia concentrations (greater than 0.5 M). The cathodic reaction (copper(II) reduction) potential was found to increase with increased copper(II) and thiosulfate (up to 0.1 M) concentrations, but decreased with increasing ammonia and anion concentrations. Notably, all these effects correlate with the copper(II) stability.

## Chapter 7

# *Dissolution of Gold in Aging Thiosulfate Leach Solutions*

## 7.1 Introduction

A detailed study of the gold dissolution process in fresh thiosulfate leach solutions was presented in Chapter 6. However, the thiosulfate leach solution composition continually changes in the absence and presence of oxygen as previously detailed in Chapters 3 and 5 respectively. The objective of this chapter is thus to investigate the dissolution of gold in aging thiosulfate leach solutions in the absence and presence of oxygen.

In the presence of oxygen, the oxidation of copper(I) to copper(II) maintains a minimum copper(II) concentration in the thiosulfate leach solution (Chapter 5), although at a higher rate of thiosulfate oxidation. The gold dissolution rate is expected to decrease more rapidly initially in the presence of oxygen due to the increased rate of copper(II) reduction, though the gold dissolution rate should become constant as the copper(II) concentration stabilises. A continual small decrease in the gold dissolution rate with time is then expected due to the continual oxidation of thiosulfate.

Experiments were also conducted in the absence of oxygen. An advantage of studying the gold dissolution process in the absence of oxygen is that a higher [Cu(II)]:[Cu(I)] ratio is maintained for an initial period of time; the presence of oxygen was shown in Chapter 5 to increase the initial rate of copper(II) reduction. In this initial period the higher [Cu(II)]:[Cu(I)] ratio should result in higher gold dissolution rates due to a higher copper(II) reduction potential. However, as copper(II) concentration continually decreases, the potential of the cathodic reaction (copper(II) reduction) and

hence the gold oxidation rate will continue to decrease. The effect this has on the gold dissolution rate and the anodic and cathodic reactions is shown in this chapter.

## 7.2 Experimental

The same experimental details as given in section 6.2 were used for measuring and investigating the gold dissolution process. For experiments conducted in the absence of oxygen, the solution was first purged with argon before addition of a concentrated copper-ammonia solution. The solution was then maintained under a continually purged atmosphere of argon whilst minimising air introduction during electrode insertion and removal. This approach did not totally exclude oxygen as shown in section 3.3.1. The loss of ammonia was minimised by bubbling the argon first through a solution of the same ammonia concentration. For some experiments conducted in the presence of oxygen, the thiosulfate leach solution was exposed to air via a hole in the lid of the jacketed vessel. In other experiments, the thiosulfate solution was first purged with the gas of the desired oxygen concentration before addition of a concentrated copper-ammonia solution. The gas space above the solution was then maintained by purging with the gas of the desired oxygen concentration. Ammonia losses were again minimised by bubbling the gas first through a solution of the same ammonia concentration. Sparging of the gas into the solution was not conducted in any of these experiments, hence the rate of thiosulfate oxidation and minimum copper(II) concentration are much lower than those presented in Chapter 5 and are dependent on the rate of oxygen transfer from the gas phase into solution through the solution-gas interface.

Copper(II) concentration was monitored using UV-Vis absorbance by continually pumping the thiosulfate leach solution through the UV cell as outlined in section 5.2. Changes in thiosulfate concentration are not shown, as the rates of thiosulfate oxidation were very low for the experiments presented in this Chapter (ie. thiosulfate concentration did not decrease significantly while conducting these experiments as only very low oxygen concentrations in solution were maintained).

## 7.3    Dissolution of Gold in Aging Thiosulfate Leach Solutions

### 7.3.1  Predicted Effect of Solution Aging

The effect of solution conditions on the copper(II) concentration was shown in Chapters 3 and 5. In the absence of oxygen the copper(II) concentration continues to decrease (Chapter 3). However, in the presence of oxygen a steady state copper(II) concentration is established at which point the rate of copper(II) reduction equals the rate of copper(I) oxidation (Chapter 5). Thus, mixed potential theory predicts that the gold dissolution rate will initially decrease as a fresh thiosulfate leach solution ages (all copper initially present as copper(II)). The rate of thiosulfate oxidation was also shown in Chapter 5 to be dependant on the rate of oxygen transfer into the thiosulfate leach solution. For the conditions used in all the experiments in this chapter the rate of thiosulfate oxidation is very low and hence the thiosulfate concentration can essentially be considered to remain constant.

To verify the predicted effect of solution aging on the gold dissolution process an experiment was conducted in which the gold leach rate was measured for a fresh thiosulfate leach solution containing 3 mM copper(II) and 7 mM copper(I). The measured mixed potential was expectedly found to be significantly lower at 169 mV compared to 238 mV for a fresh thiosulfate leach solution containing 10 mM copper(II). However, the measured gold leach rate of $2 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$ is only slightly lower than the $2.8 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$ measured for a fresh thiosulfate leach solution containing 10 mM copper(II). Shown in Figure 7.1 is the cathodic reaction voltammogram for a fresh thiosulfate leach solution containing 3 mM copper(II) and 7 mM copper(I). In this case copper(II) reduction is observed at potentials less than 180 mV, above which large positive currents are measured due to the oxidation of copper(I) to copper(II). Shown for comparison is the cathodic curve for a fresh thiosulfate leach solution containing 10 mM copper(II). Notably, copper(II) reduction occurs at significantly higher potentials (260 mV) in this solution. Clearly, as the [Cu(II)]:[Cu(I)] ratio decreases the potential for copper(II) reduction decreases as expected. This is reflected in the measured mixed potentials for gold leaching.

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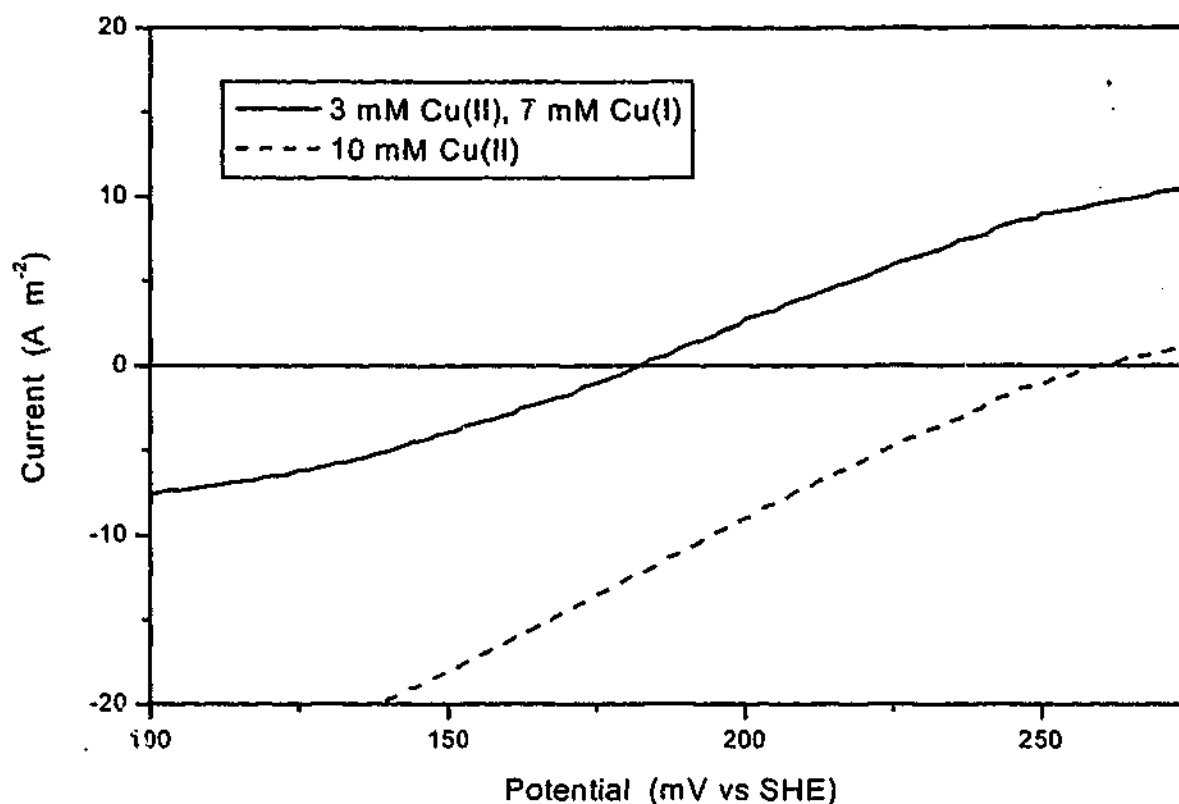
**Figure 7.1:** Linear sweep voltammograms for copper(II) reduction and copper(I) oxidation in fresh thiosulfate leach solutions: 0.4 M NH$_3$, 0.1 M Na$_2$S$_2$O$_3$, 300 rpm, 30 °C. A platinum electrode was used in these experiments.

Shown in Figure 7.2, as an Evans' type diagram, are the cathodic and anodic curves measured using the REQCM for a fresh thiosulfate leach solution containing 3 mM copper(II) and 7 mM copper(I). From the leaching experiment the actual mixed potential and reaction rate at steady state is shown in Figure 7.2 as a dot, which closely corresponds to the point of intersection of the cathodic and anodic curves. For comparison the cathodic and anodic curves for a fresh thiosulfate leach solutions containing 10 mM copper(II) are also shown in Figure 7.2. Clearly, the significant decrease in the mixed potential is attributed to the decrease in the cathodic reaction potential. The anodic curve measured for the solution containing 3 mM copper(II) and 7 mM copper(I) however is similar to that measured for the solution containing 10 mM copper(II) in the potential region in which leaching occurs. This result is consistent with the findings in section 6.3.1.5 that the anodic curve is affected by the copper concentration but independent of the copper oxidation state. Hence, the major effect of a decrease in the [Cu(II)]:[Cu(I)] ratio is a decrease in the cathodic potential which results in a lower gold leach rate.
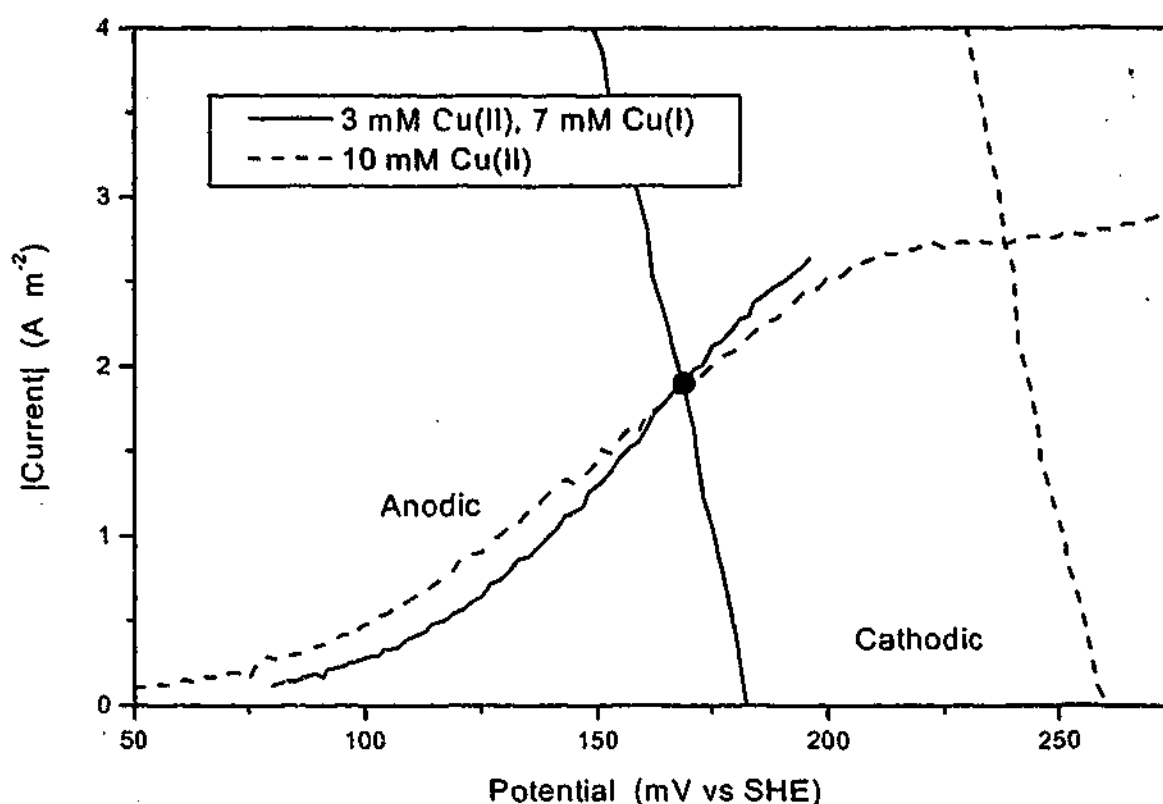
**Figure 7.2:** Evans' type diagram showing the measured cathodic and anodic curves for a fresh thiosulfate leach solution containing 3 mM copper(II) and 7 mM copper(I). Also shown (dot) is the mixed potential and reaction rate (as current density) measured during gold leaching. The cathodic and anodic curves for a solution containing 10 mM copper(II), no copper(I), are shown for comparison: $0.1$ M $Na_2S_2O_3$, $0.4$ M $NH_3$, 300 rpm, 30 °C.

## 7.3.2 Gold Dissolution in Aging Solutions in the Presence of Oxygen

The effect of oxygen on the thiosulfate leach solution chemistry was studied in detail in Chapter 5. The obvious advantage of exposing the thiosulfate leach solution to oxygen is the oxidation of copper(I) to copper(II) such that a minimum concentration of copper(II) and hence a sufficient cathodic potential are maintained for leaching to occur. The disadvantage shown though was that thiosulfate loss occurs at significantly higher rates than in the absence of oxygen; this being largely controlled by the rate of oxygen mass transfer into the solution.

### 7.3.2.1 Effect of Solution Aging on the Gold Dissolution Kinetics

As the rate of thiosulfate oxidation is dependant on the rate of mass transfer of oxygen into the thiosulfate leach solution (Chapter 5), experiments were conducted to investigate the effect of solution aging on the gold dissolution process for conditions where the oxygen mass transfer rate was low. Experimentally this was achieved by allowing the thiosulfate leach solution to be exposed to air via a hole in the lid of the jacketed vessel. The effect of solution aging in the presence of oxygen on the gold dissolution process was investigated by measuring the kinetics of gold leaching as the continually stirred (REQCM electrode) thiosulfate leach solution aged. Figure 7.3 shows some of the kinetic plots for gold dissolution recorded at various times after the solution was initially prepared. Not surprisingly, the steady state gold leach rate decreases as the thiosulfate leach solution ages. However, there is a noticeable increase in the length of the induction period which is significantly greater than those observed in this study for fresh thiosulfate leach solutions, even at low copper(II) concentrations (Chapter 6). This is attributed to intermediates or products of thiosulfate oxidation.
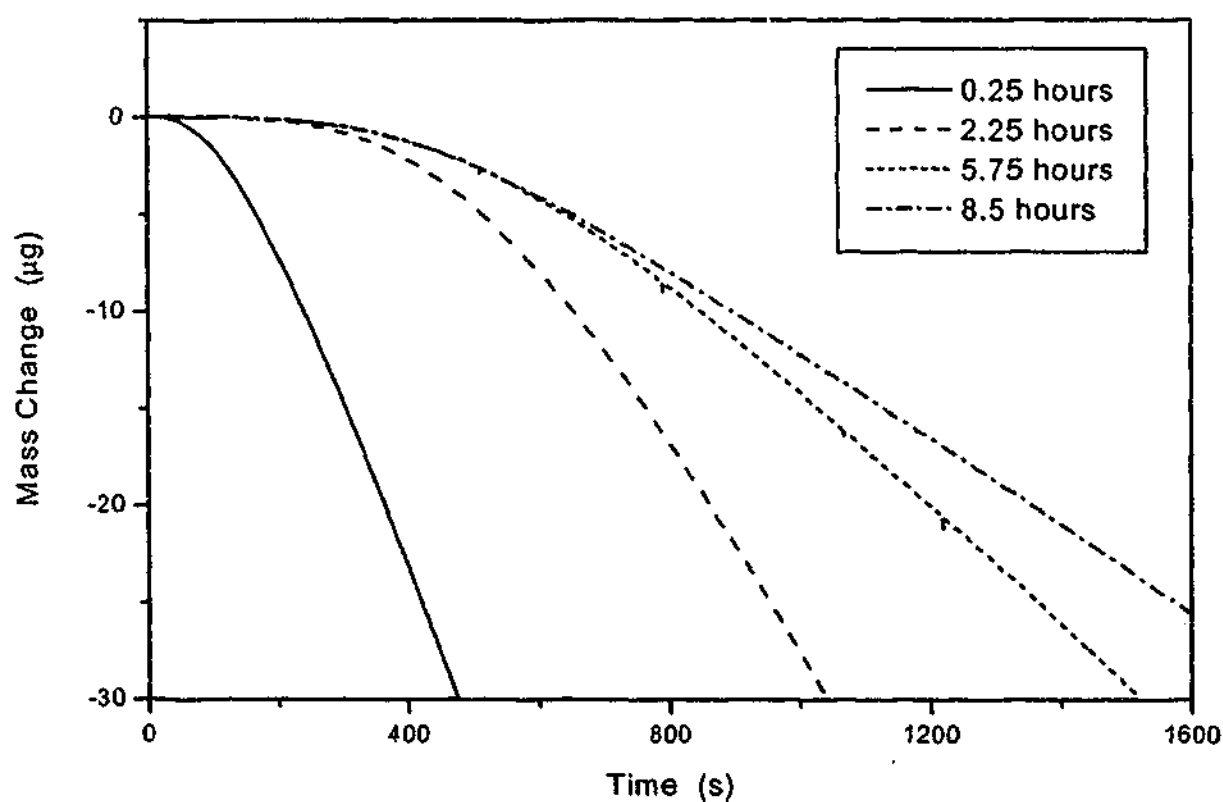


**Figure 7.3:** Kinetic plot showing the effect of solution aging in the presence of oxygen on the leaching of gold in a thiosulfate leach solution: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

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Figure 7.4 shows the effect of oxygen on the measured steady state gold dissolution rate and copper(II) concentration as the thiosulfate leach solution ages. Initially the gold dissolution rate is shown to decrease as the copper(II) concentration decreases. Noticeably though, the gold dissolution rate continues to decrease even though the copper(II) concentration becomes relatively constant after 6 hours.
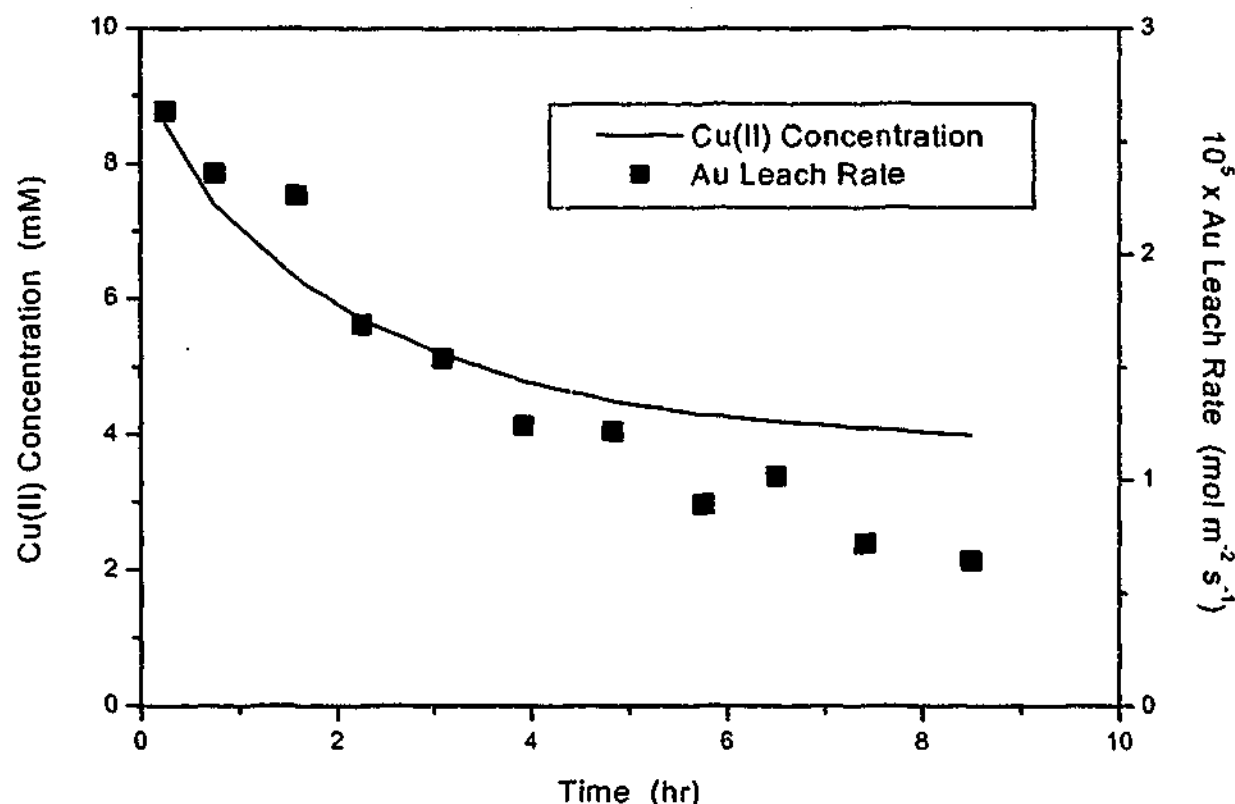


**Figure 7.4:** The effect of oxygen on the gold leach rate and copper(II) concentration in aging thiosulfate leach solutions: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

To assess the effect of oxygen on the gold dissolution rate in thiosulfate leach solutions, the results shown in Figure 7.4 were compared to the gold dissolution rates measured in fresh thiosulfate leach solutions of the same total copper concentration. Figure 7.5 clearly shows that the gold dissolution rate decreased substantially more than expected for the decrease in the [Cu(II)]:[Cu(I)] ratio. At the same [Cu(II)]:[Cu(I)] ratio, the measured mixed potential in the aging thiosulfate leach solution was slightly higher than that measured for the fresh thiosulfate leach solution. This suggests that the cathodic reaction is likely to be unaffected and that the anodic reaction (gold oxidation) is possibly hindered in solutions exposed to oxygen.
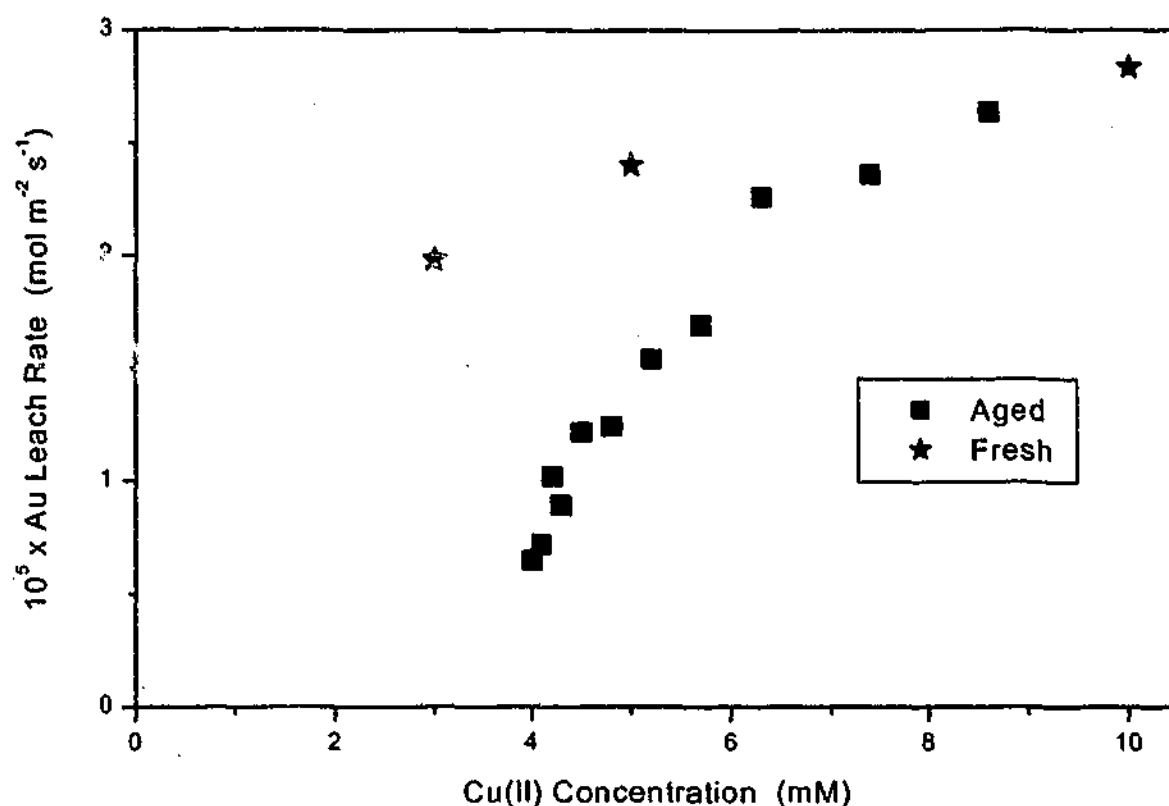
**Figure 7.5:** The effect of solution aging in the presence of oxygen on the gold leach rate plotted against the measured copper(II) concentration: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C. Also shown are the gold leach rates measured in fresh thiosulfate leach solutions containing 10 mM total copper.

One could attribute the observed decrease in the gold dissolution rate to thiosulfate or ammonia losses, though the rate of thiosulfate oxidation under these conditions is very low. Measuring the ammonia and thiosulfate concentrations at the completion of the experiment (losses less than 20%) and adding back to original concentrations did not restore the gold leach rate to those measure in fresh thiosulfate leach solutions of the same copper(II) and copper(I) concentrations; only a small increase in the gold leach was observed. These results suggest that a thiosulfate oxidation product is hindering the gold oxidation reaction.

To investigate this phenomenon further, an electrochemical study of the anodic process is required. A comparison between the anodic reaction (gold oxidation) voltammograms measured in an aged and a fresh thiosulfate leach solution using the REQCM are shown in Figure 7.6. Obviously, the gold oxidation reaction is greatly

hindered in the thiosulfate leach solution aged in the presence of oxygen. Such a result is consistent with the homogeneous reactions involving copper(II), thiosulfate and oxygen (Chapter 5) generating a reaction intermediate or product which is hindering the gold oxidation process.
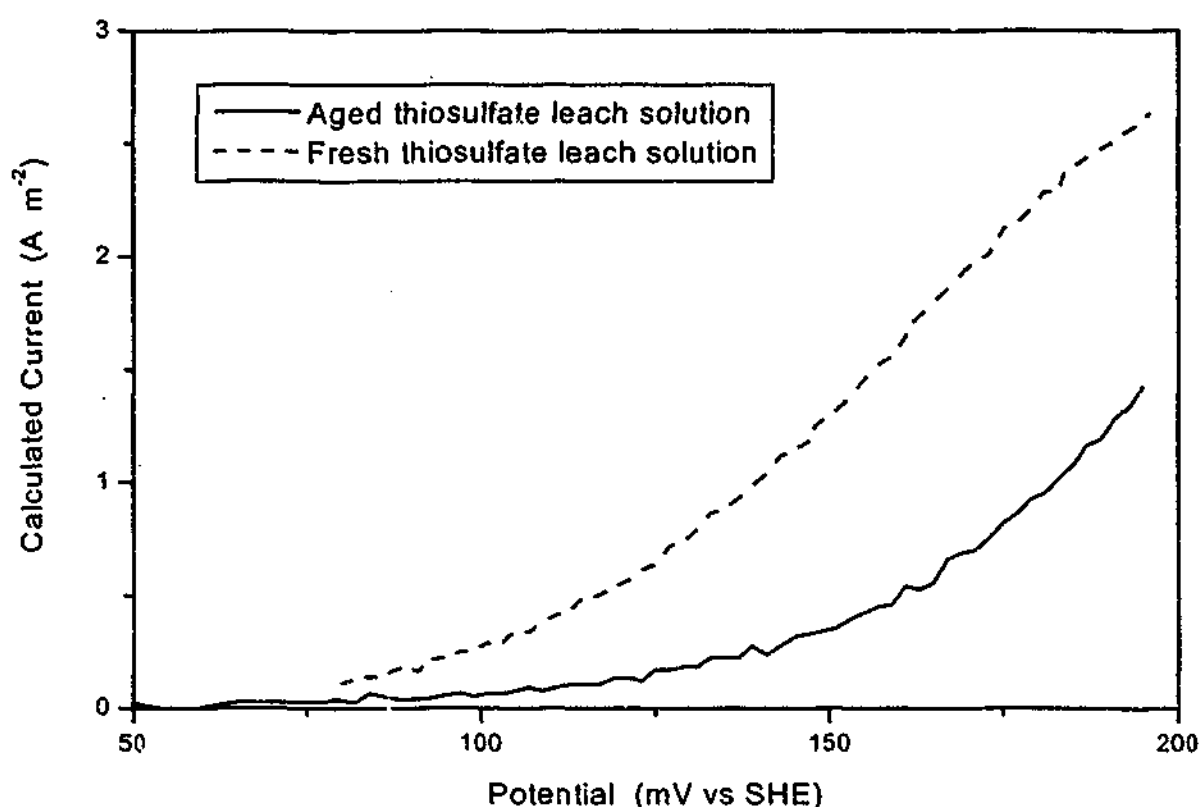


**Figure 7.6:** Anodic reaction (gold oxidation) curves measured using the REQCM for aged (at steady state copper(II) concentration) and fresh (3 mM copper(II), 7 mM copper(I)) thiosulfate leach solutions in the presence of oxygen: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 300 rpm, 30 °C.

Additional experiments were conducted where small additions of tetrathionate, trithionate or sulfate were added to a thiosulfate leach solution. It was found that these had little effect on the gold leach kinetics. If trithionate and sulfate are the final reaction products (Byerley *et al.*, 1975) and these have no effect on the gold leach kinetics in fresh solutions then it would appear that an intermediate reaction product is hindering gold leaching. The intermediate or product is unidentified at this stage but is thought to be one or more of the oxysulfur species resulting from the presence of oxygen.

Research currently being undertaken by a PhD student within Monash University is investigating this further.

### 7.3.2.2   Effect of Solution Conditions on the Gold Dissolution Kinetics

The solution conditions were previously shown by Byerley *et al.* (1975) to affect the reaction products of thiosulfate oxidation in the presence of copper(II) and oxygen. They found that at a solution pH below 10, trithionate was the sole thiosulfate oxidation product, whereas at higher pH values a mixture of trithionate and sulfate resulted. If alternative mechanisms exist as proposed by Byerley *et al.* (1975), the quantities of intermediate oxysulfur species would vary. Thus, the solution conditions could effect the passivation of the gold dissolution process as the thiosulfate leach solution ages.

An experiment was conducted in which ammonium thiosulfate was substituted for sodium thiosulfate such that the thiosulfate leach solution pH was reduced from 11.4 to 9.8. The copper(II) concentration and the gold dissolution rates measured as the thiosulfate leach solution aged in the presence of oxygen are shown in Figure 7.7. For comparison the results from Figure 7.4 for sodium thiosulfate are also shown. Expectedly, the copper(II) concentration initially decreases more rapidly and the steady state copper(II) concentration is lower for the ammonium thiosulfate solution (Chapter 5). The gold leach rate is observed to decrease initially as a result of the decrease in copper(II) concentration. However, under these conditions the gold leach rate is shown in Figure 7.7 to remain relatively constant once the copper(II) concentration becomes steady. This gold leach rate though is still lower than that expected for a fresh thiosulfate leach solution of the same copper(II) and copper(I) concentrations (Figure 7.5). Clearly, further work is required to fully understand the effect of solution aging in the presence of oxygen on the gold dissolution process.

In order to investigate the effect of solution aging over a couple of days, more controlled conditions were adopted. Here, the gas space above the solution was continually purged at a low rate with a gas consisting of nitrogen containing 1.9% oxygen. To minimise the loss of ammonia the gas was pre-equilibrated with an ammonia solution of the same concentration as the thiosulfate leach solution for which measurements were being conducted.

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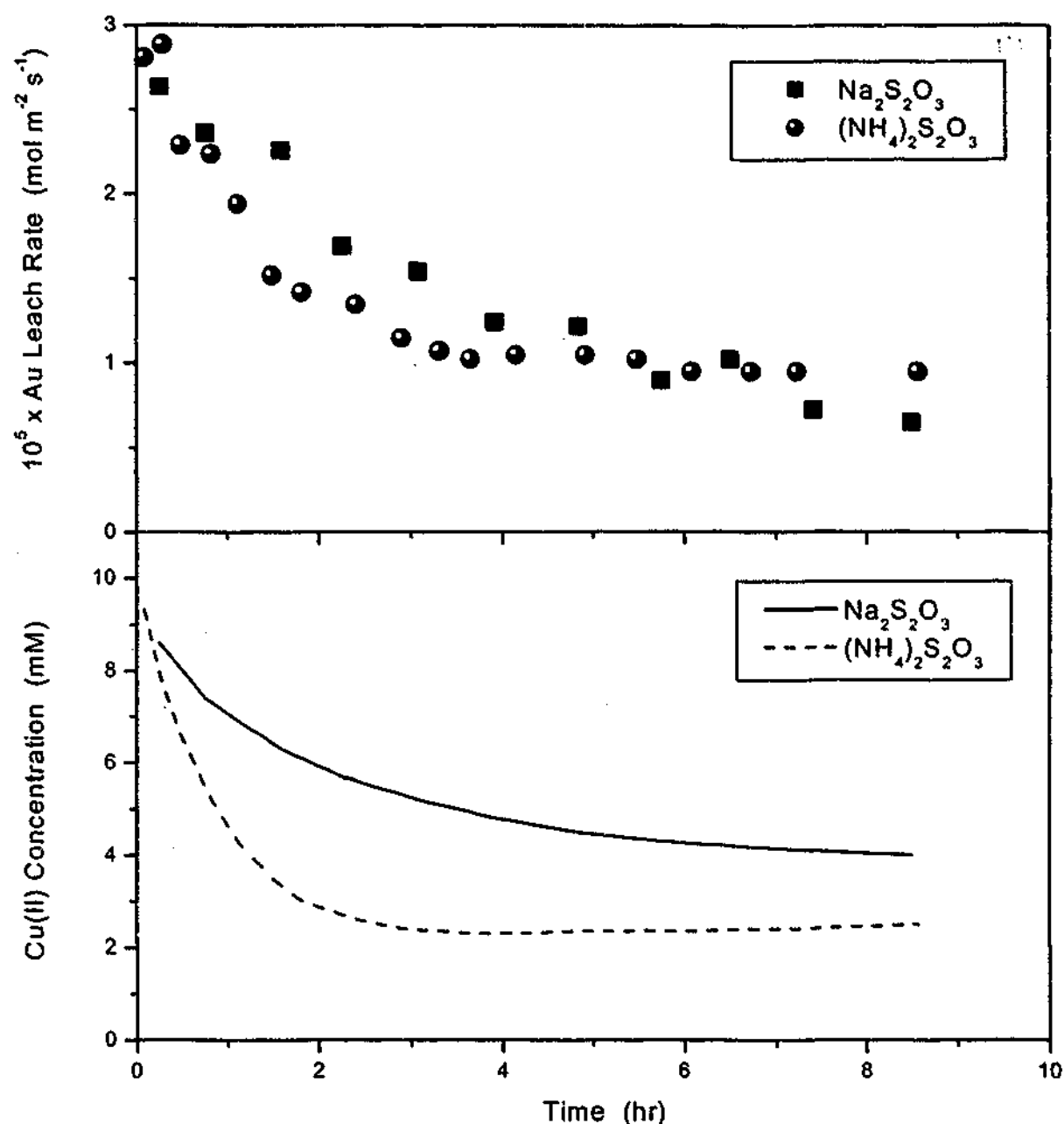
**Figure 7.7:** The effect of solution conditions and aging in the presence of oxygen on the gold leach rate and copper(II) concentration: 0.1 M $S_2O_3^{2-}$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

Figure 7.8 shows the measured gold leach kinetics for a thiosulfate leach solution maintained under these conditions for 24 and 40 hours. Also shown for comparison is the gold leach kinetics after 24 hours for the same thiosulfate leach solution conditions except where oxygen has been excluded by the use of argon. The gold leach kinetics in the thiosulfate leach solution maintained under argon shows the typical response observed whereby the gold leach rate is initially hindered but then increases until a maximum steady leach rate is observed (region (a) in Figure 7.8).

Clearly, the gold continues to leach without further hindrance as observed for fresh thiosulfate leach solutions. However, Figure 7.8 shows that the kinetics of gold leaching in thiosulfate leach solutions a͟͟ in the presence of oxygen becomes progressively slower and eventually ⸱⸱⸱⸱⸱ stops. This is consistent with passivating species taking some time ⸱ ⸱⸱ er the gold surface (likely to be concentration related) and hence some ˎ ' ' ⸱ ⸱ ⸱ is observed initially. This would account for the observed results in Figur͟
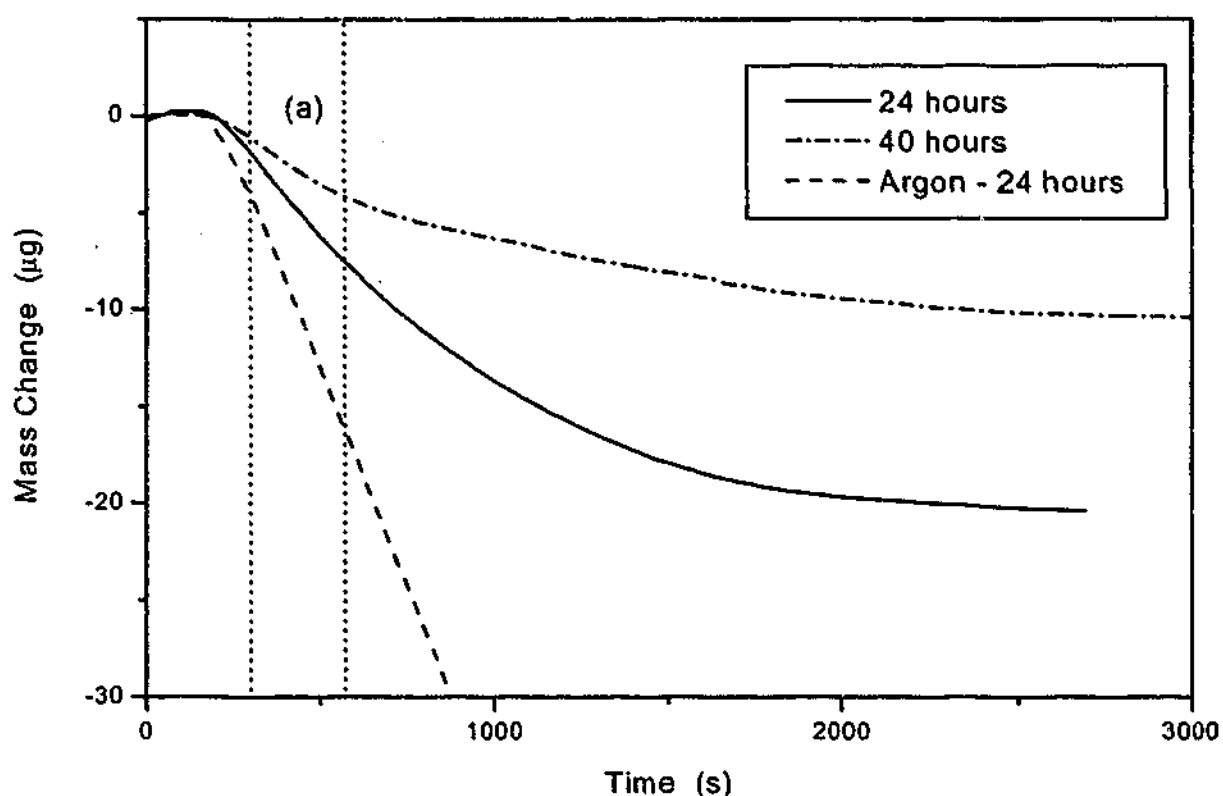


**Figure 7.8:** The effect of oxygen on the kinetics of gold leaching in an aged thiosulfate leach solution: 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$, 10 mM CuSO$_4$, 300 rpm, 30 °C.

## 7.3.2.3   Effect of Thiosulfate Concentration

In order to gain some appreciation of the effect various parameters have on the sustainable gold dissolution rate in the presence of oxygen, the thiosulfate leach solutions were allowed to age to a steady state copper(II) concentration at which point the gold dissolution rate was measured. The steady state copper(II) concentration was established by the diffusion of oxygen from the air through a hole in the lid of the vessel

and into the stagnant solution. For these conditions very little thiosulfate has been oxidised and hence the concentration of any passivating species should be very low and have little effect on the relativities of the gold leach rates.

Figure 7.9 shows the effect of thiosulfate concentration on the steady state copper(II) concentration and the gold leach rate in aged thiosulfate leach solutions. As the solution is stagnant, much lower copper(II) concentrations are observed than for Figure 7.4 where the solution was continually stirred by the REQCM electrode. Expectedly, the steady state copper(II) concentration maintained in the thiosulfate leach solution under these conditions decreases significantly with increasing thiosulfate concentration. The gold leach rates measured at the steady state copper(II) concentrations show an optimum thiosulfate concentration for gold leaching of 0.1 M. Below this thiosulfate concentration the gold leach rate decreases due to the reduced effect of thiosulfate concentration on the anodic reaction (gold oxidation) being greater than the increased cathodic potential due to the higher steady state copper(II) concentration. Above this optimum thiosulfate concentration the cathodic potential reduces due to lower steady state copper(II) concentration which results in lower gold dissolution rates.

### 7.3.2.4    Effect of Temperature

The effect of temperature on the steady state copper(II) concentration and the gold leach rate in aged thiosulfate leach solutions is shown in Figure 7.10. The effect of temperature on the copper(II) concentration was not shown in Chapter 5 but is clearly shown in Figure 7.10 to decrease the maintainable copper(II) concentration as the temperature increases. Thus, the [Cu(II)]:[Cu(I)] ratio and hence the copper(II) reduction potential decreases with increasing temperature. As the gold oxidation reaction is chemically controlled, increasing temperature significantly increases the gold oxidation rate (section 6.3.4). Thus, the gold leach rates measured at the steady state copper(II) concentrations shown in Figure 7.10 indicate an optimum operating temperature of 40 °C. Obviously, increasing the temperature up to 40 °C enhances the gold oxidation reaction more than the effect of reducing the cathodic potential. However, increasing the temperature above 40 °C further reduces the cathodic potential such that this outweighs the benefit to the gold oxidation reaction.
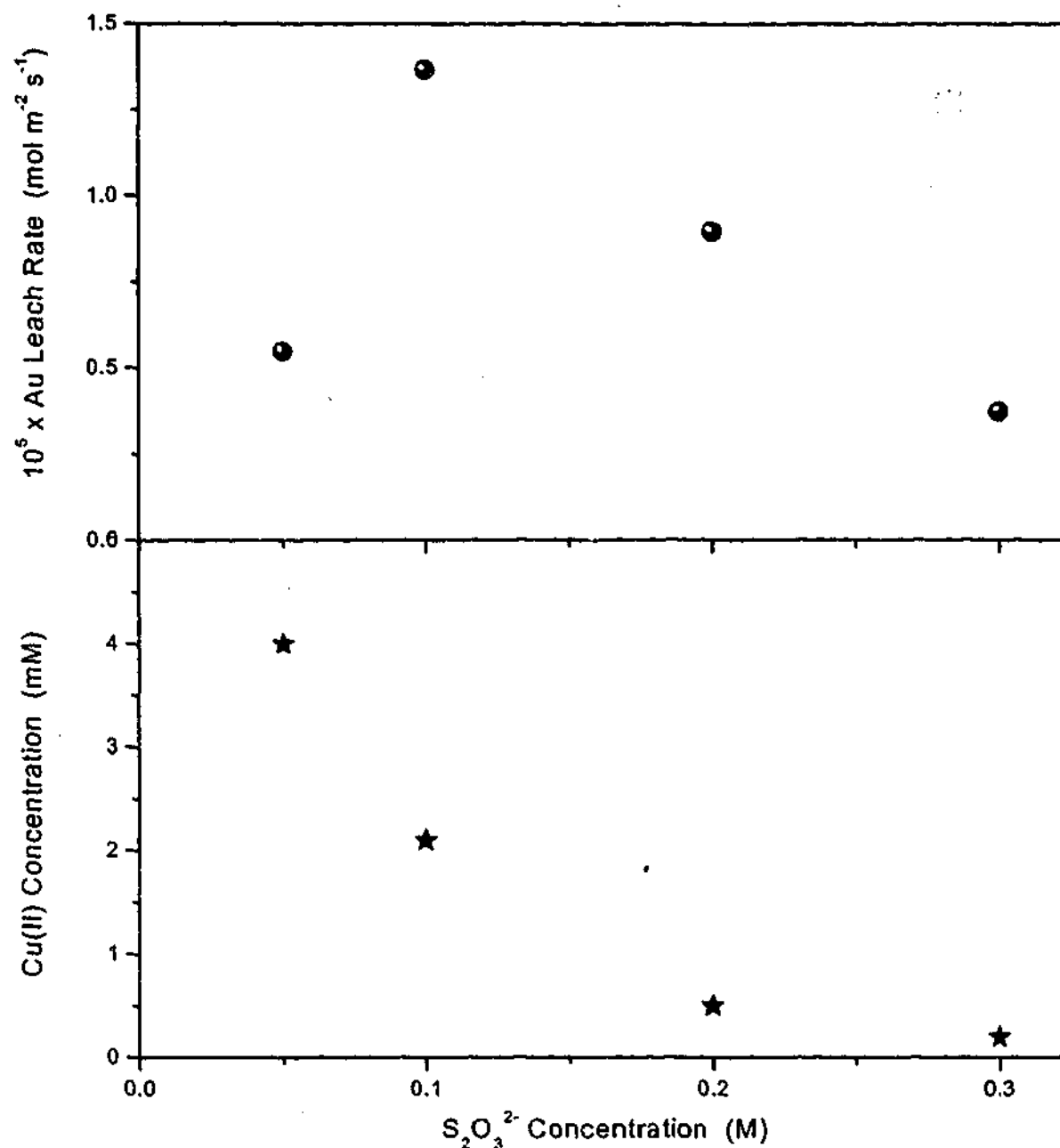
**Figure 7.9:** The effect of thiosulfate concentration on the steady state copper(II) concentration and the gold leach rate in aged thiosulfate leach solutions open to air: 0.4 M NH$_3$, 10 mM CuSO$_4$, 300 rpm, 30 °C.

## 7.3.2.5 Effect of Sulfate and pH

The effect of sulfate and pH on the steady state copper(II) concentration and the gold leach rate in aged thiosulfate leach solutions is shown in Figure 7.11. It can be seen that the addition of sulfate slightly improves the gold leach rate. In this instance the negative effects of sulfate on the cathodic and anodic reactions (section 6.3.7) is

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counteracted by the higher copper(II) concentration and hence higher cathodic potential. Lowering the solution pH with the substitution of ammonium thiosulfate for sodium thiosulfate is shown in Figure 7.11 to result in a significantly lower copper(II) concentration and thus a much lower gold dissolution rate.
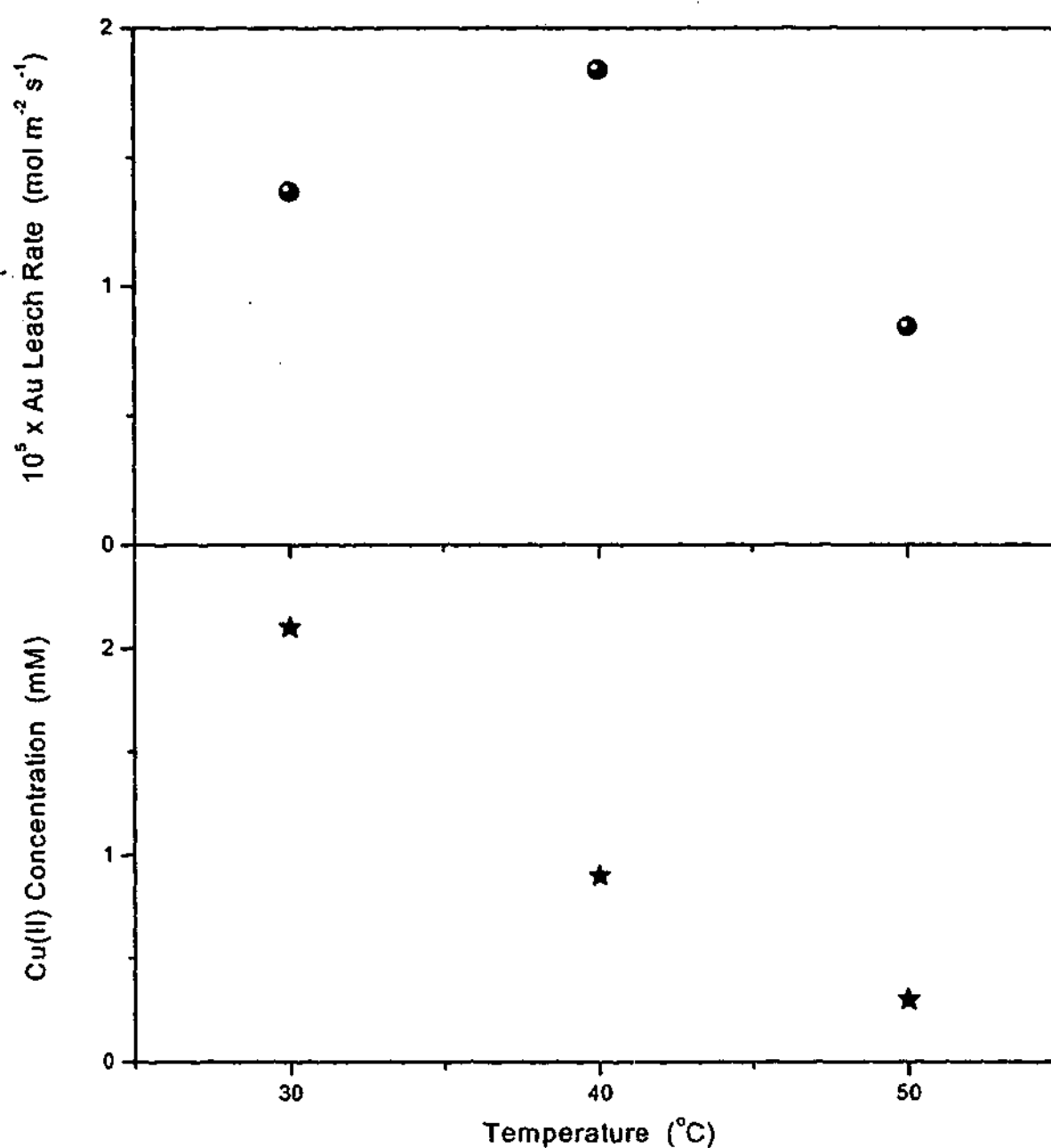


**Figure 7.10:** The effect of temperature on the steady state copper(II) concentration and the gold leach rate in aged thiosulfate leach solutions open to air: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm.
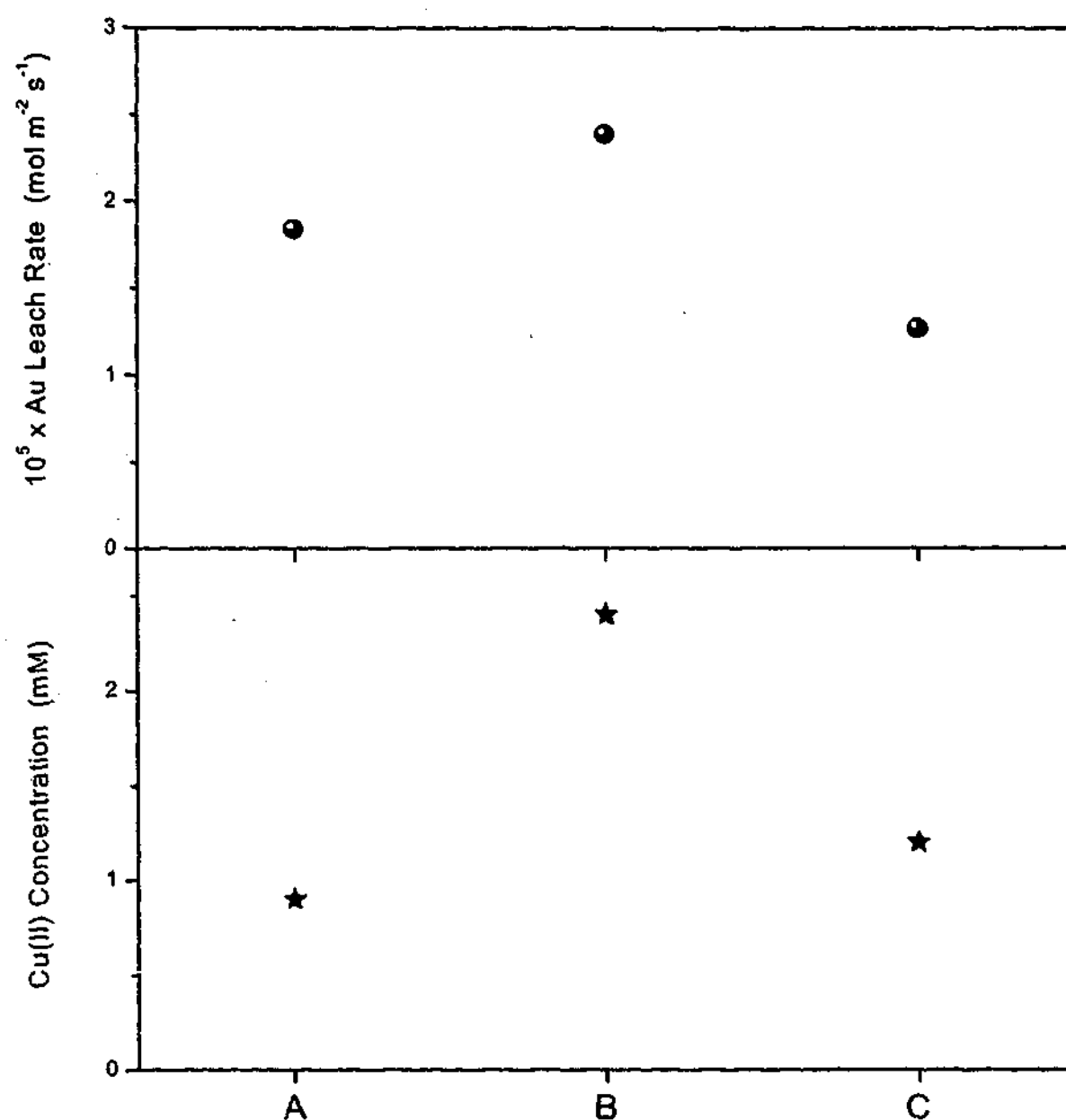
**Figure 7.11:** The effect of sulfate and ammonium ions on the steady state copper(II) concentration and the gold leach rate in aged thiosulfate leach solutions open to air. A: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 40 °C.  B: Same as A + 0.4 M $Na_2SO_4$.  C: Solution B except $Na_2S_2O_3$ replaced by $(NH_4)_2S_2O_3$.

## 7.3.3  Gold Dissolution in Aging Solutions in the Absence of Oxygen

This section looks to investigate the effect of various parameters on the gold dissolution rate as the thiosulfate leach solution ages in the absence of oxygen.  As the

copper(II) concentration will continually decrease, the gold dissolution rate is also expected to continually decrease. However, starting from fresh thiosulfate leach solutions containing copper(II) and no copper(I) there is the potential benefit for an initial period of the [Cu(II)]:[Cu(I)] ratio and hence the cathodic potential, being higher than in the presence of oxygen.

### 7.3.3.1  Effect of Solution Aging on the Gold Dissolution Kinetics

The effect of solution aging in the absence of oxygen on the gold dissolution process was firstly investigated by measuring the kinetics of gold leaching as the thiosulfate leach solution aged in the absence of oxygen. Figure 7.12 shows some of these plots recorded at various times after the solution was initially prepared. Not surprisingly, the steady state gold leach rate is observed in Figure 7.12 to decrease as the thiosulfate leach solution ages. Also, there is a significant increase in the length of the induction period as observed in Figure 7.3. This is again attributed to a reaction product or intermediate of thiosulfate oxidation.
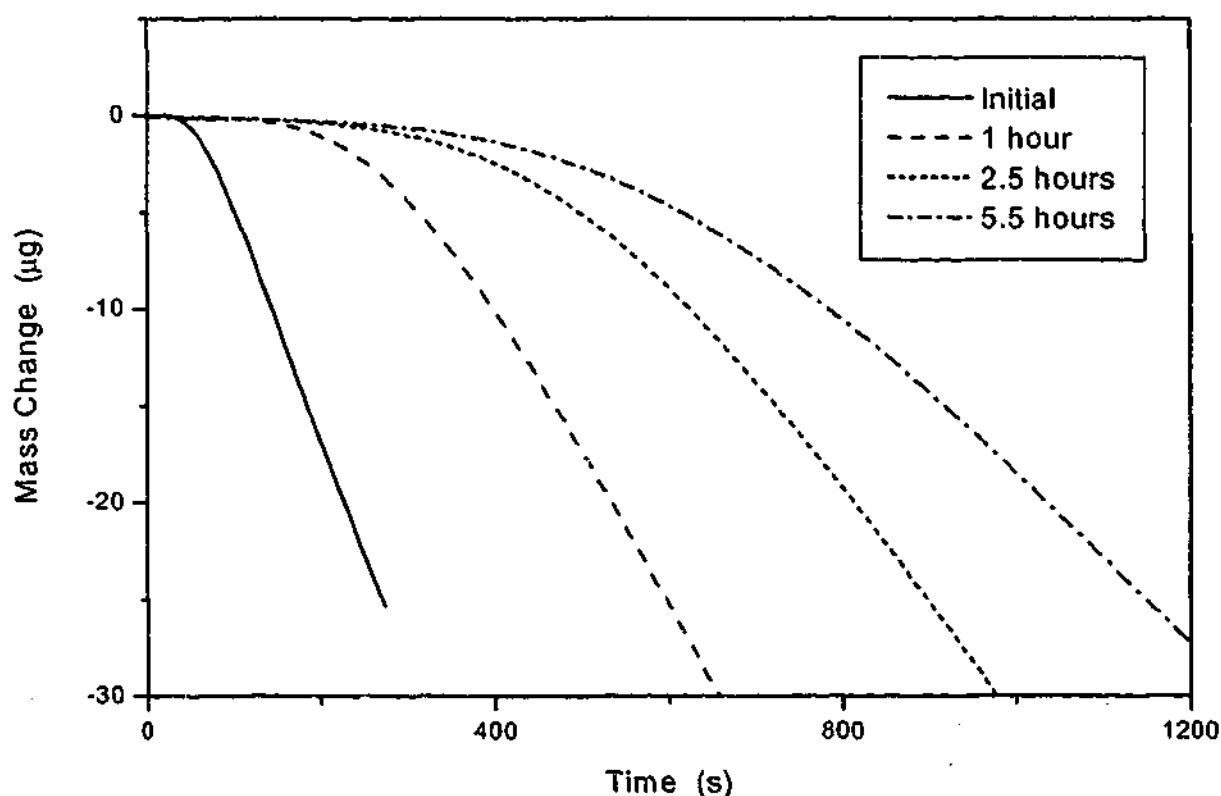


**Figure 7.12:**  Kinetic plot showing the effect of solution aging in the absence of oxygen on the leaching of gold in a thiosulfate leach solution: 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$, 10 mM CuSO$_4$, 300 rpm, 30 °C.

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Figure 7.13 presents all the steady state gold leach rates and the copper(II) concentration measured as the thiosulfate leach solution aged. It should be noted that the copper(II) concentration profile does not match that obtained in the complete absence of oxygen (as shown in section 3.3.1), which indicates the presence of trace amounts of oxygen. This is not surprising as the REQCM electrode needed to be regularly inserted and removed from the jacketed vessel. Thus, it remains unclear as to whether the reaction product or intermediate of thiosulfate oxidation that causes the increased induction period is due to the presence of oxygen or not.
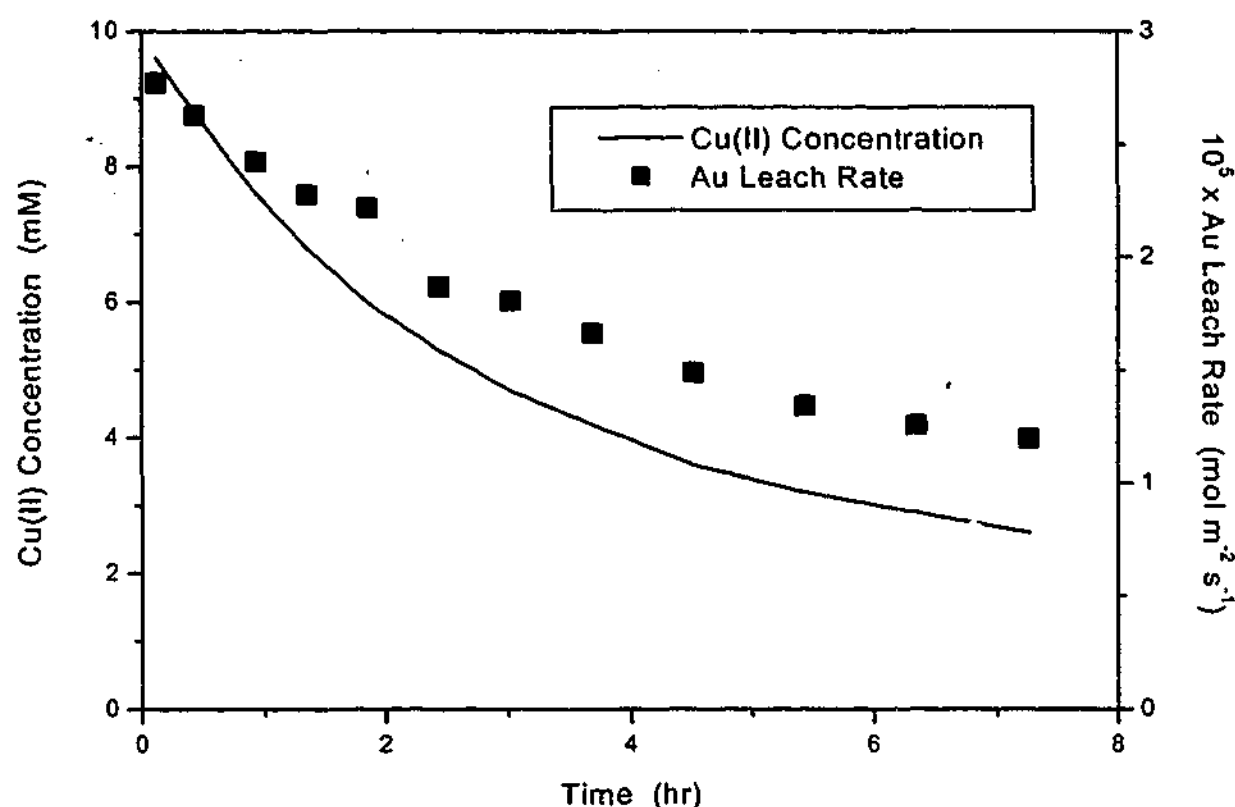


**Figure 7.13:** The effect of solution aging in the absence of oxygen on the steady state gold leach rate and the copper(II) concentration in a thiosulfate leach solution: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

It is clear from Figure 7.13 that the decrease in the gold leach rate closely follows the trend in copper(II) concentration. Here, the gold leach rate had depleted to half the initial rate after 5 hours, though the copper(II) concentration was less than half (approximately one third) the total copper concentration. The decrease in gold leach rate with decreasing copper(II) concentration in the aging thiosulfate leach solution is

best shown in Figure 7.14. Also shown in Figure 7.14 are the gold leach rates determined for fresh thiosulfate leach solutions containing 10 mM of copper. Clearly, at 3 mM copper(II) the gold leach rate in the aged thiosulfate leach solution is less than that measured in a fresh thiosulfate leach solution containing 3 mM copper(II) and 7 mM copper(I). The decrease in the gold leach rate with decreasing copper(II) concentration though is not as great as that observed in Figure 7.5 where oxygen was present for the same conditions.
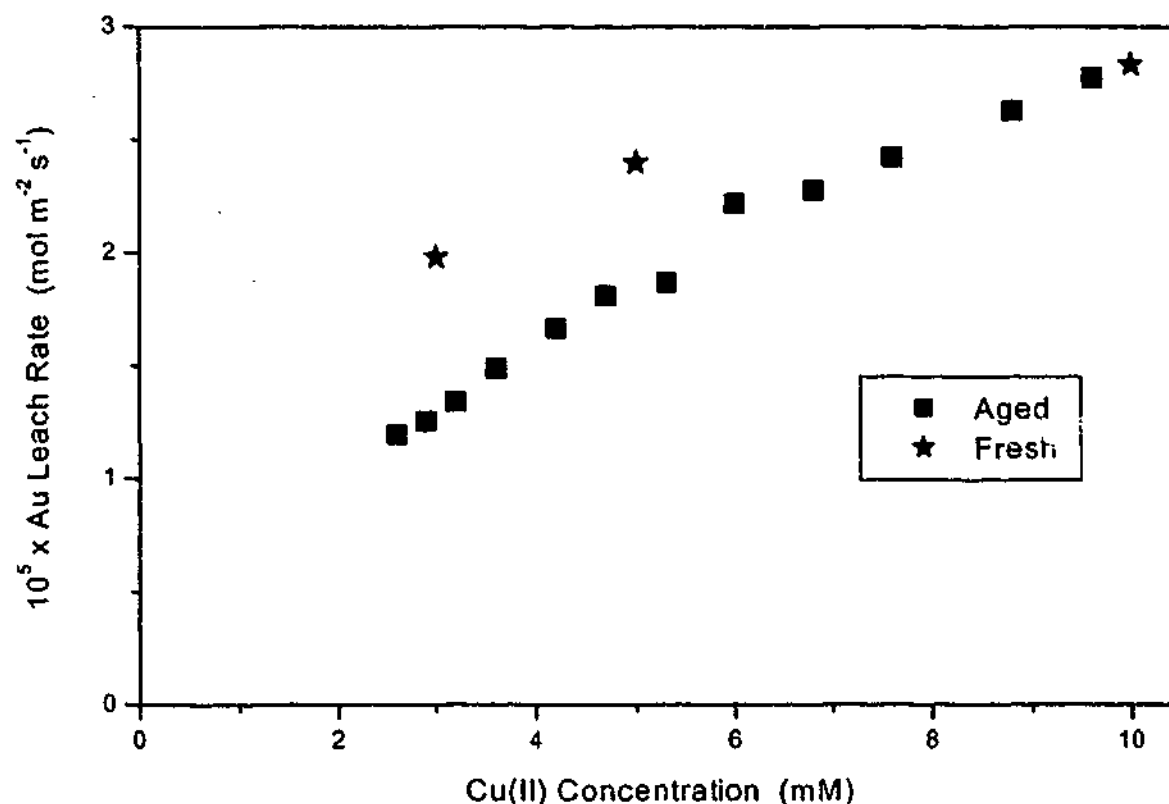


**Figure 7.14:** The effect of solution aging in the absence of oxygen on the steady state gold leach rate plotted against the measured copper(II) concentration: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C. Also shown are the gold leach rates measured in fresh thiosulfate leach solutions containing 10 mM total copper.

To further evaluate the effect of solution aging on the gold dissolution process, the effect of solution aging on the cathodic and anodic half reactions was investigated. These are shown in Figure 7.15 as an Evans' type diagram for an aged solution containing 3 mM copper(II) and 7 mM copper(I). Also shown for comparison is the

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cathodic and anodic voltammograms for a fresh thiosulfate leach solution of the same copper concentrations. Expectedly, the cathodic curves were found to be very similar and hence only one has been shown. Clearly, the lower leach rate observed in Figure 7.14 for the aged thiosulfate leach solution is due to a lower anodic reaction (gold oxidation) rate. In the absence of oxygen the thiosulfate oxidation product from the reaction with copper(II) is tetrathionate (Byerley *et al.*, 1973a); though tetrathionate was shown to be further oxidised by copper(II) in section 3.3.4. The gold oxidation reaction was shown in Figure 6.10 to be unaffected by the presence of tetrathionate. Thus, another oxysulfur reaction product appears to hinder the gold oxidation reaction and is possibly the same species responsible for the increased induction period for gold leaching as the thiosulfate leach solution ages (Figure 7.12).
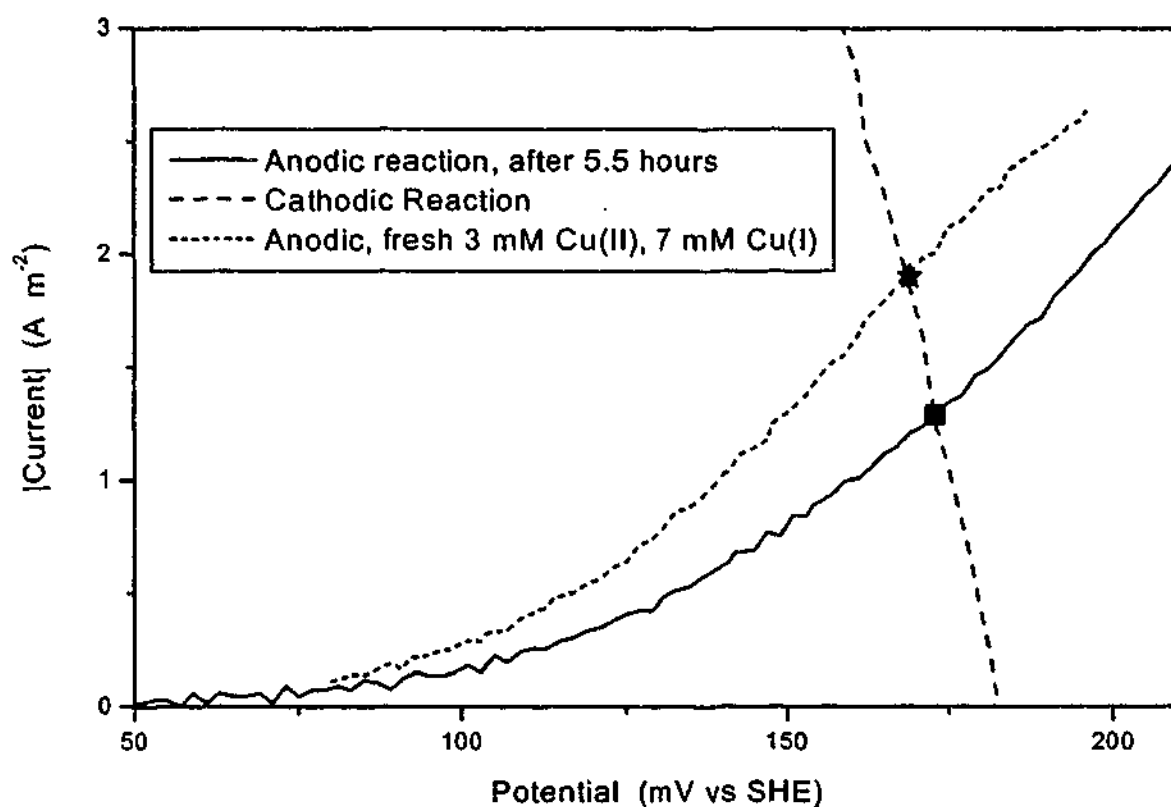


**Figure 7.15:** Evans' type diagram showing the measured cathodic and anodic curves for fresh and aged thiosulfate leach solutions containing 3 mM copper(II) and 7 mM copper(I) in the absence of oxygen. Also shown (square and star) are the mixed potential and reaction rates (as current density) measured during gold leaching in the aged and fresh thiosulfate leach solutions respectively: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 300 rpm, 30 $^\circ$C.

### 7.3.3.2 Effect of Anions

The addition of anions was shown in section 3.3.2 to significantly reduce the rate of copper(II) reduction in thiosulfate leach solutions in the absence of oxygen. However, the gold dissolution rate in fresh thiosulfate leach solutions was shown in section 6.3.7 to be reduced by the presence of high concentrations of sulfate. Thus, experiments were conducted to evaluate any benefit the addition of anions to the thiosulfate leach solution may have on maintaining an acceptable gold dissolution rate as the solution ages. The effect of sodium sulfate or sodium chloride addition on the gold dissolution rate and copper(II) concentration are shown in Figure 7.16. Clearly, the addition of anions reduces the rate of copper(II) reduction and hence the percentage decrease in the gold dissolution rate is less over the time period shown. However, despite the copper(II) concentration decreasing faster and thus being lower in the absence of added anions, the gold leach rate is at all times greater than the rates measured with the addition of sulfate or chloride. Since the gold leach rates are only slightly lower after 2 hours for the addition of 0.4 M sodium sulfate, there is the benefit of less thiosulfate oxidation having occurred and thus less of the passivating oxysulfur species formed. This may be of benefit on a longer time scale.

### 7.3.3.3 Effect of pH

The effect of using ammonium thiosulfate instead of sodium thiosulfate was shown in section 3.3.3 to result in a lower leach solution pH because of the equilibrium involving ammonium and hydroxide ions, and ammonia as shown in Equation 3.3. This results in a faster rate of copper(II) reduction (Figure 3.10). However, at lower pH only a marginal increase in the gold dissolution rate was observed for fresh thiosulfate leach solutions (Figure 6.28). Figure 7.17 shows that at lower pH values the gold dissolution rate decreases faster as a result of the faster decrease in the copper(II) concentration as the solution ages. Thus, after 1 hour the gold dissolution rate at the lower pH of 9.8 falls below that of the pH 11.4 solution due to the significantly lower copper(II) concentration. Obviously, for short term leaching (1 to 2 hours shown in Table 2.2 of the review to have been used by several researchers) there is little effect on gold dissolution of using ammonium thiosulfate. However, for longer term leaching there is

clearly a significant decrease in the gold dissolution rate in the first couple of hours, such that in the absence of oxygen very little further gold dissolution takes place.
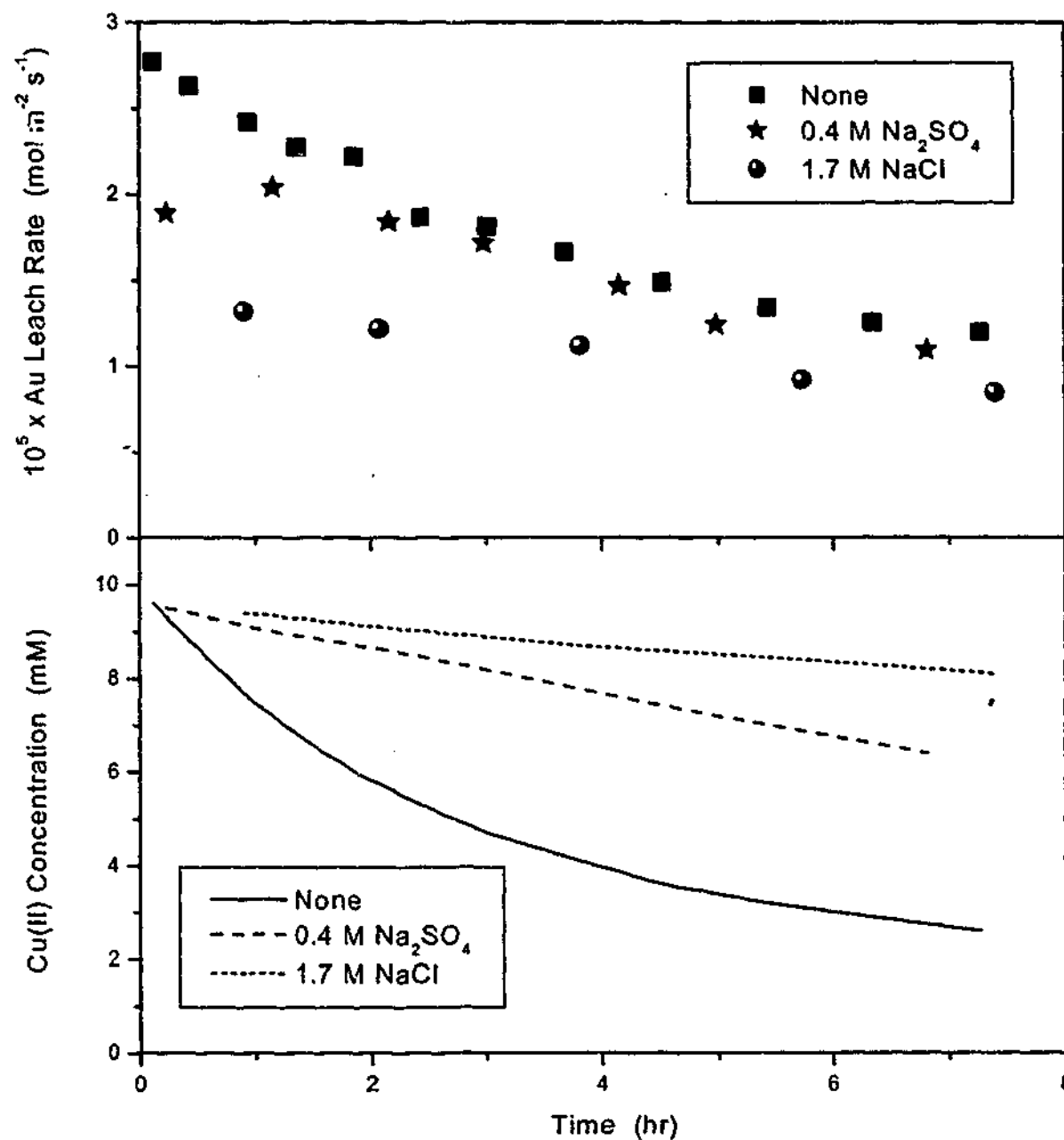


**Figure 7.16:** The effect of anions on the gold leach rate and copper(II) concentration in aging thiosulfate leach solutions in the absence of oxygen: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.
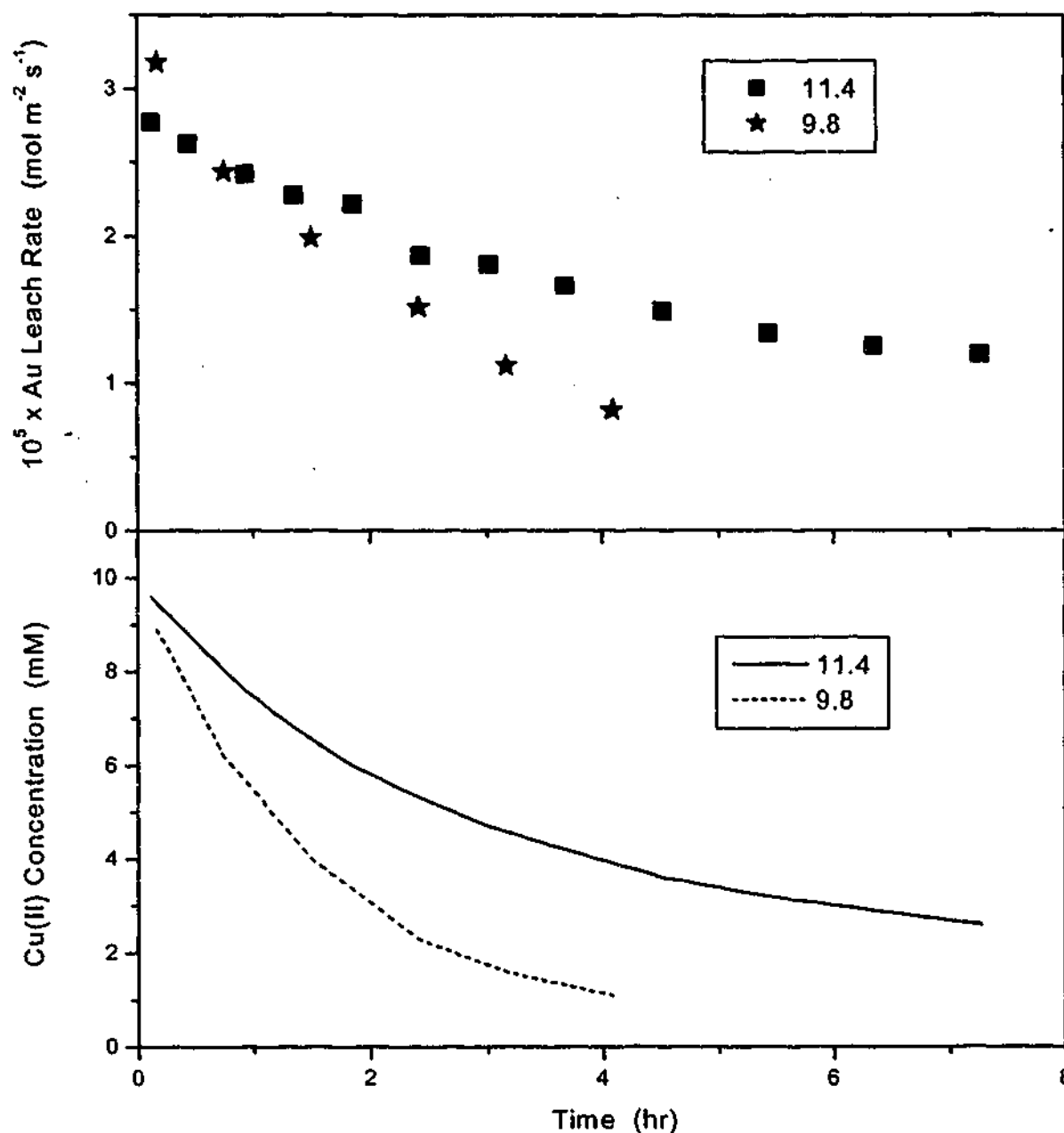
**Figure 7.17:** The effect of pH on the gold leach rate and copper(II) concentration in aging thiosulfate leach solutions in the absence of oxygen: 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

## 7.3.3.4 Effect of Temperature

The gold dissolution rates shown in the remaining 3 sections are for a fresh electroplated gold/silver alloy (2 wt% silver) as time did not permit to redo these experiments with pure gold. The effect of small quantities of silver alloyed with gold were discussed in detail in section 6.3.2.3, where it was shown that the freshly

electroplated gold/silver dissolution rate was significantly faster than for pure gold and that the dissolution rate decreased with time between electroplating and using the electrode. This later point is likely to have significantly contributed to the scatter in the data. Though, the results are not directly comparable with the pure gold data, the trends are representative of those expected if pure gold had been used.

Increasing temperature increases the reaction rate of chemically controlled processes and was shown in section 6.3.4 to significant increase the rate of gold dissolution. However, the rate of copper(II) reduction was also shown in section 3.3.7.4 to also increase significantly with an increase in temperature. As shown in Figure 7.18, there is an initial benefit of higher temperatures (40 °C) on the gold leach rate, though as the solution ages the gold dissolution rate falls below that at 30 °C after 1 hour due to the rapid decrease in the copper(II) concentration. A significant decrease in the gold dissolution rate as the thiosulfate leach solution aged at higher temperatures has also been observed by Muyunda (1996). At 25 °C the gold dissolution rate is initially lower, however the decrease with aging is slower. Clearly, after 2 hours the gold dissolution rates would suggest that a temperature of 30 °C would be optimal under these conditions. Above this temperature the copper(II) concentration decreases fast, whereas below this temperature the gold dissolution rate decreases significantly.

### 7.3.3.5    Effect of Thiosulfate

A similar trend to that observed with increasing temperature is also shown in Figure 7.19 for increasing thiosulfate concentration. Again, it should be noted that the gold dissolution rates are for freshly electroplated gold/silver (2 wt% silver). The initial gold dissolution rate increases with increasing thiosulfate concentration as shown previously in section 6.3.5, though copper(II) reduction is faster. Thus, at higher thiosulfate concentrations the gold dissolution rate also decreases faster as the thiosulfate leach solution ages. This was consistent with the results published by Muyunda (1996), which showed that the gold dissolution rate had decreased significantly over the first 2 hours at high thiosulfate concentrations. From the results shown in Figure 7.19, better gold dissolution rates are maintained as the thiosulfate leach solution ages using 0.1 M thiosulfate.
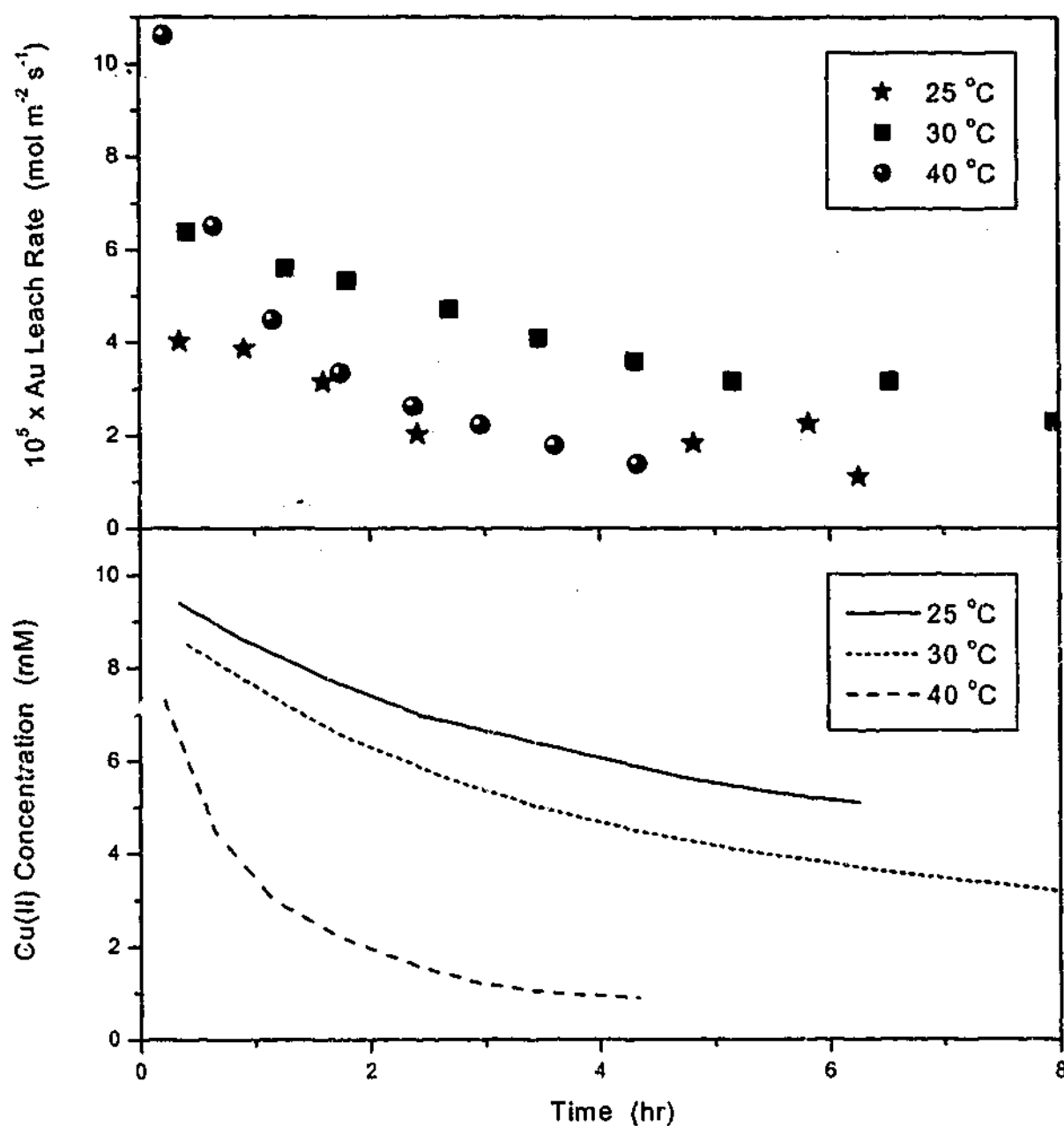
**Figure 7.18:** The effect of temperature on the gold leach rate and copper(II) concentration in aging thiosulfate leach solutions in the absence of oxygen: Au/Ag electrode (2 wt% Ag), 0.1 M $Na_2S_2O_3$, 0.4 M $NH_3$, 10 mM $CuSO_4$, 300 rpm.
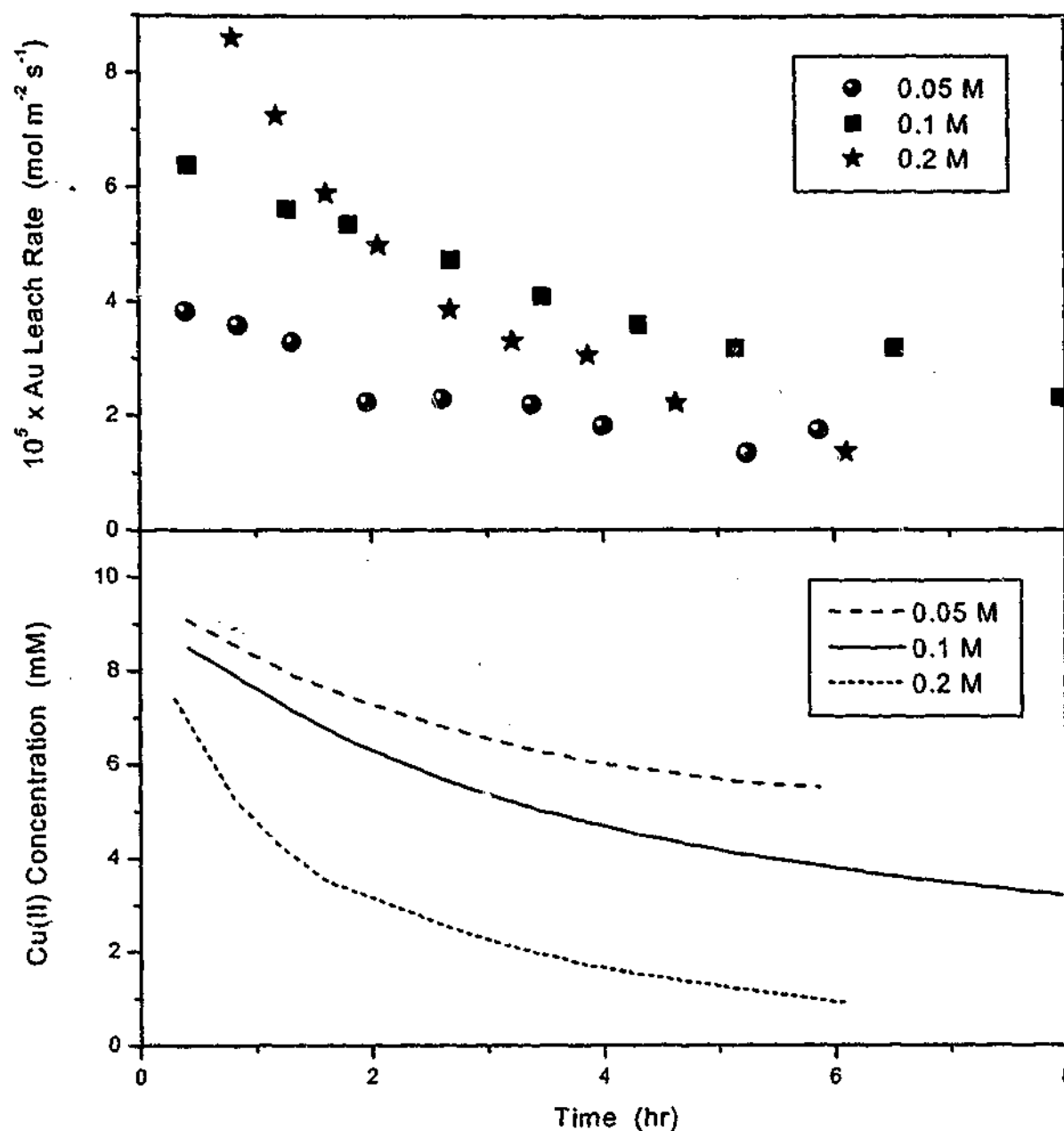
**Figure 7.19:** The effect of thiosulfate concentration on the gold leach rate and copper(II) concentration in aging thiosulfate leach solutions in the absence of oxygen: Au/Ag electrode (2 wt% Ag), 0.4 M NH$_3$, 10 mM CuSO$_4$, 300 rpm, 30 °C.

## 7.3.3.6 Effect of Ammonia

The concentration of ammonia was shown in section 6.3.6 to have little effect on the gold dissolution rate in fresh thiosulfate leach solutions. However, the effect of ammonia concentration on the rate of copper(II) reduction was shown in section 3.3.7.3 to be very significant, with increasing ammonia concentration stabilising the copper(II).

Figure 7.20 shows the effect of ammonia concentration on the gold dissolution rate as the thiosulfate leach solutions age. Again, the gold dissolution rates are for freshly electroplated gold/silver (2 wt% silver). Not surprisingly, at ammonia concentrations below 0.4 M, the copper(II) concentration decreases rapidly thus decreasing the gold dissolution rate. However, there appears to be no benefit in further stabilising the copper(II) with ammonia concentrations above 0.4 M as the gold dissolution rate at all times is lower over the period investigated.
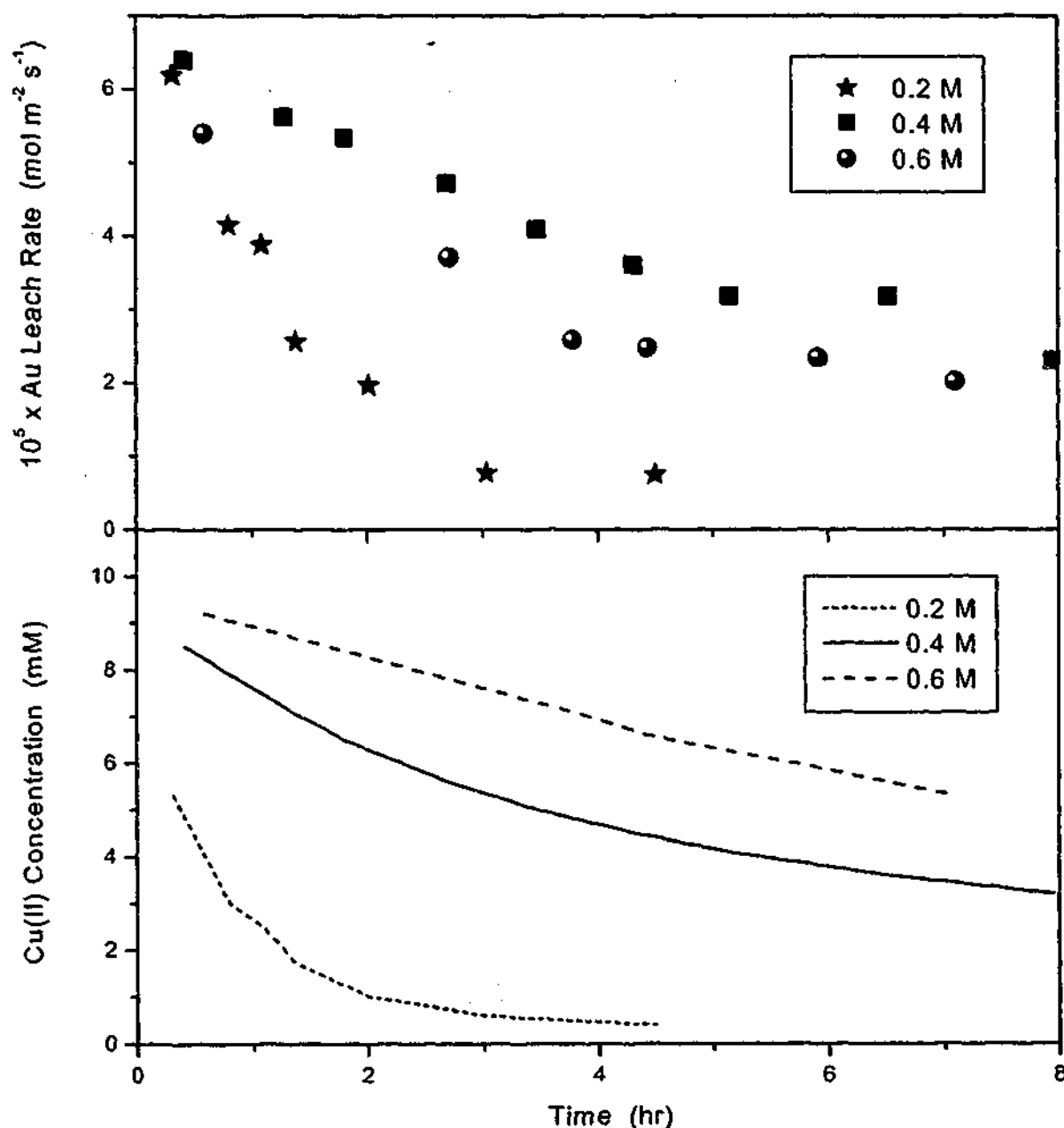


**Figure 7.20:** The effect of ammonia concentration on the gold leach rate and copper(II) concentration in aging thiosulfate leach solutions in the absence of oxygen: Au/Ag electrode (2 wt% Ag), 0.1 M $Na_2S_2O_3$, 10 mM $CuSO_4$, 300 rpm, 30 °C.

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## 7.4 Summary

The most important finding in this chapter was the observed passivation of gold during leaching in aged thiosulfate leach solutions; the gold oxidation reaction was shown to be hindered. Under certain conditions gold leaching was observed to completely stop. The species responsible for passivation was not identified but appeared to be an intermediate oxysulfur species from thiosulfate oxidation other than tetrathionate. The solution conditions were also shown to affect the passivation of the gold dissolution process. Thus, the rates of generation and disappearance of the species responsible for passivation are obviously important to the gold dissolution process and hence requires further research.

For a constant mass transfer rate of oxygen into the thiosulfate leach solution, which maintains the thiosulfate oxidation rate constant, the sustainable copper(II) concentration and associated gold leach rate were shown to be dependent on the solution conditions. Optimal thiosulfate concentration and temperature were found to be 0.1 M and 40 °C respectively. The addition of sulfate was also shown to slightly improve the gold dissolution rate. However, the use of ammonium thiosulfate instead of sodium thiosulfate, which decreases the solution pH, results in much lower gold dissolution rates.

In the absence of oxygen, the initial copper(II) reduction rate is slower, and hence the [Cu(II)]:[Cu(I)] ratio is higher for an initial period. This results in higher cathodic potentials for this initial period and thus higher gold dissolution rates. The optimal conditions for gold dissolution under these conditions are dependant on the time frame for leaching. Conditions which have high initial leach rates generally have high copper(II) reduction rates and hence low gold dissolution rates after a short period of time. For example, increasing the temperature from 30 to 40 °C almost doubles the initial gold leach rate. However after 1 hour the gold leach rate in the solution maintained at 40 °C is lower than that for the solution maintained at 30 °C due to the significantly lower copper(II) concentration.

# Chapter 8

# *Conclusions and Recommendations*

The results presented in this thesis represent a significant advancement in the fundamental understanding of the gold dissolution process in thiosulfate solutions containing copper(II) and ammonia. The role of copper(II) in the gold dissolution process was clearly identified and the homogeneous reactions involving copper(II), thiosulfate and oxygen were shown to be significantly more complex than previously thought.

The gold dissolution process in thiosulfate leach solutions was effectively studied for the first time using a rotating electrochemical quartz crystal microbalance (REQCM). This instrument allowed the gold oxidation reaction to be studied in actual thiosulfate leach solutions with copper ions present. In thiosulfate solutions the gold oxidation reaction was found to be very passive, with ammonia required in order that the reaction occurred at an appreciable rate. Most importantly, the presence of copper ions was shown to significantly enhance the gold oxidation reaction. This is the reason why copper(II) is more effective than alternative oxidants in the thiosulfate leaching process. The gold dissolution process was found to be largely chemically controlled. Thus, increasing the temperature significantly enhanced the gold oxidation rate. The gold oxidation rate was also found to increase with increasing copper(II) and thiosulfate concentrations. However, the presence of sulfate or high ammonia concentration (greater than 0.5 M), were found to reduce the gold oxidation rate. The reasons for this are unclear. Also, the gold oxidation rate was found to be dependant on the surface finish and purity of the gold.

The dominant cathodic reaction appeared to be the reduction of copper(II) tetra-ammine to a copper(I) mixed ammonia/thiosulfate complex, which proceeds quite rapidly. The potential of the cathodic reaction was found to be largely dominated by the

[Cu(II)]:[Cu(I)] ratio. To a lesser extent ammonia and thiosulfate concentrations and the presence of anions were found to also affect the cathodic potential.

It has been well known for at least 3 decades that the solution chemistry continually changes due to the undesirable reaction between copper(II) and thiosulfate. In the absence of oxygen, this reaction was shown to be generally rate limited by a second order process with respect to copper(II) concentration; a first order process is only observed at very low anion concentrations. Evidence was presented to support an inner sphere reaction mechanism in which anions compete with thiosulfate in complexing with the copper(II) at the axial sites. Phosphate was found to be the most effective anion in reducing the rate of copper(II) reduction. Increasing the ammonia concentration was also found to have a very positive effect in reducing the rate of copper(II) reduction; the estimated reaction order with respect to ammonia concentration was $-2.5$. Tetrathionate, the proposed reaction product of thiosulfate oxidation by copper(II) in the absence of oxygen, was also found to reduce copper(II) in the presence of thiosulfate via an outer sphere mechanism. Other oxysulfur species such as trithionate and sulfite were also shown to reduce copper(II) in the presence of thiosulfate and absence of oxygen via inner sphere mechanisms. These results clearly highlight the complexity of the copper(II) reduction mechanisms in thiosulfate leach solutions which involve the oxidation of thiosulfate and intermediate oxysulfur species.

In order to study the rate of thiosulfate oxidation in thiosulfate leach solutions an analytical method was developed to measure the thiosulfate concentration in such solutions, as an appropriate technique was not available. The method developed measured the silver oxidation rate which was shown with the use of the REQCM to be linearly related to the thiosulfate concentration. This method though required dilution in order to reduce the rate of silver oxidation. The thiosulfate concentration measured by this technique was also shown to be that of the free thiosulfate available for leaching, hence it does not measure thiosulfate complexed with copper(I). A flow injection analysis method was developed using a 4 electrode flow through cell containing both silver and platinum working electrodes. The integration of the difference between the measured currents of the two working electrodes during the sample injection period gave a very good estimate of the charge due to silver oxidation. This gave a very

simple, rapid and robust technique for measuring thiosulfate concentration in thiosulfate leach solutions applicable to gold leaching.

In the presence of oxygen the initial rate of copper(II) reduction was surprisingly found to be significantly faster than in the absence of oxygen. Thus, in the presence of oxygen the copper was not observed to stay mainly in the copper(II) oxidation state. The higher initial rate of copper(II) reduction in the presence of oxygen indicated that oxygen increases the rate of copper(II) reduction by thiosulfate to copper(I), though the mechanism for this remains unclear. The rate of thiosulfate oxidation was also shown to be significantly faster in the presence of oxygen. However, this rate was greater than that estimated from the initial rate of copper(II) reduction. A second mechanism for thiosulfate oxidation was shown to be consistent with thiosulfate oxidation by the intermediate superoxide and/or hydroxide radicals formed as a result of copper(I) oxidation. The thiosulfate oxidation rate was found to be largely dependant on the oxygen concentration as indicated by the dependence on the rate of oxygen mass transfer. Notably, the presence of anions had only a small effect on the thiosulfate oxidation rate compared to the significant decrease observed in the copper(II) reduction rate.

As the presence of oxygen does not maintain most of the copper as copper(II), the effect of solution conditions on the [Cu(II)]:[Cu(I)] ratio is important to the gold dissolution process as this largely governs the cathodic potential. This ratio was increased by the presence of anions or by increasing the ammonia or copper concentrations, and decreased by increasing the temperature, thiosulfate concentration or by lowering the solution pH (for example by the substitution of ammonium thiosulfate for sodium thiosulfate). Many of the parameters which enhance the gold oxidation reaction resulted in a lower maintainable copper(II) concentration and hence [Cu(II)]:[Cu(I)] ratio. Thus, optimal conditions at low oxygen mass transfer rates were found to be 0.1 M sodium thiosulfate, 0.4 M ammonia, 10 mM copper, and 40 °C. The addition of anions needs further evaluation, though the results presented in this thesis suggest a slight improvement to the gold dissolution rate with the added benefit of reducing the thiosulfate oxidation rate. Surprisingly the [Cu(II)]:[Cu(I)] ratio was found to be almost independent of oxygen concentration except at very low oxygen concentrations. Thus, to minimise thiosulfate oxidation a low solution oxygen

concentration should be maintained. This is essentially controlled by the mass transfer rate of oxygen into solution and is thus dependant on the sparge rate and oxygen concentration of the gas.

Possibly the most significant finding in this research was the passivation of the gold dissolution process with aging of the thiosulfate leach solution. Under certain condition gold leaching was observed to completely stop. The gold oxidation reaction was shown to be hindered by an unidentified species which appears to be an intermediate oxysulfur species of thiosulfate oxidation. This species was shown not to be tetrathionate. The passivation was also found to be dependant on the solution conditions.

Obviously there are several recommendations from this research for future research into the thiosulfate leaching of gold. The first of these is for further study into the roles of ammonia and copper in enhancing the gold oxidation reaction in the presence of thiosulfate. Further understanding of the hindrance to gold oxidation in thiosulfate solutions and ways to overcome this without the addition of copper, could allow alternative oxidants to be considered. Secondly, the solution chemistry in aging thiosulfate solutions containing ammonia and copper(II) needs to be studied in more detail to identify the passivating oxysulfur species and associated reactions such that it can be eliminated or its concentration minimised. Gold leaching studies conducted in aging thiosulfate leach solutions may be able to identify conditions for which this passivating species is eliminated or minimised. Thirdly, further consideration should be given to the effect of various parameters on the solution chemistry in light of the fact that the resin recovery of gold from thiosulfate leach solutions is severely hindered by a number of the oxysulfur species likely to be intermediates of thiosulfate oxidation.

Clearly, more research into the gold dissolution process in aging thiosulfate leach solutions containing ammonia and copper(II) is required if the commercial application of this process is to be successful.

# *Bibliography*

Abbruzzese, C., Fornari, P., Massidda, R. and Veglio, F. 1995, 'Thiosulphate leaching for gold hydrometallurgy', *Hydrometallurgy*, vol. 39, no. 1-3, pp. 265-276.

Antelman, M.S. and Harris, F.J. 1982, *The Encyclopedia of Chemical Electrode Potentials*, Plenum Press, New York.

Aylmore, M.G. 2001, 'Treatment of a refractory gold-copper sulfide concentrate by copper ammoniacal thiosulfate leaching', *Minerals Engineering*, vol. 14, no. 6, pp. 615-637.

Aylmore, M.G. and Muir, D.M. 2001, 'Thiosulfate leaching of gold - A review', *Minerals Engineering*, vol. 14, no. 2, pp. 135-174.

Balaz, P., Ficeriova, J., Boldizarova, E., Haber, M., Jelen, S. and Kammel, R. 2000, 'Thiosulfate leaching of gold from a mechanochemically pretreated complex sulfide concentrate', in *XXI International Mineral Processing Congress*, vol. A, Ed. Massacci, P., Elsevier, Amsterdam, pp. 74-81.

Baranova, N.N. and Ryzhenko, B.N. 1981, 'Computer simulation of the Au-Cl-S-Na-$H_2O$ system in relation to the transport and deposition of gold in hydrothermal processes', *Geochem. Int.*, vol. 18, no. 4, pp. 46-60.

Barbosa-Filho, O., Trindale, R.B.E. and Araujo, V.V. 1994, 'Dissolution of Gold in Thiosulphate Solutions: Review and Rotating Disc Investigation', *English Trans. of paper presented at Congr. Anu. Assoc. Bras. Metal. Mater.*, vol. 4, pp. 265-279.

Bard, A.J. 1973, *Encyclopaedia of Electrochemistry of the Elements*, Marcel Dekker, New York.

Bard, A.J. and Faulkner, L.R. 1980, *Electrochemical Methods. Fundamentals and Applications*, John Wiley & Sons, New York.

Berezowsky, R.M.G.S., Sefton, V.B. and Gormely, L.S. 1978, 'Recovery of Precious Metals from Metal Sulphides', U.S. Patent 4,070,182.

Bjerrum, J., Ballhausen, C.J. and Jorgensen, C.K. 1954, 'Studies on adsorption spectra. I. Results of calculations on the spectra and configuration of copper(II) ions', *Acta Chemica Scandinavia*, vol. 8, no. 7, pp. 1275-1289.

Block-Bolten, A., Daita, M.S., Torma, A.E. and Steensma, R. 1985, 'New possibilities in the Extraction of Gold and Silver from Zinc and Lead Sulphide Flotation Wastes', *Complex Sulphides, Proc. Symp.*, pp. 149-166.

Briseno, A.L., Song, F., Baca, A.J. and Zhou, F. 2001, 'Studies of potential-dependent metallothionein adsorptions using a low-volume electrochemical quartz crystal microbalance flow cell', *Journal of Electroanalytical Chemistry*, vol. 513, no. 1, pp. 16-24.

Byerley, J.J., Fouda, S.A. and Rempel, G.L. 1973a, 'Kinetics and mechanism of the oxidation of thiosulfate ions by copper(II) ions in aqueous ammonia solution', *Journal of the Chemical Society, Dalton Transactions*, pp. 889-893.

Byerley, J.J., Fouda, S.A. and Rempel, G.L. 1973b, 'The oxidation of thiosulfate in aqueous ammonia by copper (II) oxygen complexes', *Inorganic Nuclear Chemistry Letters*, vol. 9, pp. 879-883.

Byerley, J.J., Fouda, S.A. and Rempel, G.L. 1975, 'Activation of copper(II) ammine complexes by molecular oxygen for the oxidation of thiosulfate ions', *Journal of the Chemical Society, Dalton Transactions*, pp. 1329-1338.

Cao, C., Hu, J. and Gong, Q. 1992, 'Leaching Gold by Low Concentration Thiosulphate Solution', in *Randol Gold Forum '92, Vancouver*, Randol International, Golden, Co, pp. 293-298.

Chen, J.Y., Deng, T., Zhu, G.C. and Zhao, J. 1996, 'Leaching and recovery of gold in thiosulfate based system - a research summary at ICM', *Transactions of the Indian Institute of Metals*, vol. 49, no. 6, pp. 841-849.

Choo, W.L. and Jeffrey, M.I. 2001, 'An electrochemical study of copper cementation of gold(I) thiosulfate', *submitted to Hydrometallurgy*.

Dhawale, S.W. 1993, 'Thiosulfate. An interesting sulphur oxoanion that is useful in both medicine and industry - but is implicated in corrosion', *Journal of Chemical Education*, vol. 70, no. 1, pp. 12-14.

Drok, K.J. and Ritchie, I.M. 1997, 'An investigation of the selective leaching of gold over copper using ammoniacal cyanide', in *World Gold '97*, Aus.I.M.M., Melbourne, pp. 87-93.

Dulz, G. and Sutin, N. 1964, 'The effect of chloride ions on the kinetics of the oxidation of chromium(II) by iron(III)', *J. Am. Chem. Soc.*, vol. 86, pp. 829-832.

Fava, A. and Bresadola, S. 1955, 'Kinetics of the Catalytic Rearrangement of Tetrathionate', *J. Am. Chem. Soc.*, vol. 77, pp. 5792-5794.

Fleming, C.A. 2000, 'Recent advances in the development of an alternative to the cyanidation process - based on thiosulfate leaching and resin in pulp', in *Ballarat gold forum*, Ballarat, Australia.

Flett, D.S., Derry, R. and Wilson, J.C. 1983, 'Chemical study of thiosulphate leaching of silver sulphide', *Transactions of the Institute of Mining and Metallurgy*, vol. 92, pp. C216-C223.

Gallagher, N.P., Hendrix, J.L., Milosavljevic, E.B. and Nelson, J.H. 1989, 'The Affinity of Carbon for Gold Complexes: Dissolution of Finely Disseminated Gold using a Flow Electrochemical Cell', *J. Electrochem. Soc.*, vol. 136, no. 9, pp. 2546-2551.

Gallagher, N.P., Hendrix, J.L., Milosavljevic, E.B., Nelson, J.H. and Solujic, L. 1990, 'Affinity of Activated Carbon towards some Gold(I) Complexes', *Hydrometallurgy*, vol. 25, pp. 305-316.

Gering, K.L. and Rosentreter, J.J. 2001, 'Real-time measurement of aqueous cyanide in mining operations', in *Cyanide: social, industrial and economic aspects*, Eds. Young, C.A., Tidwell, L.G. and Anderson, C.G., The Minerals, Metals and Materials Society, Warrendale, Pa, pp. 141-150.

GOLDSHEET Mining Directory, 2001. [online] World Gold Production, Available: http://www.goldsheetlinks.com, [Accessed October, 2001].

Goleva, G.A., Krivenkov, V.A. and Gutz, Z.G. 1970, 'Geochemical trends in the occurence and migration forms of gold in natural water', *Geochem. Int.*, vol. 7, no. 3, pp. 518-529.

Gong, Q., Hu, J. and Cao, C. 1993, 'Kinetics of gold leaching from sulfide gold concentrates with thiosulfate solution', *Transactions of Nonferrous Metals Society of China*, vol. 3, no. 4, pp. 30-36.

Groudev, S.N., Ivanov, I.M., Spasova, I.I. and Groudeva, V.I. 1995, 'Pilot Scale Microbial Leaching of Gold and Silver from an Oxide Ore in Elshitza Mine, Bulgaria', in *Miner. Bioprocess. II, Proc. Eng. Found. Conf.*, pp. 135-144.

Groudev, S.N., Spasova, II and Ivanov, I.M. 1996, 'Two-Stage Microbial Leaching of a Refractory Gold-Bearing Pyrite Ore', *Minerals Engineering*, vol. 9, no. 7, pp. 707-713.

Guerra, E. and Dreisinger, D.B. 1999, 'A study of the factors affecting copper cementation of gold from ammoniacal thiosulphate solution', *Hydrometallurgy*, vol. 51, pp. 155-172.

Han, K.N. 2001, 'Electrochemical behaviour of the dissolution of gold in ammoniacal solutions', in *Cyanide: social, industrial and economic aspects*, Eds. Young, C.A.,

Tidwell, L.G. and Anderson, C.G., The Minerals, Metals and Materials Society, Warrendale, Pa, pp. 484-499.

Hancock, R.D., Finkelstein, N.P. and Evers, A. 1974, 'Linear free energy relationships in aqueous complex-formation reactions of the $d_{10}$ metal ions', *Journal of Inorganic Nuclear Chemistry*, vol. 36, pp. 2539-2543.

Hathaway, B.J. and Tomlinson, A.A.G. 1970, 'Copper(II) ammonia complexes', *Coordination Chemistry Reviews*, vol. 5, pp. 1-43.

Hemmati, M., Hendrix, J.L., Nelson, J.H. and Milosavljevic, E.B. 1989, 'Study on the Thiosulphate Leaching of Gold from Carbonaceous Ore and the Quantitative Determination of Thiosulphate in the Leached Solution', in *Extraction Metallurgy '89 Symposium*, Inst. Min. Metall., London, UK, pp. 665-678.

Hiskey, J.B. and Atluri, V.P. 1988, 'Dissolution Chemistry of Gold and Silver in Different Lixiviants', *Min. Proc. Extr. Metall. Review*, vol. 4, pp. 95-134.

Högfeldt, E. 1982, *Stability constants of metal-ion complexes: Pt. A. Inorganic ligands*, Pergamon, Oxford.

Hu, J. and Gong, Q. 1991, 'Substitute sulfate for sulfite during extraction of gold by thiosulfate solution', in *Randol Gold Forum '91 : Cairns, Australia*, Randol, Golden, Co, pp. 333-336.

Hurlbut, C.S. and Klein, C. 1977, *Manual of Mineralogy, 19th Edition*, John Wiley & Sons, New York.

Jeffrey, M.I. 1998, *A kinetic and electrochemical study of the dissolution of gold in aerated cyanide solutions: The role of solid and solution phase purity*, PhD Thesis, Curtin University, Bentley, Western Australia.

Jeffrey, M.I. 2000, 'The cyanide leaching of gold in solutions containing sulfide', *Minerals Engineering*, vol. 13, no. 10-11, pp. 1097-1106.

Jeffrey, M.I. 2001, 'Kinetic aspects of gold and silver leaching in ammonia-thiosulfate solutions', *Hydrometallurgy*, vol. 60, pp. 7-16.

Jeffrey, M.I. and Ritchie, I.M. 2000, 'The leaching of gold in cyanide solutions in the presence of impurities I. The effect of lead.' *Journal of the Electrochemical Society*, vol. 147, no. 9, pp. 3257-3262.

Jeffrey, M.I. and Ritchie, I.M. 2001, 'The leaching and electrochemistry of gold in high purity cyanide solutions', *Journal of the Electrochemical Society*, vol. 148, no. 4, pp. D29-D36.

Jeffrey, M.I., Zheng, J. and Ritchie, I.M. 2000, 'Development of a rotating electrochemical quartz crystal microbalance for the study of metal leaching and deposition', *Measurement Science and Technology*, vol. 11, pp. 560-567.

Ji, C. and Yu, Q. 1991, 'Research and Optimization of Thiosulphate Leaching Technology of Gold', *Rare Met.*, vol. 10, no. 4, pp. 275-280.

Jiang, T., Chen, J. and Xu, S. 1993a, 'Electrochemistry and mechanism of leaching gold with ammoniacal thiosulfate', in *XVIII International Mineral Processing Congress*, Australasian Institute of Mining and Metallurgy, Parkville, Vic., pp. 1141-1146.

Jiang, T., Chen, J. and Xu, S. 1993b, 'A Kinetic Study of Gold Leaching with Thiosulphate', in *Hydrometallurgy, Fundamentals, Technology and Innovations*, Eds. Hiskey, J.B. and Warren, G.W., AIME, pp. 119-126.

Jiang, T., Xu, S., Chen, J. and Yang, Y. 1997, 'Anodic oxidation of Thiosulphate Ions in Gold Leaching', *J. Cent. South Univ. Technol.*, vol. 4, no. 2, pp. 89-91.

Johnson, B.F.G. and Davis, R. 1973, 'Gold', in *Comprehensive inorganic chemistry*, vol. 5, Eds. Bailar, J.C., Emeleus, H.J., Nyholm, S.R. and Trotman-Dickenson, A.F., Pergamon Press, Oxford, England, p. 153.

Kerley, B.J., Jr. 1981, 'Recovery of Precious Metals from Difficult Ores', U.S. Patent 4,269,622.

Kerley, B.J., Jr. 1983, 'Recovery of Precious Metals from Difficult Ores', U.S. Patent 4,369,061.

Kirk and Othmer 1981, *Encyclopaedia of Chemical Technology*, Wiley, New York.

Koh, T. 1990, 'Analytical Chemistry of Polythionates and Thiosulphate. A Review.' *Analytical Sciences*, vol. 6, no. 1, pp. 3-14.

Labrooy, S.R., Linge, H.G. and Walker, G.S. 1994, 'Review of Gold Extraction From Ores', *Minerals Engineering*, vol. 7, no. 10, pp. 1213-1241.

Laidler, K.J. 1963, *Reaction kinetics. Volume II - Reactions in solution*, Pergamon Press, Oxford.

Laist, J.W. 1954, 'Copper, silver and gold', in *Comprehensive inorganic chemistry*, vol. 2, Eds. Sneed, M.C., Maynard, J.L. and Brasted, R.C., D. Van Nostrand Company, Inc., Princeton, New Jersey, pp. 184-238.

Langhans, J.W., Lei, K.P.V. and Carnahan, T.G. 1992, 'Copper-catalyzed thiosulfate leaching of low-grade gold ores', *Hydrometallurgy*, vol. 19, pp. 191-203.

Lappin, A.G. 1994, *Redox mechanisms in inorganic chemistry*, Ellis Harwood Limited, New York.

Li, J., Miller, J.D., Wan, R.Y. and Le Vier, K.M. 1995, 'The ammoniacal Thiosulphate System for Precious Metal Recovery', in *Proc. Int. Miner. Process. Congr., 19th*, vol. 4, Soc. for Min., Metall. and Explor., Littleton, Co, pp. 37-42.

Luo, Y., Kustin, K. and Epstein, I.R. 1988, 'Kinetics and mechanism of $H_2O_2$ decomposition catalyzed by $Cu^{2+}$ in alkaline solution', *Inorganic Chemistry*, vol. 27, pp. 2489-2496.

Marchbank, A.R., Thomas, K.G., Dreisinger, D. and Fleming, C. 1996, 'Gold recovery from refractory carbonaceous ores by pressure oxidation and thiosulphate leaching', U.S. Patent 5,536,297.

Market Information and Analysis Unit, 2001, 'Exports of primary and manufactured products. Australia 2000-01', Department of Foreign Affairs and Trade, Commonwealth of Australia.

Marsden, J. and House, I. 1992, *The Chemistry of Gold Extraction*, Ellis Horwood Ltd., Chichester, West Sussex, England.

Martell, A.E. 1983, 'Oxidation of organic substrates with dioxygen complexes as intermediates', *Pure and Applied Chemistry*, vol. 55, no. 1, pp. 125-135.

Meng, X. and Han, K.N. 1993, 'A Kinetic Model for Dissolution of Metals - The Role of Heterogeneous Reaction and Mass Transfer', *Trans. Soc. Min., Metall., Explor.*, vol. 294, pp. 128-134.

Michel, D. and Frenay, J. 1996, 'Electrochemical investigation of the thiosulfate gold leaching process', in *CIM Gold Symposium*, Canadian Institute of Mining, Montreal.

Mills, R. and Lobo, V.M.M. 1989, *Self-diffusion in electrolyte solutions. A critical examination of data compiled from the literature*, Elservier, Amsterdam.

Muir, D.M. and Aylmore, M.G. 2002, 'Thiosulphate as an alternative to cyanide for gold processing - Issues and impediments', in *Green Processing Conference*, pp. 125-133.

Muratsugu, M., Ohta, F., Miya, Y., Hosokawa, T., Kurosawa, S., Kamo, N. and Ikeda, H. 1993, 'Quartz crystal microbalance for the detection of microgram quantities of human serum albumin: relationship between the frequency change and the mass of protein adsorbed', *Analytical Chemistry*, vol. 65, no. 20, pp. 2933-2937.

Murthy, D.S.R. 1991, 'The Extraction of Gold and Silver From Lead-Zinc Sulphide Flotation Tailings Through Non-Cyanide Leachants', *Transactions of the Indian Institute of Metals*, vol. 44, no. 5, pp. 349-354.

Murthy, D.S.R. and Prasad, P.M. 1996, 'Leaching of Gold and Silver From Miller Process Dross Through Non-Cyanide Leachants', *Hydrometallurgy*, vol. 42, no. 1, pp. 27-33.

Mussatti, D., Mager, J. and Martins, G.P. 1997, 'Electrochemical aspects of the dissolution of gold in cyanide electrolytes containing lead', in *Aqueous Electrotechnologies: Progress in Theory and Practice*, Ed. Dreisinger, D., Minerals, Metals and Materials Society, Warrendale, PA, pp. 247-265.

Muyunda, C. 1996, *Thiosulphate as an alternative lixiviant for gold - kinetics and environmental aspects*, Masters Thesis, Curtin University of Technology, Bentley, Western Australia.

Naito, K., Shieh, M.-C. and Okabe, T. 1970, 'Chemical behavior of low valence sulfur compounds. V. Decomposition and oxidation of tetrathionate in aqueous ammonia solution', *Bulletin of the Chemical Society of Japan*, vol. 43, no. 5, pp. 1372-1376.

Nicol, M., Fleming, C. and Paul, R. 1987, 'The chemistry of the extraction of gold', in *The Extractive Metallurgy of Gold in South Africa*, vol. 2, Ed. Stanley, G.G., South African Institute of Mining and Metallurgy, Johannesburg, S. Africa, pp. 831-905.

Nicol, M.J. and O'Malley, G.P. 2001, 'Recovery of gold from thiosulfate solutions and pulps with ion-exchange resins', in *Cyanide: social, industrial and economic aspects*, Eds. Young, C.A., Tidwell, L.G. and Anderson, C.G., TMS, New Orleans, Louisiana, pp. 469-483.

O'Sullivan, C.K. and Guilbault, G.G. 1999, 'Commercial quartz crystal microbalances - theory and applications', *Biosensors and Bioelectronics*, vol. 14, no. 8-9, pp. 663-670.

Palmer, W.G. 1959, *Experimental inorganic chemistry*, Cambridge University Press, Cambridge.

Panchenko, A.F. and Lodeishchikov, V.V. 1971, 'Evaluation of gold solvents', *Obagashch. Rud Peskov Blagorod. Metal.*, pp. 122-124.

Perez, A.E. and Galaviz, H.D. 1987, 'Method for Recovery of Precious Metals from Difficult Ores with Copper-Ammonium Thiosulphate', U.S. Patent 4,654,078.

Pouradier, J. and Gadet, M.C. 1969, 'Electrochimie Des Sels D'or. VII. Aurothiosulphate', *J. Chim. Phys.*, vol. 66, pp. 109-112.

Power, G.P. and Ritchie, I.M. 1975, 'Metal displacement reactions', in *Modern Aspects of Electrochemistry*, vol. II, Plenum Press, London, pp. 199-250.

Power, G.P. and Ritchie, I.M. 1983, 'Mixed potentials. Experimental illustration of an important concept in practical electrochemistry', *Journal of Chemical Education*, vol. 60, no. 12, pp. 1022-1026.

Puddephatt, R.J. 1978, *The chemistry of gold*, Elsevier Scientific, Amsterdam, Netherlands.

Rabai, G. and Epstein, I.R. 1992, 'Equilibria and Kinetics of the Fast Interaction between Copper(II) and Thiosulphate Ions in Aqueous Solutions', *Inorganic Chemistry*, vol. 31, pp. 3239-3242.

Reeves, R.E. and Bragg, P. 1962, 'The amminehydroxocopper(II)-diolate chelation reaction', *Journal of American Chemical Society*, vol. 84, no. July 5, pp. 2491-2495.

Ritchie, I.M., Zheng, J., La Brooy, S.R. and Singh, P. 1994, 'Extension of electrochemical windows by the use of an electrochemical quartz crystal microbalance', in *Extended abstracts: 186th Annual meeting of the Electrochemical Society*, vol. II 94-2, Pennington, New Jersey, pp. 1044-1045.

Rolia, E. and Chakrabarti, C.L. 1982, 'Kinetics of Decomposition of Tetrathionate, Trithionate and Thiosulphate in Alkaline Media', *Environ. Sci. Technol.*, vol. 16, no. 12, pp. 852-857.

Schmitz, P.A., Duyvesteyn, S., Johnston, W.P., Enloe, L. and McMullen, J. 2001, 'Ammoniacal thiosulfate and sodium cyanide leaching of preg-robbing Goldstrike ore carbonaceous matter', *Hydrometallurgy*, vol. 60, pp. 24-40.

Shapiro, A.P. and Shvedova, N.V. 1974, 'Dissolution of gold in solutions of sulfoxide compounds', *Tr., Tsentr. Nauchno-Issled. Geologorazved. Inst. Tsvetn. Blagorodn. Met.*, vol. 111, pp. 27-29.

Simandi, L.I. 1992, *Catalytic Activation of Dioxygen by Metal Complexes*, Kluwer Acedemic Publishers, Dordrecht.

Skibsted, L.H. and Bjerrum, J. 1974, 'Studies on Gold Complexes. II. The Equilibrium between Gold(I) and Gold(III) in the Ammonia System and the Standard Potentials of the Couples Involving Gold, Diamminegold(I), and Tetramminegold(III)', *Acta Chemica Scandinavica*, vol. 28, no. 7, pp. 764-770.

Skibsted, L.H. and Bjerrum, J. 1977, 'Studies on gold complexes III. The standard electrode potentials of aqua gold ions.' *Acta Chemica Scandinavica*, vol. A31, pp. 155-156.

Skorobogaty, A. and Smith, T.D. 1984, 'Coordination and redox chemistry of some macromolecular systems', *Coordination Chemistry Reviews*, vol. 53, pp. 22-226.

Smith, R.M. and Martell, A.E. 1975, *Critical stability constants. Volume 2: Amines*, Plenum Press, New York.

Smith, R.M. and Martell, A.E. 1976, *Critical stability constants. Volume 4: Inorganic complexes*, Plenum Press, New York.

Song, Q., Wang, D. and Cheng, J. 1995, 'New Method of Extracting Gold and Silver from High Silver-Gold Concentrates', *Trans. Nonferrous Met. Soc. China*, vol. 5, no. 3, pp. 50-53.

Sullivan, A.M. and Kohl, P.A. 1997, 'Electrochemical Study of the Gold Thiosulfate Reduction', *Journal of the Electrochemical Society*, vol. 144, no. 5, pp. 1686-1690.

Sun, X., Guan, Y.C. and Han, K.N. 1996, 'Electrochemical behavior of the dissolution of gold-silver alloys in cyanide solutions', *Metallurgical & Materials Transactions B. Process Metallurgy & Materials Processing Science*, vol. 27, no. 3, pp. 355-361.

Tan, K.G. and Rolia, E. 1985, 'Chemical oxidation methods for the treatment of thiosalt-containing mill effluents', *Canadian Metallurgical Quarterly*, vol. 24, no. 4, pp. 303-310.

Ter-Arakelyan, K.A., Bagdasaryan, K.A., Oganyan, A.G., Mkrtchyan, R.T. and Babayan, G.G. 1984, 'On technological expediency of sodium thiosulphate usage for gold extraction from raw material', *Izv. V.U.Z. Tsvetn. Metallurgy*, pp. 72-76.

Thomas, K.G., Fleming, C., Marchbank, A.R. and Dreisinger, D. 1998, 'Gold recovery from refractory carbonaceous ores by pressure oxidation, thiosulphate leaching and resin-in-pulp adsorption', U.S. Patent 5,785,736.

Tozawa, K., Iniu, Y. and Umetsu, Y. 1981, 'Dissolution of Gold in Ammonical Thiosulphate Solutions', in *Annual AIME Meeting*, The Minerals, Metals and Materials Society, Warrendale, Pa, pp. A81-25 (12 pages).

Tyurin, N.G. and Kakowski, I.A. 1960, 'Behaviour of gold and silver in oxidising zone of sulfide deposit', *Izu. Buz. Tsyv. Metallurgy*, no. 2, pp. 6-13.

van Zijll de Jong, S., Feng, D. and van Deventer, J.S.J. 2001, 'Ammoniacal thiosulphate leaching of gold ores of varying mineralogy', in *6th World Congress of Chemical Engineering*, Conference Media Services Australia, Doncaster, VIC.

Wadsworth, M.E., Zhu, X., Thompson, J.S. and Pereira, C.J. 2000, 'Gold dissolution and activation in cyanide solution: kinetics and mechanism', *Hydrometallurgy*, vol. 57, pp. 1-11.

Wan, R.Y. 1997, 'Importance of solution chemistry for thiosulphate leaching of gold', in *World Gold '97*, The Australasian Institute of Mining and Metallurgy, Carlton, Vic, pp. 159-162.

Wan, R.Y. and Brierley, J.A. 1997, 'Thiosulphate Leaching following Biooxidation Pretreatment for Gold Recovery from Refractory Carbonaceous-Sulfidic Ore', *Mining Engineering*, pp. 76-80.

Wan, R.Y., Le Vier, K.M. and Clayton, R.B. 1994, 'Hydrometallurgical Process for the Recovery of Precious Metal Values from Precious Metal Ores with Thiosulphate Lixiviant', U.S. Patent 5,354,359.

Wan, R.Y., Le Vier, M. and Miller, J.D. 1993, 'Research and Development Activities for the Recovery of Gold from Noncyanide Solutions', in *Hydrometallurgy, Fundamentals, Technology and Innovations*, Eds. Hiskey, J.B. and Warren, G.W., AIME, pp. 415-436.

Wan, R.Y., Luinstra, L. and Brierley, J.A. 1995, 'Gold recovery from refractory sulfidic-carbonaceous ore. II. Thiourea leaching following biooxidation-heap pretreatment', in *EPD Congress 1995*, Minerals, Metals and Materials Society/AIME, Warrendale, PA, pp. 165-173.

Wang, X.H. 1992, 'Thermodynamic Equilibrium Calculations on Gold Silver Lixiviant Systems Relevant to Gold Extraction from Complex Ores', in *Proc. Electrochem. Soc.*, pp. 452-477.

Ward, M.D. 1995, 'Principles and applications of the electrochemical quartz crystal microbalance', in *Physical Electrochemistry: Principles, Methods and Applications*, Ed. Rubinstein, I., Marcel Dekker, New York, pp. 293-338.

Weast, R.C. Ed. (1974-75) *Handbook of chemistry and physics*, CRC Press, Cleveland, Ohio.

Webster, J.G. 1986, 'The Solubility of Gold and Silver in the System $Au-Ag-S-O_2-H_2O$ at $25^{\circ}C$ and 1atm', *Geochimica et Cosmochimica Acta*, vol. 50, pp. 1837-1845.

Yen, W.T., Aghamirian, M., Deschenes, G. and Theben, S. 1998, 'Gold extraction from mild refractory ore using ammonium thiosulfate', in *International Symposium on Gold Recovery*, CIM.

Yen, W.T., Stogram, K. and Fujita, T. 1996, 'Gold extraction from a copper bearing ore by thiosulfate leaching', *Resources Treatment Technology*, vol. 43, no. 2, pp. 83-87.

Zhang, C., Schranz, S., Lucklum, R. and Hauptmann, P. 1998, 'Mass effects of quartz resonant sensors with different surface microstructures in liquids', *IEEE Transactions on Ultrasonics Ferroelectrics & Frequency Control*, vol. 45, no. 5, pp. 1204-1210.

Zhang, H.G. 1997, *Some aspects of the use of thiourea in gold processing*, PhD Thesis, Murdoch University, Murdoch, W.A.

Zhang, H.G. and Dreisinger, D.B. 2002, 'The kinetics for the decomposition of tetrathionate in alkaline solutions', *accepted for publication in Hydrometallurgy*.

Zhang, J., Lan, X., Ding, F., Yuan, Z. and Shuai, S. 1992a, 'Leaching Gold and Silver by Lime-Sulphur-Synthetic-Solution (LSSS). Part II Treating ores with the LSSS', *Precious Met.*, vol. 16, pp. 394-398.

Zhang, J., Lan, X., Ding, F., Yuan, Z. and Yang, L. 1992b, 'Leaching Gold and Silver by Lime-Sulphur-Synthetic-Solution (LSSS). Part I. Synthesizing the LSSS and Dissolving Pure Gold and Silver with it', *Precious Met.*, vol. 16, pp. 389-393.

Zhu, G., Fang, Z. and Chen, J. 1994a, 'Electrochemical studies on the mechanism of gold dissolution in thiosulfate solutions', *Transactions of Nonferrous Metals Society of China*, vol. 4, no. 1, pp. 50-58.

Zhu, G., Fang, Z. and Chen, J. 1994b, 'Leaching of Gold from Sulphide Concentrates with Thiosulphate Polysulphide Produced by Disproportionation of Elemental Sulphur in Ammoniacal Media', *Hydrometall. '94, Pap. Int. Symp.*, pp. 541-546.

Zipperian, D., Raghavan, S. and Wilson, J.P. 1988, 'Gold and silver extraction by ammoniacal thiosulfate leaching from a rhyolite ore', *Hydrometallurgy*, vol. 19, pp. 361-375.

Zuberbühler, A.D. 1981, 'Interaction of copper(1) complexes with dioxygen', in *Metal ions in biological systems - Properties of copper*, vol. 12, pp. 325-368.

Zuberbühler, A.D. 1983, 'Copper(I), dioxygen, and catalysis', in *Copper coordination chemistry: Biochemical and inorganic prospectives*, Eds. Karlin, K.D. and Zubieta, J., Adenine Press, New York, pp. 237-258.