THE TREATMENT OF COPPER-GOLD ORES
BY AMMONIUM THIOSULFATE LEACHING

by

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ABSTRACT

The application of ammonium thiosulfate for the treatment of copper-gold ores has been investigated. Leaching studies were conducted with copper minerals, copper minerals with gold addition to solution and copper-gold samples of different copper and gold grades. The behaviour of thiosulfate, tetrathionate and sulfate in solution was studied using ion chromatography.

The copper sulfide minerals chalcopyrite and enargite seem to be unreactive toward an ammonium thiosulfate leach. Covellite and chalcocite leach to a slight extent in this leaching system. The copper extractions of the sulfide minerals seem to be independent of the availability of complexing agents. The copper oxide minerals cuprite and malachite showed high copper extractions in the presence of sufficient lixiviant.

Experiments showed that both gold extraction and thiosulfate stability are influenced by a combination of aeration and cupric ions in solution. High initial gold extractions were achieved in an aerated solution in the presence of cupric ions. However, these conditions simultaneously catalyzed thiosulfate degradation, resulting in gold precipitation. Therefore, it is important to establish a balance between providing sufficient air and cupric ions for fast gold dissolution, and to minimize the amount of air in the presence of cupric ions to prevent excessive thiosulfate degradation. A promising potential alternative to these conditions is a 24 hour leach without forced aeration.

TABLE OF CONTENTS

ABSTRACT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
LIST OF SYMBOLS.....	xi
ACKNOWLEDGMENTS.....	xii
1 INTRODUCTION	1
2 LITERATURE REVIEW	5
2.1 Aqueous Chemistry	5
2.1.1 Gold-water system	5
2.1.2 Copper-water system	8
2.1.3 Thiosulfate	10
2.2 Overview of Thiosulfate Technology for Gold Recovery	13
2.2.1 Thiosulfate leaching for gold extraction.....	13
2.2.2 Gold recovery from thiosulfate solutions	19
2.3 Chemistry of the Ammonium Thiosulfate System.....	21
2.3.1 Thermodynamic considerations.....	21
2.3.2 Copper catalysis.....	24
2.3.3 Thiosulfate degradation reactions.....	27
2.4 Ammonia technology for copper/gold leaching	33
2.4.1 Ammonia technology for gold recovery	33
2.4.2 Ammonia technology for copper recovery	35
2.5 Summary of literature.....	37
2.5.1 Thiosulfate technology	37
2.5.2 Ammonia Technology	40
2.5.3 Treatment of copper-gold ores by ammonium thiosulfate	40
3 EXPERIMENTAL METHODS	42
3.1 Materials	42
3.1.1 Copper Minerals	42

3.1.2 Copper-Gold Samples.....	44
3.1.3 Reagents.....	46
3.2 Experimental Apparatus.....	47
3.3 Experimental Procedures.....	49
3.3.1 Preliminary testwork.....	49
3.3.2 Leaching of copper minerals	50
3.3.3 Leaching of copper minerals with 5 ppm gold addition.....	51
3.3.4 Leaching of copper-gold samples.....	51
3.4 Experimental Design	52
3.4.1 Preliminary experiments.....	52
3.4.2 Leaching of copper minerals	52
3.4.3 Leaching of copper minerals with 5 ppm gold addition.....	53
3.4.4 Leaching of copper - gold samples.....	53
3.5 Sample Analysis	54
3.5.1 Copper and gold analysis.....	54
3.5.2 Thiosulfate, tetrathionate and sulfate analysis.....	55
4 RESULTS AND DISCUSSION.....	57
4.1 Eh-pH diagrams.....	57
4.2 Preliminary experiments.....	64
4.2.1 Summary.....	69
4.3 Leaching of copper minerals.....	70
4.3.1 Baseline experiments	70
4.3.2 Effect of aeration	82
4.3.3 Summary.....	86
4.4 Leaching of copper minerals with gold addition	87
4.4.1 Baseline experiments	87
4.4.2 Effect of aeration	96
4.4.3 Effect of temperature	100
4.4.4 Effect of reagent addition	103
4.4.5 Gold precipitation.....	107
4.4.6 Summary.....	108

4.5 Leaching of copper-gold samples	110
4.5.1 Overall Lobo Composite	111
4.5.2 Guanaco Composite.....	120
4.5.3 M40 Pyrite Feed	127
4.5.4 M10 Pyrite Concentrate.....	133
4.6 Sulfur balance	140
5 GENERAL SUMMARY AND CONCLUSIONS	146
6 RECOMMENDATIONS	151
7 REFERENCES	154
Appendix A: Screen analysis of copper-gold samples	160
Appendix B: Ion Chromatography	163
Appendix C: Thermodynamic data	173
Appendix D: Experimental data	174
Appendix E: Cyanidation procedures	182
Appendix F: Sulfate determination.....	186

LIST OF TABLES

Table 2.A Standard reduction potentials for gold in aqueous solution]	7
Table 2.B Stability constants for some gold complexes.....	8
Table 3.A Composition of copper mineral samples for testwork.....	43
Table 3.B Composition copper-gold concentrate and ore samples	44
Table 3.C P_{80} of the copper-gold samples.....	46
Table 3.D Overview of experiments with copper minerals	52
Table 3.E Overview of experiments with copper minerals and gold addition	53
Table 3.F Overview of experiments with copper-gold samples	54
Table 4.A Copper extractions (%) of copper minerals at different times during baseline experiments.....	109
Table 4.B Results of 24 hour cyanide leach of the copper-gold samples.....	111
Table 4.C Gold and copper extraction (%) of Overall Lobo Composite at different times.....	119
Table 4.D Gold and copper extraction (%) of Guanaco Composite at different times.....	126
Table 4.E Gold and copper extraction (%) of M40 Pyrite Feed at different times.....	132
Table 4.F Gold and copper extraction (%) of M10 Pyrite Concentrate at different times.	140
Table A.I Screen analysis of copper-gold samples.....	160

LIST OF FIGURES

Figure 2.1 Eh-pH diagram for the system Au-H ₂ O at 25°C.....	6
Figure 2.2 Eh-pH diagram for the system Cu-H ₂ O at 25°C.....	9
Figure 2.3 Eh-pH diagram for the system S-H ₂ O at 25°C	10
Figure 2.4 Eh-pH diagram for the metastable system S-H ₂ O at 25°C..	11
Figure 2.5 Structure of the thiosulfate ion.....	11
Figure 2.6 Effect of copper concentration and temperature on the dissolution of gold in 0.25 M thiosulfate, 1.0 M NH ₃ , 196 kPa O ₂ , stirring velocity 200 rpm	14
Figure 2.7 Gold-ammonia-thiosulfate-water system at 25°C	22
Figure 2.8 Effect of thiosulfate concentration on the rest potential of gold	22
Figure 2.9 Copper-ammonia-thiosulfate-water system at 25°C.....	23
Figure 2.10 Effect of copper sulfate concentration on gold leaching rate	25
Figure 2.11 Effect of the concentration ratio of ammonia to thiosulfate on gold leaching rate	26
Figure 2.12 The model of electrochemical-catalytical mechanism of ammoniacal thiosulfate leaching of gold	27
Figure 2.13 Oxidation state diagrams for sulfur at several pH values.....	28
Figure 2.14 Effect of pH/ammonia concentration on thiosulfate decomposition.....	32
Figure 2.15 Eh-pH diagram for the Au-NH ₃ -H ₂ O system at 25°C	33
Figure 2.16 Leach extraction as a function of time on three concentrates of different mineralogy	36
Figure 3.1. Schematic diagram of the experimental set-up.	48
Figure 4.1. Eh-pH diagram of the gold-thiosulfate-ammonia-water system at 25°C	59
Figure 4.2 Eh-pH diagram of the gold-thiosulfate-ammonia-water system at 25°C	60
Figure 4.3 Eh-pH diagram of the copper-thiosulfate-ammonia-water system at 25°C.....	62
Figure 4.4 Eh-pH diagram of the copper-thiosulfate-ammonia-water system at 25°C.....	63
Figure 4.5 Eh-pH diagram of the copper-ammonia-water system at 25°C.....	64
Figure 4.6. Covellite, 5 g/L copper, 0.1 M S ₂ O ₃ , 0.47 M NH ₃ , pH 9.5, aeration, 35°C.....	67
Figure 4.7 Covellite, 5 g/L copper, 0.20 M (NH ₄) ₂ S ₂ O ₃ , aeration, 35°C	71
Figure 4.8 Chalcocite, 5 g/L copper, 0.20 M (NH ₄) ₂ S ₂ O ₃ , aeration, 35°C.....	72
Figure 4.9 Chalcopyrite, 5 g/L copper, 0.20 M (NH ₄) ₂ S ₂ O ₃ , aeration, 35°C	73

Figure 4.10 Enargite, 1 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	74
Figure 4.11 Cuprite, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	75
Figure 4.12 Malachite, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	76
Figure 4.13 Chalcocite, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no aeration, 35°C	83
Figure 4.14 Cuprite, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no aeration, 35°C	84
Figure 4.15 Covellite, 5 ppm gold, 1 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	88
Figure 4.16 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	90
Figure 4.17 Chalcocite, 5 ppm gold, 1 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	92
Figure 4.18 Chalcopyrite, 5 ppm gold, 1 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	93
Figure 4.19 Enargite, 5 ppm gold, 1 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	94
Figure 4.20 Cuprite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	95
Figure 4.21 Malachite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C	97
Figure 4.22 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no aeration, 35°C	98
Figure 4.23 Cuprite, 5 ppm gold, 1 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no aeration, 35°C	99
Figure 4.24 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 20°C	101
Figure 4.25 Cuprite, 5 ppm gold, 1 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 20°C	102
Figure 4.26 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 0.05 M SO_3^{2-} , aeration, 35°C	104
Figure 4.27 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 0.05 M SO_4^{2-} , aeration, 35°C	105
Figure 4.28 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 0.4 M NH_3 , aeration, 35°C	106
Figure 4.29 Effect of dilution factor on detected thiosulfate concentration	108
Figure 4.30 Overall Lobo Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35°C	113
Figure 4.31 Overall Lobo Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35°C, reground.	114
Figure 4.32 Overall Lobo Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, no aeration, 35°C	115
Figure 4.33 Overall Lobo Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no cupric addition, aeration, 35°C	116

Figure 4.34 Overall Lobo Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no cupric addition, aeration, 35°C, duplicate.....	117
Figure 4.35 Guanaco Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35°C	121
Figure 4.36 Guanaco Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, no aeration, 35°C	122
Figure 4.37 Guanaco Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no cupric addition, aeration, 35°C	123
Figure 4.38 Guanaco Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ (Thiogold™ grade), 1 g/L cupric addition, aeration, 35°C	125
Figure 4.39 M40 Pyrite Feed, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35°C	128
Figure 4.40 M40 Pyrite Feed, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, no aeration, 35°C	129
Figure 4.41 M40 Pyrite Feed, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no cupric addition, aeration, 35°C	130
Figure 4.42 M40 Pyrite Feed, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no cupric addition, no aeration, 35°C	131
Figure 4.43 M10 Pyrite Concentrate, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35°C	134
Figure 4.44 M10 Pyrite Concentrate, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, no aeration, 35°C	135
Figure 4.45 M10 Pyrite Concentrate, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, no aeration, 35°C, 24 hours.....	136
Figure 4.46 M10 Pyrite Concentrate, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no cupric addition, aeration, 35°C	137
Figure 4.47 M10 Pyrite Concentrate, 0.72 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35°C	139
Figure 4.48 Ion Chromatograms of the AS4A column representing the sulfate concentration at different times during the leaching of 1g/L Chalcocite with 5 ppm gold addition.....	142
Figure 4.49 Ion Chromatograms of the Omnipax column showing (from left to right) thiosulfate, trithionate and tetrathionate at different times during the leaching of 1g/L chalcocite with 5 ppm gold addition	143
Figure A.1 Particle size distribution of Overall Lobo Composite	161
Figure A.2 Particle size distribution of Guanaco Composite	161
Figure A.3 Particle size distribution of M40 Pyrite Feed	162
Figure A.4 Particle size distribution of M10 Pyrite Concentrate	162

Figure D.1 (a) Diagram showing the separation of a mixture of components A and B by column elution chromatography. (b) The output of the signal detector at the various stages of elution shown in (a)	164
Figure D.2 Chromatogram of the AS4A column.....	165
Figure D.3 Chromatogram of the Omnipax column.....	166

LIST OF SYMBOLS

E^0 Standard potential versus a reference electrode, V

F Faraday constant; 96500 C/mol

ΔG_f^0 Standard free energy of formation; kJ/mol

ΔG^0 Standard free energy change; kJ/mol

K_{stab} Stability constant

M Molarity, mol/L

R Ideal gas constant; 8.314 J/mol K

T Temperature; K

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1 INTRODUCTION

Cyanide leaching is the conventional method used to extract gold from ores; it is economical, biodegradable and achieves excellent recoveries from a wide range of ores [Michaelis, 1987]. However, the use of lixiviants other than cyanide for gold recovery is a subject that has received considerable attention in the past few years. There are two reasons for this increased interest:

- 1) Potential environmental restraints on the use of cyanide in some areas;
- 2) Poor leaching characteristics of some ore-bodies to cyanidation, the so-called refractory ores.

Refractory ores are not amenable to cyanide treatment due to the presence of impurities (such as copper, arsenic, antimony, tellurium, and manganese), sulfide or silicate encapsulation or preg-robbing characteristics, which cause unsatisfactory gold recovery and high cyanide consumption. Refractory ore-bodies are becoming an increasingly important source of gold, because of the decreasing supply of ores which are amenable to cyanide treatment.

The application of other lixiviants for gold recovery, such as thiourea, chloride, bromide, and ammonium thiosulfate has been extensively researched in the last few years. These lixiviants would be particularly attractive if they improve the gold recovery or result in a savings in reagent cost [Michaelis, 1987]. Ideally the lixiviant is cheap or recyclable, selective, non-toxic, and compatible with down-stream recovery processes [Avraamides, 1982]. In practice, meeting all these criteria is difficult.

Thiosulfate has the ability to complex gold and silver. Moreover, ammonium thiosulfate has been used for many decades as a fertilizer and consequently, from an environmental standpoint,

has a definite advantage over cyanide [Atluri, 1987]. Comparing reagent unit costs, ammonium thiosulfate is far cheaper than sodium cyanide (US \$0.13/kg vs. US \$1.80/kg). Consequently, with similar or even slightly higher lixiviant consumption, the application of thiosulfate for gold recovery can be economical and compete directly with cyanidation.

The ammonium thiosulfate system has three indispensable components: thiosulfate, ammonia and copper ions. Thiosulfate stabilizes gold in solution, while copper and ammonia accelerate the leach reaction. Research into the ammonium thiosulfate system for gold recovery has shown that the chemistry is complex and not yet fully understood. Another complication of the system is that thiosulfate is prone to degradation. Thiosulfate is a metastable sulfur species which will eventually decompose in aqueous solutions.

Ammonium thiosulfate has been proposed for the treatment of refractory gold ores in which carbon components are intimately associated with the gold, the carbonaceous ores. The carbonaceous matter in the ore adsorbs the solubilized gold complexes from the leach solutions back into the ore and thus reduces gold extraction. Several patents [Kerley, 1981, 1983; Perez and Galaviz, 1987; Wan et al, 1994; Marchbank et al, 1996] describe a process development that uses an ammonium thiosulfate leach solution containing copper as a catalyst for gold recovery. A soluble gold-thiosulfate complex is formed, which is not adsorbed by the carbon content of the ore. Gold can then be recovered from solution by several methods including cementation by zinc or copper and ion exchange methods.

Copper-gold ores form another type of refractory gold ore. Large quantities of this ore type are available for processing. Cyanide treatment of ores with a high cyanide soluble copper to gold ratio results in unfavourable economics due to high cyanide consumption resulting from the formation of copper-cyanide complexes.

The objective of this work is to investigate the application of ammonium thiosulfate for the leaching of copper-gold ores. Ammonium thiosulfate is particularly attractive as an alternative to cyanide for the treatment of copper-gold ores; the presence of copper is desired in a thiosulfate leach, whereas it is detrimental in a cyanide leach. Moreover, copper leaching may occur at the same time as gold is leached, provided enough lixiviant (thiosulfate and ammonia) is available, and thus gold and copper may be recovered. At the moment copper recovery from a cyanide leach solution has not found wide commercial application.

To study the application of ammonium thiosulfate for the treatment of copper-gold ores an experimental program consisting of three different sets of experiments was performed. First, the leaching behaviour of sulfide (chalcocite, covellite, chalcopyrite and enargite) and oxide (cuprite and malachite) copper minerals in the ammonium thiosulfate system was studied. It has been reported that copper plays a catalytic role during a thiosulfate leach, however, no information is available regarding the leaching of copper minerals in an ammonium thiosulfate solution.

To observe the behaviour of gold in combination with the copper minerals, gold was added to the leach solutions in a second set of experiments. The experimental program was completed by subjecting several copper-gold concentrates of different copper and gold grades to the

ammonium thiosulfate system. Special attention is given to the behaviour of thiosulfate during the different experimental sets, in order to gain an understanding of the leach reactions taking place.

This thesis contains five chapters. The second chapter gives a review of existing literature on the ammonium thiosulfate system for gold recovery, and a brief background on ammonia technology for the recovery of copper and gold. The experimental methods are described in chapter three, followed by a discussion of the experimental results in chapter four. The summary and conclusions are presented in chapter five, followed by the recommendations in the final chapter.

2 LITERATURE REVIEW

The chemistry of the ammoniacal thiosulfate system for gold recovery involves many interrelated chemical equilibria which are not yet fully understood. This complexity can be attributed to the presence of three essential components which define the ammoniacal thiosulfate leaching environment: ammonia, thiosulfate and copper. Many reactions may occur between these species, dissolved metal ions, atmospheric gases and ore minerals.

This chapter gives a brief review of the aqueous chemistry of copper and gold, followed by a summary of the research conducted over the years in the field of ammonium thiosulfate leaching for the recovery of gold. Some background is also given regarding the recovery of gold from thiosulfate solutions. The chemical reactions involved in ammonium thiosulfate leaching and the degradation of thiosulfate are discussed next.

Ammonia, itself, is an important lixiviant for copper recovery and research has been conducted on the recovery of gold with ammonia. Both topics are discussed briefly. The chapter ends with a summary of the presented literature.

2.1 Aqueous Chemistry

2.1.1 Gold-water system

Gold occurs in two oxidation states, as +1 (aurous) and +3 (auric) in aqueous solutions. As can be seen in Figure 2.1, the Eh-pH diagram of the gold-water system shows no area of stability of Au^{3+} relative to water, i.e. the standard reduction potential for Au^{3+}/Au is greater than

the upper stability limit of water (Equation (II.1) and (II.3)) [Bard et al, 1985]. The value of the standard reduction potential for Au^+/Au is even larger (Equation (II.2)) which makes this ionic species even less stable in water (the dashed lines delineate the stability limits of water).

Figure 2.1 Eh-pH diagram for the system Au-H₂O at 25°C. The activity of soluble gold species is 10⁻⁴.

As predicted by the Nernst equation for Au^+ (Equation II.4), a decrease in the activity of free gold ions will lead to a lowering of the standard reduction potential.

$$E = 1.83 + 0.059 \log[\text{Au}^+] \quad (\text{II.4})$$

Complexing the dissolved gold ions with ligands such as cyanide or thiosulfate therefore results in a dramatic lowering of the reduction potentials (see Table 2.A).

Table 2.A Standard reduction potentials for gold in aqueous solution, [Bard et al, 1985]

Ligand	$E^\circ, \text{Au}^+/\text{Au}$ (Volts)	$E^\circ, \text{Au}^{3+}/\text{Au}$ (Volts)
H_2O	+1.83	+1.52
Cl^-	+1.154	+1.002
Br^-	0.960	0.854
I^-	0.578	0.56
NH_3	$+0.563 \pm 0.006$	$+0.325 \pm 0.003$
$\text{S}_2\text{O}_3^{2-}$	ca. +0.153	ca. +0.10*
CN^-	-0.595 ± 0.002	-0.50*

*Avraamides [1982]

From Table 2.A it can be concluded that all the ligands listed form water-stable complexes with gold, i.e. the resulting standard reduction potentials are below that of water.

Therefore, from a thermodynamic viewpoint there are two basic requirements for a successful leaching system for gold [Avraamides, 1982]:

1. The presence of an oxidizing agent;
2. The presence of a suitable complexing ligand.

Some stability constants associated with these gold complexes are shown in Table 2.B.

Table 2.B Stability constants for some gold complexes [Avraamides, 1982]

Au⁺		Au³⁺	
Complex	K_{stab.}	Complex	K_{stab.}
Au(CN) ₂ ⁻	2 x 10 ³⁸	Au(CN) ₄ ⁻	ca. 10 ⁵⁶
Au(S ₂ O ₃) ₂ ³⁻	5 x 10 ²⁸	AuI ₄ ⁻	5 x 10 ⁴⁷
AuI ₂ ⁻	4 x 10 ¹⁹	AuBr ₄ ⁻	10 ³²
AuBr ₂ ⁻	10 ¹²	AuCl ₄ ⁻	10 ²⁶
AuCl ₂ ⁻	10 ⁹		

From this data, ligands for complexing gold may be chosen, which, when combined with a suitable oxidant, could form a successful leaching system. Then, parameters such as kinetics, selectivity, reagent stability and reagent consumption need to be determined to assess the applicability of the system.

2.1.2 Copper-water system

In the absence of complexing substances, copper is a relatively noble metal. Copper can exist in oxidation states of +1 (cuprous) and +2 (cupric) in aqueous solutions. Copper forms a large number of complexes [Atluri, 1987]:

- for the +1 valency complexes with Cl⁻, CN⁻, NH₃ and S₂O₃²⁻, which are colorless;
- for the +2 valency the yellow CuCl⁺ complexes, the intense blue ammine complexes and the brown complexes with SCN⁻.

Figure 2.2 Eh-pH diagram for the system Cu-H₂O at 25°C. The activity of soluble copper species is 10⁻⁴.

The Eh-pH diagram for the copper-water system is presented in Figure 2.2. The equilibrium constant for the disproportionation reaction in water

is 10⁶ (at 25°C) and therefore only small amounts of Cu⁺ can exist unless it is stabilized by complexing agents [Baes and Mesmer, 1976]. The only significant hydrolysis product of Cu⁺ is Cu₂O, which has a low solubility. Cu₂S is very insoluble ([Cu⁺]² [S²⁻] = 10⁻⁴⁹) and will likely form in a reducing environment in the presence of sulfide [Baes and Mesmer, 1976].

The Cu²⁺ ion at practical concentrations begins to hydrolyze above pH 4 and precipitates as oxides or hydroxides soon thereafter, i.e. solution hydrolysis occurs to a slight extent at moderate concentrations before precipitation occurs [Atluri, 1987].

Copper complexes with NH_3 are notably stable (Equation (II.6) and (II.7)) [Sillén, 1971].

Other copper(II)ammonia complexes form in addition to the ones given in Equation (II.6) and (II.7). However, these will not dominate in the pH range of interest (pH 9 to 10).

2.1.3 Thiosulfate

The Eh-pH diagram of the sulfur-water system demonstrates that thiosulfate has no dominant region in aqueous solution (Figure 2.3). It is only when sulfate formation is omitted in the construction of the Eh-pH diagram for the sulfur-water system, that the metastable sulfur species appear (Figure 2.4).

Figure 2.3 Eh-pH diagram for the system S- H_2O at 25°C. The activity of sulfur species is 0.4.

Figure 2.4 Eh-pH diagram for the metastable system S-H₂O at 25°C. The activity of sulfur species is 0.4 M (ΔG_f° (S₂O₃²⁻) = -518.8 kJ/mol).

Thiosulfates are compounds containing the group S₂O₃²⁻ which is a structural analog of sulfate with one oxygen atom replaced by a sulfur atom. The two sulfur atoms are not equivalent (Figure 2.5).

Figure 2.5 Structure of the thiosulfate ion [Kirk Othmer, 1983]

The unique chemistry of the thiosulfate ion, S₂O₃²⁻ or SSO₃²⁻, is dominated by the sulfide-like sulfur atom which is responsible for the reducing properties and complexing abilities of thiosulfates [Kirk-Othmer, 1983].

Chemical properties of thiosulfate include:

- I. Tendency to be oxidized (by O_2 , Cu^{2+} etc., see section 2.3.3)
- II. Tendency to hydrolyse at $pH < 5.5$
 - A. to S^0 and HSO_3^{2-} at mildly acid pH [Skoog and West, 1976]
 - B. to more complex mixtures in strong acid [Smith and Hitchen, 1976]
- III. Relative hydrolytic stability in basic solution [Pryor, 1960]
- IV. Thiosulfate forms complex ions with a variety of metals, e.g. gold, silver, copper (Cu^+ and Cu^{2+}), iron (Fe^{3+}) etc. [Burns et al, 1981]. The stability of these complexes depend on the solution conditions.
- V. Formation of metal sulfides, e.g. with copper, silver, mercury [Burns et al, 1981]
- VI. Reductive stability toward reduction to free sulfide or sulfur; the E^0 of Equation (IV.8) is $-0.643 V_{SHE}$

The best known reaction of thiosulfate is its oxidation to tetrathionate ($S_4O_6^{2-}$) by iodine, which is widely used in analytical chemistry. The two most important salts of thiosulfate are sodium thiosulfate, $Na_2S_2O_3$ or $Na_2S_2O_3 \cdot 5H_2O$, and ammonium thiosulfate, $(NH_4)_2S_2O_3$. The latter one was used for this research.

2.2 Overview of Thiosulfate Technology for Gold Recovery

2.2.1 Thiosulfate leaching for gold extraction

The use of thiosulfate for the recovery of precious metals was first proposed in the 19th century and is known as the “Patera Process”. It was applied in 1858 by Von Patera for silver recovery. The process utilizes the solubility of silver chloride in a solution of sodium thiosulfate. The ore was treated by a chloridizing roast followed by a sodium thiosulfate leach. Sodium sulfide was used to precipitate silver sulfide [Liddell, 1945].

Berezowsky and Gormely [1978] revived the interest in the thiosulfate leaching system for precious metals recovery by developing an atmospheric ammoniacal thiosulfate leach system to recover gold and silver from ammoniacal oxidative pressure leach residues of sulfidic copper concentrates. The residues were comprised predominantly of hydrated ferric oxides and unleached sulfides. Extractions of 88-95% for gold and 83-98% for silver were achieved after 2 to 4 hours leaching with 0.4 to 0.8 M $S_2O_3^{2-}$ at 40 to 60°C. The parameters affecting the gold solubilization were thiosulfate, ammonia and cupric ion concentrations, temperature, and residence time. To minimize oxidation of the thiosulfate leach conditions initial testwork was performed under a nitrogen atmosphere.

In some experiments, a decrease in gold extraction with time was observed. Berezowsky and Gormely [1978] attributed this phenomenon to thiosulfate degradation; thiosulfate decomposition in the presence of copper causes the precipitation of copper sulfide which coats the gold particles and thus inhibits gold leaching and recovery. Therefore, an optimal leach time exists; the leach time should not be needlessly prolonged.

A direct thiosulfate leaching test was performed on a chalcopyrite concentrate with 3 to 5 g/L Cu^{2+} addition and mild air sparging. A gold extraction of 97% was obtained after 1 hour. Analysis of the leach liquors for thiosulfate indicated that 90-95% of the thiosulfate was accounted for and could be recycled [Berezowsky and Sefton, 1979].

The dissolution of metallic gold in ammoniacal thiosulfate solution containing copper ions was investigated by Tozawa et al [1981]. The experiments were conducted in an autoclave under various conditions. The following results were reported (Figure 2.6):

1. In the absence of $\text{Cu}(\text{NH}_3)_4^{2+}$ the kinetics of dissolution of gold are very slow.
2. At leaching temperatures between 65 to 100°C the dissolution of gold is inhibited by the formation of a copper sulfide coating.
3. Vigorous stirring and high temperature (>140°C) decrease the gold dissolution due to excessive oxidation of thiosulfate ions.

Figure 2.6 Effect of copper concentration and temperature on the dissolution of gold in 0.25 M thiosulfate, 1.0 M NH_3 , 196 kPa O_2 , stirring velocity 200 rpm, [Tozawa et al, 1981]

The same authors also investigated the effect of oxygen partial pressure on the dissolution of gold in thiosulfate medium. Maximum gold dissolution occurred at 98 kPa oxygen partial pressure. At higher oxygen pressures the dissolution of gold decreased because of thiosulfate oxidation.

Kerley [1981,1983] patented a process for the recovery of precious metals from refractory ores, particularly those containing manganese and/or copper, by lixiviation using an ammonium thiosulfate leach solution. The patent claims to improve upon the thiosulfate leaching of the patent of Berezowsky and Gormely [1978] by providing better control of the stability of the thiosulfate ion (see section 2.3.3).

The leach solution contains 1.2 to 1.35 M $S_2O_3^{2-}$, 1 to 4 g/L Cu^{2+} , sufficient ammonia to maintain a pH of 7.5 or higher, and a minimum of 0.05% sulfite ions to control the stability of the solutions during leaching. Kerley [1981] claims that sulfite ions inhibit the decomposition of thiosulfate according to Equation (II.9) and thus prevent precipitation of metal sulfides.

This reaction is however unlikely to occur at pH 7.5, since the sulfide ion is not stable in this pH region (see Figure 2.4 and section 2.3.3). The precious metals can be recovered by conventional methods, such as cementation or electrolysis.

The process patented by Kerley was carried out in a plant in Mexico, but the scale-up from laboratory to plant-size failed. Perez and Galaviz [1987] describe the modifications required to

make plant operation feasible. The most important process adjustment was the pH value which should be maintained at a minimum level of pH 9.5, instead of 7.5 as suggested by Kerley [1981].

This higher pH inhibits the action of substantial amounts of metallic iron and ferric salts that are present in the lixiviating solution as a result of grinding the ore in a ball mill prior to lixiviating. According to Perez and Galaviz [1987] the ferric ion accelerates the oxidation of thiosulfate to tetrathionate (Equation II.10) which has no lixiviating action on gold or silver.

The ferrous ion displaces silver and gold from solution according to:

At high pH (9.5 and higher) ammonia hydrolysis produces hydroxide ions which react with the ferrous ions according to Equation (II.12) and (II.13), thus preventing iron from displacing silver and gold from solution.

Zipperian and Raghavan [1988] identified the parameters of importance in the dissolution of gold and silver values from a rhyolite ore with a high manganese content using ammoniacal thiosulfate solutions containing copper. The effect of thiosulfate, ammonia concentration, temperature, and copper sulfate addition was researched. Optimum conditions were established at 2 M $\text{S}_2\text{O}_3^{2-}$, 4.1 M NH_3 , 6 g/L Cu^{2+} , 50°C, and 2 hours leaching in the absence of oxygen.

In the absence of cupric ions only 14% gold was solubilized. Initial rates of gold extraction were enhanced by increasing cupric ion concentration, but the ultimate extraction was not influenced by the cupric ion concentration in the range investigated (up to 6 g/L Cu). Further, it was concluded that maintaining optimal pH and Eh conditions (pH 10 and 200 mV) are necessary to prevent precipitation of copper as Cu_2S . Half of the thiosulfate in the lixiviant solution at pH 9.5-10 was reported to be consumed during the dissolution process.

The consumption of the reagents and the recycling of the lixiviant over a long period of time was researched by Gong and Hu [1990]. It was reported that the consumption of thiosulfate depends on the amount of air used, the temperature, agitation and configuration of the reactor. If these variables are optimized the lixiviant solution can be recycled and the losses are minimal. However, details regarding agitation and reactor configuration are not described. Over 95% gold extraction was achieved under the conditions of 0.8 to 1M $\text{S}_2\text{O}_3^{2-}$, 1.8 to 2.2 M NH_3 , 0.1 M Na_2SO_3 , 1 g/L Cu^{2+} , 40°C, 1.5 hours and an oxygen atmosphere. The pH was adjusted to 10.

Hemmati et al [1989] studied the application of ammoniacal thiosulfate leaching for gold recovery on various types of ores. It was found that the highest gold extractions were achieved at 0.7 M $\text{S}_2\text{O}_3^{2-}$, 3 M NH_3 , pH of 10.5, 35°C (over the range of 25 to 85°C) and an oxygen partial pressure of 103 kPa. Gold extraction of 73% was accomplished under these conditions. No impact was found on either gold extraction or thiosulfate consumption by variation of the oxygen pressure in the range of 0 to 206 kPa. Hemmati et al [1989] reported that the efficiency of thiosulfate leaching depends upon ore type. For treating carbonaceous ores, thiosulfate was found to be chemically superior and economically advantageous over cyanide.

Langhans et al [1992] focused on maximizing gold extraction while minimizing thiosulfate consumption at low reagent concentrations and ambient temperatures and a pH between 9 and 11. The range of the thiosulfate concentration tested was 0.05 to 0.2 M. The research was conducted on low-grade oxidized gold ores with application to heap, dump, or in-situ leaching techniques and found to be competitive with conventional cyanidation. After leaching for 48 hours, 83% gold extraction was achieved with 0.2 M $S_2O_3^{2-}$, 0.09 M NH_4OH , 0.00625 M Na_2SO_3 , 63.5 ppm Cu^{2+} with 0.4 kg $S_2O_3^{2-}$ consumed per tonne of ore. Langhans et al [1992] concluded that these results compare favorably with 86% gold extraction after 24 hours with 0.21 kg CN⁻ consumed per tonne of ore using standard cyanidation methods.

The effectiveness of low thiosulfate concentrations was confirmed by Cao et al [1992], who studied the effects of the concentrations of thiosulfate, copper and ammonia on the extraction of gold and silver from a sulfide concentrate. Leaching was performed with a 0.2 M thiosulfate solution at 2 hours retention time which yielded 95% gold extraction. The sparge air was treated with ammonia in order to keep the ammonia concentration constant. Cao et al [1992] also researched the influence of sulfate addition to the system, in order to reduce the thiosulfate consumption, but found no effect (see section 2.3.3).

Wan et al [1994] patented a process using a thiosulfate lixiviant for the treatment of carbonaceous gold ores on a heap leach without applied pre-treatment. The pH of the solution should be in the range of 9 to 10 with a thiosulfate concentration of 0.1-0.2 M.

Newmont Gold Company evaluated the application of ammonium thiosulfate on a demonstration heap leach of 327,000 metric tonnes of low-grade carbonaceous sulfidic ore that was pretreated by bio-oxidation. The average gold recovery for thiosulfate heap leach at a particle size of minus 1.9 cm was found to be approximately 55 per cent. Ammonium thiosulfate consumption was about 5 kg/tonne for low sulfide carbonaceous ores (without bio-oxidation) and 12-15 kg/tonne for bio-oxidised ores. Typical leach solutions used contained 0.1 M $\text{S}_2\text{O}_3^{2-}$, 0.1 M NH_3 and 30 ppm Cu^{2+} [Wan, 1997]. Construction started for a commercial size heap leach operation, but was halted due to the current low gold price.

The application of a thiosulfate salt lixiviant to recover gold from an oxidative pressure leach slurry is described in a patent granted to Marchbank et al [1996]. An ore slurry of refractory sulfidic and refractory carbonaceous ore is subjected to pressure oxidation in an autoclave under neutral or alkaline conditions followed by leaching with a thiosulfate salt in stirred tank reactors. Typical leaching conditions are 0.025 to 0.1M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 50 to 100 ppm Cu^{2+} , 40 to 55°C and a minimum sulfite concentration of 0.001 M, while maintaining a pH between 7 and 8.7.

2.2.2 Gold recovery from thiosulfate solutions

Process options for the recovery of gold from thiosulfate solutions are:

- Cementation
- Carbon adsorption
- Direct electrowinning
- Reductive precipitation
- Ion exchange
- Solvent extraction

Most researchers report the application of cementation for the recovery of gold from thiosulfate solutions [Berezowsky and Sefton, 1979; Kerley, 1983; Perez and Galaviz, 1987; Wan et al, 1994; Marchbank et al, 1996]. Suggested precipitants are zinc, copper, aluminum, iron or soluble sulfides. The use of copper as precipitant is preferred since it enables the precipitation of gold without also causing precipitation of copper from the lixiviant solution.

Gallagher [1987] found that activated carbon has a very low affinity for the gold(I)thiosulfate complex. McKee and Lulham [1991] reported that gold was effectively recovered by the addition of a near stoichiometric amount of cyanide to the leach solution, enabling the recovery of the gold cyanide complex by activated carbon or an anion exchange resin.

The direct electrowinning of a gold thiosulfate leach solution onto a steel cathode at 40°C was investigated by Abbruzzese et al [1995]. The kinetics of electrowinning were reported to be fast and the precious metal recovery was quantitative (99%). No qualitative information was given. The current efficiency was 4% due to the concurrent parasitic reactions at the electrodes (oxygen evolution at the anode and reduction of water and dissolved oxygen at the cathode).

Awadalla and Ritcey [1991] reported the use of sodium borohydride for the reduction of gold and silver in acidic solutions of thiosulfate. Complications of this process option are: low pH (around 6) and Cu^{2+} ions decrease the efficiency of borohydride.

Atluri [1987] studied the use of three anion exchange resins (Amberlite IRA-400, Amberlite IRA-68 and Amberlite IRA-94) for the selective recovery of gold and silver from simulated

thiosulfate leach liquors containing copper, gold and silver. All the three resins investigated were not selective to silver and gold over copper. Another process option mentioned is solvent extraction [Marchbank et al, 1996]. However, no literature was found which covered the selective extraction of gold from a thiosulfate solution.

This brief review of recovery methods indicates that the recovery of gold from thiosulfate solutions is not easily accomplished, and offers opportunities for more research.

2.3 Chemistry of the Ammonium Thiosulfate System

This section reviews some fundamental aspects of the ammonium thiosulfate system: thermodynamics, copper catalysis and the degradation pathways of thiosulfate.

2.3.1 Thermodynamic considerations

Thermodynamically, the ammonium thiosulfate system is not stable. Both ammonia and thiosulfate will be lost through escape or decomposition. Therefore, true equilibrium diagrams cannot be constructed for this system. By omitting the more stable species such as sulfate ions from the system, the features of the metastable species can be examined (see Figure 2.4). The species considered are: NH_4^+ , NH_3 , $\text{S}_2\text{O}_3^{2-}$, S^0 , $\text{S}_x\text{O}_6^{2-}$ ($x \geq 2$), SO_3^{2-} , HSO_3^{2-} . The stability of the thiosulfate ion will be discussed in section 2.3.3.

The Eh-pH diagram for the gold-ammonia-thiosulfate-water system at 25°C is presented in Figure 2.7.

Figure 2.7 Gold-ammonia-thiosulfate-water system at 25°C, Activity of species: 0.1 M thiosulfate, 0.1 M ammonia, 5×10^{-4} M gold [Li et al, 1995]

According to Figure 2.7, under alkaline conditions ($\text{pH} > 9$), $\text{Au}(\text{NH}_3)_2^+$ is expected to be the most stable gold species. However, rest potential measurements performed by Li et al [1996] suggest that the predominant gold species is $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ since the gold rest potentials varied with thiosulfate concentrations and not with ammonia concentrations (in the range of 0 to 0.5 M NH_3) (Figure 2.8).

Figure 2.8 Effect of thiosulfate concentration on the rest potential of gold [Li et al, 1996]

The half-cell reaction for gold thiosulfate is:

It can be noted from Figure 2.7 that gold remains in the metallic state if potentials are too low throughout the pH range of 6-12. Thus thermodynamics predicts that potentials exceeding 0.05 V_{SHE} are required for gold leaching.

Figure 2.9 shows that copper(I)thiosulfate is the predominant species in solution at most common potentials and appears to be in equilibrium with copper(II)ammine (see section 2.3.2). Thus the excess copper(I)thiosulfate ions will be converted back to copper(II)ammine ions to maintain the equilibrium as dictated by potential [Li et al, 1996]. At low potentials and high pH, the decomposition of thiosulfate may lead to the precipitation of copper sulfides.

Figure 2.9 Copper-ammonia-thiosulfate-water system at 25°C, 0.1 M thiosulfate, 0.1 M ammonia, 5×10^{-4} M copper [Li, 1995]

2.3.2 Copper catalysis

The rate of gold leaching in an ammoniacal thiosulfate solution is enhanced greatly by a catalytic copper reaction [Berezowsky and Sefton, 1979, Zipperian et al, 1988, Tozawa et al, 1981]. However, conflicting opinions exist on the exact role of the copper in the leach chemistry.

Agreement does exist concerning the dissolution reaction of gold in thiosulfate solutions in the presence of oxygen (Equation II.15).

The above reaction can be modified to incorporate the influence of the catalytic action of the cupric ion during gold dissolution [Li et al, 1995; Marchbank et al, 1996]]:

Copper minerals in some ores can act as a source of cupric ion or copper sulfate may be added to the leach solutions. The appropriate copper half cell reaction is:

Li et al [1996] states that oxygen in the absence of a catalyst may be an oxidant for gold leaching, but with much slower kinetics. It was found that in the absence of copper, the gold leaching rate in ammonium thiosulfate becomes negligible (Figure 2.10).

Figure 2.10 Effect of copper sulfate concentration on gold leaching rate [Li et al, 1996]

At low copper levels, an increase in the copper concentration results in a dramatic rise in the gold dissolution rate. However, too high copper concentrations significantly inhibit gold leaching. Li et al [1996] explained this by a deficiency of lixiviant for complexing gold, because the copper combines with most of the ammonia and thiosulfate in solution. Furthermore, thiosulfate degradation is accelerated by high copper concentrations (see section 2.3.3). Either way, loss of reactants results in slower leaching kinetics.

It is evident from Equation (II.17) that to enable the regeneration of the cupric ion, it is necessary to keep the concentration ratio of ammonia to thiosulfate in a certain range. Increasing the concentration of only one of the ligands will have a limited positive effect on the gold leaching process. However, this may have a negative effect, as an excess of either ammonia or thiosulfate may make the reaction depicted in Equation (II.17) less reversible [Li et al, 1996]. This effect is illustrated in Figure 2.11.

Figure 2.11 Effect of the concentration ratio of ammonia to thiosulfate on gold leaching rate [Li, 1996]

Jiang et al [1993] proposed a model for gold dissolution in ammoniacal thiosulfate solutions on the basis of electrochemical investigations (Figure 2.12). According to this study, ammonia preferentially complexes gold, and the $\text{Au}(\text{NH}_3)^+$, which forms at the anodic surface then reacts with $\text{S}_2\text{O}_3^{2-}$ and is converted to the more stable $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$. The $\text{Cu}(\text{NH}_3)_4^{2+}$ gains an electron at the cathodic surface and is reduced to $\text{Cu}(\text{NH}_3)_2^+$ which is then oxidized by oxygen into $\text{Cu}(\text{NH}_3)_4^{2+}$ after entering the bulk solution.

In this model, a prominent role is ascribed to oxygen in the system, and the effect of the ratio of ammonia to thiosulfate does not seem to play a role on the regeneration of the cupric ion. This is in contradiction to the observations of Li et al [1996]. The two models display the complexity of the ammonia thiosulfate leaching system and the need for more fundamental research.

Figure 2.12 The model of electrochemical-catalytical mechanism of ammoniacal thiosulfate leaching of gold [Jiang et al, 1993]

2.3.3 Thiosulfate degradation reactions

The variables affecting the stability of thiosulfate solutions are [Skoog and West, 1976]

- pH;
- The presence of microorganisms and redox catalysts;
- The concentration of the solution;
- The presence of oxygen;
- Exposure to sunlight.

Experiments indicate that in the absence of strong oxidants or catalysts, the stability of thiosulfate solutions is at a maximum in the pH range between 9 and 10 [Skoog and West, 1976]. Bacterial activity appears to be at a minimum at this pH, which explains the maximum stability in this pH region since bacterial activity is reported to be the most prominent cause of instability.

Thiosulfate decomposition is catalyzed by copper(II), and iron(III) ions as well as by the reaction products of the decomposition. Skoog and West [1976] report that the decomposition rate is greater in more dilute solutions.

In the case of oxidative decomposition of thiosulfate, sulfur may exist in many different oxy-sulfur species in the +2 or higher oxidation states. These include $S_5O_6^{2-}$ (+2), $S_2O_3^{2-}$ (+2), $S_4O_6^{2-}$ (+5/2), $S_2O_4^{2-}$ (+3), $S_3O_6^{2-}$ (+10/3), SO_3^{2-} (+4), $S_2O_6^{2-}$ (+5), SO_4^{2-} (+6), $S_2O_8^{2-}$ (+7), SO_5^{2-} (+8). Thermodynamically, sulfate is the most stable sulfur species under the preferred leaching conditions (alkaline pH, oxidative potential). This is visible in Figure 2.13, the oxidation state diagram for sulfur at several pH values. By drawing a line between HS^- and SO_4^{2-} at pH 10, it is visible that most sulfur species are unstable (all species lie above the line). The nearest species to the line are S^0 and $S_2O_3^{2-}$ which indicates that relative stability for these species in the pH 10 range.

Figure 2.13 Oxidation state diagrams for sulfur at several pH values [Peters].

Smith and Hitchen [1976] described the oxidation of thiosulfate to tetrathionate in the presence of cupric ion:

or, in basic solution:

Tetrathionate may then decompose according to a variety of pathways, leading to the following stoichiometry for the overall oxidation of thiosulfate via the tetrathionate pathway:

Byerley et al [1973] cited the following reactions to describe the disproportionation of $\text{S}_4\text{O}_6^{2-}$ to higher and lower polythionates:

These reactions will take place at $\text{pH} > 7$ [Smith and Hitchen, 1976]. The trithionate ($\text{S}_3\text{O}_6^{2-}$) species only decomposes under harsh conditions ($\text{pH} > 13$ and boiling) to form thiosulfate and

sulfite. Marsden and House [1992] used Equation (II.26) to explain why $S_2O_3^{2-}$ is relatively stable under basic conditions.

Pryor [1960] showed that $S_2O_3^{2-}$ is relatively stable in basic solution, i.e. in the absence of catalysts. The disproportionation of thiosulfate in water or aqueous buffers at 250-280°C follows Equation (II.27) and is irreversible.

This base hydrolysis was found to be very slow in basic solution, even at 250°C, and sulfite was found not to be an intermediate in the reaction.

According to several authors the addition of sulfite ions (SO_3^{2-}) to an ammoniacal thiosulfate solution has a beneficial effect on the stability of thiosulfate [Kerley, 1981; Perez and Galaviz, 1987; Zipperian et al, 1988; Gong and Hu, 1990]. The sulfite ions react with sulfide as to regenerate thiosulfate and consequently prevent the precipitation of precious metal values with the sulfide ions. Different reactions are proposed to explain this effect:

- Zipperian et al [1988]:

- Gong and Hu [1990]:

- Kerley [1981, 1983], Perez and Galaviz [1987]:

It is questionable that the reactions described in Equation (II.28) to (II.30) take place under typical thiosulfate leaching conditions (around pH 9-10, Eh 150 to 250 mV_{SHE}). Little free sulfide ions and hydrogen sulfide ions will exist at these pH and Eh values (Figure 2.4). Equation (II.30) describes the formation of thiosulfate under acidic conditions. This is unlikely since thiosulfate tends to hydrolyze under acidic conditions [Skoog and West, 1976].

There are a few reactions in which sulfite can participate. An advantage of sulfite addition can be the oxidation of sulfite to sulfate (Equation II.31). When this reaction is kinetically favored over the oxidation of thiosulfate to sulfate, sulfite can improve the stability of thiosulfate in solution.

A further beneficial effect of sulfite addition is described by Wasserlauf and Dutrizac [1982]. Sulfite ions accelerate the decomposition of $\text{S}_x\text{O}_6^{2-}$, $x \geq 4$, in alkaline to mildly acidic solutions. The products are trithionate, thiosulfate and protons. The reaction with tetrathionate is given in Equation (II.24). Also, elemental sulfur may react with sulfite under alkaline conditions, to form thiosulfate (Equation II.32) [Wasserlauf and Dutrizac, 1982]:

Several authors described the substitution of sulfate for sulfite, in order to stabilize thiosulfate [Gong and Hu, 1994; Cao et al, 1992]. Since sulfate is quite stable toward reduction [Burns et al, 1980], no effect of sulfate with respect to thiosulfate degradation would be anticipated.

Li et al [1996] reported the effect of ammonia concentration on thiosulfate degradation. Increasing ammonia concentration increased the rate of thiosulfate decomposition significantly (Figure 2.14). Since this effect is more evident after several days, it is unlikely to play a significant role in stirred tank leaching, but has to be accounted for in heap leach operations. No explanation was given for this phenomena.

Figure 2.14 Effect of pH/ammonia concentration on thiosulfate decomposition [Li et al, 1996].

It can be concluded from the above overview that the exact degradation pathways of thiosulfate are very complex. Many reactions are possible between existing and generated species in solution. The reactions quoted by the literature do not reflect this complexity, and even tend to simplify the reactions taking place. A good example of this simplification is the explanation repeatedly cited in the literature regarding the beneficial effect of sulfite addition.

2.4 Ammonia technology for copper/gold leaching

Leaching of copper using ammonia/ammonium salts has been well established. Up to now ammonia has found no application for the extraction of gold and silver from ores due to the very slow dissolution rate of gold and silver in the absence of proper oxidants, and high temperatures and pressures.

A brief overview of ammonia technology for gold and copper is given, followed by a discussion of relevant chemistry.

2.4.1 Ammonia technology for gold recovery

Gold dissolves in ammonia as the gold(I)ammonia complex, $[\text{Au}(\text{NH}_3)_2]^+$, within the range of water stability over a range of pH values (Figure 2.15). The gold(III)ammonia complex, $[\text{Au}(\text{NH}_3)_4]^{3+}$ is thermodynamically unstable in the region of water stability.

Figure 2.15 Eh-pH diagram for the Au-NH₃-H₂O system at 25°C. Activity of ions is 10⁻⁴; NH₃=1.0 M [Meng and Han, 1993]

The dissolution of gold is thermodynamically feasible at room temperature. However, kinetic experiments showed that gold was essentially not leached. A practically acceptable dissolution rate was not observed unless the leaching temperature was greater than 120°C in the presence of an oxidant [Meng and Han, 1993].

Various oxidants such as oxygen, cupric, cobaltic (Co^{3+}) and manganic (Mn^{4+}), alone or in combination, can be used in a solution containing ammonia and ammonium salts (e.g. ammonium chloride, ammonium carbonate or ammonium sulfate) for the leaching of gold [Han and Meng, 1992]. Oxygen in itself insufficient as an oxidant. Han and Meng [1992] reported the most desirable combination of oxidants to be: oxygen, hypochlorite and cupric ion at an appropriate ratio (the ratio was not further specified). Meng and Han [1993] found oxygen (100 kPa) and cupric ion (10 g/L Cu^{2+}) as the preferred combination.

Other important variables apart from time and particle size, are temperature and ammonia concentration. Meng and Han [1993] reported that there appears to be a temperature-controlled solubility limit for the gold(I)ammonia complex: at 180°C this value is about 80 mg/L Au.

Extractions of 80-96% Au from three gold ores and one concentrate in 3-4 hours were obtained by using an autoclave. Conditions were 190°C, Cu^{2+} 5 to 10 g/l, free NH_3 5.5 M, $(\text{NH}_4)_2\text{SO}_4$ 0.5 M, oxygen pressure 600-1000 kPa, particle size minus 0.147 mm, and a pulp density of 10 to 25% solids.

2.4.2 Ammonia technology for copper recovery

Ammonia leaching of copper and nickel has been well established. Sherritt Gordon developed an ammonia pressure leach process for extracting copper, nickel, cobalt and sulfur from high grade nickel concentrates [Forward and Mackiw, 1955].

Anaconda designed the Arbiter process for the treatment of copper concentrates with a low-pressure ammonia-ammonium sulfate leach [Kuhn et al, 1974]. A suitable mixing technology was applied to overcome the necessity of high oxygen partial pressure rather than using high pressure reactors. The process requires the use of oxygen rather than air. The leach takes place at temperatures ranging from 60 to 90°C.

The simplified leaching chemistries of chalcocite, covellite and chalcopyrite are shown in Equations (II. 33) to (II.35) [Kuhn et al, 1974]:

Chalcocite is probably the most amenable copper sulfide mineral to ammonia leaching. It has been demonstrated that half of the copper in chalcocite is essentially free and dissolves readily, leaving a covellite mineral matrix. As long as there is sufficient ammonia available to complex the copper and sufficient oxygen provided, it is expected that the leaching of chalcocite and covellite reaches completion [Kuhn et al, 1974].

When leaching chalcopyrite, the iron present in the mineral forms a hematite layer on the copper particle, thus becoming the rate-controlling factor in the leaching of chalcopyrite [Williams and Light, 1978].

A general formulation of enargite leaching is given in Equation (II.36) [Kuhn et al, 1974]:

Figure 2.16 shows the copper extraction as a function of leaching time for three different minerals. Kuhn et al [1974] did not explain the slow leaching characteristics of the enargite mineral, other than that the rate of enargite leaching appears to be dependent on the relative specific surface area of the mineral.

Figure 2.16 Leach extraction as a function of time on three concentrates of different mineralogy. ○ Weed chalcocite; Δ Twin Buttes chalcopyrite; □ Butte enargite [Kuhn et al, 1974]

In summary, according to Kuhn et al [1974] the leaching of copper sulfide minerals in the ammonia-ammonium sulfate environment depends mainly on oxygen mass transfer through the bulk solution to the surface and diffusion through an iron oxide layer, if present. Several studies

support this theory [Halpern, 1953, Fisher and Halpern, 1956]. According to Kuhn et al [1974], the solution to this mass-transfer problem lies in the mixing system. By increasing the stirrer speed, the chemical reaction rate is made to be the rate-controlling mechanism, instead of oxygen mass transfer, and ammonia leaching can be accomplished in a low-pressure system.

However, Beckstead and Miller [1978] stated that a change in mixing system changes the morphology of the hematite deposit which causes a change in surface reaction kinetics, rather than improving the oxygen mass transfer. This was noted before by Forward and Mackiw [1955] who found that intense agitation tends to reduce the iron oxide layer thickness.

For copper oxide minerals, the following relations can be written [Fisher and Halpern, 1956]:

In the presence of NH_4^+ the dissolution of the copper oxide is favored.

2.5 Summary of literature

2.5.1 Thiosulfate technology

From the literature review it was realized that the thiosulfate concentrations applied for the recovery of gold have decreased over the years of study. The patents granted in the early 1980's applied thiosulfate concentrations ranging from 0.4 to 2 M thiosulfate, while recent studies mention the addition of 0.1 to 0.2 M thiosulfate. The application of lower thiosulfate

concentrations while still achieving high gold extractions render the ammonium thiosulfate process more economical and should therefore be pursued in current and future investigations.

The pH of the recently developed leaching processes is generally maintained between 9 to 10. This pH range is dictated by the ammonia/ammonium buffer point (9.25 at 25°C), since the presence of ammonia has to be ensured in order to solubilize copper as the copper(II)ammonia complex. Testing at higher temperature and lower pH values are possible because the buffer point shifts to lower values with increasing temperatures. This is probably the reason why Marchbank et al [1996] were successful in leaching at pH's of 7 to 8.7 at 50°C. The thiosulfate stability will however decrease at higher temperatures and lower pH values. Therefore, a pH of 9 to 10 is generally preferred at ambient temperature because thiosulfate appears to be less prone to degradation in this region and the copper(II)ammonia complex is stable.

When evaluating the optimum ammonia concentration two factors should be considered. Firstly, there has to be sufficient ammonia present in the leaching system to solubilize the copper partially as an ammonia complex. Secondly, the ammonia to thiosulfate ratio should be kept in a certain range, preferably around 1 to 2. This effect is illustrated in Figure 2.9. A too high ammonia concentration might stabilize copper as the copper(II)ammonia complex, or a too high thiosulfate concentration might result in the stabilization of copper as the copper(I)thiosulfate complex according to Equation (II.39), thus limiting the catalytic action on gold extraction:

Another significant difference between early studies and recent ones is the difference in cupric

ion addition. In the patent of Kerley [1981, 1983] a cupric addition of 1 to 4 g/L is described and Berezowsky and Gormely [1978] mention an addition of 1-10 g/L. Cupric ion concentrations of 50-100 ppm are mentioned in the patents granted more recently [Wan et al, 1994; Marchbank et al, 1996]. Low cupric ion concentrations seem to be favourable, since high cupric ion concentrations accelerate thiosulfate degradation.

The addition of sulfite ions to an ammonium thiosulfate solution in order to stabilize the thiosulfate ion is widely practiced. As discussed in section 2.3.3., the reactions referred to in the literature seem unlikely to take place. Sulfite might, however, participate in different reactions, such as the reaction with tetrathionate to form trithionate and thiosulfate, and thus influence the leaching reactions (see section 2.3.3).

The main factors effecting the thiosulfate stability in an ammoniacal thiosulfate leach solution are: cupric ions, oxygen pressure and temperature. Some authors reported a negative effect on thiosulfate consumption with high oxygen pressures, others however, did not observe any negative effect when applying higher oxygen pressures. At high temperatures ($>60^{\circ}\text{C}$) excessive thiosulfate consumption and the formation of a copper sulfide coating on gold particles have been observed. At slightly higher than ambient temperatures, the kinetics of leaching are favoured, without causing excessive thiosulfate consumption.

In conclusion, ammonium thiosulfate leaching for gold recovery preferably should be performed at:

- Low thiosulfate concentrations, ranging from 0.1 to 0.2 M;
- An ammonia to thiosulfate ratio of 1 to 2;

- Copper concentrations ranging from 50 to 100 ppm;
- An alkaline pH, preferably 9 to 10;
- Ambient temperatures to 50°C.

2.5.2 Ammonia Technology

The leaching of copper sulfide minerals in ammonia solution has been extensively studied throughout the years. Less information is available concerning the behaviour of copper oxide minerals in an ammonia solution.

Most studies investigated the leaching of copper minerals at higher temperatures and pressures, only in the Arbiter process ammonia leaching is accomplished in a low-pressure system with sufficient oxygen availability and high stirrer speed [Kuhn et al, 1974].

The optimum conditions for the leaching of gold in ammonia thiosulfate solution are at low temperatures and atmospheric pressure (section 2.5.1). It can be concluded that there is no data available regarding the behaviour of copper minerals under these conditions.

2.5.3 Treatment of copper-gold ores by ammonium thiosulfate

Copper-gold ores are available in large quantities. However, treatment of these ores by cyanide is unfavourable for several reasons. Firstly, the use of cyanide is restricted in many areas. Secondly, cyanidation of gold ores containing cyanide soluble copper, results in high cyanide consumption. Since cyanide is an expensive reagent (US\$ 1.80/kg), and the recovery of cyanide from copper cyanide complexes is not widely applied, this reagent consumption can be detrimental for the economics of a project.

Ammonium thiosulfate might be a potential alternative for the treatment of these ores. Copper is required as a catalyst in the leaching reaction, and thiosulfate is cheap compared to cyanide (US\$0.13/kg). Furthermore, ammonium thiosulfate is used as a fertilizer, thus from an environmental standpoint it has an advantage over cyanide.

Little research is available regarding the treatment of copper-gold ores by ammonium thiosulfate. The research reported by Berezowsky and Sefton [1979] concerned the treatment of ammonia pressure oxidation residues, which contained 0.54 to 2.58 % copper. Several studies were performed by Gong and Hu [1990] and Cao et al [1992] on a gold sulfide concentrate containing 3.16 % Cu.

All of these studies were performed at high thiosulfate concentrations (0.4 to 1 M), and high ammonia concentrations (1 to 2 M). The catalytic effect of copper on gold extraction was recognized by these researchers, but only Berezowsky and Sefton [1979] mentioned the detrimental effect of copper on thiosulfate stability. None of the studies attempted to investigate the behaviour of copper and thiosulfate during the leach.

This study is directed towards developing an economical leach process for copper-gold ores using ammonium thiosulfate. Therefore, the reagent concentrations should be as low as possible. Furthermore, an understanding should be obtained of the behaviour of copper, gold and thiosulfate in an ammonium thiosulfate leach solution.

3 EXPERIMENTAL METHODS

This chapter first discusses the materials and reagents used for testing, followed by a description of the experimental apparatus, the experimental procedures and an overview of the performed test work. The chapter concludes with a description of the analytical methods used in this work.

3.1 Materials

3.1.1 Copper Minerals

To study the behaviour of copper minerals in ammonium thiosulfate solutions, samples of natural occurring copper minerals were obtained from Ward's Natural Science Establishment, Inc. These include covellite, chalcocite, chalcopyrite, cuprite and malachite. A mineral sample of enargite was received from the Montana Bureau of Mines and Geology.

The mineral samples were reduced in size by subjecting the samples to a series of cone crushers, followed by a disk grinder. A narrow particle size fraction between 230 (63 μm) and 270 mesh (53 μm) was obtained by screening. This fraction was analysed for copper and iron content.

X-ray diffraction (XRD) was used to determine the main mineral phases present. The results of these analyses are summarized in Table 3.A.

Table 3.A Composition of copper mineral samples for testwork

Mineral Sample	%Cu*	%Fe*	Mineral phases
Covellite (CuS)	63.1 (66.4)	2.5 (0)	Covellite, Chalcocite
Chalcocite (Cu ₂ S)	53.9 (79.8)	8.43 (0)	Chalcocite, Bornite (Cu ₅ FeS ₄)
Chalcopyrite (CuFeS ₂)	28.5 (34.6)	27.7 (30.4)	Chalcopyrite
Enargite (Cu ₃ AsS ₄)	23.2 (48.4)	7.0 (0)	Enargite, Chalcopyrite, Tennantite ((Cu,Fe) ₁₂ As ₄ S ₁₃)
Cuprite (Cu ₂ O)	38.9 (88.8)	13.9 (0)	Cuprite, Goethite (FeOOH)
Malachite (Cu ₂ (CO ₃)(OH) ₂)	47.7 (57.5)	0.6 (0)	Malachite

*in brackets represents the percentage of Cu or Fe in a 100% pure mineral

From this table, it can be concluded that all mineral samples contain several mineral phases other than the desired copper mineral phase. For example, XRD showed the presence of goethite (FeOOH) in the cuprite mineral sample which explains the high iron content. Upgrading these copper minerals by flotation was deemed very difficult; therefore, it was decided to conduct testing with the samples in the as-received condition.

Oxidation of the copper sulfide minerals after particle size reduction was prevented by purging the sample bottles containing the copper minerals with nitrogen and sealing the lids.

3.1.2 Copper-Gold Samples

The following copper-gold concentrates and ores were obtained for the leaching studies:

- Overall Lobo Composite from Teck Corporation
- Guanaco Composite from Amax Gold Inc.
- M40 Pyrite Feed and M10 Pyrite Concentrate from Newcrest Mining Ltd.

The Overall Lobo Composite and Guanaco Composite are whole ores, whereas the M40 Pyrite Feed and M10 Pyrite Concentrate are flotation products. Gold and copper content and the copper mineral phases present in the samples are listed in Table 3.B.

Table 3.B Composition copper-gold concentrate and ore samples

Copper-gold samples	Au (ppm)*	Cu (ppm)*	Cu mineral phases
Overall Lobo Composite	2.11	1,120	Chalcopyrite, Covellite, Chalcocite
Guanaco Composite	2.06	3,320	Enargite, Cuprite, Malachite
M40 Pyrite Feed	7.10	5,920	Chalcopyrite
M10 Pyrite Concentrate	45.5	16,600	Chalcopyrite

*Assayed by Chem Met Consultants, Vancouver, B.C.

Mineralogical examination of the Overall Lobo Composite revealed that the ore was characterized by highly altered rock fragments and lesser granular vein quartz with minor finely disseminated sulfides and iron oxides/oxyhydroxides. Copper mineralization was dominated by chalcopyrite (CuFeS_2 , 76%), with minor covellite (CuS , 24%), trace chalcocite (Cu_2S , <1%) and rare bornite (<0.2%). Trace gold / electrum was identified as small grains (<15 μm), and was found associated with silicates and iron oxides / oxyhydroxides [Lakefield Research Limited, 1997].

The Guanaco Composite was comprised of rather strongly oxidized ore with minor remnant pyrite (FeS_2), enargite (Cu_3AsS_4), and sphalerite (ZnS). The oxidation suite includes goethite (FeOOH), with lesser amounts of psilomelane ($\text{BaMn}^{2+}\text{Mn}^{4+}_8\text{O}_{16}(\text{OH})_4$), cuprite (Cu_2O), and copper oxysalts minerals (malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$), azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), and olivenite ($\text{Cu}_2(\text{AsO}_4)(\text{OH})$) [Honea, 1998]. No information is available about the gold occurrence or association in this composite.

The M40 Pyrite Feed was characterized by 78% pyrite (FeS_2) and 10% quartz (SiO_2). Some minor chalcopyrite (CuFeS_2 , 1.6%) and calcite (CaCO_3 , 1%) was present and the remainder was comprised of mainly clay minerals. The M10 Pyrite Concentrate was found to be similar with 76% pyrite and 7% quartz as the main minerals present. Minor chalcopyrite (1.6%) and calcite (2.5%) and some dolomite ($\text{CaMg}(\text{CO}_3)_2$, 5.0%) were identified [Oretest, 1997]. Details regarding gold association are not available for these concentrates.

The Lobo composite and Guanaco composite samples were reduced in particle size by a series of cone crushers, followed by pulverization using a disk pulverizer. The product was split into smaller quantities (about 400 grams) suitable for testwork. Size reduction for the M40 Pyrite Feed and M10 Pyrite Concentrate was not necessary. The concentrates were also split into smaller quantities for testwork. The screen analyses of the copper-gold samples are given in Appendix A; the 80% passing size (P_{80}) was determined for every material (Table 3.C).

Table 3.C P_{80} of the copper-gold samples

Copper-gold samples	P_{80} (μm)
Overall Lobo Composite	141
Guanaco Composite	160
M40 Pyrite Feed	75
M10 Pyrite Concentrate	46

The P_{80} of the Guanaco and Overall Lobo Composite is high for leaching experiments, however, both size fractions are already the result of a regrind. Further reduction of the P_{80} was deemed difficult with the equipment available, therefore, testing was continued with this particle size distribution.

3.1.3 Reagents

- Soluble gold was added to some leaching solutions. A 1,000 ppm Au reference standard solution was used. In this solution (10% hydrochloric acid) gold is present as a chloride complex (AuCl_4^-).
- Unless otherwise stated, analytical grade ammonium thiosulfate in powder form was used. Tessenderlo-Kerley provided Thiogold™ grade ammonium thiosulfate solution. The solution contains between 50 - 60 % ammonium thiosulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_3$), 40 - 50 % water and 0 - 4 % ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$).
- Other reagents used during testing were cupric sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, anhydrous sodium sulfite, Na_2SO_3 , and anhydrous sodium sulfate, Na_2SO_4 . Concentrated sodium hydroxide (50% solution in water) was used for pH adjustments. Ammonia solutions (1 and 3

M) were prepared from concentrated reagent grade ammonium hydroxide (NH_4OH) solution. Preliminary experiments used anhydrous ammonia gas (99.99% purity) to adjust the pH of the leach solution and 1M sulfuric acid (H_2SO_4) prepared from reagent grade sulfuric acid. Air (19.5-23.5% O_2) was supplied via a gas cylinder.

3.2 Experimental Apparatus

A schematic diagram of the experimental set-up used for the batch leaching tests is given in Figure 3.1. The experiments were carried out in a 1500 mL cylindrical glass vessel with a removable high density polyethylene lid. The vessel was vertically baffled with a baffle width of 11 mm which is 1/10 of the tank diameter. The baffles were made of acrylic. The solutions were stirred by a stainless steel Rushton impeller (35 mm diameter, 1/3 of the vessel diameter, 6 blades) on a stainless steel shaft connected to a variable speed DC motor. All experiments were performed at an impeller speed of 1695 RPM. It was experimentally determined that this was the minimum impeller speed required for complete particle suspension.

Figure 3.1. Schematic diagram of the experimental set-up.

Unless otherwise stated, experiments were performed at 35°C. The glass vessel was placed in a water bath heated by an immersion heater connected to a PID controller. A thermocouple was placed in the reactor to provide temperature control. Air was added to the solutions via a stainless steel sparger placed directly under the Rushton impeller. A gas flowmeter controlled the flow of air into the reactor.

Controlled pH experiments were performed by ammonia gas and sulfuric acid addition. Two solenoid valves, connected to the pH controller, regulated the flow of the ammonia gas from a gas cylinder and the flow of sulfuric acid from a burette. The pH was controlled in a range of ± 0.10 pH. The ammonia gas was added to the solution via the air sparger.

A gel-filled combination pH probe with a silver/silver chloride reference electrode was used to monitor the pH of the solutions. The redox potential was measured using a platinum combination redox electrode with a silver/silver chloride reference electrode. The E^0 of this reference electrode at the experimental temperature of 35°C was 189 mV. In order to report the experimentally observed Eh values versus the potential of the standard hydrogen electrode (SHE), all values were corrected by adding 189 mV.

3.3 Experimental Procedures

Four sets of experiments were performed:

1. Preliminary testwork
2. Leaching of copper minerals
3. Leaching of copper minerals with 5 ppm gold addition
4. Leaching of copper-gold samples

The procedure for each set varied and will be discussed separately.

3.3.1 Preliminary testwork

The preliminary testwork involved the leaching of the copper minerals in one litre of deionized water. Depending on the copper content of the different minerals (Table 3.A), sufficient mineral feed was added to the solution such that upon 100% copper dissolution, the copper concentration would be 5 g/L. Due to the limited amount of the 53-63 μm material available, the preliminary testwork was conducted with the <53 μm fraction.

The initial slurry of copper mineral feed was heated to the desired temperature. Once the desired temperature was attained, aeration of the slurry was initiated (0.23 L/min), and the ammonium thiosulfate was added. The pH was adjusted to the desired value with either ammonia gas or 3 M ammonia solution. This time was noted as time zero.

In pH uncontrolled experiments, the pH was allowed to drift. During pH controlled experiments, the pH was adjusted with either ammonia or sulfuric acid in a range of ± 0.1 pH. Slurry samples of 7 mL were withdrawn at selected intervals and centrifuged for liquid/solid separation. The resulting solutions were prepared for copper, gold, thiosulfate, tetrathionate and sulfate analyses.

Experiments continued until the redox potential of the solution stabilized (typically 6 - 8 hours). At the end of the experiment the solution was filtered, the residue was washed with deionized water, dried, and collected.

3.3.2 Leaching of copper minerals

After the preliminary testwork, some adjustments were made in the experimental procedure. As above, experiments were performed in one litre of deionized water. Sufficient mineral feed was added to the solution such that upon 100% copper dissolution, the copper concentration would be either 5 g/L or 1 g/L copper. The fraction 53-63 μm of the copper minerals was used for this set of experiments.

Heating, aeration and reagent addition followed the same procedure described above. The pH of the slurry was adjusted to 10 for all experiments with concentrated sodium hydroxide and the time was set to zero. The pH was allowed to drift in all experiments.

Slurry samples of 7 mL were withdrawn at 30, 60, 120, 180, 240 and 360 minutes, centrifuged and analysed for copper, thiosulfate, tetrathionate and sulfate. In several experiments, a solution sample was taken after 5 minutes. However, this sample time was discontinued at a later stage in order to reduce the time necessary to perform the analytical procedure with the ion chromatograph after the experiment (section 3.5). The experiments lasted 6 hours, after which the solution was filtered. The residues and the wash water were collected. The amount of residue remaining after the experiments was not deemed sufficient for copper analysis (see section 3.5).

3.3.3 Leaching of copper minerals with 5 ppm gold addition

The experimental procedure for this series of experiments is similar to that described in section 3.3.2 with the exception that 5 ppm of gold from the standard reference was added to the deionized water. Accordingly, solution samples were also analysed for gold.

3.3.4 Leaching of copper-gold samples

The experiments involving the concentrates were performed at a pulp density of 30% by weight (360 grams of concentrate and 840 grams of deionized water). The pulp was heated to desired temperature, after which the reagents were added. Experiments were continued as described in section 3.3.2. One adjustment was the sample volume. Because of the higher pulp density 8 mL samples were taken. Solution samples for copper, gold, thiosulfate, tetrathionate and sulfate analysis were prepared. Wash water samples were analysed for gold content. The residues were analysed for copper and gold.

3.4 Experimental Design

The experimental design is discussed according to the four different series of experiments mentioned in section 3.3.

3.4.1 Preliminary experiments

Preliminary experiments (at controlled pH and uncontrolled pH) were conducted with the copper minerals at 0.05 and 0.1 M ammonium thiosulfate at pH's ranging from 8 - 9.5. All experiments were performed at a temperature of 35°C.

3.4.2 Leaching of copper minerals

So-called baseline experiments were first conducted, after which the effects of several parameters could be studied (Table 3.D). Baseline tests included: aeration of the system, 0.2 M ammonium thiosulfate, pH 10 (uncontrolled), a copper mineral addition which would achieve 5 g/L copper or 1 g/L copper upon 100% dissolution, and 35°C. The experiments lasted 6 hours. Two experiments were performed without aeration.

Table 3.D Overview of experiments with copper minerals

Copper minerals	Baseline	No aeration
Covellite	X	
Chalcocite	X	X
Chalcopyrite	X	
Enargite	X	
Cuprite	X	X
Malachite	X	

3.4.3 Leaching of copper minerals with 5 ppm gold addition

The experiments were performed under the same conditions as described in section 3.4.2. However, several other parameters were evaluated in this test series; aeration, leach temperature, ammonia concentration, sulfite concentration and sulfate concentration (Table 3.E).

Table 3.E Overview of experiments with copper minerals and gold addition

Copper mineral	Baseline	No aeration	Temperature 20°C	0.4 M NH ₃	0.05 M SO ₃ ²⁻	0.05 M SO ₄ ²⁻
Covellite	X					
Chalcocite	X	X	X	X	X	X
Chalcopyrite	X					
Enargite	X					
Cuprite	X	X	X			
Malachite	X					

3.4.4 Leaching of copper - gold samples

Baseline experiments of this test series included: aeration of the system, 0.2 M ammonium thiosulfate, pH 10 (uncontrolled), 30 % pulp density, and 1 g/L copper addition (as cupric (CuSO₄.5H₂O)) and 6 hours. The parameters studied in this series are (see Table 3.F): aeration of the system, leaching time, ammonia thiosulfate concentration, copper addition and ammonium thiosulfate grade.

Table 3.F Overview of experiments with copper-gold samples

Copper-gold samples	Baseline	No aeration	No aeration, 24 hours	No cupric	No aeration, no cupric	Extra ATS*	Thiogold™ Grade
Overall Lobo Composite	X	X		X			
Guanaco Composite	X	X		X			X
M40 Pyrite Feed	X	X		X	X		
M10 Pyrite Concentrate	X	X	X	X		X	

*ATS = Ammonium Thiosulfate

3.5 Sample Analysis

3.5.1 Copper and gold analysis

All the copper and gold assays on solution and solid samples were performed by Chem Met Consultants in Vancouver. Selected solution samples were analysed for gold and copper content. The solution samples (exactly 20 mL) for copper were prepared for atomic absorption spectrophotometry (AAS) by treatment with hydrogen peroxide to destroy any thiosulfate present since thiosulfate interferes with AAS measurements. After this, nitric acid was added to dissolve any precipitates resulting from the hydrogen peroxide addition. The solution volume was adjusted to known volume and the copper content measured by AAS.

Between 3-5 mL of sodium cyanide was added to the samples for gold analysis, to keep gold in solution. The gold content was determined by evaporating 25 mL of solution to dryness in a lead foil boat, followed by fire assay and cupellation. The resulting bead was digested and the gold content of the resulting solution was determined by AAS.

The residues of the copper-gold samples were analysed for copper and gold for mass balance purposes. A representative sample of the residues was obtained by coning and splitting. Copper content of the residues was determined by acid digestion and AAS analysis of the resulting solution. Gold content of the residues was determined by fire assay and cupellation. The resulting bead was digested and the gold content of the resulting solution was determined by AAS.

3.5.2 Thiosulfate, tetrathionate and sulfate analysis

All solution samples were analysed for thiosulfate, tetrathionate and sulfate by high performance liquid chromatography (HPLC) methods directly following the experiment. A Dionex Series 4500i Chromatograph was used for the analysis. The ion chromatography methods and procedures are discussed in more detail in Appendix B.

Solution samples produced from the experiments were diluted to a concentration suitable for detection by the ion chromatograph (< 20 ppm). The typical dilution factor was 1,000 times. The diluted samples were kept refrigerated and in the dark to reduce the rate of thiosulfate degradation. The samples were allowed to warm to room temperature just before analysis.

It should be noted that only the free ion concentrations are detected by ion chromatography. Sulfur species complexed with metal ions will either not be retained by the column (when the complex has no charge) or have such a high affinity for the ion exchange sites on the column that the complex does not elute; for example the copper(I)tri-thiosulfate complex which has a -5 charge.

Further, for most experiments the presence of sulfite and trithionate was detected by ion chromatography. However, these species could not be quantified.

4 RESULTS AND DISCUSSION

The experimental results are presented and discussed in this chapter. As mentioned in Chapter 3, four different sets of experiments were conducted: preliminary testwork, leaching of copper minerals, leaching of copper minerals with gold addition to solution and leaching of copper-gold samples. The experimental results are discussed accordingly. First, the construction of Eh-pH diagrams which represent the experimental conditions are discussed.

4.1 Eh-pH diagrams

To understand and characterize the chemistry of copper-thiosulfate-ammonia solutions containing gold, Eh-pH diagrams were constructed which reflect the experimental conditions used in this research. Eh-pH diagrams represent the thermodynamic equilibria in a system and do not give information regarding the kinetics of the reactions represented in the diagram. This has to be considered when interpreting Eh-pH diagrams.

The thermodynamic data used for the various copper and gold species expected to be present in these solutions are presented in Appendix C. The diagrams were constructed with the use of the computer program CSIRO Thermochemistry [Turnbull, 1986]. An Eh range of -1.5 to 1.5 V_{SHE} and a pH range of 6 to 14 were considered. The pH range was chosen between 6 and 14; below pH 6 complex reactions involving the hydrolyses of thiosulfate start to take place which are not pertinent to this research (see section 2.3.3). The pH values of interest are around 9-10 (see section 2.5). According to the literature, the Eh values during thiosulfate leaching are generally in the range of 150 to 250 mV_{SHE} [Atluri, 1987].

The Eh-pH diagrams were constructed for 25°C, while the experiments were conducted at 35°C. Entropy data are required to calculate the free energy of a species at 35°C. This data is not available for several sulfur species (e.g. $\text{S}_2\text{O}_3^{2-}$, $\text{S}_x\text{O}_6^{2-}$, $x \geq 2$). The diagrams were therefore constructed at 25°C. The change of the ammonia/ammonium buffer point with temperature can be calculated and changes from pH 9.25 at 25°C to pH 8.96 at 35°C. This change in pH value is not incorporated on the Eh-pH diagrams, but has to be considered when interpreting the experimental results.

Moreover, Eh-pH diagrams are theoretical thermodynamic diagrams and should therefore be constructed using ionic activities. In dilute solutions these activities can be replaced by molalities (mol/kg of solvent). Due to the complex nature of the solutions in this system, representative activity coefficients are not readily available. The experimental solutions cannot be considered to be dilute either, since at least 0.4 M NH_3 and 0.2 M $\text{S}_2\text{O}_3^{2-}$ are present. The diagrams were constructed using molarities, which in this instance, is the most practical alternative.

The Eh-pH diagram for the gold-thiosulfate-ammonia-water system appears in Figure 4.1. The gold activity is $2.5 \cdot 10^{-5}$ M (5 ppm), the thiosulfate activity is 0.2 M and the ammonia activity is 0.4 M. It can be seen that the gold(I)thiosulfate complex is stable in the whole pH range shown.

Figure 4.1. Eh-pH diagram of the gold-thiosulfate-ammonia-water system at 25°C. The activities of the species are 2.5×10^{-5} Au (5 ppm), 0.2 $\text{S}_2\text{O}_3^{2-}$ and 0.4 NH_3 . $\Delta G_f^0(\text{S}_2\text{O}_3^{2-}) = -518.8$ kJ/mol.

Comparing Figure 4.1 with the Eh-pH diagrams given in the literature (see Figure 2.7), it can be observed that the gold(I)ammonia complex has no region of stability in Figure 4.1, while Figure 2.7 shows a region of stability for this complex. A closer examination of the literature revealed that the free energy of formation value of the thiosulfate species was different. In Figure 4.1 a value of -518.8 kJ/mol was used for the thiosulfate species [Bard et al, 1985]. The Handbook of Chemistry and Physics [Weast, 1975] lists a value of -532.2 kJ/mol for thiosulfate, resulting in the Eh-pH diagram presented in Figure 4.2, which resembles Figure 2.7.

Figure 4.2 Eh-pH diagram of the gold-thiosulfate-ammonia-water system at 25°C. The activities of the species are 2.5×10^{-5} Au (5 ppm), 0.2 $\text{S}_2\text{O}_3^{2-}$ and 0.4 NH_3 . $\Delta G_f^0(\text{S}_2\text{O}_3^{2-}) = -532.2$ kJ/mol.

The gold(I)ammonia complex now appears next to the gold(I)thiosulfate complex. This large effect of this relatively small change in free energy is explained when the following equation is considered:

The free energy change for this reaction, calculated using the ΔG_f^0 value of -518.8 kJ/mol for thiosulfate, is + 22.5 kJ which indicates that this reaction is not favoured. When the free energy change is recalculated using the ΔG_f^0 value of -532.2 kJ/mol for thiosulfate, the value -4.3 kJ is obtained which indicates that the formation of the gold(I)ammonia complex is now favoured. It can be concluded that a small change in the free energy of the thiosulfate species has a great

impact on the thermodynamic equilibria presented in the Eh-pH diagram of the gold-thiosulfate-ammonia-water system.

According to Figure 4.2, the gold(I)ammonia complex is the most stable species at pH 10, which does not agree with experimental observations. As Li et al [1996] remarked, it is generally accepted that the gold(I)thiosulfate species is the more stable species at pH 10 and Li et al [1996] confirmed this by rest potential measurements (see section 2.3.1). These rest potential measurements are easily explained by Figure 4.1. This example illustrates that Eh-pH diagrams have to be interpreted with the necessary precautions.

In Figure 4.1 a decrease in thiosulfate concentration results in a slight decrease in area of stability for the gold(I)thiosulfate complex over the entire pH range considered. In Figure 4.2 a decrease in thiosulfate concentration results in a larger area of stability for the gold(I)ammonia complex. When thiosulfate disappears, thermodynamically the gold(I)ammonia complex becomes the stable species over the whole pH range. In this study the concentrations of gold in ammoniacal thiosulfate solutions are usually very low (in range of 5 to 30 ppm). Hence, a variation in gold concentration should not significantly affect the thermodynamics of the system.

The copper-thiosulfate-ammonia Eh-pH diagram, calculated using the value of -518.8 kJ/mol for thiosulfate, is presented in Figure 4.3. The copper(I)tri-thiosulfate complex occupies the whole pH range and is stable in the area of the leaching conditions; pH 10 and an Eh range of 150-250 mV_{SHE}. The copper(I)di-thiosulfate complex is stable at low pH values. A slight lowering of the Eh will result in the precipitation of copper as CuS.

Figure 4.3 Eh-pH diagram of the copper-thiosulfate-ammonia-water system at 25°C. The activities of the species are 0.015 Cu (0.95 g/L), 0.2 $\text{S}_2\text{O}_3^{2-}$ and 0.4 NH_3 . $\Delta G_f^\circ (\text{S}_2\text{O}_3^{2-}) = -518.8$ kJ/mol.

The copper(II)ammonia complex has a small stability region around the ammonia/ammonium buffer point. As mentioned before, this buffer point will shift towards pH 8.96 at 35°C. This area lies slightly above the $\text{O}_2/\text{H}_2\text{O}$ line, and will therefore not exist at significant concentrations. This complex will have a region of stability within the water lines, when the thiosulfate concentration decreases. A decrease in copper concentration increases the width of the region of the copper(II)ammonia complex. The dominant copper species at the Eh-pH conditions of the experiments is not affected by a decrease in thiosulfate concentration.

Calculating the same diagram with the thiosulfate value of -532.2 kJ/mol, results in Figure 4.4.

Figure 4.4 Eh-pH diagram of the copper-thiosulfate-ammonia-water system at 25°C. The activities of the species are 0.015 Cu (0.95 g/L), 0.2 $S_2O_3^{2-}$ and 0.4 NH_3 . $\Delta G_f^0(S_2O_3^{2-}) = -532.2$ kJ/mol.

When comparing Figure 4.4 to Figure 4.3, two observations can be made. The region of interest is pH 10. In Figure 4.4, the area for the copper(I)thiosulfate complex is greatly reduced compared to Figure 4.3. At Eh values lower than 0 V_{SHE} , the Cu_2S species has an area of stability directly below the copper(I)thiosulfate species instead of CuS in Figure 4.3. Furthermore, the region of stability of the copper(II)ammonia complex increases to lower Eh values when compared to Figure 4.3.

Figure 4.5 shows the copper-ammonia-water system. This Eh-pH diagram represents the leaching conditions when thiosulfate is no longer present in solution.

Figure 4.5 Eh-pH diagram of the copper-ammonia-water system at 25°C. The activities of the species are 0.015 Cu (0.95 g/L) and 0.4 NH₃.

The copper(I)ammonia complex now appears as a stable species in the area of interest. The areas of the copper(I)ammonia and copper(II)ammonia decrease in width with higher copper concentrations and lower ammonia concentrations. At very low ammonia concentrations the stability region of the copper(II)ammonia complex completely disappears.

4.2 Preliminary experiments

The preliminary experiments were performed to obtain an understanding of the behaviour of copper minerals in an ammonium thiosulfate solution under conditions that are typical for the leaching of gold (see section 2.5.1). The results of these experiments were used to determine the experimental conditions for further testwork.

Conditions

As described in section 3.3.1 the preliminary experiments were performed with the copper minerals (section 3.1.1), particle size of minus 270 mesh (53 μm). A copper mineral addition was employed which would achieve 5 g/L copper in solution upon 100% dissolution. In the remainder of this chapter this will be referred to as a 5g/L copper addition. 5 g/L copper was chosen as a representative amount for an industrial operation. This would be equivalent to 0.5% copper in an ore, with leaching at 50% pulp density.

As outlined in the literature review (section 2.5.1) it is necessary to apply low ammonium thiosulfate concentrations, ranging from 0.05 - 0.20 M, to achieve an economical process for the recovery of gold by ammonium thiosulfate leaching. Therefore, testing started with concentrations of 0.05 and 0.1 M ammonium thiosulfate. Since the thiosulfate to copper ratio in the copper(I)thiosulfate complex is 3 to 1 (the $\text{Cu}(\text{S}_2\text{O}_3)_2^{3-}$ complex is not stable under these conditions), there was not enough thiosulfate present in solution to complex all the copper (maximum of 5 g/L copper (=0.079 M copper)).

The same applies to the ammonia concentration; the ammonia to copper ratio in the copper(II)ammonia complex is 4 to 1 and thus not enough ammonia is present to complex all the copper if 100% dissolution would occur. However, ammonia was used for pH adjustment, resulting in sufficient ammonia concentrations at high pH values (≥ 9.0).

The pH range tested was from 8 to 9.5. Testing was started at lower pH values, considering the shift of the ammonia/ammonium buffer point to pH 8.96 at 35°C. First, the experiments were pH

controlled in a narrow range (± 0.1 pH). After several experiments, however, it was realized that by allowing the pH to drift during the experiment, a better understanding of the chemical reactions occurring in the leach solution can be obtained. Accordingly, the pH was allowed to drift in all further experiments.

Results

All preliminary experiments showed that the thiosulfate disappeared quickly. Thiosulfate was not detected in the leach solutions after 2 to 3 hours. An example is presented in Figure 4.6., the leaching of covellite with 0.10 M ammonium thiosulfate at pH 9.5.

The first graph reflects the pH (primary y-axis) and Eh (secondary y-axis) changes during the experiment. The negative time on this plot reflects the heating of the solution to 35°C, in the absence of reagents. The addition of the reagents to the solution was noted as time zero. The large increase of pH and sharp decrease of the Eh result from the reagent addition. The bottom graph shows the results of thiosulfate and tetrathionate analyses by ion chromatograph on the primary y-axis, and the copper extraction on the secondary y-axis. Sulfate concentrations are not available for this experiment.

Figure 4.6. Covellite, 5 g/L copper, 0.1 M S₂O₃, 0.47 M NH₃, pH 9.5, aeration, 35°C

A more detailed discussion of the leaching of covellite is given in a later section (4.3.1). This graph is presented here for two reasons:

- The thiosulfate concentration in solution decreases quickly. This was also observed during the leaching of the other copper minerals.
- Copper extraction is low, just above 20% (of 5 g/L), which is about 1 g/L of copper.

Based on these results it was decided to try to maintain thiosulfate in solution by increasing the thiosulfate concentration to 0.2 M. The pH was set to 10 for further experiments. At this pH thiosulfate is quite stable (see section 2.3.3) and the presence of ammonia instead of ammonium in solution is ensured. At lower pH values the leaching of the copper sulfide minerals might be prevented because of an ammonia deficiency.

Moreover, the experimental procedure was changed. Exposing the copper minerals to deionized water resulted in a unique solution pH for each mineral. By adjusting the pH with ammonia, a different ammonia concentration was obtained for each experiment. To ensure the same ammonia concentration for all experiments, concentrated sodium hydroxide was used for pH adjustment. By adding the same amount of ammonium thiosulfate to every experiment and raising the pH to 10 by sodium hydroxide, the concentrations of thiosulfate and ammonia will be similar for every experiment (small differences in concentration will exist due to the fact that the amount of sodium hydroxide required to raise the pH to 10 is mineral dependent).

Furthermore, some difficulties were experienced with the dilution of solution samples to concentrations within the range of the ion chromatograph (2-20 ppm). Several samples turned

turbid upon dilution. Ammonia was added to the solutions to redissolve solid precipitates, enabling the measurement of the samples by ion chromatograph. It was realized that this addition changed the solution chemistry. For the next series of experiments it was recorded to which samples ammonia was added (Appendix D).

The ammonia addition may affect the solution chemistry in the following way: ammonia could displace any thiosulfate complexed with copper, resulting in a higher measured free thiosulfate concentration than actually present in the leach solution. In most experiments, ammonia was only added to the last samples (240, 360 minutes) resulting in no effect since in most experiments thiosulfate was no longer present after 180 minutes. For experiments with high initial copper extraction, ammonia was added to all samples. Again, this resulted in a minimum effect, since thiosulfate degraded quickly in the leach solutions because of the high copper concentration.

4.2.1 Summary

The main conclusion that can be drawn from the preliminary experiments is that thiosulfate was not detected after 2 to 3 hours under the experimental conditions applied. To extend the presence of thiosulfate in solution the thiosulfate concentration was increased to 0.2 M for further testwork.

The copper extractions for the sulfide minerals were not very high and this was thought to be due to low pH values, i.e. at low pH values ammonium will be the dominant species instead of ammonia. To ensure the presence of ammonia in the leach solution, the pH was increased to 10

in later testwork. This pH value might also positively affect the thiosulfate stability, since it is reported to be at a maximum in solutions of pH 9 to 10 (see section 2.3.3).

4.3 Leaching of copper minerals

In these experiments copper minerals were leached in an ammonium thiosulfate solution (see Table 3.D). The baseline experiments included a mineral addition which upon 100% copper dissolution would result in 5 g/L copper in solution, 0.20 M ammonium thiosulfate (~ 22 g/L thiosulfate), pH 10, 35°C and aeration. The pH was allowed to drift. The behaviour of thiosulfate, tetrathionate, sulfate and copper was recorded. The effect of aeration was studied. Experimental data and observations made during the experiments, such as solution colours are presented in Appendix D. All % extraction calculations are based on the head assays of the copper minerals.

4.3.1 Baseline experiments

The results of the baseline experiments are presented in Figures 4.7 to 4.12. The top graphs represent the pH and Eh values during the leach, whereas the bottom graphs show the sulfur species and copper extractions. Instrumental difficulties prevented the determination of sulfate concentrations for some experiments.

Figure 4.7 Covellite, 5 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

Figure 4.8 Chalcocite, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C

Figure 4.9 Chalcopyrite, 5 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

Figure 4.10 Enargite, 1 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

Figure 4.11 Cuprite, 5 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

Figure 4.12 Malachite, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35°C

An examination of the top graphs of the figures reveals that all figures, except Figure 4.10, show an initial pH increase followed by a pH decrease after a certain time period. The solution pH is influenced by several reactions which occur simultaneously:

- The oxidation of thiosulfate to tetrathionate (Equation IV.2), coupled with the reduction of oxygen to hydroxide (Equation IV.3), resulting in the production of hydroxide ions:

- Concurrently, hydroxide will be consumed by the hydrolysis of tetrathionate in a basic solution:

- Hydroxide is also consumed because ammonia is removed from the system due to evaporative losses and complexation reactions. The equilibrium depicted in Equation (IV.5) changes accordingly:

The reactions depicted in Equations (IV.2) and (IV.3) are dominant while thiosulfate is present. When the thiosulfate is gone, the hydroxide consuming reactions become more prominent and consequently, the pH decreases. This sequence of reactions is visible in for example, Figure 4.7, the leaching of covellite. The pH increases as long as thiosulfate is present, followed by a pH decrease around the same time (about 240 minutes) that thiosulfate was no longer detected in solution (bottom graph).

A closer look at Figure 4.7 reveals that the Eh remains constant for a long time and then suddenly increases around 240 minutes. This time coincides with the instant that the pH starts to drop and thiosulfate is no longer present. Further, the colour of the leach solution changes: after about 180 minutes the solution colour changes from colourless to light blue indicating that the copper(II)ammonia complex has formed (see Appendix D). Moreover, the copper extraction curve shows a steady increase after thiosulfate is gone, which can only be explained by copper complexing with ammonia, since there is no thiosulfate present in solution. It can be remarked that the copper extraction is low.

Figure 4.5, the Eh-pH diagram of the copper-ammonia system at 25°C, can be used to interpret these results. It can be seen from the bottom graph that the copper concentration is only about 0.006 M. This means that the stability regions of the copper(I)ammonia and copper(II)ammonia complex are slightly larger than represented in Figure 4.5. The pH and Eh value measured indicate that it is likely that the copper(I)ammonia complex forms under these conditions. The copper(I)ammonia complex oxidizes rapidly, in the presence of sufficient oxygen, to form the copper(II)ammonia complex, explaining the colour change of the solution and the rise in Eh.

Figures 4.7 to 4.12 show that the pH and Eh trends described above are applicable to all figures, except for the leaching of enargite (Figure 4.10). However, this figure too confirms the reactions postulated above. No decrease in pH value is observed, which indicates that thiosulfate was present throughout the entire experiment. Consequently, no change in Eh value should occur, which is confirmed by the Eh curve in Figure 4.10.

Chalcocite (Figure 4.8) shows an increase in potential after about 40 minutes, thereafter stabilizing until at 180 minutes the Eh increases again to a higher potential. As discussed in the literature review, section 2.4.2, half of the copper in chalcocite is essentially free and leaches rapidly leaving a covellite matrix behind (ΔG^0 of Equation (IV.6) is -313.1 kJ/mol, using -518.8 kJ/mol for $S_2O_3^{2-}$):

Figure 4.8 shows that copper extraction decreases slightly and then rises again. It was observed that the solution colour changed from colourless to light blue after 30 minutes. This indicates that the copper(I)thiosulfate complex, the copper(I)ammonia and the copper(II)ammonia complex could be present under these conditions. According to the Eh-pH diagram in Figure 4.3 the copper(I)thiosulfate species is dominant. However, the Eh-pH diagram presented in Figure 4.4. shows that under these conditions the copper(II)ammonia complex can also be present, which is indicated by the solution colour.

When most of the copper is present as the copper(I)thiosulfate complex, free thiosulfate has to be present in solution to keep the equilibrium depicted in Equation (IV.6) to the right. When the thiosulfate degrades, the copper(I)thiosulfate complex also decomposes following the equilibrium. When thiosulfate is no longer present, copper dissolves again forming complexes with ammonia, which results in an Eh rise (copper(I)ammonia to copper(II)ammonia) and an increase in copper extraction. Chalcopyrite shows similar behaviour with an increase in copper extraction after the thiosulfate is no longer present (Figure 4.9).

The patterns are different for the leaching of the copper oxide minerals, cuprite and malachite (Figure 4.11 and 4.12). High copper extractions are achieved at the start of the experiment, followed by a decrease in extraction and then a steady increase once the Eh changes. Cuprite leaches according to Equation (IV.7) (ΔG^0 of Equation (IV.7) is -117.5 kJ/mol, using -518.8 kJ/mol for $S_2O_3^{2-}$):

The high concentration of sulfate after 5 minutes and its steady decline does not seem to correlate with the patterns previously observed. By summing up the concentrations of thiosulfate, tetrathionate and sulfate, a sulfur balance can be calculated at every moment of the experiment (Appendix D). This balance will be discussed in more detail in section 4.6. The resulting sulfur balance for this experiment is quite close to the 0.4 M sulfur (0.2 M $S_2O_3^{2-}$) which was originally added to the system. A closer examination of the graph revealed that the results can be explained by sample degradation.

The samples are analyzed as soon as possible by ion chromatograph. Practically, however, the time between taking the sample and analysis by ion chromatograph can be up to 7 to 10 hours for the first few samples (taken at 5, 30, 60 minutes) and less than 7 hours for the last samples. When a lot of copper is present in solution, as is the case when leaching the copper oxide minerals, and the cupric ion is generated in the presence of air, the degradation of thiosulfate is accelerated (see section 2.3.3).

Re-examining Figure 4.11, the leaching of cuprite results in a high copper extraction. The graph

also shows that there is a relatively high tetrathionate concentration and very high sulfate concentration. Both are the products of thiosulfate degradation. The previous graphs show similar trends, but to a lesser extent because the copper concentrations are lower.

Figure 4.11 shows that after the initial high copper extraction the copper concentration declines and stabilizes after about 240 minutes. The same explanation given for the leaching of chalcocite applies to cuprite. At 30 minutes copper is complexed with both thiosulfate and ammonia, because there is not enough thiosulfate in solution to complex copper and give a free thiosulfate concentration of 5 g/L thiosulfate (see bottom graph, Figure 4.11). This is confirmed by the blue colour of the solution, indicating the presence of the copper(II)ammonia complex. From this, it can be concluded that Figure 4.4. seems to represent the actual solution more accurately, instead of Figure 4.3.

If the copper was mainly complexed with ammonia during the entire experiment, the decline in copper extraction would not have been observed, since the ammonia concentration remains fairly constant during the experiment. There will only be a slight ammonia loss to the atmosphere. The same explanation can be applied to malachite (Figure 4.12).

For the enargite mineral sample the conditions were different. After several experiments it was concluded that the 5g/L addition was too high in order to observe the leaching of copper with both thiosulfate and ammonia, since there was a deficiency of thiosulfate. It was decided to lower the mineral addition such that upon 100% copper dissolution, the copper concentration would be 1 g/L. In the remainder of this chapter this will be referred to as a 1 g/L copper addition.

From Figure 4.10 it can be observed that enargite barely dissolves in ammonium thiosulfate under the applied experimental conditions. The effect of a low copper concentration in solution on thiosulfate degradation can be clearly observed from this experiment. The copper that dissolves is probably converted to cupric in the presence of air, but the concentration is too low to significantly affect thiosulfate stability. The pH of the solution changes only slightly and only small amounts of tetrathionate and sulfate are detected.

4.3.2 Effect of aeration

In these experiments no forced aeration of the solution was applied, however, the vessel was not sealed airtight. It can be assumed that air was able to enter the reactor and the leach slurry, especially since a high stirring speed was applied (see section 3.2).

Comparing Figure 4.8 and Figure 4.13 clearly illustrates the effect of aeration on thiosulfate degradation. Figure 4.13 shows that the thiosulfate concentration remains high; degradation does not occur appreciably. This is confirmed by the constant pH value. Because the system is not aerated the potential of the solution is lower. The erratic nature of the potential indicates that the system has not yet stabilized. The copper extraction shows a steady increase but remains fairly low. Compared to the leaching of chalcocite in an aerated system the final copper extractions do not differ significantly. It appears that the thiosulfate concentration in solution does not affect the final copper concentration in solution. The erratic behaviour of the sulfur species is explained by sample degradation.

The leaching of cuprite in a non-aerated system is shown in Figure 4.14. Thiosulfate remains in

Figure 4.13 Chalcocite, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no aeration, 35°C

Figure 4.14 Cuprite, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no aeration, 35°C

solution. The low thiosulfate concentrations in the first half of the experiment are explained by sample degradation. The later samples are more representative of the true leaching conditions, because the length of time between sampling and analyses was less for these samples.

As for copper extraction, it can be observed that the initial extraction is just as high as with aeration. The major difference is that, without aeration, the copper extraction remains high throughout the course of the experiment. This indicates that the decline in copper concentration presented in Figure 4.11 is due to the degradation of thiosulfate. The colour of the solution is light blue during the experiment, indicating copper is complexed by both thiosulfate and ammonia. The stable Eh and pH of the solution reflect the minimal thiosulfate degradation. The Eh shows a small increase directly after the start of the experiment, indicating the quick dissolution of cuprite.

From this study, it can be concluded that both air and cupric ion concentration play an important role in thiosulfate degradation. With copper in solution as cupric, thiosulfate degradation occurs readily and the cupric ion is converted to cuprous (Equation IV.8). The cuprous ions in solution will be easily re-oxidized by air to cupric ions resulting in a fast rate of thiosulfate degradation (Equation IV.9). The overall reaction is represented by Equation (IV.10). When no aeration is applied, the cuprous ion is not as readily oxidized to the cupric ion, resulting in greater thiosulfate stability.

Overall reaction:

4.3.3 Summary

In general it can be observed that the leaching of copper sulfide minerals in an ammonium thiosulfate solution with and without aeration, results in low copper extractions, around 0.5 to 1 g/L copper. Chalcopyrite and enargite seem to be unreactive toward ammonium thiosulfate leaching. The copper oxide minerals show high initial copper extractions, followed by a decline in extraction in the case of aeration. The copper extractions remain high without aeration.

The Eh-pH diagram of the copper-thiosulfate-ammonia-water system presented in Figure 4.4 seems to give a more accurate representation of the actual solution conditions, then the Eh-pH diagram given in Figure 4.3.

The following effects were observed regarding thiosulfate degradation:

- A combination of aeration and copper, whereof a significant amount will be present as the cupric ion in the presence of air, results in fast thiosulfate degradation.
- In the absence of aeration, even a substantial amount of copper in solution (~ 1 to 4 g/L) does not constitute a detrimental effect on thiosulfate stability.
- In the presence of a small amount of copper (~0.1 g/L) and aeration, thiosulfate remains longer in solution (leaching of enargite (Figure 4.10)).
- The continuing occurrence of thiosulfate degradation in samples has to be taken into consideration when interpreting the ion chromatograph analyses.

4.4 Leaching of copper minerals with gold addition

In this set of experiments, the copper minerals were leached with a 5 ppm gold addition to solution (see Table 3.E). The effect of the different variables on the leach reaction are only investigated with regard to chalcocite and cuprite.

For the next two sections the following comment regarding the gold extraction curves is highlighted. Three solution samples were analyzed for gold content per experiment (30, 120 and 360 minutes). In the figures lines are drawn through those three sample points. This is to indicate a trend; it is not intended to imply that the gold extraction actually follows this curve. For a few experiments more samples were analyzed, resulting in a more accurate understanding of the behaviour of gold. All % copper extraction calculations are based on the head assays of the copper minerals. Gold extractions (%) are based on the 5 ppm gold addition.

4.4.1 Baseline experiments

Figure 4.15 shows the leaching of covellite at 1 g/L copper addition. Comparing this figure to Figure 4.7, the leaching of covellite at 5 g/L without gold, a few differences can be observed. Firstly, the pH during heating (at “negative” time) is lower. This is due to the addition of the gold to the solution (as chloride complex in 10% hydrochloric acid, see section 3.1.3). The pH of the solution was immediately raised to pH 10 with concentrated sodium hydroxide after the ammonium thiosulfate addition, to avoid any hydrolysis of the ammonium thiosulfate at the low pH (see section 2.1.3).

Figure 4.15 Covellite, 5 ppm gold, 1 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

The pH follows the pattern described previously. Since the thiosulfate is still present at the end of the experiment, the reduction of oxygen is the dominant reaction which produces hydroxide ions resulting in a steady increase in pH. The potential of the solution remains fairly stable, and at the same value as the potential in Figure 4.7 before the thiosulfate disappeared.

The total amount of copper extracted is lower in the experiment with 1 g/L addition compared to the 5 g/L addition (0.15 g/L copper vs. 0.85 g/L copper). It seems that the copper extraction is independent of thiosulfate or ammonia availability. Further, it can be noted that the gold remains in solution during the leaching of covellite.

The bottom graph illustrates the effect of lower copper concentration on thiosulfate degradation. Comparing the detected thiosulfate concentration with the concentration plotted in Figure 4.7 it can be concluded that the thiosulfate degrades at a slower rate when less copper is present in solution. Thiosulfate is still detected after 6 hours with lower copper concentration. This effect has already been discussed in the leaching of enargite.

The leaching of chalcocite in the presence of gold shows the same patterns for pH, Eh, thiosulfate, tetrathionate and copper compared to the leaching of chalcocite without gold addition (Figure 4.16). The high sulfate concentration and its subsequent decline can be attributed to sample degradation. The behaviour of the gold in solution is quite different from the previous discussed experiment (Figure 4.15). The line is dashed to indicate that it is unknown how the gold extraction behaves between the points. More samples were not available for analysis.

Figure 4.16 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

This experiment was also performed with an addition of 1 g/L copper (Figure 4.17). It has to be remembered that gold was added as a solution. The fact that the gold extraction at time 120 minutes is higher than at time 30 minutes is therefore difficult to explain. It might be that gold precipitated during heating and that it was resolubilized by the thiosulfate. When thiosulfate is no longer present in solution, gold precipitates, although more gold remains in solution compared to the experiment with 5 g/L copper addition.

Before this phenomena is discussed the results of the leaching of the other copper minerals with gold addition are examined. Chalcopyrite shows a stable Eh and pH which only rises at the end of the experiment indicating that almost no thiosulfate degradation takes place until the end of the experiment (Figure 4.18). This is confirmed by the measured thiosulfate concentrations. Copper extraction is low, even lower compared to the experiment with a 5 g/L copper addition.

The gold extraction shows the same pattern as with chalcocite; slightly lower extraction at 30 minutes than at 120 minutes. The gold remains in solution throughout the entire experiment, similar to covellite. Enargite (Figure 4.19) shows almost exactly the same behaviour as the experiment without gold addition (Figure 4.10). The gold also remains in solution throughout the entire experiment.

The leaching of cuprite (Figure 4.20) follows the same patterns as those presented in Figure 4.11. The initial tetrathionate concentration is very high. Coupled with the very low initial thiosulfate concentration and its subsequent increase and a high copper concentration, this pattern indicates sample degradation. It can be seen that gold precipitates slightly.

Figure 4.17 Chalcocite, 5 ppm gold, 1 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

Figure 4.18 Chalcopyrite, 5 ppm gold, 1 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

Figure 4.19 Enargite, 5 ppm gold, 1 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

Figure 4.20 Cuprite, 5 ppm gold, 5 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

Sample degradation is also visible in the leaching of malachite (Figure 4.21). The very low initial thiosulfate concentration, its increase later, the high tetrathionate, sulfate and copper concentration indicate sample degradation. Gold is not affected and remains in solution. It has to be commented that the overall copper extraction for cuprite and malachite is lower with the 1 g/L copper addition than the 5 g/L copper addition.

It can be seen for chalcocite, cuprite and malachite that there is no thiosulfate left in solution after 180 to 240 minutes, this opposed to the covellite, chalcopyrite and enargite where thiosulfate remains present for 6 hours. The experiments with the first three minerals showed gold precipitation, whereas gold remains in solution during the experiments of the latter three minerals.

4.4.2 Effect of aeration

Experiments without aeration were performed for chalcocite (Figure 4.22) and cuprite (Figure 4.23). The same conditions apply as described in section 4.3.2. Chalcocite shows a stable pH and potential, which is confirmed by the thiosulfate concentration which barely changes. The resulting copper extraction is lower than previous experiments. This is probably due to the low potential, which is lower than previous experiments with chalcocite ($\sim 50 \text{ mV}_{\text{SHE}}$ vs. $250 \text{ mV}_{\text{SHE}}$). As opposed to the experiment with aeration, gold remains in solution during the whole experiment.

Figure 4.21 Malachite, 5 ppm gold, 5 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35°C

Figure 4.22 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no aeration, 35°C

Figure 4.23 Cuprite, 5 ppm gold, 1 g/L copper, 0.20 M (NH₄)₂S₂O₃, no aeration, 35°C

The sulfur analysis of Figure 4.23 shows high tetrathionate and sulfate concentrations and a thiosulfate concentration which increases after 180 minutes. This trend indicates sample degradation of the first 5 samples. Copper extraction is high (1 g/L copper addition), however, the copper extraction of cuprite at 5 g/L with aeration is higher. It was observed that copper and gold extraction declined with time when aeration was applied. Figure 4.23 shows that copper and gold remain in solution without aeration. The above results indicate that the retention of gold in solution is ensured by the presence of thiosulfate.

4.4.3 Effect of temperature

Two experiments were performed at 20°C to investigate the effect of temperature on thiosulfate stability. Comparing the figures representing the leaching of chalcocite and cuprite at 35°C (Figures 4.17 and 4.20) with those obtained at 20°C (Figures 4.24. and 4.25), it can be observed that the thiosulfate degradation is slightly delayed in the case of chalcocite. The effect is barely noticeable for the leaching of cuprite. The ion chromatograph analysis for cuprite suggest the occurrence of sample degradation for the initial samples indicated by the high tetrathionate and sulfate concentrations.

The recorded pH and potential show that the patterns for both minerals are similar to those obtained during leaching at 35°C, only slightly delayed. The behaviour of gold and the copper extraction follow the same pattern at 20 and 35° for chalcocite. For cuprite, the results cannot be compared since the mineral feed was not the same (5 g/L copper vs. 1 g/L copper).

Figure 4.24 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 20°C

Figure 4.25 Cuprite, 5 ppm gold, 1 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 20°C

4.4.4 Effect of reagent addition

As discussed in chapter 2, section 2.3.3, several papers attribute a positive effect to the addition of sulfite and sulfate to an ammonium thiosulfate leach solution. The additions are supposed to stabilize the thiosulfate in solution. The effects of the additions were investigated with the copper mineral chalcocite and the results are presented in Figure 4.26 (addition of sulfite) and 4.27 (addition of sulfate).

Comparing these results to Figure 4.17, it can be observed that the additions did not significantly improve the stability of thiosulfate. The Eh increases are slightly delayed in time, indicating that thiosulfate remains slightly longer in solution. Copper and gold behaviour are similar in all three experiments. The only visible difference is the increase in sulfate concentration when sulfite and sulfate are added. This endorses the statement postulated in section 2.3.3 that sulfite acts as a sacrificial reagent, oxidizing to sulfate. The effect of sulfate cannot be explained with the data available.

Low copper extractions were observed during the baseline experiments. It was thought that this might be due to a low ammonia concentration. One experiment was performed with an additional 0.4 M ammonia resulting in a total ammonia concentration of 0.8 M (Figure 4.28). It can be seen that the extra ammonia had no beneficial effect on the copper extraction, and decreased the thiosulfate stability.

Figure 4.26 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 0.05 M SO_3^{2-} , aeration, 35°C

Figure 4.27 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 0.05 M SO_4^{2-} , aeration, 35°C

Figure 4.28 Chalcocite, 5 ppm gold, 5 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 0.4 M NH_3 , aeration, 35°C

4.4.5 Gold precipitation

At the instant that thiosulfate is no longer present in solution, the following reaction is driven to the left and gold precipitates, unless it is complexed by something else in solution:

Thermodynamically, ammonia should be able to complex the gold, but that does not seem to occur. The discussion in section 4.1 already indicated that it seems that Figure 4.1 represents more accurately the actual solution conditions instead of Figure 4.2. However, it can be noticed that in several cases the gold extraction does not completely go to zero, although there is no thiosulfate present in solution. Several explanations can be given for this phenomena:

- Ammonia complexes gold to a certain extent. The literature reports 10 to 20% gold extraction in the presence of ammonia and cupric ions [Zipperian et al, 1988; Cao et al, 1992].
- Gold precipitates as colloidal gold, and is therefore detected in solution.
- There is still a small amount of thiosulfate left in solution not detected by ion chromatographic analysis, providing enough background for gold to remain in solution to a certain extent

The presence of a background concentration of thiosulfate is confirmed by ion chromatograph measurements (Figure 4.29). Typical dilution factor for all experiments was 1000 times. This dilution factor ensured that the samples could be measured within the calibration range (2-20 ppm, see Appendix B). A disadvantage was that concentrations below 1-2 ppm were not detected. This implies that, with a 1000 times dilution factor, concentrations below 1-2 g/L

thiosulfate could still be present in solution. Figure 4.29 shows the measurement of a sample at 1000, 500 and 50 times dilution. At 1000 and 500 times no thiosulfate is detected, whereas a small thiosulfate concentration is detected at 50 times dilution. This indicates that about 0.1 g/L of thiosulfate is in solution, providing enough background for gold to remain in solution. More research has to be performed to determine the nature of the gold precipitates.

Figure 4.29 Effect of dilution factor on detected thiosulfate concentration (retention time thiosulfate is 1.9 minutes)

4.4.6 Summary

It can be concluded that in the presence of chalcocite, cuprite and malachite gold precipitates out of solution, while gold remains in solution in the presence of covellite, chalcopyrite and enargite.

This seems to correlate with the fast degradation of thiosulfate observed during the leaching of

the first three minerals. High copper concentrations were achieved during the leaching of those three minerals, thus increasing the presence of cupric ion in solution, which enhances the degradation of thiosulfate. The copper extractions achieved during the baseline experiments of this series and the series discussed in section 4.3 are summarized in Table 4.A. It is evident from Table 4.A that the copper extractions did not improve by lowering the mineral feed addition and thus increasing lixiviant availability.

Table 4.A Copper extractions (%) of copper minerals at different times during baseline experiments.

Mineral	% Copper leached at time (in minutes)							
	Feed addition	Leaching of copper minerals			Feed addition	Leaching of copper minerals + gold addition		
		30	120	360		30	120	360
Covellite	5 g/L Cu	5.8	6.7	16.5	1 g/L Cu	8.8	14.3	15.1
Chalcocite	5 g/L Cu	26.0	17.8	24.0	5 g/L Cu	29.5	26.3	18.3
Chalcocite	-	-	-	-	1 g/L Cu	19.7	35.7	46.4
Chalcopyrite	5 g/L Cu	2.7	5.1	8.9	1 g/L Cu	3.78	9.9	14.5
Enargite	1 g/L Cu	3.8	6.3	9.2	1 g/L Cu	3.19	5.7	9.2
Cuprite	5 g/L Cu,	79.1	36.2	22.8	5 g/L Cu,	80.9	32.2	24.4
Malachite	5 g/L Cu	64.8	62.5	44.5	1 g/L Cu	87.0	86.1	83.5

No beneficial effect of lower temperature, sulfite and sulfate addition on thiosulfate stability was observed. Lower copper extractions with 1 g/L copper addition were observed compared to the copper extractions achieved with 5 g/L copper addition. This cannot be attributed to an ammonia deficiency since an extra addition of ammonia did not improve copper extractions. It may be

that the copper minerals are not provided with sufficient oxidizing agents and/or the leach temperature is too low, resulting in poor copper extractions.

Regarding the use of the Eh-pH diagrams given in Figure 4.1 to Figure 4.4 to explain the experimental results presented in section 4.3 and 4.4. the following can be concluded:

- For the gold-thiosulfate-ammonia-water system, Figure 4.1 (using the free energy value of -518.8 kJ/mol for thiosulfate) seems to give a more accurate representation of the actual leaching conditions
- For the copper-thiosulfate-ammonia-water system, Figure 4.4 (using the free energy value of -532.2 kJ/mol for thiosulfate) seems to explain the experimental results better.

More fundamental research is necessary to investigate this phenomenon.

4.5 Leaching of copper-gold samples

The experimental results of the copper-gold samples are discussed per copper-gold sample, to directly observe the influence of the different variables (Table 3.F). In this series baseline experiments were performed and the effects of aeration and cupric addition were studied. The gold extraction calculations are based on calculated head, the copper extraction calculations on solids head assay.

The cyanide consumption and copper and gold extraction of the copper-gold materials were determined by a 24 hour cyanide leach at a constant 1 g/L cyanide level. The experimental conditions are described in Appendix E. The results are summarized in Table 4.B.

Table 4.B Results of 24 hour cyanide leach of the copper-gold samples

Copper-gold samples	Gold extraction (%)	Copper extraction (%)	Cyanide consumption (kg/t ore)
Overall Lobo Composite	81.4	41.4	4.38
Guanaco Composite	84.3	70.4	6.77
M40 Pyrite Feed	94.7	34.9	6.40
M10 Pyrite Concentrate	47.5	28.3	9.91
M10 Pyrite Concentrate*	81.2	50.3	n.a.

*Data obtained from Newcrest Mining Ltd. [Oretest, 1997]

Cyanide leaching of all copper-gold samples resulted in high cyanide consumption, and consequently a high reagent cost must be anticipated when treating these samples with cyanide.

It can be seen that a substantial amount of the copper in all samples is cyanide soluble.

Two test numbers are listed for the M10 Pyrite Concentrate. The first was obtained during the leach described in Appendix E, the second was provided by Newcrest Mining Ltd; a 24 hour cyanidation at an initial cyanide concentration of 1.25 g/L cyanide, maintained at 0.75 g/L cyanide. The first number is believed to be low because of the following reaction:

which indicated the presence of free cyanide, while in reality it was complexed with copper.

4.5.1 Overall Lobo Composite

Figure 4.30 gives the results of the leaching of the Overall Lobo Composite with a 1 g/L cupric ion addition in an aerated system. Similar patterns as described in the previous sections are

observed for the pH and Eh. The pH initially increases, and starts decreasing around 180 minutes which coincides with an increase in Eh. The initial Eh, during heating of the solution without any reagents present, shows a sharp decrease. Apparently, a component is present in the ore which strongly consumes oxygen.

The line representing the thiosulfate concentration is dashed, the 180 minutes sample was not analyzed for sulfur species. The line implies that the thiosulfate concentration is about 5 g/L after 180 minutes and zero around 240 minutes. However, the pH and Eh patterns indicate that most thiosulfate was gone after 180 minutes. The erratic pattern of tetrathionate is attributed to sample degradation.

Gold extractions are stable around 40%. Initially copper is high which can be explained by the 1g/L cupric addition. The decline in copper extraction with time can be attributed to the disappearance of thiosulfate, a pattern that has been observed previously. The experiment was conducted with coarse material ($P_{80} = 253 \mu\text{m}$) and the aeration of the system did not work properly (the sparger plugged). The experiment was duplicated with reground material ($P_{80} = 141 \mu\text{m}$) and the results are presented in Figure 4.31.

Most patterns are comparable to those of Figure 4.30. The thiosulfate concentration goes to zero after 180 minutes and the tetrathionate, sulfate and copper values are resembling those of Figure 4.30. Two differences can be observed. The Eh value shows a steady increase during the second half of the experiment, and the gold extraction is lower during the second experiment.

Figure 4.30 Overall Lobo Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35°C

Figure 4.31 Overall Lobo Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35°C, reground.

Figure 4.32 Overall Lobo Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, no aeration, 35°C

Figure 4.33 Overall Lobo Composite, 0.20 M (NH₄)₂S₂O₃, no cupric addition, aeration, 35°C

Figure 4.34 Overall Lobo Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no cupric addition, aeration, 35°C, duplicate

The experiment with 1 g/L cupric addition without aeration is shown in Figure 4.32. As shown with the previous series of experiments without aeration, thiosulfate remains in solution during the whole experiment, copper is present at a constant value. Gold slowly dissolves and the final extraction is similar to the one achieved in the first experiment. The irregular pattern of the Eh cannot be explained; after the increase it stabilizes again at its previous value.

Figure 4.33 shows the effect of aeration without cupric addition. A higher gold extraction was achieved and the thiosulfate concentration remains very high. This is confirmed by the stable pH and Eh values. A duplicate of this experiment was performed to ensure that sufficient aeration had been applied (Figure 4.34). The results are very similar, except for gold extraction, which indicates that the reproducibility of the experiment is good. When no cupric is added to the solution, the resulting copper extraction is very low; the composite contains mainly chalcopyrite (see section 3.1.2) which shows comparable low copper extraction (Figure 4.18).

Summary

The leaching of the Overall Lobo Composite results in moderate gold extractions. The absence of both aeration and cupric ion addition have a positive effect on the thiosulfate stability and result in the case of no cupric ion addition (with aeration) in a gold extraction of 66%. Copper in this composite seems to be unreactive towards ammonium thiosulfate leaching. The beneficial effect of cupric ions addition on the gold extraction is not demonstrated in these experiments. The copper and gold extractions of the experiments are summarized in Table 4.C.

From Table 4.C, it can be concluded that most of the copper(II)sulfate initially added to the leach solution, precipitates. Compared to the cyanidation results (81.4 % Au, 41.4 % Cu after 24 hours) it can be concluded that comparable gold extractions are achieved in the experiment with aeration and no cupric ion addition. Copper extractions with the ammonium thiosulfate leach are very low compared to the cyanidation.

Table 4.C Gold and copper extraction (%) of Overall Lobo Composite at different times.

Experimental Conditions	%Gold extracted at time (minutes):				%Copper extracted at time (minutes):		
	30	120	360	Total*	30	120	360
Aeration	42.0	41.6	41.2	62.1	36.9	20.4	11.6
Aeration, duplicate	16.2	15.9	15.5	44.8	35.0	13.8	11.3
No aeration	b.d.	b.d.	35.8	n.a.	48.0	48.6	48.7
Aeration, no cupric	34.6	67.9	66.0	73.5	9.3	11.7	12.6
Aeration, no cupric, duplicate	b.d.	34.2	66.5	74.3	7.9	10.4	12.6

*Total represents total gold extraction, including wash water

b.d.= below detection limit

n.a.= not available

The thiosulfate consumption for the 24 hours experiment was around 15.7 kg/tonne ore, which results in a reagent cost of US\$2.04/tonne ore (US\$0.13/kg). The concentrate contains 2.11 g/tonne gold which yields US\$20.3/tonne (at US\$300/oz gold). Thus, the reagent cost constitutes about 10% of the total metal value. Cyanidation would result in a reagent cost of US\$7.88 (cyanide consumption of 4.38 kg/tonne ore). Thiosulfate leaching compares favourable to cyanidation for this experiment, however both leaches are not very economical.

4.5.2 Guanaco Composite

The leach behaviour of the Guanaco Composite presented in Figures 4.35 to 4.37, resembles closely the patterns observed during the leaching of the Overall Lobo Composite. Aeration of the solution with cupric ion addition resulted in the disappearance of thiosulfate which is confirmed by the pH and Eh patterns (Figure 4.35). The gold extraction declines to zero when the thiosulfate is no longer present. The initial copper extraction is slightly higher than the final extraction.

When cupric is added and no aeration is applied, the Eh of the system is very erratic and shows an upward trend (Figure 4.36). The lowering of the thiosulfate concentration is not reflected in the pH curve, and thus indicates sample degradation. Initially, there is not a lot of copper in solution, and thus sample degradation should not significantly occur. The samples taken after 120 minutes contain more copper and therefore sample degradation is catalyzed.

Both gold and copper follow an upward trend. Especially copper shows a large increase. It seems that due to the low Eh value at the start of the experiment, the added cupric ions precipitated. The solution colour changed around 240 minute from colourless to very light blue. This indicates that initially the copper could be complexed as the thiosulfate and copper(I)ammonia complex, which are both colourless. The oxidation of the copper(I)ammonia to the copper(II)ammonia complex progresses slow in the absence of an abundant amount of air, but explains the steady rise in Eh and copper extraction.

Figure 4.35 Guanaco Composite, 0.20 M (NH₄)₂S₂O₃, 1 g/L cupric addition, aeration, 35°C

Figure 4.36 Guanaco Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, no aeration, 35°C

Figure 4.37 Guanaco Composite, 0.20 M (NH₄)₂S₂O₃, no cupric addition, aeration, 35°C

Aeration and no cupric ion addition resulted in thiosulfate degradation, as opposed to the result of the leaching of the Overall Lobo Composite (Figure 4.37). The copper concentration is higher in this solution explaining the occurrence of thiosulfate degradation. However, compared to Figure 4.35, leaching of the composite in the presence of air and with cupric ion addition, the thiosulfate degradation is slightly delayed. This implies that the addition of cupric ions results in faster thiosulfate degradation. Copper extraction remains fairly constant and gold extraction decreases at the end of the experiment.

When comparing the three figures it can be concluded that the same gold extractions are achieved every experiment, however, at different times. When aeration is applied, initial gold extractions of around 40% are achieved, which is the same as the final gold extraction of the experiment without aeration. However, the experiment without aeration implies that higher gold extractions can be achieved when the experiment is allowed to last longer, since thiosulfate is still present in solution.

One experiment was performed with Thiogold™ grade ammonium thiosulfate (see section 3.1.3). The results are presented in Figure 4.38. The high initial gold extraction is due to an analytical error. The conclusion that can be drawn from this experiment is that the purity of the thiosulfate solution has no effect on the gold extraction.

Figure 4.38 Guanaco Composite, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ (Thiogold™ grade), 1 g/L cupric addition, aeration, 35°C

Summary

Similar gold extractions are achieved under all conditions, however, at different times. Initial gold extractions are higher in an aerated system, while final extractions are higher in a non-aerated system. Copper extractions are low when thiosulfate is not present during the entire experiment. In the presence of thiosulfate higher copper extractions are achieved. Like the Overall Lobo Composite there is no obvious beneficial effect observed on gold extraction with cupric ion addition. Table 4.D lists the gold and copper extractions of the experiments.

Table 4.D Gold and copper extraction (%) of Guanaco Composite at different times.

Experimental Conditions							
	%Gold extracted at time (minutes):				%Copper extracted at time (minutes):		
	30	120	360	Total*	30	120	360
Aeration	33.6	33.0	b.d.	0.0	47.0	34.9	32.5
No aeration	b.d.	b.d.	39.6	44.0	9.0	28.7	59.2
Aeration, no cupric	51.6	50.6	24.6	30.7	30.4	31.5	24.7
Aeration, Thiogold™	112.3	36.8	35.7	36.7	46.5	37.3	36.9

*Total represents total gold extraction, including wash water
b.d. = below detection limit

Compared to the cyanidation results (84.3% Au, 70.4 % Cu at 24 hours cyanidation) it can be seen that the extractions achieved with ammonium thiosulfate are low. For this composite, the experiment with no forced aeration should be extended to a 24 hours leach, enabling a more accurate comparison with the cyanidation test results.

4.5.3 M40 Pyrite Feed

As can be seen in Figures 4.39 to 4.42, the experimental results of the M40 Pyrite Feed generally follow the same patterns as observed previously. One additional experiment was performed in which no cupric was added to the solution and no aeration was applied (Figure 4.42). Both the experiments shown in Figure 4.41 and 4.42 were conducted at 0.24 M ammonium thiosulfate.

Comparison of the experiments with aeration and cupric addition (Figure 4.39) and aeration without cupric addition (Figure 4.41) shows that the cupric addition accelerates the thiosulfate degradation. This is visible from the pH, Eh and thiosulfate curves. The experiment without cupric addition shows a steady increase in copper extraction.

Comparison of the experiments presented in Figure 4.40 and 4.42, both without aeration and one with cupric addition and one without, show that similar low gold extractions are achieved. The cupric addition does not seem to influence the leaching of gold. High tetrathionate concentrations were detected (Figure 4.40) and it is difficult to predict whether this occurred in the leach solution or was due to sample degradation. The low copper extraction in Figure 4.42 demonstrates that the copper in the M40 Pyrite Feed, which is mainly chalcopyrite, is unreactive toward an ammonium thiosulfate leach. This corresponds to the results of the leaching of chalcopyrite (Figure 4.18).

Figure 4.39 M40 Pyrite Feed, 0.20 M (NH₄)₂S₂O₃, 1 g/L cupric addition, aeration, 35°C

Figure 4.40 M40 Pyrite Feed, 0.20 M (NH₄)₂S₂O₃, 1 g/L cupric addition, no aeration, 35°C

Figure 4.41 M40 Pyrite Feed, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no cupric addition, aeration, 35°C

Figure 4.42 M40 Pyrite Feed, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, no cupric addition, no aeration, 35°C

Summary

Highest gold extractions were achieved in an aerated system around 120 to 180 minutes. The gold precipitates when the thiosulfate starts degrading significantly. Low gold extractions were achieved in the non-aerated system, however, thiosulfate is still present. This implies that higher gold extraction could be achieved when the residence time is prolonged. Cupric addition did not show a pronounced effect on gold extractions, in both an aerated and non-aerated system. The copper in the concentrate seems unreactive towards an ammonium thiosulfate leach. Copper and gold extractions for all experiments are summarized in Table 4.E.

Table 4.E Gold and copper extraction (%) of M40 Pyrite Feed at different times.

Experimental Conditions	%Gold extracted at time (minutes):				%Copper extracted at time (minutes):		
	30	120	360	Total*	30	120	360
Aeration	11.1	32.8	10.6	14.1	30.4	29.3	32.0
No aeration	10.5	10.3	19.9	21.3	30.2	29.1	28.6
Aeration, no cupric	13.3	26.1	12.7	14.5	11.5	13.9	21.4
No aeration, no cupric	10.1	9.9	19.3	22.7	7.2	7.1	7.4

*Total represents total gold extraction, including wash water

The results of the ammonium thiosulfate leach are very low compared to the cyanidation test results (94.7% Au, 34.9% Cu with 24 hours leach). It is uncertain why this concentrate shows such low overall extractions.

4.5.4 M10 Pyrite Concentrate

The experiments involving the M10 Pyrite Concentrate are presented in Figures 4.43 to 4.47. From Figure 4.43, it can be observed that gold extractions of 80% were achieved after 120 minutes. The same experiment without cupric addition resulted in 50% gold extraction, indicating a positive effect of the cupric ion addition (Figure 4.45). The final copper concentrations were low in both cases and very similar. This indicates that a portion of the cupric ions added to the solution precipitated during the experiment.

The experiment performed without aeration resulted in a gold extraction of 50% (Figure 4.43). It was decided to duplicate this experiment and extend the leaching time to 24 hours, to observe the effect on thiosulfate concentration and gold extraction. The results are presented in Figure 4.45. A gold extraction of 80% was achieved and thiosulfate is still present in solution. A plausible explanation for the increase in thiosulfate concentration from 5 to 500 minutes is sample degradation; the samples were analyzed after about 30 hours. The copper extraction remained stable during the entire 24 hours.

Two observations can be made from the series of experiments presented in section 4.15 to 4.46:

- Gold precipitates when no thiosulfate is present in solution.
- The copper extractions remain low, perhaps because of the presence of insufficient complexing agents (M10 Pyrite Concentrate contains 16,600 ppm copper).

Figure 4.43 M10 Pyrite Concentrate, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35°C

Figure 4.44 M10 Pyrite Concentrate, 0.20 M (NH₄)₂S₂O₃, 1 g/L cupric addition, no aeration, 35°C

Figure 4.45 M10 Pyrite Concentrate, 0.20 M (NH₄)₂S₂O₃, 1 g/L cupric addition, no aeration, 35°C, 24 hours

Figure 4.46 M10 Pyrite Concentrate, 0.20 M (NH₄)₂S₂O₃, no cupric addition, aeration, 35°C

To investigate this, an experiment was performed with an initial ammonium thiosulfate concentration of 0.36 M (Figure 4.47). Every hour, at 60, 120, 180, 240 and 300 minutes, an additional 0.072 M of ammonium thiosulfate was added to the solution, resulting in a total ammonium thiosulfate concentration of 0.72 M. Every ammonium thiosulfate addition gave rise to a slight decrease in pH and Eh. As can be seen from the graph, 80% gold extraction was also achieved in this experiment, and the final thiosulfate concentration is almost zero. The copper extraction is not affected by the additional thiosulfate and ammonia.

The M10 Pyrite Concentrate contains a considerable amount of copper (16,600 ppm), which means that 0.72 M ammonium thiosulfate does not provide sufficient thiosulfate to complex all the copper, but it does supply sufficient ammonia to complex all the copper. The copper is mainly present as chalcopyrite, which does not leach very well in ammonium thiosulfate solutions, as observed in section 4.3 and 4.4.

Summary

The combination of aeration and cupric addition results in high gold extraction (80%) early in the experiment (around 120 minutes), but is followed by gold precipitation due to the degradation of thiosulfate. Similar gold extractions were obtained in a 24 hour leach without aeration and a leach with a total addition of 0.72 M thiosulfate. Cupric addition resulted in higher initial gold extractions and total copper extraction is not significantly influenced by any of the variables tested: cupric addition, aeration, leaching time, reagent concentration. Table 4.F summarizes the copper and gold extractions achieved.

Figure 4.47 M10 Pyrite Concentrate, 0.72 M (NH₄)₂S₂O₃, 1 g/L cupric addition, aeration, 35°C

Table 4.F Gold and copper extraction (%) of M10 Pyrite Concentrate at different times.

Experimental Conditions	%Gold extracted at time (minutes):				%Copper extracted at time (minutes):		
	30	120	360	Total*	30	120	360
Aeration	39.2	87.1	5.9	7.2	21.2	20.5	27.4
No aeration	14.1	29.7	50.0	55.6	20.1	20.8	21.0
No aeration, 24 hours	13.2	29.8	76.1**	83.3	20.3	21.6	21.7**
Aeration, no cupric	39.8	49.3	3.99	5.8	11.9	12.9	23.6
0.72 M (NH ₄)S ₂ O ₃	49.1	74.3	76.1	84.4	23.6	25.5	29.2

*Total represents total gold extraction, including wash water

** at time 1440 minutes (24 hours)

The gold extractions achieved during the 24 hour leach compare very well to the cyanidation test results (81.4% Au, 50.3% Cu at 24 hours). It should be noted that the resulting copper extractions are very low. The thiosulfate consumption for the 24 hours experiment was around 40 kg/tonne ore, which results in a reagent cost of US\$5.2/tonne ore (US\$0.13/kg). The concentrate contains 45.5 g/tonne gold which yields US\$436/tonne (at US\$300/oz gold). Thus, the reagent cost constitutes about 1.2% of the total metal value. The cyanide consumption was not available.

4.6 Sulfur balance

A closer examination of the curves representing the sulfur species in the figures discussed above, reveals that not all the sulfur that was added to the solution (0.2 M ammonium thiosulfate) is

accounted for by the sulfur species detected by the ion chromatograph. A good example is given in Figure 4.47, the leaching of the M10 Pyrite Concentrate with a total addition of 0.72 M ammonium thiosulfate. After 360 minutes a negligible amount of thiosulfate and tetrathionate is detected and about 5 g/L sulfate. Since the experiment indicates that thiosulfate degrades, it is expected that a large amount of tetrathionate and sulfate are present. If all the thiosulfate converted to sulfate, 138 g/L of sulfate should be present. However, the ion chromatography analyses did not detect high concentrations of either sulfate or tetrathionate.

In Appendix D the sulfur balances for all experiments are presented, which clearly indicates that the sulfur balance of most experiments is not correct. To investigate where the sulfur reported to, several leach solutions were analyzed for sulfate using barium chloride (Appendix F). The experiments indicated that the sulfate levels were not significantly high compared to the ion chromatograph analyses. Next, several copper mineral residues were analysed for sulfur species (S^{total} , S^0 , and S^{2-}) to determine whether the sulfur reported to the residues. The analyses showed that the sulfur levels did not increase significantly in the residues.

Several solutions were also analyzed for total sulfur and these results indicated that the sulfur was still present in solution. The ion chromatograph detected along with the thiosulfate, tetrathionate and sulfate species, two other sulfur species: sulfite (SO_3^{2-}) and trithionate ($\text{S}_3\text{O}_6^{2-}$). The sulfite peak appears just before the sulfate peak on the ion chromatogram (Figure 4.48) and the trithionate appears between the thiosulfate and tetrathionate peak (Figure 4.49). It should be noted that the identification of these peaks was based on previous experience and not on an actual identification.

Figure 4.48 Ion Chromatograms of the AS4A column representing the sulfate concentration at different times during the leaching of 1g/L Chalcocite with 5 ppm gold addition

Figure 4.49 Ion Chromatograms of the Omnipax column showing (from left to right) thiosulfate, trithionate and tetrathionate at different times during the leaching of 1g/L chalcocite with 5 ppm gold addition

At first hand it seems unlikely that these ions are present at high concentrations, since their peak area is very small (Figure 4.49). However, a study by Steudel [1986] indicated that the response factor of trithionate is about 18 times lower than tetrathionate. This means that when trithionate and tetrathionate have the same area, the trithionate concentration is 18 times larger. Using this knowledge, the sulfur balance was recalculated for several experiments (Appendix D). This resulted in improved sulfur balances.

This indicates that the decomposition of tetrathionate to higher and lower polythionates, as presented in Equation (IV.13), takes place (section 2.3.3):

As mentioned in chapter 2 (section 2.3.3), trithionate is a relatively kinetically stable sulfur species under the leaching conditions applied. It decomposes quickly under harsh conditions: boiling and $\text{pH} > 13$. This indicates that if trithionate formed, it is very likely that it remains for a while in solution.

Two comments have to be made:

1. The determination of the response factor in the study quoted, was performed using different equipment. This study was only used to show that the concentration of trithionate might be higher than would be expected from the size of the peak area.
2. The trithionate peak areas were determined with the tetrathionate calibration curve. The trithionate peak areas were all below 1 mg/L, which is below the minimum detection limit, resulting in inaccurate area measurements.

Summary

The sulfur balances for the leach experiments did not account for all the sulfur added to the solutions. Further research revealed that it is very likely that most of the sulfur ends up as the trithionate species in solution.

5 GENERAL SUMMARY AND CONCLUSIONS

This study investigated the application of ammonium thiosulfate for the treatment of copper-gold ores. Leaching studies were conducted with copper minerals, copper minerals with gold addition and copper-gold samples of different copper and gold grade. On the basis of the experimental results, the following conclusions were drawn:

Leaching of copper minerals in ammonium thiosulfate solution

General observations

- The copper sulfide minerals covellite and chalcocite do not leach appreciably in an ammonium thiosulfate solution. Chalcopyrite and enargite seem to be unreactive toward an ammonium thiosulfate leach. Copper extraction seems to be independent of the availability of complexing agents; leaching of less material in the presence of the same amount of lixiviant did not result in higher copper extractions.
- The copper oxide minerals cuprite and malachite, showed fast dissolution resulting in high initial copper extractions (around 80%). The final copper extractions were dependent on lixiviant availability; copper extractions decreased with declining thiosulfate concentrations, high copper extractions were achieved when thiosulfate remained in solution. The exact role of ammonia in copper solubilization is not clear. It can be further remarked that 80% copper extraction was achieved independent of the amount of material subjected to the leach; both mineral additions of 5 g/L copper and 1 g/L copper resulted in 80% copper extraction.

- The amount of copper solubilized was in all cases, except enargite and chalcopyrite (both at a mineral feed of 1 g/L copper), enough to catalyze the degradation of thiosulfate in solution. After about 180 to 240 minutes thiosulfate was no longer present in solution. Because enargite and chalcopyrite barely leaches in an ammonia thiosulfate solution, little copper was solubilized which resulted in increased thiosulfate stability; the thiosulfate was still present after 360 minutes.

It can therefore be concluded that the leaching of the copper minerals in the presence of air resulted in the solubilization of copper as cupric, which catalyzed thiosulfate degradation. Thiosulfate degradation reduces overall copper extraction.

The following observations were made when soluble gold was added to the leach solution in the presence of copper minerals:

- Copper concentrations of 0.3 g/L or higher result in enhanced rates of thiosulfate degradation. The consequent reduction of thiosulfate concentration causes gold to precipitate.
- In the presence of low copper concentrations (around 0.1 g/L Cu) thiosulfate degradation is reduced and gold remains in solution.

Further study should be undertaken to determine exactly at which copper concentration a negative effect on thiosulfate stability is observed.

The above shows that gold solubilization is dependent on the presence of thiosulfate. Ammonia is known as a complexing agent for gold, but does not appear to play a role under the experimental conditions investigated.

Effect of aeration

As stated above, an aerated solution in combination with as little as 0.3 g/L copper in solution causes fast thiosulfate degradation, resulting in gold precipitation. Thiosulfate degradation is less in the absence of aeration, even in the presence of high copper concentrations. Cuprous ions are easily regenerated into cupric in the presence of air, resulting in fast thiosulfate degradation. The oxidation of cuprous to cupric is a lot slower in the absence of air, resulting in greater thiosulfate stability, and thus gold remains in solution.

Effect of temperature

A leach temperature of 20°C instead of 35°C did not result in a measurable effect on thiosulfate degradation, copper extraction and gold solubilization.

Effect of reagent addition

In this study, the addition of sulfite and sulfate was not observed to affect thiosulfate stability, as suggested in the literature. An increase in ammonia concentration did not result in higher copper extractions, and the thiosulfate stability was negatively affected by the increase in ammonia concentration.

Leaching of copper-gold samples in ammonium thiosulfate solution

General observations

These experiments confirmed the above conclusion: when the thiosulfate concentration declines, gold extraction decreases. Thiosulfate degradation depends on aeration and cupric ion

concentration. Gold extractions ranged from low to high depending on the experimental conditions. The copper-gold samples tested did not show appreciable co-extraction of copper during an ammonium thiosulfate leach. Compared to the cyanidation test results, the ammonium thiosulfate treatment of the Overall Lobo Composite and M10 Pyrite Concentrate showed that similar gold extractions were achieved at lower reagent cost.

Effect of aeration

High initial gold extractions are achieved in a well aerated system. Without aeration, but not in an airtight system, gold dissolves a lot slower and low gold extractions are achieved after 6 hours of leaching. An extended residence time of 24 hours for the M10 Pyrite Concentrate resulted in gold extractions of 83%.

It can be concluded that a balance has to be found between providing enough oxidant for fast gold dissolution, and minimizing the amount of oxidant in the presence of cupric ions to prevent excessive thiosulfate degradation. The alternative is slow gold dissolution and low thiosulfate consumption in a non-aerated system with extended residence time.

Effect of cupric ion addition

A high cupric ion concentration in combination with aeration results in fast thiosulfate degradation. The leaching of the M10 Pyrite Concentrate and M40 Pyrite Feed showed higher initial gold extraction with the addition of cupric ions in combination with aeration. This indicates a catalytic effect of cupric ions on the dissolution of gold in an ammonium thiosulfate solution, which is described in the literature (see section 2.3.3). In the absence of aeration, no

beneficial effect was observed from the addition of cupric ions. For the two composites (Overall Lobo and Guanaco), higher gold extractions were observed without the addition of cupric ions. This effect was not further investigated.

Analytical

- Part of the sulfur could not be accounted for in the leach solutions. Initial research indicates that a large portion of the sulfur initially present does not end up as sulfate, the thermodynamically predicted final degradation product of thiosulfate, but as trithionate ($\text{S}_3\text{O}_6^{2-}$).
- It is very difficult to prevent early thiosulfate degradation in the samples, resulting in an inaccurate portrayal of the actual leaching conditions.

Eh-pH diagrams

- Different ΔG^0 values are used for the thiosulfate species (-518.8 kJ/mol and -532.2 kJ/mol), which result in a totally different representation of the thermodynamic equilibria in the ammonium thiosulfate system.

6 RECOMMENDATIONS

This work investigated the application of ammonium thiosulfate for the treatment of copper-gold ores. From the previous chapter it can be concluded that the application of ammonium thiosulfate for the treatment of copper-gold ores offers definite opportunities; however, more research should be conducted in the following areas:

Process development

- High gold extractions were achieved with a 24 hour leach in a non-aerated system. Additional experiments should be conducted to optimize the gold extraction and at the same time minimize thiosulfate consumption. Factors to be studied to optimize the leaching are thiosulfate concentration and the effect of the solution pH.
- High initial gold extractions were achieved in an aerated system. It might be valuable to investigate the possibility of separating solution and solids at that instant without causing thiosulfate degradation and thus gold precipitation. Further, the amount of aeration should be studied, to optimize gold extraction and minimize the thiosulfate degradation.
- Low copper extractions were achieved with the experimental conditions specified. More research should be performed to determine why low copper extractions were achieved. The copper species in solution should be more closely examined using UV spectrophotometry. This may reveal more information regarding the mechanism of copper complexation in solution; whether mainly copper thiosulfate or copper ammonia complexes form and which copper ammonia complexes form: the copper(I)ammonia or the copper(II)ammonia complex.
- If trithionate is the predominant degradation product of thiosulfate in this system, it should be researched how trithionate can be prevented from building up in the system. Furthermore,

trithionate may have a significant effect on adsorption processes for gold and copper recovery and these effects must be quantified.

Fundamental Research

- Fundamental research should be performed to provide more insight in the leaching chemistry. Because the chemistry of the ammonia thiosulfate system is not yet fully understood and has proven to be very complex, it is difficult to optimize and control the leaching conditions, especially on an industrial scale.
- Efforts should be undertaken to obtain correct values for the free energies of the species present in ammonium thiosulfate solutions. This will enable a more accurate representation of the thermodynamic equilibria.
- More research is required to determine the mechanism of gold precipitation when thiosulfate is no longer present in solution. This is coupled with the question of whether or not ammonia plays a role in gold solubilization in this system.

Analytical

- Difficulties were encountered in preventing thiosulfate degradation from occurring in the solution samples for ion chromatography analyses. Sample treatment, with for example ion exchange resins, might offer a solution to this problem.
- Moreover, it was only possible to detect the free species and not the complexed species by ion chromatography during this research. By developing methods for sample treatment, it might be possible to quantify both the free and complexed species.

- Not all sulfur species could be quantified by ion chromatography, e.g. sulfite and trithionate. Since it appears that trithionate plays an important role in the solution, methods should be developed for quantifying these sulfur species by ion chromatography. Furthermore, the response factor for trithionate has to be determined for the ion chromatograph set up used in this research.
- UV spectrophotometry should be applied to qualitatively determine which copper ammonia complexes are present in solution.

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Appendix A: Screen analysis of copper-gold samples

The particle size distributions of the Overall Lobo Composite and Guanaco Composite were determined by taking a 500 gram representative sample of the pulverized ore, and subjecting it to screening. Results are presented in Table A.I.

Table A.I Screen analysis of copper-gold samples

Size (μm)	Lobo Composite		Guanaco Composite		M40 Pyrite Feed		M10 Pyrite Concentrate	
	Mass(g)	Mass %	Mass(g)	Mass %	Mass(g)	Mass %	Mass(g)	Mass %
300	0.38	0.08	0.83	0.17	27.87	1.41	-	-
212	3.16	0.64	19.04	3.85	54.09	2.73	8.30	0.42
150	73.38	14.85	99.42	20.10	74.86	3.78	17.20	0.87
106	142.02	28.74	81.27	16.43	94.37	4.76	35.90	1.81
75	61.62	12.47	75.83	15.33	150.94	7.61	87.50	4.41
45	113.6	22.99	86.2	17.43	330.52	16.67	256.00	12.90
-45	100.02	20.24	132.02	26.69	1250.13	63.05	1578.85	79.59
Totals	494.18	100.0	494.61	100.0	1982.78	100.0	1983.75	100.0
P80(μm)	141		160		75		46	

The particle size distributions of the M40 Pyrite Feed and M10 Pyrite Concentrate were obtained from Newcrest Mining Ltd (Table A.I). The P_{80} of the four materials was determined by plotting the cumulative weight percentage passing against the screen sizes (see Figure A.1 to A.4)

Figure A.1 Particle size distribution of Overall Lobo Composite

Figure A.2 Particle size distribution of Guanaco Composite

Figure A.3 Particle size distribution of M40 Pyrite Feed

Figure A.4 Particle size distribution of M10 Pyrite Concentrate

Appendix B: Ion Chromatography

Chromatography is an important method that permits the separation and analysis of ionic species. In this research ion exchange chromatography was used. A small amount of liquid sample is injected into a moving stream of liquid (termed the mobile phase), that passes through an immiscible stationary phase (resins with ion exchange sites), which is fixed in a column or on a solid surface. Separation is based on ions partitioning into the ion exchange phase to varying degrees.

This process is illustrated in Figure D.1. At time t_0 , the sample, contained in the mobile phase, is introduced at the head of the column. The components of the sample distribute themselves between the two phases. Introduction of additional mobile phase (the eluent) forces the mobile phase containing a part of the sample down the column, where further partition between the mobile phase and fresh portions of the stationary phase occurs (time t_1). Continuous flow of the mobile phase carries analyte molecules down the column in a continuous series of transfers between the mobile and the stationary phases.

Because movement of sample components can only occur in the mobile phase, the average rate at which a species migrates depends upon the fraction of time it spends in that phase. For components that are strongly retained by the stationary phase (compound B in Figure D.1) this fraction is small, whereas the fraction is large for components that are weakly retained by the stationary phase (component A). Ideally, the components are separated into bands (time t_2), which can be detected at the end of the column (time t_3 and t_4) [Skoog, D.A., 1992].

Figure D.1 (a) Diagram showing the separation of a mixture of components A and B by column elution chromatography. (b) The output of the signal detector at the various stages of elution shown in (a) [Skoog, D.A., 1992]

If the signal of the detector is plotted as a function of time, a series of peaks is obtained, as shown in the lower part of Figure D.1. This plot is called a chromatogram, and is a tool for both qualitative and quantitative analysis. The positions of peaks on the time axis may serve to identify the components of the sample; the areas under the peaks provide a quantitative measure of the amount of each component. This is achieved by calibrating using standards that contain known components of known concentrations.

Ion chromatography in this work

Two methods were used in this work to measure the different sulfur species in solution. The IonPac AS4A-SC analytical column and IonPac AG4A-SC guard column combined with a conductivity detector and anion micro membrane suppressor were used for sulfate analyses.

An example of a chromatogram is given in Figure D.2.

Figure D.2 Chromatogram of the AS4A column: sulfate (retention time of 4.7 minutes)

An OmniPac PAX-100 analytical and Omni Pac- PAX-100 guard column with a UV detector was used for thiosulfate and tetrathionate determination. An example chromatogram is shown in Figure D.3. Detailed procedures for both columns are described on the next pages.

Figure D.3 Chromatogram of the Omnipax column: thiosulfate (retention time of 2 minutes) and tetrathionate (retention time of 5.1 minutes)

Determination of thiosulfate and tetrathionate (S_2O_3 and S_4O_6)

by Ion Chromatography [Lakefield Research Ltd.]

Objective

To determine thiosulfate and tetrathionate in solutions by ion chromatography

Range:

1.0 mg/L to 20 mg/L (maximum detection limit), if there are no interferences and no dilution factor. Concentrations higher than 20 mg/L should be diluted to below maximum detection limit.

Interferences:

High thiocyanate interferes with the thiosulfate peak

Sample Requirements:

The sample is not preserved, and should be analysed the same day as the experiment took place.

Apparatus:

1. Liquid chromatograph with UV detector
2. OmniPac Pax-100 analytical column
3. OmniPac Pax-100 guard column
4. 1 mL syringe for sample injection
5. 0.45 μ m syringe filter

Reagents:

1. Sodium Perchlorate eluent (0.038 M) with 10 % methanol: dissolve 10.675 g $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (HPLC grade) in DI water, add 200 mL methanol, and dilute to 2 L with DI water using a 2L beaker. Filter the solution through a 0.45 μm filter.
2. Calibration standards (prepare fresh every day)

Thiosulfate

Prepare 1000 mg/L S_2O_3 standard by dissolving 1.4117 g of $\text{Na}_2\text{S}_2\text{O}_3$ (anhydrous sodium thiosulfate) in DI water and dilute to 1000 mL in a volumetric flask

Tetrathionate

Prepare 1000 mg/L stock solution by dissolving 0.1368 g $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ (sodium tetrathionate dihydrate) in water and dilute to 100 mL in a volumetric flask

Prepare from these 1000 mg/L stock solutions calibration standards containing 2, 10, 15 and 20 ppm thiosulfate and tetrathionate

Procedure:

1. Set up the ion chromatograph according to the instructions in the ion chromatograph manual
2. Guard column -OmniPac PAX - 100, analytical column - OmniPac PAX-100
3. Eluant: 0.038 M NaClO_4 in 10% methanol
4. Flow rate: 1.1 mL/min
5. sample loop volume - 50 μL
6. Detector: UV, measure at 215 nm
7. Inject one of the calibration standards and run the chromatogram of thiosulfate and

tetrathionate to determine the retention times. Standardize the instrument on these conditions

8. Calibrate the machine with the 2, 10, 15 and 20 ppm calibration standards and check the calibration plot
9. If the calibration is successful, determine the chromatograms of the samples (use syringe filters for injection)

Ion Retention Time*

S_2O_3 1.8 - 2.2 minutes

S_4O_6 4 - 6 minutes

*Note: difference in retention time depends on condition of the column

Quality Control:

The following samples must be analyzed after an analytical run

- i. Replicate calibration standard: choose the calibration standard close to prevalent concentration
- ii. Replicate sample: select random a sample and perform a second analytical run

Note: the anhydrous sodium thiosulfate can be prepared from hydrated sodium thiosulfate

($Na_2S_2O_3 \cdot 5H_2O$) via a procedure described by Woolf [1982]. It can also be purchased in a granular form.

Determination of sulfate by Ion Chromatography

[Lakefield Research Ltd., 1990]

Objective:

To determine sulfate in solutions by ion chromatography

Range:

0.5 mg/L to 20 mg/L (maximum detection limit), if there are no interferences and no dilution factor. Concentrations higher than 20 mg/L should be diluted to below maximum detection limit.

Interferences:

There can be overestimation of sulfate values with low pH samples

Sample Requirements:

The sample is not preserved, and should be analysed the same day as the experiment took place.

Apparatus:

1. Liquid chromatograph with conductivity detector and anion micro membrane suppressor (AMMS)
2. IonPac AS4A-SC analytical column
3. IonPac AG4A-SC guard column
4. 1 mL syringe for sample injection
5. 0.45 μm syringe filter

Reagents:

1. Sodium carbonate - sodium bicarbonate eluent with 10 % methanol: prepare 1.8 mM Na_2CO_3 + 1.7 mM NaHCO_3 by weighing 0.382 g of Na_2CO_3 anhydrous and 0.286 g of NaHCO_3 anhydrous into DI water. Add 200 mL methanol, and dilute to 2 L with DI water using a 2L beaker. Filter the solution through a 0.45 μm filter.
2. Sulfuric acid (25 mN H_2SO_4): 100 ml 1N sulfuric acid into 2 L beaker, dilute to 2 L.
3. Calibration standards

Sulfate

Prepare 1000 mg/L SO_4 standard by dissolving 1.4796 g of Na_2SO_4 (anhydrous sodium sulfate) in DI water and dilute to 1000 mL in a volumetric flask. Prepare from this 1000 mg/L stock solution calibration standards containing 2, 10, 15 and 20 ppm sulfate

Procedure:

1. Set up the ion chromatograph according to the instructions in the ion chromatograph manual
2. Guard column IonPac AG4A-SC, analytical column - IonPac AS4A-SC
3. Eluant: 1.8 mM Na_2CO_3 + 1.7 mM NaHCO_3
4. Flow rate: 2.0 mL/min
5. Sample loop volume - 50 μL
6. Suppressor: Anion Micro Membrane Suppressor (AMMS)
Regenerant: 25 mN H_2SO_4 at flow rate 3-5 mL/min
7. Detector: conductivity
8. Inject one of the calibration standards and run the chromatogram of sulfate to determine the retention time. Standardize the instrument on these conditions

9. Calibrate the machine with the 2, 10, 15 and 20 ppm calibration standards and check the calibration plot
10. If the calibration is successful, determine the chromatograms of the samples (use syringe filters for injection). If the sample contains thiosulfate, the peak will appear around 15-20 minutes on the chromatogram, depending on the condition of the column

Ion Retention Time*

SO₄ 4-6 minutes

S₂O₃ 15-20 minutes

*Note: difference in retention time depends on condition of the column

Quality Control:

The following samples must be analyzed after an analytical run

- i. Replicate calibration standard: choose the calibration standard close to prevalent concentration
- ii. Replicate sample: select random a sample and perform a second analytical run

Appendix C: Thermodynamic data

Formula	ΔG^0 , kJ/mol
H ₂ O	-237.18
OH ⁻	-157.29
NH ₃	-26.6
NH ₄ ⁺	-79.37
S	0
S ²⁻	86.31
S ₂ ²⁻	79.5
S ₃ ²⁻	73.6
S ₄ ²⁻	69
S ₅ ²⁻	65.7
SO ₃ ²⁻	-486.6
SO ₄ ²⁻	-744.63
S ₂ O ₃ ²⁻	-518.8
S ₂ O ₃ ²⁻	-532.2*, ***
S ₂ O ₄ ²⁻	-600.4
S ₂ O ₅ ²⁻	-791.
S ₂ O ₆ ²⁻	-966.
S ₂ O ₈ ²⁻	-1110.4
S ₃ O ₆ ²⁻	-958.
S ₄ O ₆ ²⁻	-1022.2
S ₅ O ₆ ²⁻	-956.
HS ⁻	12.05
H ₂ S (aq)	-27.87
HSO ₃ ⁻	-527.81
HSO ₄ ⁻	-756.01
Au	0

Formula	ΔG^0 , kJ/mol
Au ⁺	176.
Au ³⁺	440.
AuO ₃ ³⁻	-51.9
HAuO ₃ ²⁻	-142.
H ₂ AuO ₃ ⁻	-218.
Au(OH) ₃ (aq)	-283.5
Au(OH) ₃ (s)	-317
Au(NH ₃) ₂ ⁺	-41.1**
Au(S ₂ O ₃) ₂ ³⁻	-1048.**
Cu	0
Cu ⁺	50.30
Cu ²⁺	65.70
Cu ₂ O	-148.10
CuO	-134.
Cu(OH) ₂ (s)	-359.50
HCuO ₂ ⁻	-258.90
CuO ₂ ²⁻	-183.90
Cu(NH ₃) ₂ ⁺	-63.
Cu(NH ₃) ₂ ²⁺	15.60
Cu(NH ₃) ₂ ²⁺	-30.50
Cu(NH ₃) ₃ ²⁺	-73.20
Cu(NH ₃) ₄ ²⁺	-111.50
Cu(S ₂ O ₃) ₂ ³⁻	-1083.66***
Cu(S ₂ O ₃) ₃ ⁵⁻	-1623.39***
Cu ₂ S	-87.60
CuS	-53.20

All data from Bard [1986], except * from CRC Handbook of Chemistry and Physics [1975] and ** from Atluri [1987] and Wang [1992] and *** from Duby [1977]

Appendix D: Experimental data

Mineral	CuS	Cu ₂ S	CuFeS ₂	Cu ₃ AsS ₄	Cu ₂ O
	Baseline	Baseline	Baseline	Baseline	Baseline
Grams added	7.92	9.28	17.56	4.31	12.85
Residue	6.06	7.78	15.87	3.97	11.29
NaOH added (g)	24.84	24.89	24.89	24.96	22.02
NaOH added (mL)	16.40	16.43	16.43	16.48	14.53
Colour samples					
Time (min.) = 5	colourless	colourless	colourless	colourless	l.blue
30	colourless	l.blue	colourless	colourless	blue
60	colourless	blue	colourless	colourless	blue
120	colourless	blue	colourless	colourless	blue
180	l.blue	blue	very l.blue	colourless	blue
240	blue	blue	l.blue	colourless	blue
360	blue	blue	blue	colourless	blue
Addition of NH ₃ to samples:	only t240, 360	all except t5,30	only t240, 360	to none	to all
Colour filtrate	blue	d.blue	blue	v.l.blue	d.blue
Colour washwater	colourless	colourless	colourless	colourless	colourless
Ion chromatograph analyses					
	g/L S-species	g/L S-species	g/L S-species	g/L S-species	g/L S-species
Thiosulfate	5	19.83	15.48		6.72
	30	15.59	10.04		4.80
	60	12.41	9.41		2.67
	120	8.70	3.36		3.30
	180	2.09	0.09		1.31
	240	0.00	0.19		0.05
	360	0.02	0.00		0.02
Tetrathionate	5	0.53	1.20		3.21
	30	1.73	1.47		2.94
	60	1.76	0.49		2.10
	120	0.82	0.04		0.68
	180	0.40	0.00		0.63
	240	0.03	0.00		0.00
	360	0.00	0.00		0.00
Sulfate	5		0.24		23.98
	30		0.56	0.00	20.59
	60		1.54	0.00	18.00
	120		0.78	0.00	8.80
	180		3.65	0.00	3.82
	240		5.23	0.00	3.62
	360		5.46	0.77	4.07
Sulfur balance at every sample time (thiosulfate, tetrathionate and sulfate)					
			g/L S	g/L S	g/L S
	5		12.65		13.69
	30		12.25	13.09	11.30
	60		11.31	13.06	8.74
	120		8.62	12.67	5.22
	180		3.41	12.14	2.38
	240		2.17	11.63	1.24
	360		1.89	10.31	1.37
Trithionate 360			5.51	-	7.28
Total Sulfur balance at t=360, incl.trithionate:			7.40	10.31	8.66

- = no trithionate present, or too small to measure

Sample calculation:

CuFeS₂, baseline, t=5: 21.55×0.572 (% S in S₂O₃) + 0.42×0.572 (% S in S₄O₆) + 0.24×0.334 (% S in SO₄) = 12.65

Mineral		CuCO ₃	Cu ₂ S	Cu ₂ O	CuS+Au	Cu ₂ S+Au
		Baseline	no aeration	no aeration	Baseline	Baseline
Grams added		10.48	9.28	12.85	1.58	9.28
Residue		5.33	7.42	6.73	1.24	7.82
NaOH added (g)		23.3	25.52	23.03	24.95	25.58
NaOH added (mL)		15.38	16.84	15.20	16.47	16.88
Colour samples						
Time (min.) =	5	l.blue	colourless	l.blue	colourless	colourless
	30	blue	colourless	l.blue	colourless	l.blue
	60	blue	colourless	l.blue	colourless	blue
	120	blue	colourless	l.blue	colourless	blue
	180	blue	colourless	l.blue	colourless	blue
	240	blue	colourless	l.blue	colourless	blue
	360	blue	colourless	l.blue	v.l.blue	blue
Addition of						
NH₃ to samples:		to all	to none	to all	none	to all, except t5
Colour filtrate		d.blue/purple	v.l.blue	l.blue	l.blue	v.dark blue
Colour washwater		colourless-l.blue	colourless	l.bl-green	colourless	l.blue
Ion chromatograph analyses						
		g/L S-species	g/L S-species	g/L S-species	g/L S-species	g/L S-species
Thiosulfate	5	4.88	21.53	2.18	21.88	13.31
	30	3.49	20.35	3.25	21.19	3.27
	60	4.41	19.10	1.60	20.93	3.58
	120	2.23	15.00	3.11	18.92	3.75
	180	0.12	15.12	3.42	17.09	2.36
	240	0.07	11.22	6.93	14.08	0.00
	360	0.16	19.03	12.85	2.93	0.06
Tetrathionate	5	4.37	0.24	2.99	0.00	2.20
	30	3.07	0.55	2.60	0.22	2.41
	60	2.05	1.08	2.91	0.51	1.55
	120	0.48	2.09	3.11	0.72	0.76
	180	0.00	1.99	2.94	0.47	0.08
	240	0.00	2.88	2.56	0.13	0.00
	360	0.00	1.26	1.84	0.00	0.00
Sulfate	5	18.88	1.63	23.56	0.15	11.44
	30	15.73	2.58	22.73	0.15	21.40
	60	10.03	4.48	23.61	0.15	16.26
	120	4.41	12.77	22.26	0.15	9.03
	180	2.93	13.97	22.61	0.15	5.01
	240	3.15	17.59	19.27	0.15	5.40
	360	3.79	6.99	17.85	1.72	6.07
Sulfur balance at every sample time (thiosulfate, tetrathionate and sulfate)						
		g/L S	g/L S	g/L S	g/L S	g/L S
	5	11.60	13.00	10.82	12.57	12.69
	30	9.01	12.81	10.94	12.30	10.40
	60	7.04	13.04	10.47	12.31	8.37
	120	3.03	14.04	10.99	11.28	5.59
	180	1.05	14.45	11.19	10.10	3.07
	240	1.09	13.94	11.86	8.18	1.80
	360	1.36	13.94	14.37	2.25	2.06
Trithionate		360	4.93	-	3.73	8.34
Tot. S.balance at t=360:		6.29	13.94	14.37	5.98	10.40

- = no trithionate present, or too small to measure

Mineral		$\text{Cu}_2\text{S}+\text{Au}$	CuFeS_2+Au	$\text{Cu}_3\text{AsS}_4+\text{Au}$	$\text{Cu}_2\text{O}+\text{Au}$	CuCO_3+Au
		Baseline	Baseline	Baseline	Baseline	Baseline
Grams added		1.86	3.31	4.31	12.85	2.1
Residue		1.16	3.02	3.89	10.95	0.36
NaOH added (g)		25.6	24.2	30.19	22	24.22
NaOH added (mL)		16.90	15.97	19.93	14.52	15.99
Colour samples						
Time (min.) =	5	colourless	colourless	colourless	blue	v.l.blue
	30	colourless	colourless	colourless	blue	v.l.blue
	60	v.l.blue	colourless	colourless	blue	l.blue
	120	l.blue	colourless	colourless	blue	blue
	180	blue	colourless	colourless	blue	blue
	240	blue	colourless	colourless	blue	blue
	360		colourless		blue	blue
Addition of						
NH ₃ to samples:		to 240, 360	none	to none	all	to 120, 180, 240
Colour filtrate		blue	v.l.blue	v.l.blue	blue	d.blue/purple
Colour washwater		colourless	colourless	colourless	l.blue	v.l.blue
Ion chromatograph analyses						
		g/L S-species	g/L S-species	g/L S-species	g/L S-species	g/L S-species
Thiosulfate	5		22.47		0.54	0.00
	30	23.68	22.19	22.17	1.95	0.17
	60	16.36	22.96	21.71	2.33	2.01
	120	8.04	21.10	20.76	2.69	2.77
	180	1.98	19.18	19.76	0.24	0.53
	240	0.00	18.09	18.49	0.07	0.00
	360	0.00	12.68	15.75	0.04	0.00
Tetrathionate	5		0.00		2.87	3.11
	30	2.32	0.28	0.12	2.69	3.02
	60	1.16	0.59	0.22	1.83	2.07
	120	0.73	0.95	0.35	0.59	0.66
	180	0.00	1.10	0.40	0.00	0.00
	240	0.00	1.01	0.38	0.00	0.00
	360	0.00	0.54	0.11	0.00	0.00
Sulfate	5		0.00			11.93
	30	0.17		0.66		
	60	0.38	0.27	0.65		4.71
	120	1.35		0.69		3.23
	180	2.39	0.03	0.73		3.59
	240	5.07	0.07	0.76		4.07
	360	5.70	1.04	0.91		4.65
Sulfur balance at every sample time (thiosulfate, tetrathionate and sulfate)						
		g/L S	g/L S	g/L S		g/L S
	5		12.85			5.76
	30	14.93	12.85	12.97		1.83
	60	10.15	13.56	12.77		3.91
	120	5.47	12.61	12.31		3.04
	180	1.93	11.61	11.78		1.50
	240	1.69	10.95	11.04		1.36
	360	1.90	7.91	9.38		1.55
Trithionate	360	5.94	2.99	-		6.38
Tot. S.balance at t=360:		7.84	10.90	9.38		7.94

- = no trithionate present, or too small to measure

Mineral		Cu ₂ S+Au	Cu ₂ O+Au	Cu ₂ S+Au	Cu ₂ O+Au	Cu ₂ S+Au	Cu ₂ S+Au
		no aeration	no aeration	20°C	20°C	0.4 M NH ₃	Sulfite addn.
Grams added		9.28	2.57	1.86	2.57	1.86	1.86
Residue		7.86	1.26	1.25	1.31	1.14	1.2
NaOH added (g)		25.54	23.54	21.27	19.31	33.58	18.33
NaOH added (mL)		16.86	15.54	14.04	12.75	22.17	12.10
Colour samples							
Time (min.) =	5	colourless	colourless	colourless	colourless	l.blue	colourless
	30	colourless	colourless	colourless	l.blue	l.blue	colourless
	60	colourless	colourless	colourless	l.blue	blue	v.l.blue
	120	colourless	colourless	v.l.blue	blue	blue	l.blue
	180	colourless	colourless	v.l.blue	blue	blue	blue
	240	colourless	colourless	l.blue	blue	blue	blue
	360	colourless	colourless	blue	blue		
Addition of							
NH ₃ to samples:		none	none	to 360	to 120, 180, 240	to none	to 240, 360
Colour filtrate		very l.blue	l.blue	d.blue	d.blue/purple	d.blue	blue
Colour washwater		colourless	colourless	colourless	colourless	colourless	l.blue
Ion chromatograph analyses							
		g/L S-species	g/L S-species	g/L S-species	g/L S-species	g/L S-species	g/L S-species
Thiosulfate	5	21.08	0.00	22.08	0.00		
	30	21.21	0.00	19.86	0.00	15.93	20.20
	60	20.99	0.00	12.60	0.00	11.92	17.17
	120	19.06	0.00	8.62	2.05	1.93	7.73
	180	17.59	0.00	5.16	0.94	0.00	2.11
	240	17.33	0.84	1.59	0.00	0.00	0.30
	360	19.83	4.32	0.00	0.00	0.00	0.00
Tetrathionate	5	0.22	2.51	0.32	3.39		
	30	0.39	2.65	1.07	4.32	1.79	0.03
	60	0.58	2.72	2.75	0.99	0.90	0.24
	120	0.96	2.71	2.71	2.04	0.15	0.49
	180	1.19	2.81	1.04	0.00	0.00	0.21
	240	1.20	2.91	0.00	0.00	0.00	0.00
	360	0.77	3.13	0.00	0.00	0.00	0.00
Sulfate	5		11.38	0.56	14.95		
	30			0.65	12.46	0.86	1.92
	60		12.55	1.24	6.35	0.65	2.91
	120			1.69	2.79	1.41	4.39
	180		5.73	1.69	2.38	2.87	5.67
	240		5.21	1.67	3.01	3.22	8.72
	360		0.92	3.28	3.13	3.68	9.48
Sulfur balance at every sample time (thiosulfate, tetrathionate and sulfate)							
		g/L S	g/L S	g/L S	g/L S	g/L S	g/L S
	5	5.24	13.00	6.93			
	30	1.51	12.19	6.63	10.42	12.21	
	60	5.75	9.19	2.69	7.55	10.93	
	120	1.55	7.05	3.27	1.66	6.17	
	180	3.52	4.11	1.33	0.96	3.22	
	240	3.88	1.47	1.01	1.07	3.08	
	360	4.57	1.09	1.05	1.23	3.17	
Trithionate	360	-	7.38	-	6.47	5.29	
Tot. S.balance at t=360:		4.57	8.48	1.05	7.70	8.45	

- = no trithionate present, or too small to measure

Mineral	Cu ₂ S+Au	Lobo	Lobo	Lobo	Lobo
	Sulfate addn.	Baseline	Baseline, dupl.	no aeration	no Cu ²⁺ addn.
Grams added	1.86	360	360	360	360
Residue	1.1	342.66	336.53	339.42	335.09
NaOH added (g)	25.08	23	22.63	22.45	21.63
NaOH added (mL)	16.55	15.18	14.94	14.82	14.28
Colour samples					
Time (min.) = 5	colourless	v.l.blue	v.l.blue	colourless	colourless
30	colourless	v.l.blue	v.l.blue	colourless	colourless
60	v.l.blue	v.l.blue	v.l.blue	colourless	colourless
120	l.blue	l.blue	l.blue	colourless	colourless
180	blue	l.blue	l.blue	colourless	colourless
240	blue		blue	colourless	colourless
360					
Addition of					
NH ₃ to samples:	to 240,	to none	to none	to none	to none
Colour filtrate	blue	blue	blue	v.l.blue	colourless
Colour washwater	colourless	colourless	l.blue	colourless	colourless
Ion chromatograph analyses					
	g/L S-species	g/L S-species	g/L S-species	g/L S-species	g/L S-species
Thiosulfate					
5					
30	21.42	13.91	13.01	4.58	21.87
60	17.65	13.30	10.62	9.22	21.44
120	12.19	8.78	3.30	7.10	20.52
180	4.99	0.00	0.00	11.58	19.52
240	0.79	0.00	0.00	10.29	18.70
360	0.00		0.00	15.17	16.86
Tetrathionate					
5					
30	0.54	2.03	2.26	3.36	0.51
60	0.92	0.97	0.94	3.04	0.66
120	0.38	5.40	0.17	3.16	0.78
180	0.22	0.00	0.00	2.61	0.82
240	0.00	0.00	0.00	2.68	0.81
360	0.00		0.00	1.97	0.65
Sulfate					
5					
30	4.80	2.40	2.83	3.88	0.94
60	4.69	2.10	2.91	3.86	0.95
120	4.93	4.38	3.71	3.45	0.96
180	6.18	6.25	6.30	3.22	0.97
240	7.15	6.55	6.63	3.17	0.98
360	9.46		7.37	2.29	0.99
Sulfur balance at every sample time (thiosulfate, tetrathionate and sulfate)					
	g/L S	g/L S	g/L S	g/L S	g/L S
5					
30	14.17	9.92	9.68	5.84	13.12
60	12.19	8.87	7.58	8.30	12.96
120	8.84	9.58	3.23	7.02	12.51
180	5.04	2.09	2.10	9.19	11.96
240	2.84	2.19	2.21	8.48	11.49
360	3.16	0.00	2.46	10.57	10.35
Trithionate 360	4.07	4.00	5.45	-	3.09
Tot. S. balance at t=360:	7.23	4.00	7.91	10.57	13.44

- = no trithionate present, or too small to measure

Mineral		Lobo	Guanaco	Guanaco	Guanaco	Guanaco
		no Cu ²⁺ addn., dupl.	Baseline	no aeration	no Cu ²⁺ addn.	Thiogold
Grams added		360	360	360	360	360
Residue		338.78	343.13	339.72	338.65	341.97
NaOH added (g)		21.74	22.76	22.76	20.69	24.11
NaOH added (mL)		14.35	15.02	15.02	13.66	15.91
Colour samples						
Time (min.) =	5	colourless	l.blue	colourless	colourless	l.blue
	30	colourless	blue	colourless	v.l.blue	blue
	60	colourless	blue	colourless	l.blue	blue
	120	colourless	blue	colourless	blue	blue
	180	colourless	blue	colourless/v.l.b.	blue	blue
	240	colourless	blue	v.l.b.	blue	blue
	360					
Addition of						
NH3 to samples:		to none	to all	to none	to 180, 240, 360	to all
Colour filtrate		colourless	blue	l.blue	blue	d.blue/purple
Colour washwater		colourless	blue	v.l.b.	l.blue	blue
Ion chromatograph analyses						
		g/L S-species	g/L S-species	g/L S-species	g/L S-species	g/L S-species
Thiosulfate	5					
	30	22.73	12.54	22.24	15.94	11.32
	60	22.03	9.37	19.86	14.64	7.82
	120	21.09	3.07	14.55	6.84	0.66
	180	20.09	0.00	12.96	1.50	0.00
	240	19.60	0.00	13.52	0.00	0.00
	360	17.52	0.00	14.36	0.00	0.00
Tetrathionate	5					
	30	0.45	1.78	0.34	1.88	0.97
	60	0.64	0.78	0.98	1.12	0.45
	120	0.67	0.12	2.03	0.43	0.00
	180	0.72	0.00	2.36	0.00	0.00
	240	0.76	0.00	2.40	0.00	0.00
	360	0.57	0.00	2.41	0.00	0.00
Sulfate	5					
	30	0.88	3.47	2.54	1.46	3.93
	60	0.87	3.62	2.86	1.36	4.04
	120	0.94	4.02	3.43	2.17	6.35
	180	0.92	6.27	3.61	3.61	7.43
	240	1.00	6.70	3.52	5.21	7.75
	360	1.06	7.10	3.13	5.83	8.41
Sulfur balance at every sample time (thiosulfate, tetrathionate and sulfate)						
		g/L S	g/L S	g/L S	g/L S	g/L S
	5					
	30	13.55	9.35	13.77	10.69	8.35
	60	13.26	7.01	12.88	9.47	6.08
	120	12.75	3.17	10.63	4.88	2.50
	180	12.21	2.09	9.97	2.07	2.48
	240	11.98	2.24	10.28	1.74	2.59
	360	10.70	2.37	10.64	1.95	2.81
Trithionate	360	2.89	8.34	-	5.17	6.15
Tot. S.balance at t=360:		13.59	10.71	10.64	7.12	8.96

- = no trithionate present, or too small to measure

Mineral		M40	M40	M40	M40	M10
		Baseline	no aeration	no Cu ²⁺ addn.	no Cu ²⁺ , no air	Baseline
Grams added		360	360	360	360	360
Residue		334.39	336.6	336.35	338.04	333.4
NaOH added (g)		21.5	19.85	25.63	24.72	20.94
NaOH added (mL)		14.19	13.10	16.92	16.32	13.82
Colour samples						
Time (min.) =	5	v.l.blue	colourless	colourless	colourless	l.blue
	30	l.blue	colourless	colourless	colourless	l.blue
	60	blue	colourless	colourless	colourless	blue
	120	blue	colourless	colourless	colourless	blue
	180	blue	colourless	l.blue	colourless	blue
	240	blue	colourless	blue	colourless	blue
	360	blue	colourless	blue	colourless	blue
Addition of						
NH3 to samples:		to all, except 5	to none	to 360	to none	to all, except 5
Colour filtrate		d.blue/purple	colourless, yello	blue	colourless, yellowis	d.blue/purple
Colour washwater		l.blue	colourless	v.l.blue	colourless	blue
Ion chromatograph analyses						
		g/L S-species	g/L S-species	g/L S-species	g/L S-species	g/L S-species
Thiosulfate	5	1.60	9.04	23.87	19.67	8.67
	30	7.32	12.11	17.67	25.13	8.06
	60	4.51	9.45	15.25	25.81	7.02
	120	0.66	11.95	10.34	26.18	2.55
	180	0.00	11.71	10.28	25.04	0.00
	240	0.00	12.02	1.36	25.05	0.00
	360	0.00	12.95	2.20	24.78	0.00
Tetrathionate	5	3.68	3.89	1.09	5.45	0.00
	30	3.08	3.41	2.37	0.63	4.27
	60	0.62	3.67	2.32	0.52	3.07
	120	0.00	3.07	1.57	0.66	1.49
	180	0.00	3.09	1.38	0.52	0.30
	240	0.00	2.82	0.12	0.53	0.00
	360	0.00	2.68	0.24	0.72	0.00
Sulfate	5	7.93	4.54	1.94	0.27	4.46
	30	4.66	4.12	2.33	2.09	4.75
	60	5.04	5.09	2.63	0.46	3.93
	120	5.00	4.24	3.31	0.15	3.97
	180	6.62	4.41	3.88	0.55	5.66
	240	7.39	3.98	6.86	0.00	6.55
	360	8.76	3.81	7.95	0.00	8.22
Sulfur balance at every sample time (thiosulfate, tetrathionate and sulfate)						
		g/L S	g/L S	g/L S	g/L S	g/L S
	5	5.67	8.91	14.92	14.46	6.45
	30	7.50	10.26	12.24	15.44	8.64
	60	4.62	9.21	10.93	15.21	7.08
	120	2.05	10.00	7.92	15.40	3.64
	180	2.21	9.94	7.97	14.81	2.06
	240	2.47	9.82	3.14	14.63	2.19
	360	2.93	10.21	4.05	14.59	2.74
Trithionate	360	5.17	-	5.68	-	8.10
Tot. S.balance at t=360:		8.09	10.21	9.73	14.59	10.85

- = no trithionate present, or too small to measure

Mineral		M10	M10	M10	M10
		no aeration	no aeration	no Cu ²⁺ addn.	0.72 M ATS
Grams added		360	360	360	360
Residue		335.52	341.73	333.81	337.71
NaOH added (g)		21.58	21.48	21	38.49
NaOH added (mL)		14.24	14.18	13.86	25.41
Colour samples		Time			
Time (min.) =	5	v.l.blue 30	v.l.blue	colourless	l.blue
	30	v.l.blue 120	v.l.blue	v.l.blue	blue
	60	v.l.blue 300	v.l.blue	l.blue	blue
	120	v.l.blue 480	v.l.blue	blue	d.blue
	180	v.l.blue 1440	l.blue	blue	d.blue
	240	v.l.blue		blue	d.blue
	360	v.l.blue		blue	
Addition of NH3 to samples:		to none	to 1440	to 120,180,240	to none
Colour filtrate		l.green	l.blue	d.blue/purple	d.blue/purple
Colour washwater		v.l.green	v.l.blue	blue	blue
Ion chromatograph analyses					
		g/L S-species	g/L S-species	g/L S-species	g/L S-species
Thiosulfate	5	7.37		0.51	
	30	4.10	4.90	2.09	12.87
	60	10.71	5.76	2.67	17.56
	120	9.06	7.11	0.14	12.55
	180	10.13	9.57	0.00	8.75
	240	9.42	7.97	0.00	6.04
	360	12.54		0.00	1.09
Tetrathionate	5	4.10		3.18	
	30	3.92	3.81	2.67	5.25
	60	3.42	3.29	0.93	3.14
	120	3.52	2.92	0.00	3.74
	180	3.12	2.46	0.00	3.24
	240	3.01	1.14	0.00	2.14
	360	2.48		0.00	0.24
Sulfate	5	5.95		6.92	
	30	7.61	6.81	3.43	6.15
	60	4.65	6.40	4.28	5.33
	120	5.12	5.72	5.72	5.63
	180	4.55	5.03	7.07	5.24
	240	8.31	5.35	8.02	5.46
	360	3.05		9.72	5.76
Sulfur balance at every sample time (thiosulfate, tetrathionate and sulfate)					
		g/L S	g/L S	g/L S	g/L S
	5	8.55		4.42	
	30	7.13	7.26	3.87	12.42
	60	9.64	7.32	3.49	13.62
	120	8.90	7.65	1.99	11.20
	180	9.10	8.56	2.36	8.61
	240	9.89	7.00	2.68	6.50
	360	9.61		3.25	2.69
Trithionate	360	-	2.95	5.86	21.08
Tot. S.balance at t=360:		9.61	2.95	9.11	23.76

- = no trithionate present, or too small to measure

Appendix E: Cyanidation procedures

Cyanidation Test Report

Sample: Overall Lobo Composite

Date: May 9/1998

Test Conditions:

Slurry Weight [g]:	100.12	Ca(OH) ₂ added [g]:	0.11
Target pulp density:	30	Initial NaCN concentration [g/L]:	1
H ₂ O to add [g]:	233.61	NaCN to add [g]:	0.234
Mass of solids [g]:	100.12	Leach time [hrs]:	24
Mass of liquids [g]:	233.613	Temperature [°C]:	19.7
Pre-lime pH:	5.47	Stirrer speed [rpm]:	512
Post-lime pH:	9.12		

Leach Data

Time [hr]	NaCN [g/L]	NaCN added [g]	NaCN cumul. [g]	pH	Ca(OH) ₂ added [g]	pH
0	1.00	0.234	0.234	9.86	0.18	10.50
2	0.38	0.147	0.381	10.36	-	10.54
4	0.75	0.062	0.443	10.61	-	10.66
8	0.76	0.059	0.502	10.61	-	10.67
12	0.78	0.055	0.557	10.81	-	10.85
24	0.45	0	0.557	10.75	-	-

Solids Balance

	mass [g]	Au [ppm]	Cu [ppm]
Solids	100.12	2.11	1120
Residue	99.39	0.4	640

Solution Balance

	mass [g]	Au [ppm]	Cu [ppm]
Filtrate	234.38	0.64	1.75
Tit. waste	100	0.24	34

Au extraction [%]	81.4
assayed head [ppm]	2.11
calculated head [ppm]	2.14

Cu extraction [%]	41.1
assayed head [ppm]	1120
calculated head [ppm]	1080.27

Reagent Consumption

NaCN [kg/t]	4.38
Ca(OH) ₂ [kg/t]	2.90

Notes:

1. Sodium cyanide concentration was determined by titration of 5 mL solution samples with silver nitrate and rhodanine indicator at selected time intervals. The solution samples were collected and analyzed for copper and gold content (Tit. Waste)
2. The extractions are based on calculated head

Cyanidation Test Report

Sample: Guanaco Composite

Date: May 9/1998

Test Conditions:

Slurry Weight [g]:	100.04	Ca(OH) ₂ added [g]:	0.03
Target pulp density:	30	Initial NaCN concentration [g/L]:	1
H ₂ O to add [g]:	233.43	NaCN to add [g]:	0.233
Mass of solids [g]:	100.04	Leach time [hrs]:	24
Mass of liquids [g]:	233.427	Temperature [°C]:	20.7
Pre-lime pH:	7.93	Stirrer speed [rpm]:	514
Post-lime pH:	9.72		

Leach Data

Time [hr]	NaCN [g/L]	NaCN added [g]	NaCN cumul. [g]	pH	Ca(OH) ₂ added [g]	pH
0	1.00	0.233	0.233	10.49	0.02	10.59
2	0.09	0.213	0.446	10.27	-	10.74
4	0.45	0.131	0.577	10.58	-	10.78
8	0.55	0.107	0.684	10.46	-	10.64
12	0.68	0.079	0.763	10.70	-	10.76
24	0.33	0	0.763	10.34	-	-

Solids Balance

	mass [g]	Au [ppm]	Cu [ppm]
Solids	100.04	2.06	3320
Residue	99.78	0.28	1500

Solution Balance

	mass [g]	Au [ppm]	Cu [ppm]
Filtrate	236.697	0.6	1460
Tit. waste	100	0.08	109

Au extraction [%]	84.3
assayed head [ppm]	1.6
calculated head [ppm]	1.78

Cu extraction [%]	70.4
assayed head [ppm]	3320
calculated head [ppm]	5061.47

Reagent Consumption

NaCN [kg/t]	6.77
Ca(OH) ₂ [kg/t]	0.50

Notes:

1. Sodium cyanide concentration was determined by titration of 5 mL solution samples with silver nitrate and rhodanine indicator at selected time intervals. The solution samples were collected and analyzed for copper and gold content (Tit. Waste)
2. The extractions are based on calculated head

Cyanidation Test Report

Sample: M40 Pyrite Feed

Date: May 10/1998

Test Conditions:

Slurry Weight [g]:	100.06	Ca(OH) ₂ added [g]:	0.07
Target pulp density:	30	Initial NaCN concentration [g/L]:	1
H ₂ O to add [g]:	233.47	NaCN to add [g]:	0.233
Mass of solids [g]:	100.06	Leach time [hrs]:	24
Mass of liquids [g]:	233.473	Temperature [°C]:	19.7
Pre-lime pH:	6.03	Stirrer speed [rpm]:	505
Post-lime pH:	9.89		

Leach Data

Time [hr]	NaCN [g/L]	NaCN added [g]	NaCN cumul. [g]	pH	Ca(OH) ₂ added [g]	pH
0	1.00	0.233	0.233	10.40	0.02	10.62
2	0.09	0.213	0.446	9.91	-	10.63
4	0.46	0.129	0.575	10.84	-	10.96
8	0.59	0.099	0.674	10.78	-	10.86
12	0.66	0.082	0.756	10.70	-	10.81
24	0.46	0	0.756	10.16	-	-

Solids Balance

	mass [g]	Au [ppm]	Cu [ppm]
Solids	100.06	7.1	5920
Residue	99.85	0.5	3680

Solution Balance

	mass [g]	Au [ppm]	Cu [ppm]
Filtrate	239.283	3.36	775
Tit. waste	100	0.96	117

Au extraction [%]	94.7
assayed head [ppm]	7.1
calculated head [ppm]	9.5

Cu extraction [%]	34.9
assayed head [ppm]	5920
calculated head [ppm]	5645.93

Reagent Consumption

NaCN [kg/t]	6.40
Ca(OH) ₂ [kg/t]	0.90

Notes:

1. Sodium cyanide concentration was determined by titration of 5 mL solution samples with silver nitrate and rhodanine indicator at selected time intervals. The solution samples were collected and analyzed for copper and gold content (Tit. Waste)
2. The extractions are based on calculated head

Cyanidation Test Report

Sample: M10 Pyrite Concentrate

Date: May 10/1998

Test Conditions:

Slurry Weight [g]:	100.06	Ca(OH) ₂ added [g]:	0.13
Target pulp density:	30	Initial NaCN concentration [g/L]:	1
H ₂ O to add [g]:	233.47	NaCN to add [g]:	0.233
Mass of solids [g]:	100.06	Leach time [hrs]:	24
Mass of liquids [g]:	233.473	Temperature [°C]:	20
Pre-lime pH:	5.76	Stirrer speed [rpm]:	494
Post-lime pH:	9.57		

Leach Data

Time [hr]	NaCN [g/L]	NaCN added [g]	NaCN cumul. [g]	pH	Ca(OH) ₂ added [g]	pH
0	1.00	0.233	0.233	10.34	0.04	10.73
2	0	0.233	0.466	10.20	-	11.08
4	0.07	0.217	0.683	10.86	-	11.21
8	0.16	0.196	0.879	11.01	-	11.20
12	0.23	0.182	1.061	11.08	-	11.23
24	0.29	0	1.061	10.25	-	-

Solids Balance

	mass [g]	Au [ppm]	Cu [ppm]
Solids	100.06	45.5	16600
Residue	98.39	21.5	11400

Solution Balance

	mass [g]	Au [ppm]	Cu [ppm]
Filtrate	242.103	7.6	1750
Tit. waste	100	1.32	192

Au extraction [%]	47.5
assayed head [ppm]	45.5
calculated head [ppm]	41.54

Cu extraction [%]	28.3
assayed head [ppm]	16600
calculated head [ppm]	15645.27

Reagent Consumption

NaCN [kg/t]	9.91
Ca(OH) ₂ [kg/t]	1.70

Notes:

1. Sodium cyanide concentration was determined by titration of 5 mL solution samples with silver nitrate and rhodanine indicator at selected time intervals. The solution samples were collected and analyzed for copper and gold content (Tit. Waste)
2. The extractions are based on calculated head

Appendix F: Sulfate determination

Determination of sulfate as barium sulfate (derived from Jeffery, [1989])

The method consists in slowly adding a solution of barium chloride to a solution of the sulfate:

Normally this procedure is carried out at boiling temperature, to obtain large barium sulfate crystals. For this study, the measurement was performed at room temperature.

To determine if it was possible to obtain representative sulfate numbers at room temperature the following procedure was followed:

- Prepare standard solutions of 0.1 M ammonium thiosulfate and 0.1 M ammonium sulfate and 1M barium chloride
- Measure out 100 mL of the first two solutions and transfer them into an 300 mL erlenmeyer
- While stirring add slowly 1 M of barium chloride
- Filter, wash and dry precipitate

The sulfate concentration was calculated from the resulting weight of the barium sulfate precipitate. The amount of sulfate added was 0.96 gram, the method gave 1.08 gram.

The filtrates resulting from the leach experiments were subjected to the same procedure, only 50 mL of filtrate was used.