
School of Engineering and Computing

Department of Civil Engineering

**Gold Leaching in Thiosulfate Solutions and Its
Environmental Effects Compared With Cyanide**

Elsayed A. Oraby

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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature:.....

List of Publications

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Abstract

Nowadays, keeping mining and the environment sustainable is a major concern all over the world. Using toxic chemicals such as cyanide and mercury in the gold leaching process is one of the main factors that need to be considered in terms of the environment. Finding alternative lixivants is one solution that would decrease the uses of these toxic chemicals. Thiosulfate is one of the most promising alternative substitutes to cyanide kinetically and environmentally.

Gold leaching in thiosulfate solutions was evaluated environmentally and kinetically in different ways: (1) applying a closed system to leach gold (2) evaluating the environmental and metallurgical optimum thiosulfate leaching characteristics for pure gold and pure silver and gold silver alloys (4, 8, 20 and 50 wt % silver), (3) studying the electrochemical behavior of gold, silver, and gold/silver alloys (4) optimizing the leaching conditions of gold ore samples supplied from Centamin Egypt Limited Company, (5) finally, studying the ability of thiosulfate solutions to dissolve mercury and evaluating gold, copper, and mercury recovery from ion-exchange resins.

The study showed that the leaching rate of gold and silver in the closed vessel was greater than that obtained in the open vessel by 30% and 45% respectively. To avoid the losses of ammonia a closed leaching system is recommended. Gold and silver leaching in thiosulfate solution is preferable kinetically and environmentally if conducted in a closed vessel system.

The effect silver alloyed with gold was evaluated and the result showed that the dissolution rate of pure gold is higher than that from 4 and 8 wt% Ag alloys. And the dissolution rate of gold from 20 and 50% silver alloys is more than that obtained for pure gold. The silver dissolution rate is sensitive to copper(II) concentration being $1.67 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ at an initial copper(II) concentration of 1.25 mM and $6.6 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ at an initial copper(II) concentration of 10 mM. Silver dissolution is more sensitive to ammonia than gold.

From the electrochemical study on gold/silver alloys, it was found that an increase in silver in the alloy results in an increase of the current density from both gold and silver oxidation in thiosulfate solutions in the range of potentials 0.242-0.542 V. Also, it was found that in thiosulfate solutions containing thiourea, the oxidation current of gold/silver alloys decreased and the oxidation current from pure

gold after the standard potential for gold oxidation (150 mV) is higher than the total oxidation current from gold-silver alloys.

Leaching of a selected gold ore using thiosulfate solutions for 24 hours suggested the optimum conditions to leach the ore to be 0.2 – 0.4 M thiosulfate, 400 mM NH₃, 10 - 20 mM Cu(II), 30 °C, 300 rpm, no air supplied, solid/liquid ratio 20%, and mean particle size of < -106 μm.

Finally, the study showed that mercury dissolves in thiosulfate solutions as it dissolves in cyanide. Mercury dissolves in thiosulfate solutions in the order: HgS₂ < Hg⁰ < Hg₂Cl₂ < HgCl₂. The effect of mercury on gold and copper loading and recovery from resins was evaluated and the results showed that mercury does not influence gold and copper loading and recovery. Also, it was found that mercury elution from the loaded resin is slower than the recovery of gold and copper.

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Chapter 1 Introduction

1.1 Mining and the Environment

Mining by its nature always disturbs the natural air, earth and water systems with the main challenge for the mining industry being to find, extract, and process mineral and metal resources with the least possible disturbance to the environment. The waste product of extracting valuable minerals or metals, known as tailings, may contain hazardous chemicals and dissolved toxic metals. Tailings are produced from the unit extraction processes commonly found in mineral processing (flotation, gravity concentration, amalgamation, leaching, etc.). One of the main sources of pollution from tailings into the air, earth and water is the chemical reagents that are sometimes used extensively to beneficiate the minerals or to extract the metals from the ore.

Chemicals are used extensively in extraction of gold and silver. Traditionally mercury was used and is still used extensively with artisanal extraction while, cyanide is the main chemical used for large scale extraction of these precious metals. These two chemical reagents are classified as highly toxic to humans, and can cause considerable harm to other living organisms and the environment.

This study concentrates on gold processing, which has had wide environmental impacts that have been compounded by the use of mercury and cyanide in the extraction process. The best way to secure the environment from the negative effects of using mercury and cyanide in gold processing is using a less toxic substitute. Alternatives reagents to cyanide are considered with the focus of the research on the most promising, thiosulfate.

1.2 Gold Overview

Gold is classified as a noble metal because it does not easily oxidise under normal conditions. Its chemical symbol “Au” is derived from the Latin word for gold “aurum”. The average concentration of gold in the earth’s crust is about 0.005 g/t, which is lower than most of other metals such as silver (0.07 g/t) and copper (50 g/t) (Marsden & House, 2006).

Gold ores may contain different amounts of silver, copper, nickel, arsenic, antimony, mercury, thallium, sulfur, base metal sulfides, other precious metals, and sulfosalts. The amount of these constituents depends on the nature of the deposit and the amount of weathering that has occurred. Consequent alteration of the ore by oxidation influences both gold recovery and dissolution of the other gangue minerals (EPA, 1994).

Gold readily forms alloys with many other metals. Native gold contains generally 8 to 10% silver, but can contain over 20% silver. Gold containing more than 20% silver is known as electrum. As the silver percent in gold increased, the gold colour turns whiter and its density gets lower (Cryssoulis & McMullen, 2005).

Many countries around the world produce gold. South Africa is the highest gold producing country followed by Australia and the United States in third position as shown in Figure 1.1.

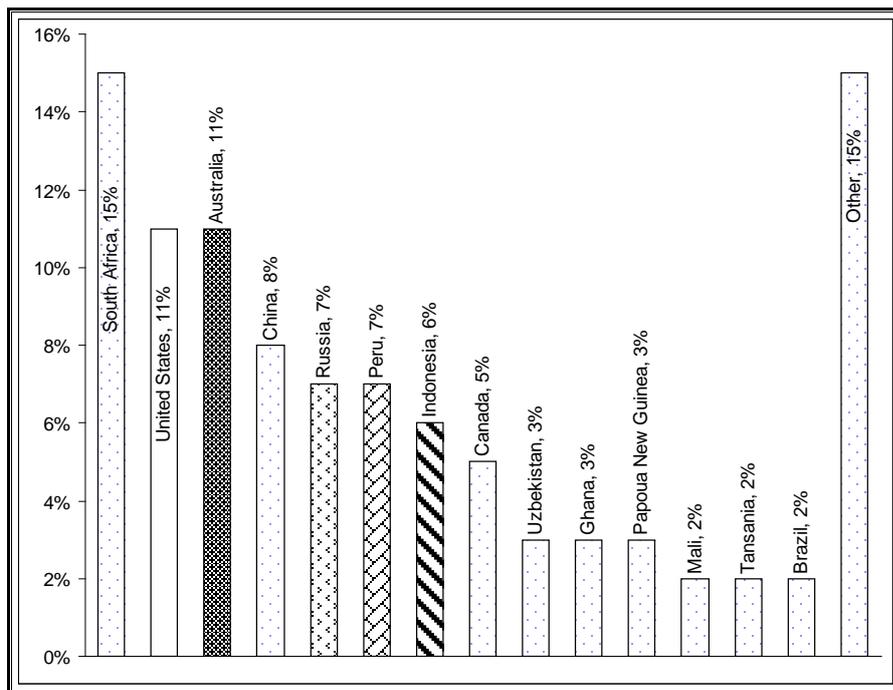


Figure 1.1: The estimated gold mine production by country in 2003 (Gold Fields Mineral Services Ltd, 2004).

1.2.1 Gold Properties

The density of pure gold is around $19,300 \text{ kg/m}^3$, though native gold typically has a density of $15,000 \text{ kg/m}^3$. Gold is very soft, ductile, and malleable (1 oz of gold can be beaten into an area of 30 cm^2) with Vickers and Mohs hardness numbers of 40

to 95 kg/mm² and 2.5 to 3, respectively (Marsden & House, 2006). Pure gold is an excellent electrical and thermal conductor. The melting and boiling points of gold are 1064 °C and 2808 °C, respectively. Some other properties of gold are listed in Table 1.1.

Table 1.1: Some physical and mechanical properties of gold (Marsden & House, 2006).

Property	Value
Atomic weight	196.97
Melting point (°C)	1064 °C
Boiling point (°C)	2808 °C
Atomic radius, nm	0.1422
Density at 273 K (g/cm ³)	19.32
Tensile strength (MPa)	123.6 – 137.3
Elongation (annealed at 573 K) (%)	34-45
Vapour pressure (Pa)	
At 1000 (K)	5.5 x 10 ⁻⁸
At 2000 (K)	82 x 10 ⁻⁸
Thermal conductivity at 273 K (W/m.K)	311.4
Electrical resistivity at 273 K (Ω. cm)	2.05 x 10 ⁻⁵

1.2.2 Gold Minerals and Ores

There are many different gold minerals found in the Earth's crust such as native gold, electrum, gold tellurides, gold with bismuth (maldonite), and gold with copper (auricupride and tetra-auricupride). The gold minerals are associated with oxide and/or sulfide minerals (arsenopyrite, pyrite, tetrahedrite, and chalcopyrite) forming gold ore. A comprehensive classification of gold ores with respect to the ease of gold extraction using cyanide (cyanidation) was given by Marsden and House (2006) as presented below:

1. **Free milling ores:** from which cyanidation can extract approximately 95% of the gold when the ore is ground to a size of 80% <75 μm. The two main classes of free milling ores are palaeoplacer and quartz vein gold.

2. **Oxidised ores:** the ore material has been oxidised or weathered in these ores. Generally the degree of gold liberation is increased by oxidation. The most common of these ores are the iron oxides such as hematite, magnetite, goethite, and limonite.
3. **Iron sulfides:** gold is principally unliberated in an iron sulfide matrix, or the behaviour of the iron sulfide affects process selection or operation conditions. The most common iron sulfide minerals are pyrite, marcasite, and pyrrhotite.
4. **Arsenic sulfides:** gold ores should be considered in this class if the gold is associated with an arsenic sulfide or arsenide matrix. The most common arsenic minerals are arsenopyrite, orpiment, and realgar.
5. **Copper sulfides:** ores containing gold associated with copper sulfide minerals that affect process selection or operating conditions are considered in this class. It is relatively uncommon for gold to be associated solely with copper minerals, and there is usually some pyrite present. Chalcopyrite is the most abundant copper mineral. Chalcosite and covellite also are important copper ore minerals.
6. **Tellurides:** are the only gold minerals other than metallic gold and gold-silver alloys that are of economic significance. The most important tellurides encountered in gold ores are calverite, petzite, hessite, krennerite, and maldonite. Gold telluride ores usually contain some native gold, together with metal tellurides.
7. **Carbonaceous ores:** these gold ores contain carbonaceous components that adsorb dissolved gold during cyanidation, thereby reducing gold extraction. These gold ores sometimes require oxidative pre-treatment prior to cyanide leaching.

1.2.3 Uses of Gold

Most corrosive agents such as heat, moisture, and oxygen have very little alteration effects on gold, making it as ideal metal to use in coins and jewellery. Gold is also used in jewellery due to its beauty, properties, and rarity. Gold has a long history of use as money or as a reserve backing for other forms of money, but that role is shrinking as gold is gradually being demonetized in the industrial nations.

Gold also has special combinations of physical and chemical properties (Table 1.1) that make it a very good material for use in a wide range of electronic conductors and semi-conductors, and medical applications. Figure 1.2 shows the different uses gold is put to around the world. It is clear from Figure 1.2 that decoration and jewellery use is the major use (with 66% consumption) followed by bar hoarding which consumes 19% of gold.

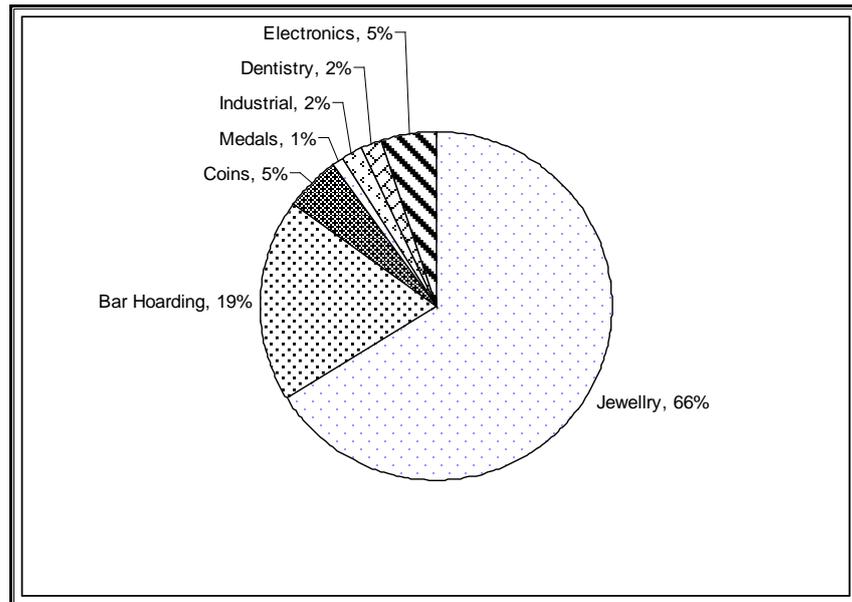


Figure 1.2: The distribution of gold uses (Marsden & House, 2006).

1.3 Gold Mining and the Environment

Although gold mining is one of the main sources of income for many countries, it can have a significant detrimental impact on the environment. Large amounts of toxic chemicals such as mercury and cyanide are used to extract gold from its ore. Based on recent knowledge of toxicity principles and updated environmental standards, the activity of the mines that use mercury and cyanide needs to be carefully regulated. Small-scale producers widely use the historic amalgamation technique. This technique creates mercury vapour emissions as well as liquid and solid wastes with toxic constituents (Müezzinoğlu, 2003).

Cyanidation is the most widely used method to extract gold from its ore, because of its relatively low cost and selective efficiency gold dissolution. The main disadvantage of using cyanide is its detrimental environmental impacts on soil, surface and underground water (tailing and drainage water), and air (hydrogen cyanide emission). The following section notes, in brief, some of the alternative reagents to cyanide.

1.4 Alternatives to Cyanide

For more than 100 years, cyanide has been the leaching reagent of choice in gold mining due to its high efficiency in gold recovery, stability, simplicity of use,

and relatively low cost. On the other hand, cyanide can have wide detrimental environmental impacts. Thus, several other chemical reagents had been considered for gold extraction from ores, not only to lessen the environmental impacts and overcome the restrictions to the use of cyanide, but also for other reasons including: 1) potential of having faster gold leaching kinetics than cyanide, 2) possibility of their use in acidic media, which is suitable in the treatment of refractory ores, and 3) a greater degree of selectivity than cyanide for gold over other metals (Navarro et al., 2007).

Unfortunately, most cyanide alternatives have not progressed past the laboratory or pilot plant scale. To select a gold lixiviant for gold leaching, economics, efficiency, and environmental concerns should all be considered (Gos & Rubo, 2000). In recent years, many scientists aimed to identify and develop less toxic leaching reagents. Only a few ligands form gold complexes of sufficient stability and at a suitable rate for their use in gold leaching operations. Alternatives to sodium cyanide are summarised by McNulty (2001) in Table 1.2.

Table 1.2: Most of the alternatives to sodium cyanide (McNulty, 2001).

Reagent type	Reagent type
1. Ammonia	14. Bisulfate/sulphur dioxide
2. Ammonia/cyanide	15. Bacteria
3. Ammonium thiosulfate	16. Natural organic acids
4. Slurry CN-electrolysis	17. DMSO, DMF
5. Sodium sulphide	18. Bromine/bromide
6. Alpha-hydroxynitriles	19. Thiourea
7. Malononitrile	20. Thiocyanate
8. Alkali cyanoforn	21. Aqua regia
9. Calcium cyanide	22. Acid ferric chloride
10. Alkaline polysulphides	23. Ethylene thiourea
11. Hypochlorite/chloride	24. Haber process
12. Bromocyanide	25. High temperature chlorination
13. Iodine	

1.5 Objectives of the Study

The main challenge in producing a suitable substitute for cyanide in gold processing, lies in developing an equally effective and degradable leach reagent, which at the same time, has less environmental impacts. One of the alternative systems to cyanide that may achieve the environmental and gold leaching rate objectives is the thiosulfate system. The optimum conditions for leaching gold using the thiosulfate system are not clearly defined as there are a wide range of variables that impact on the thiosulfate leaching system for gold. One of the variables that limited research is the effect of silver on gold leaching rates in thiosulfate solutions. Therefore the objectives of this project are to:

- (1) optimise gold and silver using thiosulfate solutions in both closed and open vessels;
- (2) evaluate the metallurgical optimum thiosulfate leaching characteristics for pure gold, pure silver and gold-silver alloys (4, 8, 20 and 50 wt% silver) in both closed and open vessels;
- (3) study the electrochemical nature of thiosulfate leaching using gold, silver, and gold-silver alloys with linear sweep voltammetry and coulometric electrochemical techniques at fixed potential values;
- (4) optimise the thiosulfate leaching of gold ore samples supplied from the Centamin Egypt Limited Company; and
- (5) study the possibility of mercury dissolution in different thiosulfate and cyanide solutions and the recovery of gold from ion-exchange resins in the presence of mercury.

A flowchart of the goals and procedures of this project is presented in Figures 1.3a and 1.3b.

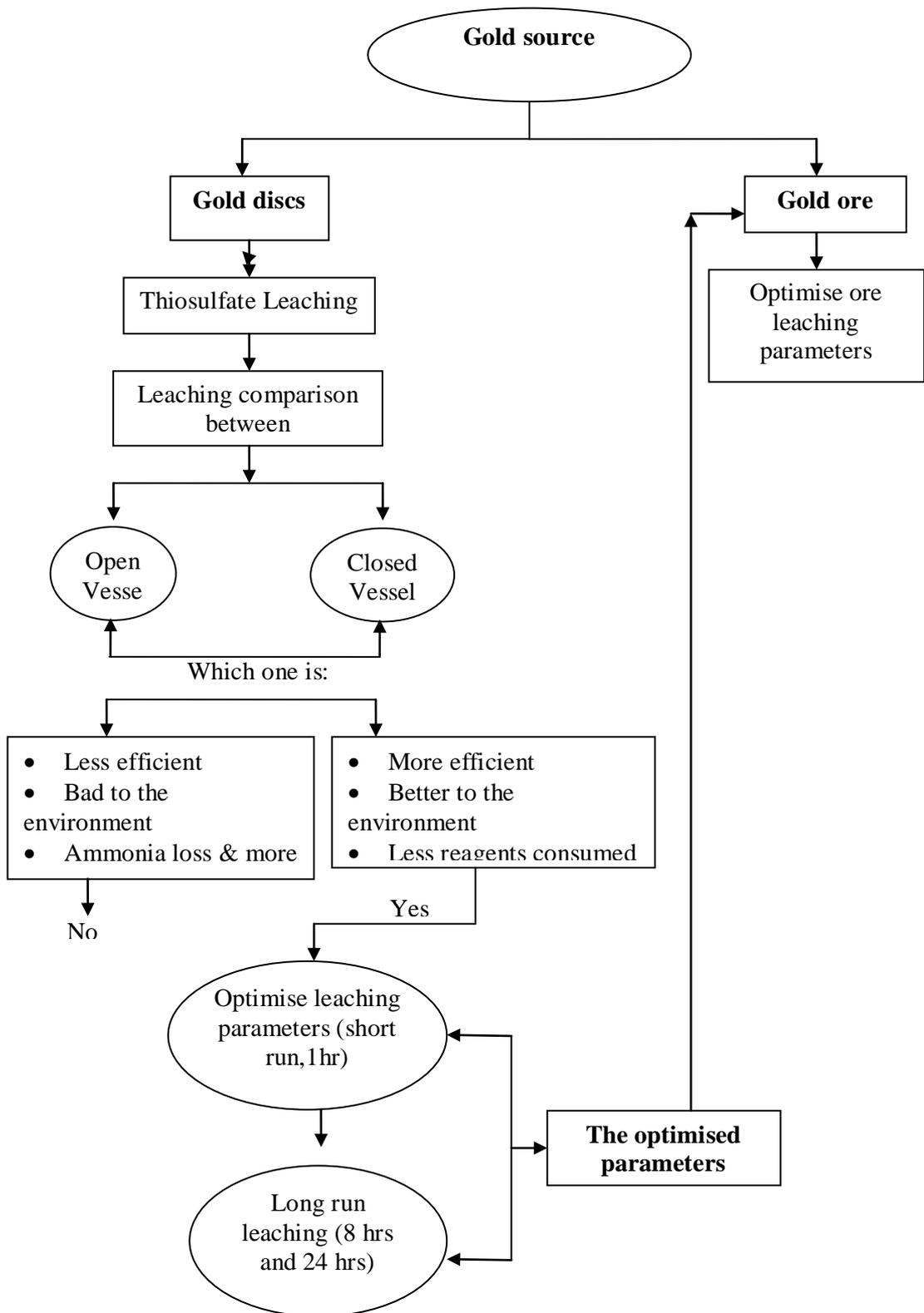


Figure 1.3a: Flowchart of the goals and procedures of the project (part I).

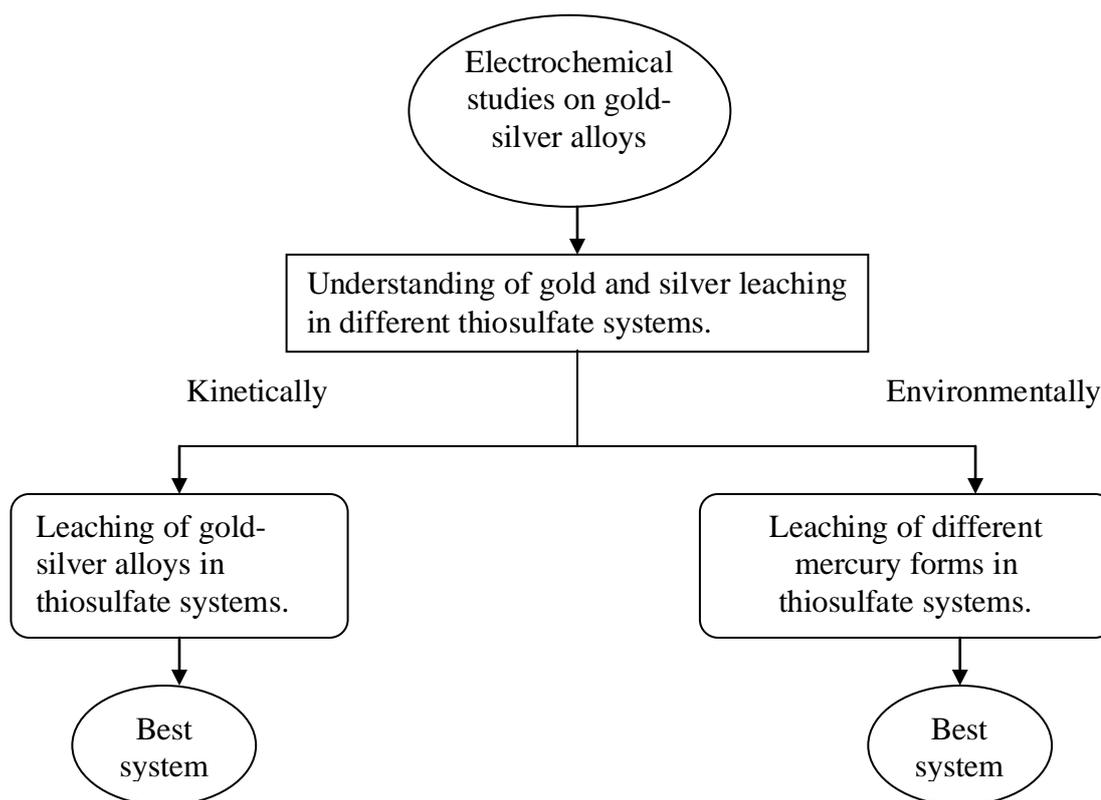


Figure 1.3b: Flowchart of the goals and procedures of the project (part II).

1.6 Methodology of the Study

The methodology used in this study was:

- review previous published work on the environmental impacts of mercury and cyanide in the gold mining industry;
- review previous work related to the application of the thiosulfate leaching system to gold leaching;
- apply the thiosulfate leaching system to pure gold and pure silver discs and gold-silver alloy discs (4, 8, 20, 50 wt% silver) in open and closed vessels;
- evaluate the variables that affect thiosulfate leaching by testing the dissolution of pure gold and pure silver discs and a range of gold and silver alloy discs (4, 8, 20, 50 wt.% silver) in open and closed vessels;
- study through electrochemical methods the effects of the different reagents, additives and electrolytes on the dissolution of the gold, silver and gold-silver alloys;
- evaluate the variables that affect thiosulfate leaching of gold ore samples using a rotating disc electrode technique; and

- evaluate the dissolution of different mercury forms in different thiosulfate and cyanide solutions.

1.7 Thesis Organization

This thesis consists of nine chapters as follows:

- **Chapter 1** is an introduction which presents a general overview on gold, notes some cyanide alternatives and summarises the objectives of this work;
- **Chapter 2** is a literature review of the environmental impacts of using mercury and cyanide in gold processing;
- **Chapter 3** is a review of the use of thiosulfate for gold leaching and this provides the present state of advancement and understanding of the thiosulfate leaching system;
- **Chapter 4** presents the methodology and materials that have been used in this study;
- **Chapter 5** presents and discusses the results of experiments that were conducted on pure gold and gold-silver alloys to evaluate open and closed leach vessels;
- **Chapter 6** is the results and discussion of electrochemical experiments applying linear sweep voltammetry and coulometry on pure gold and gold-silver alloys to provide a better understanding of the thiosulfate leaching system;
- **Chapter 7** applies the optimum leaching reagent concentrations that were determined from Chapter 5 to the leaching of gold ores from Sukari Gold Mine;
- **Chapter 8** looks at the dissolution of mercury in different thiosulfate systems and the cyanide system;
- **Chapter 9** is the conclusions and recommendations derived from this work; and
- **Chapter 10** is the references for this work.

Chapter 2 Environmental Impacts of Gold Mining: Literature

Review

2.1 Introduction

Generally, the gold mining industry has a negative environmental image due to its historically high polluting rates in soil, water, and air. The major environmental problems caused by gold mining include: 1) acid mine drainage, 2) noise, 3) dust, and 4) air and water pollution from toxic chemicals such as arsenic, cyanide, and mercury.

Gold mining forms a significant part of the economic system in many countries but, on the other hand, it can have wide environmental impacts to many sections of the ecosystem. Non toxic gas emissions alter the normal constitutions of air, while many toxic gas emissions have highly hazardous effects on human health. The Pan American Health Organization (PAHO) reported that the gold mining industry is frankly responsible for the high levels of air and water pollution and health problems in Latin America and the Caribbean (Gatti, 2004).

Gold mining begins by extracting the ore from the earth. Often to access the ore large amounts of waste rock needs to be removed. The volume of waste rock and ore mined continues to increase, especially as open cut mining methods expand.

The ore is generally processed by cyanidation to remove the gold. Recently, there has been growing arguments in many countries on the extensive use of cyanide for gold leaching (McNulty, 2001). Many attempts have been made to find a more environmentally friendly alternative.

The tailings that remain after cyanidation are usually deposited in a tailings storage facility. The tailings contain toxic chemicals used in the gold extraction process and heavy metals coextracted from the ore with gold. Waste rock movement and tailings management need to be under tight control in most gold mines (Mudd, 2007).

Two highly toxic chemical reagents that are used widely in gold processing are mercury and cyanide. In the following sections the environmental impacts of using mercury and cyanide in gold processing will be reviewed.

2.2 Environmental Impacts of Mercury in Gold mining

2.2.1 Introduction

Mercury is widely considered to be one of the most serious environmental pollutants. It is a hazardous metal that has represented in the last decades a serious source of environmental contamination and human toxicity in numerous locations around the world.

As mercury has the property to adhere with metallic gold and silver forming amalgams, this characteristic of mercury has been utilised as an effective technique to concentrate and extract gold and silver from ores. The amalgamation method was used on a large scale until the beginning of the twentieth century when it declined due to the exhaustion of silver reserves in Colonial South and Central America and later due to the invention of cyanidation. Unfortunately, recently, due to economic and social factors in most of the developing countries located in the tropics, a new rush for gold by individual miners, for whom mercury amalgamation is a cheap, easy and reliable extraction process (Valenzuela & Fytas, 2002) has began.

2.2.2 Mercury Overview

Mercury is a natural component of the earth, with significant local variations and an average abundance of approximately 0.05 mg/kg in the Earth's crust. Elemental mercury also is known as Quicksilver (symbol Hg for hydrargyrum). Mercury is considered as one of the most hazardous chemicals that impacts upon the global environment. It is among the best known and most poisonous metals in the environment which causes serious human health problems; even death due to inhalation of vapour and ingestion of contaminated food has been reported.

Mercury occurs in different forms:

- elemental or metallic mercury;
- inorganic mercury compounds; and
- organic mercury compounds (Eisler, 2006).

2.2.3 History of Mercury

Mercury was known to the ancient Chinese and Hindus, and has been discovered in Egyptian tombs that date from 1500 BC (Eisler, 2006). The use of

mercury in the extraction of gold by the amalgamation technique has been used for more than 4500 years (Malm, 1998).

The main source of mercury, cinnabar (mercuric sulfide), has been mined since 415 BC. In the 1800s, mercury was used in medical and electrical instruments, and since 1900, it has been used in pharmaceuticals, in agricultural fungicides and the production of plastics. During the Spanish colonial period of South America (mainly Mexico, Peru, and Bolivia), mercury was widely used for silver and gold recovery (Clarkson & Marsh, 1982). Over 260,000 metric tons of mercury was emitted into the environment in the period from 1550 to 1930. After this period, the mercury amalgamation process was not efficient to treat the remaining low grade ores. The amalgamation extraction process was replaced partially by the cyanidation process (UNEP, 2003).

The world production of mercury decreased from 7100 to 1800 metric tons in the period from 1980 to 2000. Table 2.1 shows the decline of mercury production from the year 1981 to the year 2000.

Table 2.1: Maximum and minimum recorded global primary production of mercury since 1981, metric tons/year (UNEP, 2003).

Period	1981-1985	1986-1989	1990-1995	1996	1997	1998	1999	2000
annual, mercury production (in metric tons)	5500-7100	4900-6700	3300-6100	2600-2800	2500-2900	2000-2800	2100-2200	1800

2.2.4 Occurrence

The main source of atmospheric mercury is natural from volcanic eruptions and ocean emissions (USGS, 2000). In addition to natural sources, mercury is released into the air and water by human activities such as small-scale gold mining (using amalgamation), coal-fired power plants, cement kilns, medical incinerators, and other industries. The most important primary mercury minerals are cinnabar (HgS) and its polymorph metacinnabar (HgS) and livingstonite (HgSb₄S₇). Native

mercury (Hg^0) is, by comparison, relatively rare in primary deposits but is found more commonly in oxidation zones of such deposits (Valenzuela & Fytas, 2002).

2.2.5 Mercury Properties

Mercury exist in a large number of physical and chemical forms with a wide range of physical, chemical, and eco-toxicological properties (Ebinghaus et al., 1999). Mercury is a silver-white metal that is liquid at room temperature and highly volatile. It exists in three oxidation states: elementary mercury (Hg^0), mercurous ion (Hg_2^{2+}), and mercuric ion (Hg^{2+}). It can form both inorganic and organic compounds (USEPA, 1980). The mercuric species are the most toxic inorganic chemical form, but all three forms of inorganic mercury may have a common molecular mechanism of damage in which Hg^{2+} is the toxic species (Clarkson & Marsh, 1982).

The physical properties of mercury are summarised in Table 2.2. Mercury freezes at about $-39\text{ }^\circ\text{C}$ and when heated, the metal expands uniformly; boiling at $357\text{ }^\circ\text{C}$ at 760 mmHg, and has a vapour pressure of 0.0018 mmHg at $25\text{ }^\circ\text{C}$. Mercury vapour is colourless.

Table 2.2: Summary of the physical properties of mercury (Robert, 1967).

Property	Value
Melting point, $^\circ\text{C}$	39
Boiling point, $^\circ\text{C}$	357
Specific gravity	13.54 at $22\text{ }^\circ\text{C}$
Density, g/mL	13.55
Vapour pressure, mmHg	0.0018 at $25\text{ }^\circ\text{C}$
Relative vapour density (Air =1)	7.0
Heat of vaporization, J/g	295.6

2.2.6 Mercury Uses

Mercury is the only metal that is found in a liquid form at room temperature and atmospheric pressure. The following unique characteristics of mercury make mercury useful in a large number of applications and processes:

- being liquid at room temperature;
- a good electrical conductor;
- having very high density and high surface tension;

- expanding/contracting uniformly over its entire liquid range in response to changes in pressure and temperature; and
- being toxic to micro-organisms (including pathogenic organisms) and other pests (UNEP, 2003).

The world usage of mercury in recent years is estimated at 10,000 to 15,000 metric tons annually; major producers of mercury now include the former Soviet Union, Spain, the former Yugoslavia, and Italy (Eisler, 2006). As noted in section 2.2.3 the primary production of mercury was 1800 metric tones, hence a large percentage of usage is through recycling. Table 2.3 shows the application of mercury in different industries. Mercury is used widely in gold and silver processing as well as in many medical and electrical applications.

Table 2.3: Some examples of mercury uses in different industry applications (UNEP, 2003).

Examples of mercury uses
As a metal (among others):
<ul style="list-style-type: none">• for extraction of gold and silver (for centuries)• as a catalyst for chlor-alkali production• in manometers for measuring and controlling pressure• in thermometers• in electrical and electronic switches• in fluorescent lamps• in dental amalgam fillings
As chemical compounds (among others):
<ul style="list-style-type: none">• in batteries (as a dioxide)• biocides in paper industry, paints and on seed grain• as antiseptics in pharmaceuticals• laboratory analyses reactants• catalysts• pigments and dyes• detergents• explosives

2.2.7 Mercury Toxicity and Standards

Mercury and its compounds are very toxic and must be handled with care and under controlled conditions. Persons working with mercury should be monitored regularly (EPA, 2007). Toxicologically, there are three forms of mercury (Eisler, 2006): (1) elemental mercury; (2) inorganic mercury compounds; and (3) organomercurials.

The TLV value for metallic mercury in Germany is 0.1 mg/m^3 (0.01 ppm) and for mercury vapour, the TLV value is 0.05 mg/m^3 . In 1994, the American Conference of Governmental Industrial Hygienists (ACGIH) decreased the threshold limit value (TLV) from 0.05 mg/m^3 as a Time Weighted Average (TWA) for 10h/day to 0.025 mg/m^3 as an 8h/day exposure or 40h/week time weighed average (ACGIH, 1997).

The odour threshold for mercury is 13 mg/m^3 . With metallic mercury, inorganic mercury compounds, and organic non-alkyl mercury compounds, mercury values in urine should not exceed 150 mg/L and blood levels should be less than 35 mg/L. With organic alkyl mercury compounds, the maximum allowable blood level is 75 mg/L. Acute poisoning occurs when mercury ion concentrations reach 0.2 mg per 100 mL of blood. Daily 5h exposure to inhaled mercury vapour concentrations of 0.1 mg/m^3 leads to severe mercury poisoning (Simons et al., 1997).

2.2.8 Mercury Effects on Human Health

The World Health Organization (WHO, 1976) reported that acute exposure, 4-8 hours, to the calculated elemental mercury levels of 1.1 to 4.4 mg/m^3 result in chest pain, dyspnea, cough, hemoptysis, and impairment of pulmonary function. Furthermore, WHO indicated that acute exposure to mercury vapour results in profound central nervous system effects, including psychotic reactions characterized by delirium, hallucinations, and suicidal tendency. Mercury poisoning is manifested in various neuromuscular malfunctions ranging from numbing of the extremities to the loss of eye sight, paralysis, and even death (Barkay, 1992; WHO, 1990 & 1976)

The first case of fatal inorganic mercury poisoning in humans was reported in 1865 with two men exposed in a European chemical laboratory, and the first documented human poisoning from agricultural exposure to an organo-mercury compound was reported in 1940 (Das et al., 1982).

Mercury species differ greatly in their properties, however they are all toxic. Elemental mercury (Hg^0) volatilizes readily, emitting mercury vapour, which is readily absorbed in the lungs; however, elemental mercury is very poorly absorbed through the skin or gastrointestinal (GI) tract. Inorganic mercurial salts (Hg^+ and Hg^{2+}) have a wide range in solubility and absorptive properties. All mercury compounds are toxic to humans and animals, but the organic forms, in particular methylmercury and dimethylmercury, have the highest toxicity. Methylmercury is the form found most widely in nature where it bio-accumulates in the food chain. It is the form to which most human exposure occurs (Gochfeld, 2003).

2.2.9 Mercury Releases to the Environment

Mercury is a widely spread pollutant due to its unique characteristics such as low melting and boiling points, conversion between chemical forms and participation in biological cycles. The pre-industrial deposition rate of mercury from the atmosphere was approximately 4 ng/L in the western USA. The atmospheric mercury value can be increased by 4-6 times during volcanic eruptions (USGS, 2000). The global atmospheric mercury emissions rate is now nearly three times higher than in pre-industrial times and has increased by a factor of 2-10 in and around most industrialised regions (Lamborg et al., 2002; Bergan et al., 1999; Meili, 1995).

A study by Horvat et al. (2002) found that for every gram of gold produced by amalgamation around 1.2 to 1.5 grams of mercury are lost to the environment. Nearly 20% of the mercury is lost to tailings, soils, stream sediments and water with 70.8% emitted into the atmosphere.

In 1995, approximately 1900 metric tons of mercury entered the atmosphere, most of it (about 75%) from the combustion of fossil fuels (Pacyna & Pocyina, 2002). Mercury enters the environment as a pollutant from various industries (EPA, 2007) including:

- coal-fired power plants are the largest aggregate source (40% of USA emissions in 1999);
- large gold mines - the three largest point sources for mercury emissions in the US are the three largest gold mines;
- gas fired power plants fueled with gas from mercury prone reservoirs where the mercury has not been removed;
- small-scale gold mining;

- industrial processes;
- medical applications, including vaccinations; and
- laboratory work involving mercury compounds.

Before the cyanidation process replaced the amalgamation process, gold and silver mines using mercury were one of the major sources of mercury emission to the environment. In addition, mercury can be released to the environment during the recovery of precious metals from deposits that contain mercury as a minor component, including volcanogenic massive sulfide and sedimentary exhalative deposits (Shaw et al., 2006; Lacerda & Marins, 1997; Lacerda, 1997; Nriagu, 1993). Figure 2.1 shows the different pathway of mercury emissions into the atmosphere from gold and silver mining.

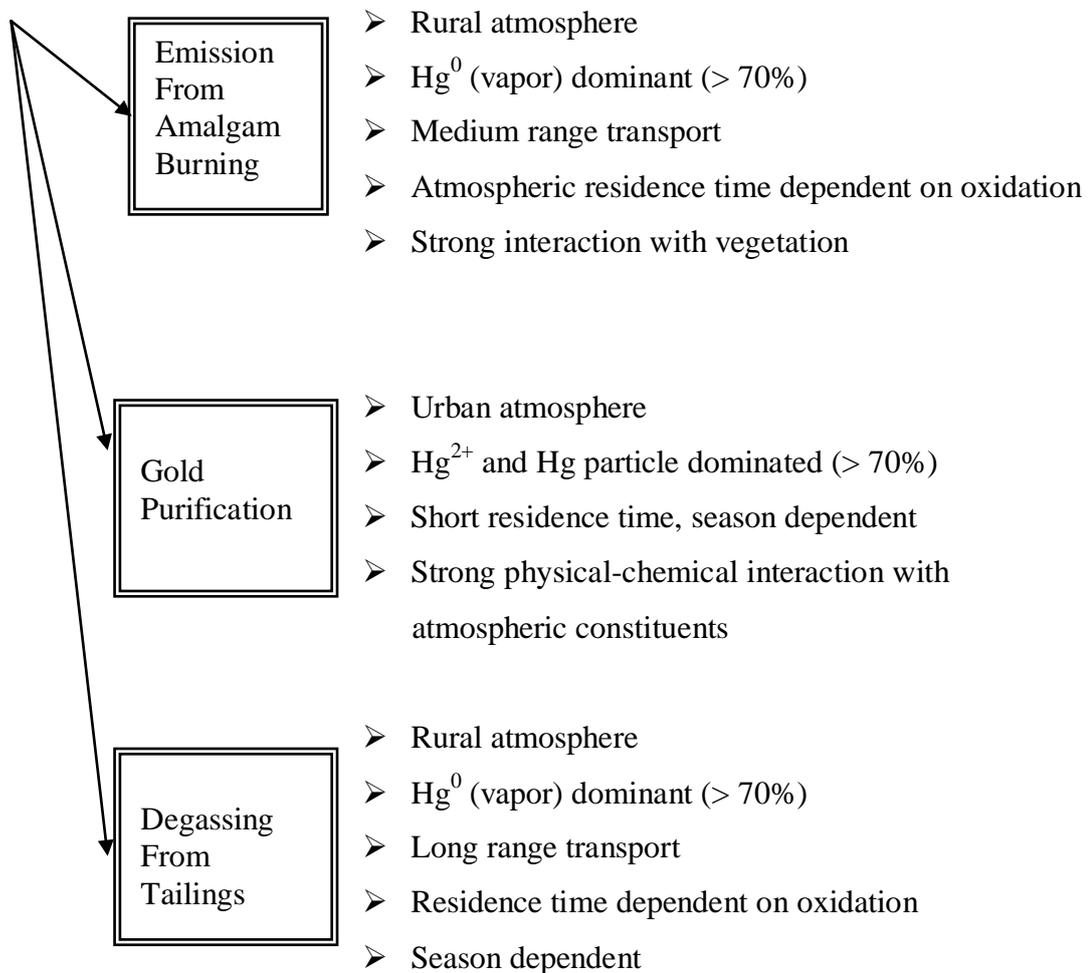


Figure 2.1: Atmospheric mercury pathways in areas of gold and silver mining (de Lacerda & Salomons, 1998).

2.2.10 The Principle of the Amalgamation Process

Amalgamation is the main gold extraction technique used in small scale gold mines. In general, gold processing requires a method to separate gold from the impurities in the ore. This can be achieved by mixing metallic mercury with the ore, which has a high affinity for gold, forming a gold-mercury amalgam. The amalgam is separated from barren ore residue and heated in a process called burning. This heats up the amalgam driving off the mercury as vapour, leaving gold metal.

A variation on amalgamation of gold, as an alternative to the ancient sheepskin collection and water shaking methods, was developed by the Roman. In this method sands or ground ores containing gold were mixed with metallic mercury to produce gold amalgam and the mixture was put into leather bags. Amalgam would leak out of the bag and residual solids would be retained inside. By distillation of the amalgam, mercury would be condensed for recycling and gold was recovered (Müezzinoğlu, 2003).

Donoghue (1998) summarised the process of amalgamation for gravity gold on a medium scale by the following sequence of steps:

1. the mining of placer gold is undertaken by hydraulic excavators which extract river bed gravel;
2. the gold-bearing gravel is delivered to a processing plant where the fine gold bearing material is separated by rotary screens and vibrating tables. It is then examined closely so that free gold particles can be collected;
3. the remaining gold-bearing sands are mixed with metallic mercury in barrels to extract the gold in the form of a mercury-gold amalgam;
4. after washing in water to remove any remaining sand, the amalgam is placed in a sealed retort and heated until the mercury has been evaporated off, condensed, and collected under water; and
5. the remaining gold along with free gold obtained at the tabling stage is then placed in a crucible, smelted on a furnace and cast into ingots.

2.2.11 Mercury and Gold mining

Numerous small-scale miners all over the world use mercury to extract gold and silver. The environmental impacts of mercury affect not only the mine and workers, but also on the surrounding environment. Any mercury released into the

environment circulates through the ecosystem where it can bio-accumulate and stay active.

Starting from the 16th century, Hg amalgamation was the major technique used for the mining of precious metals (de Lacerda & Salomons, 1998). Around one million tons of metallic mercury has been extracted from cinnabar and other ores during the past five centuries. About half of this amount has been used for mining of gold and silver (Hylander & Meili, 2003). Many studies report that most of the mercury released to the environment is generally associated with mercury mining and precious metal mines that utilises amalgamation methods (da Costa et al., 2007; Shaw et al., 2006; Valenzuela & Fytas, 2002; Malm, 1998; Salomons, 1998; Malm et al., 1995; Salomons, 1995).

Telmer (2006) reported that about 15 million small-scale gold miners around the world use mercury to trap fine particles of gold. The inefficient recovery of mercury amalgam and excess free mercury and the release of fugitive mercury vapours during burning release mercury into the environment.

About 1,000 tons of mercury are released into the environment each year, affecting up to 100 million people. In 1995, China produced 105 tons of gold, about one third of which was from small-scale mines (alluvial ore, rock ore, and coexisting ore). The small gold mines usually extracted gold with mercury amalgamation (Lin et al., 1997). Haygrath and Jones (1992) reported that burning of mercury amalgam or purification of the extracted precious metal bullion may produce various mercury species such as Hg vapour (Hg^0), HgO , and Hg^{2+} , and Hg adhered or condensed onto solid particles. The areas near to gold mines may be contaminated with at least two forms of mercury, inorganic mercury, and methylmercury (Me.Hg) (Horvat et al., 2002).

For large scale operation using cyanidation, the loss of mercury from gold mining tailings to the surrounding environment is thought (Shaw et al., 2006) to occur through two main processes:

1. leaching of soluble Hg to the groundwater in the form of Hg-CN complexes; and
2. diffusion of Hg gas (Hg^0) to the atmosphere.

2.2.11.1 Environmental Problems of using Mercury in Gold mining

Environmental problems caused by the utilization of mercury in gold and silver mining have been reported since Roman times. Around 77 A.D, Roman

authorities were importing 5000 kg/year of mercury from Spain to be used in gold amalgamation in Italy (de Lacerda & Salomons, 1998).

One of the main problems of using mercury is that it is continuously present in the environment. A study conducted by Lacerda (1997) found that most of the mercury released to the atmosphere through gold and silver mining during the last 500 years may still participate in the mercury cycle through re-mobilization from abandoned tailings and other contaminated areas. Wong et al. (2002) studied the toxicity of metals from abandoned gold mine tailings at Goldenville, Nova Scotia, Canada where large quantities of mercury were used in the gold recovery process. There are around 3 million tons of tailings left from the mining processing. The results showed that these tailings may contain up to 6.8 tons of mercury and there is a continuous emission of mercury and other metals from the tailing field which causes contamination of the surrounding environment.

Ikingura et al. (1997) studied the environmental impacts of using mercury in gold extraction in Tanzania and reported elevated mercury concentrations in environmental samples from the mining areas and average mercury concentrations in river sediments and soils of 4.19 $\mu\text{g/L}$ and 3.39 $\mu\text{g/g}$ respectively. Another study carried out by García-Sánchez et al. (2006) showed that the soil, mud, and waste rock samples from gold mining areas where mercury is used in El Callao (Venezuela), have high concentrations of mercury (around 0.5-500 $\mu\text{g/g}$). This concentration is very high if compared with the normal mercury concentrations ($<0.1 \mu\text{g/g}$). In the areas around the Murray Brook gold deposit, located in northern New Brunswick, Canada, high mercury levels have been detected in the ground water (11,500 $\mu\text{g/L}$) and 32 $\mu\text{g/L}$ in the surface water (Shaw et al., 2006). In Brazil, the major source of mercury pollution is gold mining and average mercury emissions are 77.9 ton per year. The mercury emissions are more concentrated in the Amazon region with an approximate concentration of 16 g/km^2 (Lacerda & Marins, 1997).

In the Philippines, the effect of mercury in areas around an abandoned gold mine located southeast of Manila proved disastrous with around 1 million tons of tailings dumped into Honda Bay where about 2000 inhabitants live (Maramba et al., 2006). High concentrations of total mercury were detected at locations with extensive small-scale gold mining activities. All water mercury concentrations from the sampling sites were higher than the WHO limit of 0.001 mg/L for drinking water.

- **Problems of Mercury in the Cyanidation Process**

The cyanidation process (section 3.4) uses cyanide to dissolve gold and silver from the ore. The soluble gold cyanide complex is adsorbed onto activated carbon to remove it from the ore slurry. Elution with sodium hydroxide and sodium cyanide strips the gold cyanide complex from the activated carbon allowing electrowinning to recover crude gold metal. The crude gold is upgraded by smelting. The eluted activated carbon is regenerated by heating to about 700°C and reused.

During the cyanidation process, cyanide also leaches mercury and some other metals present in the mined ore, including Co, Fe, Ni and Zn (Shaw et al., 2006; Smith & Mudder, 1991). Mercury cyanide complexes are adsorbed on activated carbon along with gold and silver and other metal complexes. Mercury is then recovered at the same time with the gold and silver in the elution circuit and consequently electrowinning. Mercury contained in the electrowinning sludge can present both environmental and industrial problems (Washburn & Hilldoi, 2003) when the sludge is heated during smelting. Mercury left on the activated carbon is vapourised to the atmosphere during the carbon regeneration.

An alternative to the carbon adsorption process is to filter the ore from the solution and precipitate gold by using zinc metal (Merrill-Crowe process). As mercury is also precipitated with gold and silver it reports to the smelting furnace and causes processing, occupational health and safety and environmental concerns.

2.3 Environmental Impacts of Cyanide

2.3.1 Introduction

Cyanide was first applied commercially in New Zealand over a century ago in the extraction and recovery of gold and silver. Although cyanide has determinable toxicological effects, it has a wide application in many different fields. There is much public concern about the use and toxicity of cyanide around the world. Some countries such as the Czech Republic, and Turkey, and some states in the USA, such as Colorado, Wisconsin, and Montana have campaigned to ban cyanide in mineral processing applications (Arima et al., 2004; Anonymous, 2000; De Voto & McNulty, 2000).

Most of the hydrogen cyanide emitted into the atmosphere stays in the lower troposphere. Environmental monitoring of free cyanide (FCN), weak acid dissociable

cyanide (WAD) and total cyanide levels in the environment is required in all the mines that utilise cyanide (Cicerone & Zellner, 1983).

The environmental degradation of hydrogen cyanide from surface waters usually occurs through volatilization, biodegradation, hydrolysis, and sorption. Volatilization and sorption are the two main physical processes that remove cyanide from surface waters. Volatilization rates of hydrogen cyanide are dependent upon pH (at lower pH, HCN emission rate is higher) and aeration. The pH should be controlled because if the pH of the solution is <9.2, most of the free cyanide in the solution exists as hydrogen cyanide. The most common cyanide salts (sodium and potassium cyanide) may be lost from surface water through volatilization; whereas, the soluble metal cyanides (copper, nickel, zinc) are removed from water mostly by sedimentation and biodegradation (USEPA, 1992).

Oxidation and decay compounds derived from cyanide such as cyanate, cyanogen chloride and thiocyanate (Souren, 2000) may also exit in process waste solutions. In addition, cyanide can dissolve in water forming metal cyanide ions (Klenk et al., 1996).

2.3.2 Chemistry of Cyanide

Cyanide is a chemical ion that contains one atom of carbon (C) and one atom of nitrogen (N) represented by the chemical formula CN^- . It is a triple-bonded molecule with a negative one charge, where the carbon is in the +2 oxidation state and the nitrogen in the -3 oxidation state (Franson, 1992).

Simple cyanide salts, such as sodium, potassium, and calcium cyanide, dissolve and ionize in water to form their respective metal cation and free cyanide ions as described by Equation 2.1 for sodium cyanide.

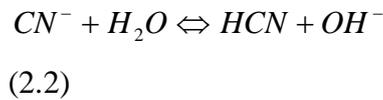


The solubility and the relative cyanide content of the different cyanide salts are shown in Table 2.4. Sodium and potassium cyanide are more soluble than calcium cyanide.

Table 2.4: Properties of simple cyanide salts (Marsden & House, 2006).

Compound.	Available cyanide %	Solubility in water at 25 °C
NaCN	53.1	48
KCN	40.0	50
Ca(CN) ₂	56.5	Decomposes

Cyanide ions hydrolyse in water to form molecular hydrogen cyanide (HCN) and hydroxide ions, with a corresponding increase in pH as described in Equation 2.2.



Hydrogen cyanide is a weak acid, which incompletely decomposes in water as shown in Equation 2.3.



Figure 2.2 shows the extent of this dissociation reaction at equilibrium as a function of pH. At pH 6.0, 100% of the total cyanide exists as hydrogen cyanide and at pH 12, all the total cyanide exists as free cyanide. From the same figure, at approximately pH 9.3, half of the total cyanide exists as hydrogen cyanide and half as free cyanide ions.

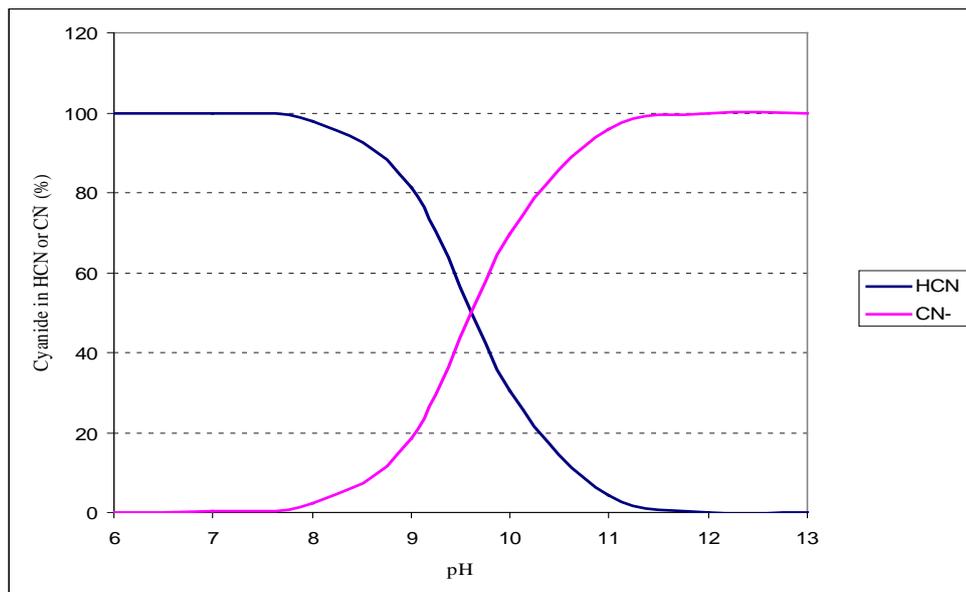


Figure 2.2: The speciation of free cyanide and hydrogen cyanide in aqueous solution as a function of pH.

Free cyanide forms complexes with many metal species, principally the transition metals as described by Equation 2.4 (Marsden & House, 2006), which vary in stability and solubility



where $K_{diss} = [M^{x+}].[CN^-]^y / M(CN)_y^{(y-x)-}$

Metal cyanides can be represented by the formula $M(CN)_x$, where M is a metal and x is the number of cyano-groups, dependant on the valence number of the metal ion. The stability constants of some of the more important metal cyanide complexes are shown in Table 2.5.

Table 2.5: Stability constants for some selected metal cyanide complexes (Tien, 1994).

Chemical Formula	Quantity
HCN	$\text{Log}K_1 = 9.21$
$\text{Fe}(\text{CN})_6^{4-}$	$\text{Log } \beta_6 = 35.4$
$\text{Fe}(\text{CN})_6^{3-}$	$\text{Log } \beta_6 = 43.6$
$\text{Ni}(\text{CN})_4^{2-}$	$\text{Log } \beta_4 = 30.22$
$\text{Cu}(\text{CN})_3^{2-}$	$\text{Log } \beta_3 = 21.66$
$\text{Zn}(\text{CN})_4^{2-}$	$\text{Log } \beta_4 = 19.62$
$\text{Ag}(\text{CN})_3^{2-}$	$\text{Log } \beta_3 = 21.40$
$\text{Au}(\text{CN})_2^-$	$\text{Log } \beta_2 = 39.3$
$\text{Cd}(\text{CN})_4^{2-}$	$\text{Log } \beta_4 = 17.92$
$\text{Co}(\text{CN})_6^{4-}$	$\text{Log } \beta_6 = 19.1$

With respect to table 2.5 cyanide and cyanide complex may be divided into three main categories, based on their stability (Morgan, 1991).

- free cyanide (HCN, CN^-);
- weak acid dissociate (WAD) cyanide complexes (for which $\log K \leq$ approximately 30); and
- strong cyanide complexes (for which $\log K >$ approximately 30).

The ability of cyanide to form strong complexes and stabilise gold and silver allows it to be used in the cyanidation process. Besides stabilising gold and silver in solution, cyanide forms complexes with other metals, such as mercury, zinc, copper, iron and nickel that leads to:

- increases in the consumption of cyanide in gold extraction circuits;
- waste waters that may be difficult to treat; and
- complications in the analysis of cyanide solutions (Mudder et al., 2001).

Both hydrogen cyanide and cyanide ion can be oxidized to cyanate in the presence of oxygen and under suitably oxidizing conditions as illustrated in the E_h -pH diagram for the CN^- - H_2O system in Figure 2.3.

The important reactions (Mudder et al., 2001) are:



These reactions are undesirable during leaching, because they reduce the free cyanide concentration, and the cyanate species formed does not dissolve gold.

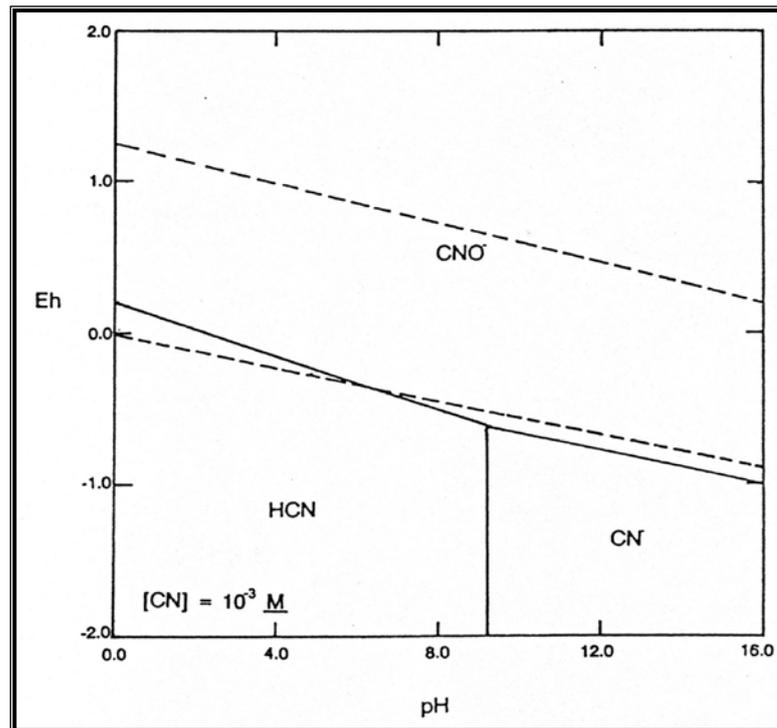


Figure 2.3: Eh-pH diagram for the CN- H₂O system at 25 °C (Smith, 1988).

Hydrogen cyanide is miscible with water, giving a weak acid. The CN triple bond is readily hydrolysed by strong alkali or acid giving formic acid and ammonia, with higher temperature favouring these reactions.

2.3.3 Production of Sodium Cyanide

Most cyanide that is produced is in the form of hydrogen cyanide (HCN) or one of the simple alkali metal cyanides such as sodium cyanide (NaCN), potassium cyanide (KCN) or calcium cyanide (Ca(CN)₂).

Sodium cyanide was first prepared in 1834 by heating sodium carbonate and Prussian blue (a mixture of cyanogen compounds of iron) with sodium cyanide extracted from the cooled mixture using alcohol. Today, almost all sodium cyanide is produced by reacting hydrogen cyanide with sodium hydroxide solution (NaOH) and

evaporating off the water. This is often called the neutralisation-wet process as described in Equation 2.7 (Williams, 2001).



The wet process typically uses 50% (by weight) NaOH and purified anhydrous hydrogen cyanide (liquid or vapour) replacing the alkali metal of the hydroxide to produce the corresponding alkaline metal cyanide. As an example if KOH is used, KCN will be produced

In most commercial sodium cyanide plants, reaction between the hydrogen cyanide and NaOH occurs followed by the evaporation of water and crystallisation of NaCN (for solid NaCN). The control of this system is important to avoid the formation of hydrogen cyanide polymer and sodium formate, and to maximise crystal size. One estimation by Towill et al. (1978) stated that 84% of North American hydrogen cyanide production is used to produce organic cyanide, also called nitriles. Some of the remaining hydrogen cyanide is used to produce 130,000 tons of sodium cyanide per year of which about 90% is used in gold mining.

2.3.4 Uses and Sources of Cyanide

Although many attempts have been made to find chemical replacements for cyanide, it remains the main lixiviant of choice in the precious metals industry worldwide.

The superiority of cyanide to other chemicals in this industry is due its:

- availability;
- effectiveness;
- low cost; and
- the ability to use it with acceptable risk to people and the environment if it is used under control (Mudder & Botz, 2001).

Sodium cyanide is the most widely used type of cyanide by the precious metal mining industry, though $\text{Ca}(\text{CN})_2$ and KCN are used in select locations.

Mudder (2001) reported that up to 90% of gold is produced using cyanide. About 1.4 Mt of hydrogen cyanide are produced annually. About 13% of this amount is converted into sodium cyanide and used in the extraction of gold and silver as shown in Figure 2.4. The remaining 87% of the hydrogen cyanide is used in the production of different products such as adhesives, computer electronics, fire retardants,

cosmetics, dyes, nylon, paints, pharmaceuticals, Plexiglas, rocket propellant, and road and table salts (Williams, 2001).

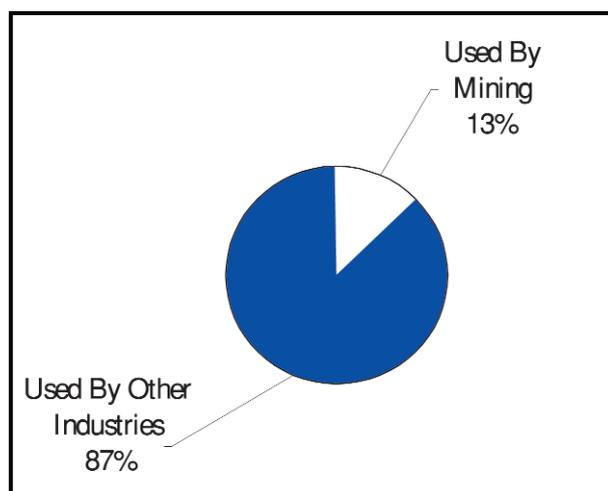


Figure 2.4: Industrial uses of hydrogen cyanide (Williams, 2001).

In fact, natural production of cyanide occurs throughout the world. Cyanide and chemically related compounds are generated in nature by different species of bacteria, algae, fungi, plants, and insects (Fish & Wildlife Service, 1991; Knowles, 1976). Cyanide is naturally present in the biosphere in both simple and complex forms. Interestingly, for many years' cyanide and cyanide compounds have been referred to as the first organic compounds on earth, from which the remaining compounds of life were derived (Oparin, 1983; Lehninger, 1970).

2.3.5 History of Cyanide in Gold mining

A short chronology of the history of the use of cyanide in gold processing is summarised as follows (Logsdon et al., 1999):

- in 1704, Dippel and Diesbach discovered “Prussian blue” (iron ferrocyanide);
- the earliest well-documented work on Scheele’s studies in Sweden in 1783 is on the solubility of gold in cyanide solutions;
- by 1840, Elkington held a patent for the use of potassium cyanide solutions for electroplating gold and silver;
- Elsner’s equation describing the extraction of gold from ores by cyanide was known by 1846;

- in 1887 and 1888, McArthur and the Forrest brothers effectively established the current gold extraction process, dissolution by cyanidation and precipitation using zinc;
- the first commercial-scale cyanidation plant started operating at the Crown Mine in New Zealand in 1889; and
- by 1904 cyanidation processes were also in place in South Africa, Australia, The United States of America, Mexico and France and the use of cyanide to extract gold from low-grade ores was a fully established metallurgical technology.

To date, cyanide is still the main lixiviant used in gold and silver processing, and there is no proven alternative for cyanide in the industry.

2.3.5 Cyanide Toxicity

Cyanide is poisonous with its toxicity depending on the type of cyanide complexes that are present. Despite cyanide ions in process waste solutions and hydrogen cyanide as gas emissions from cyanidation being monitored and measured regularly, the accurate determination of cyanide concentrations in the field is difficult to achieve due to sampling, and analytical errors associated with loss and interferences following collection (Donato et al., 2007).

The principal toxicological hazard of cyanide is acute exposures, such as rapid ingestion of cyanide-containing forage or solutions. Cyanides are absorbed through inhalation, ingestion, or skin contact and are readily distributed throughout the body via blood. Inhalation of cyanide salts is highly hazardous because the cyanide dissolves on contact with moist mucous membranes (Mudder & Botz, 2001). Ingestion of cyanide salts may be deadly with as little as 200 mg. Also solutions of cyanide salts can be absorbed through intact skin or through the conjunctiva of the eye. The dosage required to kill 50% of a population of rats under standard test conditions, LD₅₀, is generally used as a measure of cyanide toxicity. Table 2.6 shows the LD₅₀ values that represent the toxicity of cyanide and its derivatives.

Table 2.6: Toxicity of cyanide and cyanide derivatives (Lowehein & Moran, 1975).

Substance	Boiling point, °C	Expousre limit (ppm)	LD ₅₀ (mg/Kg)	Cyanide releasing
Bromobenzylcyanide	Solid		3500	+
Cyanamide	Solid	2 mg/m ³	1000	0
Cyanide salts	Solid	5 mg/m ³	2	+
Cyanoacetic acid	108	-	2000	0
Cyanogen	gas	10	13	+
Cyanogen chloride	61	0.3	13	+
Ferric-cyanide	Solid	-	1600	0
Ferroc-cyanide	Solid	-	1600	0
Hydrogen cyanide	26.5	10	0.5	+
Malonitrile	Solid	3	6	+
Methylcyano-acrylate	liquid	2	-	+
Methyliso-cyanate	39	0.02	2ppm	-
Nitoprusside	Solid	-	10	+
O-Tolunitrile	204	-	600	0

Note: + release free cyanide 0 No free cyanide released - No specification

Environmental issues generally related with cyanide are due to its high toxicity. Cyanide eliminates fish of the trout species at concentrations as low as 0.04 mg/L of cyanide ion in water. According to the National Institute of Occupational Safety and Health (NIOSH) of the USA, for HCN gas for humans (Muyunda, 1996):

- 270 ppm is immediately fatal;
- 180 ppm is fatal after 10 minutes;
- 135 ppm is fatal after 30 minutes;
- 110 ppm can be fatal;
- 45-55 ppm can be tolerated for up to 60 minutes without immediate effects; and
- 18-36 ppm results in symptoms of poisoning several hours after exposure.

Low dissolved oxygen and low pH are the main factors that increase the toxicity of free cyanide in aquatic ecosystems (Alabaster et al., 1983). The acute toxicity of cyanide on fish in solutions containing only free cyanide decreases with increasing pH. Figure 2.1 shows that as pH increase the proportion of total cyanide present as hydrogen cyanide increases. Hence more hydrogen cyanide is present at low pH values and Alabaster et al (1983) report that hydrogen cyanide (HCN) is more toxic (nearly 2.3 times) than the anionic form (CN⁻).

2.3.5.1 Occupational Exposure to Cyanide

The occupational exposure standard or threshold limit value (TLV) for cyanide dust is 5 mg/m³, and for hydrogen cyanide is 10 ppm (Mudder & Botz, 2001). Workers must use engineering and work practice controls to reduce exposure to or below an 8-hour time-weighted average (TWA) of 10 ppm of hydrogen cyanide. The exposure to cyanide in gold mining should be controlled with physical elimination methods and chemical treatment and recovery of cyanide to maintain the levels of WAD cyanide below 5 mg/L (Mudder & Botz, 2001).

Respirators must be provided and used during the time period necessary to install or implement feasible engineering and work practice controls (Ballantyne, 1988). The US Environmental Protection Agency has proposed a limit of 0.2 mg/L cyanide in drinking water. German and Swiss regulations have set limit of 0.01 mg/L for cyanide for surface water and 0.5 mg/L in sewers (Desai et al., 1998).

2.3.5.2 Recent Cyanide Accidents

A series of recent environmental accidents at various gold mines around the world has precipitated widespread concerns over the use of cyanide as a leach reagent. The majority of these accidents occurred either by cyanide leakage through holes or tears in protective heap leach liners, or by losses in tailings storage areas (Korte & Coulston, 1998). The number of cyanide tailing dam failures around the world has increased from 10 in the years between 1969–1979 to 21 in the years between 1989–1999 (Stenson, 2006).

Some examples of cyanide spills and mine-related accidents in the world and the resulting environmental impacts are presented in Table 2.7. In each of these accidents many tonnes of cyanide were released into the environment. For example in the disaster at the Omai gold mine in Guyana, 1995, about 2.9 million m³ of cyanide tailings and wastewater was released by a collapse of the tailings dam, polluting the Essquibo River. Another accident occurred, in Romania, 2000, where about 100 ton of cyanide contaminated the Danube River (Hilson & Monhemius, 2006). Gold mining in the Portovelo-Zaruma district in southern Ecuador is causing considerable environmental impact; the main environmental impact of this mine is the discharge of cyanide, mercury and metal rich tailings into rivers of the Puyango catchment area (Tarras-Wahlberg et al., 2001).

Table 2.7: Examples of cyanide spills and mine-related accidents and the environmental impacts (Mudder et al., 2001; Moran, 1998).

Mine/country	Year of occurrence	Impact
Galactic Resources Ltd.'s Summitville Mine	Colorado, USA, 1992	Severe environmental problems along a 17-mile stretch of the Alamosa River
Pegasus Corporation's Zortman–Landusky Mine	Montana, USA, 1997	Severe contamination of groundwater; substantial wildlife deaths
Echo Bay's McCoy/Cove Gold Mine	Nevada, USA, 1989 and 1990	Eight cyanide leaks over a two-year period released almost 900 lbs of cyanide.
Harmony mine, South Africa	February, 1994	10 miners killed by cyanide-laced mud.
Omai gold mine, Guyana	August, 1995	All aquatic life forms in a creek that runs into the Essquibo river were killed.
Kumtor mine, Kyrgyzstan	May 20, 1998	Truck transporting cyanide to Kumtor mine plunged off a bridge, spilling 2 tons of sodium cyanide. Four people died.
Baia Mare, Romania	January, 2000	Thousand of tons of fish died in the Tiza and Danube Rivers. Rare Osprey, birds, river otters, fox, and other mammals died from eating cyanide contaminated fish.
Tolukuma mine, Papua New Guinea	March, 2000	Dome helicopter dropped a crate containing 1 tonne of sodium cyanide pellets into the water system in the rainforest.
Ghana <ul style="list-style-type: none"> ▪ Bogoso Goldfields 1994 ▪ Teberebie Goldfields 1996 ▪ Ashanti Goldfields 1998 ▪ Goldfields (S.A.) 2001 ▪ 2001 – second spill occurred in the same area after 2 weeks 	1994–2001	Communities were re-located, waters polluted, there were reported cases of avian mortality, and crops were affected. There were serious health impacts including skin rashes.
Placer Dome tailings disposal, The Philippines	1975–1991	Loss of aquatic life forms in Mogpog River and Calancan Bay.
Grasberg Mine, Indonesia	1996	The spill affected aquatic life forms in Ajkwa River and surrounding communities.

With the many incidences of cyanide release into the environment and the subsequent environmental damage control measures have been increased. Four major directions are being pursued:

1. reduction in cyanide use in cyanidation plants;
2. replacement of cyanide with less toxic reagents;
3. destruction of excess cyanide after cyanidation; and
4. recovery and reuse of excess cyanide after cyanidation.

The next section, 2.3.6 reviews the methods available for the destruction and recovery of cyanide after cyanidation.

2.3.6 Treatment and Recovery of Cyanide

The increase in global mining activity coupled with greater environmental awareness has generated renewed interest in developing processes for the treatment of metallurgical solutions and other mine waters. To minimize the environmental impact of cyanide and make cyanidation acceptable, a variety of verified and reliable chemical, physical, and biological processes have been developed for the treatment and recovery of cyanide and related compounds, which are present in mine waters.

Due to the widespread use of cyanide in mining operations, the recovery and destruction of cyanide is important both from the environmental aspects of wastewater and effluent treatment, and in some cases, from the economic aspects associated with high reagent consumption by the process itself. The following sections will present, in brief, some methods of cyanide treatment and destruction.

2.3.6.1 Activated Carbon Adsorption

The use of activated carbon adsorption for cyanide removal originated from attempts to employ it as a catalyst in the oxidation of cyanide with oxygen. It was noted that the cyanide was first adsorbed, and then catalytically oxidized. The presence of metal ions, particularly copper, enhanced the removal of cyanide through formation of the copper cyanide complex. The best application of granular activated carbon is in a polishing step for the removal of low levels of WAD cyanide and cyanide complexed metals (Mudder et al., 2001).

Reed (1971) investigated the removal of cyanide using granular activated carbon without oxidation. The addition of copper or nickel was necessary for the

removal of cyanide. The process involves the addition of metal ions, followed by a complexation period where metal cyanide complexes are formed, followed by adsorption of these complexes onto the granular activated carbon.

2.3.6.2 Alkaline Chlorination

Alkaline chlorination is a widely used process that generally is used to oxidise free and WAD forms of cyanide. This process is the oldest of the cyanide destruction processes, with the first industrial applications being in the treatment of metal plating and finishing waste water. The use of alkaline chlorination in mine water treatment resulted from the chemical similarity noted between metal plating and mine waters.

The alkaline chlorination process is best applied as a method on clear solutions when WAD cyanide, thiocyanate and/or ammonia are required to be removed (Moran, 1998). In this process, firstly free and WAD forms of cyanide are converted to cyanogen chloride (CNCl) using chlorine (Cl₂) or hypochlorite (OCl⁻). The first stage of the alkaline chlorination process is described by Equations 2.8 and 2.9 (Mudder et al., 2001):



In the first stage, the control of pH is important in order to eliminate the volatilization of cyanogen chloride, which occurs if the pH is less than about 8.0; therefore, this reaction step is ideally carried out at a pH in the range of 10.5 to 11.5. In this pH range, cyanogen chloride hydrolyses to yields cyanate:



The second stage of the oxidation includes the hydrolyses of the cyanate in the presence of chlorine or hypochlorite to yield ammonia and carbonate according to the reaction represented by the Equation 2.11:



2.3.6.3 Biological Treatment

Biological processes have proven effective in the treatment of elevated concentrations of cyanide. Although biological treatment of cyanide is a relatively

new phenomenon in the gold mining industry, there are several references to it dating from as early as the 1950s (Mudder & Botz, 2001).

In this method, chemical and/or physical processes may be included, but the primary treatment occurs through biologically mediated reactions. Biological treatment occurs under carefully controlled conditions using a large number of micro-organisms selected to remove one or more constituents (Moran, 1998).

In the biological treatment, the cyanide is converted to thiocyanate then about 90% of the thiocyanate is decomposed into NH_4^+ , CO_2 and SO_4 . This decomposition is not affected by the feed flow-rate and the pollutant concentrations (Dictor et al., 1997). The biological method is better than other physical and chemical destruction methods, (Akciil, 2003) as the bio-treatment of cyanide tailings can be less expensive than chemical and physical methods, but much faster than natural oxidation. In addition, Mosher and Figueroa (1996) reported that chemical treatments of cyanide are expensive and can bring some additional environmental problems such as by-products of the cyanide oxidation (i.e. CNO^-) possibly generating ammonia, which has an environmental impact the same as the cyanide. Finally, Nelson et al. (1998) conclude that the biological treatment methods have a higher capital cost, but a significantly lower operating cost.

One of the limitations of the biological treatment system for cyanide is that it can not be used to destroy raw electroplating wastewater (EPWW) because of the low organic matter concentration of 10 ± 3 mg-BOD₅₀/L and toxicity of the high cyanide concentration of 23.0 ± 2.2 mg-CN/L (Sirianuntapiboon et al., 2008).

2.3.6.4 Caro's Acid

In the early 1990s, Caro's acid was postulated as a reagent for possible use in oxidizing cyanide in cyanidation solutions. Caro's acid, also known as peroxymonosulphuric acid (H_2SO_5), is a strong oxidizing agent and has been used for many years in industrial chemical formulations and bleaching agents. It has recently been applied at a few mining operations for tailings detoxification, particularly for tailings slurry. The mechanism of treating the cyanide with Caro's acid is that it reacts with both free and WAD cyanides to produce cyanate and sulphuric acid according to reaction 2.12.

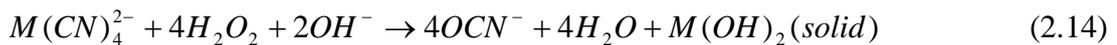


Caro's acid is the product of the reaction between concentrated hydrogen peroxide and sulphuric acid and the treatment of cyanide with Caro's acid is rapid, and it is complete within only a few minutes (Norcross, 1996).

2.3.6.5 Hydrogen Peroxide

Cyanide treatment by hydrogen pyroxide was investigated in the 1980s. The first full application of a hydrogen peroxide treatment in the mining industry was operated by Degussa at the Ok Tedi Mine in Papua New Guinea (Knorre & Griffiths, 1984).

The mechanism and the chemistry of the hydrogen peroxide cyanide destruction process can be explained by Equations 2.13 and 2.14 for the oxidation of free and weakly complexed metal cyanides (i.e., M = cadmium, copper, nickel and zinc):



Using copper as a catalyst in reactions 2.13 and 2.14 can increase the reaction rate. The copper may be present naturally in the solution as a result of gold-silver cyanidation or can be added as a reagent copper solution (Mudder et al., 2001).

There are many other methods used to treat and recover cyanide from the cyanide tailings, such as natural attenuation, precipitation of cyanide, ion exchange, and ozone oxidation.

The detrimental effects of cyanide can be alleviated by destroying excess cyanide in tailings. An alternative is to eliminate cyanide from gold processing by using another lixiviant. The alternative must be as efficient as cyanide at complexing gold and silver and have less adverse environmental impacts. In the following sections alternative lixiviants to cyanide are reviewed.

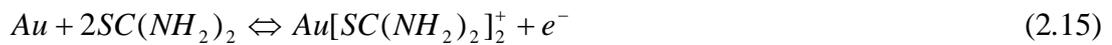
2.3.7 Alternatives to Cyanide

Many attempts have been made to find an efficient alternative to the cyanide that can extract gold and silver with high recovery levels and less environmental impacts. Some of the most promising alternatives including, thiourea, thiocyanate, halides, thiosulfate, and ammonia (Gos & Rubo, 2000), will be discussed in this section.

2.3.7.1 Thiourea

The thiourea process has been chosen as one of the alternatives to cyanide to be reviewed because thiourea is less detrimental to the environment, is less toxic to humans and the dissolution of gold in thiourea solutions is much faster than in cyanide solutions.

The use of thiourea (NH_2CSNH_2) as a gold extraction agent has shown considerable promise. Thiourea leaching usually is applied in acidic conditions. It dissolves gold to form a cationic complex; the reaction is rapid and gold extraction of up to 99% can be achieved (Yannopoulos, 1991). The anodic reaction of this system is described in Equation 2.15.



Groenewald (1976) used solutions containing 1.2 M thiourea to extract gold from its ore within an hour; under these conditions the consumption of thiourea was about 1.4 kg thiourea per ton of ore treated. The thiourea consumption could be reduced to 0.4 kg/ton if 0.1 M thiourea was used; complete extraction of the gold then occurred within eight hours.

Li and Miller (2007) studied the reaction kinetics for gold dissolution in acid thiourea solutions using ferric sulfate as an oxidant. They concluded that the thiourea-ferric sulfate system has rapid kinetics for gold dissolution. No passivation of the gold surface or retardation of the leaching rate was observed during this study. The use of thiourea to extract gold and silver from ore in an acidic medium was studied by Chen et al. (1980). In this study, the leaching solution contained 1.0% thiourea, 0.5% sulfuric acid, and 0.1% ferric ions, and the rate of gold and silver dissolution was over 10 times faster than in a solution containing 0.5% sodium cyanide and 0.05% calcium oxide.

After the optimisation of experimental conditions (Ubal dini et al., 1998) obtained about 80% gold recovery using thiourea with low reagent consumption (5 g/kg of thiourea, 5 g/kg of sulfuric acid and 0.5 g/kg of ferric sulfate). Presad (1991) reports the optimum parameters for thiourea leaching are: pH: 1.4 adjusted accordingly with H_2SO_4 ; redox potential: max 250 mV, min 150 mV; thiourea concentration: 1%; thiourea consumption: 2 kg/t; and leach time: 10–15 hours. Other recent work conducted to evaluate and optimise thiourea gold leaching include studies by Li and Miller (2007), Zheng et al. (2006) and Tanriverdi et al. (2005).

Acidic thiourea as a leaching reagent for gold has a number of problems such as high consumption of thiourea compared with cyanide, serious corrosion of equipment in acidic solutions compared with steel passivation in alkaline cyanide solutions, no selectivity for gold over gangue minerals compared with excellent selectivity for cyanide, and complicated regeneration and purify procedures of the thiourea lixiviant (Zheng et al., 2006). Due to these problems, thiourea has not been applied on an industrial scale to date.

2.3.7.2 Thiocyanate

Thiocyanate (SCN^-) is produced as a product of the reaction between cyanide and sulfur species during cyanide leaching. In 1905, a study demonstrated that thiocyanate dissolved gold effectively in the presence of a suitable oxidising agent (White, 1905). The leaching of gold with thiocyanate, if performed between pH 1 and 2, enables the use of iron (III) as an oxidising agent. The chemistry and thermodynamics of thiocyanate were described by (Barbosa-Filho & Monhemius, 1994). The authors concluded that thiocyanate is an effective lixiviant for gold in acidic conditions, yielding dissolution rates that are comparable to those obtained with thiourea whilst offering the advantage of much greater stability against oxidative decomposition. Also Kholmogorov et al. (2002) found that more than 95% of gold was dissolved in weak acidic solutions (pH=2–5) at a KSCN concentration of 0.4 mol/L.

Thiocyanate solutions have a lower toxicity than sodium and potassium cyanide and better stability in various media. Moreover, it can be regenerated and obtained as a by-product in technological processes.

Kholmogorov et al. (2002) compared the rate of gold leaching for the different complex-forming reactants: thiocarbamide in H_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, KSCN, and NaCN. It was found that the leaching rate in KSCN is slightly lower than that in thiocarbamide solutions and is much greater than that in NaCN or $\text{Na}_2\text{S}_2\text{O}_3$ solutions.

Broadhurst and du Perez (1993) studied the chemistry and thermodynamics of the dissolution of gold in an acidic aqueous thiocyanate medium using iron (III) sulfate as an oxidant. They found that thiocyanate is an effective reagent for dissolving gold at fast rates. Gold thiocyanate can be adsorbed from solution onto ion exchange resins. The recovery of gold from ion exchange resins can be achieved by thiocarbamide solutions in H_2SO_4 at room temperature.

2.3.7.3 Halides

The halides, Cl, Br, and I have been used for many years to extract gold, in fact the use of halide systems for gold dissolution predates cyanidation (La Brooy et al., 1994).

- **Chloride**

Gold is leached rapidly by chlorine at low pH (Equation 2.17): The optimum conditions for the chlorination process are low pH, high chloride and chlorine levels, elevated temperatures, and high ore surface areas. Chlorine can be generated in slurries and solutions via electrolysis of NaCl solution or by the addition of MnO₂ to hydrochloric acid as shown in Equation 2.16 (Yannopoulos, 1991).



Although gold dissolution with chlorine is substantially faster than with cyanide, low concentrations of sulfides or other reactive components in the ore can make reagent consumption excessive and can reduce AuCl₄⁻ back to metallic gold (Hilson & Monhemius, 2006). Baghalha (2007) noted that calcium hypochlorite produced sluggish gold leaching kinetics, requiring twice the time (46 h) to achieve the maximum gold recovery of 58% compared to sodium hypochlorite. The amount of HCl added and hence the initial pH has a major impact on gold leaching kinetics and the maximum gold recovery. Very slow gold leaching kinetics are obtained without the addition of acid.

- **Iodide**

Gold can dissolve in an iodine solution at moderate oxidizing potentials, but insoluble gold iodine will be formed, which will hinder further reaction between gold and the iodine solution.

Angelidis et al. (1993) concluded that the gold dissolution rate in the iodide system depends upon the concentration of iodine and iodide as well as the ionic strength. A fresh gold surface can be leached at a greater rate by iodine-iodide solution than is possible by thiourea and by conventional cyanidation techniques.

- **Disadvantages of Halides**

Because the reaction conditions for gold leaching with halogens require a high redox potential, (Equations 2.18, 2.19, 2.20) and further extraction processes are necessary to complete gold extraction, this method is not at present an alternative to cyanidation (Anhong, 1997).

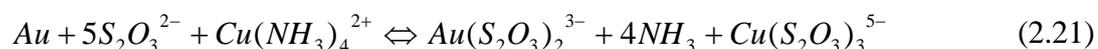


The high oxidation potentials required in the halide systems for the leaching of gold require bromine (Br₂) or iodine (I₂) as an oxidant, but these are toxic with a time weighted exposure average limit of 0.1 mg/L (Lewis, 1997).

2.3.7.4 Thiosulfate

Thiosulfate (S₂O₃)²⁻ is a less toxic alternative to cyanide. Up to 12 g of thiosulfate can be taken daily by mouth with no ill effects (Lewis, 1997), hence thiosulfate is usually classified as GRAS (generally recognized as safe). Thiosulfate has a low toxicity with an LD₅₀ (dose needed to kill 50% of a population) of 7.5 ±0.752 g/kg (Grayson, 1983) for mice. It is commonly used as a fertilizer and an indirect and direct human food ingredient (Langhans et al., 1992).

In the thiosulfate leaching system for gold, thiosulfate is used as the principle reagent but, both ammonia and cupric ions are required. Ammonia is required to stabilize copper(II) as copper(II) tetraamine and also to adjust pH. Thiosulfate leaching has emerged as one of the more attractive alternatives to cyanide (Molleman & Dreisinger, 2002; Navarro et al., 2002; Aylmore & Muir, 2001a); because thiosulfate is considered a non-toxic reagent and can leach gold faster than cyanide. On the other hand, the main disadvantage of the thiosulfate leaching system is high reagent consumption and the lack of a suitable gold recovery method. The oxidation of gold to the aurous Au⁺ ion in ammoniacal thiosulfate in the presence of Cu(II) can be represented by Equation 2.21 (Muir & Aylmore, 2004).



The thiosulfate leaching system will be reviewed in detail in Chapter 3.

2.3.7.5 Ammonia

Ammonia is more commonly known as an additional reagent used to reduce cyanide consumption in the cyanidation of copper containing gold ores. The advantages of using ammonia as a leaching reagent are its availability, price and the simplicity of recycling ammonia. The gold oxidation reaction with ammonia is shown in Equation 2.22.



Ammonia has a threshold limit value (TLV) of 14 mg/m³ and in this context is very similarly to HCN (Gos & Rubo, 2000). In addition, ammonia is classified as a water contaminant. Hence, ammonia and other reagents containing ammonia can not be considered as having a more favourable profile than cyanide with regard to toxicity and exposure aspects. Despite the possibility of gold dissolution at ambient temperature according to the reaction in Equation 2.22, the gold dissolution and leaching kinetics may be slow and small (McNulty, 2001).

2.3.7.6 The Toxicity of Different Alternative Leaching Reagents

Table 2.8 summarises toxicity data for some selected alternatives to cyanide. The TLV of an air contaminant is that concentration to which it is believed that most workers can be exposed daily without adverse effects (effectively, the threshold between safe and dangerous concentrations). Bromine is the most toxic alternative to cyanide; its threshold limit value (TLV) is 0.6 mg/m³. Thiosulfate is the most promising alternative to cyanide according to handling, toxicity, and water contamination shown in Table 2.8.

2.4 Summary

Studying the environmental and kinetic problems resulting from using cyanide and most of its alternative lixivants has shown that, of the alternative reagents, thiosulfate seems to be the most promising alternative to cyanide. Thiosulfate is less-toxic, cheaper than cyanide and it has the potential to be utilised for a number of applications in which cyanidation is not efficient such as the treatment of carbonaceous (preg-robbed) ores or when it is not possible to use cyanide due to political or environmental factors. Because of that, thiosulfate was selected to be used for gold leaching in this study.

Table 2.8: Toxicity data for selected lixiviants (Gos & Rubo, 2000).

Reagent	Emission	Toxicity/Handling		Exotoxicity/transport spillages	
		LD ₅₀ /LC ₅₀	TLV	Water contaminant (WGK)	LC ₅₀ /EC ₅₀ Lethal concent.
Thiourea	NH ₃ , H ₂ S	LD ₅₀ 1750 mg/kg	none	2	LC ₅₀ >100mg/L
Thiosulfate (sodium)	H ₂ S	LD ₅₀ 4000 mg/kg		0	LC ₅₀ >10000mg/L
Thiosulfate (ammonium)	NH ₃ , H ₂ S	LD ₅₀ 2890 mg/kg		1	Consider ammonia/ammonium
Thiocyanate (sodium)		764 mg/kg		1	EC ₅₀ > 100mg/L
Thiocyanate (ammonium)		LD ₅₀ 15 g		1	Consider ammonia/ammonium 280- 300 ppm/1h killed sunfish.
Ammonia		LD ₅₀ 350 mg/kg	14 mg/m ³	2	LC ₅₀ 0.53 mg/L
Chlorine		LD ₅₀ 293 ppm/1h	1.45 mg/m ³	2	LC ₅₀ 0.05 mg/L
Bromine		LD ₅₀ 14 mg/kg	0.6 mg/m ³	3	LC ₅₀ 10 mg/L/10h
Iodine		LD ₅₀ 14000 mg/kg	1.1 mg/m ³	1	LC ₅₀ 0.083 mg/L
Cyanide (sodium)		LD ₅₀ 6.4 mg/kg	5 mg/m ³	3	LC ₅₀ 0.16 mg/L/96h
Cyanide (hydrogen)		LD ₅₀ 3.7 mg/kg	5 mg/m ³	3	LC ₅₀ 2.29 mg/L/96h

Where:

LD₅₀ = Lethal Dosage

LC₅₀ = Lethal concentration

EC₅₀ = Exotoxicity concentration

WGK is an indicator letters of water contaminant

WGK = 0 is not water contaminant

WGK = 1 is slight water contaminant

WGK = 2 is water contaminant

WGK = 3 is strong water contaminant

Chapter 3 Thiosulfate Leaching of Gold: Literature Review

3.1 Introduction

In this chapter, a review of the published literature relating to gold and silver leaching in thiosulfate solutions is presented. Also for comparison, in brief, a review of the cyanidation process is presented.

The first use of thiosulfate leaching of gold and silver was in the late nineteenth century in the Von Patera process. Recently, the thiosulfate leaching system was proposed for use on refractory ores and concentrates, such as ores that contain large amounts of: cyanide-consuming copper, carbonaceous preg-robbing materials, refractory sulfides, and the products of partial oxidative pre-treatment of refractory sulfides that contain cyanide-consuming sulfur species (Marsden and House, 2006).

Most of the published work related to thiosulfate leaching has used copper(II) as an oxidant and ammonia as an oxidant ligand. However, other studies suggest using nickel(III) (Arima et al., 2004) or iron(III) as an oxidant and oxalate or EDTA as a ligand (Chandra & Jeffrey, 2005). Despite thiosulfate leaching showing promise with high gold leaching rates, the application of the thiosulfate system on an industrial scale may still be a long way off, due to high reagent consumption and the difficulties of gold and silver recovery from the leach solution. However, recently, extensive worldwide research has been conducted to optimise and model the thiosulfate leaching system to advance it to an industry process.

3.2 History of Gold Production

Gold was first extracted from streambed gravels, where the gold occurred as free native metallic gold. Gold recovery methods have ranged from the historic gravity panning, sieving, and sheepskin collection techniques to amalgamation, chlorination, and the presently practiced cyanidation methods. Despite the advances in gravity concentration and amalgamation, they are unsuitable for the recovery of fine gold and gold associated with sulfide minerals, hence cyanidation has developed as the predominate gold recovery process.

Native metallic gold was found and used by prehistoric man as a tool. The recovery of native gold by gravity concentration dates back at least 6000 years

(Puddephatt, 1978). The art of working gold and silver into jewellery/coins seems to have arisen in Sumer, Egypt, and Crete at roughly the same time, probably around 3000 B.C. (Butterman & Amey, 2005).

Chlorination was first used commercially to treat Deetken ore in California in 1858 (Schnabel, 1921). By the mid 1860s various chlorination processes were used in the United States, South Africa, and Australia.

In the first half of the 19th century, Russia was the main source of gold, supplying 60% of the world's production. The main mining activity was gravity concentration by panning, although steam and water power driven trammels and strakes were also used (Marsden & House, 2006). The environmental implications of hand picking and mechanical hand sieving were low as there were no chemical lixivants and production was on a small scale (Müezzinolu, 2003).

The dissolution of gold in aerated cyanide solutions and the role of oxygen in the mechanism were investigated by Elsner in 1846 (Elsner, 1846). The cyanidation process, as it is now known, was patented between 1887 and 1888 by MacArthur and the Forrest brothers and the first commercial application of the cyanide process was in New Zealand in 1889 (McNulty, 1989).

Due to the environmental considerations of using cyanide, research is being undertaken to find suitable alternatives. The most promising reagent from both a metallurgical and environmental standpoint is thiosulfate. The first proposed use of thiosulfate to recover precious metals was in the early 1900s (White, 1905). In a process known as the Von Patera process, gold and silver ores were first subjected to a chloridising roast and then leached with thiosulfate. Thiosulfate was first used in the silver mining industry for the recovery of silver from very high grade ores (Gowland, 1930).

3.3 An overview of Thiosulfate

Sodium and ammonium thiosulfate are the two main commercial sources of thiosulfate and the most common thiosulfate salt forms used in research on thiosulfate leaching of gold and silver. The common thiosulfate salts (Na^+ , K^+ , Ca^{2+} and NH_4^+) are biodegradable and are regarded as non-hazardous by Worksafe Australia (NOHSC, 1999). These thiosulfate salts are 'Generally Recognised As

Safe' (GRAS) in the US, and are not considered to be dangerous substances by European standards (Grosse et al., 2003; EEC/FDA, 2001).

3.3.1 Chemistry of Thiosulfate

Thiosulfate salts have been used in industry for more than two and a half centuries (Schmidt, 1962). The chemical symbol for the thiosulfate anion is $S_2O_3^{2-}$. The thiosulfate anion, shown in Figure 3.1, is tetrahedral in shape and is notionally derived by replacing one of the oxygen atoms by a sulfur atom in a sulfate anion. The sulfur to sulfur (S-S) distance indicates a single bond, implying that the sulfur bears a significant negative charge and the S-O interactions have more double bond character.

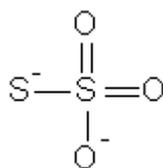


Figure 3.1: The chemical structure of the thiosulfate ion.

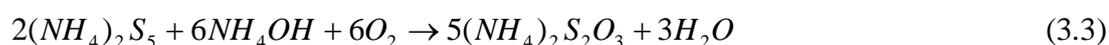
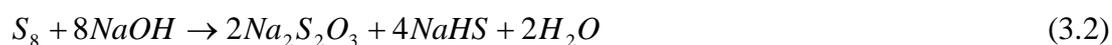
The thiosulfate anion is metastable and is a natural sulfur donor, disproportionating to form sulfite and sulfur or an active sulfur species. Although this tendency is medically useful, it can contribute to the corrosion of metals and other materials. Thiosulfate is also subject to attack by microorganisms.

3.3.1.1 Production of Thiosulfate

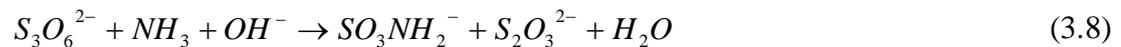
Thiosulfate can be produced from elemental sulfur and sulfite at an elevated temperature as shown by Equation 3.1.



Under alkaline conditions, thiosulfate can be produced as a product of the reaction between sulfur or sulfide and hydroxide as described by Equations 3.2 and 3.3 (Shieh et al., 1965).



Thiosulfate is sometimes regenerated from tri, tetra, or penta thionates in an alkaline aqueous ammonia solution as shown in Equations 3.4 to 3.8 (Zhang & Dreisinger, 2002; Aylmore & Muir, 2001a; Naito et al., 1970).



Sodium sulfide, or sodium hydrosulfide, is oxidised to form sodium polysulfide and sodium hydroxide, which may be further oxidized to sodium thiosulfate and sodium hydroxide. The oxidant is air, oxygen or oxygen in combination with other gases; the reductant is aqueous sodium sulfide or sodium hydrosulfide; and the reaction is carried out with both reactants in non-flooded contact with a solid catalyst material, of which a typical example is a particulate carbon treated with polytetrafluoroethylene (PTFE) (Smith & Sanders, 1979).

3.3.1.2 Uses of Thiosulfate

The use distribution (Bean, 1996) of ammonium thiosulfate is shown in Figure 3.2. The greatest proportion of ammonium thiosulfate use is in the agriculture industry as a fertilizer, where the sulfur and ammonium content are both important plant nutrients. Photochemical grade ammonium thiosulfate is primarily used in the development of photographic film by the dissolution of silver halides from the negatives and prints.

Other uses of sodium thiosulfate include:

- an alternative solvent to cyanide for extraction of gold;
- in pH testing of bleach substances;
- the tanning of leather;
- removal of excess chlorine in paper and textile bleaching;
- preparation of matches;
- flue gas desulfurisation; and
- as a chemical reagent.

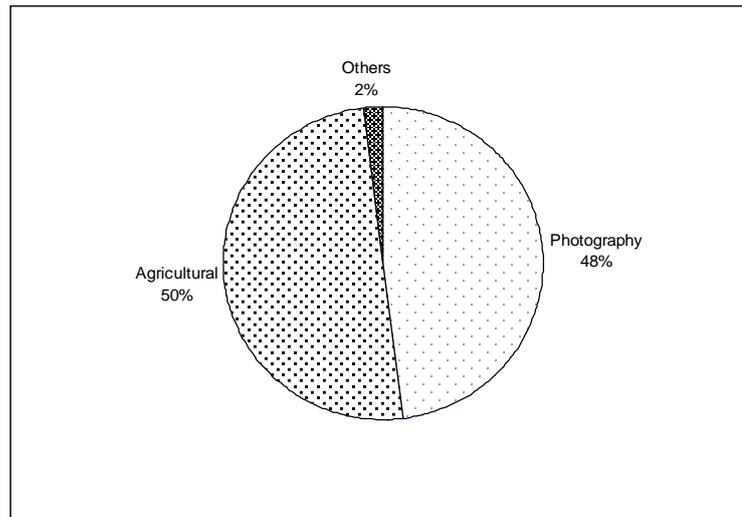


Figure 3.2: The use distribution of ammonium thiosulfate (Bean, 1996).

3.3.1.3 The Stability of Thiosulfate

One of the major problems that hinders the application of thiosulfate in the gold production industry is the high consumption of thiosulfate during the leaching of gold ores, consequently increasing operating costs. Unlike cyanide, thiosulfate is metastable and tends to undergo chemical decomposition. In short, with regard to gold leaching, many factors influence the stability of thiosulfate solutions (Dhawale, 1993):

- the purity of the water used as the solvent;
- the concentration and pH of the solution;
- the presence of certain metals or alloys;
- the presence of certain metals and sulfur bacteria; and
- the exposure to ultraviolet light

It has been reported that thiosulfate decomposition increases in thiosulfate solutions with increasing copper concentration. Also, it was found that oxygen has a major negative effect on the stability of thiosulfate and oxygen use should be controlled in thiosulfate solutions (Jeffrey et al., 2003). From the data shown in Table 3.1, the consumption of thiosulfate in the process of gold leaching is very high and depends on the type of ore minerals associated with the gold.

Table 3.1: Thiosulfate consumption during gold leaching as a function of ore type.

Author	Thiosulfate consumption	Ore type
Yen et al. (1996)	30 kg/t	Copper bearing gold ore
Wan and Brierley (1997)	8.9 kg/t	Carbonaceous gold ore
Zipperian et al. (1988)	50% consumed	Rhyolite ore
Langhans et al. (1992)	0.4 kg/t	Low grade gold ore
Aylmore (2001)	36-70 kg/t	Gold – copper sulfide
Arima (2003)	23 kg/t	Gold silicate ore (16g/t)
Xia et al. (2003)	30 kg/t	Copper bearing gold ore

• **Effect of pH**

Thiosulfate is gradually decomposed to tetrathionate in the pH range from neutral to alkaline. In acidic conditions, thiosulfate forms dihydrogen thiosulfate which gradually decomposes to hydrogen sulfide and sulfite as shown in Equation 3.9 (Aylmore & Muir, 2001b).



The chemical speciation of thiosulfate decomposition products were determined by Jeffrey and Brunt (2007). They showed that tetrathionate and pentathionate are the main reaction products from thiosulfate oxidation at pH 8.5 and 9, while trithionate and sulfate are generated at pH 10.4. The study concluded that thiosulfate decomposition is greater at pH 9.0 than pH 10.4.

• **Effect of Copper**

The presence of the cupric ion in a thiosulfate solution increases the thiosulfate oxidation rate according to Equation 3.10 (Byerley et al., 1975; Byerley et al., 1973b; Naito et al., 1970).



During gold leaching the presence of copper greatly lowers the stability of ammonium thiosulfate in solution due to copper-catalyzed thiosulfate oxidation and the formation of copper sulfides or hydroxides, depending on the leaching conditions (Zhang & Dreisinger, 2002). A decrease in the copper concentration in gold leach

solutions by a factor of 5 only decreased the rate of thiosulfate oxidation by a factor of 2 (Breuer & Jeffrey, 2003b).

• **Effect of Oxygen**

Another more significant factor that affects thiosulfate stability and consumption is the amount of oxygen or air in thiosulfate solutions. Breuer and Jeffrey (2003b) measured thiosulfate concentration as a function of time for a 0.1 M thiosulfate gold leach solution sparged with air or maintained under argon. The results showed that the rate of thiosulfate consumption is very high in the presence of oxygen or air, with all of the thiosulfate being oxidised in one hour. In comparison, less than 5% of the thiosulfate was oxidised under argon for the same time period.

Another study carried out by Molleman and Dreisinger (2002) concluded that using air or oxygen in a thiosulfate leach solution has a significant positive effect on gold extraction but it decreases thiosulfate stability. Chu et al. (2003) indicate that, in order to reduce the rate of thiosulfate oxidation, low partial pressure and flowrate of oxygen is required. At these conditions, the rate of polythionate formation will also be low; hence, the gold oxidation rate is considerably higher.

• **Effect of Impurities**

The effect of pyrite on the decomposition rate of thiosulfate ($S_2O_3^{2-}$) and the formation rates of its decomposition products, sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), and tetrathionate ($S_4O_6^{2-}$), were investigated in aqueous solutions of pH 2.9–8.6 at 20°C by Xu and Schoonen (1995). They concluded that the pyrite surface catalyzed oxidation of $S_2O_3^{2-}$ to $S_4O_6^{2-}$ by dissolved oxygen is the dominant $S_2O_3^{2-}$ decomposition mechanism. Feng and Deventer (2007a) studied the effect of hematite on thiosulfate decomposition and unlike pyrite found that hematite catalysed the oxidative decomposition of thiosulfate to polythionates in the presence of oxygen.

Senanayake (2004) summarised some of the published data (Muir & Aylmore, 2004; West-Sells et al., 2003; Nicol & O'Malley, 2002; Abbruzzese et al., 1995; Zipperian et al., 1988) of the effect of thiosulfate decomposition on the leaching of gold with thiosulfate as:

- (i) high reagent cost;
- (ii) decrease in rate of gold dissolution caused by the decrease in concentration of copper(II) and thiosulfate;

- (iii) formation of insoluble products especially in thiosulfate and/or ammonia deficient solutions; and
- (iv) interference of polythionates with gold separation and recovery stages subsequent to the leaching stage.

3.4 Cyanide Leaching of Gold (Cyanidation)

Cyanide has been used in the gold mining industry since its value as a leach reagent for gold ores was recognised by John Stewart MacArthur in the 1880s. About 1.4 Mt of hydrogen cyanide is produced each year worldwide, 13% of which is converted into sodium cyanide and used in gold and silver extraction from their ores (Mudder et al., 2001). The major factors affecting the dissolution rate of gold in cyanide solutions are the cyanide and oxygen concentrations, temperature, pH, surface area of gold exposed, agitation speed, gold impurity, and the presence of other ions in the solution.

During the application of cyanide to treat precious metals, waste has to be disposed of or treated properly to achieve the environmental requirements. In spite of procedures to decrease the hazardous effects of using cyanide, sometimes the concentration of cyanide in waste processes reaches up 2000 mg/L total cyanide (Barriga-Ordonez et al., 2006).

In this section, gold leaching in cyanide solution is briefly reviewed, as it is the standard that any other leaching agent must be compared against.

3.4.1 Chemistry of Cyanide

Simple cyanide salts, such as sodium, potassium, and calcium cyanide, dissolve and ionise in water to form their representative metal cation and free cyanide ions, as shown by Equations 3.11a, 3.11b, and 3.11c.



Both hydrogen cyanide and free cyanide can be oxidized to cyanate in the presence of oxygen under suitably oxidizing conditions. The oxidation of hydrogen cyanide and free cyanide is represented by Equations 3.12 and 3.13:



3.4.2 Gold Dissolution in the Cyanide System

The dissolution of gold in cyanide solutions includes an anodic reaction (gold oxidation) and a cathodic reaction (oxygen reduction). Both reactions are discussed in this section.

3.4.2.1 The Anodic Reaction

In aqueous, alkaline cyanide solutions, gold is oxidised and dissolved to form the Au(I) cyanide complex, $Au(CN)_2^-$. For dissolution the oxidation of gold will be the anodic reaction in this system, the opposite of the standard reduction reaction shown in Equation 3.14 (Marsden & House, 2006):



The gold anodic reaction can be affected negatively or positively by the presence of impurities in the leaching solution. Heavy metals such as lead and mercury can have a positive effect on gold oxidation by reducing passivation of the gold surface (Jeffrey & Ritchie, 2000b; Hughes et al., 1984; Nicol, 1980). On the other hand, the presence of sulfur forms a passive layer on the gold surface which reduces gold oxidation and leaching rate (Wang & Forssberg, 1990).

3.4.2.2 The Cathodic Reaction

The mechanism of the cyanidation process includes several parallel and series cathodic reactions. The cathodic dissolution reaction in cyanide solutions containing oxygen is represented by Equations 3.15 to 3.17 (Habashi, 1966).



The hydrogen peroxide formed is a strong oxidizing agent, which may take part in further oxidation reactions:

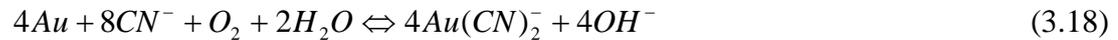


Finally oxygen may be directly reduced to hydroxide ions, as described in Equation 3.17.



3.4.2.3 Overall Dissolution Reaction of Gold

The overall dissolution reaction of gold in alkaline cyanide solutions in the presence of oxygen or air, considering both the anodic and the cathodic half-reaction, is most accurately described by Equation 3.18.



The component reactions of gold dissolution in the cyanide system are illustrated schematically in Figure 3.3.

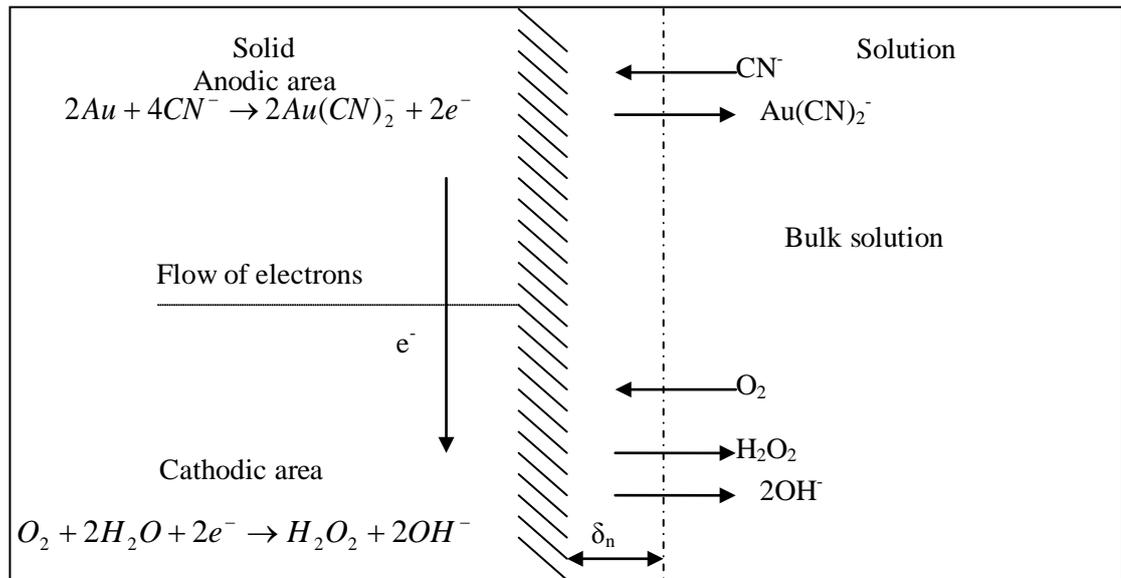


Figure 3.3: Schematic representation of the local corrosion cell at a gold surface in contact with an oxygen containing cyanide solution (Marsden & House, 2006).

3.5 Thiosulfate Leaching of Gold

Cyanide, a very toxic chemical is presently used in the gold leaching process. Thiosulfate is one of the most promising alternatives and substitutes to cyanide, kinetically and environmentally. In comparison with conventional cyanide processing, the thiosulfate process shows promise of greater efficiency, less expense, and lower environmental impacts compared with cyanide.

Langhans et al. (1992) indicated that thiosulfate leaching may be competitive with conventional cyanidation for application to heap, dump, or in situ leaching where longer leach times are normally utilized. Newmont mining was the first mining company to undertake a pilot scale thiosulfate heap leaching as a means of recovering gold from carbonaceous pre-robbing ores (Wan, 1997).

Navarro et al. (2002) observed that by using ammonium thiosulfate leaching, the initial rate of extraction is enhanced, allowing about 90% gold dissolution from a concentrate after 10 hours. The same percentage dissolution was reached by cyanidation, but after about 46 hours.

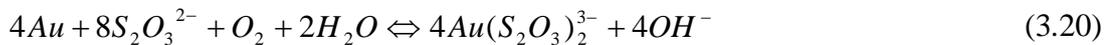
Thiosulfate leaching has significant potential as an effective leaching agent and metal can be recovered from the thiosulfate solution using a variety of procedures (i.e. adsorption onto ion exchange resins), (Navarro et al., 2007). The following sections (3.5.1 and 3.5.2) review the literature on the mechanism and variables that influence thiosulfate leaching of gold and silver.

3.5.1 Reaction Mechanism

Gold forms a stable complex with thiosulfate $(S_2O_3)^{2-}$ in an aqueous solution, as shown in the half Equation, 3.19:



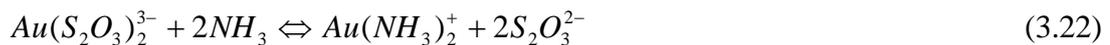
In alkaline thiosulfate solutions, in the presence of oxygen as an oxidant, the complete redox reaction is shown in Equation 3.20:



The thiosulfate leaching of gold in the presence of oxygen according to Equation 3.20 is very slow in the absence of a suitable catalyst. Copper(II) is a very efficient catalyst for this reaction, which is used with ammonia that stabilises the copper(II) in solution as the Cu(II) tetraamine complex $(Cu(NH_3)_4)^{2+}$ as shown in Equation 3.21 (Breuer & Jeffrey, 2003a).



Gold forms stable complexes ($\beta = 3 \times 10^{19}$) in ammonia solutions (Skibsted & Bjerrum, 1997). Therefore, in an ammoniacal thiosulfate solution, both thiosulfate and ammonia (Equation 3.22) have the ability to form complexes with gold.



The E_h -pH diagram that best represents the equilibrium species in the Au, NH_3 , $\text{S}_2\text{O}_3^{2-}$, H_2O system is shown in Figure 3.4 (Senanayake et al., 2003).

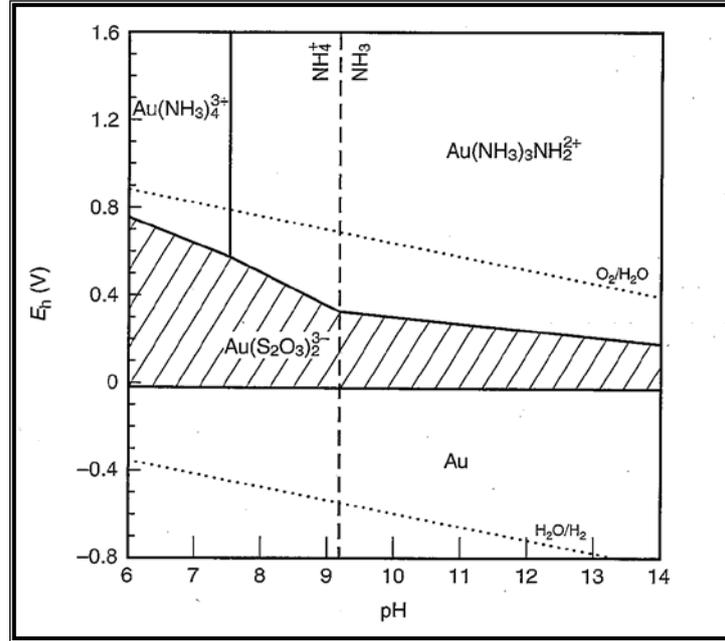
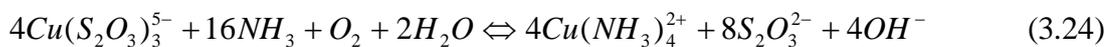


Figure 3.4: E_h - pH diagram for the Au - NH_3 - $\text{S}_2\text{O}_3^{2-}$ - H_2O system at 25 °C: 10^{-5} M Au(I), 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, 1 M ($\text{NH}_3 + \text{NH}_4^+$).

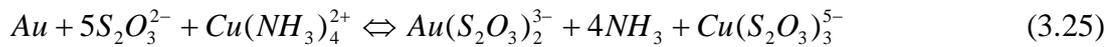
The chemistry of the ammoniacal copper-thiosulfate system is complex due to the side reactions that may occur in the system, such as the reduction of copper(II) to copper(I) and the decomposition of thiosulfate to the different species of polythionates due to reaction between copper(II) and thiosulfate. The exact mechanism of gold dissolution and the catalytic action of Cu(II) is still not completely understood (Breuer & Jeffrey, 2003b; Lam & Dreisinger, 2003; Senanayake et al., 2003; Chen et al., 1993). As the $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ complex is more stable than $\text{Cu}(\text{NH}_3)_2^+$ under the conditions applied for effective gold dissolution the major reduction reaction is given by Equation 3.23:



The reduction of Cu(II) tetramine is accompanied by oxidation of thiosulfate to tetrathionate. The oxidant species, Cu(II), is then regenerated by oxidation of $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ by oxygen:



From Equations 3.23 and 3.24, the overall dissolution reaction for gold in ammoniacal copper-thiosulfate solutions has been proposed (Hiskey & Atluri, 1988) as:



The presence of ammonia is critical to stabilize Cu(II) in the solution as the Cu(II) tetraamine ion, to prevent the formation of Cu(OH)₂ and to prevent passivation of the gold surface by preferential adsorption (i.e., avoiding coating with sulfur species). The mechanism of gold dissolution in the ammoniacal copper-thiosulfate system is illustrated schematically in Figure 3.5.

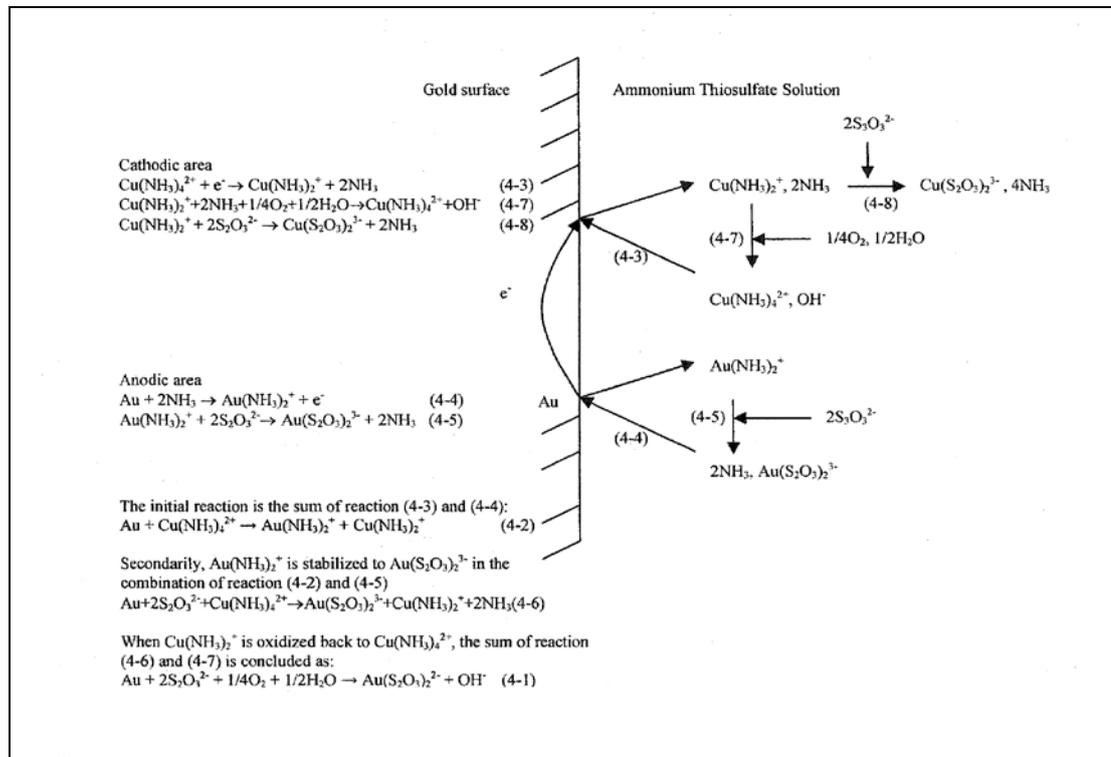


Figure 3.5: Schematic dissolution mechanisms in ammonium thiosulfate solution on gold surface (Aylmore & Muir, 2001a).

3.5.2 The Effect of Reagent Concentration and Reaction Conditions

Many published studies (Aylmore & Muir, 2001a; Abbruzzese et al., 1995; Anhong, 1997; Breuer, 2002; Briones & Lapidus, 1998; Jeffrey, 2001; Jeffrey et al., 2001) have reported the effects of the reagent concentration and reaction conditions on the gold dissolution rate and the oxidation of thiosulfate. The most studied variables are thiosulfate, copper(II), ammonia and oxygen concentration and, agitation speed, temperature pH of solution, and the effect of impurities. Most of the

published results from these studies showed that gold and silver dissolution rate is dependent on the thiosulfate and Cu(II) concentration, up to a certain concentration (Jeffrey, 2001).

3.5.2.1 Effect of Thiosulfate

It has been reported that increasing thiosulfate concentration increases the gold leaching rate (Arima, 2003; Navarro et al., 2002; Jeffrey, 2001; Briones & Lapidus, 1998; Muyunda, 1996; Abbruzzese et al., 1995; Langhans et al., 1992).

Thiosulfate concentration is an important variable, particularly given the small driving force for the leaching reaction shown in Equation 3.25 (Jeffrey, 2001). Thiosulfate concentrations ranging from 0.05 to 2.0 M have been investigated to determine their affect on gold and silver leaching. Both sodium and ammonium thiosulfate have been used as the primary reagent for the thiosulfate leaching system. A number of studies have examined the effects of thiosulfate concentration on gold dissolution; one of these studies was carried out by Chai (1997). The results showed that the amount of gold extracted was only 10% in the absence of thiosulfate but in the presence of ammonia and copper sulfate. The amount of gold extracted increased with increasing initial thiosulfate concentration up to 0.287 M, but decreased at higher initial thiosulfate concentrations.

The rate of gold leaching is reduced at lower thiosulfate concentrations due to both the oxidation of thiosulfate, and the reduction of copper(II) amine to copper(I) thiosulfate (Breuer & Jeffrey, 2000). In oxygenated thiosulfate solutions, the thiosulfate concentration needs to be optimised to increase the dissolution of gold and to decrease the effect of thiosulfate on copper(II) reduction and hence, the [Cu(II)]:[Cu(I)] ratio (Breuer & Jeffrey (2003b).

The following results summarise the effect of thiosulfate on gold and silver leaching from some of the published studies:

- increasing thiosulfate concentration from 0.1 M into 0.2 M, gold recovery increased from 76% into 90%, but thiosulfate consumption increased from 18 kg/t-ore to 32 kg/t-ore (Arima, 2003);
- Langhans et al. (1992) concluded that high gold extractions (90%) were obtained at higher thiosulfate concentrations;
- gold and silver extraction increases with an increase in thiosulfate concentration (Zipperian et al., 1988);

- gold extraction is enhanced by the increase in thiosulfate concentration up to 0.3 M but a negligible effect on gold dissolution is obtained at higher thiosulfate concentrations (Navarro et al., 2002); and
- leaching at high thiosulfate concentrations, the rate of gold extraction is high: a recovery of about 60% after the first hour of attack is achieved (Abbruzzese et al., 1995).

To conclude, gold dissolution is very low in the absence of thiosulfate however, it is enhanced by increasing the thiosulfate concentration up to an optimum value according to the type of gold ore. On the other hand, an increase in the thiosulfate concentration increases the reduction of copper(II) to copper(I).

3.5.2.2 Effect of Ammonia

Ammonia is one of the important reagents in the thiosulfate leaching system of gold as it initially dissolves gold and complexes the copper as the copper tetraamine complex. The two dominant functions of ammonia in thiosulfate solutions are explained by Chai (1997) as follows:

1. ammonia reacts with gold first to form $Au(NH_3)_2^+$, which then reacts with $S_2O_3^{2-}$ to form $Au(S_2O_3)_2^{3-}$ in the anodic reaction; and
2. ammonia stabilises the cupric ion by reacting with it to form the cupric amine complex, which is a strong oxidizing agent.

The gold ammonia complex is substituted by thiosulfate ions and releases ammonia according to Equation 3.26 (Chen et al., 1996).



The effect of ammonia concentration was studied by Jeffrey (2001) who found that the gold leaching rate varies with ammonia concentration as shown in Table 3.2. For example, at low ammonia concentrations (0.2 and 0.4 M), the gold leach rate is higher than that obtained at higher ammonia concentrations (0.84 and 1.68 M).

Chai (1997) reported a gold recovery of only 9% with thiosulfate in the absence of ammonia. However, after adding 0.5 M ammonia to the solution, the extracted gold was found to increase significantly with the optimum concentration of ammonia was determined to be 2 M. In another study (Arslan et al., 2008), an increase in ammonia concentration up to 1 M, increased the gold and silver leaching

rates, but ammonia concentrations higher than 1M were found to decrease the gold leaching rate. Briones and Lapidus (1998) found that the silver dissolution rate also decreased at higher ammonia concentrations. Silver extraction is more sensitive to changes in ammonia concentration than gold (Zipperian et al., 1988).

Table 3.2: Effect of ammonia concentration on the gold leaching rate in 0.4 M thiosulfate and 25 mM copper(II) (Jeffrey, 2001).

NH ₃ (M)	10 ⁵ x Rate (mol m ⁻² s ⁻¹)
0.2	10.2
0.4	11.9
0.84	9.9
1.68	6.3

Increasing ammonia concentration has no noticeable effects on the thiosulfate oxidation rate, however, an increase in the sustainable copper(II) concentration is noticed (Arima, 2003; Breuer & Jeffrey, 2003a,b; Wan & LeVier, 2003; Aylmore, 2001; Muyunda, 1996).

Ammonia prevents gold passivation by being preferentially adsorbed on gold surfaces over thiosulfate (Jiang et al., 1993). Furthermore, the presence of ammonia prevents the dissolution of iron oxides, silica, silicates and carbonates, the most common gangue minerals found in gold bearing ores (Abbruzzese et al., 1995). In conclusion, it is important to optimise the ammonia concentration to ensure the stability of copper(II) in solution as the copper(II) amine complex and to decrease the reaction between free copper(II) ions and thiosulfate in the solution.

- **Environmental Impacts of Ammonia**

Although ammonia is an important reagent of the gold thiosulfate leaching system, it poses environmental and toxicity problems both as a gas and dissolved in solutions. The US National Institute for Occupational Safety and Health (NIOSH) recommend an airborne exposure limit of 25 ppm (18 mg/m³) averaged over a 10-hour work-shift, with a limit of 35 ppm (27 mg/m³), not to be exceeded during any 15 minute work period (NIOSH, 2000). Ammonia is relatively stable, but it may eventually metabolize to nitrate, which has the potential to promote algal growth and

to pollute ground water; hence precautions have be considered to control ammonia emissions, usually from tanks or heaps, and to prevent its release into the environment (Muir & Aylmore, 2004).

3.5.2.3 Effect of Copper

Copper(II) has an important role in the thiosulfate leaching system as an oxidant for the gold, hence, (Breuer and Jeffrey, 2003b) the gold leaching rate in thiosulfate solutions without copper is extremely poor. The copper concentration has a significant effect on the observed sustainable copper(II) concentration and the [Cu(II)]:[Cu(I)] ratio. As copper concentration decreases, the [Cu(II)]:[Cu(I)] ratio and hence the cathodic potential for gold leaching also decreases significantly (Breuer & Jeffrey, 2003b).

Gold recovery increased from 75% to 90% with an increase of copper(II) concentration from 5 mM to 10 mM, however, an increase of copper concentration up to 50 mM was reported to have no effect on gold recovery (Arima, 2003). In the absence of cupric ion, Chai (1997) reported gold extraction could only reach 34% however, when cupric ion was added 76% extraction was achieved. The gold extracted increased with the increase of cupric ion until the concentration of copper sulfate became 0.12 M. The reason for the disparity in the recovery (Wan & LeVier, 2003; Langhans et al., 1992) is that the optimum concentration of copper in the leach solution depended on the ore characteristics and the concentration of thiosulfate used.

Silver extraction like gold has been found to increase as the copper concentration increases (0.15% to 1.5%) (Zipperian et al., 1988). Silver is quite sensitive to the variation in the concentration of copper (Langhans et al., 1992).

The best gold leach rate is achieved when the copper sulfate concentration is 0.01 M and the rate of gold leaching sharply decreased at higher concentration (Arima, 2003). Muyunda (1996) stated that gold dissolution rates increased by increasing the copper concentration up to 0.025 M.

Generally (Arima, 2003; Breuer & Jeffrey, 2003a,b; Wan & LeVier, 2003; Aylmore, 2001; Breuer & Jeffrey, 2002; Briones & Lapidus, 1998; Abbruzzese et al., 1995 Langhans et al., 1992; Zipperian et al., 1988), it is reported that increasing copper(II) concentration enhances gold and silver dissolution rates, but has the side effect of increasing the thiosulfate oxidation rate.

In conclusion, although copper(II) can affect gold and silver leaching rates positively, it also has a negative effect on the thiosulfate oxidation. Gold leaching recoveries decrease significantly after a certain value of copper(II) concentration. The main reason for this may be that an increase in Cu^{2+} ion concentration reduces the stability region of the $\text{Cu}(\text{NH}_3)_4^{2+}$ complex while widening the stability region of the solid copper compounds such as CuO , Cu_2O , CuS , and Cu_2S (Arslan et al., 2008).

3.5.2.4 Effect of pH

The correct pH of thiosulfate solutions is essential to ensure the presence and the stability of the required reagents and concentrations in the system. Many published studies have studied the effect of the pH of thiosulfate solutions containing copper and ammonia. Table 3.3 shows a list of the various pH values published within the literature related to gold leaching using thiosulfate solutions.

Table 3.3: List of various pH values used in thiosulfate solutions published in different studies.

pH	Author
8.5-9.5	Wan and LeVier (2003)
9-11	Breuer and Jeffrey (2003b); Senanayake et al. (2003)
10.5-12	Muyunda (1996)
10	Arima, (2003); Jiang et al. (1993c); Zipperian et al. (1988)
10.2	Aylmore (2001)
11	Yen et al. (1996); Langhans et al. (1992)
9-10	Navarro et al. (2002)
9	Wan (1997); Dasgupta et al. (1997)
8.5-10.5	Abbruzzese et al. (1995)

Using ammonium thiosulfate instead of sodium thiosulfate in thiosulfate leach solutions changes the solution pH according the equilibrium shown in Equation

(3.27). The pK_a for ammonia is 9.25 (Equation 3.27) hence, the pH of thiosulfate solutions containing ammonia should be greater than 9.25 in order to maintain ammonia in the system which is essential to stabilise copper (II) as the copper (II) ammonia complex (Breuer & Jeffrey, 2003b).



According to the studies shown in Table 3.4 some conclusions can be summarized as follows:

- pH of thiosulfate solution should be between 8.5 and 9.5 depending on the ore characteristics (especially sulfide content) and acidity/alkalinity levels prior to thiosulfate leaching (Wan & LeVier, 2003);
- Muyunda (1996) studied and noted the effects of pH on gold leaching rates in thiosulfate solutions as follows:
 - the dissolution of gold is extremely poor at a pH lower than 9.2;
 - at low pH values, thiosulfate decomposes into sulfur and polythionate components and sulfur may then coat the surface of gold and stop the process of gold dissolution;
 - at high pH values, above 12.0 with or without ammonia, gold dissolution rates are very poor; and
 - a pH of 11- 12 is required for better dissolution rates in thiosulfate solutions than those of cyanide;
- gold dissolution was found to increase with the increase in the solution pH up to a value of about 9.2. However, a further increase was reported to have no effect on the rate of gold dissolution (Dasgupta et al., 1997);
- a pH value of 10.0 is the optimum value for high gold extraction and lesser thiosulfate consumption. Increasing pH up to 10.7 decreases the gold recovery and increases thiosulfate consumption (Arima, 2003); and
- Senanayake et al. (2003) stated that, typically, leaching is carried out between pH 9 and 11. Below pH 9, however, the Cu(I) triamine $Cu(NH_3)_3^+$ complex becomes prevalent, making the copper species less effective as a catalyst.

3.5.2.5 Effect of Agitation Speed

The interaction between the reacting material in a heterogeneous reaction (a solid and liquid reaction) may proceed via different steps (Habashi, 1970):

- diffusion of reacting molecules to the interface;
- absorption at the interface;
- reaction at the interface;
- desorption of the products; and
- diffusion of the products from the interface.

When the diffusion of the reactants and/or products is the slow step, the reaction is said to be diffusion controlled. If the reaction is diffusion controlled, the rate will depend on (i) the thickness of the diffusion layer, (ii) the concentration gradient across the diffusion layer, (iii) the diffusion rate across the diffusion layer, and, (iv) the surface area of the solid reactant.

In diffusion controlled reactions, the rate should be inversely proportional to the thickness of the diffusion layer and directly proportional to the stirring speed. Chai (1997) found that the amount of gold extracted using a mechanical stirrer was 14% more than without agitation. This result is likely due to the increase in the surface area of the ore sample exposed to the solution by the agitation suspending and separating the ore particles.

A Levich plot was constructed for the gold leaching system in a study done by Jeffrey (2001). The Levich plot was not linear indicating that the dissolution of gold in thiosulfate solutions containing copper and ammonia is not a diffusion controlled reaction. The same study showed that the gold leaching rate slightly increased with increasing agitation speed.

Muyunda (1996) studied the effects of agitation speed on gold dissolution in the thiosulfate system containing copper and ammonia. The results showed that when the rotation speed increased, there was no change in the gold dissolution rate. This result confirms that the gold leaching reaction is not a diffusion controlled reaction. On the other hand, the leaching of silver in thiosulfate solutions is a diffusion controlled reaction and hence, the leaching of silver depends on the agitation speed (Jeffrey, 2001).

3.5.2.6 Effect of Temperature

Temperature has a significant effect on the rate of a leaching process if the reaction is chemically controlled but, little effect on diffusion controlled reactions. As will be described in this section temperature is an important variable during gold

extraction with thiosulfate because of its positive effects on the gold extraction rate; and its negative effects on the decomposition of thiosulfate and the evaporation of ammonia.

A chemically controlled reaction will be affected by a temperature change according to the proportion of the reactant species with sufficient energy to overcome the chemical activation energy. The activation energy can be calculated from the reaction rate constant according to Equation 3.28.

$$k = Ae^{-E_a / RT} \quad (3.28)$$

where

k is the reaction rate constant,

R is the gas constant (8.31 J/K/mole),

T is the temperature, K,

A is the frequency factor, and

E_a is the activation energy.

Zipperian et al. (1988) found that the initial rate of extraction for both gold and silver is enhanced as the leach temperature increases, but the rate falls off dramatically after approximately one hour of leaching. Nearly 90% of gold is leached at higher temperatures in less than one hour.

Muyunda (1996) studied the effect of temperature on the gold leach rate. The results showed that by increasing the temperature from 25 °C to 35 °C, the gold leach rate was doubled but, at high temperatures (55 °C), almost 95% of the gold leach rate was obtained after an hour of leaching. By increasing the temperature, the ammonia loss from an open leach vessel is increased as shown by Manunda (1996) whose results are tabulated in Table 3.4.

Table 3.4: The effect of temperature on ammonia concentration after 2 hours of leaching (Muyunda, 1996).

Temperature, °C	Ammonia remaining after 2 hours (% of original)
25	98.4
35	96.8
45	45.1
55	22.6

Chai (1997) found that gold extraction was preferably carried out at a temperature of 60 °C, because when the temperature is below 40 °C, the rate of the reaction will be adversely affected; and at a temperature more than 60 °C, the volatilization of ammonia will be fast.

Breuer and Jeffrey (2000) concluded that the rate of gold leaching increases with increasing temperature. Temperature has a significant effect on the gold leaching reaction rate (which is expected for chemically controlled reactions). Also the authors found that the activation energy of the leaching reaction was $60 \pm 10 \text{ kJ mol}^{-1}$. This result confirms that the reaction is chemically controlled. The rate of copper(II) reduction also increases with increasing temperature. Arslan et al. (2008) stated that increasing the temperature has positive influences on the gold leaching efficiency but only up to a certain point. After 60°C gold leaching recoveries rapidly decreased.

Conversely, Abbruzzese et al. (1995) observed that the temperature does not have any positive effects on gold dissolution and an increase of temperature from 25 to 60°C produces a decrease in gold recoveries. The authors explained that by using high temperature the speed of cupric sulfide film formation becomes very fast, hindering gold dissolution. In addition, increasing the temperature to 60°C enhances the thiosulfate decomposition into sulphur compounds. Zipperian et al. (1988) concluded that the increase in temperature above 40 °C accelerated the loss of ammonia and the reduction of copper(II). Temperatures of 25-40°C may, therefore, be regarded as ideal, reducing volatilisation and maintaining ammonia levels. Also it was found that the extraction of silver is more temperature sensitive than that of gold.

Based on several published studies, it can be concluded that a controlled temperature at 30-40 °C in the thiosulfate system is indeed required to achieve the best results of gold dissolution and minimizes the amount of ammonia losses and copper(II) reduction.

3.5.2.7 Effect of Impurities

Gold in ore is associated with other various minerals which act as impurities in thiosulfate leaching solutions. Some of them can enhance the gold dissolution rate but most of them reduce the gold dissolution rate and increase thiosulfate oxidation.

Hematite: Feng and Deventer (2007a) studied the effect of hematite on gold recovery. The results clearly showed that hematite significantly reduced the dissolution of gold and this negative effect became more obvious with increasing hematite concentration. This may be due to hematite formed coatings on gold surfaces, which would prevent the leach solution from diffusing to the gold surface. Feng and Deventer (2007a) also showed that hematite catalysed the oxidative decomposition of thiosulfate to polythionates in the presence of oxygen.

Sulfite: Arslan et al. (2008) found that almost 100% gold and silver recoveries were observed with the addition of sodium sulfite during leaching. Increasing the sulfite concentration reduced thiosulfate consumption from 95.6 to 22.2 kg/t over a 4-hour leaching period. Kerley (1983) also reported that the presence of sulfite inhibits the decomposition of thiosulfate. Free sulfite ions regenerate thiosulfate according to Equation 3.29.



Manganese: The addition of a small amount of manganese dioxide in the thiosulfate leaching of sulfide bearing gold ores improved both the kinetics and the overall gold extraction without much impact on thiosulfate consumption (Feng & van Deventer, 2007b).

Sulfur: The presence of the sulphur species, tetrathionate, trithionate and sulfur ions has a significant effect on the thiosulfate leaching of gold in both pure gold and ore leaching systems. Gold dissolution increased with the addition of the sulfur species at low levels, while the amount of dissolved gold decreased at high levels. The presence of these sulfur species significantly reduced thiosulfate decomposition, and this beneficial effect became more prominent at high levels of the sulfur species (Feng & van Deventer, 2007b).

Lead and Zinc: Feng and Van Deventer (2002) found that the presence of lead(II) and zinc(II) ions affects thiosulfate degradation as well as gold oxidation by ammoniacal copper(II) solutions. The effect of lead(II) and zinc(II) ions on thiosulfate consumption is negligible, but the presence of lead(II) and zinc(II) shows beneficial effects on gold dissolution. On the other hand, Navarro et al. (2002) stated that by using a concentration of 4.5 g/L zinc in the thiosulfate solution, recovery

from a gold concentrate after 10 hours decreased from 92% gold without zinc addition to 86%.

Pyrite: The presence of pyrite significantly reduced gold dissolution in ammoniacal thiosulfate solutions and this detrimental effect became more prominent with higher pyrite content. Pyrite has a catalytic effect on the decomposition of thiosulfate (Feng & van Deventer, 2006).

3.5.2.8 Effect of Oxygen

Oxygen is required to convert copper(I) to copper(II) for further gold leaching, but, oxygen concentration should be controlled in thiosulfate solutions in order to reduce the degree of thiosulfate decomposition and hence, the gold dissolution rate. The decrease in the gold dissolution rate in the thiosulfate system upon the addition of oxygen could be attributed to: (a) the decrease in mixed potential, (b) the decrease in thiosulfate concentration (Chu et al., 2003).

Breuer and Jeffrey (2003b) found that the rate of thiosulfate oxidation is very rapid when the solution is injected with pure oxygen; all the thiosulfate is decomposed in less than 25 min, compared to 1 hour for air. However, when the solution is sparged using a gas composed of 1.9% oxygen in nitrogen, the thiosulfate oxidation rate is significantly reduced, and after 2 hours only 10% of the thiosulfate has been destroyed. Chu et al. (2003) also found that the gold-thiosulfate leaching reaction is hindered when oxygen is present in the solution and although the decrease in thiosulfate concentration due to its oxidation by oxygen does affect the leaching process, this alone could not account for the slow leaching kinetics observed in the presence of oxygen.

Some other studies reported that the presence of oxygen in the thiosulfate leaching system has an adverse effect on both gold recovery and thiosulfate oxidation. In addition, the presence of oxygen should be controlled in order to get an optimum balance between the gold extraction and thiosulfate consumption (Feng & van Deventer, 2007c; Zhang et al., 2004; Jeffrey et al., 2003; Muyunda, 1996; Byerley et al., 1975 & 1973a,b)

On the other hand, Wan and LeVier (2003) noted that oxygen availability in the system is of vital importance, as in the absence of oxygen, Cu(I) ions can not return to the Cu(II) state which causes copper sulfide precipitation from the solution.

Jeffrey et al. (2003) noted that without oxygen added to the leach solution, gold leaching was very slow. Only small amounts of oxygen are required to enhance the gold dissolution rate. Jenkins also found that gold leaching decreased when oxygen was added in excess amounts due to the decomposition of thiosulfate.

From the discussion provided in this section, it is important to control the use of oxygen or air in thiosulfate solutions in order to achieve high rates of gold leaching and low rates of thiosulfate decompositions. The optimum level of oxygen or air required in thiosulfate solutions is a function of the ore characteristics used.

3.5.2.9 Effect of Pulp Density

Pulp density is defined as the ratio between the weight of ore in kilograms and the volume of solution in litres. Navarro et al. (2002) concluded that using 10% pulp density increased the percentage of gold extracted compared to 25 and 40%. Arslan et al. (2008) stated that an increase in the solid-liquid ratio decreased gold and silver leach recoveries with the optimum solid-liquid ratio as 10%.

Xia et al. (2003) studied the effects of pulp density on both thiosulfate consumption and the amount of gold extracted. As the pulp density increased from 28.6% to 61.5%, the thiosulfate consumption for 24 hours was reduced from 77.9 to 17.4 kg/t. At the lower pulp density, the gold extraction increased but the difference was very small; around 1.9% difference between the pulp density of 28.6% and 61.5%.

3.5.3 Optimum Leaching Conditions

From the previous discussion on the effects of different reagent concentrations and experimental conditions on gold leaching rate, it is possible to tabulate the optimum leach conditions for gold ore, concentrate and pure gold (as disc or foil) as shown in Table 3.5.

From the data shown in Table 3.5, it can be concluded that the reported optimum reagent concentrations and leaching parameters have a wide range and the optimum leaching conditions were affected by the type of the gold source used.

Table 3.5: The optimum reagent concentrations and leaching parameters in thiosulfate solutions reported by various authors.

Author	Optimum conditions	Type of gold
Arslan et al. (2008)	0.5 M S ₂ O ₃ ²⁻ , 1 M NH ₃ , 10 mM Cu(II), S/L ratio 10 %, 20 °C	Gold ore (6.4 g/t Au and 10.4 g/t Ag)
Arima (2003)	0.4 M S ₂ O ₃ ²⁻ , 3 M NH ₃ , 30 mM Cu(II), room temperature.	Gold ore (16g/t)
Xia et al. (2003)	0.3 MS ₂ O ₃ ²⁻ , 3 M NH ₃ , 30 mM Cu(II), pH 10.2	Copper-bearing ore
Aylmore (2001)	0.8 M S ₂ O ₃ ²⁻ , 4 M NH ₃ , 50 mM Cu(II),	Au-Cu sulfide
Jeffrey (2001)	Heap leaching: 0.2 M S ₂ O ₃ ²⁻ , 0.4 NH ₃ , 5 mM Cu(II); Standard gold leaching circuits: 0.4 M S ₂ O ₃ ²⁻ , 0.6 M NH ₃ , 10 mM Cu(II)	Gold/Silver disc
Breuer and Jeffrey (2000)	0.2 M S ₂ O ₃ ²⁻ , 0.09 M NH ₃ , 1 mM Cu(II), 6.25mM SO ₃ ²⁻	Gold disc
Chai (1997)	0.287 M S ₂ O ₃ ²⁻ , 2 M NH ₃ , 0.12 M Cu(II), 60 °C, aeration	Gold ore
Muyunda (1996)	0.4 M S ₂ O ₃ ²⁻ , 0.84M NH ₃ , 25 mM Cu(II), pH 10.5, 35 °C	Pure gold disc
Abbruzzese et al. (1995)	2 M S ₂ O ₃ ²⁻ , 4 M NH ₃ , 0.1 M Cu(II), 25 °C	Ore (51.6 g/t Au)
Langhans et al. (1992)	0.1 M S ₂ O ₃ ²⁻ , 0.4 M NH ₃ , 10 mM Cu(II), 30 °C, pH > 11.4	Low-grade Ore

3.6 Electrochemical Reactions

Electrochemical reactions are caused by, and can result in, an electron transfer. The electrochemical driving force is a potential (voltage difference) which results in a flow of electrons (an electrical current). Any electrochemical process must have two half reactions; one is the oxidation (anodic reaction) and the other is the reduction reaction (cathodic reaction).

3.6.1 Measurement of Solution Potentials

Actual electrode potentials in aqueous solutions can be measured using suitable indicator and reference electrodes. There are many different types of reference electrodes. Care should be taken to ensure that the potential measurements are compared against similar reference electrodes, or appropriate adjustments are made to measurements. The most commonly used reference electrodes are as follows (Marsden & House, 2006):

- platinum/calomel with saturated potassium chloride (HgCl_2), $E^0 = 0.242 \text{ V}$ vs. SHE (standard hydrogen electrode);
- platinum/mercury sulfate, 0.618 V vs. SHE; and
- silver/silver chloride, 0.222 V vs. SHE.

The most suitable electrodes for measuring potentials are those that are unreactive in the conditions used.

Potential sweep voltammetry methods are among the most powerful methods of investigating electrochemical reaction rates. The most important and easiest to use is a linear potential sweep. Among the electrochemical methods, voltammetry is one of the most popular methods for investigation of the overall electrochemical reaction, since it combines the advantages of short time scales and large potential variations. It consists in applying to the electrode under study a linear potential sweep between two potential limits, E_a and E_c , and recording the current flowing through the electrode as a function of the applied potential (Bockris et al., 1992). The output of this method is a relation between the applied potential and the measured current.

From this method, the potential at which the reactions take place can be compared to the thermodynamics to identify the reactions that may occur. Solid or solution reaction products can be determined from the effects of the sweep rate, and the formation of solid surface species that may cause passivation can be determined.

3.6.2 Electrochemical Reactions in Thiosulfate Solution

The leaching of gold occurs as a result of the oxidation of gold (anodic reaction) and the reduction of the oxidant (cathodic reaction).

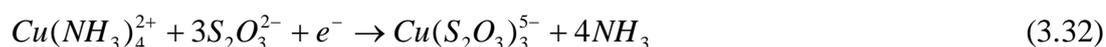
In the thiosulfate leaching system, the fundamental electrochemistry of the anodic oxidation of gold and of the cathodic reduction of oxygen and redox mediators such as the copper(II)/copper(I) couple have not been studied extensively (Zhang & Nicol, 2005).

The overall stoichiometric reaction for the dissolution of gold in aqueous alkaline thiosulfate solutions in the presence of oxygen is described in Equation 3.20. This consists of two reaction equations, the oxidation of gold, and the reduction of oxygen as shown in Equations 3.30 and 3.31.



However, this reaction has been found to be very slow in the absence of ammonia due to the formation of a sulfur-like film as a result of decomposition of thiosulfate on the gold surface (Zhang & Nicol, 2005 & 2003; White, 1905).

In the presence of copper(II) and ammonia in the thiosulfate solution, however, there is another reaction. Copper(II) is reduced by thiosulfate to copper(I). This reduction reaction is represented by Equation 3.32.



In the electrochemistry of gold in thiosulfate solutions containing copper and ammonia, the cathodic half reaction, the reduction of copper(II), occurs readily in the potential region where gold should be oxidised to gold thiosulfate. However, the gold oxidation half reaction in thiosulfate solutions without ammonia is hindered; the presence of ammonia is required for the reaction to occur at an appreciable rate (Breuer and Jeffrey, 2002).

To investigate an electrochemical process, each half reaction should be studied independently. Sections 3.6.2.1 and 3.6.2.2 will present the electrochemical mechanism of gold dissolution in thiosulfate solutions.

3.6.2.1 The Anodic Reaction (Gold Oxidation)

The oxidation of gold in thiosulfate has been studied using traditional electrochemical techniques (Zhang & Nicol, 2005; Chandra & Jeffrey, 2004; Chai &

Wang, 2003; Zhang & Nicol, 2003; Jiang et al., 1997 & 1993a; Zhu et al., 1994).

Polarisation curves were recorded by Breuer and Jeffrey (2002) for a gold electrode in a solution containing 0.1 M thiosulfate and 0.4 M ammonia. The data has been plotted in Figure 3.6, which shows that at the potential region 150–300 mV, there is an oxidation reaction occurring, although at a low rate. At potentials more positive than 300 mV, the current density increases rapidly.

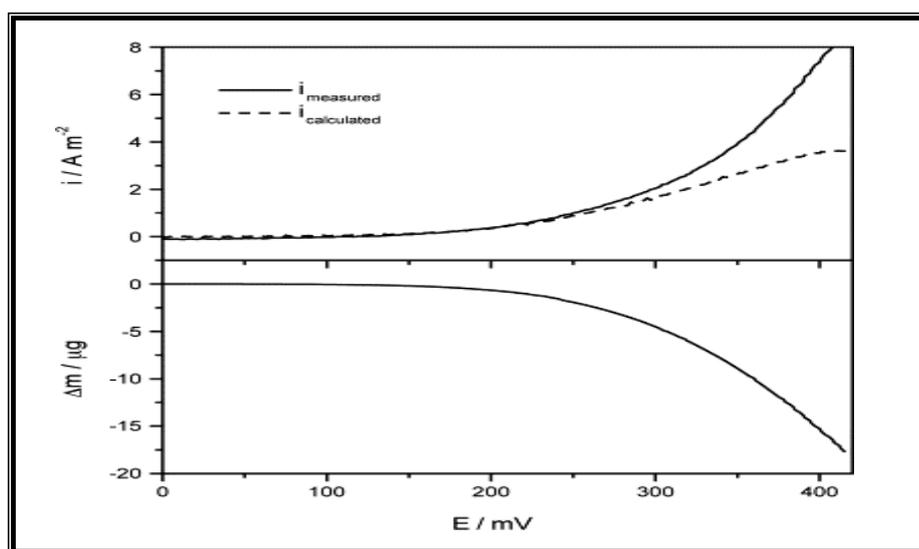


Figure 3.6: Linear sweep voltammogram showing the oxidation of gold to gold thiosulfate. Also shown is the mass change measured using the REQCM, and the partial current density ($i_{\text{calculated}}$) derived from this (Breuer & Jeffrey, 2002).

Voltammetry and electrochemical impedance spectra (EIS) experiments were conducted by Zhu et al. (1994). The results indicated that the anodic voltammetric curves of the gold electrode in thiosulfate solution did not indicate the features of gold dissolution, but passivation of the gold occurred. With the addition of ammonia into the system, however, the passivation of gold is completely eliminated, and gold dissolution increased. On the other hand, Dasgupta et al. (1997) concluded that the rate of dissolution of gold was not affected by the total ammonia ($\text{NH}_3 + \text{NH}_4$) concentration of the solution.

The effect of copper on the anodic dissolution of gold was studied electrochemically by Zhang and Nicol (2005) and they concluded that copper has a positive effect on the anodic dissolution of gold, with increasing concentrations of copper resulting in higher dissolution rates of gold at a potential of 0.3V.

The oxidation of gold in ammoniacal solutions at 75 °C was evaluated using electrochemical techniques by Dasgupta et al. (1997). The results showed that the dissolution current increased with the increase of the overpotential before gold became oxidised at 0.46 V vs. SCE in ammoniacal solutions. A current density peak during anodic polarization at 0.46 V vs. SCE is believed to be due to the formation of Au(OH)₃.

Electrochemical experiments were carried out by Chandra and Jeffrey (2004) using solid gold/silver alloy containing 2% silver. The linear sweep voltammograms for pure gold and the gold/silver alloy (Figure 3.7) show that when silver is present as an alloying element, the current density for gold/silver oxidation in thiosulfate solutions at all potentials is higher than that of pure gold.

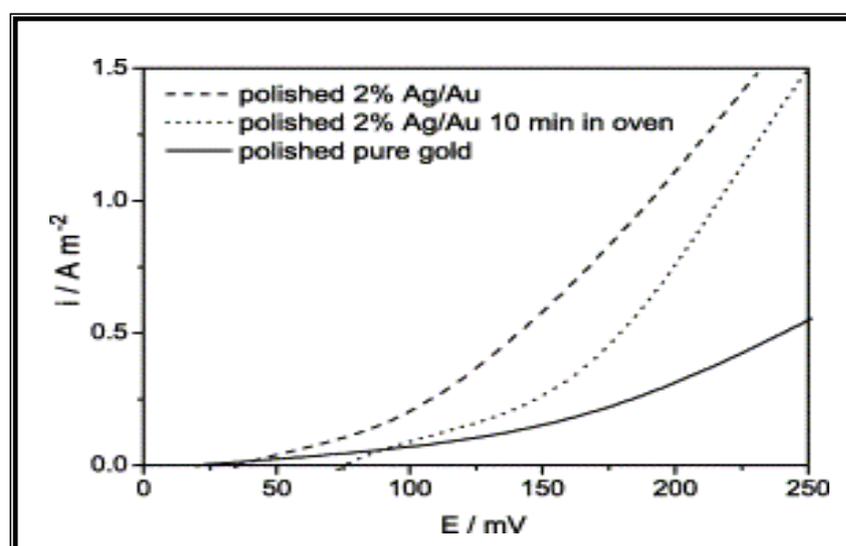


Figure 3.7: Linear sweep voltammograms showing the oxidation of a gold/silver alloy containing 2% silver in 0.2 M ammonium thiosulfate (Chandra & Jeffrey, 2004).

Chandra and Jeffrey (2004) also studied the effects of additives on the gold oxidation half reaction. In ammonium thiosulfate solutions containing 5 mM of either xanthate or thiourea, the addition of thiourea was found to be beneficial to the oxidation of gold, with the current density rapidly increasing as the potential is increased above 125 mV (Figure 3.8).

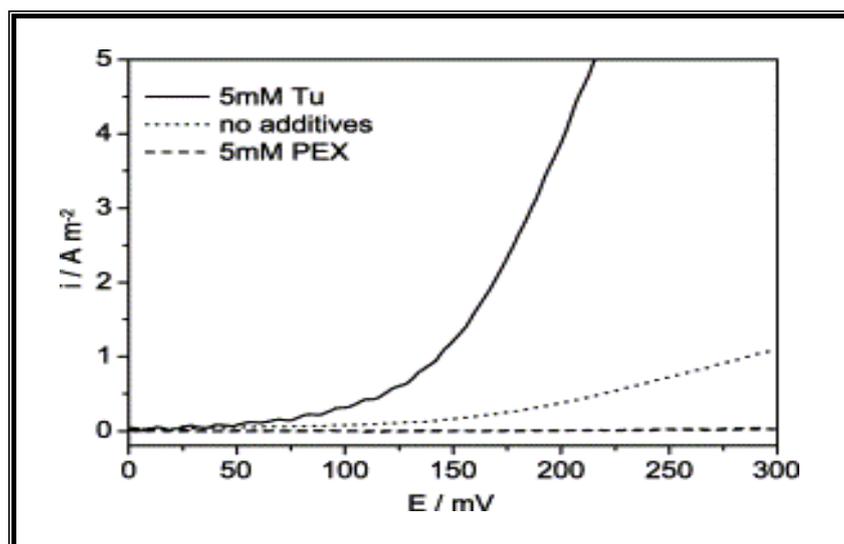


Figure 3.8: Linear sweep voltammograms showing the effect of thiourea (Tu) and potassium ethyl xanthate (PEX) on the gold oxidation half reaction in 0.2 M ammonium thiosulfate (Chandra & Jeffrey, 2004).

3.6.2.2 The Cathodic Reaction (Copper(II) Reduction)

The main reduction reaction in thiosulfate solutions is the reduction of copper(II) into copper(I) as shown in Equation 3.31. Breuer and Jeffrey (2002) from an electrochemical study on thiosulfate solutions found that the cathodic half reaction, the reduction of copper(II), occurs readily in the potential region where gold should be oxidised to gold thiosulfate.

Although there are limited published work on the cathodic reaction in thiosulfate solutions, Breuer and Jeffrey (2002) studied the cathodic reaction by replacing the gold electrode with an inert platinum electrode. Figure 3.9 shows the linear sweep voltammograms for three systems, these systems are:

Ammonia-thiosulfate: In air-saturated solutions containing ammonia and thiosulfate there are two possible reactions: the reduction of dissolved oxygen and the reduction of thiosulfate. It can be seen that both oxygen and thiosulfate reduction occurs at potentials more negative than 50 mV.

Copper-ammonia: For the solution containing cupric tetraamine without thiosulfate, there is the possibility of reducing copper(II) to copper(I), as the copper(I)-amine

complex is also stable in alkaline solutions. It can be seen that this reaction occurs at potentials more negative than 150 mV.

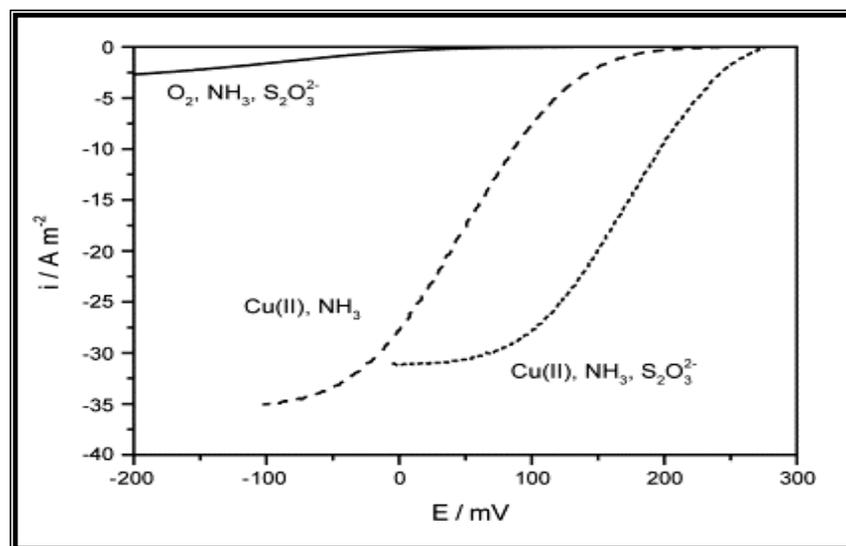


Figure 3.9: Linear sweep voltammograms for the reduction of oxygen in ammonia-thiosulfate solutions, and for the reduction of copper in ammonia and ammonia-thiosulfate solutions. A platinum electrode was used in these experiments (Breuer & Jeffrey, 2002).

Copper-ammonia-thiosulfate: In the presence of thiosulfate, there is the possibility of forming both thiosulfate and ammonia complexes of copper(I) (Breuer & Jeffrey, 2002). 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 the copper(II) ion is more readily reduced in a solution containing thiosulfate. Other studies (Michel & Frenay, 1996; Jiang et al., 1993a) have also found that increasing the concentrations of copper(II) and ammonia has a positive effect on the polarisation curve potentials of copper(II) reduction to copper(I).

Chapter 4 Materials and Methods

This section describes the materials and methods used in this research. Section 4.1 is the leaching kinetic experiments. These experiments were conducted on gold, silver and gold-silver alloys and a sample of gold ore from the Sukari Gold Mine. Section 4.2 describes the experimental procedure for electrochemical experiments performed on the gold, silver and gold-silver alloy discs. Section 4.3 is the dissolution of mercury, a common element found in gold ores and section 4.4 the recovery of gold, copper and mercury onto ion exchange resins.

4.1 Leaching Kinetic Experiments

The kinetic aspects of gold and silver leaching in thiosulfate solutions using pure gold, pure silver, and four different compositions of gold-silver alloys were studied using the rotating disc technique in open and closed 1 L vessels. Then, gold ore samples were used to optimise the process of gold leaching in thiosulfate and cyanide solutions.

4.1.1 Gold and Silver Sources

In this study, the sources of gold and silver were as follows:

- 1) Discs: Pure gold (99.99), pure silver (99.99), and gold-silver alloys of 4, 8, 20, and 50% silver; and
- 2) Ore samples: Gold ore samples were provided from the Sukari Gold Mine, Eastern Desert, Egypt, by the Centamin Egypt Limited Company.

4.1.1.1 Gold and Silver Discs

The gold and silver discs were made from 99.99% pure gold and silver (Perth Mint). A 17 mm diameter by 2 mm thick disc (with a surface area of 2.27 cm²) was formed in a stainless steel mould and embedded in a black phenolic (PremoldsTM) resin. The resin specimen mount was polished away to reveal one disc face. A hole was then drilled and tapped into the opposite side of the mount to attach a stainless steel shaft, which in turn could be attached to an agitator.

Pure gold, pure silver and gold-silver discs of silver compositions 4, 8, 20, and 50 wt.% silver were constructed (Figure 4.1).

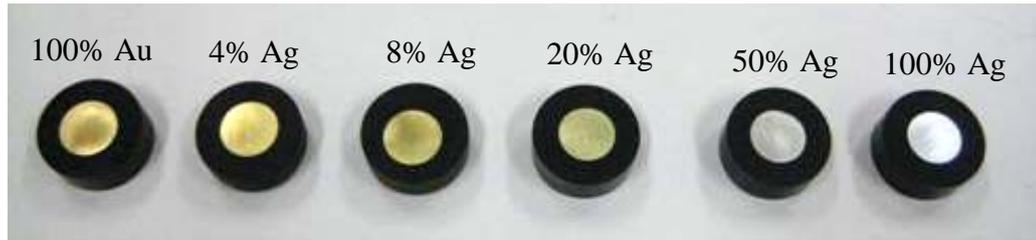


Figure 4.1: Pure gold, pure silver and gold-silver discs of different silver composition: 4, 8, 20, and 50 wt.% silver.

4.1.1.2 Gold Ore Samples

Gold ore samples were supplied from the Sukari Gold Mine, Eastern Desert, Egypt, by Centamin Egypt Limited. The ore consisted of about 50 kg of drill core pieces around 10 to 15 cm in length and 5 cm in diameter. The ore samples were separated according to weathered (near surface drill core) and unweathered (deep core) samples. Both the weathered and unweathered samples were crushed, firstly by a hydraulic Enerpack crusher (Enerpack model RR 308) shown in Figure 4.2. The crushed ore samples were sieved at a sieve size of 707 μm (25 mesh). The minus 707 μm fraction was collected for grinding and the plus 707 μm fraction was recycled back to the crusher. The crushed samples were ground by a bench top ring mill, which is shown in Figure 4.3.

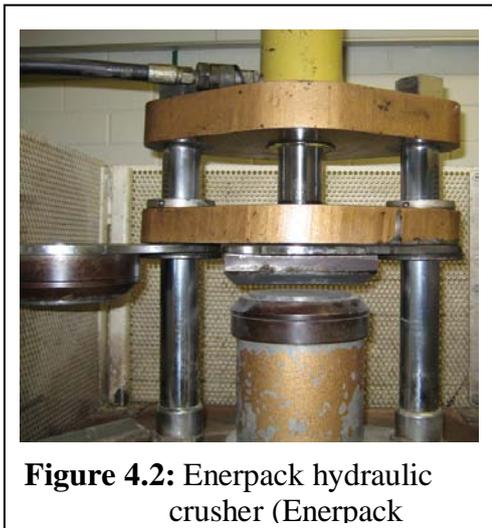


Figure 4.2: Enerpack hydraulic crusher (Enerpack)



Figure 4.3: Bench top ring mill and its internal components.

The ground weathered sample was mixed well by a rotary splitter and a subsample of the weathered ore and all the unweathered ore sieved at a size of $-106\ \mu\text{m}$. The sieved ore samples ($-106\ \mu\text{m}$) were passed through the splitter two times to homogenise them and then 250 g samples were split and packed into sample bags for use in the leaching experiments.

In order to study the gold leaching rate of different ore size fractions, about one kilogram of the weathered ground ore sample was screened into different size fractions by using sieves of 38, 75, 106, and 125 μm . Four size fractions, -38 , $-75+38$, $-106+75$, and $-125+106\ \mu\text{m}$, were collected. Finally, each size fraction was mixed well using the splitter and then 100 g samples were packed for the leaching experiments.

Quantitative X-Ray Diffraction (XRD) was used to determine the mineralogy of each size fraction for the weathered samples (Table 4.1) and the minus 106 μm material of the weathered and unweathered samples (Table 4.2). The XRD analysis was carried out in the X-Ray Analytical Science Laboratory, Faculty of Science, Curtin University of Technology.

Table 4.1: Quantitative XRD analysis (Wt.%) of the gold ore samples (weathered) for size fractions: -38 , $-75+38$, $-106+75$, and $-125+106\ \mu\text{m}$.

Phase	Sample			
	$-38\mu\text{m}$	$-75+38\mu\text{m}$	$-106+75\mu\text{m}$	$-125+106\mu\text{m}$
Quartz	25.0	30.9	31.3	30.4
Albite	49.5	46.4	46.1	48.2
Muscovite	13.3	10.5	8.3	10.5
Calcite	2.6	0.6	1.7	1.9
Microcline	8.6	9.4	9.5	6.9
Niningerite	-	0.9	1.0	0.3
Gupeite	0.3	0.6	0.5	0.5
Pyrite	0.7	0.7	1.6	1.3

An element analysis for each size fraction was performed by Ultratrace Laboratories, Perth, Western Australia, tabulated in Tables 4.3 and 4.4. The analysis was performed by acid digestion of the ore, followed by ICP–OES determination.

Table 4.2: Quantitative XRD analysis (Wt.%) for weathered and unweathered gold ore samples (size fraction $-106\ \mu\text{m}$).

Phase	Samples	
	Weathered ($-106\mu\text{m}$)	Unweathered ($-106\mu\text{m}$)
Quartz	29.6	24.7
Albite	50.3	63.4
Muscovite	9.3	3.5
Calcite	1.9	-
Microcline	7.2	4.8
Niningerite	0.5	-
Gupeite	0.6	0.2
Pyrite	0.6	1.1
Ankerite	-	2.3

Table 4.3: The elementary analysis (Wt.%) of the weathered gold ore for size fractions: -38 , $-75 +38$, $-106+75$, and $-125+106\ \mu\text{m}$.

Element	$-38\mu\text{m}$	$-75+38\mu\text{m}$	$-106+75\mu\text{m}$	$-125+106\mu\text{m}$
Au, ppm	4.12	4.23	5.39	3.22
Si, %	66	68	70.5	67.6
Al, %	15.1	14.6	13.6	14.6
Ca, %	2.08	1.6	1.28	1.6
Fe, %	4.5	4.19	3.68	4.22
K, %	2.14	2.15	1.95	2.17
Mg, %	0.44	0.47	0.4	0.48
Na, %	5.37	5.15	4.95	5.09
P, %	0.04	0.04	0.035	0.04
S, %	0.29	0.38	0.4	0.42
Ti, %	0.34	0.33	0.3	0.34
Mn, %	0.08	0.08	0.07	0.08

Table 4.4: The elementary analysis (Wt.%) for both weathered and unweathered gold ore samples of size fraction (-106 μm).

Element	Weathered (-106μm)	Unweathered (-106μm)
Au, ppm	3.71	4.59
Si, %	68.9	68.4
Al, %	14.3	13.4
Ca, %	1.61	1.37
Fe, %	3.97	4.2
K, %	1.95	1.05
Mg, %	0.35	0.59
Na, %	5.35	6.55
P, %	0.036	0.07
S, %	0.26	3.22
Ti, %	0.31	0.37
Mn, %	0.07	0.09

4.1.2 Rotating Disc Experimental Method

The following sections present the experimental setup and method for gold, silver and gold-silver disc leaching.

4.1.2.1 The Experimental Setup

- **Setup Using Discs**

The leaching of gold, silver, and gold-silver discs in the thiosulfate solutions was conducted using a rotating disc technique. The experiment setup for this consisted of:

- a mechanical agitator;
- a stainless steel rod;
- 1 L glass reactor, water bath with a thermostat;
- a five-necked glass cover (for closed vessel experiments);
- gold, silver and gold-silver alloy discs; and
- Teflon seals.

- **Setup Using Ore Samples**

The leaching of gold ore samples was conducted using a mechanical stirrer. The experiment setup consisted of the same components of the leaching disc setup except using a plastic agitation stirrer instead of the disc.

For both disc and ore leaching, a closed vessel system was used. In this system, a 1 L glass vessel was sealed by a five-necked glass cover and a mechanism that permits the stirrer rod to rotate in a Teflon seal in the middle neck of the cover. The same setup was used for the open vessel experiments, but the reactor vessel was left open to the ambient atmosphere. Figure 4.4 shows the experimental setup of the open and closed vessel systems.



Figure 4.2: The experimental setup of the open and closed vessels.

4.1.2.2 Disc Polishing

Before each experiment, the surface of the gold or silver or gold-silver disc was polished to obtain a clean and shiny surface to ensure that the surface in direct contact with the solution was free of passivation layers. The disc polishing was conducted with a waterproof silicon carbide paper (FEPA # 2400) and 3 micron aluminium oxide powder. Finally, the disc was washed with distilled water and allowed to dry for 5 minutes.

4.1.2.3 Disc Leaching Procedure

In this study, gold and silver leaching from pure gold, pure silver and 4, 8, 20, and 50% of silver gold-silver discs were used to evaluate the effect of silver on the gold leaching rate in thiosulfate solutions. In the leaching experiment for each alloy in thiosulfate- copper- ammonia solutions, a solution volume of 500 mL was used in both the open and closed 1 L vessel experiments, maintained at a constant temperature to ± 0.1 °C. Unless specified, the standard conditions used in the open and closed vessel experiments for the short run (1 hour) and the long run (8 hours

and 24 hours) were 0.2 M sodium thiosulfate, 10 mM copper(II) sulfate, 0.4 M ammonia, 30 °C and 300 rpm. All the experiments were conducted at a fixed pH of 11.5 and without air or oxygen injection.

4.1.2.4 Ore Leaching Procedure

During ore samples leaching, all experiments were carried out using solutions prepared from analytical reagents and de-ionized water. The main size fraction of the gold samples for most of the leaching experiments was -106 µm. One hundred grams of the ground ore was put into a 1L glass vessel as described in the experimental setup (section 4.1.2.1). A solution volume of 400 mL containing 0.2 M sodium thiosulfate, 10 mM Cu(II) sulfate, and 0.4 M ammonia was added to the ore sample to achieve a solid/liquid ratio of 20% weight to volume. The temperature was adjusted at 30 °C, and the rotation speed to 300 rpm. The leaching experiments were run for 24 hours.

Gold analysis was carried out using atomic absorption spectrophotometry (AAS) on filtered samples taken after 3, 8, 12, and 24 hours of leaching. At the end of each experiment, the solution was filtered and collected for assay. The residue was then washed by 50 mL of de-ionized water 3 times to ensure that all dissolved gold was washed from the residue. The gold concentration was measured using AAS. The solid residue was dried in an oven for 24 hours at 60 °C.

The dried solid residue was analysed for gold by firing a 40 gram (approx) portion of the sample (fire assay analysis), and the gold in the dore bead determined by the Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). The percentage of extracted gold was calculated from the gold in the leached residue, the main solution and the wash solution as follows:

$$\text{Gold Extraction (\%)} = \frac{\{(Au)_{main.sol.} + (Au)_{wash.sol.}\}}{\{(Au)_{main.sol.} + (Au)_{wash.sol.} + (Au)_{residue}\}} \times 100$$

where:

$(Au)_{main.sol.}$: total amount of gold in the main solution (mg);

$(Au)_{wash.sol.}$: total amount of gold in the wash solution (mg); and

$(Au)_{residue}$: total amount of gold in the residue solution (mg).

4.1.2.5 Gold and Silver Analysis

The analysis of the dissolved gold and silver from each disc during the open and closed vessel experiments was measured by atomic adsorption spectrophotometry.

4.1.2.6 Thiosulfate Analysis

The concentration of thiosulfate in the leach solution for both gold-silver disc and ore experiments was determined by the idometric titration method (Lenahan & Murray-Smith, 1986) during, and at the end of each test. The principle and procedure of this method are as follows.

- **Principle**

The principle behind thiosulfate analysis depends on the determination of thiosulfate, sulfite, and sulfide in the solution. In an acidic solution, sulfite, sulfide and thiosulfate are oxidized by iodine to sulfate, sulfur and tetrathionate respectively according to Equations 4.1, 4.2, and 4.3.



Titration, based on these reactions, provides an accurate method for the determination of all three species. The sample to be analysed is divided into three portions. One portion is titrated with a standard iodine solution: the result obtained is the combined concentration of the three ions. A second portion of the sample is treated with formaldehyde with which the sulfite reacts (Equation 4.4).



The hydrosulfonate thus formed does not react with iodine. By iodometric titration, the combined concentration of sulfide and thiosulfate is therefore obtained. A third portion of the sample is treated with zinc acetate to precipitate zinc sulfide (Equation 4.5).



Iodometric titration then determines the combined sulfite and thiosulfate. Subtraction of this value, from the value obtained from the first titration, provides the

sulfide content. By deduction of the combined concentration of sulfite and sulfide from the total value, the thiosulfate concentration is derived.

Exposure of the sample to air should be minimised to prevent oxidation. Certain metal ions, such as Cu^{2+} , may catalyse the oxidation of sulfite to sulfate on exposure of the sample to air. As a general precaution against auto-oxidation, solutions should be analysed no later than six hours after the time of sampling.

- **Solutions**

The solutions and their concentrations used in the thiosulfate determination were:

- (a) Standard iodine solution: 0.05 M I_2 ;
- (b) Starch solution: 5 g/L;
- (c) Acetic acid: glacial;
- (d) Formaldehyde solution: 370 g HCHO/L;
- (e) Sodium hydroxide solution: 6 M NaOH (Stored in a plastic bottle); and
- (f) Zinc acetate solution: 1 M $\text{Zn}(\text{CH}_3\text{COO})_2$.

- **Procedure**

Into each of three 250 cm^3 Erlenmeyer flasks, the appropriate volume of the sample to be analysed was pipetted.

(a) Determination of the sum of sulfite, sulfide and thiosulfate concentrations.

To the sample in the first flask, 5 cm^3 of acetic acid was added. One cm^3 of starch solution was then added and mixed. The solution was swirled and titrated with standard iodine to the first permanent blue color. The volume of iodine solution used was recorded: titre a (cm^3).

(b) Determination of the sum of sulfide and thiosulfate concentrations.

To the sample in the second flask, 35 cm^3 of formaldehyde solution was added. The pH was adjusted to 8.2 by the addition of sodium hydroxide solution. Twenty five cm^3 of water and 5 cm^3 of acetic acid were added. The solution was swirled and titrated with standard iodine to the first permanent blue color. The volume of iodine solution used was recorded: titre b (cm^3).

(c) Determination of the sum of sulfite and thiosulfate concentrations.

To the third aliquot, 5 cm^3 of zinc acetate solution was added. The pH was adjusted to 12 by the addition of sodium hydroxide solution. The solution was mixed well and

left to allow the precipitate of zinc sulfide to settle. The solution was filtered through a paper of medium porosity. To the filtrate, 5 cm³ of acetic acid and 1 cm³ of starch solution were added. The solution was swirled and titrated with standard iodine to the first permanent blue color. The volume of iodine solution used was recorded: titre c (cm³).

From the iodometric titrations, the thiosulfate concentration was calculated by Equation (4.6)

$$\text{Concentration of thiosulfate, (mg/L)} = \frac{(b + c - a) \times M \times 224 \times 1000}{V} \quad (4.6)$$

where:

a is the titre (cm³) of the sum of sulfite, sulfide and thiosulfate;

b is the titre (cm³) of the sum of sulfide and thiosulfate;

c is the titre (cm³) of the sum of sulfite and thiosulfate;

M is the concentration of the iodine solution (0.05M); and

V is the volume of sample (cm³).

At the end of each ore leaching experiment, the final concentration of thiosulfate obtained from Equation (4.6) was subtracted from the initial thiosulfate concentration and the thiosulfate consumption during leaching calculated using Equation (4.7).

$$\text{Sodium thiosulfate consumption, (kg/t-ore)} = \frac{V \times (S_2O_3^{2-})_{consumed}}{W} \quad (4.7)$$

where:

V is the volume of thiosulfate solution used in the leaching experiment, L;

$(S_2O_3^{2-})_{consumed}$ is the amount of thiosulfate consumed in the experiment, mg/L; and

W is the weight of the ore sample used in the experiment, g.

4.1.2.7 Copper(II) Analysis

Copper(II) is the main oxidant in the thiosulfate leaching system and its concentration has a significant influence on the gold leach rate. Copper(II) concentrations were measured by using UV-Vis spectrophotometry in order to monitor the concentration of the copper(II) ammine complex. The maximum absorbance of this component (copper(II) ammine) was found at a wavelength of 605 nm in concordance with Breuer (2002). Figure 4.5 shows the absorbance of copper(II) ammine as a function of wavelength at different concentrations of Cu(II).

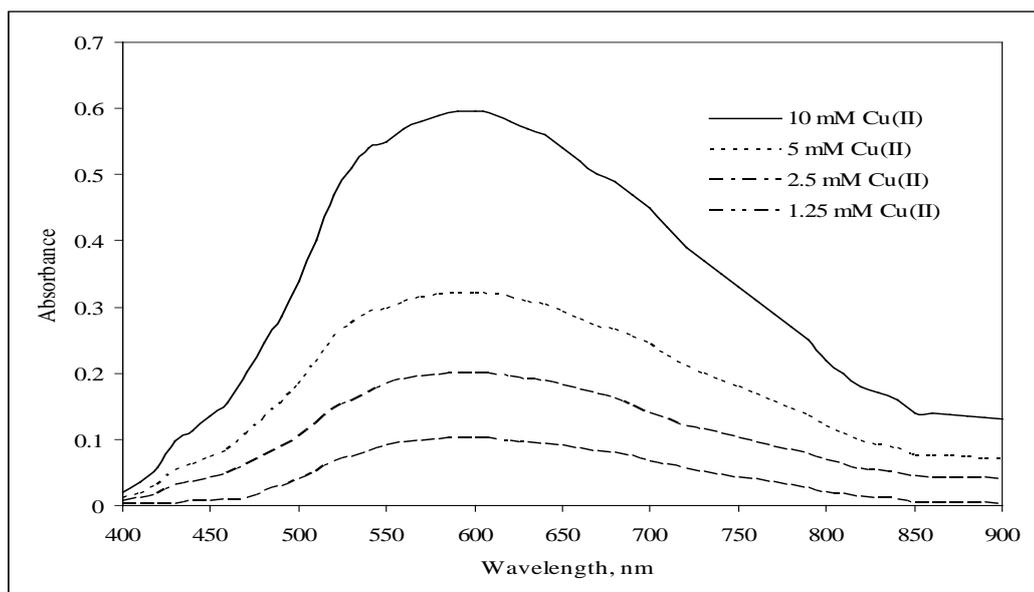


Figure 4.3: The absorbance of copper(II) ammine in solutions containing 400 mM ammonia and 100 mM sodium thiosulfate at 30 °C using UV-Vis spectrophotometer.

• **Procedure**

The procedure to determine copper(II) concentration is given in the following steps:

1. A blank solution containing only 0.4 M ammonia and 0.2 M sodium thiosulfate was prepared;
2. A stock solution of 100 mM Cu(II) as copper ammine complex was prepared. To decrease the contact reaction time between thiosulfate and copper(II), another stock solution of 1 M sodium thiosulfate was prepared separately. These solutions were stored in sealed volumetric flasks (500 mL) maintained at a constant temperature 30 ± 0.1 °C;
3. The appropriate volumes of copper(II) ammine complex and thiosulfate stock solutions were mixed in 50 mL volumetric flasks to form Cu(II) standards of 1.25, 2.5, 5, 10, and 20 mM Cu(II). A sample was taken from each standard solution, as well as the blank, and these were sealed within UV cells which were placed in a covered cell holder of a SHIMADZU (UV mini1240) UV-Vis spectrophotometer;
4. Firstly, the absorbance of the blank sample was read and the instrument was adjusted to read zero absorbance. This step removes the effects of ammonia and thiosulfate on the absorbance at the wavelength 605 nm;
5. The absorbance at 605 nm was measured for each copper(II) standard;

6. From the previous step, a calibration curve was constructed, as shown in Figure 4.6; and
7. Finally, the absorbance of the samples from each experiment at different times were recorded, and the absorbance readings were converted into copper(II) concentrations using the calibration curve (Figure 4.6).

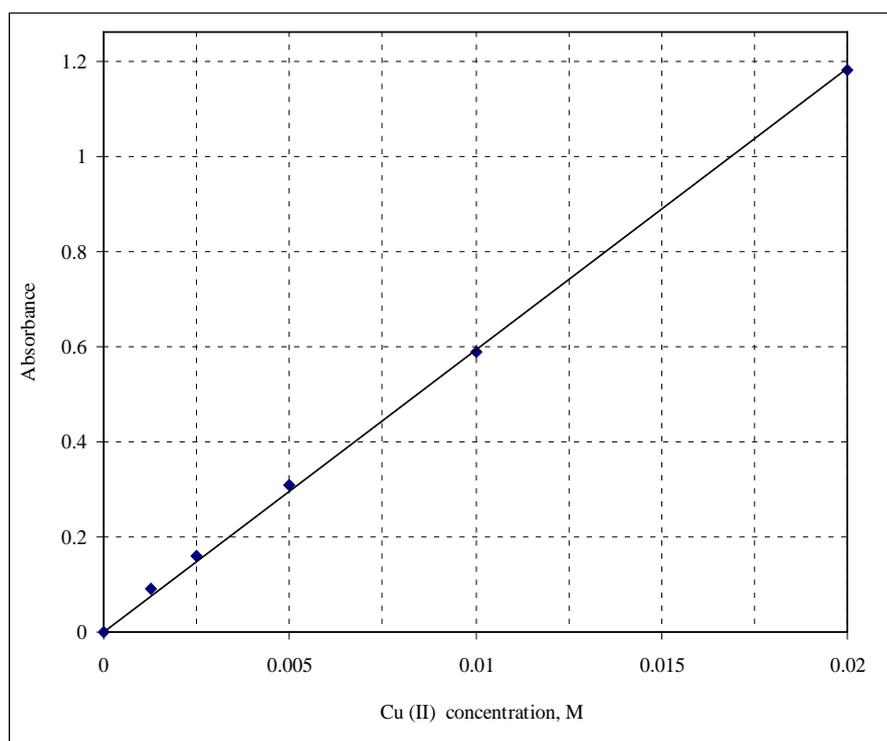


Figure 4.4: The calibration curve of copper(II) ammine.

4.1.2.8 Ammonia Analysis

For all gold leaching experiments conducted in the open and closed vessels, the ammonia analysis was carried out by the phenate method as described by Greenberg et al. (1992).

- **Principle**

In an alkaline solution (pH 10.4-11.5), ammonia reacts with hypochlorite and phenol catalyzed by a manganous salt to form the blue coloured indophenol. The concentration of ammonia is then determined spectrophotometrically using a UV mini 1240 UV-Vis spectrophotometer. To ensure the peak value of indophenol was at a wavelength of 630 nm, a wavelength scan of a 3.05 mg/L ammonia standard was conducted, as shown in Figure 4.7.

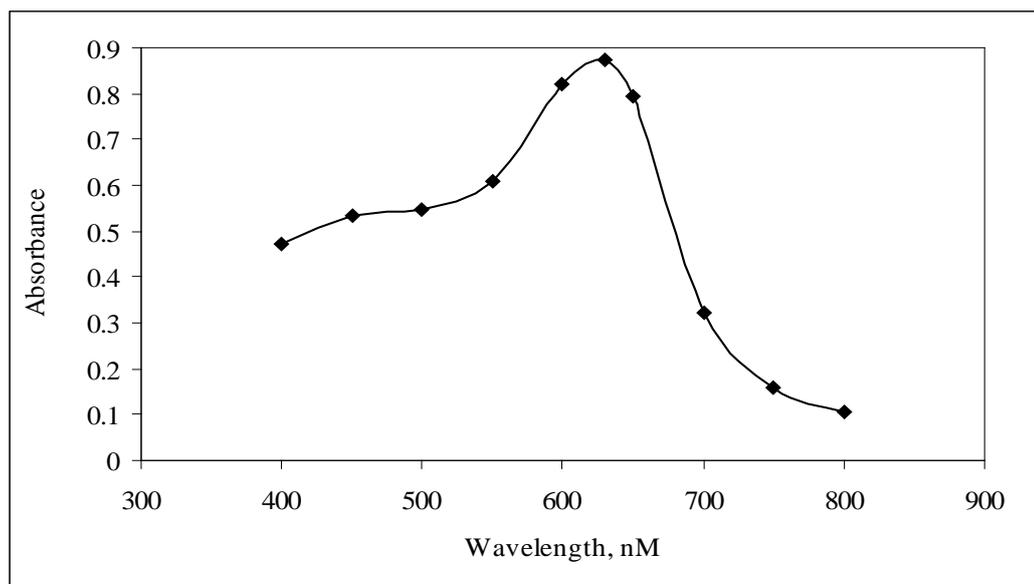


Figure 4.5: Wavelength scan of the absorbance of an ammonia standard solution using UV-Vis spectrophotometry.

- **Solutions**

The solutions and their concentrations used in the determination of ammonia were:

- Phenol (C_6H_5OH): Dissolve 2.5 g NaOH and 10g phenol in 100 mL water;
- Sodium hypochlorite solution: To 40 mL water, 10 mL (5-6% NaOCL solution) was added and the pH adjusted to 6.5 to 7 with HCl (Prepared Weekly);
- Manganese sulfate (0.05 mL $MnSO_4$); and
- Stock ammonia solution: 0.3819 g of the dried salt (ammonium chloride , NH_4Cl) was dissolved in water in a 1000 mL volumetric flask and diluted to the mark with water. The solution is stable for six months when stored in a refrigerator.

- **Procedure**

The procedure for ammonia determination by this method was:

1. Preparation of the standards: a calibration curve in the range from 0 to 12 mg/L was prepared;
2. 5.0 mL of each of these standard solutions and 5.0 mL of water were transferred to a 30 mL test tube;
3. One drop (0.05 mL $MnSO_4$) solution was added;
4. 0.5 mL sodium hypochlorite was added and mixed well;

- 0.6 mL phenol was added and mixed well until a blue colour is formed;
- The sample was then transferred to a 10 mm UV cell and the absorbance was measured at 630 nm;
- A calibration curve, plotting the absorbance of each of the standard solutions against its concentration of ammonium, was prepared; and
- In order to check for ammonium in the reagents, a photometric reading of a reagent blank (0.00 mg NH_3^+ /L) against water was taken. The absorbance should not exceed 0.020.

To analyse the samples, firstly, they were diluted to suit the calibration curve values, and then 5.0 mL of the sample and 5.0 mL of water were transferred to a 30 mL test tube. The procedure followed the instructions, as in points 3, 4 and 5. The spectrophotometric readings of the sample were converted to mg NH_3^+ /L by means of the calibration curve shown in Figure 4.8.

If the pH-value of the sample was lower than 3, the sample was neutralized. If the sample was turbid, both the sample and the blank was filtered through a white band filter.

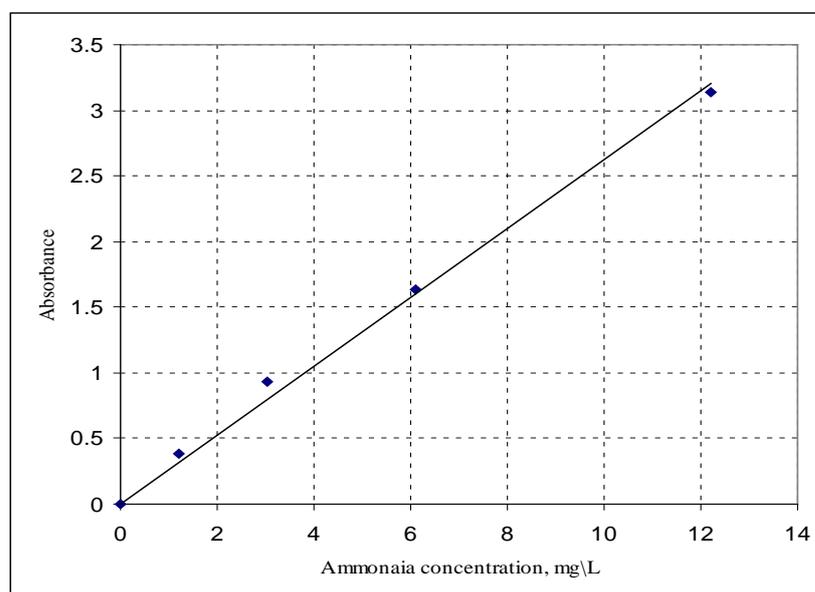


Figure 4.6: The calibration curve of different ammonia standards.

4.2 Electrochemical Rotating Disc Experiments

Electrochemical rotating disc experiments were carried out using pure gold, pure silver and 4, 8, 20, and 50% silver gold-silver discs using two different

electrochemical techniques: (1) linear sweep voltammetry, and (2) coulometry at a fixed potential value.

4.2.1 Linear Sweep Voltammetry

4.2.1.1 Solution and Disc Preparations

All experiments were carried out using 50 mL of solutions prepared from analytical reagents and Millipore water.

The solutions used in these experiments were:

- Ammonium thiosulfate (ATS) or sodium thiosulfate (STS) only;
- Ammonium thiosulfate (ATS) or sodium thiosulfate (STS) and ammonia;
- Ammonium thiosulfate (ATS) or sodium thiosulfate (STS) and ammonia and copper sulfate; and
- Ammonium thiosulfate (ATS) or sodium thiosulfate (STS) and thiourea.

All solutions were deaerated using nitrogen gas for 20 minutes and performed at 30 °C, with a rotation rate of 300 rpm, and at the natural pH of the solution, which was typically pH 11-11.5. Before each experiment, the surface of the gold or silver or gold-silver disc was polished as described in section 4.1.2.2.

4.2.1.2 Experimental Setup

Linear sweep voltammetry was carried out using a Radiometer PGP201 potentiostat. All experiments were performed at a scan rate of 1 mV s⁻¹. All potentials were measured relative to the saturated calomel electrode (+0.242 V vs. SHE), but are reported relative to the standard hydrogen electrode (SHE). The current was measured at a range of potentials between -22 mV and 300 mV.

4.2.2 Coulometric Experiments

The electrochemical coulometric experiments were carried out to study the effects of ammonium thiosulfate (ATS), sodium thiosulfate (STS), ammonia, copper(II), and thiourea concentrations on the total leach rate (gold and silver) from pure gold and t gold-silver alloys.

4.2.2.1 Solution and Disc Preparation

All experiments were carried out using in 50 mL of solution prepared from analytical reagents and Millipore water.

The solutions used were:

- Ammonium thiosulfate (ATS) only;
- Ammonium thiosulfate (ATS) and ammonia;
- Ammonium thiosulfate (ATS), ammonia and copper(II); and
- Ammonium thiosulfate (ATS) and thiourea.

Before each experiment, the surface of the gold or silver or gold-silver disc was polished as described in section 4.1.2.2.

4.2.2.2 Experimental Setup

Coulometric experiments were conducted at fixed potentials on pure gold and gold-silver alloys in an electrochemical cell containing thiosulfate solutions for 30 minutes. All experiments, unless specified, were performed at a rotation speed of 300 rpm and at a temperature of 30 °C for 30 minutes at different fixed potential values. All the solutions were deaerated using nitrogen for 20 minutes.

The produced current in the electrochemical cell was measured and the electric charge density ($\text{mC}\cdot\text{cm}^{-2}$) was obtained by the integration of the current-time plot. After each experiment, a sample was collected and analysed for gold and silver by ICP-OES. The setup of the electrochemical cell that was used in the electrochemical experiments is shown in Figure 4.9.

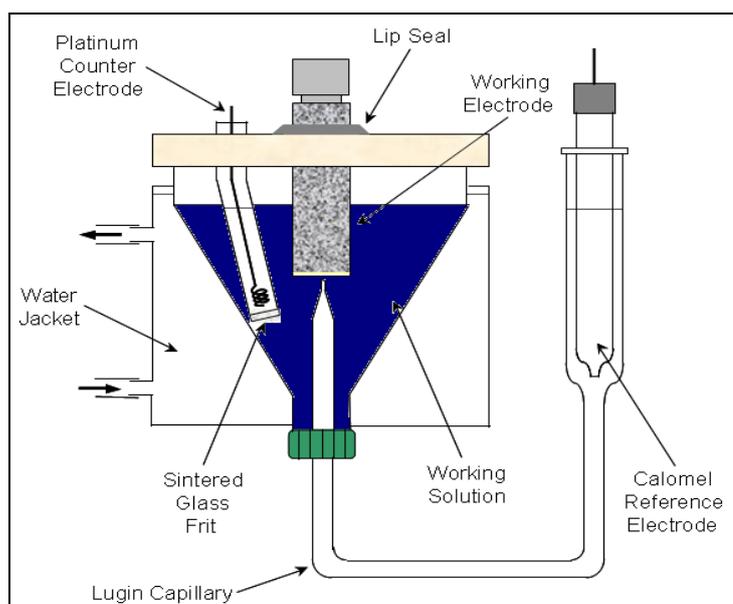


Figure 4.7: The electrochemical cell setup used to conduct the different experiments.

4.3 Mercury Dissolution

In this project, the ability of thiosulfate and cyanide solutions to dissolve different mercury compounds was evaluated. All the mercury compounds used were analytical reagents grade. In this section, the dissolution of each mercury form in thiosulfate and cyanide solutions was studied.

4.3.1 Mercury Dissolution Experiments

The dissolution of the different mercury compounds in thiosulfate and cyanide solutions was studied. The different mercury compounds used were: elementary mercury (Hg^0), mercuric chloride (HgCl_2), mercurous chloride (Hg_2Cl_2), and mercury sulfide (HgS). All the mercury leaching experiments were conducted using the bottle roll technique. One hundred millilitres of solution was used in 250 mL plastic bottles.

The thiosulfate and cyanide solutions used were:

- 2.5 g/L NaCN solution;
- 50 mM ammonium thiosulfate (ATS), 400 mM NH_3 , 10 mM Cu^{2+} ;
- 50 ATS, 1 mM Cu^{2+} ;
- 50 ATS, 10 mM thiourea (Tu), 12.5 mM ferric oxalate, 5 mM FeCl_3 ; and
- 50 ATS, 10 mM Tu, 5 mM FeEDTA.

The initial pH of the solution was: 12 for the cyanide system solution; 11.4 for the ATS, copper, ammonia solution; 10 for the ATS, 1 mM Cu^{2+} solution; 5.5 for the solution containing Ferric Oxalate; and, 7 for the solution containing FeEDTA. Following the addition of the mercury compound, the solutions were rolled on an electric roller for 48 hours at ambient temperature and at a rotation speed of 60 rpm. For mercury analysis, 12 mL samples were taken after 5, 24, and 48 hours leaching, and filtered immediately with a 0.5 mm micro filter. Ten mL from each filtered sample was treated with 1 mL of 0.1 M tetra-sodium EDTA to stabilise the mercury. All the samples were analysed for mercury by the ICP-OES.

4.4 Gold, Copper and Mercury Recovery

The recovery of gold, copper and mercury from pregnant ammonium thiosulfate (ATS) solutions using a strong anion-exchange resin was evaluated. Commercially available anion-exchange resin, Purolite A500/2788, was obtained in

its wet form. The physical and chemical properties of the resin will be shown in Chapter 8 (Table 8.4). The metal loading and recovery was conducted using two different experiments: (1) loading-stripping and (2) loading-elution.

4.4.1 Loading-Stripping Experiments

The anion-exchange resin experiments were carried out using plastic bottles (500 mL) that were sealed and placed on an electric roller at 60 rpm at room temperature (24 - 25 °C). Loading was accomplished by contacting 0.667 g of the resin with 250 mL of solution for 5 hours. The stock loading solution consisted of 100 mM ammonium thiosulfate (ATS), 4 mM trithionate ($S_3O_6^{2-}$), 1 mM $CuSO_4 \cdot 5H_2O$, and 5 mM gold (Au) as gold thiosulfate $[Au(S_2O_3)_2]^{3-}$. Different mercury concentrations of 0, 2, 3, 5, 7, 10, 15, and 20 mg/L Hg as $HgCl_2$ were added to the stock loading solution. At the start of each experiment, two samples of 10 mL were taken for analysis, one for gold and copper and the second for mercury. After 5 hours of loading, the experiment was stopped and two more samples were taken from the solution to measure the amount of gold, copper, and mercury left unloaded in each solution.

The loaded resin was stripped two times for 30 minute each using 25 mL of 0.5 M sodium perchlorate ($NaClO_4 \cdot H_2O$). The concentration of gold, copper, and mercury were analysed before loading ($t= 0$ hour), after loading ($t= 5$ hours), and after each stripping batch using ICP-OES. Solution speciation for thiosulfate and polythionates was carried out using HPLC after loading ($t= 5$ hours) and for each stripping batch.

4.4.2 Solution Speciation

Solution speciation for thiosulfate and polythionate components after 5 hours loading and for each stripping batch was carried out using a high performance liquid chromatography (HPLC) system. The HPLC system comprised a Dionex AS16 strong base anion exchange column (4×250 mm) with AG16 guard, coupled with a Waters 2695 separation module. Detection of UV active components was accomplished using a Waters 2996 UV Photodiode Array (PDA) detector ($\lambda = 190\text{--}400$ nm). An isocratic elution with perchlorate at 1 mL/min flow rate was used to separate the anionic sample components. Waters Empower software was used for

analysis of component peak areas, and the concentration determined were based on comparisons with calibration standards (Jeffrey & Brunt, 2007).

4.4.3 Loading-Elution Experiments

Six grams of wet resin were loaded overnight in 1.5 L of solution containing 100 mM ammonium thiosulfate (ATS), 4 mM trithionate ($S_3O_6^{2-}$), 1 mM $CuSO_4 \cdot 5H_2O$, 5 mM gold (Au) as gold thiosulfate $[Au(S_2O_3)_2]^{3-}$, and 5 mg/L Hg as $HgCl_2$. The solution and the resin were put in a 2 L volumetric flask and stirred overnight at a speed of 150 rpm. The loaded resin was washed with de-ionised water, and then 8 mL of the loaded resin was measured by a volumetric cylinder and transferred into the elution column. The loaded resin was eluted using 100 mL of an eluant solution containing 2 M NaCl and 0.2 M Na_2SO_3 . The solution was pumped into a column at a flow rate of 14.8 mL/h. An automatic fraction collector was adjusted to collect 8 mL fractions. Each fraction was analysed for gold, copper, and mercury using ICP-OES. Finally, the rest of the loaded resin was stripped two times in series for 30 minutes using a solution of 0.5 M perchlorate ($NaClO_4 \cdot H_2O$). After each batch was stripped, samples were collected for gold, copper, and mercury analysis.

Chapter 5 Thiosulfate Leaching in Open and Closed Vessels

5.1 Introduction

One of the main advantages of using thiosulfate is that it has less adverse environmental impact than cyanide. However, of environmental concern when using thiosulfate is that ammonia is required to stabilise the copper(II) ions in solution as the copper(II) tetraamine complex. In this chapter, the main objective is to compare both the leaching kinetics and associated environmental issues of using open and closed leaching tanks with thiosulfate leaching in the presence of ammonia. After determining whether an open or closed tank gave the best leaching kinetics and which was more environmentally acceptable, an optimisation of different leaching reagent concentrations was conducted in the chosen system for short run (1 hour) and long run (8 hours) leaching experiments. Figure 5.1 shows the procedure adopted to achieve the objectives of this section of the project.

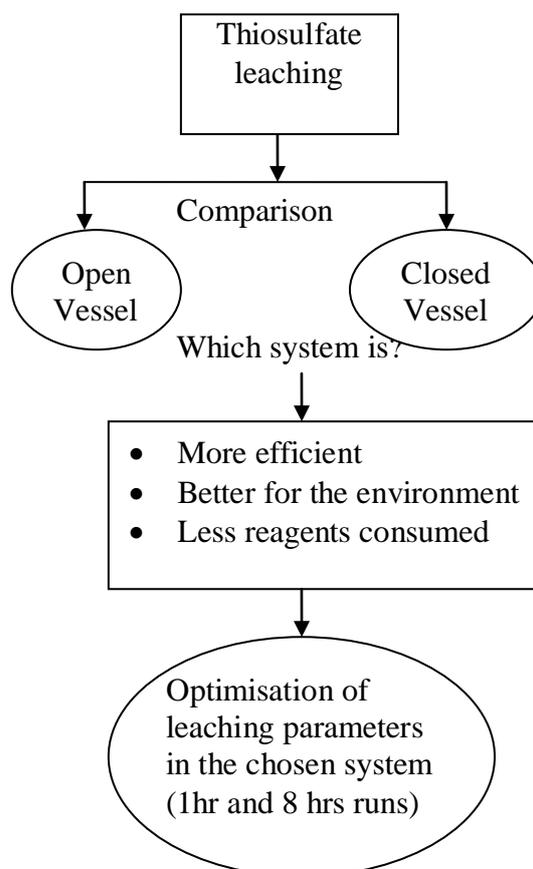


Figure 5.1: Procedure to achieve the goals and achievements.

5.2 Thiosulfate Leaching in Open and Closed Vessels

The kinetic aspects of sodium thiosulfate leaching of gold and silver were studied using a rotating disc technique in open and closed vessels to compare which one of them is more efficient for gold and silver leaching, has less environmental impact and lower reagents consumption. The setup of the experiment for leaching in open and closed vessels has been shown in Figure 4.4 (Chapter 4). Both the open and closed vessel experiments were conducted with 500mL of leaching solutions in a 1L vessel thermostatted to ± 0.1 °C. For the open vessel experiments, the vessel was left open to the atmosphere providing a 100mm diameter interface between the solution and the atmosphere. For the closed vessel experiments, the vessel was sealed with a glass cover, which provided a head space above the solution of approximately 500mL (Figure 4.4).

5.2.1 Gold and Silver Leaching in Open and Closed Vessels (1 hour run)

The standard leaching conditions used to compare the gold and silver leaching in open and closed vessels were selected from the previous published studies: 0.2 M sodium thiosulfate, 10 mM copper(II) sulfate, 0.4 M ammonia, 30 °C, and 300 rpm. The pH was fixed at a value of 11.5. Leaching began when the gold or silver disc was inserted into the leaching solution. The leaching experiment lasted an hour with samples being extracted after 15, 30, 45 and 60 minutes. Figure 5.2 shows the amount of gold and silver dissolved from both open and closed vessel runs in solutions containing the selected standard leaching conditions.

The data in Figure 5.2 shows that the amount of gold and silver dissolved in thiosulfate solutions using the closed vessel for the 1 hour run is slightly higher than that for the open vessel. It can be seen that silver dissolution in the thiosulfate solution is higher than that of gold. This observation has also been observed in cyanide solutions by Jeffrey, (2001). Jeffrey noted that gold dissolves nearly seven times slower than silver with the dissolution rate of silver and gold about $26.6 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ and $3.9 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ respectively. According to Lide (1990), the chemical bond strength of Au-Au ($53.8 \pm 0.5 \text{ kcal/mol}$ at 25 °C) is higher than that of Ag-Ag ($39 \pm 2.0 \text{ kcal/mol}$) indicating that the dissolution rate of silver is higher than that of gold.

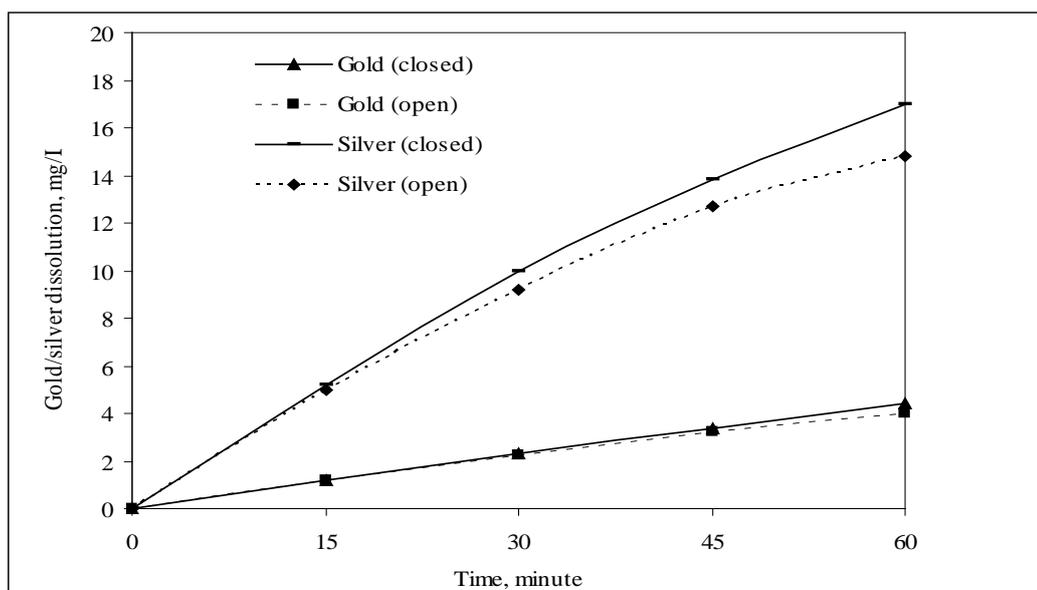


Figure 5.2: The amount of gold and silver dissolved in both open and closed vessels.

Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, pH= 11.5 and 30 °C.

In order to determine the reason for the difference in gold and silver leaching between the open and closed vessels, the concentrations of thiosulfate, ammonia, and copper(II) were analysed after 30 and 60 minutes of gold leaching using pure metal. The results are shown and discussed in sections (5.2.1.1, 5.2.1.2, & 5.2.1.3).

5.2.1.1 Thiosulfate Depletion in Open and Closed Vessels

Sodium thiosulfate concentrations were assayed in the open and closed vessels by idometric titration (Lenahan and Murray-Smith, 1986). Figure 5.3 shows the thiosulfate concentration as a function of time in solutions initially containing 0.2 M thiosulfate, 10 mM copper sulfate, 0.4 M ammonia without any air or oxygen injection. The results show that there is a slight decrease in the thiosulfate concentration (around 3.5% loss) after 60 minutes leaching in both open and closed vessels. The greater decrease in thiosulfate in the open vessel may be due to the reaction of thiosulfate with the oxygen from the ambient atmospheric air. This result is similar to that of Breuer and Jeffrey (2003), where it was found that only 5% of thiosulfate was decomposed after 1 hour of leaching without air or oxygen injections.

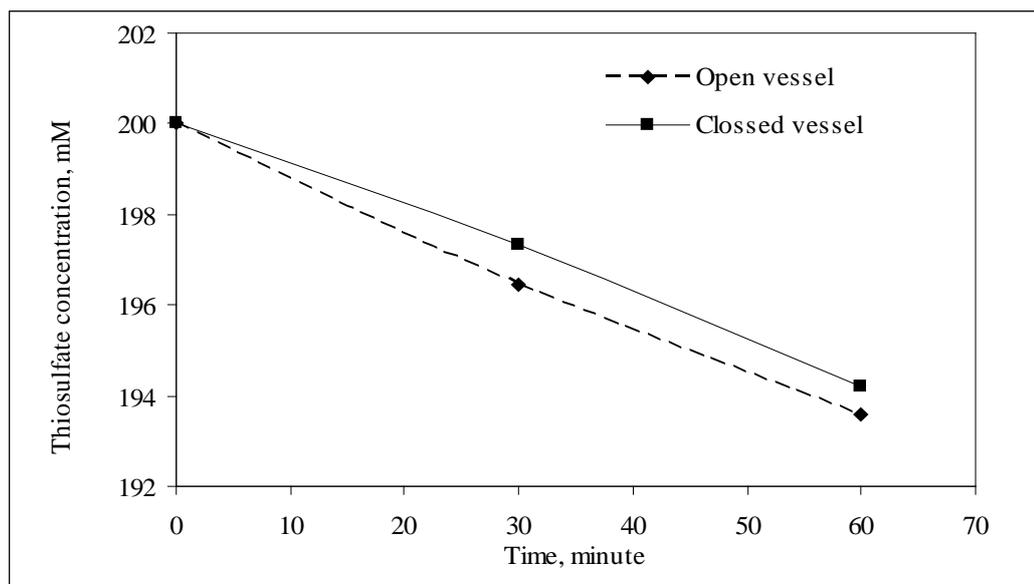


Figure 5.3: Thiosulfate concentrations in open and closed vessels after 30 and 60 minutes leaching. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, pH= 11.5 and 30 °C.

5.2.1.2 Ammonia Analysis in Open and Closed Vessels

The concentration of ammonia was analysed after 30 and 60 minutes leaching. Figure 5.4 shows the concentration of ammonia as a function of time. The analysis of ammonia in the open and closed vessels was carried out by the phenate method (Greenberg, et al., 1992). It was found that loss of ammonia from the open vessel was higher than that from the closed one and hence, the stability of Cu(II) tetraammine complex may have been compromised allowing greater reduction of Cu(II) by thiosulfate. Keeping ammonia in the leaching solution is necessary to stabilise the copper(II) in the system. Ammonia loss from the open vessel might have a secondary detrimental effect causing environmental problems. Therefore, it would be preferable, kinetically and environmentally, to run the thiosulfate leaching of gold or silver in the presence of ammonia in a closed vessel.

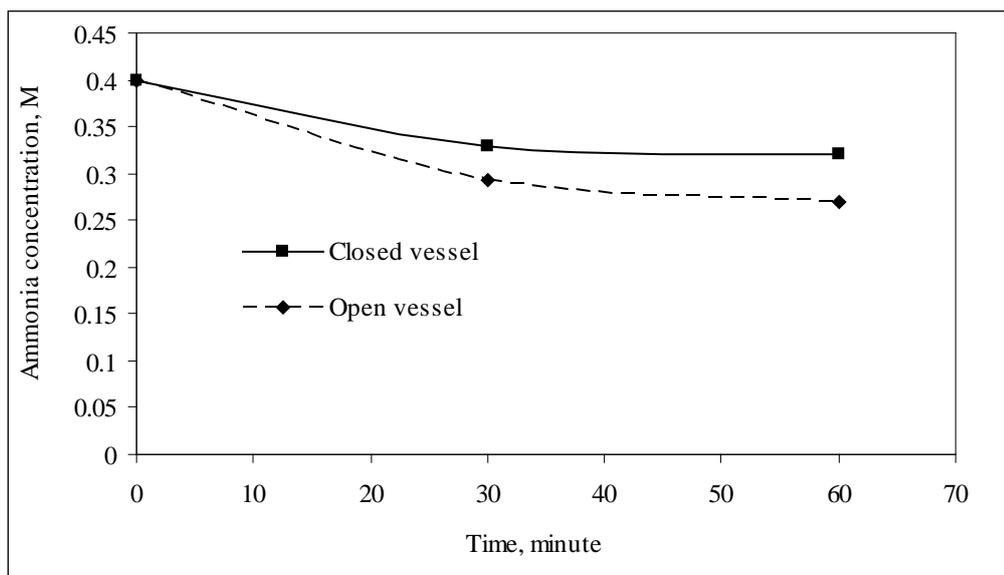


Figure 5.4: Ammonia concentrations in open and closed vessels after 30 and 60 minutes leaching. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, pH= 11.5 and 30 °C.

5.2.1.3 Copper(II) Analysis in Open and Closed Vessels

In order to understand all the effects of the open vessel compare to the closed, copper(II) concentration was analysed by UV-Vis spectrophotometry. The absorbance of copper(II) tetraammine was measured at a wavelength of 605 nm. Figure 5.5 shows a comparison between the concentrations of copper(II) for open and closed vessels. It can be observed that the concentration of copper(II) remains slightly higher in the closed vessel experiments compared with the open vessel experiments. The higher copper(II) concentrations in the closed vessel may be due to the high percentage of ammonia retained in the closed vessel hence, the stability of the copper(II) tetraamine complex is increased in the closed vessel leaching.

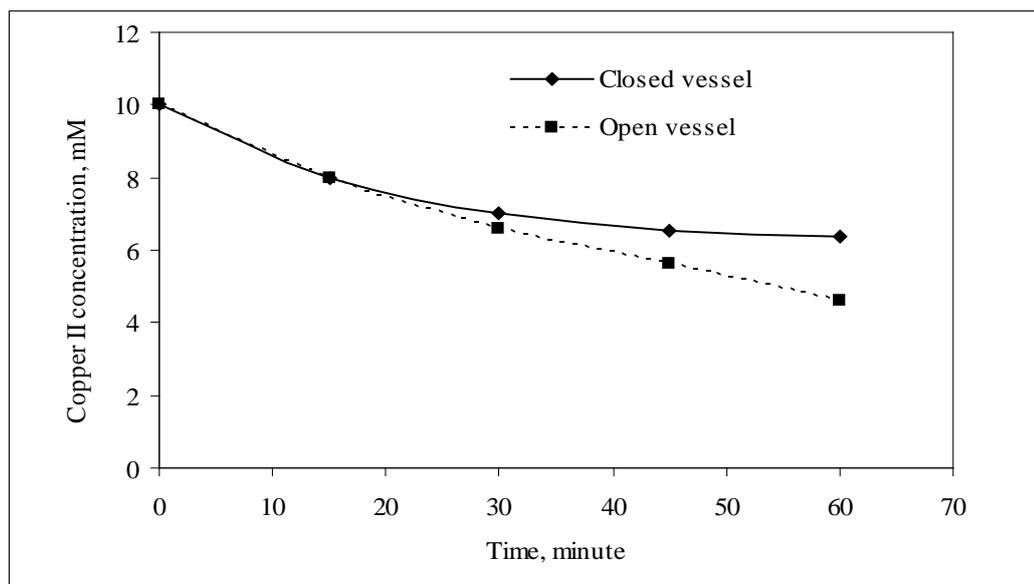


Figure 5.5: Copper(II) concentrations in open and closed vessels after 30 and 60 minutes leaching. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, pH= 11.5 and 30 °C.

5.2.1.4 Gold and Silver Leaching Rates in Open and Closed Vessels (one hour)

The kinetic aspects of gold and silver dissolution from pure gold and silver in thiosulfate solutions containing copper and ammonia for a short run experiments (one hour leaching) in both open and closed vessels were studied using rotating discs at the standard leaching conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, pH= 11.5 and 30 °C. The amount of gold and silver dissolved were determined after 15, 30, 45, and 60 minutes of leaching from which the gold and silver leaching rates were calculated and the results are shown in Figure 5.6. It can be seen that silver dissolved in the thiosulfate solution at a faster rate than gold. Both gold and silver leached faster in the closed vessel than in the open vessel. The leach rate decreased slightly over the leach period which, can be attributed to the decrease in the reagent concentrations, thiosulfate, ammonia, and copper(II) as demonstrated in sections 5.2.1.1, 5.2.1.2, and 5.2.1.3.

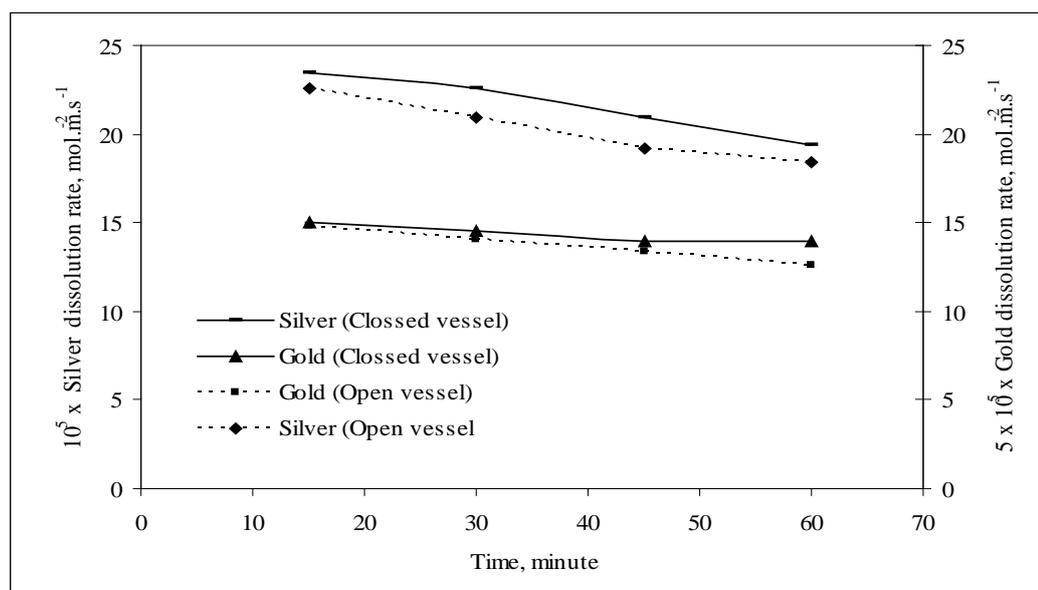


Figure 5.6: Gold and silver dissolution rates in open and closed vessels for 1 hour experiments. Initial experiment conditions: 10 mM CuSO_4 , 0.4 M NH_3 , 0.2 M $(\text{S}_2\text{O}_3)^{2-}$, 300 rpm, pH = 11.5 and 30 °C.

It is obvious that the dissolution rate of gold and silver in the closed vessel are greater than that in the open vessel for the 1 hour leaching experiments. To ensure and understand these differences in gold and silver leaching rates in both open and closed vessels, the leaching run time was increased to 8 hours.

5.3 Effect of Reagent Concentrations and Leaching Parameters (8 hours run)

The gold and silver dissolution rates for thiosulfate solutions (Figure 5.6) are comparable to those for cyanide solutions. This indicates the leaching residence time for ores on plants using thiosulfate solutions would be longer than the one hour time frame used so far in these experiments. Another series of experiments were conducted to determine the effect of thiosulfate, ammonia and copper concentrations, temperature, pH and rotation speed over an extended time period of 8 hours. Both open and closed vessels were evaluated.

5.3.1 Effect of Temperature

In this section, the effect of temperature on gold and silver dissolution rates, the volatilization of ammonia, the reduction of copper(II) to copper(I), and the

oxidisation of thiosulfate in both open and closed vessels are presented and discussed.

5.3.1.1 Effect of Temperature on Gold and Silver Dissolution

The volatilization of ammonia and hence, the stability of the copper-ammonia- thiosulfate leach system depends on the temperature of the solution. The effect of temperature on the dissolution of gold and silver was determined under standard leaching conditions of 0.2 M sodium thiosulfate, 10 mM Cu(II) sulfate, 0.4 M ammonia, 30 °C, and 300 rpm. All experiments were carried out at a fixed pH of 11.5.

Figure 5.7 shows the effect of temperature on gold dissolution from pure gold in open and closed vessels. Gold dissolution increased with increasing temperature in both open and closed vessels, but the dissolution was higher in the closed vessel. From the decrease in the slope of the lines in Figure 5.7, the gold dissolution rate decreased with time. The decrease in dissolution rate is particularly evident for the 50 °C leach in the open vessel which became the slowest towards the end of the eight hour leach.

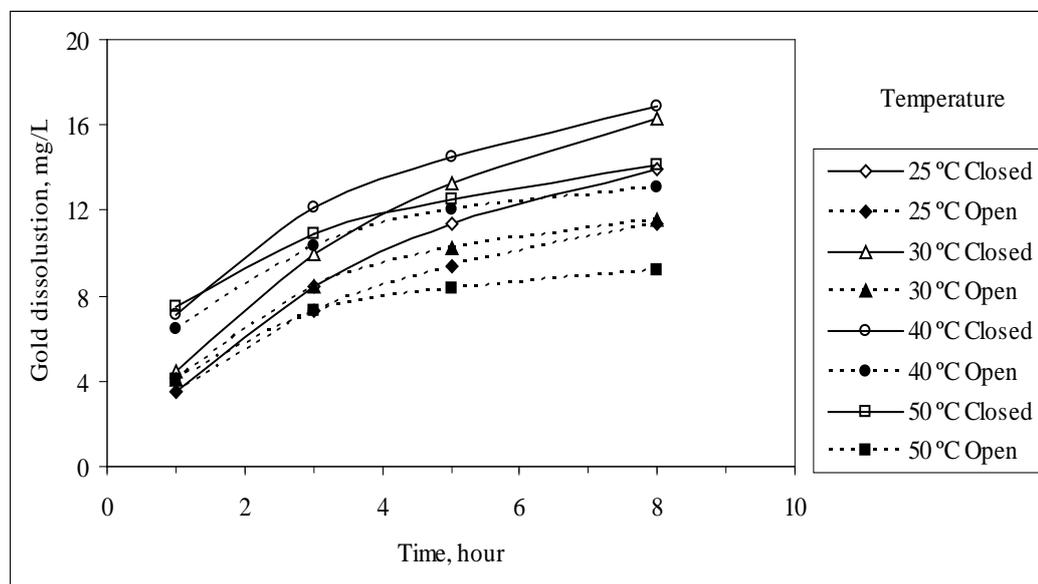


Figure 5.7: Effect of temperature on gold leaching in open and closed vessels. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, and pH= 11.5.

Fig. 5.8 shows the effect of temperature on silver dissolution from pure silver in the open and closed vessels. The dissolution of silver is sensitive to the temperature with the greatest dissolution, after 8 hours of leaching occurring at 30 °C.

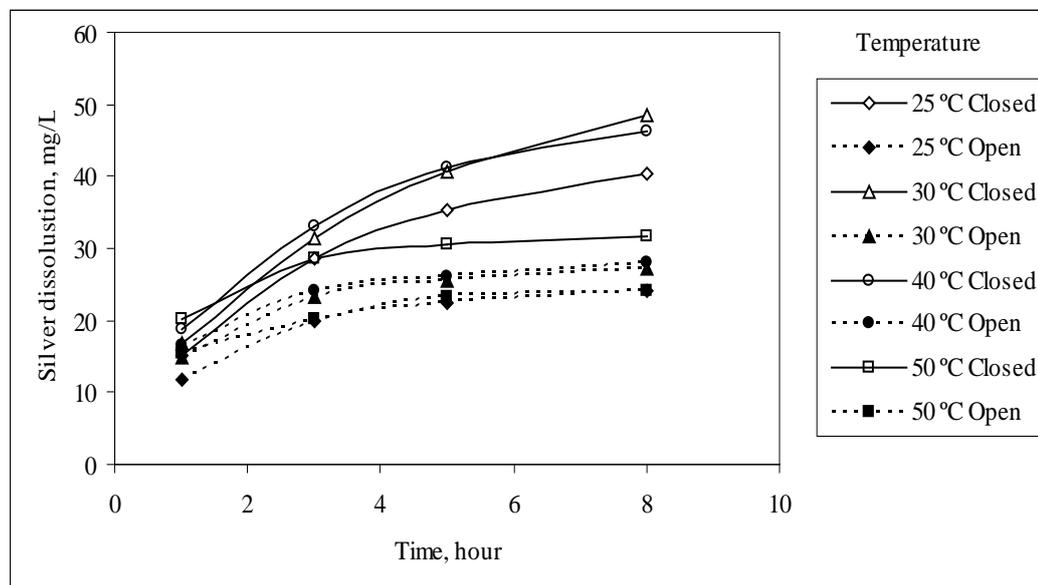


Figure 5.8: Effect of temperature on silver leaching in open and closed vessels.

Initial leaching conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, and pH= 11.5.

Table 5.1 shows the dissolution rate of gold, from pure gold, after 1, 3, 5 and 8 hours of leaching at different temperatures in the open and closed reaction vessels. The initial rate of gold extraction is enhanced by an increase in the leach temperature but the rate falls off sharply after a leach time of approximately one hour for both open and closed vessels. The average dissolution rate of gold over the 8 hour leaching period is around 18% more in the closed than in the open vessel at 25 °C, while this percentage increased up to about 35% at 50 °C.

Table 5.2 shows the dissolution rate of silver, from pure metal, after 1, 3, 5 and 8 hours of leaching at different temperatures in open and closed vessels. The dissolution rates of silver after 8 hours in the open vessel at any temperature were lower than the closed vessel. The silver dissolution rates after one hour of leaching increased with increasing temperature but the rates decreased over time being about 25% of the initial rate after 8 hours of leaching. As a percentage there is a slight difference in silver dissolution rates in the open and closed vessels after 1 hour of

leaching, but the difference increases to more than 43% at a temperature of 50 °C after 8 hours of leaching.

Table 5.1: Dissolution rates of gold after 1, 3, 5 and 8 hours at different temperatures in open and closed reaction vessels.

Temp., °C	Gold dissolution rate, $10^5 \times \text{mol.m}^{-2}.\text{s}^{-1}$							
	Open vessel				Closed vessel			
	1hr	3 hrs	5 hrs	8 hrs	1hr	3 hrs	5 hrs	8 hrs
25	2.16	1.52	1.17	0.88	2.18	1.74	1.41	1.08
30	2.52	1.74	1.27	0.89	2.79	2.06	1.65	1.27
40	3.99	2.14	1.50	1.02	4.44	2.52	1.81	1.31
50	2.55	1.51	1.04	0.71	4.65	2.26	1.56	1.10

Table 5.2: The dissolution rates of silver after 1, 3, 5, and 8 hours at different temperatures in the open and closed reaction vessels.

Temp., °C	Silver dissolution rate, $10^5 \times \text{mol.m}^{-2}.\text{s}^{-1}$							
	Open vessel				Closed vessel			
	1hr	3 hrs	5 hrs	8 hrs	1hr	3 hrs	5 hrs	8 hrs
25	13.32	7.57	5.07	3.41	17.22	10.84	8.01	5.71
30	16.79	8.85	5.77	3.88	19.23	11.87	9.21	6.90
40	18.88	9.11	5.92	3.99	21.19	12.54	9.36	6.55
50	17.53	7.60	5.27	3.43	22.84	10.81	6.90	4.49

A comparison between Tables 5.1 and 5.2 indicates that the dissolution rate of silver is more than 6.5 times greater than the dissolution rate of gold. In addition, the differences in the average gold and silver dissolution rates over the eight hour of leaching at 50 °C in open and closed vessels were 35% and 43% respectively. The decrease in dissolution over time for both gold and silver and the greater decrease observed in the open vessel may be attributed to:

- the volatilization of ammonia and hence a decrease of the Cu(II) tetraammine complex stability;

- an increase in the reduction rate of Cu(II) to Cu(I); and
- the decomposition of thiosulfate and the passivation of the gold surface by the products of thiosulfate decomposition.

5.3.1.2 Effect of Temperature on the Volatilization of Ammonia

The open vessel experiments allowed free volatilization of ammonia from the solution surface; therefore, volatilization was followed in the open vessel experiments to determine the amount of ammonia loss. Figure 5.9 shows the ammonia concentration decrease during the leaching experiments for the open vessel, indicating that ammonia loss increased rapidly with increasing temperature.

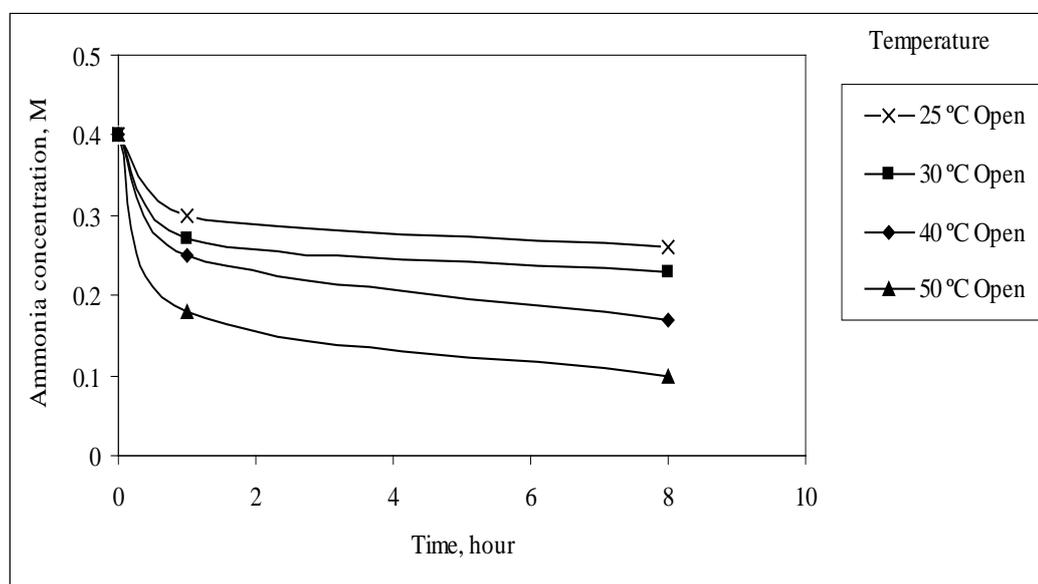


Figure 5.9: Effect of temperature on ammonia volatilization in the open vessel.

Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, °C, and pH= 11.5.

From the amount of ammonia remaining in the open vessel solution, the average volatilization rates of ammonia ($g/m^2.s$) over the eight hour experiment was calculated by using the diameter of the open vessel of 10 cm. The results are tabulated in Table 5.3. The volatilization of ammonia increased as the temperature increased and doubled when the temperature was increased from 25 to 50 °C.

Table 5.3: The average volatilization rate of ammonia in the open vessel over the eight hours of leaching at different temperatures.

Temperature, °C	25	30	40	50
Volatilization rate of ammonia, g/m ² .s x 10 ²	1.053	1.278	1.729	2.256

The volatilization of ammonia is of metallurgical and environmental concern especially during heap leaching where a closed system can not be used. Temperature should be minimized in the thiosulfate leaching system in order to avoid the loss of ammonia from the solution, but this must be balanced against the lower dissolution rates at lower temperatures.

5.3.1.3 Effect of Temperature on Cu(II) Reduction

The volatility of ammonia and temperature are confounding variables on the stability of the copper(II) tetraammine complex in the ammoniacal thiosulfate leaching system. The concentration of Cu(II) was measured in open and closed vessels after 1 and 8 hours of leaching at different temperatures (Figure 5.10). The rate of Cu(II) reduction increased with increasing temperature. At temperatures greater than 40 °C, the concentration of Cu(II) in the open vessel was virtually zero after 2 hours of leaching.

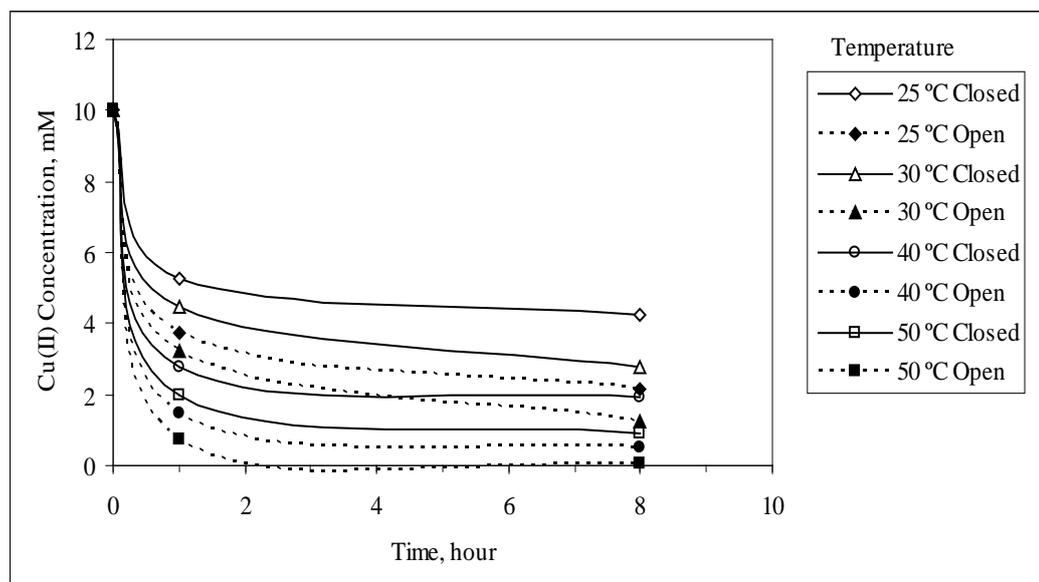


Figure 5.10: Effect of temperature on Cu(II) concentration in open and closed vessels. Initial experiment conditions: 0.2 M (S₂O₃)²⁻, 10 mM CuSO₄, 0.4 M NH₃, 300 rpm, °C, and pH= 11.5.

The results of Figure 5.10 show, also, that reduction of Cu(II) in the open vessel was greater than for the closed vessel. Moreover, loss of ammonia from the open vessel was high and hence, the stability of Cu(II) tetraamine complex in the solution may have been reduced allowing greater reduction of Cu(II) to Cu(I) by thiosulfate.

5.3.1.4 Effect of Temperature on the Decomposition of Thiosulfate

It has been found that temperature has positive influences on gold leaching efficiency. However, raising temperature increases copper(II) reduction and thiosulfate decomposition rates (Arslan et al., 2008; Breuer and Jeffrey, 2000; Abbruzzese et al., 1995). Because of this, the effect of temperature on the decomposition of thiosulfate in the open and closed vessels was studied and the results are shown in Figure 5.11. There exists a general decrease in thiosulfate concentration with increasing temperature, however, the concentration of thiosulfate remains slightly higher in the closed vessel experiments compared with the open vessel experiments. Comparison of the copper reduction and the thiosulfate decomposition experiments indicate that thiosulfate continues to decompose even when the copper(II) ions in solution are exhausted.

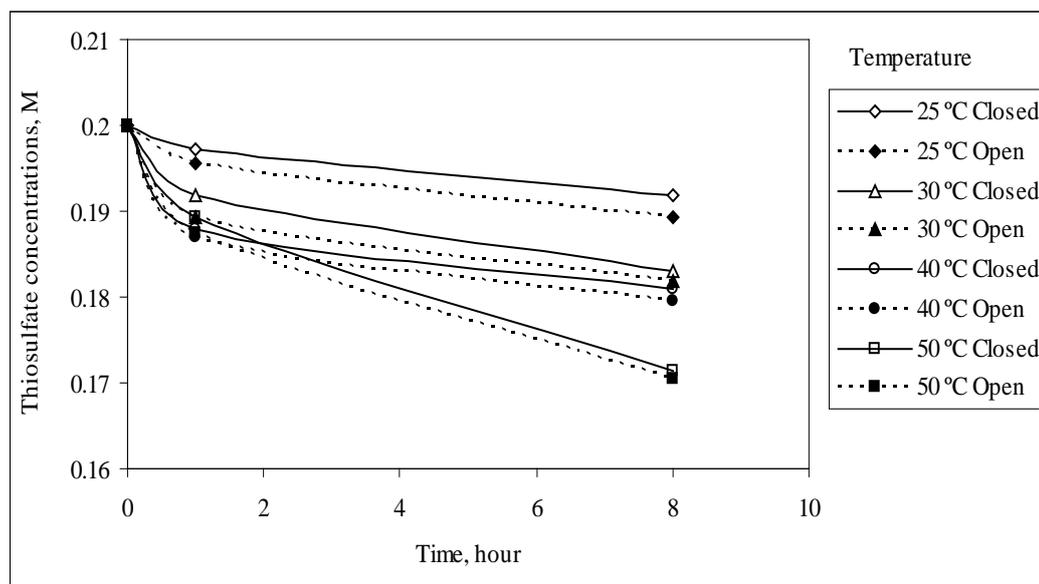


Figure 5.11: Effect of temperature on the decomposition of thiosulfate in open and closed vessels. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, °C, and pH= 11.5.

5.3.2 Effect of Initial Ammonia Concentration

In the following sections, the effect of ammonia concentration ranging from 0.2 to 0.8 M on gold and silver dissolution rates, ammonia volatilization, and copper(II) reduction in open and closed vessels are reported and discussed.

5.3.2.1 Effect of Initial Ammonia Concentration on Gold and Silver Dissolution

In this section the effect of initial ammonia concentration on the dissolution rate of pure gold and pure silver in both open and closed vessels were studied. The results in Figure 5.12 show that for all initial ammonia concentrations, the dissolution rate of gold in the closed vessel was greater than the open vessel, which can be attributed to the loss of ammonia from the open vessel and hence, the reduced stability of the Cu(II) tetraammine complex.

The results indicate that the dissolution of gold increased with increasing initial ammonia concentration up to 0.6 M then decreased at 0.8 M, but the rate of gold dissolution, as shown in Table 5.4, decreased over time for all ammonia concentrations.

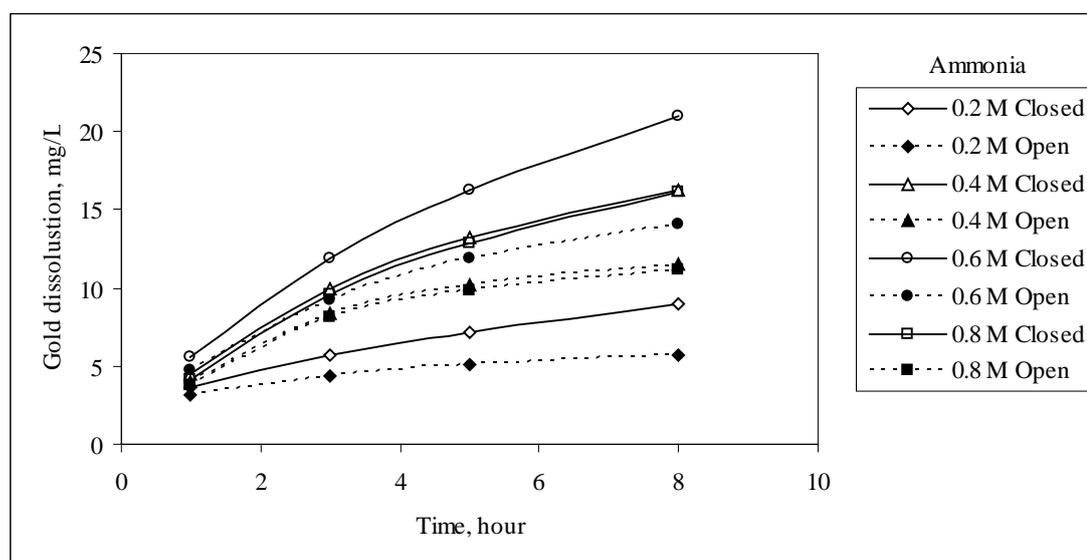


Figure 5.12: Effect of ammonia concentration on gold dissolution in open and closed vessels. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, NH_3 , 300 rpm, 30 °C, and pH= 11.5.

Table 5.4: Dissolution rates of gold after 1, 3, 5 and 8 hours at different ammonia concentrations in open and closed reaction vessels.

Ammonia Conc., M	Gold dissolution rate, $10^5 \times \text{mol m}^{-2}\text{s}^{-1}$							
	Open vessel				Closed vessel			
	1hr	3 hrs	5 hrs	8 hrs	1hr	3 hrs	5 hrs	8 hrs
0.2	1.93	0.91	0.64	0.45	2.24	1.18	0.89	0.70
0.4	2.52	1.74	1.27	0.89	2.79	2.06	1.65	1.27
0.6	2.97	1.90	1.47	1.09	3.44	2.47	2.02	1.63
0.8	2.55	1.51	1.04	0.71	4.65	2.26	1.56	1.10

As the gold dissolution rate (Table 5.4) for the 0.8 M initial ammonia experiment was below that obtained for the 0.6 M initial ammonia experiment when the ammonia concentration decreased to 0.6 M through volatilization, the decrease in rate must be attributed to a reduction in the copper (II) tetraammine concentration. Figure 5.13 shows the dissolution of silver at different initial ammonia concentrations in open and closed vessels. The dissolution of silver is very low at 0.2 M ammonia and increases rapidly with increasing ammonia concentration. Silver dissolution is more sensitive to ammonia concentration than gold as reported by Zipperian et al. (1988).

The dissolution rate of silver was calculated after 1, 3, 5, and 8 hours of leaching in open and closed vessels (Table 5.5). Again the dissolution rates are greater in the closed compared to the open vessel. Unlike gold, the dissolution rate of silver continues to increase up to an initial ammonia concentration of 0.8M. If the sole function of ammonia was to stabilize the Cu(II) ion in the system, the same optimum copper to ammonia ratio as observed for gold dissolution would have been expected.

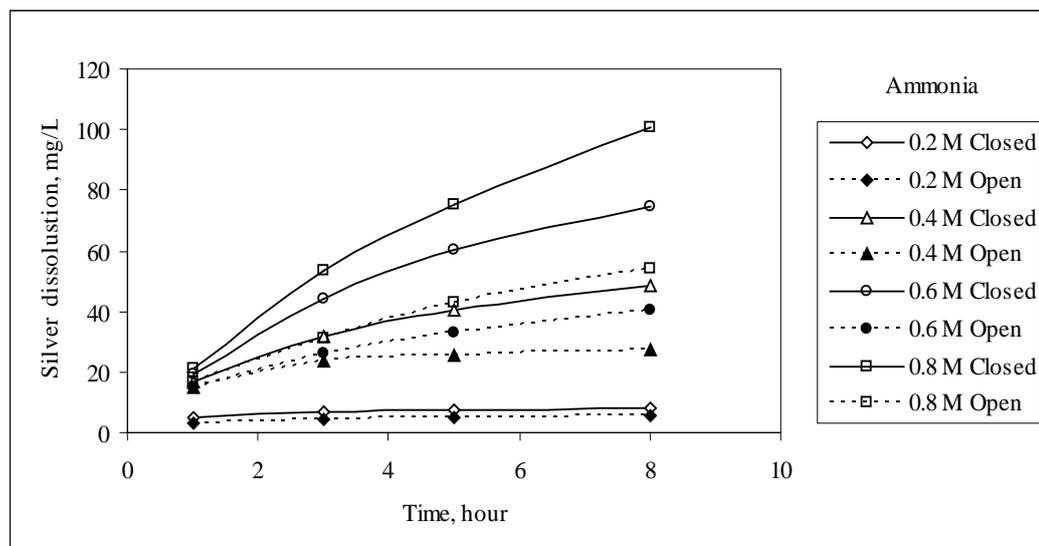


Figure 5.13: Effect of ammonia concentration on silver leaching in open and closed vessels. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, NH_3 , 300 rpm, 30 °C, and pH= 11.5.

Table 5.5: The dissolution rate of silver after 1, 3, 5, and 8 hours at different ammonia concentrations in open and closed reaction vessels.

Ammonia Conc., M	Silver dissolution rate, $10^5 \times \text{mol m}^{-2} \text{s}^{-1}$							
	Open vessel				Closed vessel			
	1hr	3 hrs	5 hrs	8 hrs	1hr	3 hrs	5 hrs	8 hrs
0.2	3.70	1.76	1.16	0.77	5.97	2.66	1.73	1.11
0.4	16.79	8.85	5.77	3.88	19.23	11.87	9.21	6.90
0.6	16.94	9.90	7.52	5.71	21.67	16.67	13.69	10.54
0.8	19.34	11.69	9.70	7.68	23.94	20.19	17.05	14.26

5.3.2.2 Effect of Initial Ammonia Concentration on Volatilization of Ammonia

The remaining ammonia concentration for different initial ammonia concentrations, in the thiosulfate system at 30 °C, in open vessels after 1 and 8 hours of leaching were analysed and the results are shown in Figure 5.14.

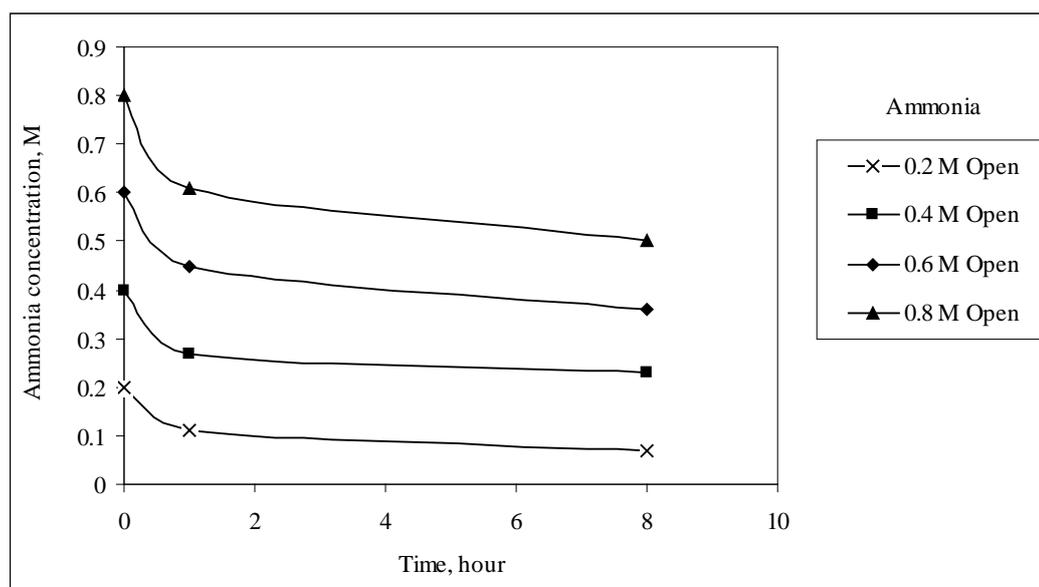


Figure 5.14: Effect of initial ammonia concentration on ammonia volatilization in the open vessel. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, NH_3 , 300 rpm, 30 °C, and pH= 11.5.

Referring to Figure 5.14, it is evident that the amount of ammonia loss increased when the initial concentration of ammonia was increased. The maximum loss was about 37% at an initial concentration of 0.8 M ammonia.

5.3.2.3 Effect of Initial Ammonia Concentration on Cu(II) Reduction

The effect of the initial ammonia concentration on Cu(II) reduction at 30°C are presented in Figure 5.15. All the copper(II) measurements in the closed vessel were higher than in the open vessel. Increasing the initial concentration of ammonia, stabilized the Cu(II) tetraammine in the solution for a longer period, hence, using the closed vessel had a positive effect on the Cu(II) concentration.

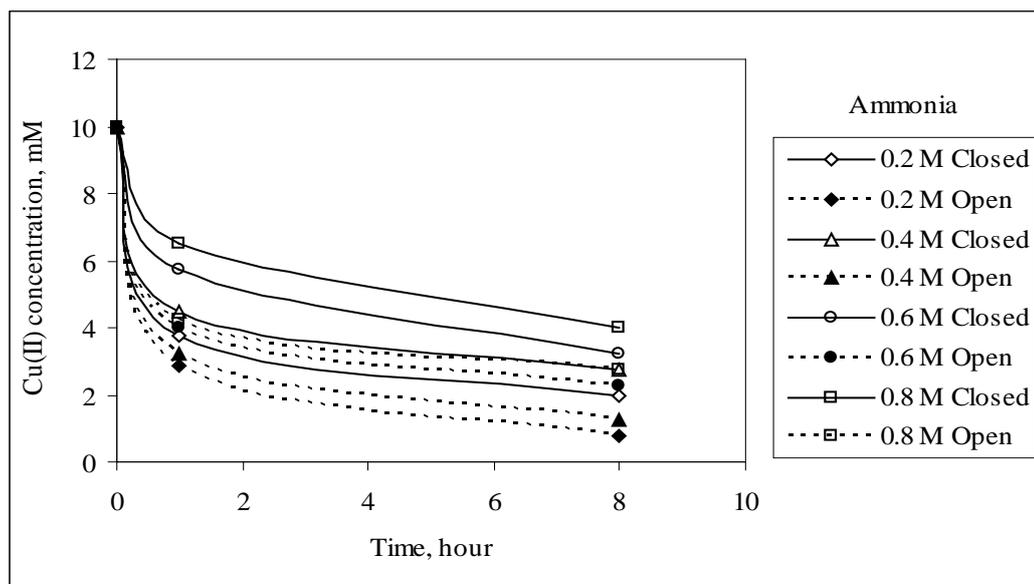


Figure 5.15: Effect of initial concentration of ammonia on Cu(II) reduction in open and closed vessels. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, NH_3 , 300 rpm, 30 °C, and pH= 11.5.

From the previous sections that compared the leaching of gold and silver in open and closed vessels, some noticeable observations are summarized as follows:

- the leaching of gold and silver in solutions containing Cu(II), ammonia and thiosulfate in a closed vessel maintains the optimum leaching conditions and enhances the leaching kinetics compared with an open vessel;
- the leaching rate of gold and silver in the closed vessel was greater than that obtained in the open vessel by approximately 35% and 43% respectively;
- higher temperatures increased the volatilization rate of ammonia during leaching in the open vessel, which raises environmental concern about using ammonia; and
- Cu(II) reduction increased in the open vessel with higher temperatures due to the loss of ammonia and hence the amount of free Cu(II) that reacts with thiosulfate.
- Temperature should be minimized in the thiosulfate system to avoid ammonia losses and the consumption of thiosulfate.

From the previous observations, it can be suggested that leaching in a closed vessel is preferred to leaching in an open vessel due to its kinetic and environmental advantages. Therefore, the closed vessel (tanks) for the leaching of gold or silver in thiosulfate solutions containing copper and ammonia was selected. In the following

sections, the leaching of pure gold, pure silver and gold-silver alloys in the selected closed vessel are presented and discussed.

5.4 Dissolution Rates of Gold, Silver and Total Metal as a Function of Silver Content

The dissolution rate of gold, silver, and total metal (gold-silver) as a function of silver content from pure gold and silver and gold-silver alloys is shown in Figure 5.16. It can be seen that the gold dissolution rate for pure gold is higher than that for 4 and 8% Ag alloys. Further increase in silver content up to 50% increased the gold dissolution rate to values higher than that for pure gold. The results also demonstrate that the silver dissolution rate from the pure metal is 6.89 times that of pure gold. The findings are consistent with those observed by Jeffrey (2001). Moreover, the silver and total metal dissolution rates increased with increasing the silver content. Not surprisingly, the silver dissolution rate is very slow at low percentages of silver, but increased significantly when the silver content was more than 20%.

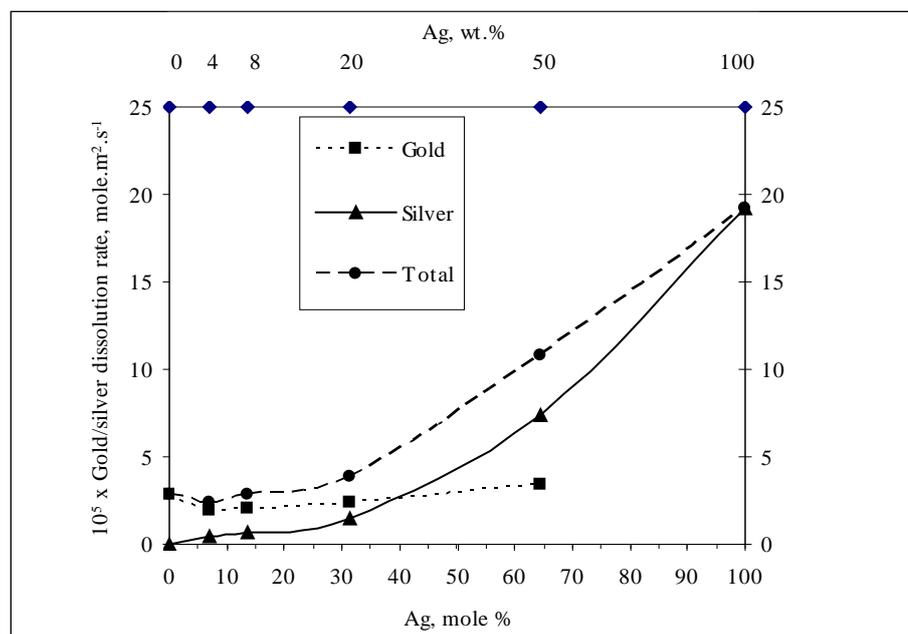


Figure 5.16: The dissolution rate of gold, silver and gold-silver alloys after 1 hour.

Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, 30 °C, and pH= 11.5.

5.5 Dissolution Rate of Gold-Silver Alloys as a Function of Time

The leaching of gold-silver alloy discs of different silver composition, 4, 8, 20, and 50% was carried out in a closed vessel. Figure 5.17 shows gold dissolution rates for each alloy after 15, 30, 45, 60 minutes using the selected initial standard concentrations of 0.2 M sodium thiosulfate, 10 mM copper sulfate, 0.4 M ammonia, 30 °C, and 300 rpm. The results of Figure 5.17 show that the gold dissolution rate under the standard conditions varied significantly with the amount of silver in the alloy. Increasing gold dissolution rate with the presence of silver was also reported in cyanide solutions by Wadsworth and Zhu (2003), Jeffrey and Ritchie, (2000), and Wadsworth et al. (2000).

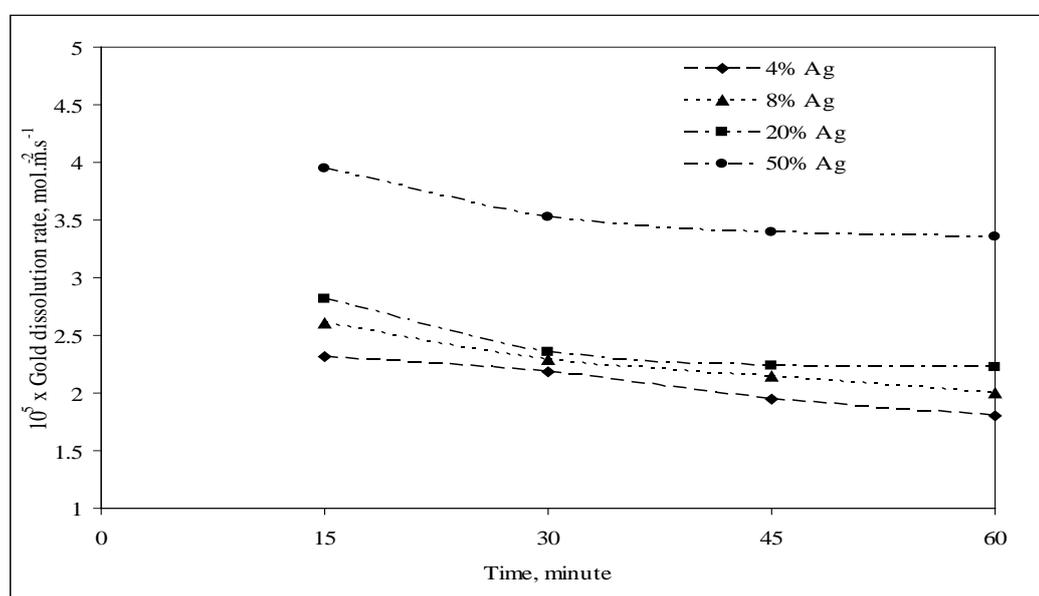


Figure 5.17: Gold dissolution rate for gold-silver alloys using a closed vessel. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, 30 °C, and pH= 11.5.

5.6 Effect of the Leaching Conditions (8 hour run)

To get a better understanding of gold, silver, and gold/silver leaching in thiosulfate solutions, the effects of different leaching conditions used in the system were investigated. Different concentrations of thiosulfate, ammonia, and copper(II) were used in this part of the project. Furthermore, the effects of temperature, pH, and agitation speed are evaluated in the closed vessel for a leaching time of 8 hours. The calculated dissolution rates throughout this investigation except the ones for the

effect of time are the average rate over 3, 5, and 8 hours of leaching. The results of these experiments are reported and discussed in this section.

5.6.1 Effect of Time on the Gold and Total Metal Dissolution

Figures 5.18 and 5.19 show gold and total metal dissolution rate from pure gold, pure silver and gold-silver alloys over 1, 3, 5, and 8 hours of leaching. The amount of gold dissolved from 20 and 50% silver alloys is higher than that from pure gold, and the 4, and 8% silver alloys for all the time periods (Figure 5.18).

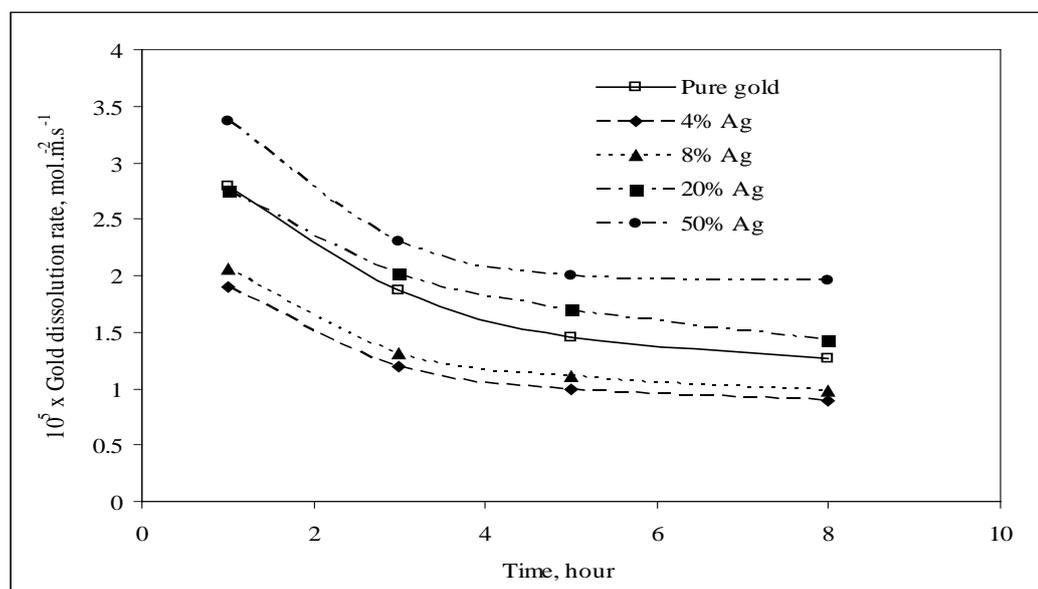


Figure 5.18: Gold dissolution rate from gold and gold-silver alloys. Initial experiment conditions: 0.2 M (S₂O₃)²⁻, 10 mM CuSO₄, 0.4 M NH₃, 300 rpm, 30 °C, and pH= 11.5.

The gold and total metal dissolution rates decreased over time due to the conditions changing with the consumption of reagents and the reduction of copper(II) to copper(I). Passivation of gold and alloy surfaces by the products of thiosulfate decomposition may also contribute to the decrease in the dissolution rate. The average dissolution rate of pure silver decreased the most, 64% compared with 55% for pure gold, when the average dissolution rate for eight hours is compared with that for 1 hour (Figure 5.19).

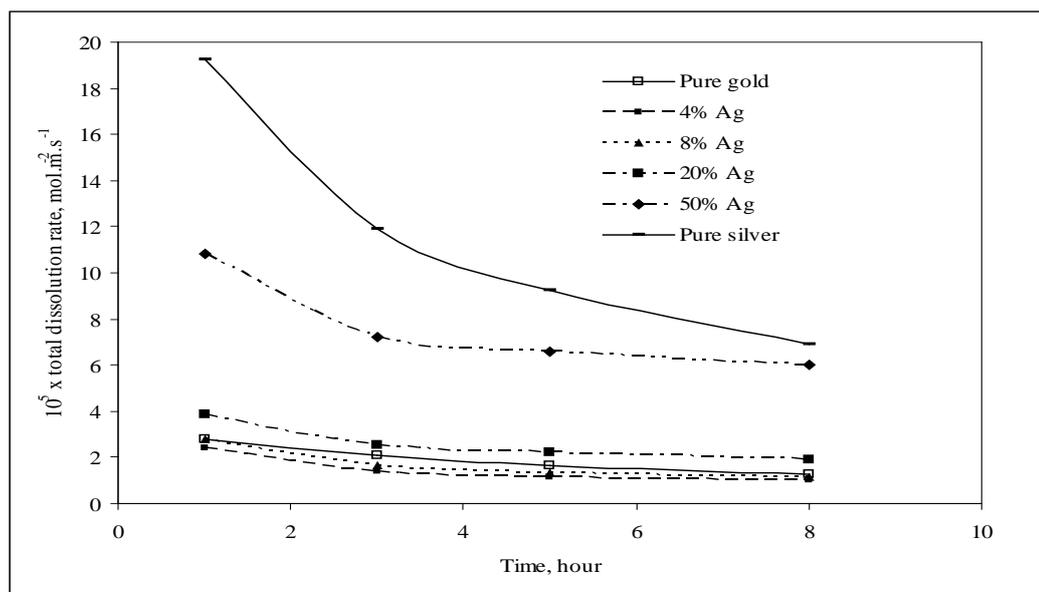


Figure 5.19: Total metal average dissolution rate for gold, silver and gold-silver alloys. Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, 30 °C, and pH= 11.5.

5.6.2 Effect of Thiosulfate Concentration on Gold, Silver, and Total Metal Dissolution

The effect of initial sodium thiosulfate concentration on gold and total metal average dissolution rate over an eight hour period is presented in Figures 5.20 and 5.21. When the initial thiosulfate concentration was increased from 0.1 M to 0.2 M to 0.4 M, the gold and total dissolution rate increased for pure gold, pure silver and the gold-silver alloys. The increased dissolution rate is due to an increase in gold and silver oxidation caused by the increase in thiosulfate concentration. However, using higher concentrations of thiosulfate leads to an increase in the reduction rate of $Cu(II)$ to $Cu(I)$ and thus, increases decomposition of thiosulfate. The results are consistent with those of Muyunda (1996) and Jeffrey (2001). The total dissolution rate (Figure 5.21) increased sharply after the silver content exceeded 20% indicating that the silver dissolution starts to increase significantly after this percentage of silver as has also been shown in section 5.5.

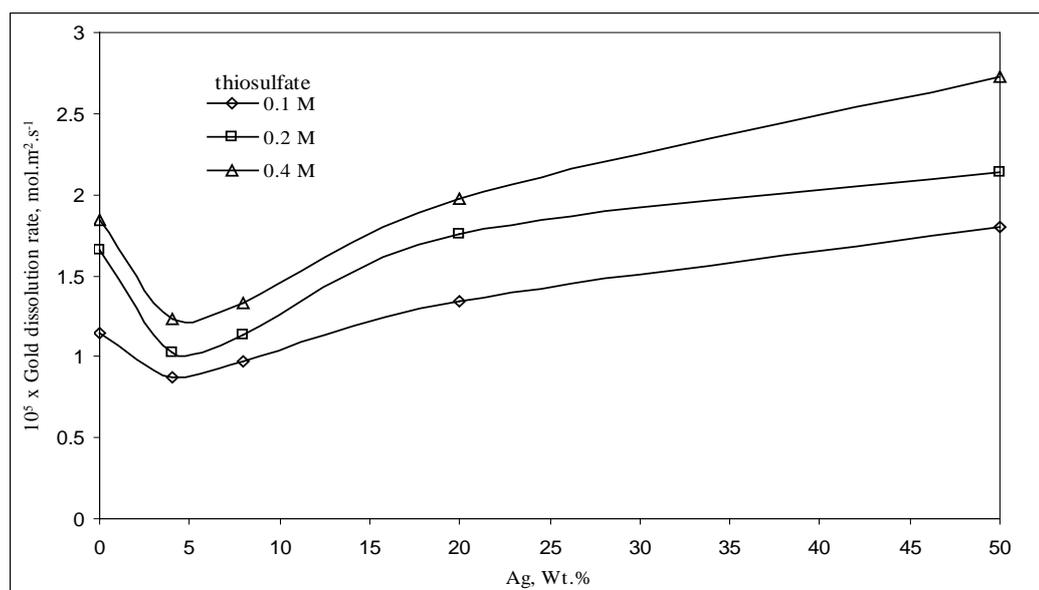


Figure 5.20: Gold average dissolution rate from pure gold and gold-silver alloys at different initial thiosulfate concentrations (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, 30 °C, and pH= 11.5.

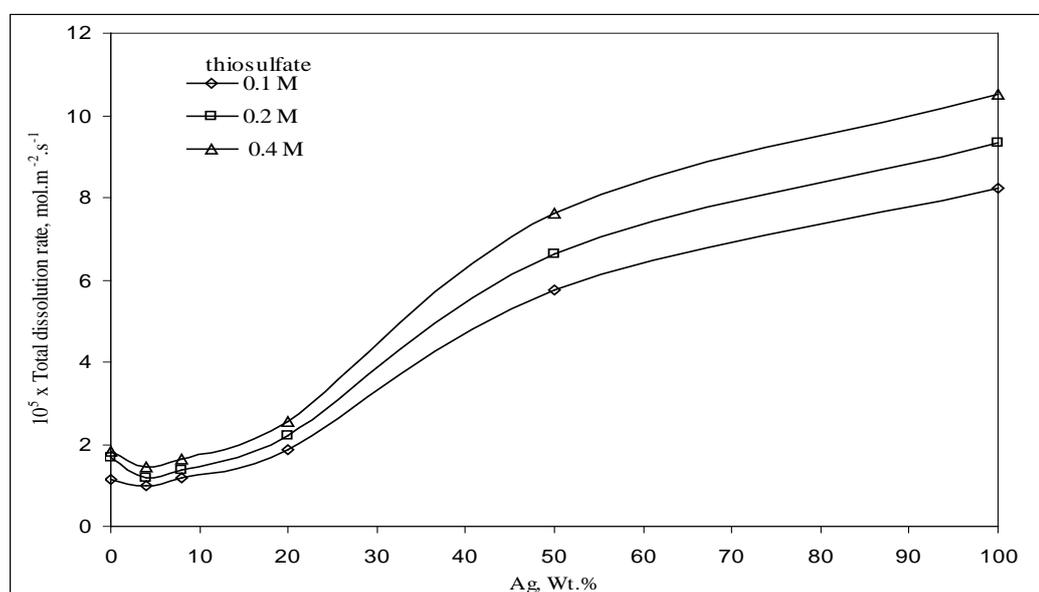


Figure 5.21: Total average metal dissolution rate from gold, silver and gold-silver alloys at different initial thiosulfate concentrations (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, 30 °C, and pH= 11.5.

5.6.3 Effect of Copper(II) Concentration on Gold, Silver and Total Metal Dissolution

The effects of changing the initial Cu(II) concentration in thiosulfate leaching solutions on average gold and total metal dissolution rates are shown in Figures 5.22 and 5.23 respectively. By increasing the initial concentration of Cu(II), the amount of gold dissolved from all the gold-silver alloys increased. In addition, the gold dissolution rate from pure gold was higher than that obtained from 4 and 8% Ag alloys and less than that from the 20 and 50% Ag alloys.

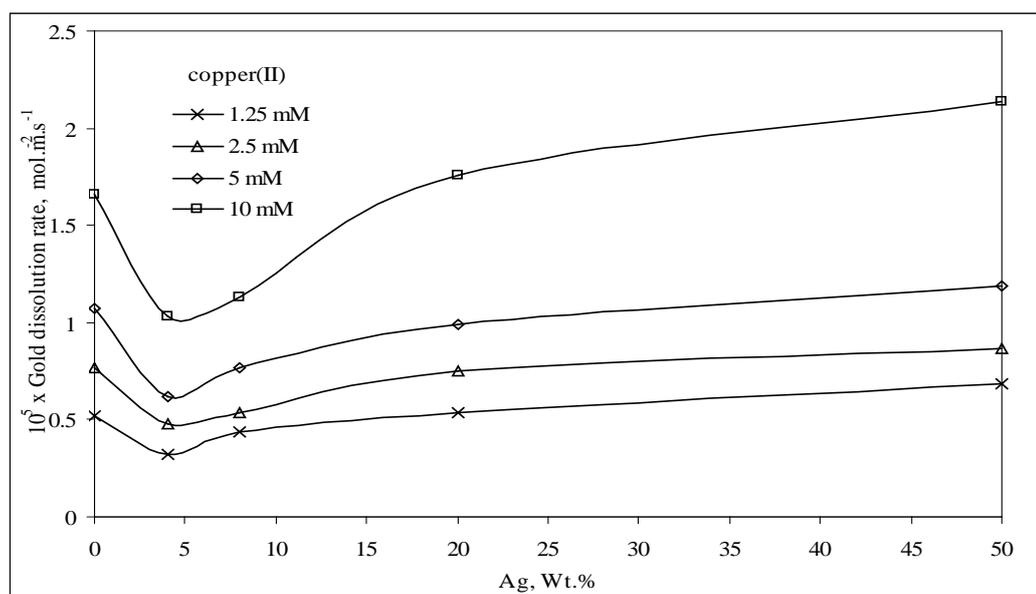


Figure 5.22: Gold average dissolution rate from gold and gold-silver alloys at different initial copper sulfate concentrations (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, $CuSO_4$, 0.4 M NH_3 , 300 rpm, 30 °C, and pH= 11.5.

Results presented in Figure 5.23 show that changing the initial Cu(II) concentration has a significant influence on the metal dissolution rate, being, $1.67 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ at 1.25 mM Cu(II) and increasing to $6.6 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ at 10 mM Cu(II) for pure silver.

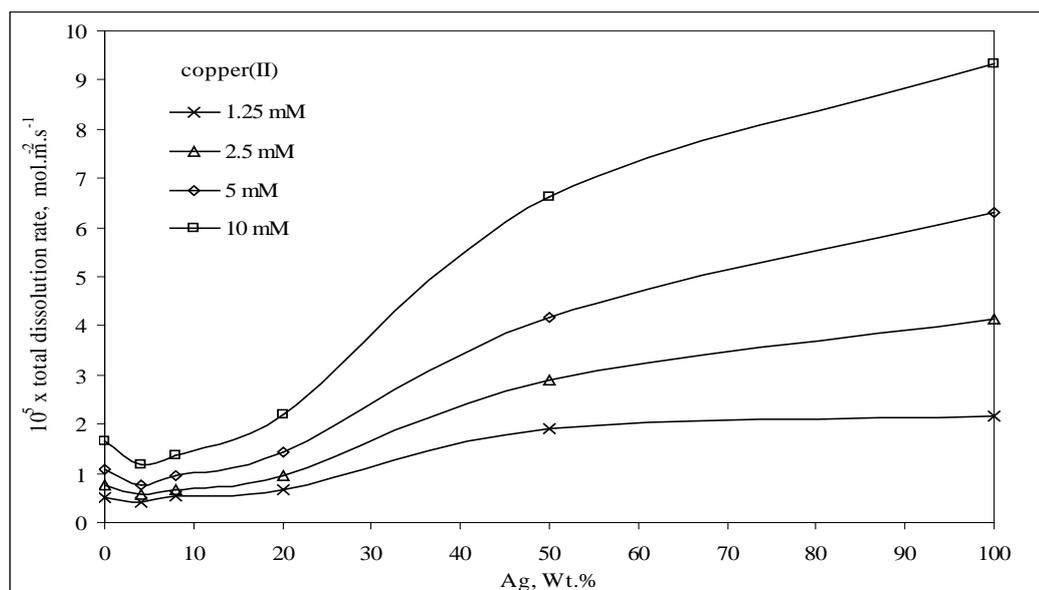


Figure 5.23: Total average metal dissolution rate of pure gold, pure silver and gold-silver alloys at different initial copper sulfate concentration (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, $CuSO_4$, 0.4 M NH_3 , 300 rpm, 30 °C, and pH= 11.5.

5.6.4 Effect of Ammonia Concentration on Gold, Silver and Total Metal Dissolution

The effect of ammonia on the average gold and total dissolution rate was conducted with ammonia concentration ranging from 0.2 to 0.8 M and the results are presented in Figures 5.24 and 5.25. It can be seen from Figure 5.24 that the amount of gold dissolved from each disc increased by increasing the concentration of ammonia up to 0.6 M but increasing the concentration up to 0.8 M decreased the amount of gold dissolved.

Alloys that contain higher concentrations of silver were more sensitive to ammonia concentration. The pure silver dissolution rate at 0.2 M ammonia was very low while the maximum dissolution rate of silver was $15.29 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ at an initial concentration of 0.8 M ammonia. For pure gold, the maximum dissolution rate was $1.63 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ at an initial ammonia concentration of 0.6 M and $1.25 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ at an initial concentration of 0.8 M ammonia. It has been observed that ammonia improves the anodic dissolution of the gold, reduces passivation of the gold surface (Jiang et al., 1993), produces Cu(II) tetra-ammine in the system, and is important to the Cu(II) ions function as an oxidant (Aylmore, 2001).

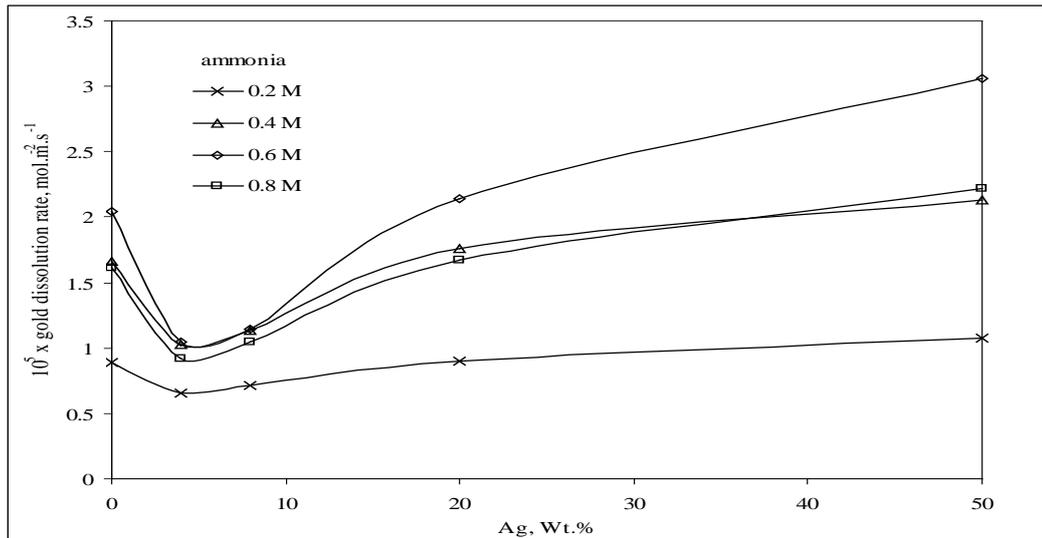


Figure 5.24: Gold dissolution rate from gold and gold-silver alloys at different initial ammonia concentrations (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, NH_3 , 300 rpm, 30 °C, and pH= 11.5.

Referring to Figure 5.25, it is evident that silver dissolution rate is enhanced by increasing the initial concentration of ammonia. The results indicate that the optimum ammonia concentration to achieve the maximum gold and silver dissolution rates were 0.6 M for gold and 0.8 M for silver.

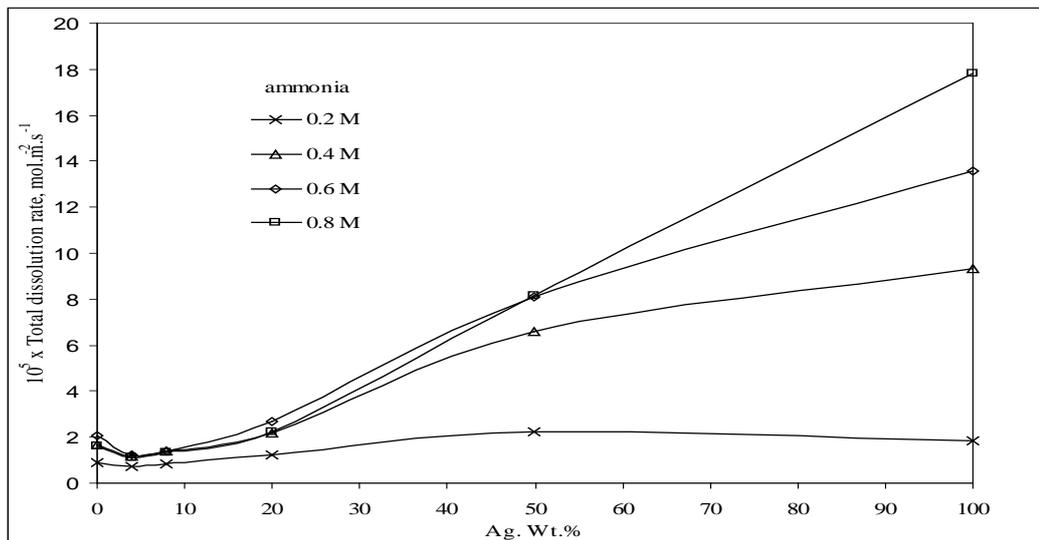


Figure 5.25: Total average metal dissolution rate of gold, silver and gold-silver alloys at different initial ammonia concentrations (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, NH_3 , 300 rpm, 30 °C, and pH= 11.5.

5.6.5 Effect of Temperature on Gold, Silver and Total Metal Dissolution

The dissolution of gold and total metal as a function of silver contents at different temperatures was studied under the leaching conditions of 0.2 M sodium thiosulfate, 10 mM Cu(II) sulfate, 0.4 M ammonia, and 300 rpm. All experiments were performed at a fixed pH of 11.5. Figure 5.26 shows the effects of temperature on the average gold dissolution rate using different percentages of silver. The results presented in Figure 5.26 indicate that gold dissolution rate varied with temperature.

An increase in temperature would be expected to enhance the activity of the solution and thus, increase the rate of gold dissolution. However, when temperature was increased from 30 °C to 50 °C, the average gold dissolution rate from all discs was significantly decreased. As can also be seen from Figure 6.27, the total metal average dissolution rate also varied with temperature. In addition, there is an increase in the average total metal dissolution rate from 25 to 30 °C, but a decrease as the temperature is increased from 30 to 50 °C. This is because at high temperatures, the rates of ammonia losses, Cu(II) reduction into Cu(I) and the decomposition of thiosulfate increase.

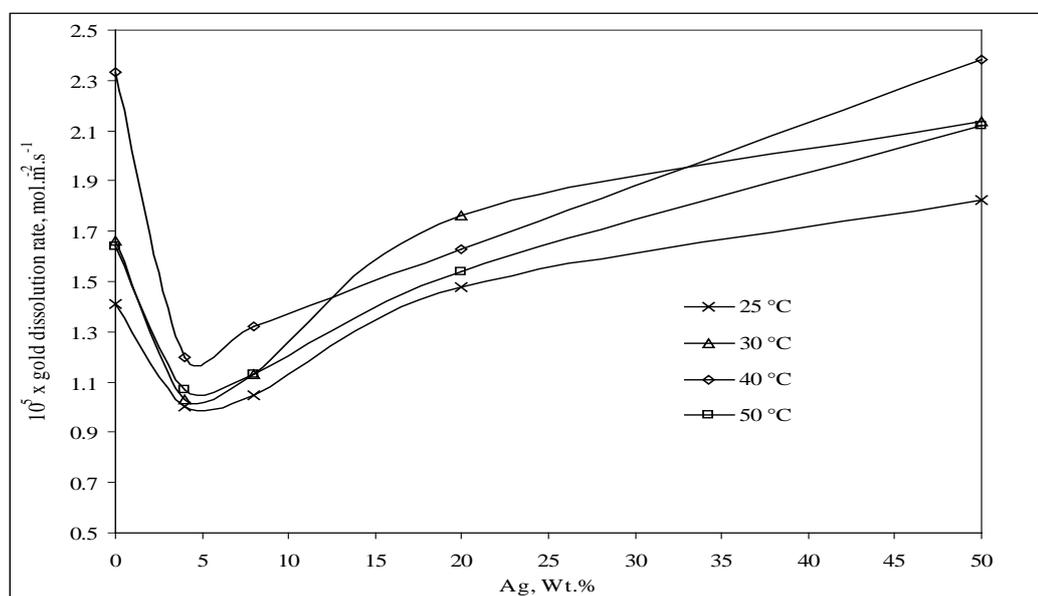


Figure 5.26: Gold dissolution rates from gold and gold-silver alloys at different temperatures (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, °C, and pH= 11.5

It is evident from the results shown in Figures 5.26 and 5.27 that there exists an optimum temperature at which maximum rates of gold and total metal dissolution will result. The results indicate that the optimum temperature for gold and silver dissolution was 30 °C.

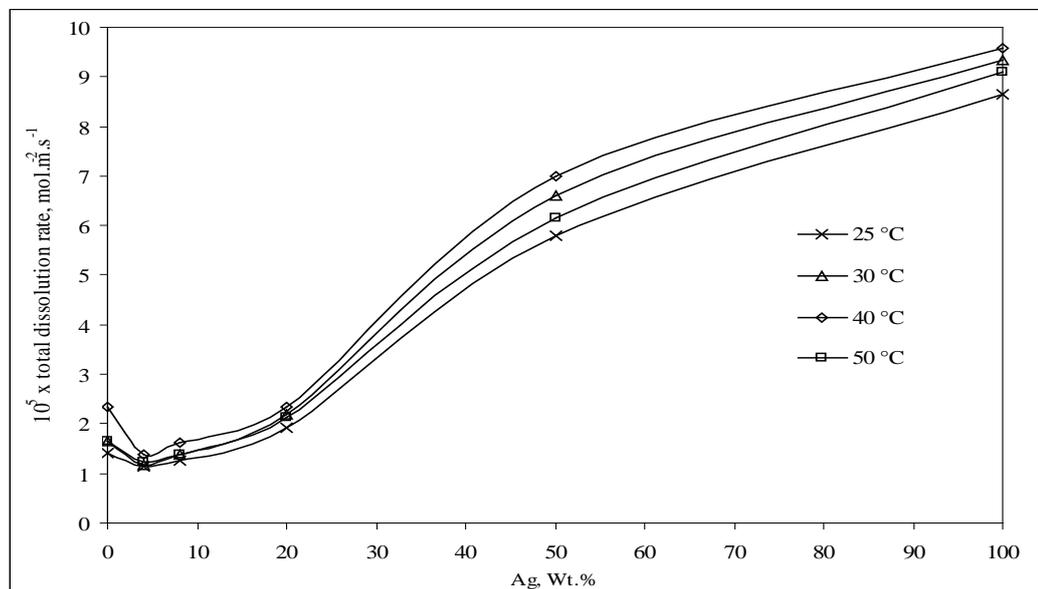


Figure 5.27: Total average metal dissolution rate of gold, silver and gold-silver alloys at different temperatures (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, °C, and pH= 11.5.

5.6.6 Effect of Rotation Speed on Gold, Silver and Total Metal Dissolution

The effects of rotation speed on the gold and total metal dissolution rate from pure gold, pure silver and gold-silver alloys was investigated at rotation speeds ranging from 300 rpm to 600 rpm. The results of these experiments are shown in Figures 5.28 and 5.29. The results show that both gold and total metal dissolution rate increased with rotation speed. However, the silver dissolution rate from the pure silver disc was more sensitive to change in rotation speed than gold from the pure gold disc. The sensitivity to rotation speed indicates that the dissolution of silver in thiosulfate solutions is a diffusion controlled reaction in which the rotation speed enhances the dissolution rate. This result is consistent with those observed by Jeffrey (2001).

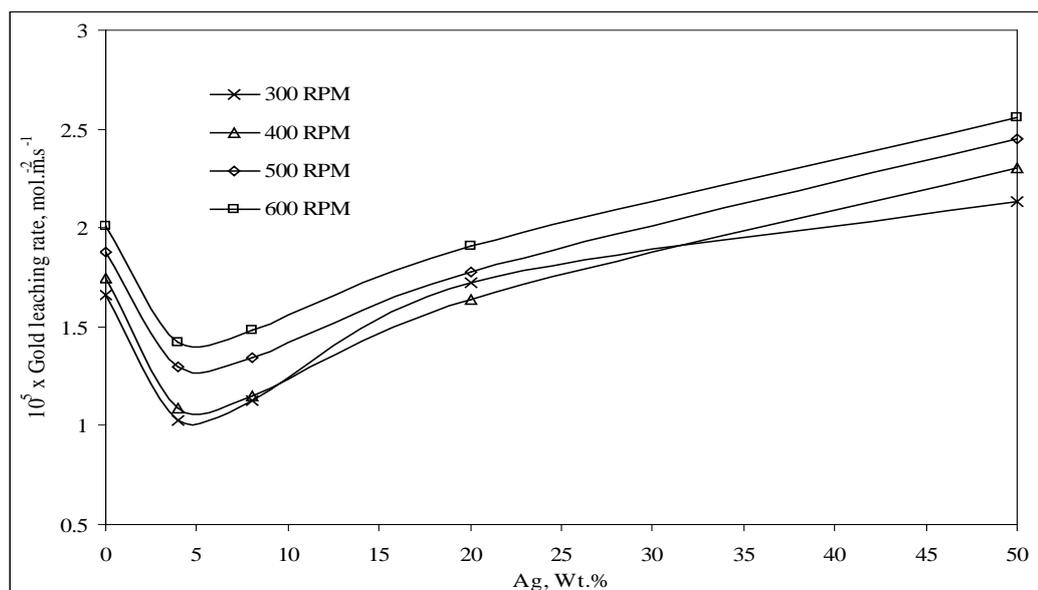


Figure 5.28: Gold dissolution rate from gold and gold-silver alloys at different rotation speeds (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , rpm, 30 °C, and pH= 11.5.

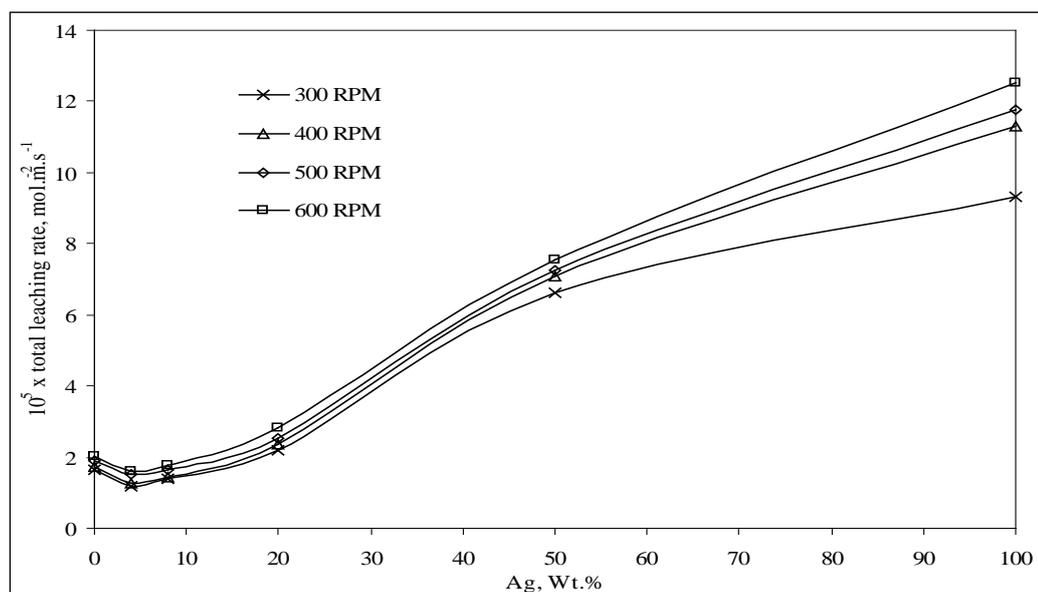


Figure 5.29: The total average metal dissolution rate of pure gold, pure silver and gold-silver alloys at different rotation speeds (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , rpm, 30 °C, and pH= 11.5

5.6.7 Effect of pH (ammonium sulfate concentration) on Gold, Silver and Total Metal Dissolution

The effect of ammonium sulfate concentration and hence pH on the total metal dissolution rate from pure gold, pure silver and gold-silver alloys was investigated and the results are shown in Figures 5.30 and 5.31. The experiments were conducted using 0, 0.01, 0.1, and 0.4 M ammonium sulfate giving solution pH values of 11.50, 10.97, 9.96, and 9.60 respectively. The average gold dissolution rate from the pure gold disc increased slightly when the pH was increased from 9.60 to 9.96. However, the total metal dissolution rates using different percentages of silver were significantly increased by increasing the pH up to 11.50. The dissolution rate of silver from pure metal decreased with increasing ammonium sulfate concentration (hence decreasing the value of pH) with the highest rate when no ammonium sulfate was present. It has to be pointed out that the optimum pH value to maximize the gold and silver dissolution rates is 11.50.

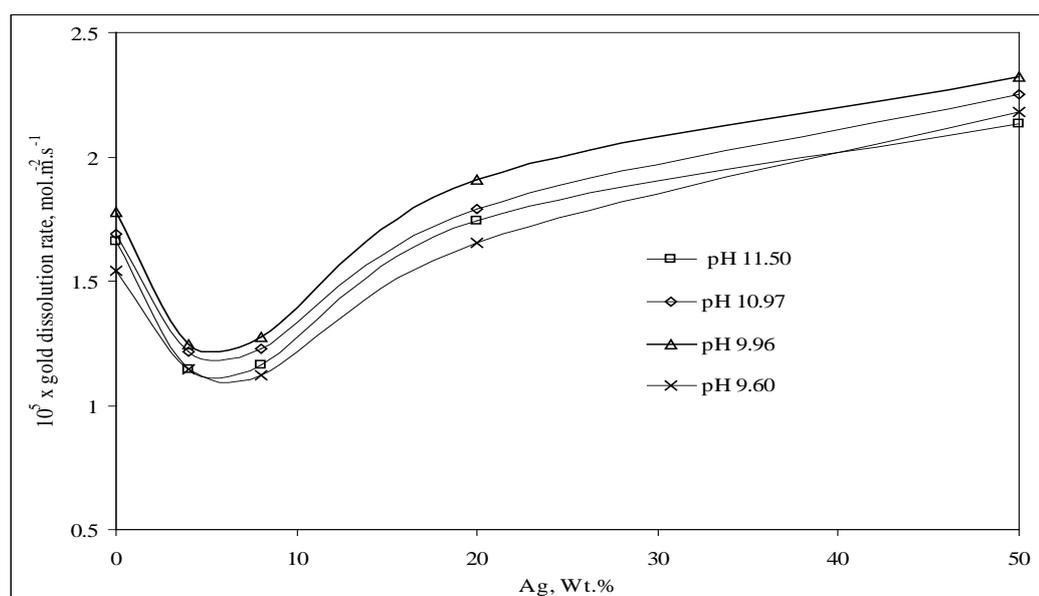


Figure 5.30: Gold dissolution rate from gold and gold-silver alloys at different pH values (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, 30 °C and pH (ammonium sulfate added).

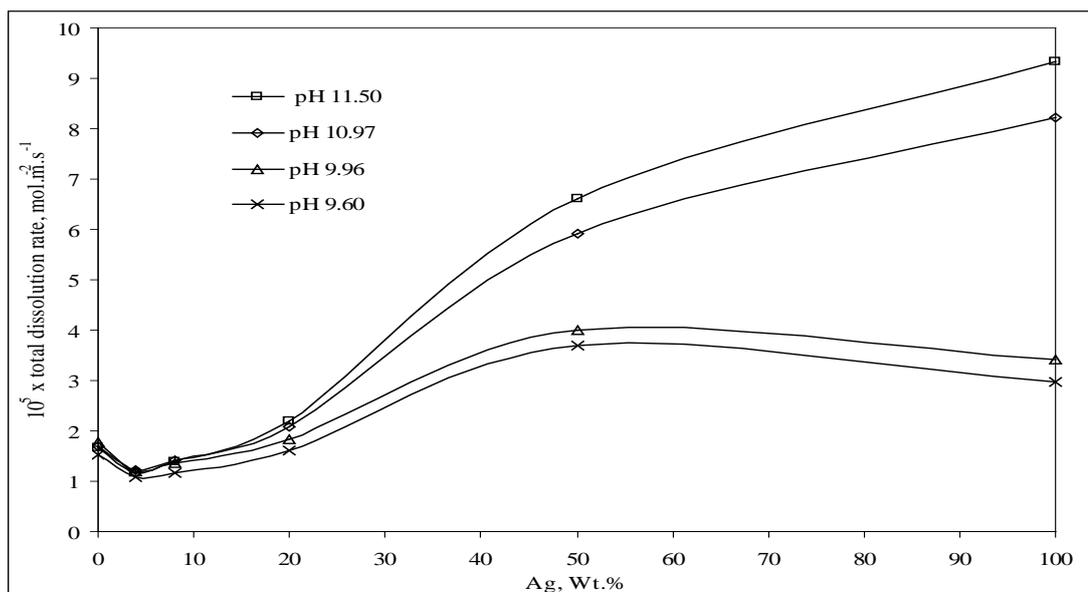


Figure 5.31: Total average metal dissolution rate of gold, silver and gold-silver alloys at different pH values (average rate of 3, 5, and 8 hours leaching). Initial experiment conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM $CuSO_4$, 0.4 M NH_3 , 300 rpm, 30 °C, and pH (ammonium sulfate added).

5.7 Summary

In this chapter, a comparison between using open and closed vessels in the thiosulfate leaching system was carried out. The experiments were conducted using pure gold, pure silver and gold-silver alloys. It was found that using a closed vessel to dissolve gold and silver in thiosulfate solutions containing Cu(II) and ammonia maintains the optimum reagents concentrations for a longer time and enhances the leaching kinetics compared with an open vessel. The leaching rate of gold and silver in the closed vessel was greater than that obtained in the open vessel by 35% and 43% respectively. Silver leaching rates were found to be more sensitive to temperature and ammonia concentration than gold. Higher temperatures increased the volatilization rate of ammonia during the leaching in the open vessel which will be of metallurgical and environmental concern. In addition, the study has shown that in thiosulfate solutions containing Cu(II) and ammonia, the gold dissolution rate was enhanced with the presence of silver.

The optimisation of leaching conditions was carried out using the closed vessel. Gold and silver dissolution rates were increased with increasing thiosulfate, copper(II), and ammonia concentrations. It was determined that the optimum leaching conditions for gold and silver were: 10 mM Cu(II), 0.6 M NH₃ for gold and 0.8 M for silver, 0.2 M (S₂O₃)²⁻, 30 °C, 300 rpm, and pH =11.5.

Chapter 6 An electrochemical study of the leaching of gold, silver, and gold-silver alloys in thiosulfate solutions

6.1 Introduction

The leaching of gold in thiosulfate solutions is an electrochemical reaction and like other electrochemical reactions, it combines of the oxidation of gold (anodic reaction) and the reduction of the oxidant copper(II) (cathodic reaction). In the present chapter, electrochemical techniques are used to study the oxidation of gold from pure gold and gold-silver discs to the gold thiosulfate complex. The anodic half reaction of gold is shown in Equation 6.1 which has a standard potential of 0.15 V (Nicol et al., 1987).



As silver often is present as an alloying element with native gold, in this chapter, the effect of silver contents on the gold oxidation half reaction is studied. Gold-silver alloys discs of 4, 8, 20, and 50 wt.% silver were used.

The experimental work was carried out in two ways: linear sweep voltammetry and coulometric electrochemical experiments at a fixed potential value. The experiments were performed at a rotation rate of 300 rpm and at a temperature of 30 °C for 30 minutes. The solutions were kept at the natural pH. After 30 minutes, samples were collected and analysed for gold and silver by ICP-OES.

6.2 Linear Sweep Voltammetry

Linear sweep voltammetry was carried out using a Radiometer PGZ 301 potentiostat. All experiments were performed at 30 °C, with a rotation rate of 300 rpm and a scan rate of 1 mV s⁻¹. Potentials were measured relative to the saturated calomel electrode (+0.242 V vs. SHE). Solutions were de-aerated using nitrogen for 20 minutes. The current was measured at a range of potential between -22 mV and 300 mV (relative to SCE). In the following sections, the effect of different reagent and additive concentrations on the gold oxidation half reaction are presented and discussed.

6.2.1 Effect of Ammonium Thiosulfate Concentration

Thiosulfate is the main reagent in the thiosulfate system and has the most noticeable effect on the rate of gold leaching. Thus, the effect of different ammonium thiosulfate (ATS) was investigated using the liner sweep voltammetry technique on pure gold, pure silver and gold-silver discs of 17 mm diameter (surface area 2.27 cm²).

6.2.1.1 Pure Gold

Figure 6.1 shows the effect of ammonium thiosulfate (ATS) concentration on the current density resulting form gold oxidation. It can be seen from Figure 6.1 that an increase in ammonium thiosulfate concentration results in an increase in the produced current due to the oxidation of gold. This result is consistent with those of Breuer and Jeffrey (2002) and Jeffrey (2001). Also this confirms the result that has been shown in the kinetics studies (Chapter 5) of this project.

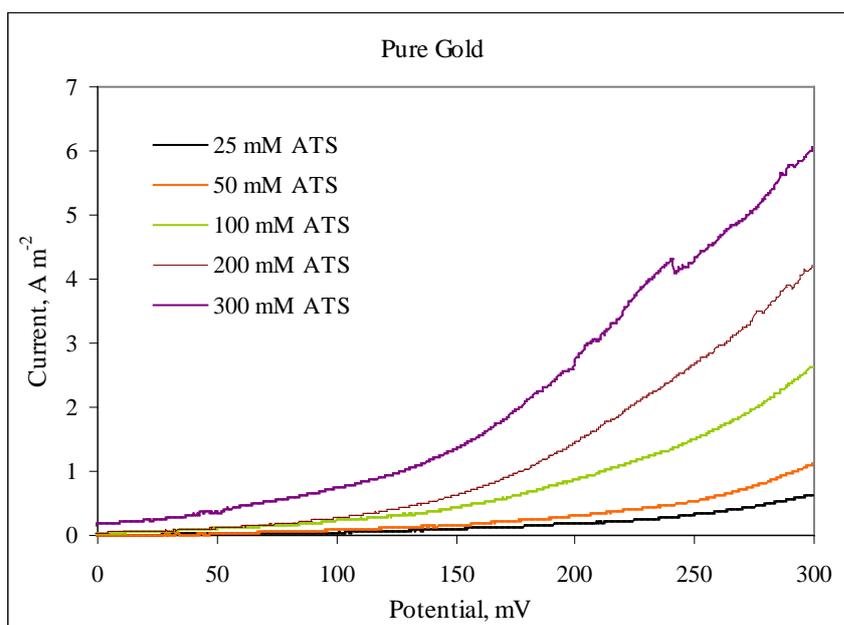


Figure 6.1: Linear sweep voltammograms showing the effect of ATS concentration on the current density of the gold oxidation for pure gold. Experimental conditions: 300 rpm, 30 °C, and natural pH of the solution.

6.2.1.2 Gold-Silver Alloys

The effect of ammonium thiosulfate (ATS) concentration on the current density of both gold and silver oxidation from gold-silver alloys in thiosulfate solutions is shown in Figure 6.2.

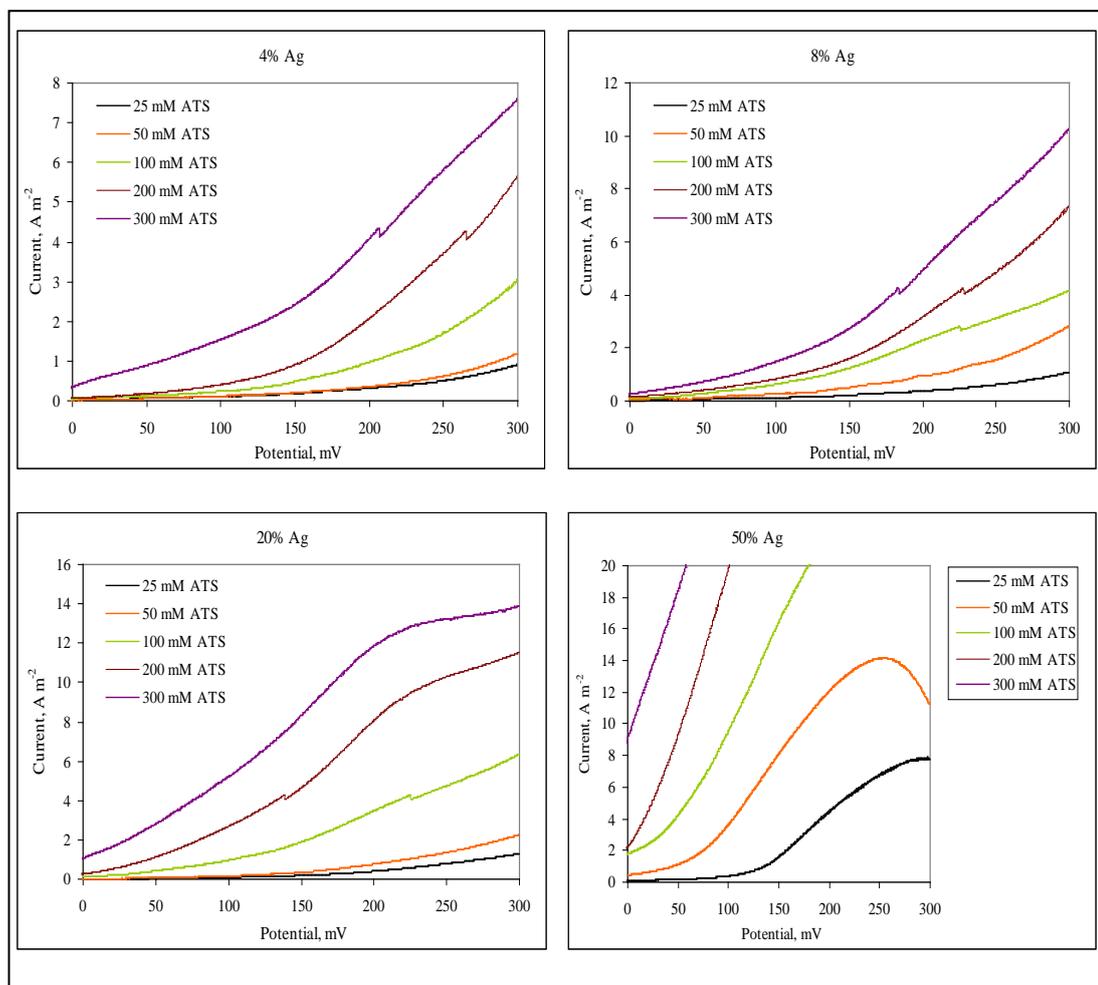


Figure 6.2: Linear sweep voltammograms showing the effect of ammonium thiosulfate concentration on the current density of both gold and silver oxidation for 4, 8, 20, and 50% Ag alloys. Experimental conditions: 300 rpm, 30 °C, and natural pH of the solution.

Figure 6.2 shows that an increase of silver percent in the alloy results in an increase of the current density for combined gold and silver oxidation in the thiosulfate solutions over the whole range of applied potentials. This result is consistent with the total leaching rate of gold and silver from these alloys obtained from the kinetics study in this project (Chapter 5). For all gold silver alloys the

current density increased with increasing concentration of ammonium thiosulfate (ATS). This result also is consistent with those observed by Chandra and Jeffrey (2004) for the oxidation of pure gold and 2% Ag.

6.2.2 Effect of Sodium Thiosulfate Concentration

To compare the effect of the two main commercial thiosulfate salts, the effect of using sodium thiosulfate (STS) concentration on the voltammograms of pure gold and gold-silver alloys was investigated.

6.2.2.1 Pure Gold

The effect of sodium thiosulfate (STS) concentration on the current density of the gold oxidation from a gold thiosulfate complex is shown in Figure 6.3. Results in Figure 6.3 show that the same trend was obtained using ammonium thiosulfate compared with STS on leaching of pure gold (Figure 6.1). A comparison between Figure 6.1 and 6.3 shows that gold oxidation is faster in ammonium thiosulfate solution than sodium thiosulfate solution. It has been shown by Chandra and Jeffrey (2004) that gold oxidation using ATS is faster than that of STS. The increase in the gold oxidation in the presence of ammonium thiosulfate can be attributed to the increased pH value with the presence of ammonium ions from the ATS.

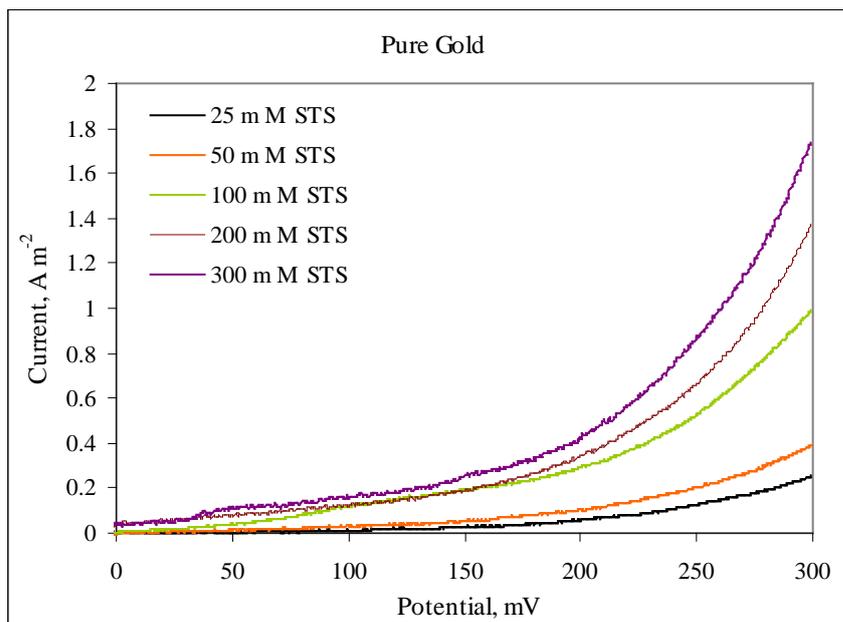


Figure 6.3: Linear sweep voltammograms showing the effect of sodium thiosulfate (STS) concentration on the current density of gold oxidation from a pure gold disc. Experimental conditions: 300 rpm, 30 °C, and natural pH of the solution.

6.2.2.2 Gold-Silver

The effect of sodium thiosulfate (STS) concentration on the current density resulting from gold-silver oxidation from gold-silver alloys in thiosulfate solution is shown in Figure 6.4. From a comparison between the data in Figures 6.3 and 6.4, the current density resulting from the gold oxidation of pure gold is slightly higher than the total metal oxidation obtained from 4, and 8% Ag alloys, however, for 20 and 50% Ag alloys the current density was much higher than for pure gold.

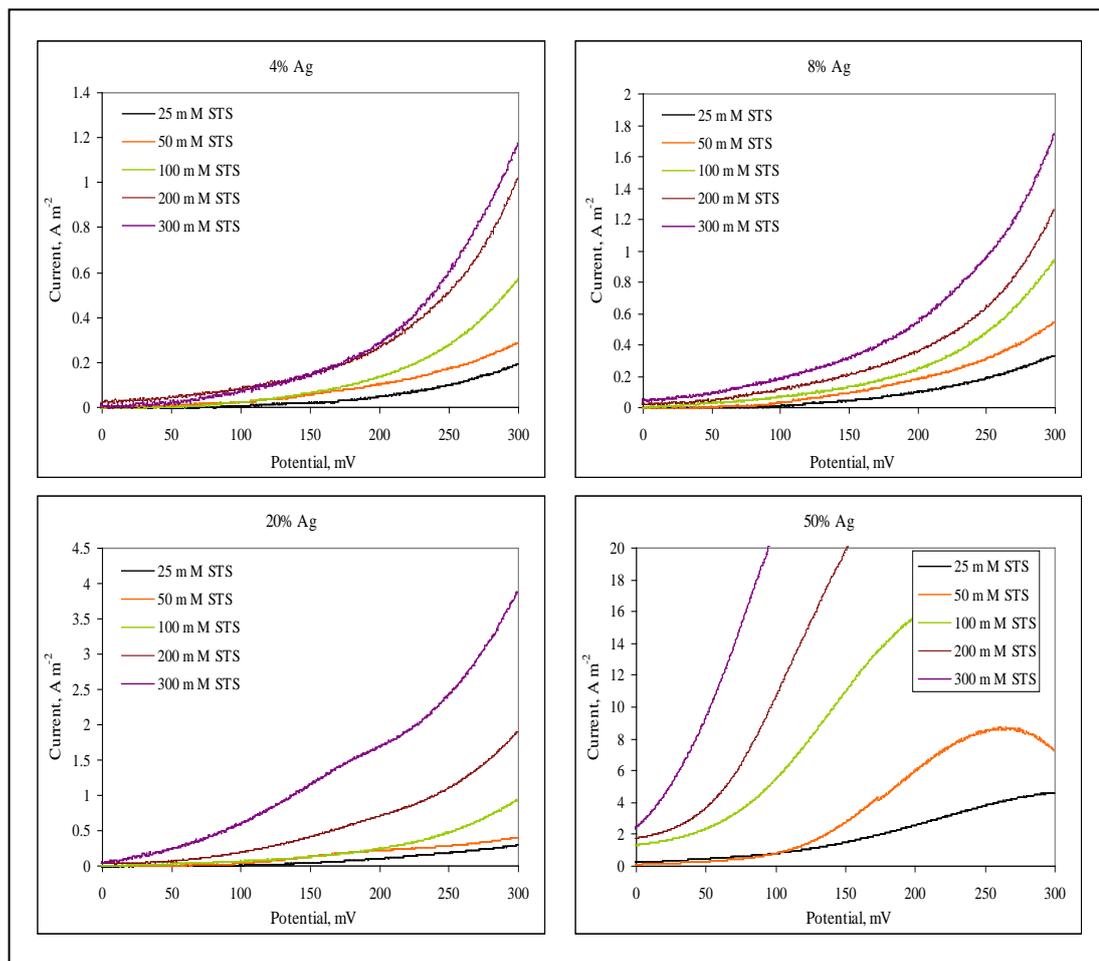


Figure 6.4: Linear sweep voltammograms showing the effect of sodium thiosulfate (STS) concentration on the combined current density of gold and silver oxidation in 4, 8, 20, and 50% Ag alloys. Experimental conditions: 300 rpm, 30 °C, and natural pH of the solution.

6.2.3 Effect of Ammonia Concentration

Ammonia is required in thiosulfate solutions in order to stabilise the copper in the copper(II) oxidation state. In this section, the effect of ammonia concentration on the gold oxidation process from pure gold and gold-silver alloys was studied using the linear sweep voltametry technique. It has been noted by Zhu et al. (1994) that the oxidation of gold in the presence of ammonia occurs in two steps, the formation of a gold-ammonia complex (Equation 6.2) and then the thiosulfate ion substitutes for the ammonia ion to form a gold-thiosulfate complex as shown in Equation 6.3.



6.2.3.1 Effect of Ammonia Concentration on Pure Gold

Figure 6.5 shows the measured current density of gold oxidation as a function of potential at different ammonia concentrations. In the absence of ammonia, the process of gold oxidation is very slow over all the potentials. However, in solutions containing high ammonia concentrations, gold oxidation occurs rapidly. This result is consistent with those of Chandra and Jeffrey (2004) and Jiang et al. (1993a).

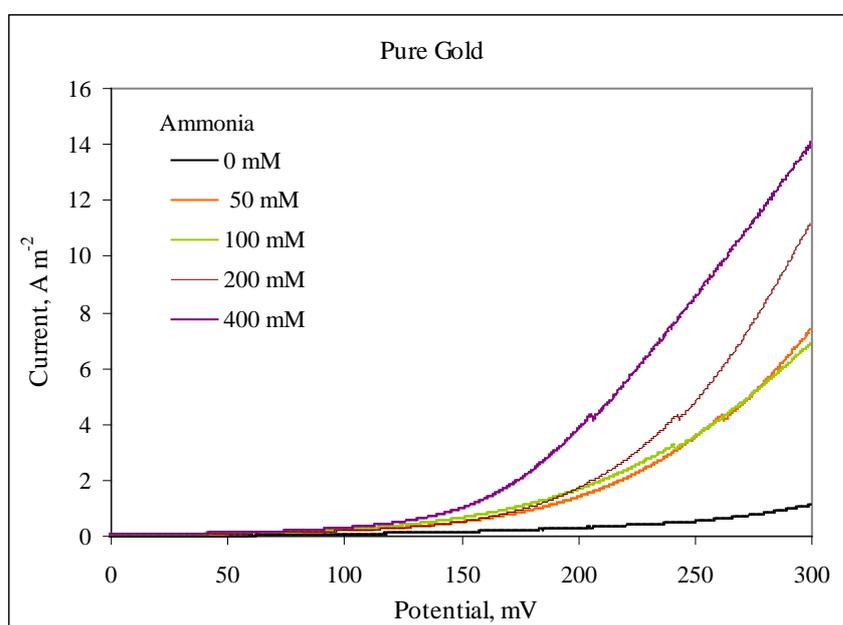


Figure 6.5: Linear sweep voltammograms showing the effect of ammonia concentration on the current density of the gold oxidation for pure gold. Experimental conditions: 50 mM ATS, 300 rpm, 30 °C, and natural pH of the solution.

6.2.3.2 Effect of Ammonia Concentration on Gold-Silver Alloys

The effect of ammonia concentration on combined gold and silver oxidation in thiosulfate solutions containing 50 mM ATS was investigated. Figure 6.6 shows the measured current density of total metal oxidation from the gold-silver alloys at different ammonia concentrations.

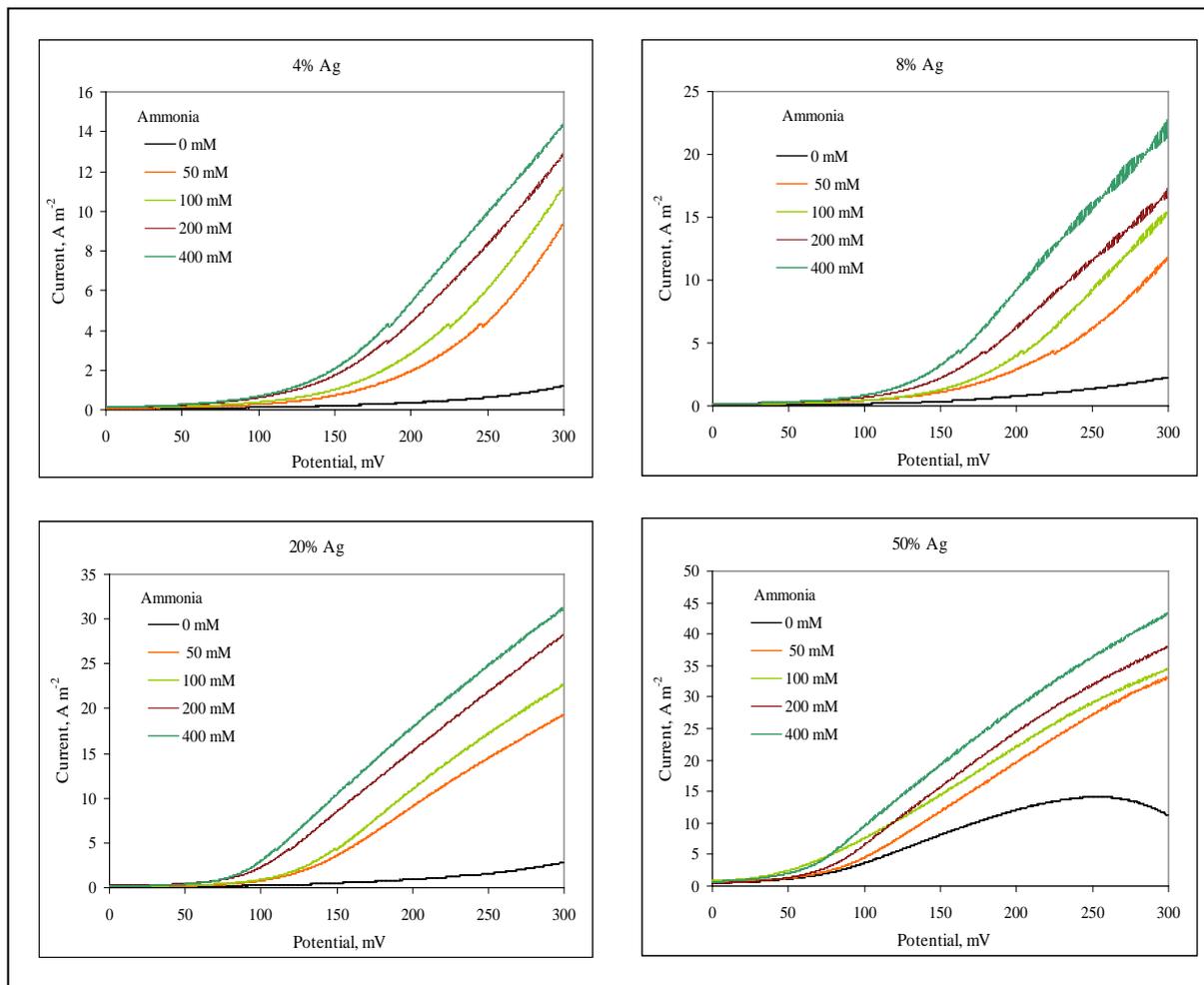


Figure 6.6: Linear sweep voltammograms showing the effect of ammonia concentration on the current density of the gold oxidation from gold-silver alloys. Experimental conditions: 50 mM ATS, 300 rpm, 30 °C, and natural pH of the solution.

It can be seen from Figure 6.6 that ammonia is an important reagent in the thiosulfate system. Moreover, the combined oxidation current of gold and silver from each alloy in the absence of ammonia is very low compared with the oxidation current in the presence of ammonia. As the percent of silver increases, the oxidation current for both gold and silver increased indicating that the leaching rate for total metal (gold and silver) increases with increasing the silver content.

6.2.4 Effect of Thiourea Concentration

From the previous electrochemical studies, it has been shown that the oxidation of gold in solution just containing thiosulfate is very slow. Therefore, high (5 mM) and low (1 mM) concentrations of thiourea were tested to evaluate its affect on the oxidation rate of gold from pure gold and gold-silver alloys. Also, the effect of thiourea on the oxidation of gold and gold-silver alloys was determined for both ammonium and sodium (50 mM) thiosulfate solutions.

6.2.4.1 Effect of Thiourea Concentration on Pure Gold

Figure 6.7 shows the effect of thiourea on the anodic dissolution of gold from a pure gold disc. There was an increase in oxidation current in the presence of thiourea which increased with increasing concentration of thiourea from 1 mM to 5 mM.

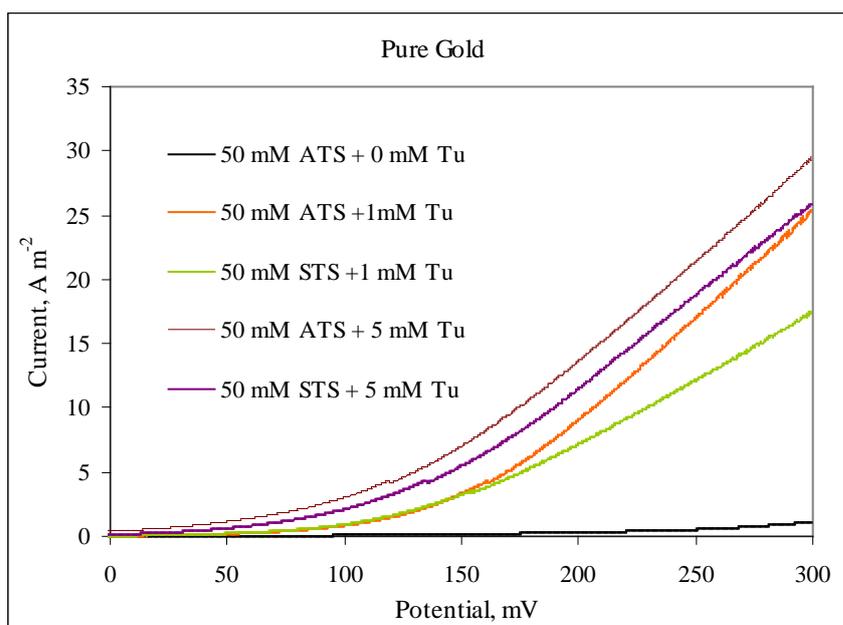


Figure 6.7: Linear sweep voltammograms showing the effect of thiourea concentration on the current density of gold oxidation from a pure gold disc. Experimental conditions: 50 mM ATS or STS, 300 rpm, 30 °C, and natural pH of the solution.

In the absence of thiourea, gold oxidation in the thiosulfate system is very slow, but in the presence of up to 5 mM thiourea the oxidation current is greatly increased. For all potentials the gold oxidation in solutions containing ammonium thiosulfate was higher than that containing sodium thiosulfate.

6.2.4.2 Effect of Thiourea Concentrations on Gold-Silver Alloys

The effect of thiourea concentration on gold-silver oxidation from different gold-silver alloys was investigated with the results shown in Figure 6.8. It is obvious that an increase in thiourea concentration results in an increase in the metal (gold and silver) oxidation current for both ammonium and sodium thiosulfate solutions.

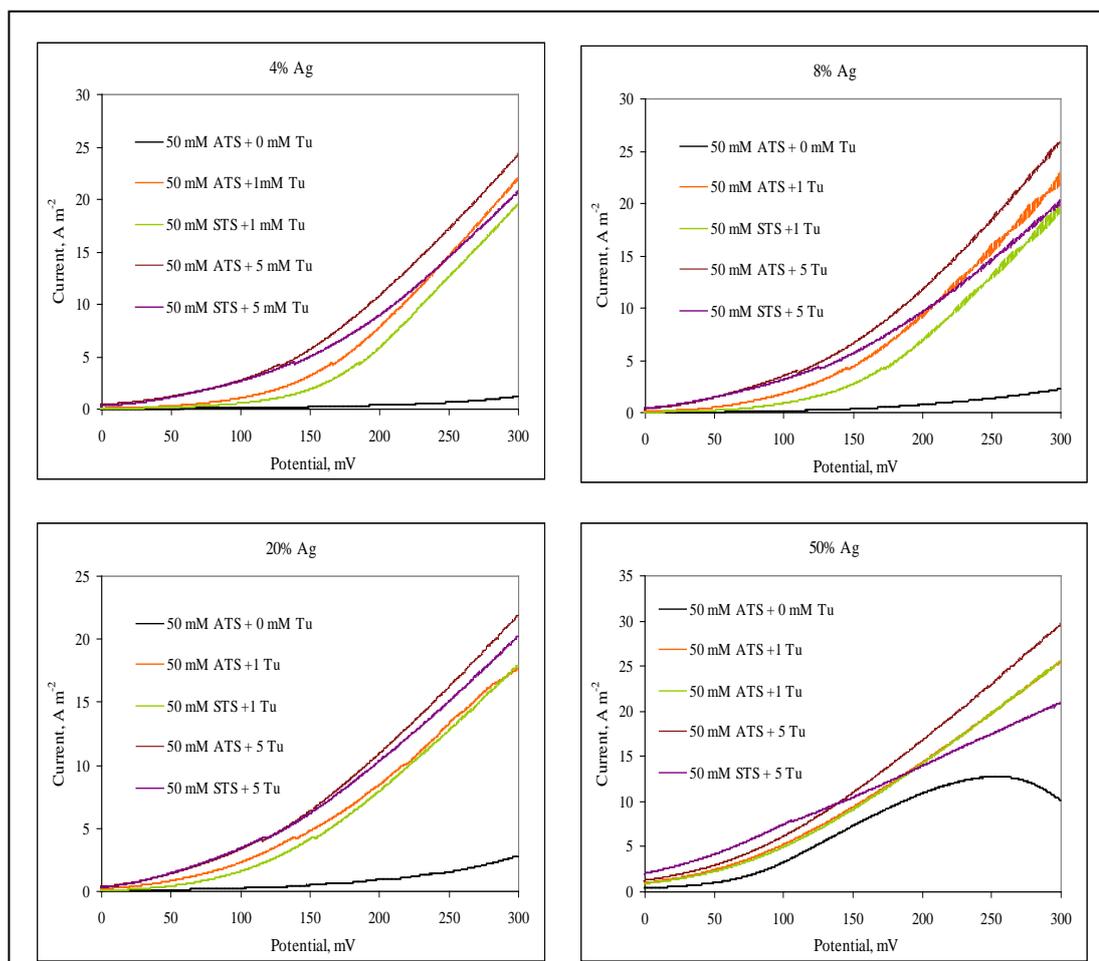


Figure 6.8: Linear sweep voltammograms showing the effect of thiourea concentration on the current density of the combined gold and silver oxidation from gold-silver alloys. Experimental conditions: 50 mM ATS or STS, 300 rpm, 30 °C, and natural pH of the solution.

Also from Figure 6.8, it can be noted, that when silver is present with gold, the oxidation current density for total metal dissolution (gold and silver) decreases. At high percentage of silver (50%), the oxidation current of gold and silver in the absence of thiourea significantly increased, compared with alloys of low silver percentages.

6.2.4.3 Effect of Silver Content in the Presence of Thiourea

To focus on the effect of silver, the polarisation curves for pure gold, 4, 8, and 20% Ag are plotted together in Figure 6.9 for a thiosulfate solution containing 50 mM ATS. In the presence of silver, the combined oxidation current of gold and silver decreased. In addition, the oxidation current from pure gold at larger potentials than the standard potential for gold oxidation of 150 mV, is higher than the total metal (gold and silver) oxidation current for all the gold-silver alloys. This phenomenon was also observed by Chandra and Jeffrey (2004). The authors observed that with the presence of 2% silver, the oxidation current is less than that of the pure gold in the presence of thiourea in the solution.

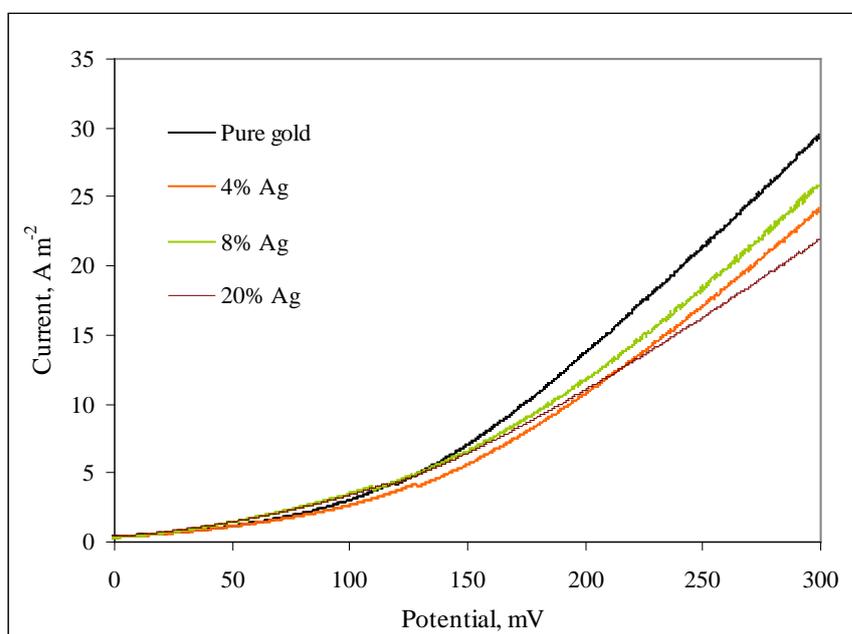


Figure 6.9: Linear sweep voltammograms showing the effect of silver content on the current density of the combined gold and silver oxidation from different gold-silver combinations in the presence of thiourea. Experimental conditions: 50 mM ATS, 5 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

6.2.4.4 Effect of Thiourea on Silver Oxidation

To determine the effect of thiourea on silver oxidation, the oxidation current of silver in the absence and the presence of thiourea in solution containing 50 mM of either ammonium or sodium thiosulfate was investigated. Figure 6.10 shows the effect of thiourea concentration on the oxidation current of silver resulting from a

pure silver (99.99%) disc. From the data shown in Figure 6.10, the addition of thiourea to the thiosulfate solution retards the oxidation of silver and the lowest silver oxidation occurs at the highest thiourea concentration.

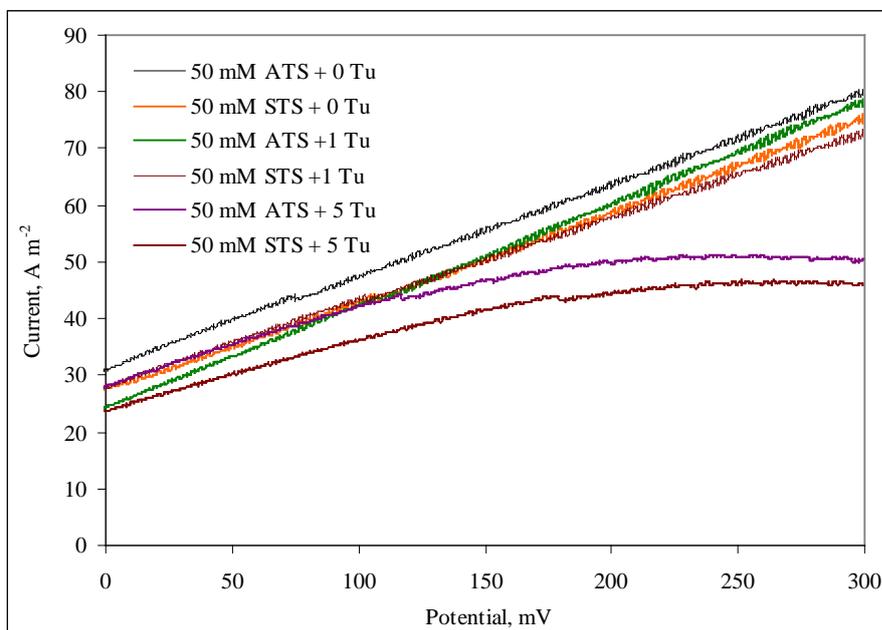


Figure 6.10: Linear sweep voltammograms showing the effect of thiourea concentration on the current density of the silver oxidation from pure silver. Experimental conditions: 50 mM ATS or STS, 300 rpm, 30 °C, and natural pH of the solution.

6.3 Coulometric Experiments at a Fixed Potential

In order to investigate the occurrence of gold and silver dissolution in different thiosulfate concentrations, coulometric experiments were carried out by applying a constant potential to pure gold and gold-silver rotating discs in the electrochemical cell. In this system, the oxidation current for gold or/and silver was measured as a function of time.

These sets of experiments were performed at a rotation rate of 300 rpm and at a temperature of 30 °C for 30 minutes. All the solutions were de-aerated using nitrogen gas for 20 minutes. The experiments were carried out at the natural pH of the solution. After 30 minutes, the solutions were analysed for gold and silver by ICP-OES. Various concentrations of reagents were added to thiosulfate solutions and the current density measured at selected potentials of 0.22, 0.256, 0.292, and 0.35V (potential values are reported relative to the standard hydrogen electrode (SHE)).

Three thiosulfate solutions were used to achieve the goals of this section: (1) thiosulfate-ammonia solution; (2) thiosulfate-ammonia-copper solution; and (3) thiosulfate-thiourea solution.

6.3.1 Coulometric Experiments at 0.22 V

The effect of thiosulfate and other reagents were studied to determine the oxidation behaviour of pure gold and gold-silver alloys in solution at a fixed potential of 0.22 V. The results are shown and discussed in the following sections.

6.3.1.1 Ammonium Thiosulfate-Ammonia Solution

Figure 6.11 shows the measured current that flowed through the electrochemical cell as a function of time for 30 minutes at a fixed potential 0.22 V in solution containing 50 mM ATS and 400 mM ammonia. These conditions were applied to pure gold and gold-silver alloys. It is clear from the data shown in Figure 6.11 that the dissolution of gold and/or silver from pure gold and 4, and 8% Ag alloys is very low at this potential. The current density increased with increasing percentage of silver up to 20%, which indicates that the alloy dissolves more easily than gold at this potential.

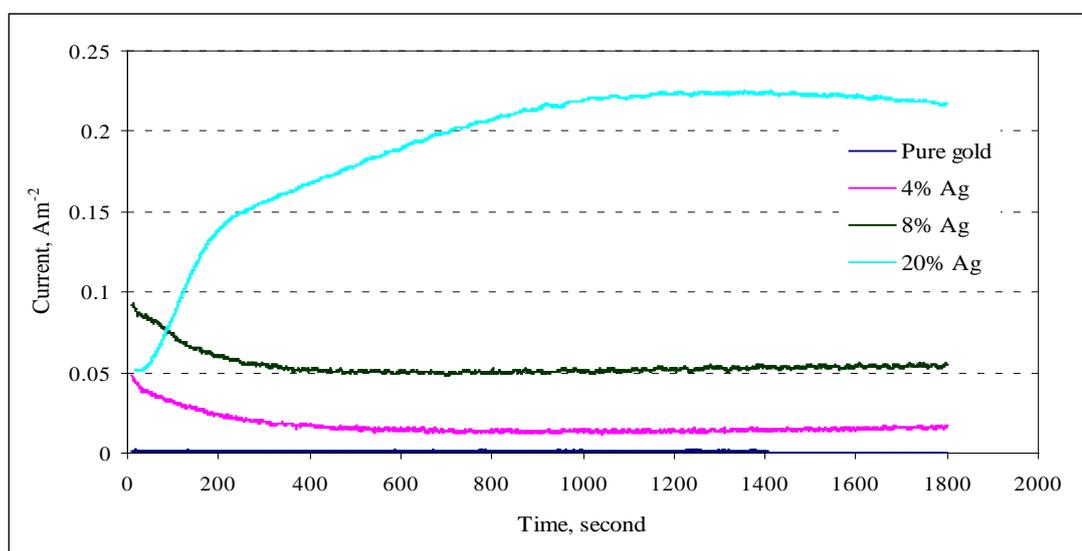


Figure 6.11: The anodic dissolution of gold and silver from a rotating disc of pure gold and 4, 8, and 20% Ag alloys. Experimental conditions: 50 mM ATS, 400 mM ammonia, 300 rpm, 30 °C, and natural pH of the solution.

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Table 6.1 shows the leaching rate of gold and silver from each disc at 0.22 V potential calculated from the ICP-OES determination of gold and silver metal dissolved in solution in 30 minutes. The data from Table 6.1 verifies the data shown in Figure 6.11 that as the percent silver increases, the total metal dissolution increases.

Table 6.1: Gold, silver, and total metal dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys at a fixed potential of 0.22 V. Experimental conditions: 50 mM ATS, 400 mM ammonia, 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Dissolution rate, $10^5 \times \text{mol.m}^{-2}.\text{s}^{-1}$		
	Gold	Silver	Total rate
Pure Gold	0.015	-	0.015
4% Ag	0.032	0.003	0.035
8% Ag	0.069	0.013	0.082
20% Ag	0.210	0.094	0.304
50% Ag	1.105	1.921	3.026

6.3.1.2 Sodium Thiosulfate-Ammonia Solution

The current that flowed through the electrochemical cell as a function of time for 30 minutes at a fixed potential of 0.22 V in solutions containing 50 mM STS and 400 mM ammonia were measured. From the amount of gold and silver dissolved, the dissolution rate of gold, silver, and total metal were calculated (Table 6.2). The data shows the same trend obtained for ammonium thiosulfate; that by increasing the percentage of silver, the gold dissolution rate, as well as the total metal dissolution rate, increased.

6.3.1.3 Thiosulfate-Ammonia-Copper Solution

The current that flowed through the electrochemical cell as a function of time for 30 minutes at a fixed potential 0.22 V in solutions containing 50 mM ATS or 50 mM STS, 400 mM ammonia, and 10 mM Cu(II) were measured. The calculated leaching rate for both gold and silver, tabulated in Table 6.3, show that gold dissolution from pure gold is faster than from 4, 8 and 20% Ag alloys. The total

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metal dissolution rate decreases for alloys of 4 and 8% Ag compared with pure gold but increases for 20 and 50% Ag alloys.

Table 6.2: Gold, silver, and total metal dissolution rates from pure gold and 4, 8, 20, and 50% Ag alloys at a fixed potential 0.22 V. Experimental conditions: 50 mM STS, 400 mM ammonia, 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Dissolution rate, $10^5 \times \text{mol.m}^{-2}.\text{s}^{-1}$		
	Gold	Silver	Total rate
Pure Gold	0.012	-	0.012
4% Ag	0.017	0.004	0.021
8% Ag	0.022	0.005	0.027
20% Ag	0.217	0.102	0.319
50% Ag	0.990	1.756	2.746

Table 6.3: Gold, silver, and total dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys at fixed a potential 0.22 V. Experimental conditions: 50 mM ATS or STS, 400 mM ammonia, 10 mM CuSO_4 , 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Dissolution rate, $10^5 \times \text{mol m}^{-2} \text{s}^{-1}$					
	Ammonium thiosulfate (ATS)			Sodium thiosulfate (STS)		
	Gold	Silver	Total rate	Gold	Silver	Total rate
Pure Gold	1.13	-	1.13	0.95	-	0.95
4% Ag	0.83	0.07	0.90	0.68	0.05	0.73
8% Ag	0.82	0.13	0.95	0.69	0.12	0.80
20% Ag	0.90	0.40	1.30	0.87	0.39	1.26
50% Ag	1.15	2.12	3.27	1.06	1.98	3.04

Figure 6.12 shows the measured current that flowed through the electrochemical cell over time for 30 minutes at a fixed potential 0.22 V in solutions containing 50 mM ATS, 400 mM ammonia, and 10 mM Cu(II) as a function of silver content. Comparison of figure 6.11 to 6.12 for the 20% Ag alloy shows that the

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current density has decreased yet the total metal dissolution rate increased. In the presence of copper(II), thiosulfate, and ammonia, the measured current does not include only the oxidation of metal to metal thiosulfate complex, but also the reduction of copper(II) to copper(I) as shown in Equation 6.4 (Breuer and Jeffrey, 2002). The standard potential for this reaction according to Jeffrey (2001) is 0.22 V and it is the sum of metal oxidation and copper reduction reactions that the coulometric experiment is measuring.

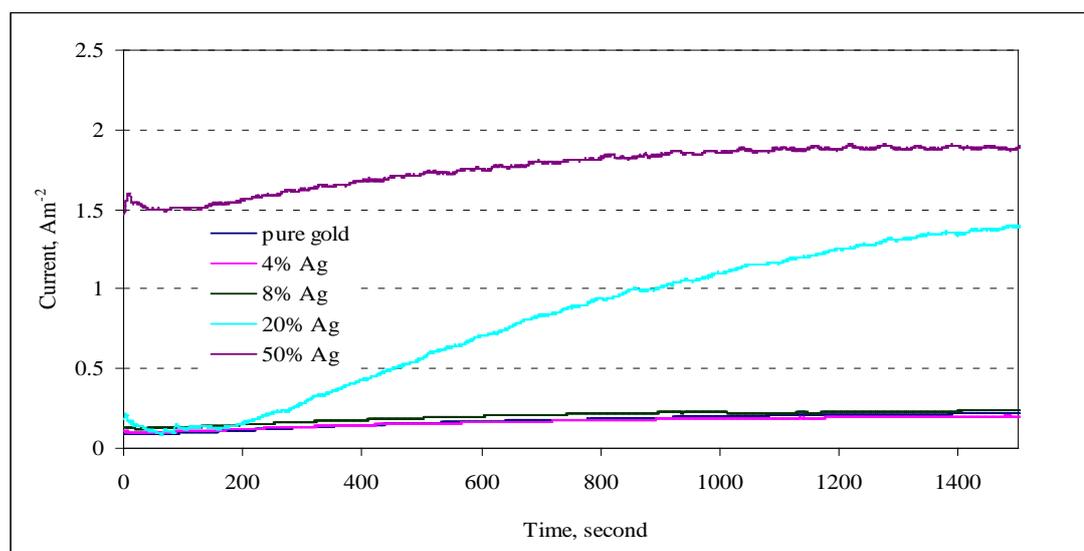
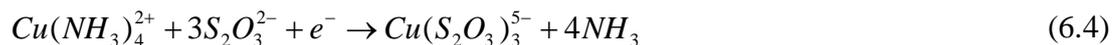


Figure 6.12: The measured current of the leaching of pure gold and gold-silver alloys in solutions containing thiosulfate-copper-ammonia at a fixed potential of 0.22 V. Experimental conditions: 50 mM ATS, 10 mM CuSO₄, 400 mM ammonia, 300 rpm, 30 °C, and natural pH of the solution.

6.3.1.4 Thiosulfate-Thiourea Solution

The effect of thiourea addition on pure gold and gold-silver alloy dissolution in thiosulfate solutions was investigated by coulometric experiments at a fixed potential of 0.22 V. The measured anodic current versus the time is plotted in Figure 6.13. The results show that the measured current increases rapidly at the start of the experiment for all alloys reaching a maximum current that depends on the percentage of silver.

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Minor passivation is observed for pure gold and for the 50% silver alloy but after about a 500 second induction time although the reason is unclear. As can also be seen from Figure 6.13, the addition of thiourea was accompanied by increasing in gold and gold/silver oxidation.

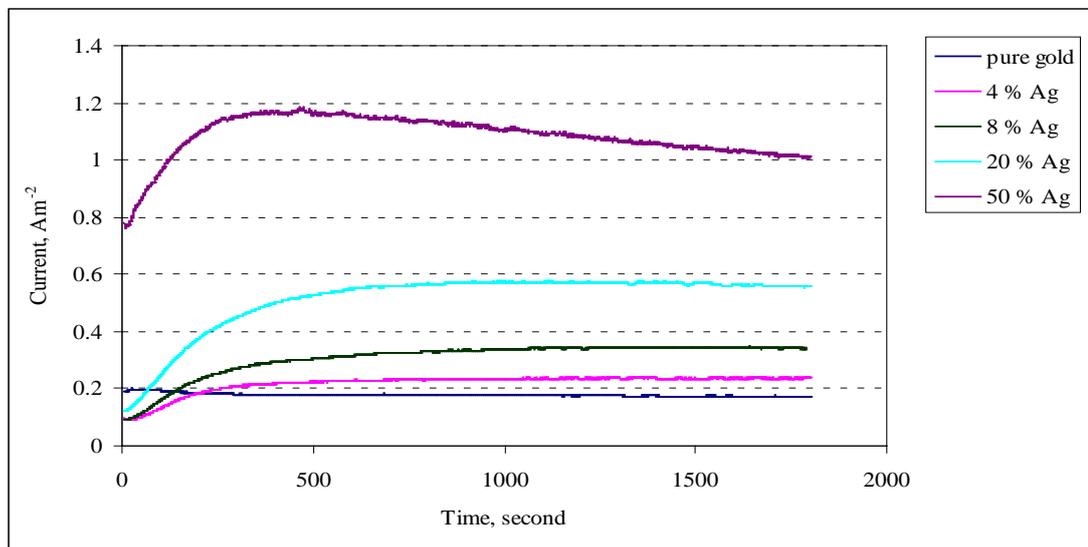


Figure 6.13: The anodic dissolution of gold and silver from pure gold, and 4, 8, 20, and 50% Ag alloys in solutions containing ammonium thiosulfate and thiourea. Experimental conditions: 50 mM ATS, 5 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

These experiments were repeated using sodium thiosulfate, the results of which are shown in Figure 6.14. It can be noticed that similar results were obtained but the anodic current is slightly higher for ammonium thiosulfate for all alloys except 4% Ag.

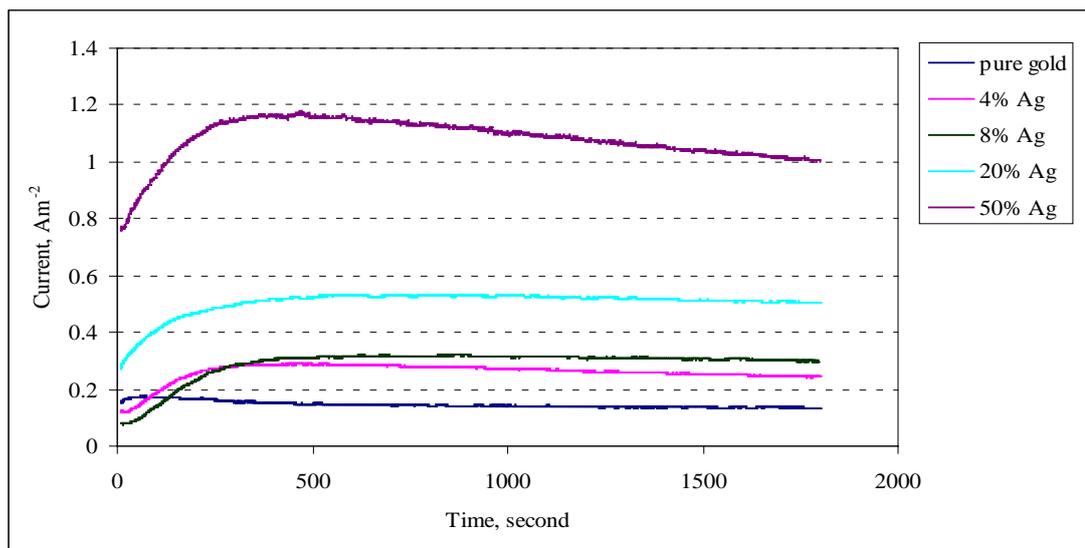


Figure 6.14: The anodic dissolution of gold and silver from pure gold and 4, 8, 20, and 50% Ag alloys in solutions containing sodium thiosulfate and thiourea. Experimental conditions: 50 mM STS, 5 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

6.3.1.5 Gold and Total Metal Dissolution Rates at 0.22 V Potential

The gold and total metal dissolution rate from pure gold and gold-silver alloys in thiosulfate solutions were calculated from ICP-OES measurements of dissolved gold and silver after 30 minutes for a fixed potential of 0.22 V. Figures 6.15 and 6.16 show the calculated gold and total metal (gold and silver) dissolution rate respectively versus the percent of silver. From the plots of gold dissolution rate after 30 minutes at a fixed potential of 0.22 V versus the percent of silver in different solutions (Figure 6.15), the trends are the same whether ammonium thiosulfate or sodium thiosulfate was used, with ammonium thiosulfate giving a slightly higher gold dissolution rate.

For either thiosulfate salt with ammonia, the gold dissolution rate increased with an increase in silver content. In comparison, when copper was added to the thiosulfate salt and ammonia solution, the dissolution rate was higher. Pure gold had a high dissolution rate which decreased with 4% Ag and then increased slowly as the silver content of the alloy was increased.

In the presence of thiourea the gold dissolution rate is higher than that obtained from thiosulfate and ammonia up to about 25% silver.

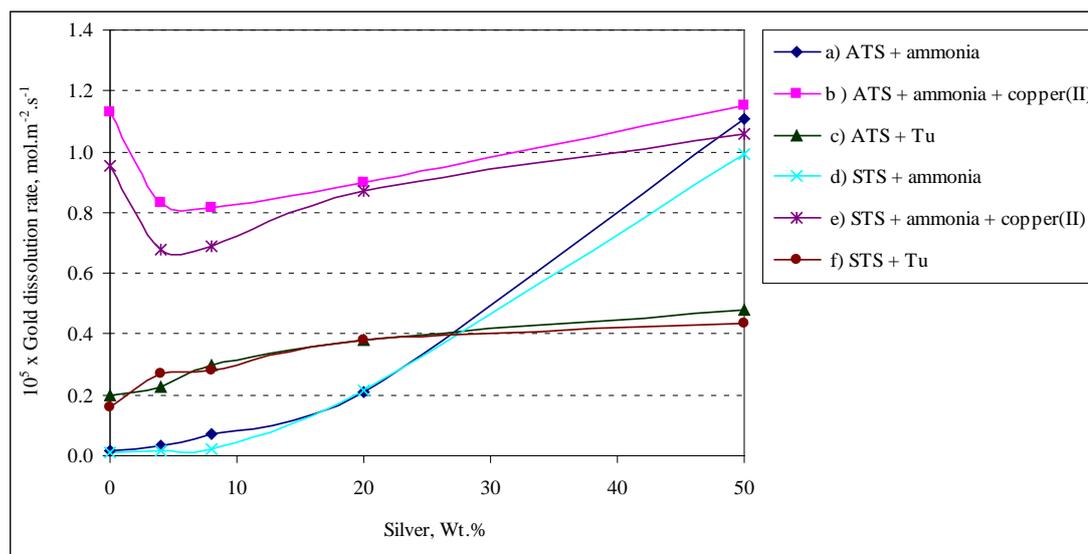


Figure 6.15: Dissolution rates of gold from a rotating disc of pure gold and 4, 8, 20, and 50% Ag alloys in thiosulfate (50 mM ATS or STS) solutions. a) ATS, 400 mM NH₃, b) ATS, 400 mM NH₃, 10 mM Cu(II), c) ATS, 5 mM Tu, d) STS, 400 mM NH₃, e) STS, 400 mM NH₃, 10 mM Cu(II), f) STS, 5 mM Tu. 300 rpm, 30 °C.

Figure 6.16, shows that solutions containing thiosulfate-copper-ammonia dissolve gold from pure metal disc faster than the total metal dissolution obtained from 4, and 8% Ag alloys. In solutions containing thiosulfate-thiourea and thiosulfate-ammonia, the total metal dissolution rate increased with an increase in silver content.

6.3.2 Coulometric Experiment at 0.256 V

Different thiosulfate solutions and reagent concentrations were studied to determine the oxidation behaviour of pure gold and gold-silver alloys in solutions at a fixed potential of 0.256 V. The results are shown and discussed in this section.

6.3.2.1 Thiosulfate-Ammonia Solution

Figure 6.17 shows the measured current that flowed through the electrochemical cell as a function of time for 30 minutes at a fixed potential of 0.256 V in solution containing 50 mM ATS and 400 mM ammonia. It can be seen from Figure 6.17 that the dissolution of gold and/or silver from pure gold and 4% Ag is very low at a potential of 0.256 V and the current density is increased with increasing percentage of silver in the alloy. Increasing oxidation current with increasing

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percentage silver is due to the dissolution of silver besides gold as the percentage of silver increases.

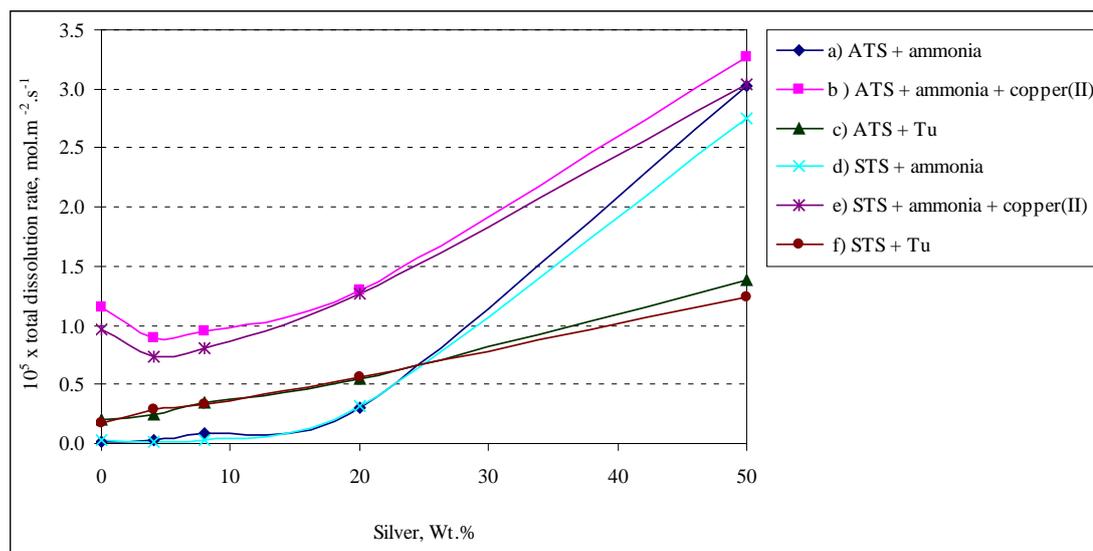


Figure 6.16: Total metal dissolution (gold and silver) rate from a rotating disc of pure gold and 4, 8, 20, and 50% Ag in thiosulfate (50 mM ATS or STS) solutions. a) ATS, 400 mM NH₃, b) ATS, 400 mM NH₃, 10 mM Cu(II), c) ATS, 5 mM Tu, d) STS, 400 mM NH₃, e) ATS, 400 mM NH₃, 10 mM Cu(II), f) STS, 5 mM Tu. 300 rpm, 30 °C.

The current passing through the cell at this potential increases rapidly at the start of the experiment (Figure 6.17) until reaching a maximum value. The time laps, before the maximum current value is obtained, decreases as the percentage of silver increases. Increasing oxidation current with increasing percentage silver indicates that the rate of alloy dissolution is dependent on the silver content.

Table 6.4 shows the calculated leaching rate of gold, silver, and total metal from each disc. The data from Table 6.4 verifies the results shown in Figure 6.17 that increasing the percentage silver leads to an increase in the total metal dissolution. For all the percentages of silver except 4%, the gold, silver, and total metal dissolution in solutions containing ammonium thiosulfate was higher than that containing sodium thiosulfate. For example, in an alloy containing 50% Ag, gold dissolution rate in solutions containing ammonium thiosulfate was higher than that from solutions containing sodium thiosulfate by 13.7%.

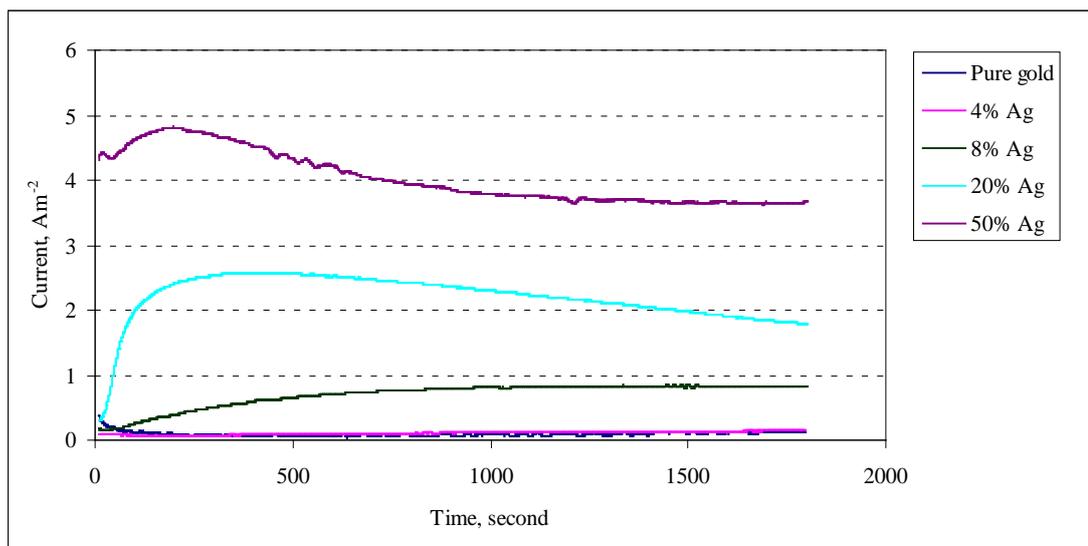


Figure 6.17: The anodic dissolution of gold and silver of a rotating disc of pure gold and 4, 8, 20, and 50% Ag alloys at a potential of 0.256 V. Experimental conditions: 50 mM ATS, 400 mM ammonia, 300 rpm, 30 °C, and natural pH of the solution.

Table 6.4: Gold, silver, and total dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys at a fixed potential of 0.256 V. Experimental conditions: 50 mM ATS or STS , 400 mM ammonia, 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Dissolution rate, $10^5 \times \text{mol.m}^{-2}.\text{s}^{-1}$					
	Ammonium thiosulfate (ATS)			Sodium thiosulfate (STS)		
	Gold	Silver	Total rate	Gold	Silver	Total rate
Pure Gold	0.03	-	0.03	0.02		0.02
4% Ag	0.09	0.01	0.11	0.19	0.01	0.20
8% Ag	0.39	0.06	0.45	0.31	0.04	0.35
20% Ag	1.99	0.98	2.97	1.85	0.72	2.56
50% Ag	2.32	4.18	6.51	2.04	3.26	5.29

6.3.2.2 Thiosulfate-Ammonia-Copper Solution

The current that flowed through the electrochemical cell as a function of time for 30 minutes at a fixed potential of 0.256 V in solutions containing 50 mM ATS or STS, 400 mM ammonia, and 10 mM Cu(II) for pure gold and different gold-silver

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alloys was measured. The measured current as a function of time (Figure 6.18) in the presence of Cu(II) as an oxidant agent, is the total current of all the electrochemical reactions occurring at the electrode-solution interface which include gold oxidation and reduction of copper(II) tetraammine into a copper(I) thiosulfate complex. At a potential of 0.256 V, there was an increase of oxidation current as the percentage of silver increased.

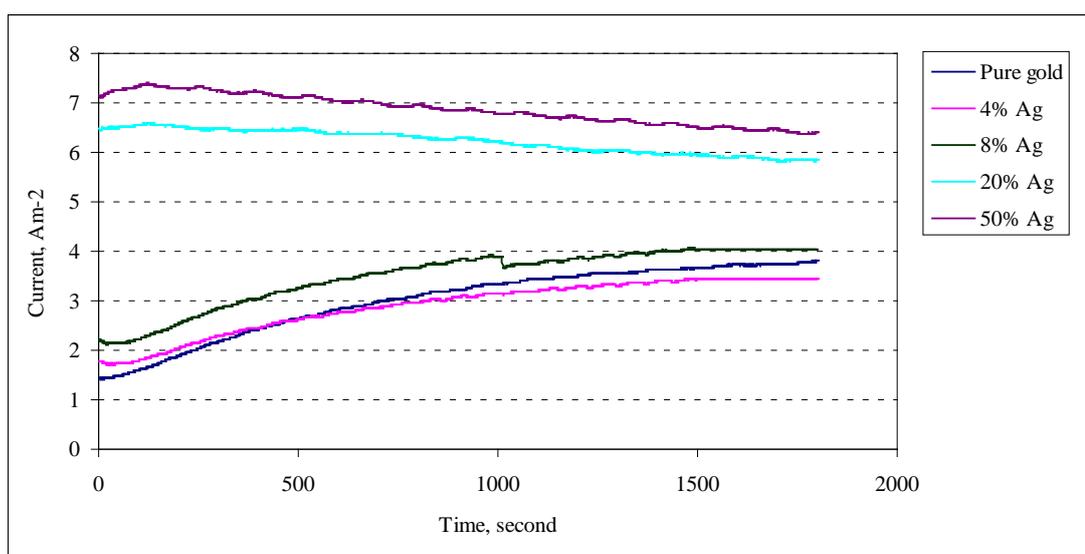


Figure 6.18: The measured current of pure gold and gold-silver alloys in solutions containing thiosulfate-copper-ammonia at a fixed potential of 0.256 V. Experimental conditions: 50 mM ATS, 10 mM CuSO₄, 400 mM ammonia, 300 rpm, 30 °C, and natural pH of the solution.

The calculated leaching rate for both gold and silver tabulated in Table 6.5 show that gold dissolution for pure gold is still faster than that of 4 and 8% Ag alloys as observed at a potential of 0.22 V. Furthermore, by increasing the percentage of silver to 20 and 50%, both gold and silver dissolution rates increased.

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Table 6.5: Gold, silver, and total metal dissolution rates from pure gold and 4, 8, 20, and 50% Ag alloys at a fixed potential of 0.256 V. Experimental conditions: 50 mM ATS or STS, 400 mM ammonia, 10 mM CuSO₄, 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Dissolution rate, 10 ⁵ x mol.m ⁻² .s ⁻¹					
	Ammonium thiosulfate (ATS)			Sodium thiosulfate (STS)		
	Gold	Silver	Total rate	Gold	Silver	Total rate
Pure Gold	1.29	-	1.29	0.98	-	0.98
4% Ag	0.86	0.06	0.93	0.73	0.08	0.81
8% Ag	0.96	0.13	1.09	0.79	0.13	0.92
20% Ag	1.11	0.47	1.58	1.03	0.43	1.46
50% Ag	1.51	2.62	4.13	1.32	2.23	3.55

6.3.2.3 Thiosulfate-Thiourea Solution

The effect of thiourea addition to thiosulfate solutions was investigated by coulometric experiments at a fixed potential of 0.256 V on pure gold and gold-silver alloys. The anodic current was plotted versus time at a fixed potential of 0.256 V. The results show that the trend is similar to that observed at a potential of 0.22 V but, the measured anodic current increased by increasing the potential, which indicates that the dissolution of gold and gold-silver alloys is faster at a potential of 0.256 V than 0.22 V.

The anodic current was measured as a function of time at a fixed potential of 0.256 V in solutions containing sodium thiosulfate and thiourea and the results are plotted in Figure 6.20. The trend is similar to what was obtained with ammonium thiosulfate (Figure 6.19) but the measured current decreased indicating that both gold and silver dissolved in sodium thiosulfate solutions slower than in ammonium thiosulfate solutions.

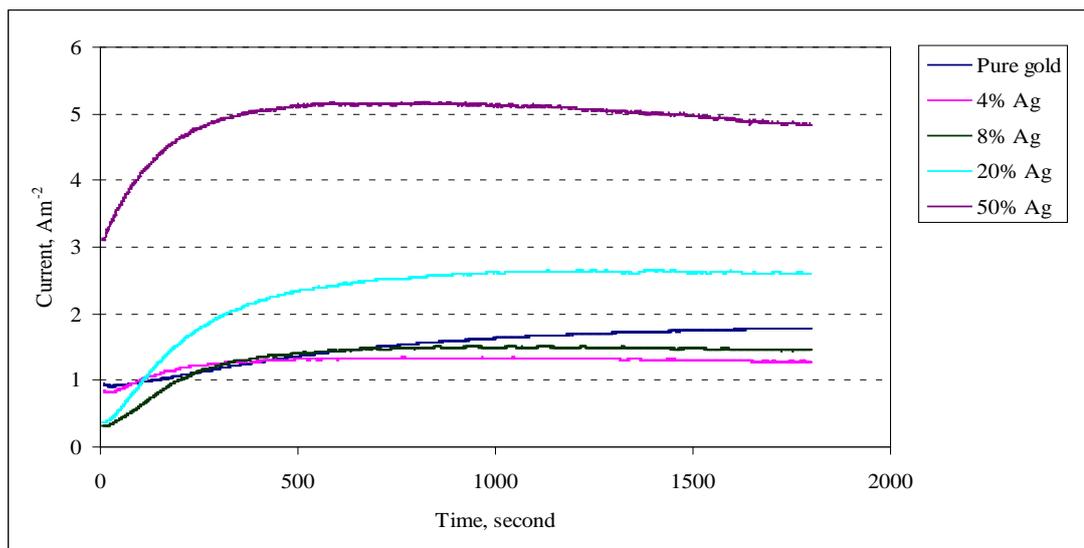


Figure 6.19: The anodic dissolution of gold and silver from pure gold and 4, 8, 20, and 50% Ag alloys in solution containing ammonium thiosulfate and thiourea. Experimental conditions: 50 mM ATS, 5 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

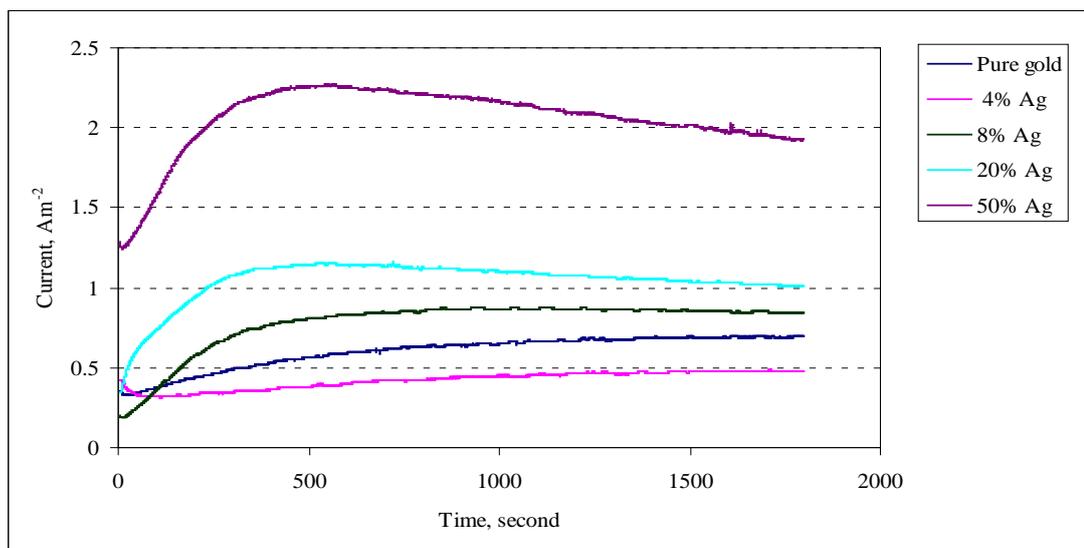


Figure 6.20: The anodic dissolution of gold and silver from pure gold and 4, 8, 20, and 50% Ag alloys in solutions containing sodium thiosulfate and thiourea. Experimental conditions: 50 mM STS, 5 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

6.3.2.4 Gold and total metal dissolution rates at 0.256 V potential

The gold and total metal dissolution rates from pure gold and gold-silver alloys in thiosulfate solutions were calculated from the metal dissolved after 30

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minutes of at a fixed potential of 0.256 V. Figures 6.21 and 6.22 show the calculated gold and total metal (gold and silver) dissolution rate as a function of the percent silver in the disc. From the results in Figures 6.21 and 6.22, it is obvious that the presence of silver enhances the gold dissolution rate in thiosulfate solutions. Comparison of gold dissolution from pure gold and gold-silver alloys in different thiosulfate solutions shows that:

- gold dissolution from pure metal is faster than that from 4 and 8% Ag but is slower than that from 20 and 50% Ag alloys in thiosulfate-ammonia-copper solutions;
- pure gold had a high dissolution rate which decreased with 4% Ag and then increased as the silver content of the alloy increased in thiosulfate-thiourea solutions;
- gold dissolution from pure metal was very slow in thiosulfate-ammonia solutions, however, the gold and total metal dissolution rate were the highest at 20 and 50% silver.

It has to be determined that with low percentages of silver (up to 8%) the best system in terms of faster gold dissolution is thiosulfate-copper-ammonia. However, with high percentages of silver, thiosulfate-ammonia has the highest gold dissolution rates.

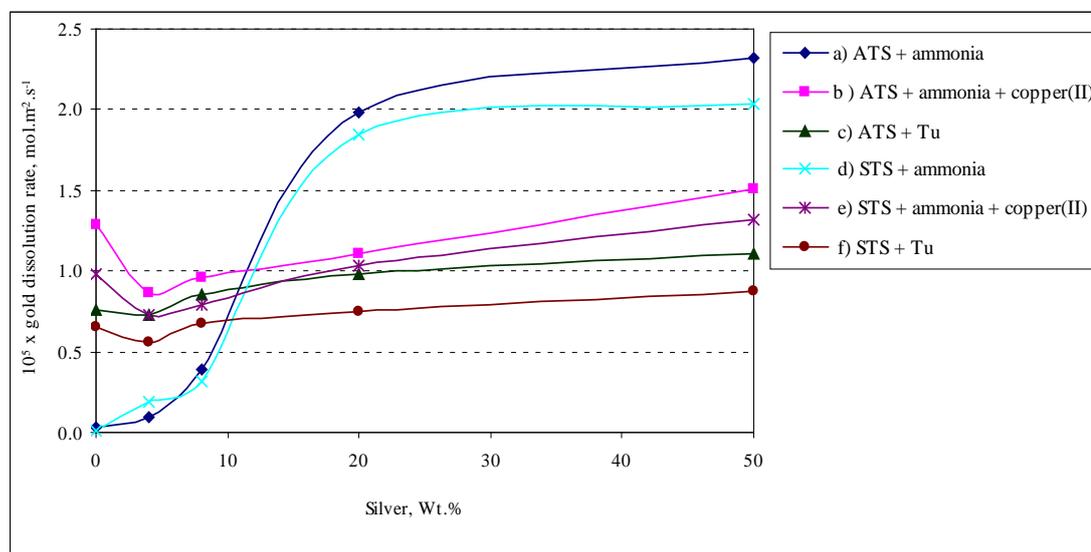


Figure 6.21: Dissolution rates of gold from pure gold and 4, 8, 20, and 50% Ag alloys in thiosulfate (50 mM ATS or STS) solutions. a) ATS, 400 mM NH_3 , b) ATS, 400 mM NH_3 , 10 mM Cu(II) , c) ATS, 5 mM Tu, d) STS, 400 mM NH_3 , e) ATS, 400 mM NH_3 , 10 mM Cu(II) , f) ATS, 5 mM Tu. 300 rpm, 30 °C.

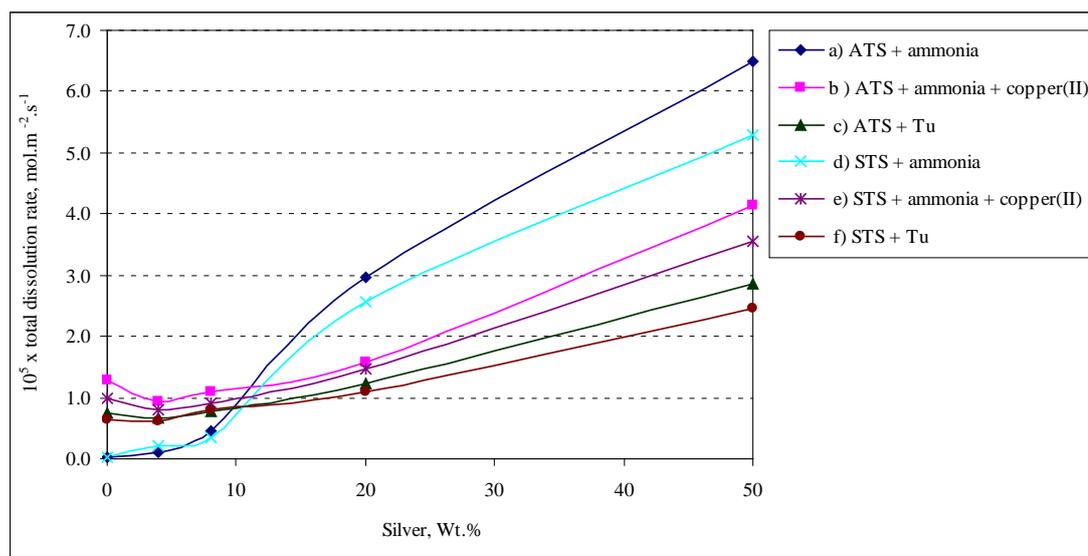


Figure 6.22: Total dissolution (gold and silver) rates from rotating discs of pure gold and 4, 8, and 20% Ag in thiosulfate (50 mM ATS or STS) solutions. a) ATS, 400 mM NH₃, b) ATS, 400 mM NH₃, 10 mM Cu(II), c) ATS, 5 mM Tu, d) STS, 400 mM NH₃, e)ATS, 400 mM NH₃,10 mM Cu(II), f) ATS, 5 mM Tu. 300 rpm, 30 °C.

6.3.3 Coulometric Experiment at 0.292 V

Different thiosulfate solutions and reagent concentrations were used to determine the oxidation behaviour of pure gold and gold-silver alloys. The experiments were conducted at a fixed potential of 0.292V and the results are shown and discussed in this section.

6.3.3.1 Thiosulfate Solutions

The effects of ammonium thiosulfate concentration on gold and silver dissolution rate from pure gold and gold-silver alloys was evaluated using the electrochemical coulometric method at a fixed potential of 0.292 V. Figure 6.23 shows the measured current that flowed through the electrochemical cell as a function of time for 30 minutes at 0.292 V in solutions containing 50 mM ATS. The results demonstrate that increasing silver content results in a higher combined oxidation current for both gold and silver. For pure gold and low percentage silver alloys, the gold and combined gold-silver oxidation is very slow in the absence of copper(II) and ammonia.

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Figure 6.24 shows the effect of increasing the ammonium thiosulfate concentration (ATS) from 50 mM to 100 mM on the anodic current resulting from the oxidation of gold and silver from pure gold and gold-silver alloys at a fixed potential of 0.292 V. The results of Figure 6.24 demonstrate that an increase of thiosulfate concentration results in an increase in the oxidation current. The maximum oxidation current for the 50% Ag alloys is around 2.2 A.m^{-2} at 50 mM ATS while this value increased to be about 6 A.m^{-2} at 100 mM ATS. The enhancement of gold oxidation by increasing thiosulfate concentrations has also been observed by Chandra and Jeffrey (2004), Zhang and Nicol (2003) and Breuer and Jeffrey (2002).

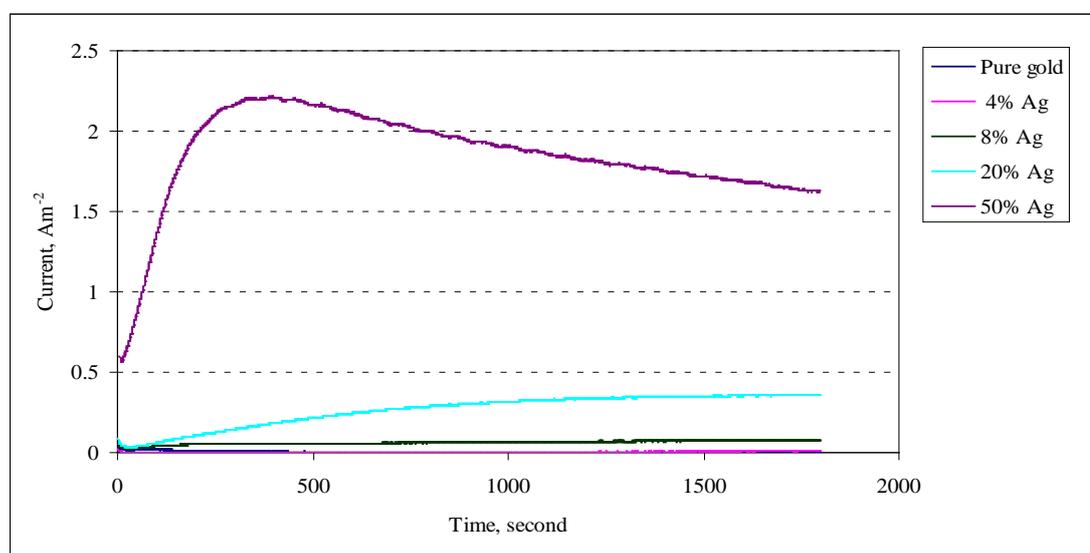


Figure 6.23: The anodic dissolution of gold and silver from pure gold and 4, 8, 20, and 50% Ag alloys in solutions containing ammonium thiosulfate. Experimental conditions: 50 mM ATS, 300 rpm, 30 °C, and natural pH of the solution.

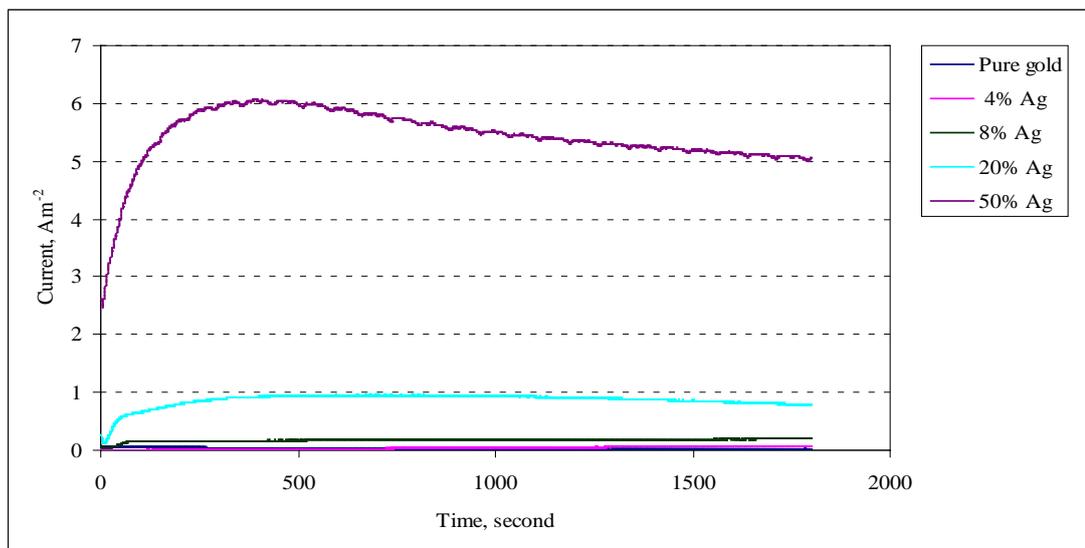


Figure 6.24: The anodic dissolution of gold and silver from pure gold and 4, 8, 20, and 50% Ag alloys in solutions containing ammonium thiosulfate. Experimental conditions: 100 mM ATS, 300 rpm, 30 °C, and natural pH of the solution.

The gold and total metal dissolution rates were calculated from the amount of gold and silver dissolved in the electrochemical cell after 30 minutes of leaching. The rate of gold and total metal dissolution was also calculated from the measured current according to Equation (6.5).

$$Q = \int_{t=0}^{t=30} I dt = NnF \quad (6.5)$$

Where: Q = the electric charge through the cell, Coulombs (Ampere.sec.);

N = number of moles of the analyte, mol;

I = current density, Am^{-2} ;

t = time, sec.;

n = number of moles of the electrons per mole of the analyte ($\text{mol} \cdot \text{mol}^{-1}$);

and

F = Faraday constant ($96485 \text{ Coulombs} \cdot \text{mol}^{-1}$)

The current efficiency was calculated as a ratio between the total dissolution rate (measured) and calculated rate from the charge. When the current efficiency is 100%, all the current can be attributed to gold/silver oxidation. Due to accuracy of gold and silver analysis, the current efficiency sometimes slightly exceeds 100%.

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The rates calculated from the current and the gold/silver dissolution and the corresponding current efficiencies at 50 mM and 100 mM ATS are shown in Table 6.6 and 6.7 respectively.

Table 6.6: The calculated rate from current and the total dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys in solution containing ammonium thiosulfate (ATS). Experimental conditions: 50 mM ATS, 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Rate from current, $10^5 \times \text{mol.m}^{-2}.\text{s}^{-1}$	Dissolution rate, $10^5 \times \text{mol.m}^{-2}.\text{s}^{-1}$	Current efficiency, %
Pure Gold	0.03	0.02	98
4% Ag	0.04	0.04	100
8% Ag	0.09	0.089	99
20% Ag	0.31	0.307	99
50% Ag	2.19	2.14	98

Table 6.7: The calculated rate from current and the total dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys in solution containing ammonium thiosulfate (ATS). Experimental conditions: 100 mM ATS, 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Rate from current, $10^5 \times \text{mol m}^{-2} \text{s}^{-1}$	Dissolution rate, $10^5 \times \text{mol m}^{-2} \text{s}^{-1}$	Current efficiency, %
Pure Gold	0.06	0.06	100
4% Ag	0.07	0.068	98
8% Ag	0.25	0.24	96
20% Ag	1.07	1.06	99
50% Ag	6.25	6.36	102

From the results shown in Tables 6.6 and 6.7, the following observations can be made:

- in solutions containing only thiosulfate, the current efficiencies are close to 100% for all the alloy compositions at different concentrations of thiosulfate. This result indicates that all the measured current is due to the oxidation of gold and silver;
- by increasing thiosulfate concentration, gold and total metal dissolution rate increased for all alloy compositions. The dissolution rate for the 50% silver alloy in 100 mM ATS reaches more than three times the value in 50 mM ATS; and
- as the percentage of silver alloyed with gold increased, gold and total metal dissolution rates increased.

6.3.3.2 Thiosulfate-Ammonia Solution

The effect of ammonia addition to thiosulfate solutions on the oxidation of gold and gold-silver alloys was studied electrochemically by adding 400 mM ammonia to thiosulfate solutions containing 50 mM ATS. Figure 6.25 shows the gold and gold/silver oxidation current from pure gold and gold-silver alloys at a fixed potential of 0.292 V. Comparing the results of Figure 6.25 (in the presence of ammonia) with those in Figure 6.23 (in the absence of ammonia), shows significant enhancement of gold and gold-silver oxidation resulting from ammonia addition into thiosulfate solutions. Because of the de-oxygenation of the solution using pure nitrogen, the only electrochemical reaction that occurs is the oxidation of gold and silver, so the measured current is a true indicator of the gold and silver dissolution rates in solutions containing thiosulfate and ammonia.

Table 6.8 shows the total metal dissolution rate, calculated from the amount of gold and silver dissolved in the electrochemical cell after 30 minutes of leaching and the measured current, in solutions containing thiosulfate and ammonia.

By comparing the data shown in Table 6.8 (in the presence of ammonia and the data in Table 6.6 (absence of ammonia), a significant effect of ammonia addition on gold and total metal dissolution rate can be seen. The total metal dissolution rate increases when a high percentage of silver is alloyed with gold. The increase of the dissolution rate, for example, for the 50% Ag alloy in solutions containing 50 mM ATS and 400 mM ammonia is more than six times the value from solutions containing 50 mM ATS.

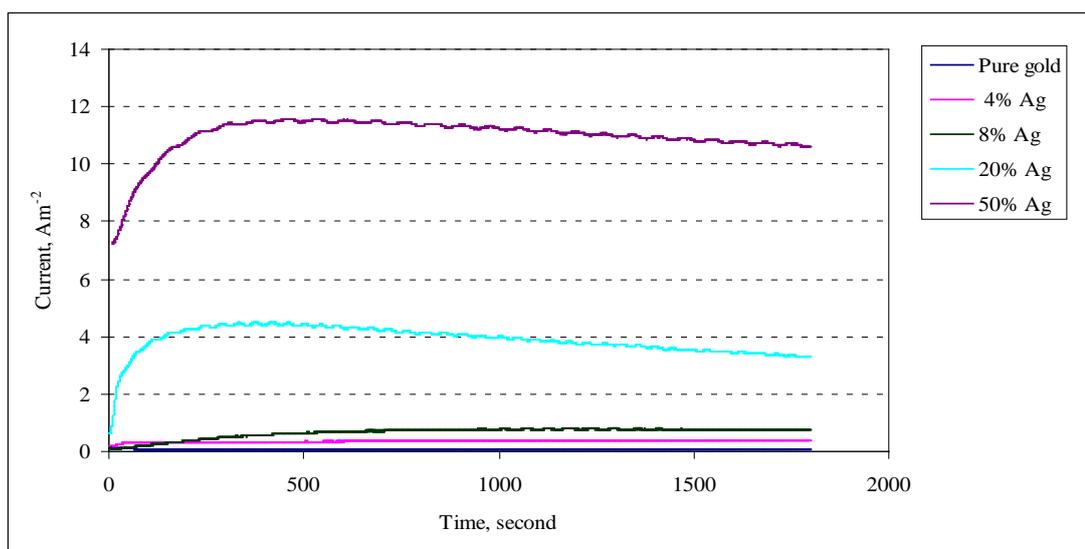


Figure 6.25: The anodic dissolution of gold and silver from a rotating disc of pure gold and 4, 8, 20, and 50% Ag alloys in solutions containing ammonium thiosulfate. Experimental conditions: 50 mM ATS, 400 mM NH₃, 300 rpm, 30 °C, and natural pH of the solution.

Table 6.8: The calculated rate from current and ICP-OES analysis for pure gold and 4, 8, 20, and 50% Ag alloys in solution containing ammonium thiosulfate (ATS). Experimental conditions: 50 mM ATS, 400 mM ammonia, 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Rate from current, Mol m ⁻² s ⁻¹	Dissolution rate, Mol m ⁻² s ⁻¹	Current efficiency, %
Pure Gold	0.06	0.05	95
4% Ag	0.43	0.45	104
8% Ag	0.79	0.82	103
20% Ag	4.61	4.48	97
50% Ag	13.16	12.61	96

6.3.3.3 Thiosulfate-Ammonia-Copper Solution

The current that flowed through the electrochemical cell as a function of time for 30 minutes at a fixed potential of 0.292 V in solutions containing 50 mM ATS, 400 mM ammonia, and 10 mM Cu(II) was measured. These conditions were applied to pure gold and gold-silver alloys with the experimental results shown in Figure

6.26. The measured current is the sum of metal oxidation and reduction of copper(II) tetraammine to a copper(I) thiosulfate complex. The results show that the addition of copper(II) leads to measured oxidation rates greater than those for thiosulfate solution containing only ammonia (Figure 6.25) even though confounded by the presence of copper(II). Figure 6.26 also shows that as a result of increasing the silver content of the alloys, the measured current increases significantly.

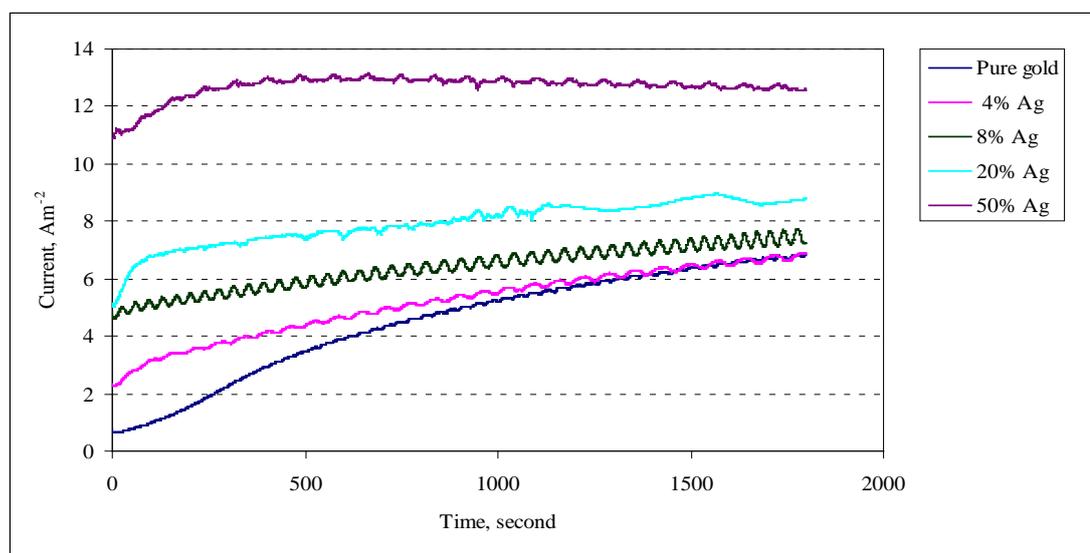


Figure 6.26: The anodic current generated on pure gold and 4, 8, 20, and 50% Ag alloys at a fixed potential of 0.292 V. Experimental conditions: 50 mM ATS, 400 mM NH₃, 10 mM Cu(II), 300 rpm, 30 °C, and natural pH of the solution.

The effect of decreasing ammonia and copper(II) concentration was also studied with the results shown in Figure 6.27. It can be seen that the trends are the same as observed using high reagent concentrations, however, with decreased oxidation currents at low ammonia and copper concentrations.

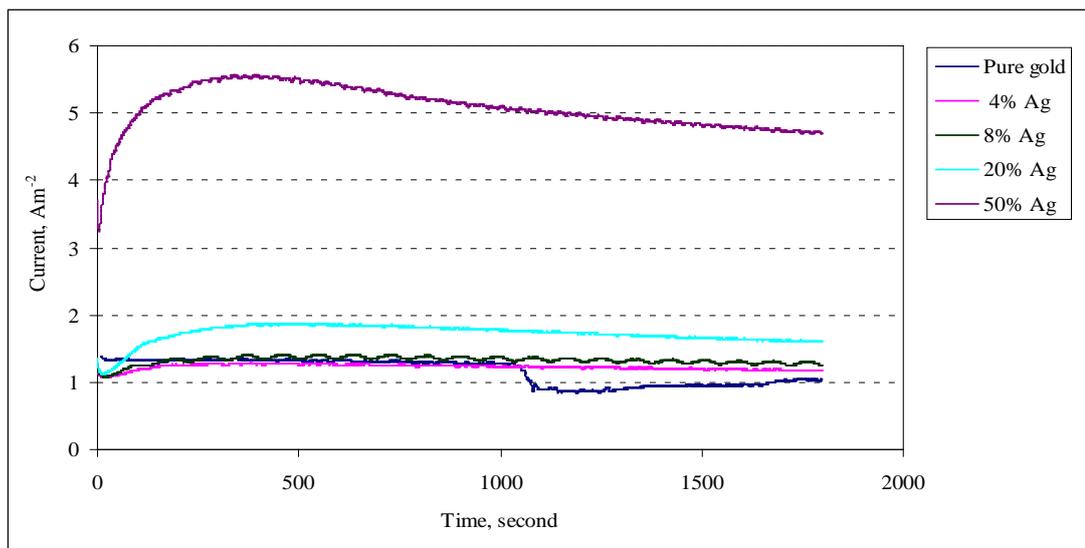


Figure 6.27: The anodic current from pure gold and 4, 8, 20, and 50% Ag alloys at a fixed potential of 0.292 V. Experimental conditions: 50 mM ATS, 100 mM NH₃, 1 mM Cu(II), 300 rpm, 30 °C, and natural pH of the solution.

Figure 6.28 shows the total metal dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys in solutions containing high and low concentrations of ammonia and copper(II). The solution concentrations used in this set of experiments were: Solution A: 50 mM ATS thiosulfate, 400 mM ammonia, and 10 mM copper(II); Solution B: 50 mM STS thiosulfate, 400 mM ammonia, and 10 mM copper(II); Solution C: 50 mM ATS thiosulfate, 100 mM ammonia, and 1 mM copper(II); and Solution D: 50 mM STS thiosulfate, 100 mM ammonia, and 1 mM copper(II).

From the data in Figure 6.28, it can be seen that increasing ammonia and copper concentration leads to higher gold and silver leaching rates from the ICP-OES analysis. Moreover, it is evident that total metal dissolution increased with increasing silver percentages alloyed with gold.

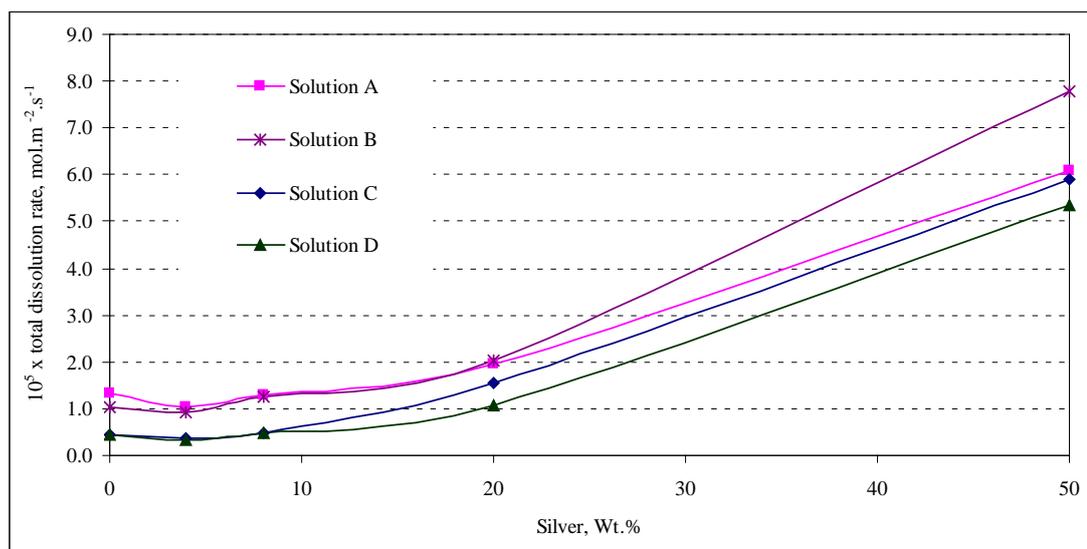


Figure 6.28: The total dissolution rate of gold and silver from pure gold and 4, 8, 20 and 50% Ag alloys at a fixed potential of 0.292 V in solutions containing thiosulfate ammonia-copper(II).

6.3.3.4 Thiosulfate-Thiourea Solution

The effect of thiourea addition to thiosulfate solutions was studied by using coulometric experiments at a fixed potential of 0.292 V on pure gold and gold-silver alloys in solutions containing 50 mM ATS and 5 mM thiourea. The measured anodic current as a function of time is plotted in Figure 6.29. It can be seen that the oxidation current increased with an increase in silver in the alloy. The results demonstrate that after an initial induction period gold oxidation is faster than total metal oxidation for 4, 8, and 20% Ag alloys. A further increase in the silver percentage up to 50% increases the total metal oxidation to a higher value than that of pure gold.

It was also found that in the presence of silver, total metal oxidation was slower in thiosulfate-thiourea solutions than in solutions containing thiosulfate-ammonia-copper(II).

The effect of decreasing thiourea concentration to 1 mM on the oxidation current is shown in Figure 6.30. As the percent of silver increased the oxidation current also increased. From Figure 6.30 it is clear that the measured current increases at the start of the experiment until it reaches a plateau value. It can also be seen that when thiourea concentration was decreased to 1 mM, the gold oxidation

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from pure metal was significantly decreased as compared with that at 5 mM thiourea (Figure 6.29).

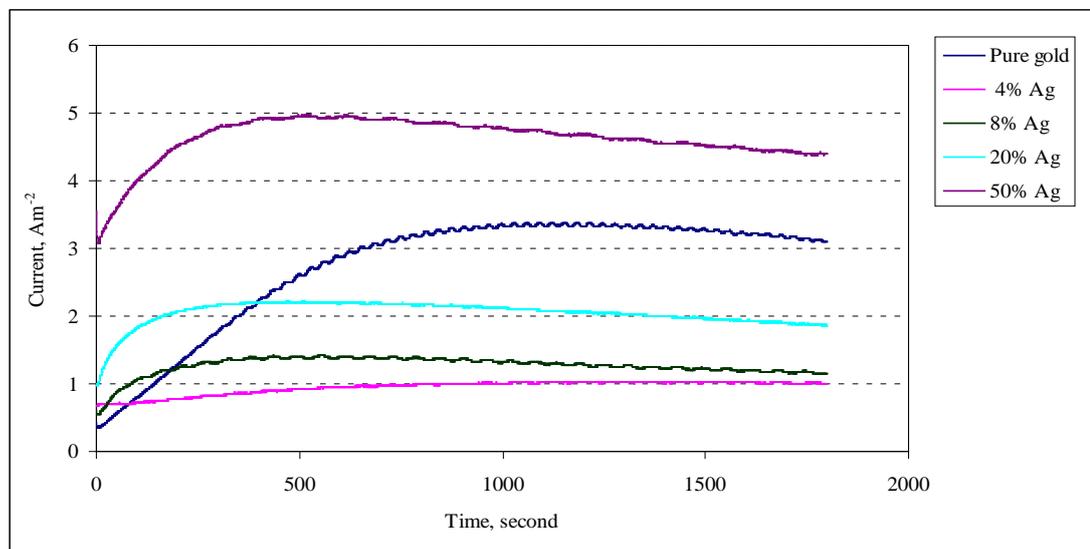


Figure 6.29: The anodic current from pure gold and 4, 8, 20, and 50% Ag discs at a fixed potential of 0.292 V in solutions containing ammonium thiosulfate and thiourea. Experimental conditions: 50 mM ATS, 5 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

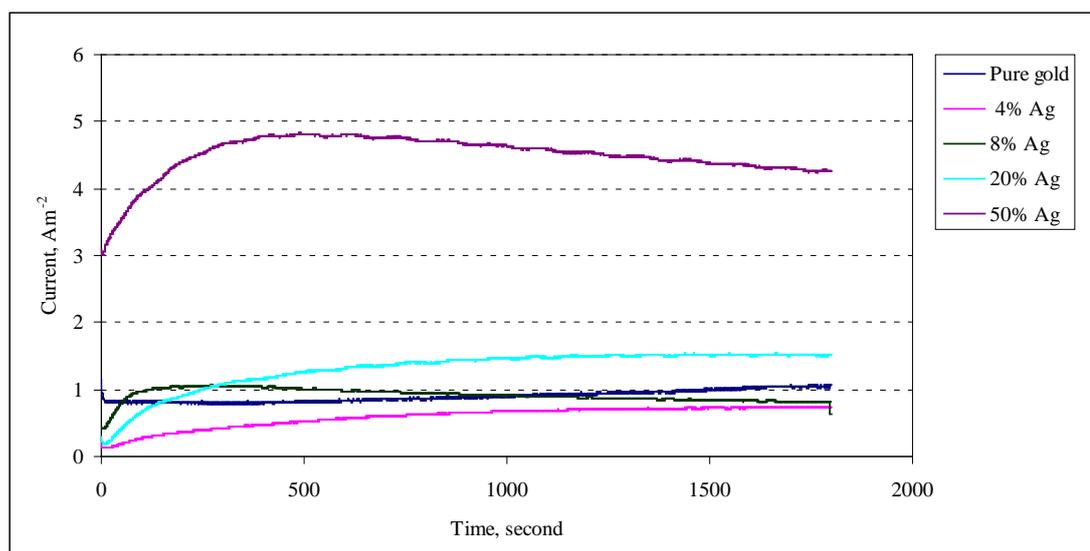


Figure 6.30: The anodic current of from pure gold and 4, 8, 20, and 50% Ag alloys at a fixed potential of 0.292 V in solutions containing ammonium thiosulfate and thiourea. Experimental conditions: 50 mM ATS, 1 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

The gold and total metal dissolution rate from pure gold and gold-silver alloys in solutions containing high and low thiourea concentrations were calculated from ICP-OES analyses of the solution after 30 minutes for a fixed potential of 0.292 V. The rates in the presence of 1 mM and 5 mM thiourea are shown in Tables 6.9 and 6.10 respectively, with the greater thiourea concentration having the higher gold and total metal leaching rate. The gold dissolution rate from pure gold is higher than that from 4 and 8% Ag alloys in solutions containing thiosulfate and a low thiourea concentration. Increasing the thiourea concentration to 5 mM increases the gold dissolution rate from pure gold with only the 50% Ag alloy having a higher rate.

Table 6.9: Calculated rate from current and the total dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys in solution containing thiosulfate-thiourea. Experimental conditions: 50 mM ATS, 1 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Rate from current, $10^5 \times \text{mol.m}^{-2}.\text{s}^{-1}$	Dissolution rate, $10^5 \times \text{mol.m}^{-2}.\text{s}^{-1}$	Current efficiency, %
Pure Gold	1.43	1.41	102
4% Ag	0.59	0.61	97
8% Ag	0.92	0.94	97
20% Ag	1.54	1.58	98
50% Ag	3.87	3.79	102

Table 6.10: The calculated rate from current and the total dissolution rate, from pure gold and 4, 8, 20, and 50% Ag alloys in solution containing thiosulfate-thiourea. Experimental conditions: 50 mM ATS, 5 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

Disc type	Rate from current, mol.m⁻².s⁻¹	Dissolution rate, mol.m⁻².s⁻¹	Current efficiency, %
Pure Gold	2.80	3.06	92
4% Ag	1.25	1.18	106
8% Ag	1.55	1.57	98
20% Ag	2.40	2.54	94
50% Ag	5.23	5.75	91

6.3.3.5 Gold and Total Metal Dissolution Rates at 0.292 V Potential

The gold and total metal dissolution rate from pure gold and gold-silver alloys in thiosulfate solutions was calculated after 30 minutes for a fixed potential of 0.292 V. Figures 6.31 and 6.32 show the calculated gold and total metal (gold and silver) dissolution rates from the ICP-OES analysis respectively as a function of percent silver. From the data in Figure 6.31, the highest gold dissolution rate from pure gold was in thiosulfate solutions containing thiourea. The gold dissolution rate was the slowest in thiosulfate solutions containing only ammonia. The important two points, here, are that (1) at a potential value of a 0.292 V in thiosulfate solutions containing thiourea, the gold-silver alloys dissolve slower than pure gold; (2) gold dissolution rates from gold-silver alloys containing high silver percentages are the highest in thiosulfate solutions containing only ammonia.

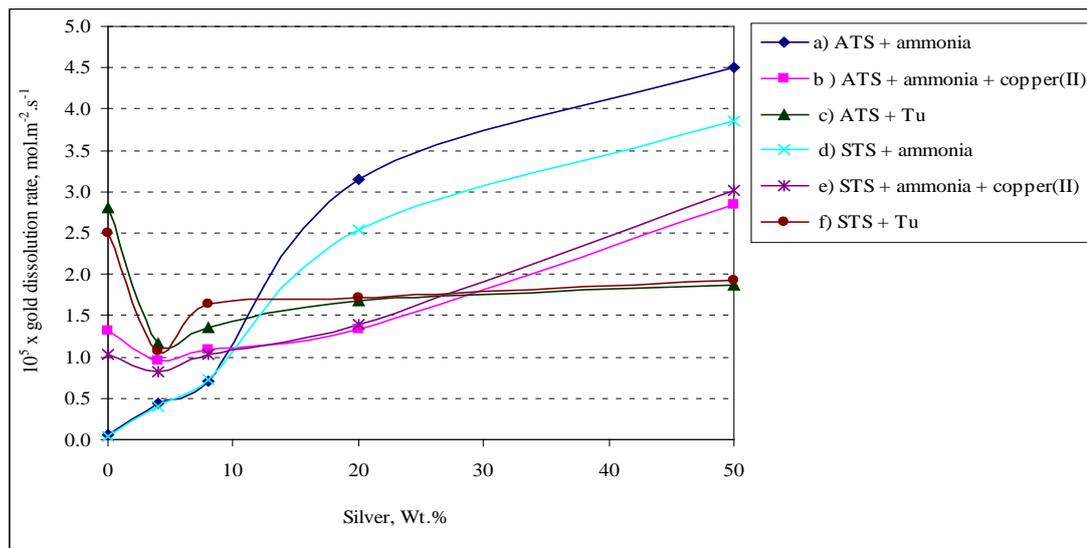


Figure 6.31: Gold dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys in thiosulfate (50 mM ATS or STS) solutions. a) ATS, 400 mM NH₃, b) ATS, 400 mM NH₃, 10 mM Cu(II), c) ATS, 5 mM Tu, d) STS, 400 mM NH₃, e) ATS, 400 mM NH₃, 10 mM Cu(II), f) ATS, 5 mM Tu. 300 rpm, 30 °C.

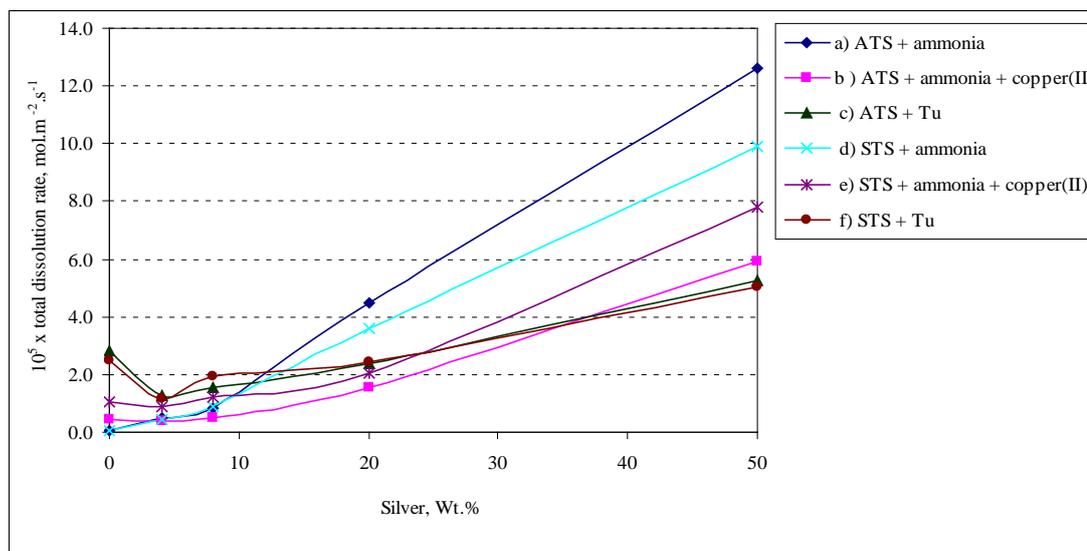


Figure 6.32: Total metal dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys in thiosulfate (50 mM ATS or STS) solutions. a) ATS, 400 mM NH₃, b) ATS, 400 mM NH₃, 10 mM Cu(II), c) ATS, 5 mM Tu, d) STS, 400 mM NH₃, e) ATS, 400 mM NH₃, 10 mM Cu(II), f) ATS, 5 mM Tu. 300 rpm, 30 °C.

6.3.4 Coulometric Experiment at 0.35 V

The effect of different thiosulfate solutions and reagent concentrations were studied to determine the oxidation behaviour of pure gold and gold-silver in thiosulfate solutions by coulometry. Coulometric experiments were conducted at a fixed potential of 0.35 V. The results are shown and discussed in this section.

6.3.4.1 Thiosulfate-Ammonia Solution

The effect of ammonia addition to thiosulfate solution on the oxidation current from pure gold and gold-silver alloys at a fixed potential of 0.35 V was studied (Figure 6.33) electrochemically by adding 400 mM ammonia to thiosulfate solution containing 50 mM ATS. The results demonstrate that the trends are the same as those at potential values of 0.22, 0.256 and 0.292 V however, the oxidation current is higher than those at lower potential values.

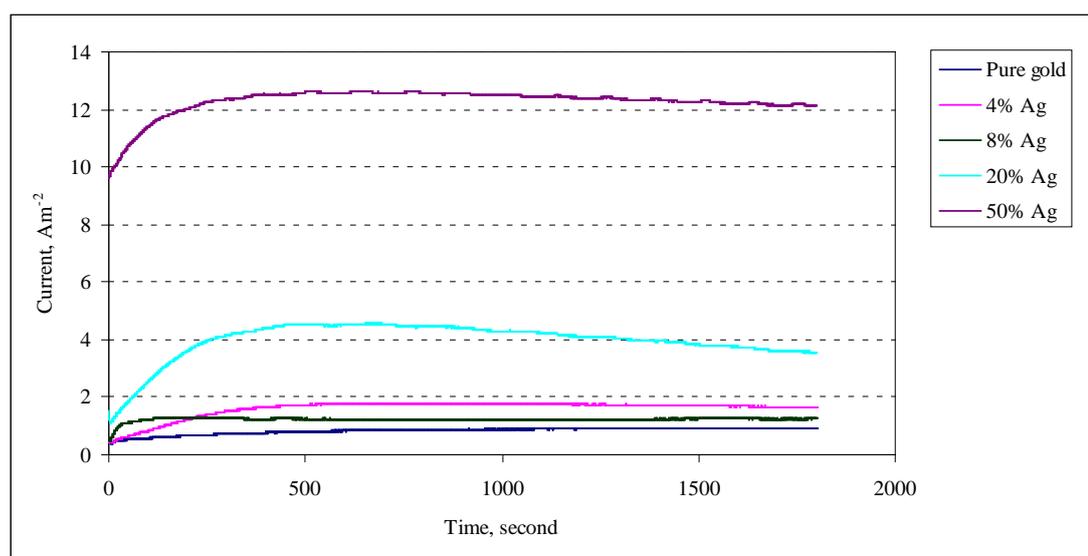


Figure 6.33: The anodic dissolution of gold and silver from pure gold and 4, 8, 20, and 50% Ag alloys in thiosulfate solution containing ammonia. Experimental conditions: 50 mM ATS, 400 mM NH₃, 300 rpm, 30 °C, and natural pH of the solution.

6.3.4.2 Thiosulfate-Ammonia-Copper Solution

The current that flowed through the electrochemical cell for 30 minutes at a fixed potential of 0.35 V in solutions containing 50 mM ATS, 400 mM ammonia, and 10 mM Cu(II) for pure gold and gold-silver alloys was measured. Figure 6.34 shows the gold and gold/silver oxidation current as a function of time in solution

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containing ammonium thiosulfate, ammonia and copper(II). At the beginning of the experiment, for each alloy, the measured current increased quickly but after a short induction period reached a nearly constant value. The oxidation current increased as the percent silver in the alloys increased.

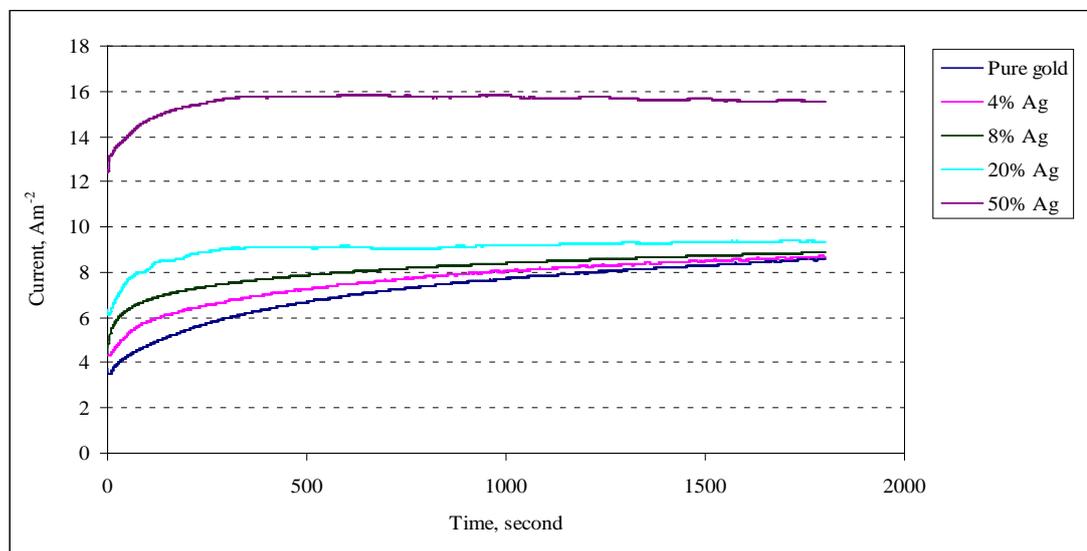


Figure 6.34: The anodic dissolution current of gold and silver from pure gold and 4, 8, 20, and 50% Ag alloys in solution containing thiosulfate-ammonia-copper(II). Experimental conditions: 50 mM ATS, 400 mM NH₃, 10 mM Cu(II), 300 rpm, 30 °C, and natural pH of the solution.

6.3.4.3 Thiosulfate-Thiourea Solution

The effect of thiourea addition to thiosulfate solution on the oxidation current from pure gold and gold-silver alloys was studied by coulometric experiments at a fixed potential of 0.35V in thiosulfate solution containing 50 mM ATS and 5 mM thiourea. Figure 6.35 shows the gold/silver oxidation current as a function of time. The measured current for thiosulfate solution containing only thiourea is representative of the gold/silver oxidation. The data shown in Figure 6.35 demonstrates that the gold oxidation rate from pure gold is higher than the total oxidation rate of gold and silver from the alloys containing 4, 8 and 20% silver.

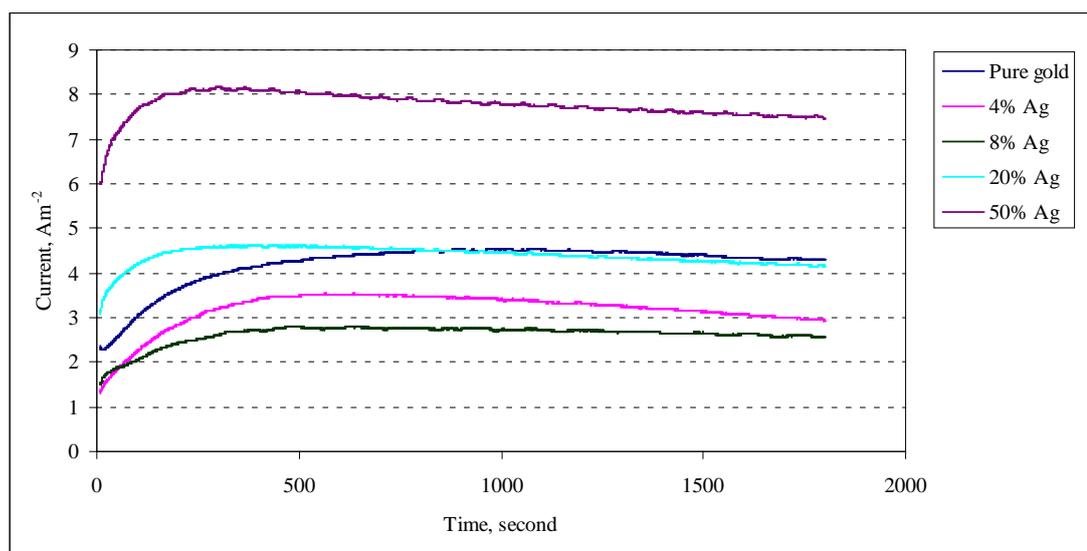


Figure 6.35: The anodic dissolution current of gold and silver from pure gold and 4, 8, 20, and 50% Ag discs in solutions containing thiosulfate and thiourea. Experimental conditions: 50 mM ATS, 5 mM Tu, 300 rpm, 30 °C, and natural pH of the solution.

6.3.4.4 Gold and Total Metal Dissolution Rates at 0.35 V Potential

The gold and total metal dissolution rate from pure gold and gold-silver alloys in thiosulfate solution were calculated from ICP-OES analysis after 30 minutes at a fixed potential 0.35 V. Figures 6.36 and 6.37 show the calculated gold and total metal (gold and silver) dissolution rates respectively as a function of percent silver. The results are consistent with those of the current-time graphs for each solution: 1) in thiosulfate-ammonia solution, gold and total dissolution rate increased as the silver content of the alloy increased :2) the same trend was observed in the thiosulfate-ammonia-copper solution; 3) for solutions containing thiosulfate and thiourea, it was observed that as the percent of silver increased, gold dissolution rate decreased (Figure 6.36).

The gold dissolution rate from the pure gold disc is higher than the total metal dissolution rate from gold-silver alloys up to 20% Ag but, for 50% Ag, the total dissolution rate is higher than the dissolution rate from pure gold (Figure 6.37). This result confirms the results shown in the current-time graph (Figure 6. 35).

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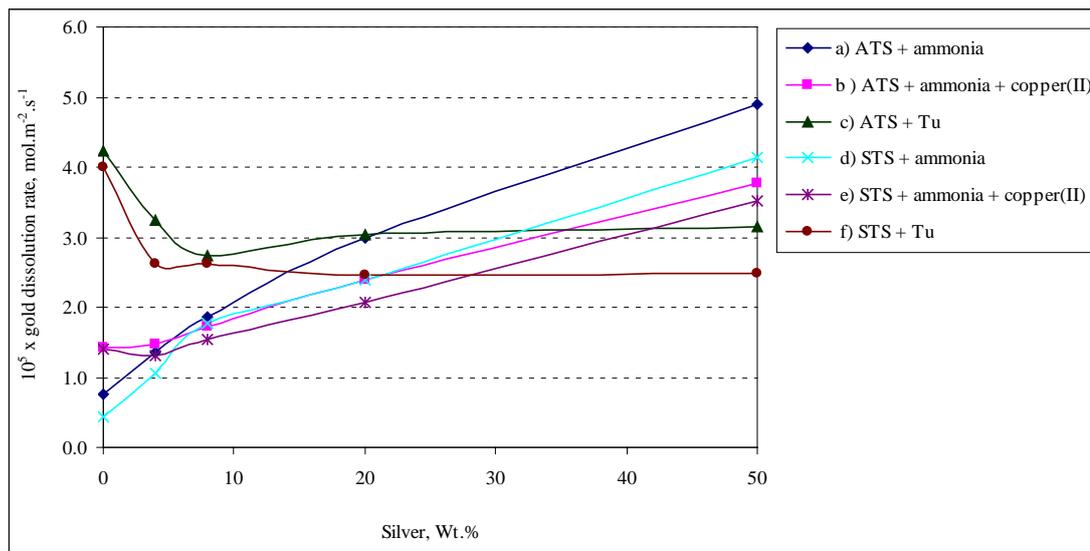


Figure 6.36: Gold dissolution rate from pure gold and 4, 8, 20, and 50% Ag alloys in thiosulfate (50 mM ATS or STS) solutions. a) ATS, 400 mM NH₃, b) ATS, 400 mM NH₃, 10 mM Cu(II), c) ATS, 5 mM Tu, d) STS, 400 mM NH₃, e)ATS, 400 mM NH₃, 10 mM Cu(II), f) ATS, 5 mM Tu. 300 rpm, 30 °C.

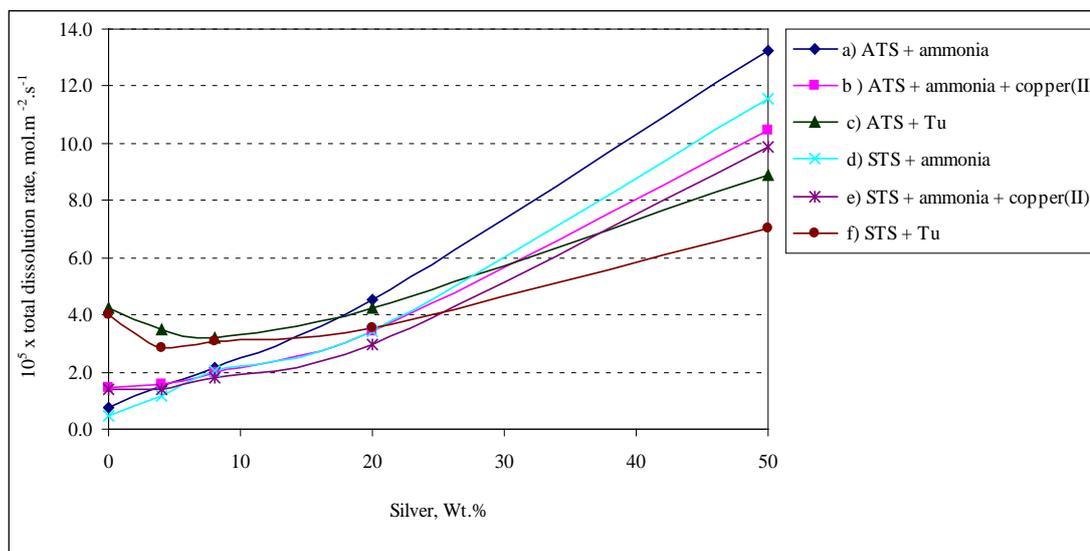


Figure 6.37: Total metal dissolution rate from pure gold and 4, 8, 20, and 50% Ag discs in thiosulfate (50 mM ATS or STS) solutions. a) ATS, 400 mM NH₃, b) ATS, 400 mM NH₃, 10 mM Cu(II), c) ATS, 5 mM Tu, d) STS, 400 mM NH₃, e)ATS, 400 mM NH₃, 10 mM Cu(II), f) ATS, 5 mM Tu. 300 rpm, 30 °C.

6.3.5 Effect of Potential on Gold and Total Dissolution (gold and silver)

Rate

The effect of potential in the range of 0.22-0.35 V on gold and total metal dissolution rate is shown in this section by plotting the dissolution rate of gold and gold silver alloys in different thiosulfate solutions as a function of potential.

- **Pure Gold**

Figure 6.38 shows the gold dissolution rate after 30 minutes of leaching pure gold in different thiosulfate solutions as a function of potential ranging from 0.22-0.35 V. An increase in the gold dissolution rate occurs when the potential is increased. The dissolution rate is increased when copper is added to the thiosulfate-ammonia solution. Moreover, it was found that the gold dissolution rate, when thiourea is present, is slow at low potentials and increases significantly at high potentials.

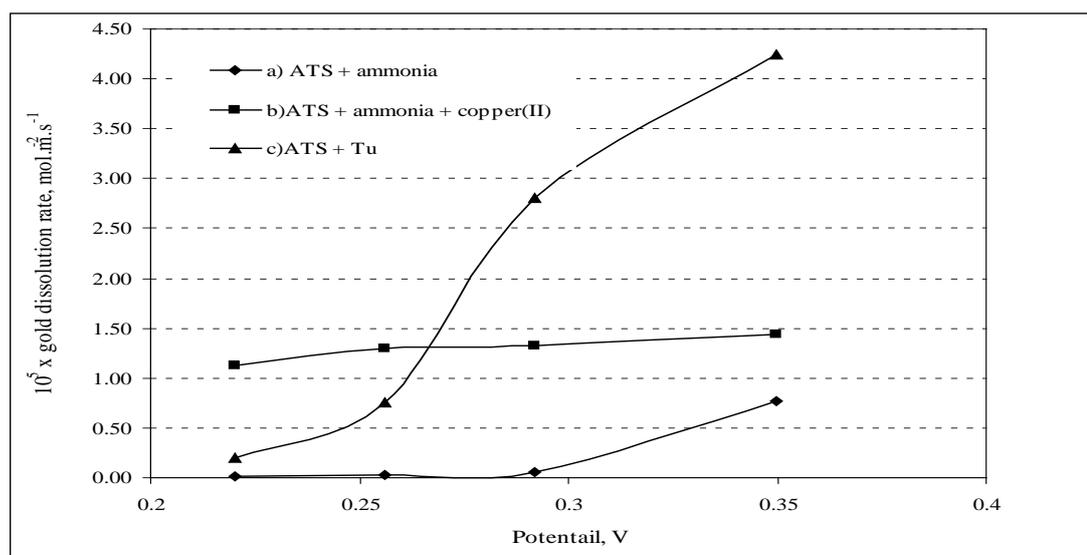


Figure 6.38: Gold dissolution rate measured after 30 min of leaching from pure gold at 300 rpm and 30 °C in thiosulfate solutions containing: a) 50 mM ATS, 400 NH₃; b) 50 mM ATS, 400 mM NH₃, 10 mM Cu(II); c) 50 mM ATS, 5 mM Tu.

- **Gold-Silver Alloys**

Figure 6.39 shows the effect of different thiosulfate solutions on the total metal dissolution rate from gold-silver alloys (4, 8, 20, and 50% silver) after 30 minutes of leaching as a function of potential ranging from 0.22-0.35 V. For all

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solutions the total metal dissolution rate increased as the percent silver in the alloy and the potential increased. A thiosulfate-ammonia-copper(II) solution was found to dissolve gold/silver at a faster rate than either a thiosulfate-ammonia or a thiosulfate-thiourea solution at a potential value of 0.22 V. However, at higher potentials the solution that gives the greatest metal dissolution is dependant on the silver concentration in the gold-silver alloy.

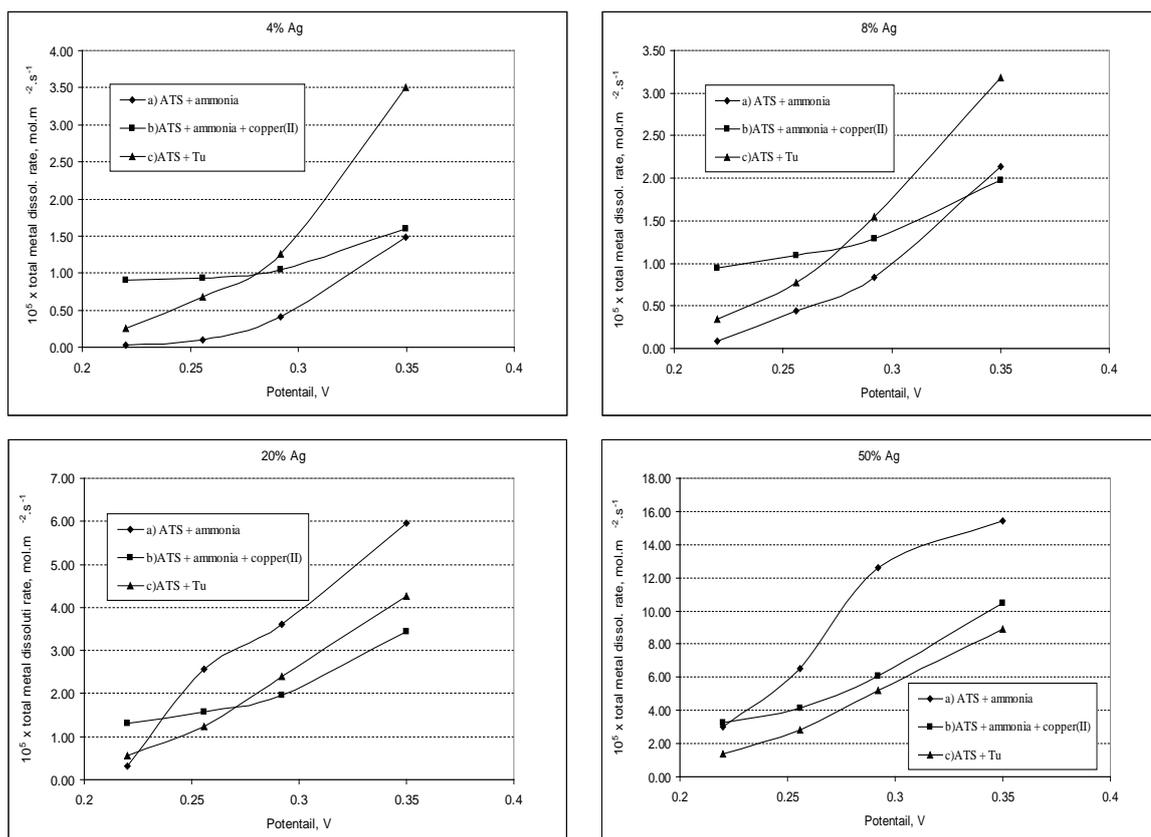


Figure 6.39: Total metal dissolution rate of gold-silver alloys at 300 rpm 30 °C measured over 30 minutes in thiosulfate solutions containing: a) 50 mM ATS, 400 NH₃; b) 50 mM ATS, 400 mM NH₃, 10 mM Cu(II); c) 50 mM ATS, 5 mM Tu.

6.4 Summary

In this chapter, a fundamental electrochemical study on the gold and gold/silver oxidation half reaction in different thiosulfate solutions has been carried out using linear sweep voltammetry and fixed potential coulometric experiments. The electrochemical experiments were conducted using rotating disc electrodes of pure gold (99.99%) and 4, 8, 20, and 50 wt% silver. The effect of potential in a range

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of 0.22–0.35 V on the gold and gold/silver oxidation half reaction was also investigated. It has also been shown that when silver is present as an alloying element with gold, it enhances the gold oxidation half reaction for all gold-silver alloy compositions investigated. This occurs only in thiosulfate-ammonia and thiosulfate-copper-ammonia solutions. For solutions containing thiosulfate and thiourea, it has been found that when up to 50% silver is present as an alloying element the gold dissolution rate at high potentials is slower than that of pure gold.

In addition, it was found that the gold dissolution rate in a thiosulfate-ammonia solution is higher than that in a thiosulfate-ammonia-copper and a thiosulfate-thiourea solution at percentages of silver more than 20%. Linear sweep voltammograms have shown that increasing thiosulfate, ammonia, and copper(II) concentrations has positive effects on the gold/silver oxidation. Moreover, it was observed that thiourea addition to thiosulfate solutions enhances the gold oxidation rate and in the presence of thiourea gold oxidises from pure gold more rapidly than gold-silver alloys.

Gold dissolution rates increased as the silver percentage increased in thiosulfate-ammonia solutions at all potential values. At high potentials and silver content it has been observed that the gold dissolution rate in thiosulfate solutions containing only ammonia is higher than in solutions containing thiosulfate-copper-ammonia and thiosulfate-thiourea.

Chapter 7 Thiosulfate leaching of gold ore in a closed vessel

7.1 Introduction

In this chapter, the application of sodium thiosulfate leaching on selected gold ore samples in a closed vessel has been studied and evaluated. The samples used in all the experiments were provided from the Sukari Gold Mine, Eastern Desert, Egypt by the Centamin Egypt Limited Company.

The main aims of the chapter are: (1) to investigate the effects of various reagent concentrations and parameter conditions on gold extraction and thiosulfate consumption in a closed vessel on a laboratory scale; (2) to compare gold ore leaching in a closed vessel to an open vessel; and in thiosulfate and cyanide solutions using the resulting optimum parameters from the first aim.

The effects of sodium thiosulfate, ammonia, and copper(II) concentration, temperature, solid-liquid ratio, and the particle size fraction of the ore sample on gold extraction and thiosulfate consumption were investigated. Primarily, the leaching of ore samples in open and closed vessels was conducted based on selected initial standard conditions of 0.2 M sodium thiosulfate, 10 mM copper(II), 0.4 M ammonia, 30 °C, 300 rpm, 20% solid-liquid (S/L) ratio; and minus 106 μm ore size. The gold ore was classified into weathered and unweathered gold samples which were ground to 100% minus 106 μm . A second portion of the weathered ore was sieved into different size fractions. Table 7.1 shows the reagent concentrations and parameters used in this section.

Table 7.1: Reagent concentrations and parameters used in the gold ore leaching experiments.

Parameter	The concentrations and values used
Sodium thiosulfate, M	0.1, 0.2, 0.3, and 0.4
Ammonia, M	0.2, 0.4, 0.6, and 0.8
Copper(II), mM	2.5, 5, 10, and 20
Temperature, °C	25, 30, 40, and 50
Rotation speed, rpm	200, 300, 400, and 500
Solid-liquid ratio, %	20, 30, 40, and 50
Particle size fraction, μm	-125+106, -106+75, -75+38, -38

Figure 7.1 illustrates the procedure undertaken on the weathered ore to achieve the objectives of this section.

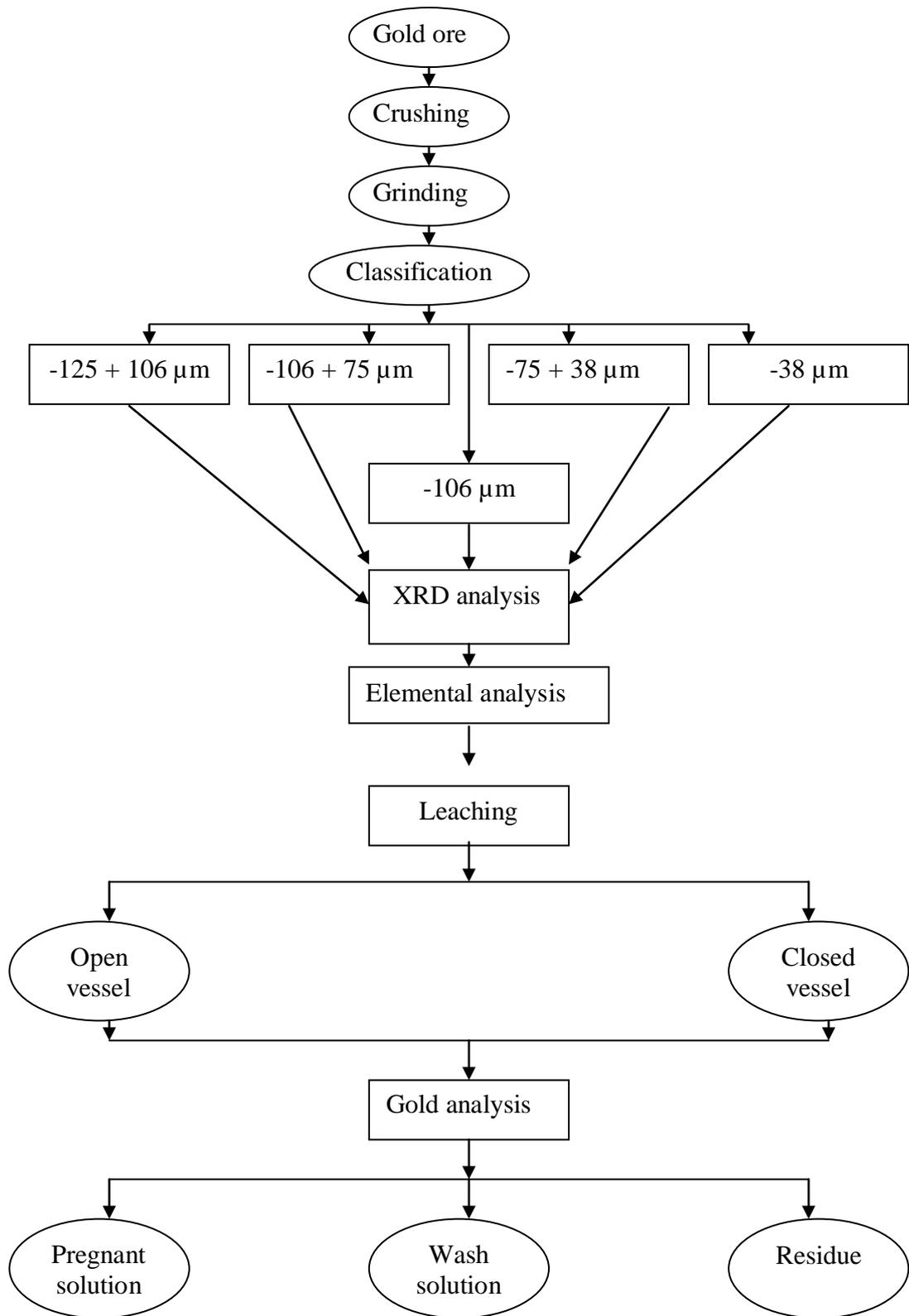


Figure 7.1: The procedure of gold ore leaching experiments.

7.2 Quantitative XRD Analysis

According to the experimental procedure shown in Chapter 4, the gold ore was classified into weathered and unweathered ore samples. A sample of the weathered ore was crushed, milled, and sieved into four size fractions of -38, -75+38, -106+75, and -125+106 μm . The rest of the weathered sample and the entire unweathered ore sample were crushed, milled, and sieved at 106 microns to produce a -106 micron fraction. Quantitative X-Ray Diffraction (XRD) was used to determine the mineralogy for the size fractions and the -106 micron samples for both weathered and unweathered ore.

Figure 7.2 shows the distribution of minerals found in each size fraction which indicates that albite, quartz, and muscovite are the dominant minerals in all size fractions. The highest mass percent of albite (63.4%) was found in the unweathered sample of size -106 μm and the lowest percent of muscovite (3.5%).

7.3 Elemental Analysis

The elemental analysis for each size fraction was performed by Ultra-trace Laboratories located in Perth, Western Australia. A list of the main elements analysed is shown in Figure 7.3. The elemental analysis was carried out by the digestion of the ore samples followed by ICP-OES determination. From the data shown in Figure 7.3, it can be seen that silicon is the most abundant element and aluminium, iron, and sodium are found as minor constituents in all the size fractions. It can also be seen that there is no difference between the weathered and unweathered samples according in the constituents of these abundant elements.

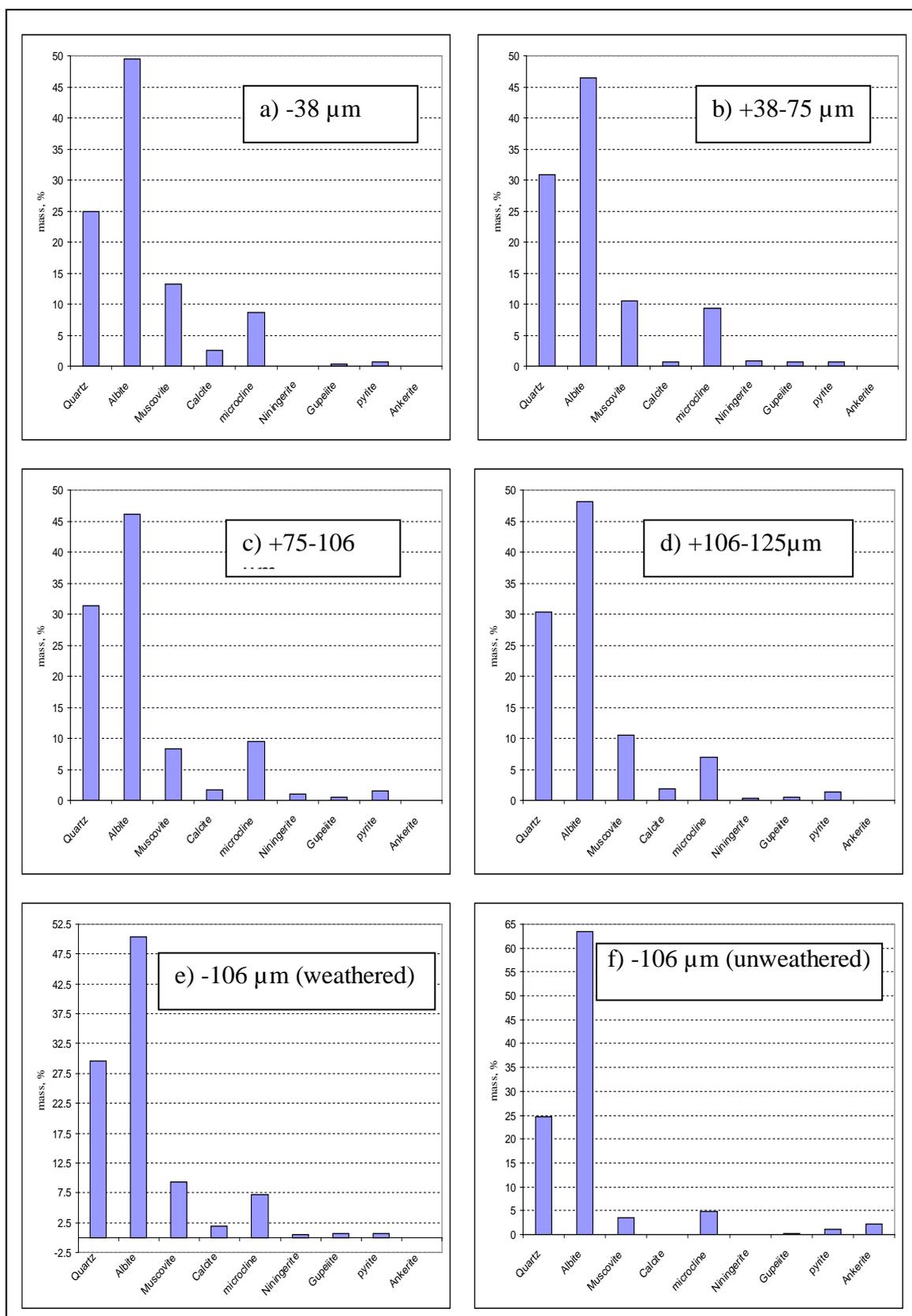


Figure 7.2: Quantitative XRD analysis of mineralogy of different size fractions of gold ore samples.

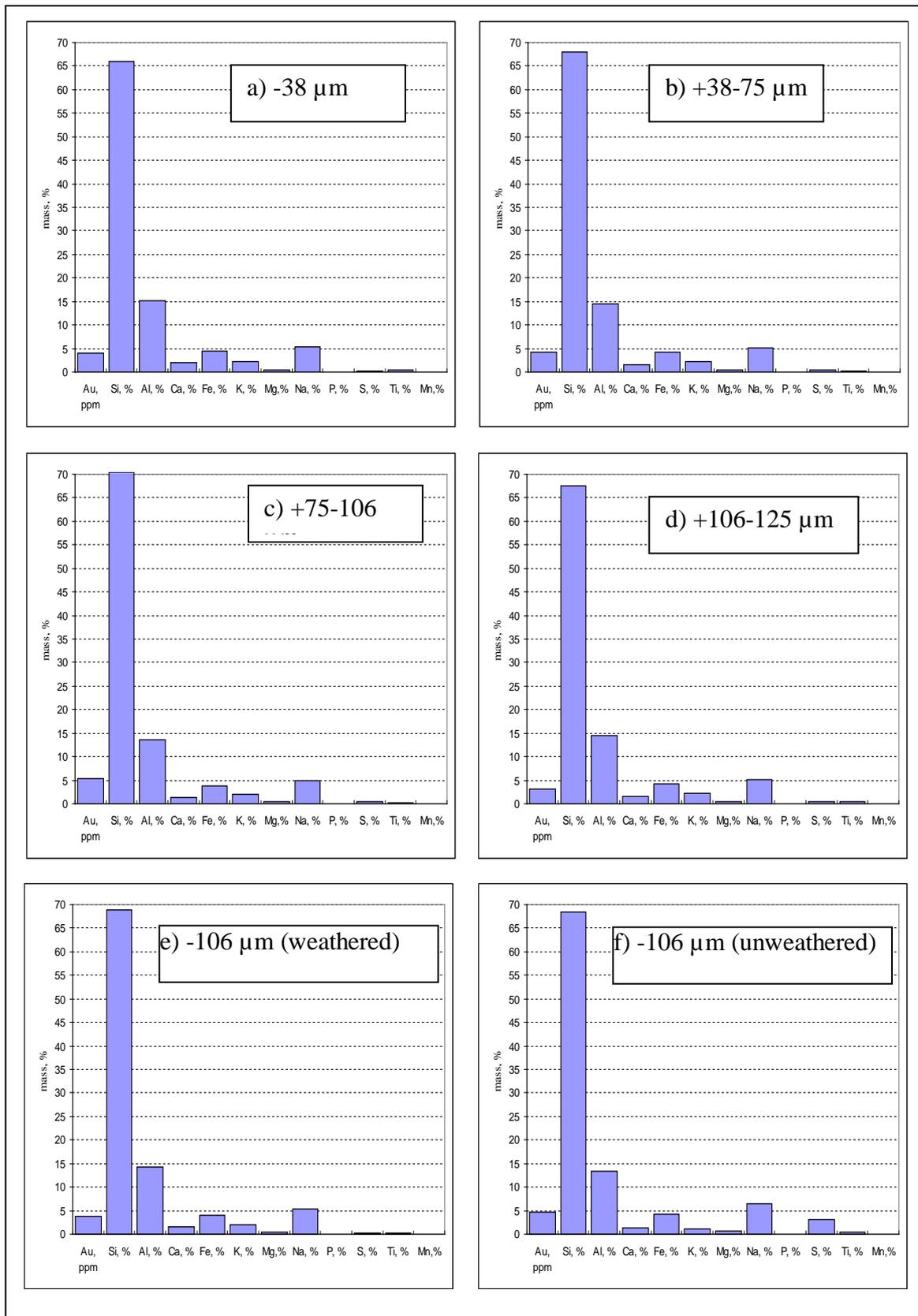


Figure 7.3: Elemental analysis of different size fractions of gold ore samples.

7.4 Ore Sample Leaching (standard conditions)

The suitability of weathered Sukari Gold Mine ore for thiosulfate leaching was determined first under standard conditions (section 7.4). Once the suitability was established then reagent concentrations and leaching parameters were optimised (section 7.5). The suitability of the weathered ore ground passing 106 μm for thiosulfate leaching was found by determining gold extraction and thiosulfate consumption in both open and closed vessels. To examine thiosulfate leaching of ore, individual size fractions of the weathered ore (Table 7.1) was subjected to leaching under standard conditions in a closed vessel.

The leaching of gold ore samples was conducted using 100 g of the ground ore (-106 μm weathered) put into a 1L glass vessel described in the experimental setup shown in Figure 4.4 (Chapter 4). A 400 mL solution containing 0.2 M sodium thiosulfate, 10 mM Cu(II), and 0.4 M ammonia was used and ore added to give a solid/liquid ratio to 20% (100 g ore and 400 mL solution). The temperature and rotation speed were adjusted to 30 °C and 300 rpm respectively. Unless specified, the leaching experiment had a duration of 24 hours.

7.4.1 Gold Extraction using Open and Closed Vessels

Using the initial standard leaching condition as specified in section (7.4), gold ore leaching experiments in open and closed vessels were conducted by the method and procedure described in Chapter 4. Figure 7.4 shows the amount of gold extracted from both open and closed vessels. It is clear that there is a slight increase of gold extraction from the closed compared to the open vessel during the first 3 hours of leaching. After 24 hours, gold extraction from the closed vessel is higher than the open vessel by nearly 5.8%. This result may be explained by increased copper(II) reduction due to ammonia losses from the open vessel as demonstrated by ammonia analyses in sections 5.2.1.2 and 5.3.1.2 (Chapter 5). This explanation is consistent with Breuer (2002) who noted the importance of maintaining sufficient ammonia in thiosulfate solutions to minimise the rate of copper reduction, consequently maximising gold extraction.

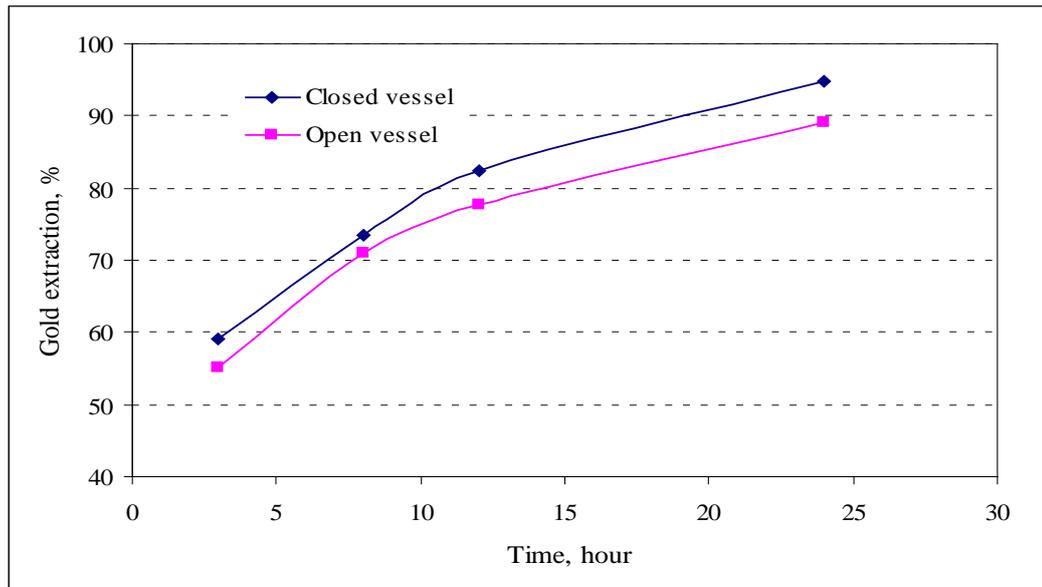


Figure 7.4: Gold extraction using open and closed vessels. Experimental initial conditions: 0.2 M $(S_2O_3)^{2-}$, 0.4 M NH_3 , 10 mM Cu(II), 30 °C, 300 rpm, 20% S/L ratio.

7.4.2 Thiosulfate Consumption in Open and Closed Vessels

Figure 7.5 shows the effect of ambient air and hence oxygen on the amount of thiosulfate consumed in open and closed vessels. The data in Figure 7.5 indicates that there is a slight difference between the amount of thiosulfate consumed in an open vessel compared to a closed vessel. This result is similar with what has been shown in gold disc leaching experiments (Chapter 5). The relatively high consumption of thiosulfate in the open vessel is due to thiosulfate oxidation by oxygen from the ambient air.

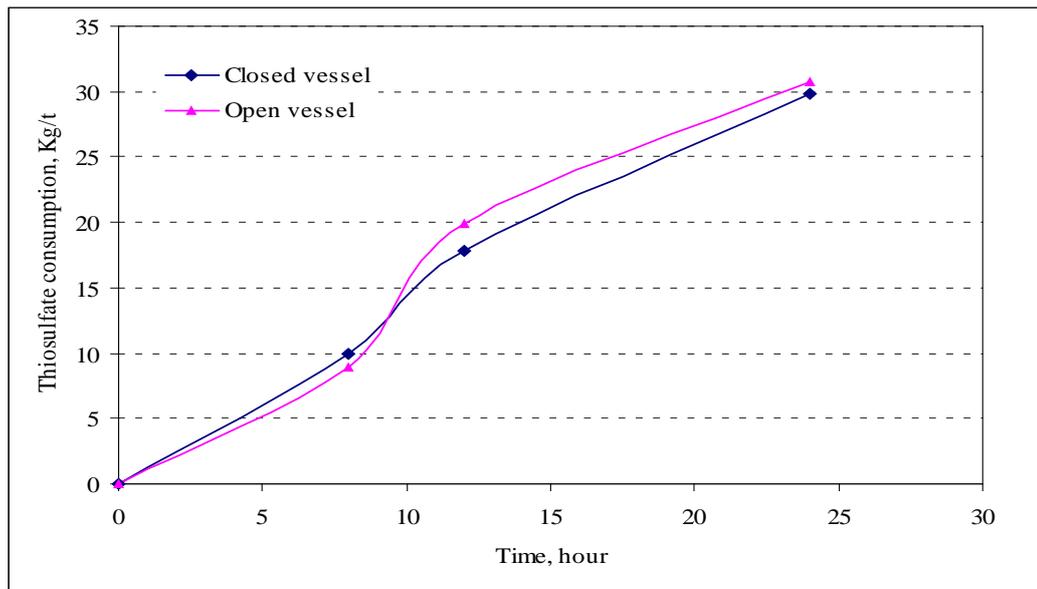


Figure 7.5: Thiosulfate consumption in closed and open vessels. Experimental initial conditions: 0.2 M $(S_2O_3)^{2-}$, 0.4 M NH_3 , 10 mM Cu(II), 30 °C, 300 rpm, 20% S/L ratio.

7.4.3 Gold Extraction from Screen Size Fractions

The weathered ore sample was used to evaluate how different screen size fractions responded with regard to gold extraction. About one kilogram of the ground ore sample was split into four size fractions (-38, -75+38, -106+75, -125+106 μm). The gold extraction results for these fractions are presented in Figure 7.6. The finer fractions had higher gold extraction while the course size fraction had the lowest gold recovery after 24 hours of leaching (Figure 7.6). This is a usual trend for gold ores, with the only link that can established between gold recovery and the mineralogy and chemical analysis being that the largest size fraction had the most silica in the ore and may have had more gold locked in silica particles and not accessible to the leaching reagent. The upward trend of the recovery versus time curves indicates that leaching was not complete for any size fraction and reagent concentrations and leach parameters need to be optimised to achieve maximum gold recovery within 24 hours.

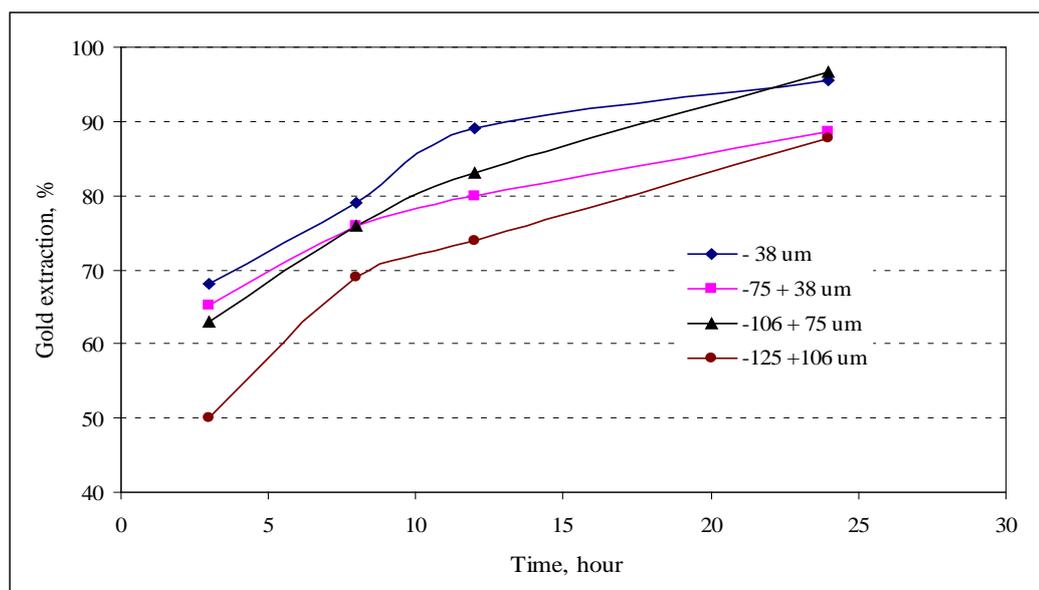


Figure 7.6: The effect of particle size fraction on gold extraction using a closed vessel. Experimental initial conditions: 0.2 M $(S_2O_3)^{2-}$, 0.4 M NH_3 , 10 mM Cu(II), 30 °C, 300 rpm, 20% S/L ratio.

7.5 Effect of Reagent Concentration and Leaching Parameters

In order to optimise and evaluate the effect of various leaching reagents and parameters on gold extraction and thiosulfate consumption, the weathered ore ground to -106 μm was used in a series of tests. One of the reagents or parameters was varied while all the others were kept constant at the initial standard conditions of 0.2 M $(S_2O_3)^{2-}$, 0.4 M NH_3 , 10 mM Cu(II), 30 °C, 300 rpm, 20% solid/liquid (S/L) ratio and natural pH of the solution (pH 11.4).

7.5.1 Effects of Thiosulfate Concentration on Gold Extraction

The effect of sodium thiosulfate concentration ranging from 0.1 to 0.4 M on gold extraction was studied as shown in Figure 7.7. With an increase of thiosulfate initial concentration from 0.1 M to 0.4 M, gold extraction increased from 74.5% to 96% after 24 hours of leaching. Initial gold extraction over the first three hours was fast but then slowed. The final recovery after 24 hours for 0.2 to 0.4 M thiosulfate was approximately the same, but much less for 0.1 M thiosulfate.

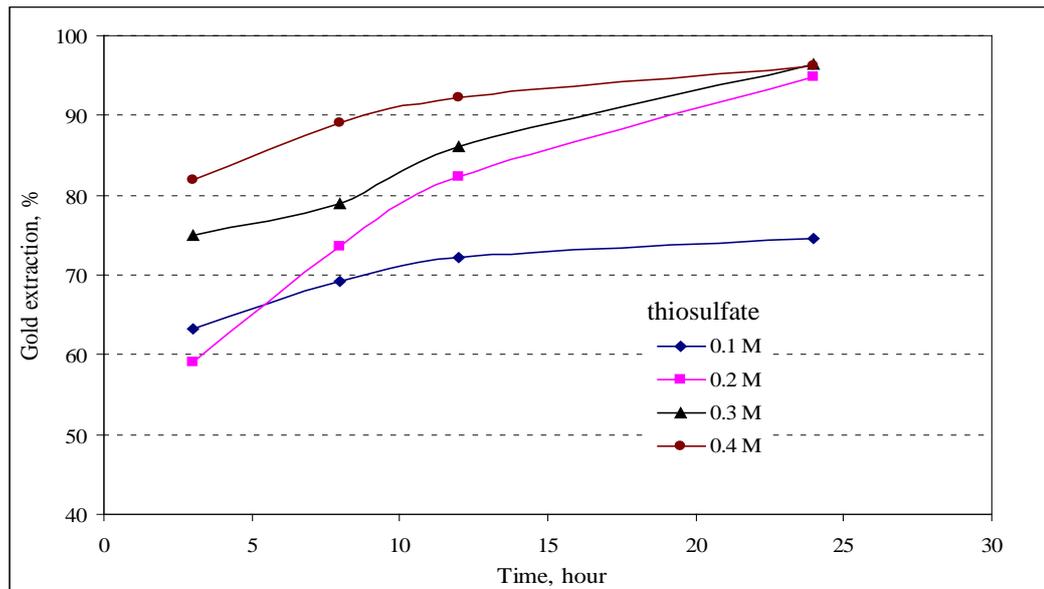


Figure 7.7: The effect of thiosulfate concentration on gold extraction. Experimental initial conditions: 0.4 M NH_3 , 10 mM Cu(II), 30 °C, 300 rpm, 20% S/L ratio.

7.5.2 Effect of Thiosulfate Concentration on Thiosulfate Consumption

Figure 7.8 shows the effects of initial thiosulfate concentration on thiosulfate consumption (kg/t-ore) after 24 hours of leaching for the experiments described in section 7.5.1. It can be seen that the initial thiosulfate concentration has an insignificant effect on thiosulfate consumption with consumption ranging from about 28 to 31 kg/t, consistent with results of Arima (2003).

As high thiosulfate concentration increases the extraction rate of gold but does not increase consumption, the possibility of using high concentration of thiosulfate and recovering and reusing the excess is available.

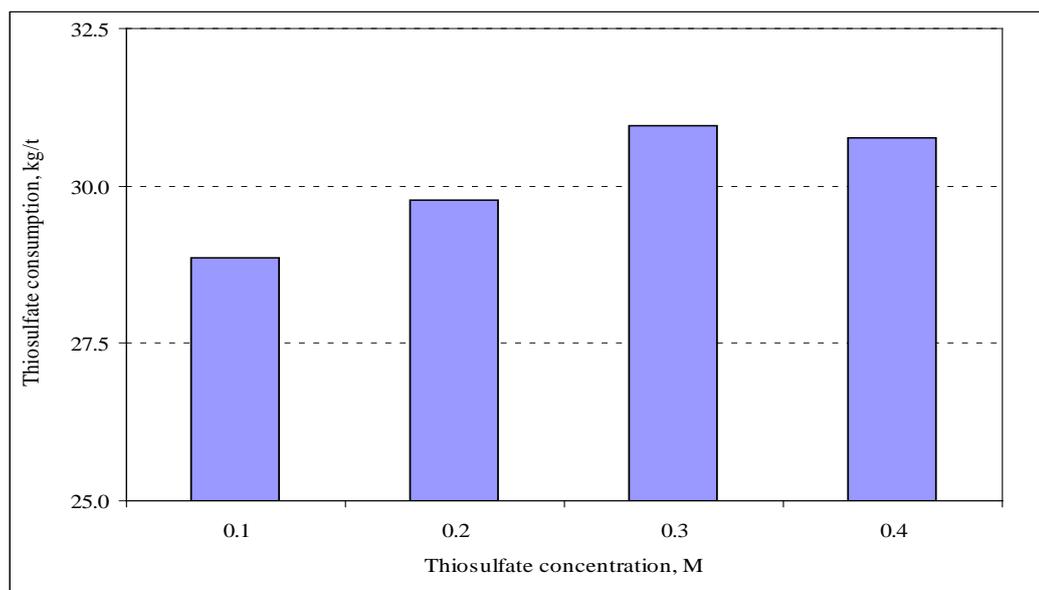


Figure 7.8: The effect of initial sodium thiosulfate concentration on its consumption. Experimental initial conditions: 0.4 M NH₃, 10 mM Cu(II), 30 °C, 300 rpm, 20% S/L ratio.

7.5.3 Effect of Copper Concentration on Gold Extraction

Copper(II) has been shown (Arima, 2003; Breuer & Jeffrey, 2003a,b; Wan & LeVier, 2003; Breuer & Jeffrey, 2000) to be essential in thiosulfate leaching solutions as an oxidising agent. In this section, the influence of copper(II) concentration on gold extraction was studied and evaluated in the range of 2.5 – 20 mM Cu(II). Figure 7.9 shows that gold extraction is enhanced from 85% to 96% after 24 hours of leaching by increasing copper concentration from 2.5 mM to 20 mM. From the 3 hour leaching extraction in Figure 7.9, copper(II) concentration has a significant effect on the initial gold extraction rate.

After 24 hours, the effect of increasing copper(II) concentration on gold extraction is not as pronounced due to high copper(II) concentration experiments approaching maximum gold extraction. A portion of the decrease in extraction rate may be due to an increase in the copper catalysed thiosulfate oxidation to tetrathionate as shown in Equation 7.1.



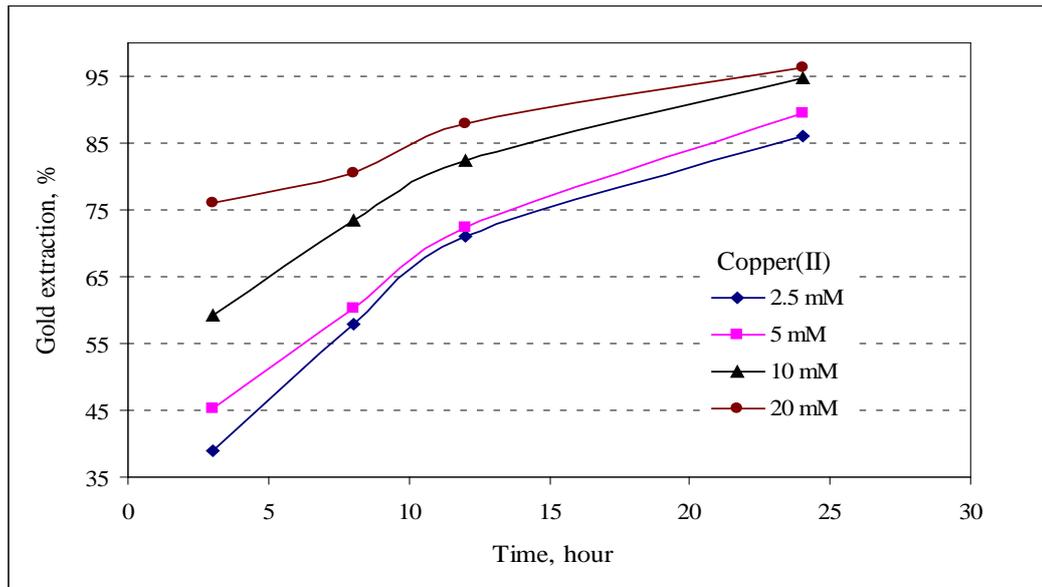


Figure 7.9: The effect of initial copper(II) concentration on gold extraction. Experimental initial conditions: 0.2 M $(S_2O_3)^{2-}$, 0.4 M NH_3 , 30 °C, 300 rpm, 20% S/L ratio.

7.5.4 Effect of Copper Concentration on Thiosulfate Consumption

Figure 7.10 shows that an increase in copper(II) concentration has a detrimental effect on thiosulfate consumption as, by increasing the concentration of copper(II) from 2.5 mM to 20 mM, thiosulfate consumption increased from 22.5 to 44.6 kg/t-ore. Thiosulfate was reduced by copper(II) as shown in the simplified overall reaction in Equation 7.2 (Byerley et al., 1973a).



Other researchers (Zhang & Dreisinger, 2002; Byerley et al., 1975; Byerley et al., 1973b) have also reported that copper has a considerable affect on the stability of thiosulfate in solution due to copper-catalyzed thiosulfate oxidation and the formation of copper sulfides or hydroxides, depending on the leaching conditions.

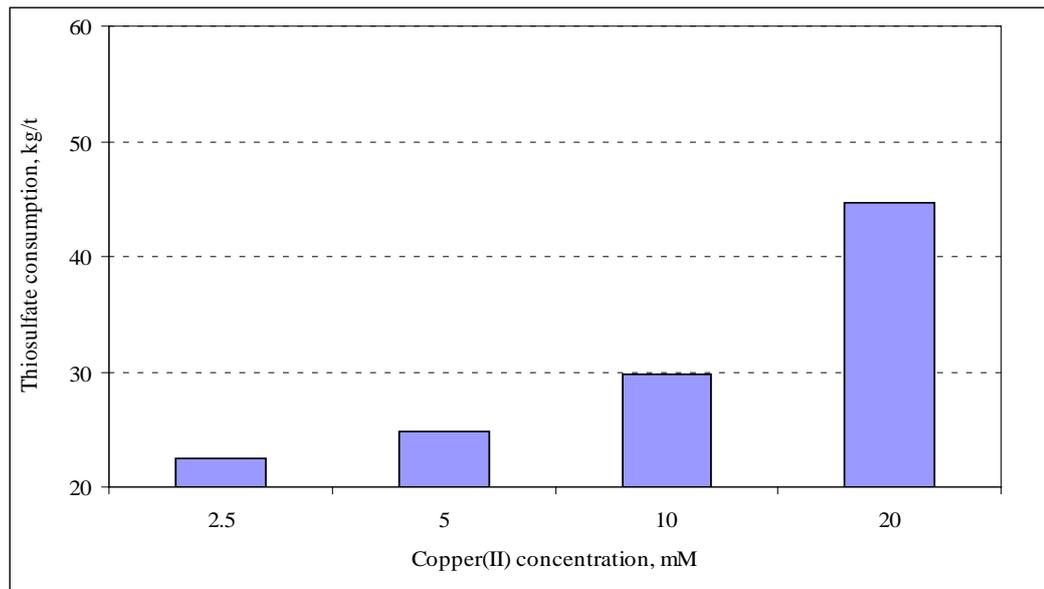


Figure 7.10: The effect of initial copper(II) concentration on thiosulfate consumption. Experimental initial conditions: 0.2 M $(S_2O_3)^{2-}$, 0.4 M NH_3 , 30 °C, 300 rpm, 20% S/L ratio.

7.5.5 Effect of Ammonia Concentration on Gold Extraction

Ammonia is required in thiosulfate solutions in order to stabilize the copper(II) ion as a cupric tetra amine complex, $[(Cu(NH_3)_4]^{2+}$ hence, minimising the decomposition of thiosulfate by its reduction to tetrathionate, as indicated in Equation 7.1.

Figure 7.11 shows the effect of ammonia concentration on gold extraction. In the absence of ammonia only 11.5% of gold can be dissolved in 24 hours but, with a concentration of 400 mM ammonia gold extraction increased to 96%, however, by increasing the concentration of ammonia to 800 mM, gold extraction decreased. This result might be attributed to higher pH values at high ammonia concentration and thus, the reduced thermodynamic stability of $Cu(S_2O_3)_2^{5-}$ and $Cu(NH_3)_4^{2+}$ with increased stability of solid copper species such as CuO and Cu_2O resulting in lower gold extraction (Arslan et al., 2008; Abbruzzese et al., 1995).

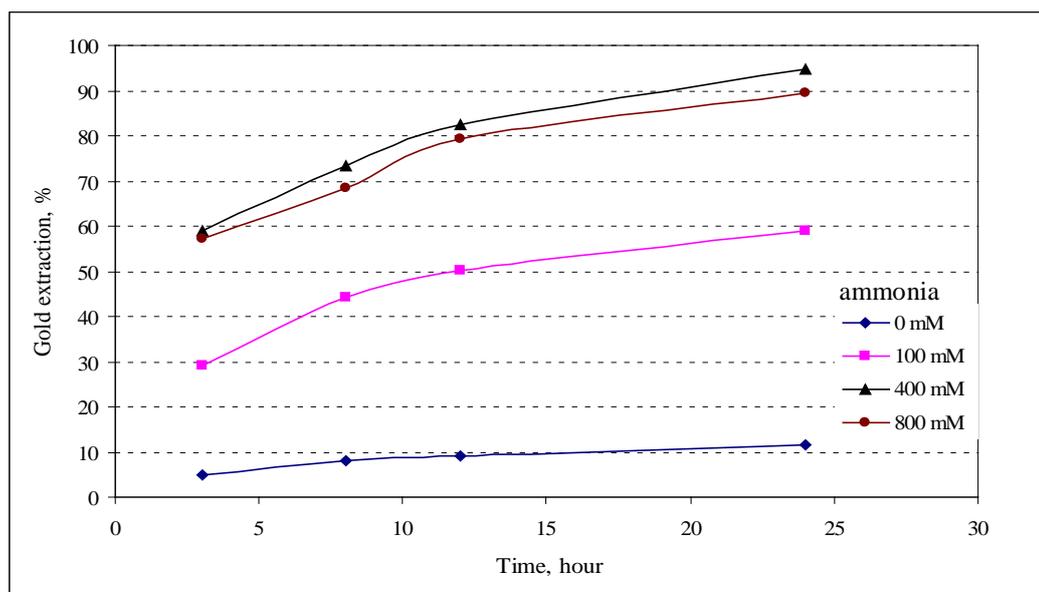


Figure 7.11: The effect of initial ammonia concentration on gold extraction. Experimental initial conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM Cu(II), 30 °C, 300 rpm, 20% S/L ratio.

7.5.6 Effect of Ammonia Concentration on Thiosulfate Consumption

Figure 7.12 shows the effect of ammonia concentration on thiosulfate consumption. In the absence of ammonia, the copper(II) ion is free in solution to react with thiosulfate consuming 70% of the initial 0.2 M thiosulfate. As the concentration of ammonia increases the increased stability of copper as the copper amine species leads to reduced thiosulfate consumption.

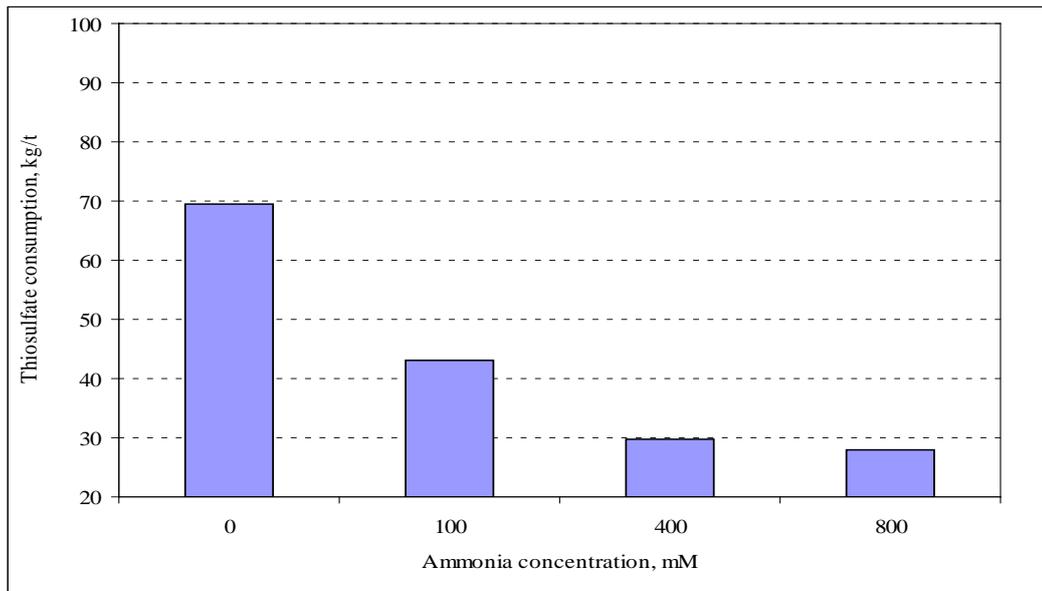
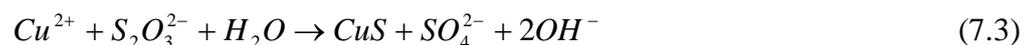


Figure 7.12: The effect of initial ammonia concentration on thiosulfate consumption. Experimental initial conditions: 0.2 M $(S_2O_3)^{2-}$, 10 mM Cu(II), 30 °C, 300 rpm, 20% S/L ratio.

7.5.7 Effect of Temperature on Gold Extraction

Temperature is one of the most important factors in thiosulfate leaching of gold as the gold oxidation rate, copper(II) reduction, thiosulfate oxidation, and the stability of ammonia in the solution depend on temperature. The effect of temperature ranging from 25 to 50 °C on gold extraction is shown in Figure 7.13. After an initial 3 hours of leaching gold extraction can be seen to increase with increasing temperature. However, the initial fast leaching rate at 50 °C declines and after 24 hours of leaching, the amount of gold extracted at 50 °C is the lowest.

The decrease in leaching rate over time at high temperatures (above 40 °C) can be attributed to two mechanisms. Passivation of the gold surface is proposed due to the formation of cupric sulfide as described in the unbalanced equation of Arslan et al., (2008) and Abbruzzese et al. (1995) (Equation 7.3) but the mechanism is likely to be more complicated than this reaction.



The second mechanism is that an increase in the reduction of copper(II) to copper(I) and the oxidation of thiosulfate and polythionate compounds occurs at higher temperatures as shown in Equation 7.4 (Breuer, 2002). Both of these

mechanisms would be supported by an increase in thiosulfate consumption with increasing temperature, which is investigated in the following section (7.5.8).

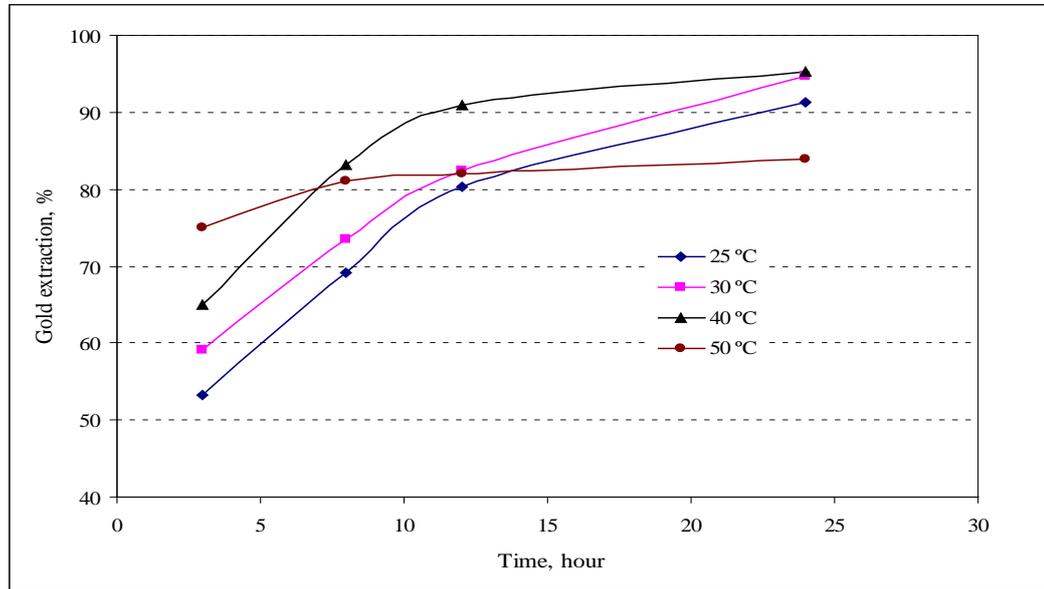


Figure 7.13: The effect of temperature on gold extraction from -106 μm weathered gold ore. Experimental initial conditions: 0.2 M $(\text{S}_2\text{O}_3)^{2-}$, 400 mM NH_3 , 10 mM Cu(II), 300 rpm, 20% S/L ratio.

7.5.8 Effect of Temperature on Thiosulfate Consumption

The effect of temperature on thiosulfate consumption is presented in Figure 7.14 for the experiments described in section 7.5.7. As the temperature increased, the amount of thiosulfate consumed increased. An increase in temperature will increase the leaching rate of gold but above about 40 °C, the detrimental effects of passivation of the gold surface and increased consumption of reagents may outweigh this advantage.

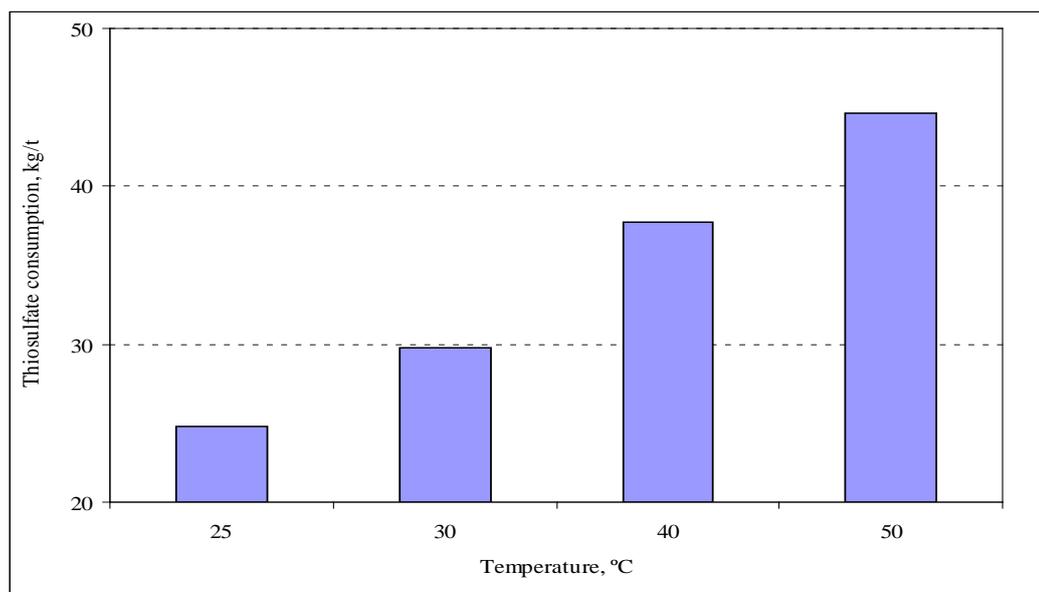


Figure 7.14: The effect of temperature on thiosulfate consumption while leaching - 106 μm weathered gold ore. Experimental initial conditions: 0.2 M $(\text{S}_2\text{O}_3)^{2-}$, 400 mM NH_3 , 10 mM Cu(II) , 300 rpm, 20% S/L ratio.

7.5.9 Effect of Air Injection on Gold Extraction

The effect of air and oxygen on gold oxidation and thiosulfate decomposition has been studied and evaluated by many authors (Arima, 2003; Breuer & Jeffrey, 2003b; Chu et al., 2003; Molleman & Dreisinger, 2002). Most of the published work recommends that air or oxygen should be controlled in thiosulfate leaching solutions. In this section the effect of airflow on gold extraction was evaluated with the results shown in Figure 7.15. The results show that for the Sukari Gold Mine weathered ore that gold leaching in thiosulfate solutions should be undertaken without the injection of oxygen or air. Gold extraction reaches more than 95% without air injection whereas it decreases when air is passed into the solution. This result is consistent with those of Breuer and Jeffrey (2003b) and Muyunda (1996).

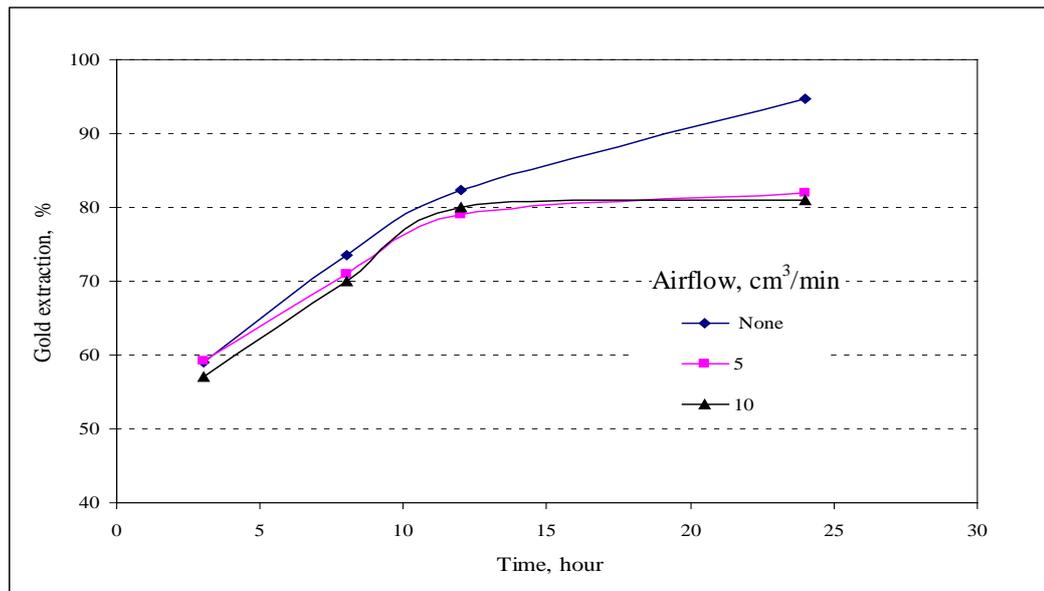


Figure 7.15: The effect of airflow on gold extraction using -106 μm weathered gold ore. Experimental initial conditions: 0.2 M $(\text{S}_2\text{O}_3)^{2-}$, 400 mM NH_3 , 10 mM Cu(II), 300 rpm, 20% S/L ratio.

7.5.10 Effect of Air Injection on Thiosulfate Consumption

It is important to evaluate why gold extraction decreased when air flow was increased into the thiosulfate leach solution. This section evaluates the effect of airflow on thiosulfate consumption after 24 hours of leaching from the experiments described in section 7.5.9. From the data shown in Figure 7.16, thiosulfate loss after 24 hours is 75% of the initial thiosulfate concentration with air injection of 10 cm^3/min , while the loss does not exceed 15% without air injection. The results indicate that the decrease in gold dissolution with air injection is due to the consumption of most of the thiosulfate in the system. This finding is supported by Breuer (2002) who evaluated the effect of high rates of airflow (1000 cm^3/min) on thiosulfate oxidation, and showed that most of the thiosulfate was consumed after only one hour of leaching.

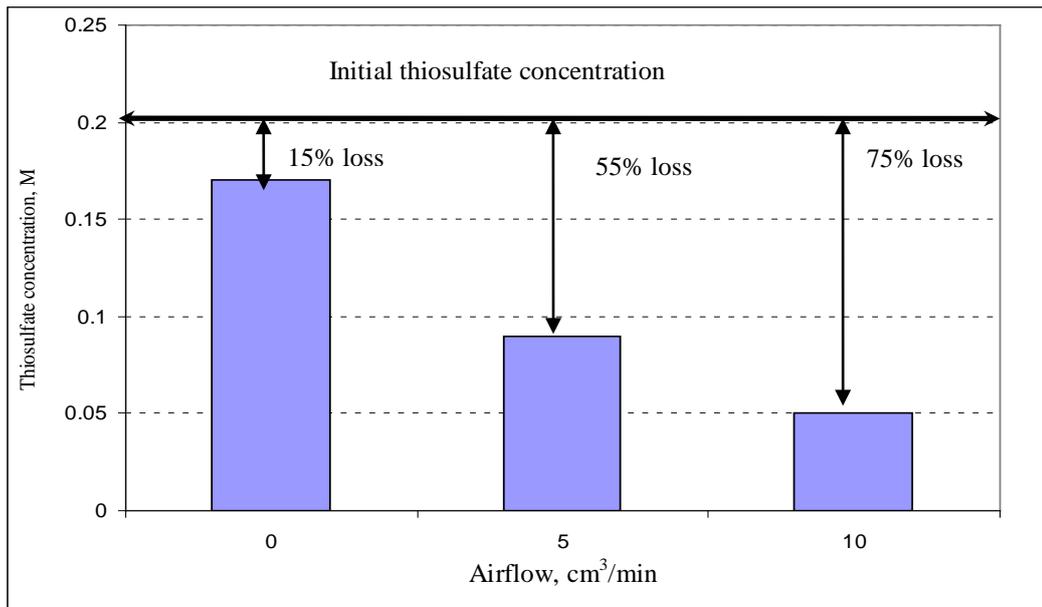


Figure 7.16: The effect of airflow on thiosulfate consumption using -106 μm weathered gold ore. Experimental initial conditions: 0.2 M $(\text{S}_2\text{O}_3)^{2-}$, 400 mM NH_3 , 10 mM $\text{Cu}(\text{II})$, 30 $^\circ\text{C}$, 300 rpm, 20% S/L ratio.

7.5.11 Effect of Pulp Density on Gold Extraction

Figure 7.17 shows the results of a series of experiments conducted to determine gold extraction at different pulp densities ranging from 20% to 50%. Gold extraction percentages increased with lower pulp density and hence, extraction is inversely proportional to the solid/liquid ratio. The trends shown in Figure 7.17 are consistent with leaching systems where a defined amount of reagent is required to dissolve metal from the ore, hence, the total amount of metal extracted increases with increased percent solids but, the extraction efficiency as a percentage decreases.

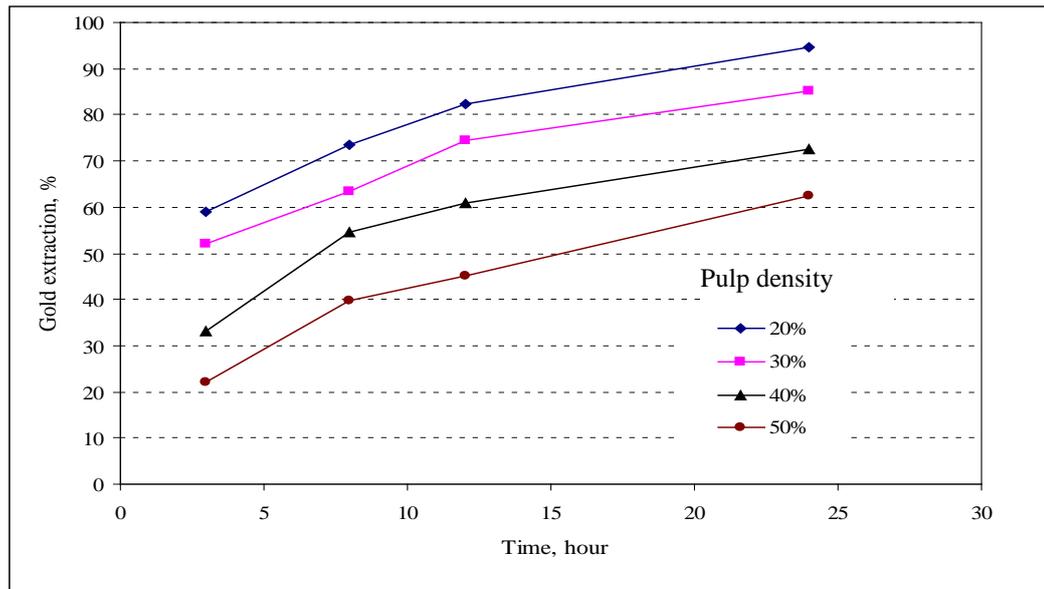


Figure 7.17: The effect of pulp density on gold extraction using -106 μm weathered gold ore. Experimental initial conditions: 0.2 M $(\text{S}_2\text{O}_3)^{2-}$, 400 mM NH_3 , 10 mM Cu(II), 30 $^\circ\text{C}$, 300 rpm.

7.5.12 Effect of Agitation on Gold Extraction

The effect of agitation measured as impellor rotation speed (RPM) can play a major role in determining the rate of gold extraction. If the reaction is diffusion controlled increased agitation will decrease the thickness of the surface boundary layer speeding the diffusion of reactant ions to the ore's surface. On the other hand, agitation does not affect the reaction itself if it is chemically controlled but, may more efficiently suspend the particles allowing uniform contact with the leaching solution. Figure 7.18 shows the results of a series of experiments conducted at different impellor rotation speeds to determine the effect of agitation on gold dissolution, which slightly increased with a higher rotation speed. This result is supportive that gold leaching in thiosulfate solutions is a chemically controlled reaction as observed by Jeffrey (2001) and Muyunda (1996).

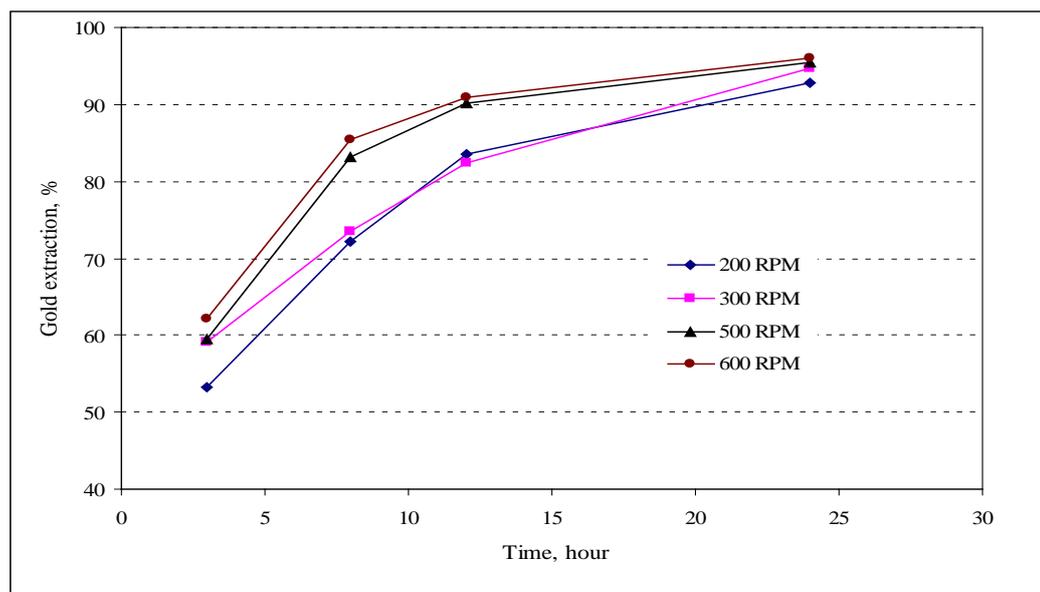


Figure 7.18: The effect of rotation speed (RPM) on gold extraction using $-106 \mu\text{m}$ weathered gold ore. Experimental initial conditions: $0.2 \text{ M } (\text{S}_2\text{O}_3)^{2-}$, 400 mM NH_3 , 10 mM Cu(II) , $30 \text{ }^\circ\text{C}$, $20\% \text{ S/L}$ ratio.

7.5.13 Effect of Ore Weathering on Gold Extraction

Two types of ore were obtained from Sukari Gold Mine, one from shallow surface drill holes (weathered) and the other from deep holes (unweathered). Leaching experiments were conducted on $-106 \mu\text{m}$ ore for both weathered and unweathered ore samples under standard leaching conditions. From the results shown in Figure 7.19 the percentage of gold extracted is slightly higher for the weathered ore. However from the chemical analysis the weathered ore had a lower gold content.

The XRD analysis shows that the mass percent of albite and microcline decreased during the weathering process and the percentage of muscovite increased. The weathering process breaks down the original minerals, liberating the gold, such that the leach solution can easily penetrate the ore particles and extract the gold. This process increased the gold recovery from about 87% in the unweathered ore to 92% in the weathered ore.

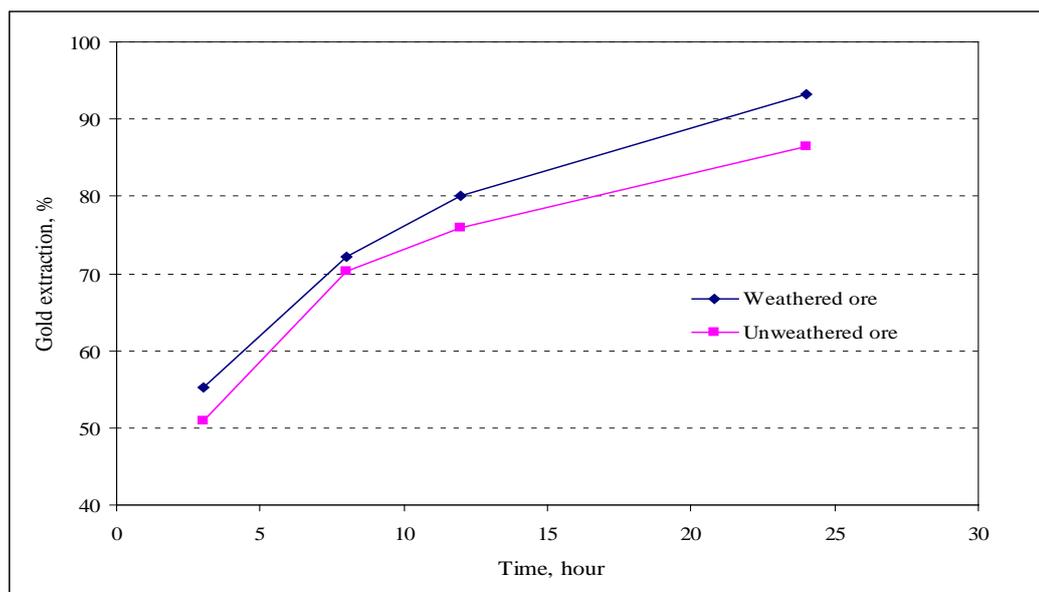


Figure 7.19: The effect of weathering on gold extraction. Experimental initial conditions: 0.2 M $(S_2O_3)^{2-}$, 400 mM NH_3 , 10 mM Cu(II), 30 °C, 300 rpm, 20% S/L ratio.

7.5.14 Ore Leaching in Thiosulfate Compared to Cyanide Solutions

A comparison of gold dissolution in thiosulfate and cyanide solutions was carried out. From the investigation of different reagent concentrations and leaching conditions, it was found that the optimum conditions are very close to the selected standard conditions with thiosulfate concentration in a range of 0.2 - 0.4 M, rotation speed in a range of 300 – 500 rpm and ammonia concentration in a range of 0.4 -0.6 M. Therefore, a thiosulfate solution containing 0.2 M $S_2O_3^{2-}$, 400 mM NH_3 and 10 mM Cu(II), at 30 °C, 300 rpm, 20% S/L ratio, and the natural pH of the solution was used. For comparison, a cyanide solution containing 1.5 g NaCN/L, 20% S/L ratio, in an open vessel at pH =11 was used to leach -106 μm weathered ore. The results are shown in Figure 7.20. Gold extraction using thiosulfate is very close to that obtained using cyanide. The difference of gold extraction in cyanide solution (96%) and in thiosulfate solution (~ 95%) was around 1%. This insignificant difference shows that thiosulfate leaching is efficient in leaching gold from ore from the Sukari Gold Mine, Eastern Desert, Egypt and competes well with cyanide in terms of gold recovery.

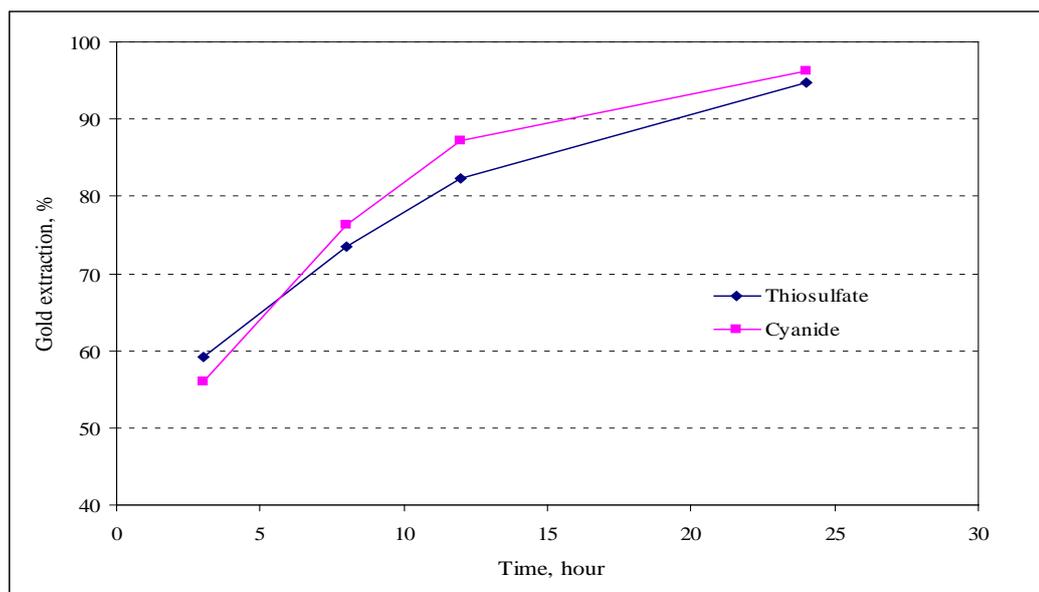


Figure 7.20: Gold extraction from thiosulfate and cyanide solutions using -106 μm weathered gold ore. Experimental initial conditions for the thiosulfate solution: 0.2 M $(\text{S}_2\text{O}_3)^{2-}$, 400 mM NH_3 , 10 mM Cu(II) , 30 $^\circ\text{C}$, 300 rpm, closed vessel, 20% S/L ratio, and natural pH of the solution and for the cyanide solution : 1.5 g NaCN/L , 20% S/L ratio, open vessel, pH =11).

7.6 Summary

In this chapter, the effect of utilising various reagent concentrations and parameter conditions on gold extraction and thiosulfate consumption in a closed vessel, a comparison between gold ore leaching in a closed vessel to an open vessel, and in thiosulfate and cyanide solutions were studied and evaluated. The results showed that there is a slight increase in gold recovery from a closed vessel compared to an open one and gold recovery from the closed vessel is higher than from an open vessel by nearly 5.8%. Increasing copper(II) concentration from 2.5 mM to 20 mM, increased gold recovery from 85% to 96% after 24 hours of leaching, but thiosulfate consumption increased from 22.5 to 44.6 kg/t-ore. With an increase in thiosulfate concentration up to 0.4 M, gold extraction increased to 96% and initial thiosulfate concentration had an insignificant effect on thiosulfate consumption. At the beginning of leaching (after 3 hours), it was found that gold recovery increased by raising the temperature, but over time gold recovered decreased at 50 $^\circ\text{C}$ to be the lowest after 24 hours, the optimum temperature being 30 $^\circ\text{C}$. Thiosulfate

consumption also increased significantly with increasing temperatures. Lower solid/liquid ratio gave higher recovery of gold from the ore. The agitation speed had an insignificant effect on gold recovery. It has been shown that the gold extraction percentage using thiosulfate is very close to that extracted using cyanide. The results showed that the thiosulfate leaching system is efficient to leach the selected gold ore. Finally, from the results of this chapter, the optimum conditions to leach the ore were determined to be 0.2 – 0.4 M thiosulfate, 400-600 mM NH₃, 10-20 mM Cu(II), 30 °C, 300 rpm, no air supplied, solid/liquid ratio 20% at a particle size of < -106 μm.

Chapter 8 Dissolution of mercury in thiosulfate and cyanide solutions: an environmental problem

8.1 Introduction

Mercury (Hg) is frequently associated with gold and silver minerals. One of the main problems in gold processing plants is that cyanide leach solutions dissolve gangue minerals as well as gold and silver. One of these gangue minerals can be metallic mercury and others may be mercury compounds. Mercury forms a strong complex with cyanide which subsequently adsorbs on carbon with gold or silver in carbon-in-column, carbon-in-pulp, and carbon-in-leach (Washburn & Hilldoi, 2003) adsorption circuits. Mercury is then partially recovered with gold and silver in the elution circuit and electroplates in the electrowinning process. When gold is recovered using the zinc-precipitation (Merrill-Crowe) process, mercury precipitates along with gold. Mercury contained in the Merrill-Crowe precipitate and in the electrowinning sludge can result in environmental and industrial problems if a retort is not used to capture it during smelting.

The loss of mercury from the tailings to the surrounding environment can occur through two main processes: (i) the leaching of soluble mercury to the groundwater in the form of Hg–CN complexes; and (ii) the diffusion of mercury gas (Hg^0) into the atmosphere (Shaw, 2006).

In this chapter, the solubility of mercury and mercury compounds in thiosulfate and cyanide solutions is evaluated. The effect that mercury has on gold and copper loading from thiosulfate solutions onto ion exchange resin is investigated. Other experimental work using ion exchange resin columns was conducted to elute gold, copper, and mercury in order to evaluate the possibility of gold loading and recovery using ion-exchange resins.

8.2 Mercury Dissolution in Thiosulfate and Cyanide Solutions

In the following sections, the dissolution of metallic mercury and mercury compounds in thiosulfate and cyanide solution is reported.

The mercury sources used in this study were: metallic mercury (Hg^0), mercury chloride (HgCl_2), mercurous chloride (Hg_2Cl_2), and mercury sulfide (HgS).

The thiosulfate and cyanide solution tested were:

2.5 g/L NaCN, pH 12;

50 mM ATS, 400 mM NH₃, 10 mM Cu²⁺, pH 11.4;

50 mM ATS, 1 mM Cu²⁺, pH 10;

50 mM ATS, 10 mM Tu, 12.5 mM Oxalate, 5 mM FeCl₃, pH 5.5; and

50 mM ATS, 10 mM Tu, 5 mM Ferric-ethylenediaminetetraacetic (Fe-EDTA), pH 7.

8.2.1 Mercury Stability in the Collected Samples

Before the dissolution of mercury in thiosulfate and cyanide leach solutions could be tested a method to stabilise mercury in the samples extracted for analyses had to be determined. Section 8.2.1 describes the experiments and results conducted to determine the stability of mercury in leach samples.

As mercury chloride (HgCl₂) is known for its high solubility in water, it was dissolved to obtain a known concentration of mercury (100 mg/L) in a range of leach solutions. Then a 10 mL filtered sample from each solution was treated with 1 mL of 0.1 M tetra-sodium EDTA. The samples of known mercury concentration were analysed for mercury by ICP-OES. The measured mercury concentration and the composition of each leach solution are shown in Table 8.1. All the results are very close to 100 mg/L indicating that adding tetra-sodium EDTA stabilises the mercury in these leach solutions and can be used as a method to stabilise samples for analyses from leaching tests. Hence EDTA was added to all leach tests sample to stabilize them until analysed.

Table 8.1: The concentration of dissolved mercury in each solution stabilized with tetra-sodium EDTA at room temperature after 48 hours.

Solution	Hg, mg/L
2.5 g/L NaCN	100.2
50 mM ATS, 400 mM NH ₃ , 10 mM Cu ²⁺	100.5
50 mM ATS, 1 mM Cu ²⁺	98.5
50 mM ATS, 10 mM Tu, 12.5 mM Oxalate, 5 mM FeCl ₃	98.4
50 mM ATS, 10 mM Tu, 5 mM FeEDTA	97.9

8.2.2 Effect of Tetrathionate on the Mercury Thiosulfate Complex

Stability

In this section the effect of tetrathionate on the stability of the mercury thiosulfate complex was evaluated using potassium tetrathionate ($K_2S_4O_6$). Two solutions (100 mL) were tested: 1) 50 mM of ammonium thiosulfate with either low tetrathionate (1 mM); or 2) high tetrathionate (10 mM). Mercury chloride ($HgCl_2$) were weighed to form 100 mg/L Hg in each solution. The experiments were conducted using the bottle roll technique with samples taken after 5, 24, and 48 hours, stabilised with tetra-sodium EDTA, and analysed for mercury. The pH of each solution was monitored at sample times. From the data in Table 8.2, tetrathionate did not effect the stability of the mercury thiosulfate complex with all analyses results within 2% of the actual value. Also, the decrease in pH in the solution, possibility due to the decomposition of thiosulfate, did not affect the stability of the mercury thiosulfate complex.

Table 8.2: The dissolved mercury in thiosulfate solutions containing tetrathionate after 0, 5, 24, and 48 hours.

Time, hour	Tetrathionate (S_4O_6) ²⁻ concentration, mM			
	1 mM		10 mM	
	Hg (mg/L)	pH	Hg (mg/L)	pH
0	99.1	6.39	101.85	5.85
5	98.50	5.84	99.71	5.66
24	98.84	5.40	99.25	4.95
48	99.01	4.88	101.10	4.09

8.2.3 The Dissolution of Mercurous Chloride (Hg_2Cl_2)

The dissolution of mercurous chloride (Hg_2Cl_2) in thiosulfate and cyanide leach solutions was tested using the bottle roll technique under the conditions described in section 8.2. Solid mercurous chloride was added to each leach solution to give 200 mg/L of Hg. Samples were taken after 5, 24, and 48 hours of leaching with the percentage mercury dissolution shown in Figure 8.1. The amount of dissolved

mercury in the cyanide, copper-ammonia, and FeEDTA solutions is much higher than in the ferric oxalate (FeOX) and ATS with 1 mM Cu^{2+} solutions. About 78% of the mercury was dissolved after 48 hours in the cyanide and FeEDTA solutions.

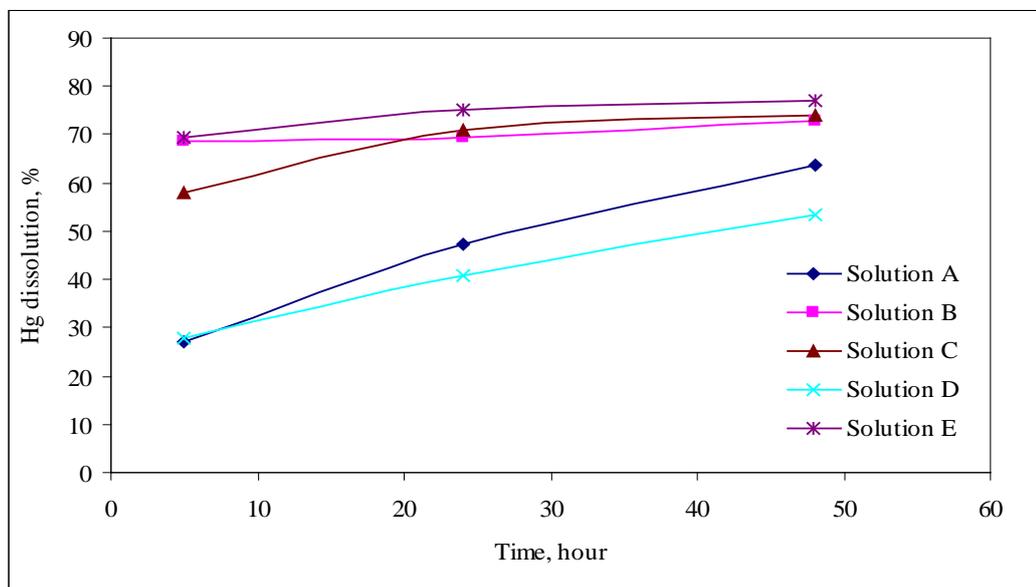


Figure 8.1: The dissolution of mercurous chloride (Hg_2Cl_2) in thiosulfate and cyanide solutions. Leaching conditions: Solution A, 50 mM ATS, 1 mM Cu^{2+} , pH 10; Solution B, 50 mM ATS, 400 mM NH_3 , 10 mM Cu^{2+} , pH 11.4; Solution C, 2.5 g/L NaCN solution, no air, pH 12; Solution D, 50 mM ATS, 10 mM Tu, 12.5 mM oxalate, 5 mM FeCl_3 , pH 5.5, and Solution E, 50 mM ATS, 10 mM Tu, 5 mM FeEDTA, pH 7.

8.2.4 The Dissolution of Mercury Sulfide (HgS)

The dissolution of mercury sulfide (HgS) in thiosulfate and cyanide solutions was tested using the bottle roll technique under the conditions described in section 8.2. Solid mercury sulfide was added to each solution to give a 100 mg/L of Hg. The percent mercury dissolved after 48 hours is shown in Table 8.3. The maximum mercury dissolution is 10.9% in 2.5 g/L NaCN solution whereas the maximum mercury dissolved from thiosulfate solutions was 3.4%. Mercury sulfide does not dissolve as easily in all the leach solutions tested as mercurous chloride.

Table 8.3: The percentage of mercury dissolved from mercury sulfide in thiosulfate and cyanide solutions after 48 hours.

Solution	Hg, %
2.5 g/L NaCN	10.9
50 mM ATS, 400 mM NH ₃ , 10 mM Cu ²⁺	3.4
50 mM ATS, 1 mM Cu ²⁺	0.4
50 mM ATS, 10 mMTu, 12.5 mM Oxalate, 5 mM FeCl ₃	0.3
50 mM ATS, 10 mMTu, 5 mM FeEDTA	0.2

8.2.4.1 Effect of Ammonium Thiosulfate Concentration on the Dissolution of Mercury Sulfide

In this section, the effects of ammonium thiosulfate concentration on the dissolution of mercury sulfide (HgS) in thiosulfate solutions was investigated using the bottle roll technique. The selected ATS concentrations were 50, 100, and 200 mM.

- **Solution A:**

The mercury sulfide dissolution as a function of ATS concentration in solution A (ATS, 1 mM Cu²⁺, pH 10) is shown in Figure 8.2. Increasing the ATS concentration from 50 mM to 200 mM, increases the amount of dissolved mercury with the maximum percentage of mercury dissolved after 48 hours not exceed 1.5%.

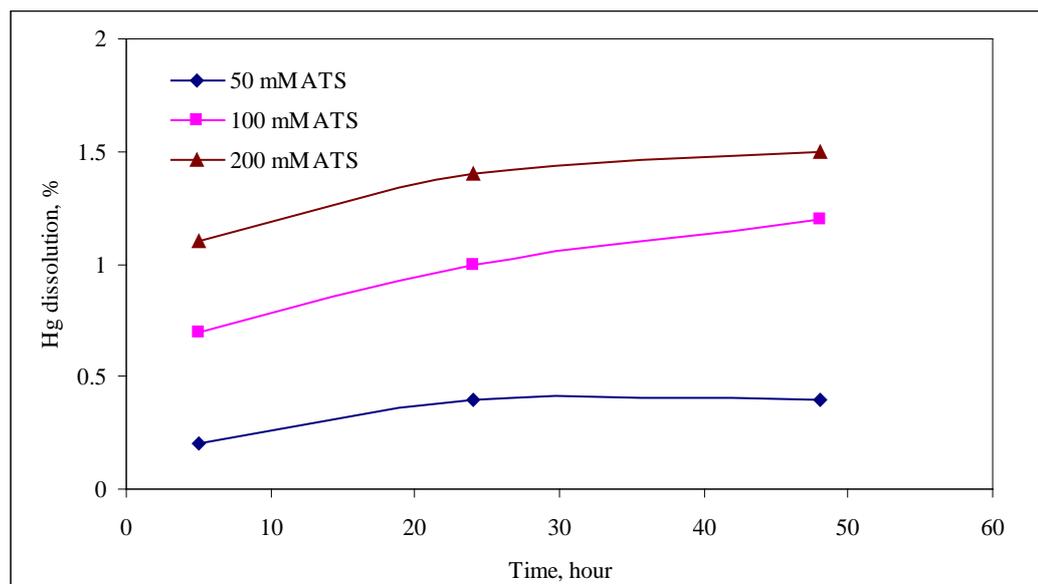


Figure 8.2: The effects of thiosulfate concentration on mercury dissolution in solution A: (ATS, 1 mM Cu²⁺, pH 10).

• Solution B:

The effects of ammonium thiosulfate concentration on mercury sulfide dissolution in solution B (ATS, 400 mM NH₃, 10 mM Cu²⁺, pH 11.4) is shown in Figure 8.3.

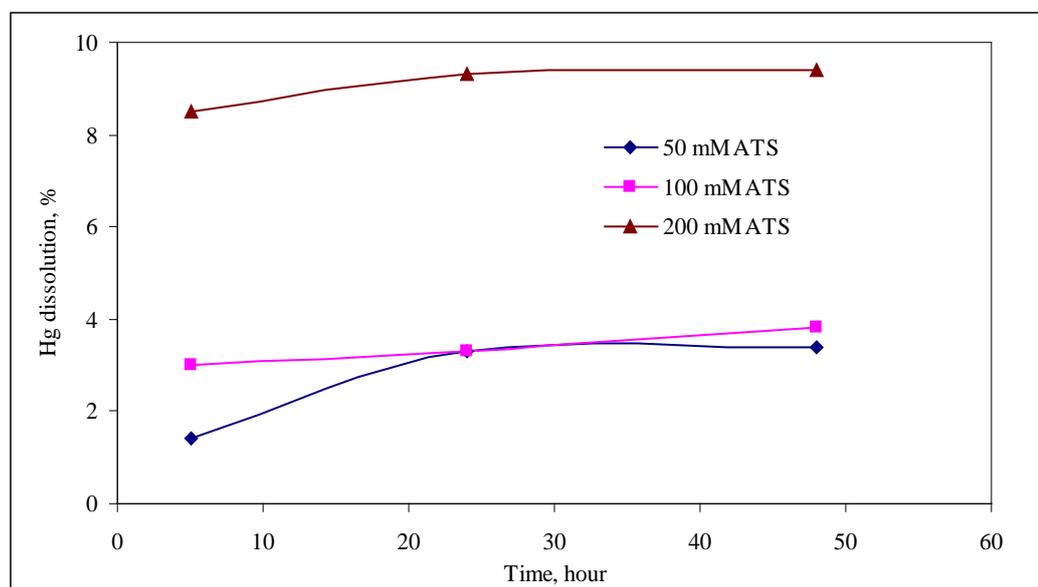


Figure 8.3: The effect of thiosulfate concentration on mercury leaching in solution B: (ATS, 400 mM NH₃, 10 mM Cu²⁺, pH 11.4).

Solution D:

Mercury sulfide dissolution as a function of ATS concentration in solution D (ATS, 10 mM Tu, 12.5 mM oxalate, 5 mM FeCl₃, pH 5.5) is shown in Figure 8.4. Mercury dissolution in this solution is much lower than in solution B and only about 1.2% of mercury dissolved in 48 hours.

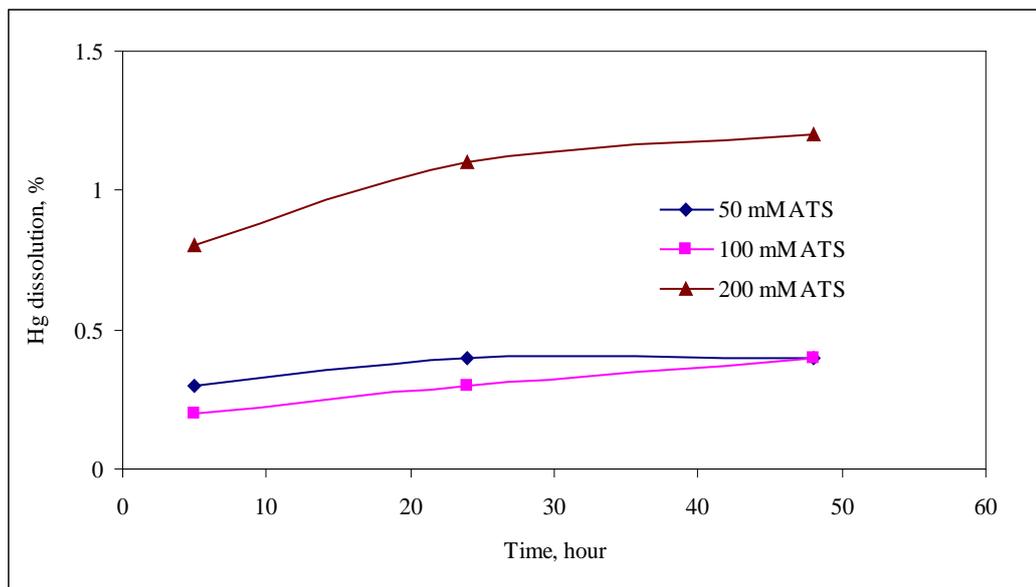


Figure 8.4: The effect of thiosulfate concentration on mercury leaching in solution D (ATS, 10 mM Tu, 12.5 mM oxalate, 5 mM FeCl₃, pH 5.5).

Solution E:

The effects of the ATS thiosulfate concentration on mercury dissolution in solution E (ATS, 10 mM Tu, 5 mM FeEDTA, pH 7) are shown in Figure 8.5. When the ATS concentration increased from 50 mM to 200 mM, the mercury dissolution after 48 hours increased from 0.3% to 2.6%.

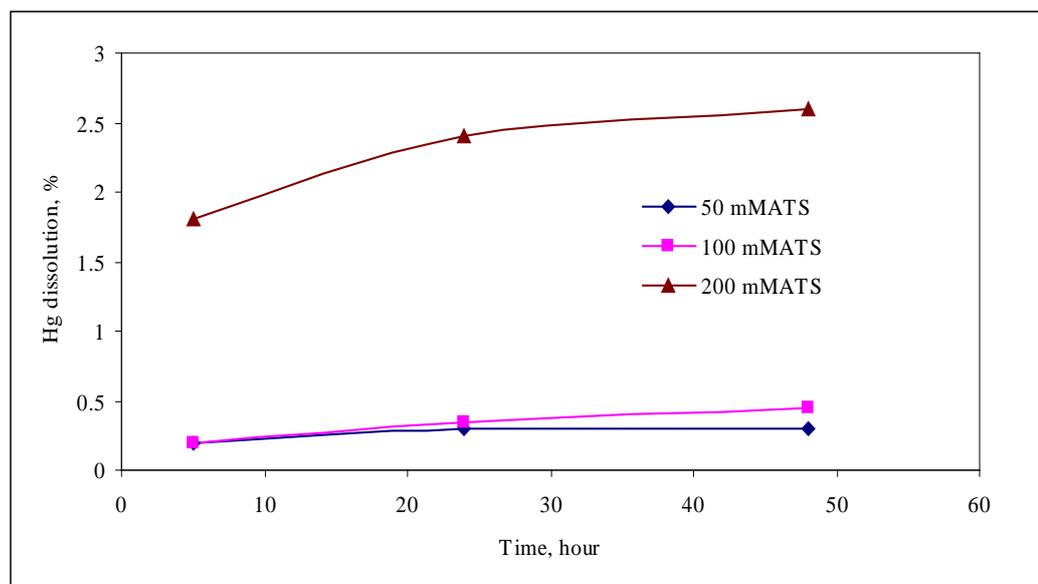


Figure 8.5: The effects of thiosulfate concentration on mercury dissolution in solution E (ATS, 10 mM Tu, 5 mM FeEDTA, pH 7).

It was found that increasing the concentration of ammonium thiosulfate to 200 mM, increases the amount of dissolved mercury from mercury sulfide in all the thiosulfate solutions but the amount of mercury dissolved was always less than that dissolved by cyanide.

8.2.5 The Dissolution of Mercury Metal (Hg^0)

The dissolution of metallic mercury (Hg^0) in thiosulfate and cyanide solutions was tested using the bottle roll technique using the conditions described in section 8.2. Mercury metal (about 0.865g as an average value) was added to each solution and samples taken after 5, 24, and 48 hours of leaching and analysed for mercury with the results shown in Figure 8.6. Mercury dissolution in the thiosulfate-copper-ammonia, Fe-Oxalate (FeOX), and cyanide solutions are higher than in FeEDTA and ATS with 1 mM Cu^{2+} solutions. The maximum dissolution of mercury metal was 20.9% after 48 hours of leaching in the thiosulfate-copper- ammonia solution (solution B).

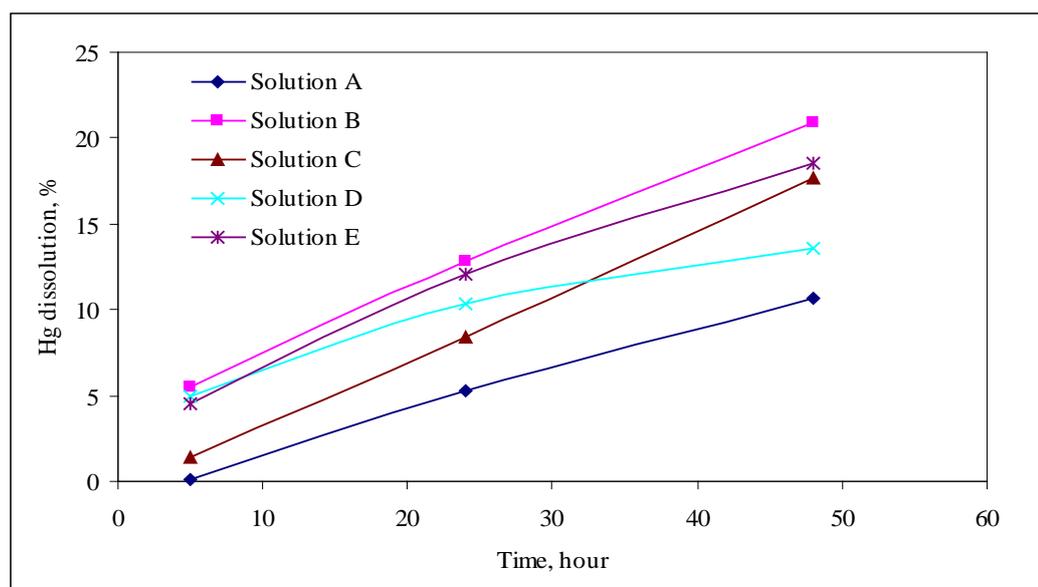


Figure 8.6: The dissolution of mercury metal (Hg^0) in thiosulfate and cyanide solutions. Experimental conditions: Solution A, 50 mM ATS, 1 mM Cu^{2+} , pH 10; Solution B, 50 mM ATS, 400 mM NH_3 , 10 mM Cu^{2+} , pH 11.4; Solution C, 2.5 g/L NaCN solution, pH 12; Solution D, 50 mM ATS, 10 mM Tu, 12.5 mM oxalate, 5 mM FeCl_3 , pH 5.5, and Solution E, 50 mM ATS, 10 mM Tu, 5 mM FeEDTA, pH 7.

The dissolution of mercury from mercurous chloride, mercury sulfide and mercury metal in a variety of thiosulfate leaching solutions was determined and compared with a cyanide solution. There was no advantage in terms of decreased mercury dissolution from mercurous chloride or mercury metal when using thiosulfate compared with cyanide solutions. However, mercury dissolution from mercury sulfide was lower for all thiosulfate solutions tested than for the cyanide leach solution.

The finding that thiosulfate solutions also dissolve mercury, as does cyanide, is a factor to be considered if thiosulfate has a future industrial application in the leaching of gold.

8.3 Effect of Mercury on Gold Loading and Recovery from Thiosulfate Solutions Using Anion-Exchange Resins

8.3.1 Introduction

Ion exchange is a technique for chemical separation, and it is to this field that it has made some of its most remarkable contributions (Rodrigues, 1986). The process of ion exchange consists of two main steps: (1) sorption of a metal ion from the pregnant solution onto the ion exchange resin and then (2) elution in which a solution is used to remove the metal ions from the resin. Ion exchange applications can be useful to (1) treatment of wastewaters (2) non metallic anions such as halides, sulfates, nitrates, and cyanides; and (3) water-soluble, ionic organic compounds.

The first attempts to apply ion exchange for metal recovery were in connection with recovery of copper from waste solutions of the cuprammonium rayon and brass industry, silver from photographic film manufacturing wastes, and chromium from electroplating wastes. Uranium was the first metal to be recovered from leach solutions by ion exchange on a large scale (Habashi, 1970).

Gold and silver production fundamentally consists of two main steps: (1) leaching of metals from its ore or concentrate and (2) recovery of the metal from the leach solution. The leaching of gold and silver can be achieved using different reagents such as cyanide, thiosulfate, thiourea, ammonia, halides, and many others. The metal recovery can be achieved by precipitation, electrowinning, solvent extraction, carbon absorption or ion exchange resin absorption.

Leaching of gold using thiosulfate is considered to be one of the most promising alternatives to cyanide. However, it is difficult to recover the gold thiosulfate complex as (Gallagher et al., 1990) the gold thiosulfate complex is not adsorb effectively onto activated carbon. The precipitation methods are not highly favoured, as they suffer from high zinc consumption, are less selective and are likely to precipitate most metals from solution in addition to the difficulty of recycling the leach liquor (Gross et al., 2003; Deschenes & Ritcey, 1990). Some success has been achieved using ion exchange resin in gold recovery from thiosulfate solution (Jeffrey & Brunt, 2007; Zhang & Dreisinger, 2004 & 2002; Fleming et al., 2001).

In this section, the recovery of gold, copper, and mercury from ammonium thiosulfate (ATS) solutions using a strong ion-exchange resin has been studied and evaluated. A commercially available ion-exchange resin, Purolite A500/2788, was

obtained in its wet form and used without conditioning. Table 8.4 presents the physical and chemical properties of Purolite A500/2788 resin.

Table 8.4: Typical physical and chemical characteristics of Purolite A500/2788 resin.

Characteristic	Ionic form	Value
Total Capacity (min.)	Cl ⁻	1.15 eq/L
Moisture Retention	Cl ⁻	53-58%
Particle Size	800-1300 μm	92%
Reversible Swelling (max.)	Cl ⁻ → OH ⁻	15%
Specific Gravity		1.08 g/mL
Shipping Weight (approx.)		670-700 g/L
Temp Limit	OH ⁻	60 °C
Temp Limit	Cl ⁻	100 °C
pH Limits		0-14 (Stability)

The loading and recovery of gold, copper, and mercury from thiosulfate solution was carried out using two different methods: (1) loading and then stripping using sodium perchlorate (NaClO₄ · H₂O) in batch tests and (2) loading and then elution using a solution composed of 2 M NaCl and 0.2 M Na₂SO₃ in elution columns. The experimental procedures for both methods have been described in Chapter 4, sections 4.4.1 and 4.4.3.

Loading-Stripping Batch Tests

The recovery of mercury, gold, and copper from a synthetic thiosulfate leach solution at different mercury concentrations (0, 2, 3, 5, 7, 10, 15, and 20 mg/L Hg as HgCl₂) was studied. The reagent concentrations of the synthetic leach solution were 100 mM ammonium thiosulfate (ATS), 4 mM trithionate (S₃O₆)²⁻, 1 mM copper sulfate, and 5 mM gold (Au) as gold thiosulfate Au(S₂O₃)₂³⁻. Resin was loaded using the synthetic leach solution and stripped in batch tests.

Loading-Elution Column Tests

In the loading-elution experiments, gold, copper, and mercury were eluted from loaded resins utilising an ion exchange column. A 1.5 L synthetic thiosulfate leach solution containing 100 mM ATS, 4 mM trithionate, 1 mM copper sulfate, 5 ppm gold as gold thiosulfate, and 5 mg/L mercury as (HgCl₂) was contacted overnight with 6 g of the strong ion-exchange resin. The loaded resin was then stripped in column tests.

8.3.2 Loading and Recovery of Gold

The amount of gold loaded on 0.667 g of resin from 250 mL of synthetic leach solution is shown in table 8.5 as a function of mercury concentration. The loaded resin was batch stripped twice with 25 mL of 0.5 M sodium perchlorate (NaClO₄·H₂O) for half an hour each. The gold stripped from the resin is shown in table 8.5. The results showed that gold loading and recovery is not affected significantly by the presence of mercury in the solution. On average, the percentage of the gold in the solution loaded onto the resin is about 76%. From the differences between the amount of gold loaded on the resin and the amount stripped it can be seen that most of the loaded gold is recovered from the resin by using sodium perchlorate as an eluant. The presence of mercury, up to 20 mg/L, has no influence on the gold loading and recovery.

Table 8.5: The amount of gold loaded on resin and stripped from the resin as a function of mercury concentration in a synthetic leach solution.

Hg, conc., mg/L	Gold, kg-Au/t-resin		Deviation, %
	Gold loaded	Gold stripped	
0	2.60	2.78	6.9
2	2.57	2.73	6.1
3	2.47	2.51	1.4
5	2.58	2.74	6.1
7	2.44	2.47	1.3
10	2.48	2.49	0.5
15	2.53	2.54	0.5
20	2.52	2.72	7.7

8.3.3 Loading and Recovery of Copper

Copper might be present in thiosulfate solutions when it used to treat gold ores containing copper or when it is added as a catalyst for gold leaching. The amount of copper loaded on 0.667 g of resin from 250 mL of synthetic leach solution containing 100 mM ammonium thiosulfate (ATS), 4 mM trithionate ($S_3O_6^{2-}$), 1 mM $CuSO_4 \cdot 5H_2O$, and 5 mM gold (Au) as gold thiosulfate $Au(S_2O_3)_2^{3-}$ is shown in table 8.6 as a function of mercury concentration. The loaded resin was batch stripped twice with 25 mL of 0.5 M sodium perchlorate ($NaClO_4 \cdot H_2O$) for 30 minutes each. The copper stripped from the resin is also shown in table 8.6. The percentage of copper from solution loaded on the resin is low with the maximum being around 18.5% when no mercury was added into the loading solution.

Table 8.6: The amounts of copper loaded on resin and stripped from resin as a function of mercury concentration in a synthetic leach solution.

Hg, conc., mg/L	Copper, kg-Cu/t-resin		Deviation, %
	Copper loaded	Copper stripped	
0	8.07	7.77	3.7
2	7.91	7.67	3.1
3	6.91	6.97	0.9
5	7.92	7.70	2.8
7	6.80	6.87	1.1
10	6.34	6.84	7.7
15	6.50	6.96	7.0
20	7.84	7.66	2.4

8.3.4 Loading and Recovery of Mercury

The amount of mercury loaded on 0.667 g of resin from 250 mL of synthetic leach solution is shown in table 8.7 for different initial mercury concentrations. The loaded resin was batch stripped twice with 25 mL of 0.5 M sodium perchlorate (NaClO₄ H₂O) for half an hour each. The mercury stripped from the resin is also shown in Table 8.7. It was found that the amount of mercury stripped was about 75% of the mercury loaded on the resin for all initial mercury concentrations.

Table 8.7: The percentages of mercury loaded on resin and stripped from resin as a function of initial mercury concentration. Possible loading is the loading if all of the mercury was removed from solution and loaded on the resin.

Possible Hg loading, kg-Hg/t-resin	Hg loaded and stripped, %	
	Mercury loaded as a % of possible loading.	Mercury Stripped as a % of possible loading
0	0	0
1.36	56.3	42.3
4.16	60.4	46.8
6.13	61.8	48.4
9.09	63.8	49.7
11.81	62.0	43.9

Figure 8.7 shows the mercury loaded on resin and stripped from resin as a function of initial mercury concentration. The amount of mercury loaded and stripped is influenced by the initial mercury concentration in the loading solution with increasing initial mercury concentration increasing the amount of loaded and recovered mercury.

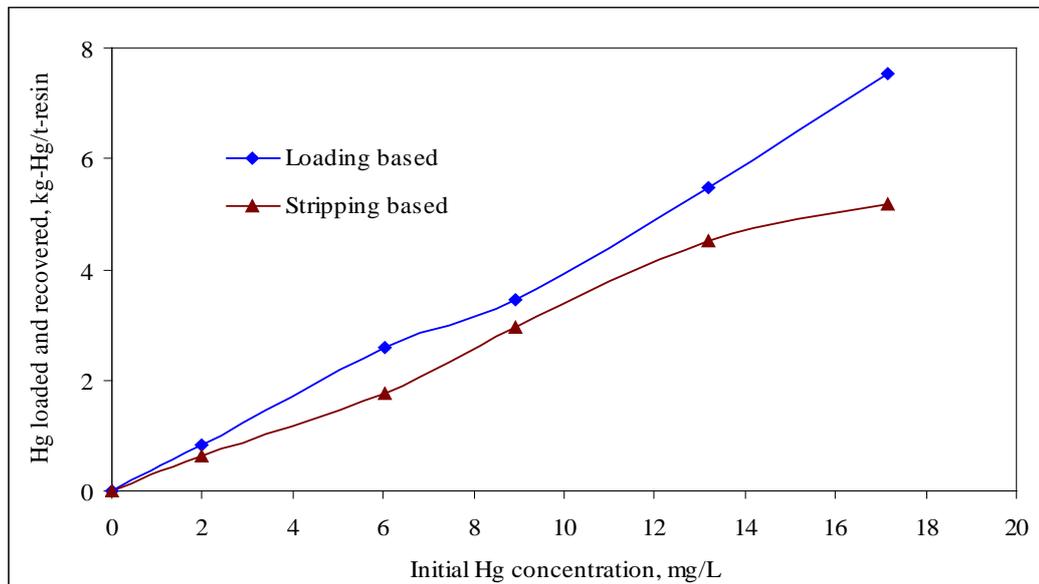


Figure 8.7: The amount of mercury loaded on resin and stripped from resin at different initial mercury concentrations.

8.3.5 Polythionate Speciation

For each loading-stripping experiment after 5 hours loading, the barren solution was analysed to determine the quantities of thiosulfate and polythionate species using a Waters 2695 HPLC separation module. The loaded resin was then stripped twice for 30 minutes each using 25 mL of 0.5 M sodium perchlorate and the polythionate speciation analysis carried out for each stripping batch. The measured speciation of the barren loading and stripping solutions are shown in Tables 8.8 and 8.9 respectively. From these tables, the thiosulfate, trithionate, tetrathionate, and pentathionate that is loaded and stripped from the resin at different mercury concentrations can be seen.

Table 8.8: Thiosulfate and polythionate speciation of the barren loading solution (Initial loading solution containing: 100 mM ammonium thiosulfate (ATS), 4 mM trithionate ($S_3O_6^{2-}$), 1 mM $CuSO_4 \cdot 5H_2O$, and 5 mM gold (Au) as gold thiosulfate).

Species	Barren solution			
	0 ppmHg	5 ppmHg	10 ppm Hg	15 ppm Hg
Thiosulfate	93.89 mM	93.92 mM	89.51 mM	90.62 mM
Trithionate	2.75 mM	2.75 mM	2.63 mM	2.56 mM
Tetrathionate	0.36 mM	0.44 mM	0.58 mM	0.57 mM
Pentathionate	0.01 mM	0.01 mM	-	-

Table 8.9: Thiosulfate and polythionate speciation of the stripping solution (25 mL of 0.5 M sodium perchlorate ($NaClO_4 \cdot H_2O$)).

Species	Stripping solution			
	0 ppmHg	5 ppmHg	10 ppm Hg	15 ppm Hg
Thiosulfate	202.4 mM	202.6 mM	195.4 mM	203.5 mM
Trithionate	353.7 mM	350.9 mM	340.9 mM	347.7 mM
Tetrathionate	66.3 mM	59.7 mM	62.2 mM	65.5 mM
Pentathionate	6.0 mM	5.1 mM	3.4 mM	3.1 mM

8.3.6 Gold, Copper and Mercury Recovery Using an Elution Column

The elution of gold, copper, and mercury from a loaded resin was carried out with an eluant solution composed of 2 M NaCl and 0.2 M Na₂SO₃. An automatic fraction collector was adjusted to collect 8 mL fractions (1 bed volume, BV). All the sample fractions were analysed for gold, copper, and mercury with a suitable method for each metal using ICP-OES. From the amount of gold, copper, and mercury loaded and eluted, the elution efficiency for each metal was calculated. The following sections present the amount of gold, copper, and mercury eluted and the elution efficiencies.

8.3.6.1 Gold Recovery

Figure 8.8 shows the concentration of gold (mg/L) eluted with each BV of solution (Elution Profile) and the elution efficiency (%). The cumulative values of the bed volumes (BV) of eluant are plotted on the x-axis. It can be seen that gold was eluted from the resin very fast and the maximum concentration of gold in the eluant was at about 2.1 BV. Most of the gold loaded was eluted completely after about 5 BV at which time the gold concentration in the eluant was less than 0.01 mg/L and the elution efficiency was 99.2%.

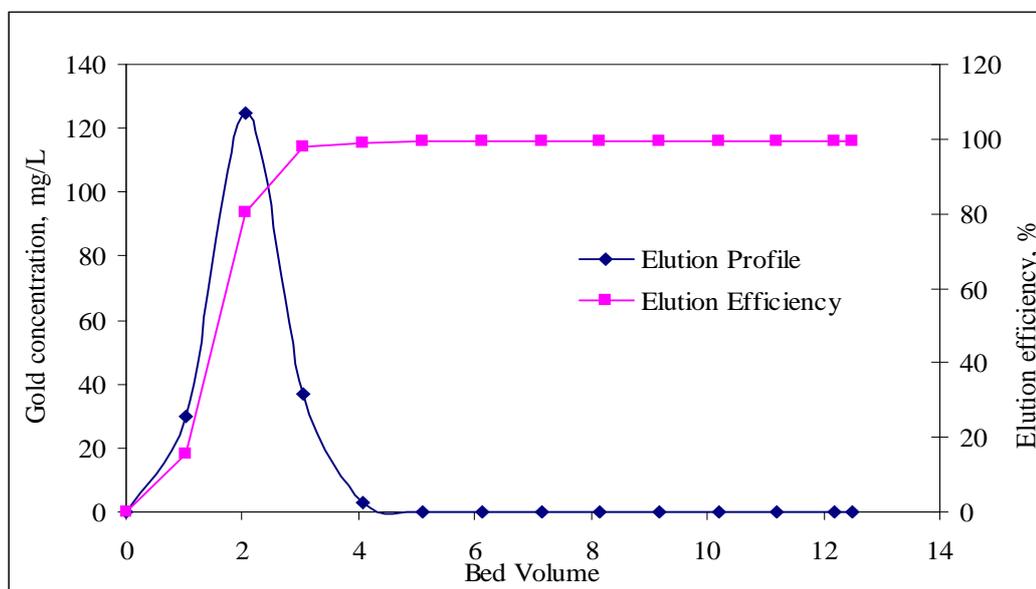


Figure 8.8: Gold eluted and elution efficiency from 8 mL of the loaded resin (Purolite A500/2788) using an eluant containing 2 M NaCl and 0.2 M Na₂SO₃.

8.3.6.2 Copper Recovery

Figure 8.9 shows the amount of copper (mg/L) eluted with each BV of solution and the elution efficiency (%). It can be seen from a comparison between Figures 8.8 and 8.9 that the elution of copper is faster than that of gold. The maximum concentration of copper in the eluant was in the first BV and most of the loaded copper was eluted by about 3 BV at which time the elution efficiency was 100% (Figure 8.9).

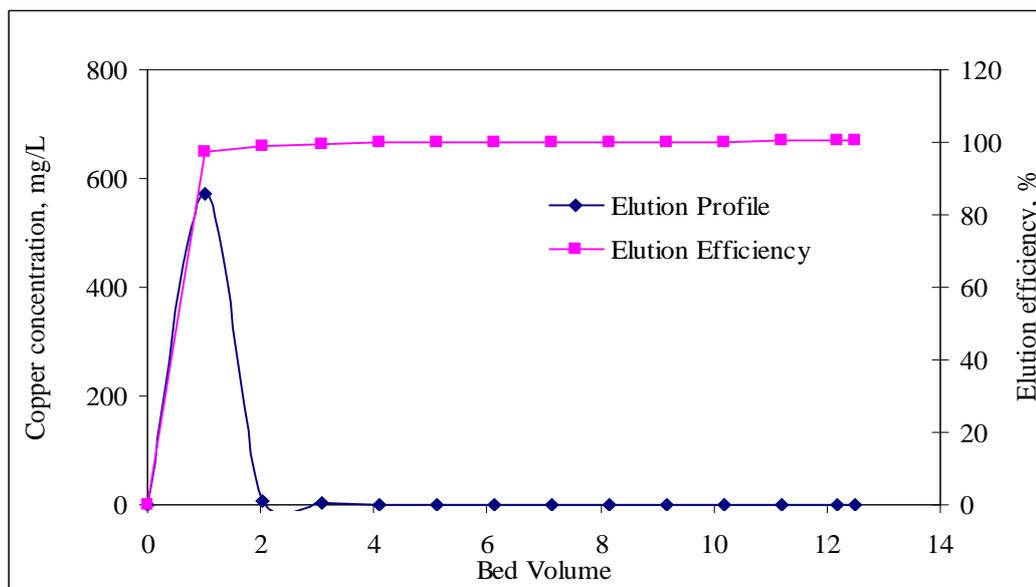


Figure 8.9: Copper eluted and the elution efficiency from 8 mL of loaded resin (Purolite A500/2788) using an eluant containing 2 M NaCl and 0.2 M Na₂SO₃.

8.3.6.3 Mercury Recovery

The amount of mercury eluted and the elution efficiency are plotted in Figure 8.10, which shows the maximum concentration of mercury in the eluant was at about 1.3 BV, but the difference between the elution of mercury and the elution of both gold and copper is that the elution of mercury is slower than for gold and copper. Complete mercury elution was achieved at about 10 BV compared with gold (5 BV) and copper (3 BV).

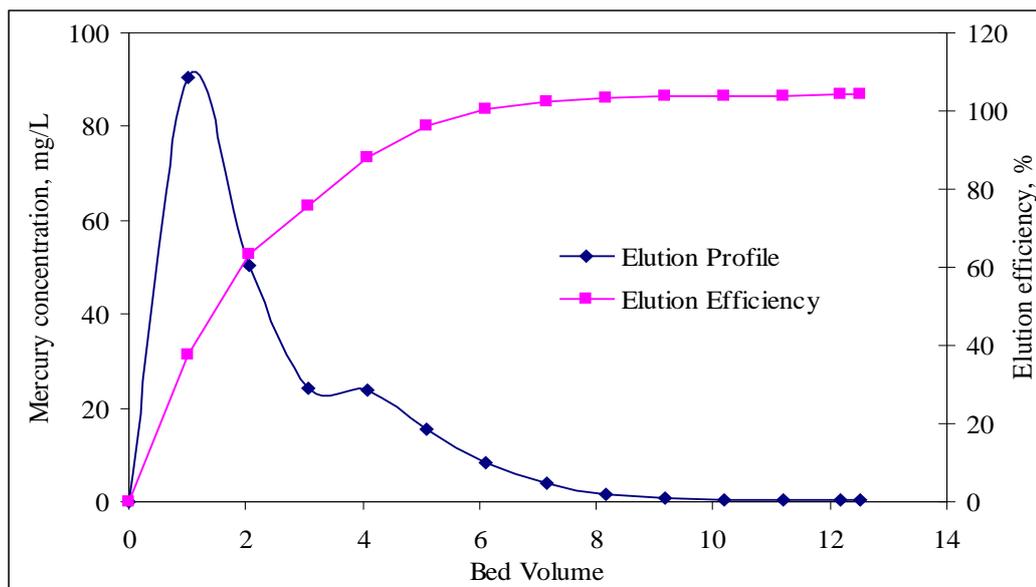


Figure 8.10: Mercury eluted and the elution efficiency from 8 mL of loaded resin (Purolite A500/2788) using an eluant containing 2 M NaCl and 0.2 M Na₂SO₃.

8.4 Summary

In this chapter, the solubility behaviour of mercury compounds (elementary mercury (Hg⁰), mercuric chloride (HgCl₂), mercurous chloride (Hg₂Cl₂), and mercury sulfide (HgS)) in ammoniacal thiosulfate leaching solutions and cyanide solutions was evaluated. The effect that mercury has on gold and copper loading from thiosulfate solution onto ion exchange resin has also been investigated. Finally, gold, copper, and mercury elution was examined using ion exchange resin columns in order to evaluate the recovery of gold and copper in the presence of mercury. It has been found that thiosulfate solutions dissolve mercury similar to cyanide, which would need to be considered when thiosulfate is used to leach gold. Mercuric chloride was the most soluble of the mercury salts tested with the order of the rate of dissolution in thiosulfate solutions being HgS < Hg⁰ < Hg₂Cl₂ < HgCl₂.

The results show that the presence of mercury does not have a significant effect on both gold loading and recovery. Finally, gold, copper and mercury were eluted using a solution composed of 2 M NaCl and 0.2 M Na₂SO₃. The results showed that gold and copper were eluted faster than mercury and that complete mercury elution was achieved at 10 BV compared to gold (5 BV) and copper (3 BV).

Chapter 9 Conclusions and Recommendations

9.1 Conclusions

The outcomes presented in this work show a significant achievement in the understanding of gold leaching with thiosulfate and the environmental impacts of mercury and cyanide in the field of gold production. The gold dissolution process using thiosulfate solutions was intensively studied in several ways: (1) gold was leached in thiosulfate solution in both closed and open vessels (kinetic and environmental comparison); (2) the metallurgical optimum thiosulfate leaching conditions for pure gold and pure silver were evaluated and the research extended to gold silver alloys (4, 8, 20 and 50 wt% silver); (3) the electrochemical nature of leaching was studied using gold, silver, and gold/silver alloys with linear sweep voltammetry and coulometric electrochemical techniques at fixed potential values; (4) the leaching of gold from ore samples supplied from the Centamin Egypt Limited Company was optimised, and (5) finally, the possibility of mercury dissolution in thiosulfate solutions and gold, copper, and mercury loading onto and recovered from ion-exchange resins was studied.

9.1.1 Gold leaching in open and closed vessels

The leaching of gold and silver in solutions containing copper(II), ammonia and thiosulfate in a closed vessel maintains optimum leaching conditions and enhances the leaching kinetics compared with an open vessel. The leaching rate of gold and silver in the closed vessel was greater than that obtained in the open vessel by 30% and 45% respectively. Silver leaching rates were found to be more sensitive to temperature and ammonia concentration than gold. Higher temperatures increased the volatilization rate of ammonia during leaching in the open vessel which is not desirable kinetically and environmentally. Copper (II) reduction increased in the open vessel with increasing temperature. Thiosulfate decomposition was also greater in an open vessel compared to the closed one and increased with increasing temperature. Temperature should be minimized in the thiosulfate system to avoid ammonia losses and the consumption of thiosulfate. In brief, gold and silver leaching in thiosulfate solutions is preferable kinetically and environmentally if conducted in a closed vessel system.

9.1.2 Optimum thiosulfate leaching characteristics of pure gold, pure silver and gold/silver alloys

From the kinetic study of the dissolution of gold, silver and gold-silver alloys in solutions containing copper (II), ammonia and thiosulfate with standard experimental conditions: 10 mM Cu(II), 0.4 M NH₃, 0.2 M S₂O₃²⁻, 30 °C, 300 rpm, pH 11.5, it is concluded that :

- Pure silver dissolution rate is around 6.89 times more than pure gold
- The dissolution rate of pure gold is higher than that from 4 and 8 wt% Ag alloys, but the dissolution rate of gold in 20 and 50% silver alloys is more than that obtained for pure gold.
- The average dissolution rate of pure gold and pure silver after 8 hours are 45 and 36% respectively of the dissolution rates after 1 hr. The average total metal dissolution rate decreased over time for all gold-silver compositions tested.
- By increasing the initial thiosulfate concentration, the average total dissolution rate after 8 hr increased for all gold–silver compositions tested.
- Silver dissolution rate is more sensitive to thiosulfate concentration than gold.
- The silver dissolution rate is sensitive to copper(II) concentration being $1.67 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ at an initial copper(II) concentration of 1.25 mM and $6.6 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ at an initial copper(II) concentration of 10 mM.
- Silver dissolution is more sensitive to ammonia than gold. The pure silver dissolution rate with 0.2 M ammonia was very low while its maximum rate was $15.29 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ with 0.8 M ammonia. For pure gold the maximum dissolution rate was $1.63 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ with 0.6 M ammonia which decreased to $1.25 \times 10^{-5} \text{ mol.m}^{-2}.\text{s}^{-1}$ with 0.8 M ammonia.

9.1.3 Electrochemical studies of gold, silver, and gold/silver alloys in thiosulfate solutions

Electrochemical experimental work was carried out in two different ways: linear sweep voltammetry and coulometric electrochemical experiments at a fixed potential value. The experiments were performed at a rotation speed of 300 rpm and at a temperature of 30 °C for 30 minutes.

From the linear sweep voltammetry experiments, an increase in ammonium thiosulfate concentration resulted in an increase in the produced current due to the oxidation of gold and/or silver. Gold was found to oxidise faster in ammonium

thiosulfate solutions than sodium thiosulfate solutions. An increase of silver percent in the alloy resulted in an increase of the total current density from both gold and silver oxidation in thiosulfate solution over the whole range of applied potentials. In the absence of ammonia gold and silver oxidation is very slow however, in solutions containing high ammonia concentration, gold oxidation occurs rapidly. The most important finding from the electrochemical and kinetic results (Chapter 6) is that the addition of thiourea into the thiosulfate solution retards the oxidation of silver and the lowest silver oxidation occurs at high thiourea concentrations. From this observation, the results suggest that choosing thiourea as an oxidant in the thiosulfate solution should be limited if the gold mineral is mixed with silver which, is usually the case with most native gold found alloyed with silver.

From the coulometric electrochemical experiments at fixed potential values of 0.22, 0.256, 0.292, and 0.35V (relative to standard hydrogen electrode (SHE)) in thiosulfate solutions, it was found that an increase in the pure gold dissolution rate can be achieved by increasing the potential. The gold dissolution rate started slowly at a low potential and increased with increasing potential in thiosulfate-thiourea solutions. The highest total (gold/silver) dissolution rate is obtained from the thiosulfate–thiourea solutions when there is a low percentage silver in the alloys. When the silver percent was increased up to 20 and 50%, the total leach rate decreased significantly. In thiosulfate-ammonia and thiosulfate-ammonia-copper solutions, the total dissolution rate increased significantly with increasing percentage of silver in the alloy.

9.1.4 Thiosulfate leaching of gold ore samples

The effect of thiosulfate concentration, ammonia, copper(II), temperature, and solid-liquid ratio on gold ore leaching was studied. The results showed that there is a slight increase in gold recovery from a closed vessel compared to an open one during the first 3 hours of leaching. After 24 hours, gold recovery from the closed vessel is higher than from an open vessel by nearly 5.8%. By increasing copper(II) concentration from 2.5 mM to 20 mM, gold recovery increased from 85% to 96% after 24 hours of leaching, but thiosulfate consumption increased from 22.5 to 44.6 kg/t-ore. With an increase in thiosulfate concentration up to 0.4 M, gold extraction increased to 96% and initial thiosulfate concentration had little effect on thiosulfate consumption. At the beginning of the leach (after 3 hours), it was found that gold

recovery increased by raising the temperature, but as time passed, it was found that the amount of gold recovered at 50 °C was the lowest, the optimum temperature being 30 °C. Thiosulfate consumption also increased significantly with increasing temperature. Lower Solid/liquid ratio gave higher recovery of gold from the ore. The agitation speed has insignificant effect on gold recovery. Finally, the study found the optimum conditions to leach the ore to be 0.2 – 0.4 M thiosulfate, 400 mM NH₃, 10 - 20 mM Cu(II), 30 °C, 300 rpm, no air supplied, solid/liquid ratio 20 %, and a particle size of -106 µm.

9.1.5 Mercury dissolutions in thiosulfate solutions and gold, copper, and mercury recovery from ion-exchange resins

The dissolution of different mercury forms in thiosulfate and cyanide solutions was carried out. The results showed that mercury dissolves in thiosulfate and in cyanide solutions. The order of the dissolution rates of different mercury forms in these solutions was $\text{HgS}_2 < \text{Hg}^0 < \text{Hg}_2\text{Cl}_2 < \text{HgCl}_2$. Mercury chloride (HgCl_2) dissolved completely in all the solutions tested. The cyanide solution sparingly leaches mercury sulfide with 10.9% dissolved after 24 hours while, the amount of mercury dissolved from the thiosulfate solution did not exceeds 3.4 % after two days of leaching.

Gold, copper, and mercury loading and stripping experiments were conducted using a strong basic ion-exchange resin. The results showed that the presence of mercury does not have a significant effect on gold loading and stripping. The study also showed that the amount of mercury stripped from the resin was about 75% of the mercury loaded at different initial mercury concentrations.

Finally, gold and copper were loaded in the presence of mercury in the loading solution and then eluted. A solution composed of 2 M NaCl and 0.2 M Na₂SO₃ was used as the eluant. The results suggested that gold and copper were eluted faster than mercury and that mercury eluted at 10 BV compared to gold (5 BV) and copper (3 BV). The presence of mercury did not have any affect on the loading or recovery of gold.

9.2 Recommendations

The study offers several recommendations for future research work directed at thiosulfate leaching of gold. First of all, the leaching of gold and silver in a closed system should be more intensively studied to evaluate the leaching kinetics of gold in the presence of low percents of silver. The environmental advantages of using a closed system in thiosulfate leaching needs to be studied on a semi-industrial scale to evaluate the amount of ammonia evaporated into the environment and that left in the final solution and its environmental impacts. Secondly, further studies should be undertaken to evaluate the effect of silver content (gold/silver as alloys and ores) on gold leaching from thiosulfate solutions containing thiourea as an oxidant. An important finding from this work is that in the presence of thiourea, the oxidation current of gold and silver decreased and the oxidation current from pure gold after the standard potential for gold oxidation (150 mV) is higher than the total oxidation current from gold-silver alloys. In the future work, the kinetic and electrochemical effects of silver content on gold leaching rate in thiosulfate solutions containing thiourea should be studied.

Finally, mercury forms with cyanide a strong complex which is adsorbed on carbon with gold or silver during the recovery processes and this causes a serious problem in the elution circuit and in the electrowinning process. An important future project suggested by this work is to study the leaching, loading, and recovery of gold in thiosulfate solutions from gold ore minerals containing different contents of mercury. The effect of mercury dissolved on gold loading and recovery should then be evaluated kinetically and environmentally.

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