

THIOSULFATE DEGRADATION DURING GOLD LEACHING IN AMMONIACAL THIOSULFATE SOLUTIONS : A FOCUS ON TRITHIONATE

By

NOELENE AHERN

B.Sc., University of Natal, 1994
B.Sc. (Hons), University of Natal, 1995
M.A.Sc., University of Cape Town, 1997

A thesis submitted in partial fulfillment of the requirements for the
degree of

Doctor of Philosophy

in

the Faculty of Graduate Studies

(Materials Engineering)

The University of British Columbia

October 2005

© Noelene Ahern, 2005

ABSTRACT

Thiosulfate has shown considerable promise as an alternative to cyanide for gold leaching. However, one of the main limitations of the thiosulfate system is the high consumption of thiosulfate. Besides increasing the cost of the process, the degradation products of thiosulfate have been claimed to passivate gold surfaces and the polythionates often produced are loaded onto resins proposed for gold recovery.

The thiosulfate degradation process is not completely understood. Of the degradation products, trithionate is a concern in the resin recovery of gold and is persistent in gold leach solutions. Very little is known about the expected behaviour of trithionate, both with respect to its formation and its interaction with other solution species.

The focus of this work was therefore to further the understanding of the behaviour of trithionate in gold leach solutions. Experimental work was carried out to determine the kinetics of trithionate degradation in systems resembling gold leaching solutions, and a kinetic model was derived for trithionate degradation. The rate of degradation of trithionate in aqueous ammoniacal solutions was expressed by Equation 1.

$$-d[S_3O_6^{2-}]/dt = (k_3[NH_4^+] + k_2[NH_3] + k_1[OH^-] + k_0)[S_3O_6^{2-}] \quad [1]$$

where $k_0 = 0.012 \text{ h}^{-1}$, $k_1 = 0.74 \text{ M}^{-1} \cdot \text{h}^{-1}$, $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$, $k_3 = 0.01 \text{ M}^{-1} \cdot \text{h}^{-1}$.

In some cases, the presence of lower concentrations of thiosulfate catalysed the reaction while excess thiosulfate inhibited it. However, under typical gold leaching conditions, thiosulfate was not expected to have a significant effect so was excluded from Equation 1. Cupric copper was not found to have any significant effect on the rate of trithionate degradation under the conditions tested.

This observed trithionate degradation rate equation was integrated with known kinetic behaviour of thiosulfate and tetrathionate based on literature findings to develop an overall model for the thiosulfate degradation and the resulting solution speciation of the sulfur oxyanions in the absence of ores. The model was evaluated against experimental data and its shortcomings were identified.

The model parameters were adjusted to obtain a best fit to the experimental data. It was found that the best-fit parameters varied with the experimental conditions, indicating inadequacies in the model. The main concern was that the understanding of the thiosulfate degradation reactions is limited, and the way in which thiosulfate degradation was described had a major impact on the model output. In particular, the effects of copper species and pH on thiosulfate degradation have not been adequately addressed in the literature.

Even taking into consideration the limitations of the model, based on the model output, decreasing the cupric concentration and increasing the ammonia concentration should help to minimise thiosulfate degradation. Solution recycle can also be used to minimise thiosulfate degradation but can result in a build up of trithionate. Limiting the reaction time would also be useful.

This investigation has led to an improved understanding of the behaviour of trithionate in gold leach solutions and the model of the thiosulfate degradation system is a first step in developing a useful assessment method for thiosulfate degradation and solution speciation under gold leaching conditions. Further research is required to refine the model, particularly with respect to thiosulfate degradation to trithionate and tetrathionate.

TABLE OF CONTENTS

Abstract.....	ii
Table of Contents.....	iv
List of Tables.....	viii
List of Figures.....	x
List of Symbols and Abbreviations.....	xviii
Acknowledgements.....	xix
1. Introduction.....	1
2. Literature Review.....	3
2.1 Introduction.....	3
2.2 The ammoniacal thiosulfate gold leaching system.....	3
2.3 Structure and thermodynamic properties of the sulfur oxyanions.....	5
2.4 Thiosulfate degradation in gold leaching – experimental observations.....	12
2.5 Thiosulfate chemistry and fundamental studies.....	18
2.5.1 Oxidative degradation in gold leaching systems.....	18
2.5.2 Disproportionation and reductive degradation of thiosulfate.....	32
2.5.3 Thiosulfate degradation inhibitors.....	33
2.6 Trithionate degradation.....	34
2.6.1 Interaction with water.....	35
2.6.2 Interaction with hydroxide.....	36
2.6.3 Interaction with ammonia.....	36
2.6.4 Interaction with thiosulfate.....	36
2.6.5 Interaction with copper.....	37
2.7 Tetrathionate degradation.....	41
2.7.1 Interaction with hydroxide.....	41
2.7.2 Interaction with ammonia.....	43
2.7.3 Interaction with copper.....	44
2.7.4 Interaction with thiosulfate.....	44
2.8 Removal of polythionates from solution.....	47
2.9 Summary of literature findings.....	48
2.10 Scope and objectives.....	49

3. Analytical Methods and Synthesis	50
3.1 Introduction	50
3.2 Analysis of sulfur oxyanions – ion chromatography	50
3.2.1 Description of method	50
3.2.2 Stability of standard solutions	51
3.2.3 Effect of other solution components on ion chromatographic analysis	53
3.3 Analysis of sulfamate	54
3.4 Analysis of total ammonia	55
3.5 Synthesis of sodium trithionate	55
3.6 Characterisation of sodium trithionate	56
3.6.1 Total sulfur	56
3.6.2 Total sodium content	57
3.6.3 Volatiles	57
3.6.4 Sulfate	58
3.6.5 Polythionates	59
3.6.6 Overall trithionate purity	61
3.7 Trace impurity analysis of chemicals used	62
4. Kinetics of Trithionate Degradation – Methodology	63
4.1 Introduction	63
4.2 Reaction kinetics theory	63
4.3 Experimental method	64
4.4 Data analysis	66
5. Kinetics of Trithionate Degradation – Results	72
5.1 Introduction	72
5.2 Stoichiometry	72
5.3 Reproducibility	74
5.4 Water	75
5.5 Hydroxide	77
5.6 Ionic strength	79
5.7 Carbonate and bicarbonate	82
5.8 Ammonium and ammonia	83

5.9	pH.....	88
5.10	Thiosulfate.....	93
5.11	Oxygen exclusion.....	95
5.12	Cupric copper.....	97
5.13	Tetrathionate.....	99
5.14	Elemental sulfur, sulfate and copper powder.....	100
5.15	Temperature.....	101
6.	Kinetics of Trithionate Degradation – Discussion and Modelling.....	104
6.1	Qualitative discussion.....	104
6.2	Modelling of trithionate degradation.....	108
7.	Modelling of Sulfur Oxyanion Speciation During Thiosulfate Degradation....	119
7.1	Introduction.....	119
7.2	Model setup.....	119
7.2.1	R1 – Thiosulfate degradation to tetrathionate.....	120
7.2.2	R2 – Tetrathionate degradation.....	121
7.2.3	R3 – Trithionate degradation.....	122
7.2.4	R4 – Thiosulfate degradation to trithionate.....	123
7.2.5	R5 – Thiosulfate degradation directly to sulfate.....	125
7.2.6	R6 – Thiosulfate degradation to sulfide.....	126
7.2.7	Incorporation of the rate equations into a model – method and constraints.....	126
7.3	Model sensitivity to model parameters.....	127
7.3.1	Proportion of thiosulfate forming tetrathionate versus trithionate.....	129
7.3.2	Rate of reaction R1 – thiosulfate degradation to tetrathionate.....	133
7.3.3	Rate of reaction R4 – thiosulfate degradation to trithionate.....	134
7.3.4	Rate of reaction R2 – tetrathionate degradation.....	135
7.3.5	Rate of reaction R3 – trithionate degradation.....	137
7.3.6	Summary – effect of model parameters.....	138
7.4	Comparison of model output with experimental results in the absence of ore.....	139
7.4.1	Experiments.....	139
7.4.2	Validation method.....	140

7.4.3	Test 1 – no copper.....	142
7.4.4	Tests 2a and 2b – low copper, pH 10.....	143
7.4.5	Test 3 – low copper, pH 9, low ammonia.....	148
7.4.6	Test 4 – low copper, pH 9, higher ammonia.....	151
7.4.7	Test 5 – high copper, pH 10.....	152
7.4.8	Summary.....	155
7.5	Comparison of experimental results with and without ore.....	159
7.6	Scope of use of model.....	163
7.7	Impact of solution conditions.....	163
7.7.1	Copper concentration.....	164
7.7.2	Total ammonia concentration.....	167
7.7.3	pH.....	170
7.7.4	Dissolved oxygen.....	172
7.7.5	Thiosulfate concentration.....	173
8.	Conclusions	180
9.	Recommendations	187
10.	References	189
	Appendix 1: Thermodynamic values used to construct Eh-pH diagrams.....	199
	Appendix 2: Thiosulfate degradation – literature data.....	200
	Appendix 3: Determination of sulfur oxyanions by ion chromatography.....	205
	Appendix 4: Chemical impurity analysis.....	208

LIST OF TABLES

2.1	Selected Gibbs free energies of formation (298 K) for species of interest in the copper-ammoniacal-thiosulfate system.....	11
2.2	Selected standard oxidation potentials (298 K).....	11
2.3	Summary of experimental observations for thiosulfate degradation.....	13
2.4	Literature data for trithionate and tetrathionate production.....	16
2.5	Formation of trithionate from thiosulfate in the presence of oxygen (oxygen pressure 725 mm Hg, 30 °C, [Cu(II)] = 1 mM, [NH ₃] = 0.2 M).....	26
2.6	Trithionate degradation in water.....	38
2.7	Trithionate degradation in ammonia.....	39
2.8	Trithionate degradation in the presence of thiosulfate.....	40
2.9	Tetrathionate degradation in alkaline solutions.....	46
2.10	Potential methods for polythionate removal.....	47
3.1	Summary of observations on stability of standard solutions of thiosulfate, trithionate and/or tetrathionate.....	52
3.2	Effect of added species on analysis of sulfur oxyanions.....	54
3.3	Sodium trithionate characterisation.....	61
5.1	Reproducibility in rate constant determination for trithionate degradation for two buffer systems using the initial rate method.....	75
5.2	Values for the observed rate constant k_{obs} for trithionate degradation in water using the initial rate method (40 °C).....	76
5.3	Effect of hydroxide concentration on the observed rate constant k_{obs} for trithionate degradation using the initial rate method (40 °C).....	77
5.4	Values for the observed rate constant k_{obs} for trithionate degradation in the presence of various salts used to adjust the ionic strength using the initial rate method.....	80
5.5	Effect of ammonium concentration on observed rate constant k_{obs} for trithionate degradation.....	88
5.6	Effect of thiosulfate on the observed rate constant k_{obs} for trithionate degradation using the integrated rate method.....	94

5.7	Effect of limiting dissolved oxygen on the observed rate constant k_{obs} for trithionate degradation in 0.1 M hydroxide solution.....	95
5.8	Effect of limiting dissolved oxygen on the observed rate constant k_{obs} for trithionate degradation ammonia / ammonium bicarbonate solution.....	96
5.9	Effect of limiting oxygen on the observed rate constant k_{obs} for trithionate degradation using the integrated rate method.....	97
5.10	Effect of cupric addition on the observed rate constant k_{obs} for trithionate degradation using the integrated rate method.....	97
5.11	Effect of cupric copper on the observed rate constant k_{obs} for trithionate degradation.....	98
5.12	Effect of elemental sulfur, sulfate and copper powder on the observed rate constant k_{obs} for trithionate degradation.....	100
5.13	Effect of temperature on the observed rate constant k_{obs} for trithionate degradation at pH 8.8 – 10.1.....	102
5.14	Effect of temperature on the observed rate constant k_{obs} for trithionate degradation using the integrated rate method.....	103
7.1	Model parameters used to test model sensitivity.....	128
7.2	Standard experimental parameters used in modelling.....	129
7.3	Experimental conditions used in tests for model validation.....	140
7.4	Adjustment of model parameters found to give improved agreement between model output and experimental data.....	156
7.5	Assay results for ore from Placer Dome used in leach tests.....	159
7.6	Effect of recycling on thiosulfate consumption and solution speciation (Initial conditions 0.2 M $\text{S}_2\text{O}_3^{2-}$, 30 mg/l Cu, 0.4 M NH_3 , 25 °C, pH 10, with model parameters set as in Table 7.2 for Test 2)....	178
7.7	Effect of recycling on thiosulfate consumption and solution speciation (Initial conditions 0.2 M $\text{S}_2\text{O}_3^{2-}$, 100 mg/l Cu, 0.3 M NH_3 , 25 °C, pH 10, with model parameters set as in Table 7.2 for Test 5)....	179

LIST OF FIGURES

2.1	Eh-pH diagram for the aqueous sulfur system (1M sulfur, 25 °C).....	6
2.2	Basic structures of selected sulfur oxyanions.....	7
2.3	Eh-pH diagram for the aqueous sulfur system with the following species omitted: SO_4^{2-} , HSO_4^- , $\text{H}_2\text{SO}_4 \cdot \text{xH}_2\text{O}$ (1M sulfur, 25 °C).....	9
2.4	Eh-pH diagram for the aqueous sulfur system with the following species omitted: SO_4^{2-} , HSO_4^- , $\text{H}_2\text{SO}_4 \cdot \text{xH}_2\text{O}$, SO_3 , SO_3^{2-} , HSO_3^- , $\text{S}_2\text{O}_6^{2-}$, HSO_5^- , $\text{S}_2\text{O}_8^{2-}$, $\text{S}_2\text{O}_5^{2-}$ (1M sulfur, 25 °C).....	10
2.5	Bimolecular nuclear substitution at the sulfenyl sulfur of trithionate.....	35
3.1	TGA/DTA for sodium trithionate batch 2.....	58
3.2	TGA/DTA for sodium trithionate batch 3.....	58
3.3	Change of measured trithionate (indicative values only) and tetrathionate concentrations with time with and without using deaerated water in solution preparation.....	60
3.4	Change of measured trithionate (indicative values only) and tetrathionate concentrations with time in the presence of 2 mM NH_4OH	60
3.5	Change of measured trithionate (indicative values only), tetrathionate and thiosulfate concentrations with time in the presence of 10 mg/l $\text{S}_2\text{O}_3^{2-}$ and 10 mg/l $\text{S}_4\text{O}_6^{2-}$	61
4.1	Concentrations of trithionate and thiosulfate with time for an integrated rate method test.....	67
4.2	Determination of reaction stoichiometry using the integrated rate method.....	68
4.3	Typical concentration profile for trithionate and thiosulfate using the initial rate method.....	69
4.4	Determination of the reaction order for the rate of trithionate degradation with respect to trithionate.....	70
4.5	Typical plot of trithionate degradation rate versus initial trithionate concentration to determine the rate constant k_{obs} from the slope.....	71

5.1	Concentration profiles for trithionate and thiosulfate.....	74
5.2	Observed rate constant for trithionate degradation k_{obs} versus $[\text{OH}^-]$ for $\text{pH} \leq 11$	79
5.3	Effect of ionic strength on observed rate constant k_{obs} for trithionate degradation using the initial rate method.....	82
5.4	Effect of ionic strength of $\text{NaHCO}_3 / \text{Na}_2\text{CO}_3$ buffer on the observed rate constant k_{obs} for trithionate degradation using the initial rate method.....	83
5.5	Effect of ammonium concentration on the observed rate constant k_{obs} for trithionate degradation using the initial rate method.....	84
5.6	Effect of ammonia concentration on the observed rate constant k_{obs} for trithionate degradation using the initial rate method.....	85
5.7	Effect of ammonium concentration on the observed rate constant k_{obs} for trithionate degradation for $(\text{NH}_4)_2\text{SO}_4 / \text{NH}_3$ and $\text{NH}_4\text{HCO}_3 / \text{NH}_3$ buffer systems using the initial rate method.....	87
5.8	Dependency of the observed rate constant k_{obs} for trithionate degradation on the ammonium concentration at various pH.....	89
5.9	Dependency of the observed rate constant k_{obs} for trithionate degradation on the ammonia concentration at various pH.....	89
5.10	Observed rate constant k_{obs} for trithionate degradation versus pH for a range of ammonia / ammonium concentrations.....	91
5.11	Observed rate constant k_{obs} for trithionate degradation versus pH at 25°C	91
5.12	Effect of pH on observed rate constant k_{obs} for trithionate degradation in sodium carbonate / bicarbonate medium.....	92
5.13	Effect of thiosulfate on the observed rate constant k_{obs} for trithionate degradation using the initial rate method.....	93
5.14	Effect of sulfur, sulfate or copper powder on trithionate concentration profile.....	101
6.1	Concentration profiles for ammonia, ammonium ions and hydroxide ions at 40°C with varying pH, using arbitrary concentration units.....	106

6.2	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0 M against pH, with modelled trend superimposed (using $k_2 = 0.0081 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	111
6.3	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.5 M against pH, with modelled trend superimposed (using $k_2 = 0.0081 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	112
6.4	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.9 – 1.2 M against pH, with modelled trend superimposed (using $k_2 = 0.0081 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	112
6.5	Plot of calculated rate constant k_{calc} versus observed rate constant k_{obs} for trithionate degradation at 40 °C for all data, using $k_2 = 0.0081 \text{ M}^{-1} \cdot \text{h}^{-1}$	113
6.6	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	114
6.7	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.1 – 0.2 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	114
6.8	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.3 – 0.4 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	115
6.9	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.5 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	115
6.10	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.7 – 0.8 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	116

6.11	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.9 – 1.2 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	116
6.12	Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 1.8 – 2.6 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$).....	117
6.13	Plot of calculated rate constant k_{calc} versus observed rate constant k_{obs} for trithionate degradation at 40 °C for all data, using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$	117
7.1	Schematic showing the basis for modelling.....	120
7.2	Logarithm of the oxygen consumption rate versus the logarithm of ammonia concentration for thiosulfate degradation to trithionate in the presence of oxygen.....	124
7.3	Logarithm of the oxygen consumption rate versus the logarithm of thiosulfate concentration for thiosulfate degradation to trithionate in the presence of oxygen.....	124
7.4	Modelled output for sulfur oxyanion speciation during thiosulfate degradation. Assumed all thiosulfate degradation is via Reaction R1.....	130
7.5	Modelled output for sulfur oxyanion speciation during thiosulfate degradation. Assumed all thiosulfate degradation is via Reaction R4.....	131
7.6	Modelled output for sulfur oxyanion speciation during thiosulfate degradation. Assumed thiosulfate degradation is via Reaction R1 and Reaction R4 ($a = 50 \%$, $b = 50 \%$).....	132
7.7	Modelled output for sulfur oxyanion speciation during thiosulfate degradation. Assumed thiosulfate degradation is via Reaction R1 and Reaction R4 ($a = 80 \%$, $b = 20 \%$).....	133
7.8	Modelled output for sulfur oxyanion speciation during thiosulfate degradation – k_{R1} increased by a factor 10.....	134

7.9	Modelled output for sulfur oxyanion speciation during thiosulfate degradation – k_{R4} increased by a factor 10.....	135
7.10	Modelled output for sulfur oxyanion speciation during 5 thiosulfate degradation – k_{R2-0} increased by a factor 10.....	136
7.11	Modelled output for sulfur oxyanion speciation during thiosulfate degradation – k_{R2-1} increased by a factor 10.....	137
7.12	Modelled output for sulfur oxyanion speciation during thiosulfate degradation – k_0 , k_1 , k_2 and k_3 increased by a factor 10.....	138
7.13	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation.....	143
7.14	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 1 \times$, $k_{R2} - 1 \times$, $k_{R3} - 1 \times$, $b_{k_{R4}} - 0 \times$	144
7.15	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 10 \times$, $k_{R2} - 1 \times$, $k_{R3} - 1 \times$, $b_{k_{R4}} - 0 \times$	145
7.16	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 14 \times$, $k_{R2} - 8 \times$, $k_{R3} - 1 \times$, $b_{k_{R4}} - 0 \times$	146
7.17	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $b_{k_{R4}} - 0.05 \times$	147
7.18	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 1 \times$, $k_{R2} - 1 \times$, $k_{R3} - 1 \times$, $b_{k_{R4}} - 0 \times$	149
7.19	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 1 \times$, $k_{R2} - 10 \times$, $k_{R3} - 1 \times$, $b_{k_{R4}} - 0 \times$	150

7.20	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 1 \text{ x}$, $k_{R2} - 10 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.1 \text{ x}$.	151
7.21	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 1.5 \text{ x}$, $k_{R2} - 10 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0 \text{ x}$.	152
7.22	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 16 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 1 \text{ x}$, $bk_{R4} - 0 \text{ x}$.	153
7.23	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 12 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 1 \text{ x}$, $bk_{R4} - 0.15 \text{ x}$.	154
7.24	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 12 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.17 \text{ x}$.	155
7.25	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 15 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.05 \text{ x}$.	161
7.26	Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation. Model parameters adjusted by the following factors: $ak_{R1} - 12 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.17 \text{ x}$.	162
7.27	Modelled thiosulfate and trithionate concentration after 24 hours at varying copper concentrations. Model parameters adjusted by the following factors: $ak_{R1} - 15 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.05 \text{ x}$.	165

7.28	Modelled thiosulfate and trithionate concentration after 24 hours at varying copper concentrations. Model parameters adjusted by the following factors: $ak_{R1} - 1 \text{ x}$, $k_{R2} - 10 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.1 \text{ x}$	166
7.29	Modelled thiosulfate and trithionate concentration after 24 hours at varying copper concentrations. Model parameters adjusted by the following factors: $ak_{R1} - 12 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.17 \text{ x}$.	167
7.30	Modelled thiosulfate and trithionate concentration after 24 hours at varying ammonia concentrations. Model parameters adjusted by the following factors: $ak_{R1} - 15 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.05 \text{ x}$.	168
7.31	Modelled thiosulfate and trithionate concentration after 24 hours at varying ammonia concentrations. Model parameters adjusted by the following factors: $ak_{R1} - 1 \text{ x}$, $k_{R2} - 10 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.1 \text{ x}$...	169
7.32	Modelled thiosulfate and trithionate concentration after 24 hours at varying ammonia concentrations. Model parameters adjusted by the following factors: $ak_{R1} - 12 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.17 \text{ x}$.	170
7.33	Modelled thiosulfate and trithionate concentration after 24 hours at varying pH. Model parameters adjusted by the following factors: $ak_{R1} - 15 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.05 \text{ x}$	171
7.34	Modelled thiosulfate and trithionate concentration after 24 hours at varying pH. Model parameters adjusted by the following factors: $ak_{R1} - 1 \text{ x}$, $k_{R2} - 10 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.1 \text{ x}$	172
7.35	Modelled thiosulfate and trithionate concentration after 24 hours at varying initial thiosulfate concentrations. Model parameters adjusted by the following factors: $ak_{R1} - 15 \text{ x}$, $k_{R2} - 8 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.05 \text{ x}$.	173
7.36	Modelled thiosulfate and trithionate concentration after 24 hours at varying initial thiosulfate concentrations. Model parameters adjusted by the following factors: $ak_{R1} - 1 \text{ x}$, $k_{R2} - 10 \text{ x}$, $k_{R3} - 5 \text{ x}$, $bk_{R4} - 0.1 \text{ x}$.	174

7.37	Modelled thiosulfate and trithionate concentration after 24 hours at varying initial thiosulfate concentrations. Model parameters adjusted by the following factors: $ak_{R1} - 12 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.17 \times$	175
7.38	Modelled output for sulfur oxyanion speciation during thiosulfate degradation over 7 days.....	176
7.39	Modelled output for sulfur oxyanion speciation during thiosulfate degradation with thiosulfate replenished every 24 hours.....	177
8.1	Typical model output against experimental data.....	183

LIST OF SYMBOLS AND ABBREVIATIONS

DO ₂	Dissolved oxygen
E°	Standard potential, volts
E _h	Redox potential, volts
E _a	Activation energy, kJ/mol
F	Faraday's constant, 96500 C/mol
ΔG°	Standard free energy of formation, kJ/mol
HPLC	High performance liquid chromatography
ICP	Inductively coupled plasma spectrophotometry
I	Ionic strength, mol/l
k	Rate constant
M	Molarity, mol/l
n	Number of electrons
RT	Room temperature
σ	Standard deviation
SHE	Standard hydrogen electrode
t	Time

ACKNOWLEDGEMENTS

I wish to acknowledge support of this project by Placer Dome, AngloGold – Ashanti, Teck Cominco and Barrick Gold, as well as the National Science and Engineering Research Council (NSERC).

I would like to thank my supervisors David Dreisinger and Gus Van Weert for their insightful advice.

Thanks to the Hydro group, especially Anita Lam and Berend Wassink, and all the staff in the Materials Engineering Department who have made life easier for me.

Thank you to Dr Michael Wolf for the loan of the cooling reactor.

I thank my parents for their encouragement, in this and all the other endeavours I have undertaken.

I am especially grateful to my husband Chris who knew that I wanted to go back to university some day and actually got me to do something about it! He is my inspiration.

1. INTRODUCTION

Cyanidation is a well established and effective process for gold recovery from ores and concentrates. However, there are increasing environmental concerns pertaining to the use of cyanide, and it is not suitable for certain ore types, particularly copper containing ores and carbonaceous refractory ores where cyanide consumption can become uneconomical and/or gold recovery low. Thiosulfate has shown considerable promise as an alternative to cyanide for gold leaching. However, one of the main limitations of the thiosulfate system is the high consumption of thiosulfate and the lack of robustness in its applicability to a large variety of ores.

Besides the fact that high reagent consumption increases the cost of the process, the degradation products of thiosulfate have been claimed to passivate gold surfaces and the polythionates often produced are loaded onto resins proposed for gold recovery (Muir and Aylmore, 2002). Degradation products may also facilitate the precipitation of gold, copper and silver sulfides, and insufficient thiosulfate lixiviant can cause the precipitation of metallic gold and silver.

While thiosulfate consumption is usually monitored and reported, the degradation process is not completely understood. It is known that trithionate, tetrathionate and sulfate are commonly present in thiosulfate leach solutions as degradation products, but the factors influencing the formation and interactions of these species are not clear. Sulfate is a thermodynamically stable degradation product, but trithionate and tetrathionate are meta-stable. Tetrathionate is less stable at the alkaline pH values used in gold leaching but trithionate is persistent in gold leach solutions. Also, of the species of interest, very little is known about the expected behaviour of trithionate, both with respect to its formation and its interaction with other solution species.

The focus of this work was therefore to further the understanding of the behaviour of trithionate in gold leach solutions. Experimental work was carried out to determine the kinetics of trithionate degradation in systems resembling gold leaching solutions, and a kinetic model was derived for trithionate degradation. This model was integrated with known kinetic behaviour of thiosulfate and tetrathionate based on literature findings to develop an overall model for the thiosulfate degradation and the resulting solution

speciation of the sulfur oxyanions. The model was evaluated against experimental data and its shortcomings were identified.

In this thesis, a literature review of thiosulfate degradation is given in Chapter 2. Analytical and synthesis methods used are discussed in Chapter 3. The methodology, results and discussion and modelling of trithionate degradation kinetics are discussed in Chapters 4, 5 and 6 respectively. In Chapter 7, a model of thiosulfate degradation and the resulting solution speciation is set up, based on literature data and on the findings in this work. Conclusions and recommendations resulting from this work are given in Chapters 8 and 9 respectively.

2. LITERATURE REVIEW

2.1 INTRODUCTION

In this review, thiosulfate degradation in gold leaching systems and the stability of tetrathionate and particularly trithionate in aqueous systems are discussed to consolidate the current understanding of sulfur oxyanion behaviour under conditions relevant to gold leaching. After a general introduction to the problem of thiosulfate degradation in gold leaching, some general structural and thermodynamic properties of the sulfur oxyanions are summarized. Next, the thiosulfate degradation and formation of other sulfur oxyanions observed experimentally in gold leaching systems are discussed. This is followed by more detailed discussions on the chemistry of thiosulfate, trithionate and tetrathionate in systems relevant to gold leaching. Finally, the overall relevance of the available literature to the understanding of the sulfur chemistry in gold leaching and the areas of shortcoming are discussed to justify the work carried out in this thesis.

2.2 THE AMMONIACAL THIOSULFATE GOLD LEACHING SYSTEM

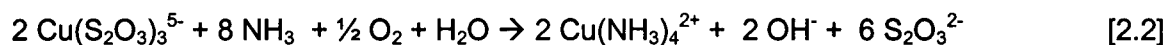
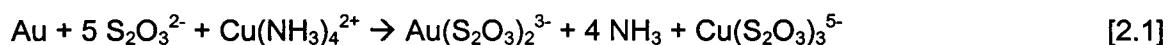
Cyanide has become the industry standard lixiviant for gold. Cyanidation is a robust and well understood process. However, the ineffectiveness of cyanide for gold recovery from preg-robbing ores and the high cyanide consumptions experienced with copper containing ores has lead to a search for an alternative lixiviant. Cyanide also has a negative public image with respect to environmental and safety concerns. However, there is an industry commitment of both gold producers and cyanide manufacturers to the International Cyanide Management Code (EMJ, 2004, Mining Magazine, 2004) that promotes best practice in the use and management of cyanide, exceeding the requirements of most governments and regulatory agencies. Even so, there remain environmental concerns with the use of cyanide, though these may be founded more on public opinion than scientific fact. Thiosulfate has been shown to be a promising alternative lixiviant for gold and silver recovery and much research has been devoted to the ammoniacal thiosulfate system in recent years.

Thiosulfate was first used in precious metals recovery in the 19th century in the Patera Process for silver recovery (Molleman, 1998). An atmospheric ammoniacal thiosulfate

leach to recover gold and silver from ammoniacal oxidative pressure leach residues of copper sulfide concentrates was developed in 1978 (Berezowsky and Gormely, 1978), renewing interest in the thiosulfate lixiviant. Since then, industrial and academic interest in the thiosulfate leaching system has grown tremendously, with the main focus on finding ways to enhance gold leaching and minimise degradation of the thiosulfate reagent.

To leach gold, a suitable oxidant and a suitable complexing lixiviant is required. Using thiosulfate as a lixiviant in ammoniacal solutions, it has been found that the presence of copper as an oxidant greatly enhanced the rate of reaction (Aylmore and Muir, 2001a). The chemistry of the system is complex and not yet fully understood.

A simplified representation of the gold leaching system is given in Equations 2.1 and 2.2, with the overall reaction given in Equation 2.3 (Abruzzese et al., 1995, Wan 1997). Cupric copper or more specifically cupric tetraammine behaves as the oxidant for gold. Thiosulfate complexes the gold ion and stabilises the gold ion in solution. In the process of gold leaching, the cupric is reduced to cuprous, so oxygen is required for its regeneration.



One of the major obstacles to thiosulfate leaching becoming a commercially viable process is the rapid degradation of the thiosulfate reagent, which is a concern economically, technically and environmentally.

Thiosulfate is a meta-stable species and can be oxidized ultimately to sulfate through a number of reaction paths. The presence of cupric copper, considered necessary by many to facilitate gold leaching, enhances thiosulfate oxidation. The decomposition products formed during gold leaching generally include trithionate ($\text{S}_3\text{O}_6^{2-}$), tetrathionate ($\text{S}_4\text{O}_6^{2-}$) and sulfate.

Even though tetrathionate, trithionate and sulfate have very little effect on the gold oxidation reaction (Chu et al., 2003), the formation of trithionate and sulfate in particular represent an irreversible loss of thiosulfate under typical gold leaching conditions.

Since activated carbon is not suitable for recovering gold from thiosulfate solutions, resins have been proposed as a favourable alternative (Fleming et al., 2000, West-Sells et al, 2003, Ji et al, 2003). However, even low concentrations of trithionate and tetrathionate (0.01 M) load strongly onto anion exchange resins, reducing gold loading (Fleming et al., 2003, Muir and Aylmore, 2002). It has been found that concentrations of 0.05 M can effectively reduce gold loading to zero (Nicol and O'Malley, 2002). These species were found not to affect the initial rate of gold loading but became important over longer times when loaded gold could be displaced (Nicol and O'Malley, 2002).

This adsorption is a serious issue for more aggressive leaching conditions where a considerable amount of thiosulfate is consumed during leaching and a considerable quantity of polythionates is produced. In one case it was claimed that mild leaching conditions (low thiosulfate, copper and ammonia concentrations, neutral pH, short time) gave relatively low concentrations of tetrathionate and trithionate (Fleming et al., 2003). However, the authors also acknowledged that in general, leach liquors still contained tetrathionate and trithionate after a few hours.

The presence of trithionate and tetrathionate is also of concern in effluent disposal, as these species have the potential for acid generation on complete oxidation to sulfate, generating 1.3 moles of acid per mole of sulfur in trithionate and 1.5 moles of acid per mole of sulfur in tetrathionate compared with the 1 mole produced per mole of sulfur in thiosulfate (Smith and Hitchen, 1976).

2.3 STRUCTURE AND THERMODYNAMIC PROPERTIES OF THE SULFUR OXYANIONS

Thermodynamically, thiosulfate is a metastable ion. Like the other metastable sulfur oxyanions, thiosulfate needs to lose or gain electrons to reach sulfate or sulfide which are stable (Williamson and Rimstidt, 1992). A typical E_h -pH diagram for aqueous sulfur

systems, shown in Figure 2.1, will therefore not include thiosulfate. All the E_h -pH diagrams shown in this thesis were generated using HSC Chemistry for Windows software (Roine, 1994, version 5.0), but species with thermodynamic data predicted by calculation in work by Williamson and Rimstidt (1992) were not included as they were acknowledged by the authors of HSC Chemistry for Windows to be unreliable and gave large stability regimes for lesser known ions such as HS_7O_3^- . The data used to generate these diagrams is shown in Appendix 1.

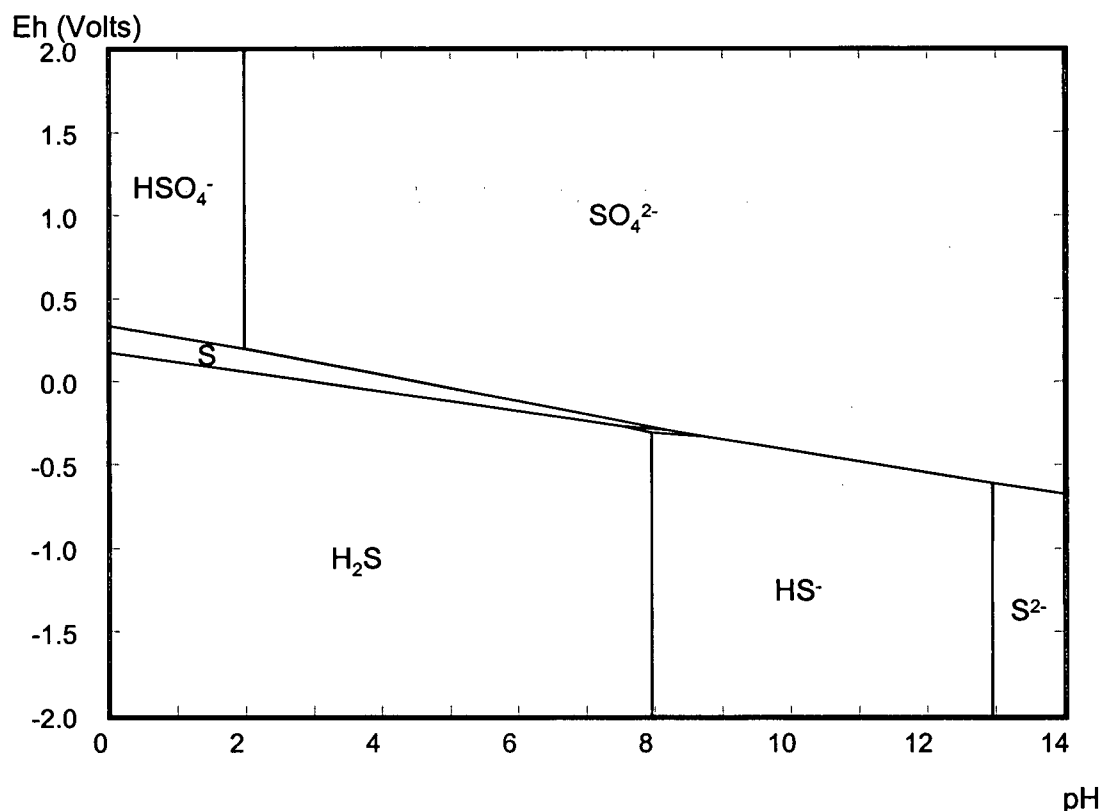
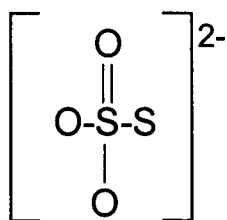
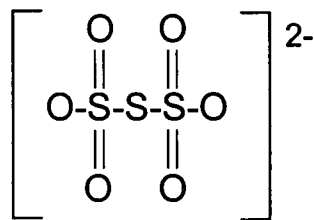


Figure 2.1 : Eh-pH diagram for the aqueous sulfur system
(1 M sulfur, 25 °C)

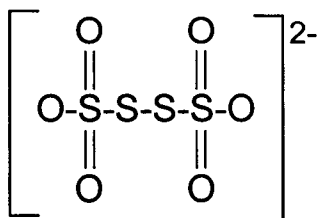
Thiosulfate can be oxidized through tetrathionate ($\text{S}_4\text{O}_6^{2-}$), trithionate ($\text{S}_3\text{O}_6^{2-}$), sulfite and other sulfur oxyanions to sulfate as the potential increases, and is reduced to sulfur in acid or bisulfide in neutral or alkaline solutions (Aylmore and Muir, 2001b). Under alkaline conditions, a number of metastable sulfur species occur, for example sulfur oxyanions and polysulfides (S_n^{2-}). Examples of the sulfur oxyanions are shown diagrammatically below in Figure 2.2. Sulfur is multivalent and therefore easily forms



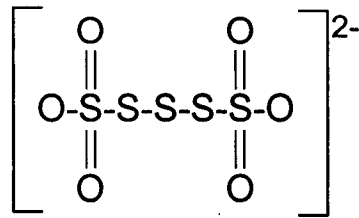
Thiosulfate $\text{S}_2\text{O}_3^{2-}$ *



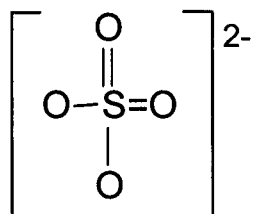
Trithionate $\text{S}_3\text{O}_6^{2-}$ *



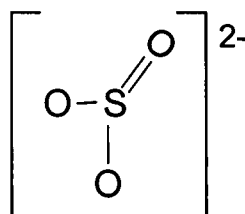
Tetrathionate $\text{S}_4\text{O}_6^{2-}$ *



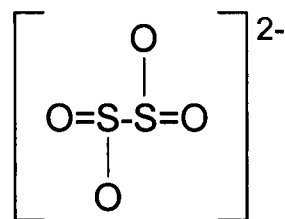
Pentathionate $\text{S}_5\text{O}_6^{2-}$



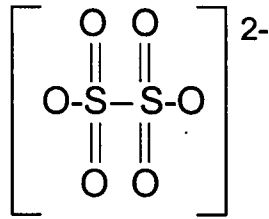
Sulfate SO_4^{2-} *



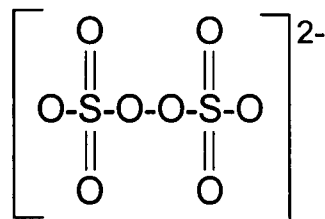
Sulfite SO_3^{2-} *



Dithionite $\text{S}_2\text{O}_4^{2-}$



Dithionate $\text{S}_2\text{O}_6^{2-}$



Persulfate $\text{S}_2\text{O}_8^{2-}$

Figure 2.2 : Basic structures of selected sulfur oxyanions

* indicates species easily quantifiable by current methods at UBC

this large range of ions, as well as polysulfides and colloidal precipitates (Aylmore and Muir, 2001b).

It is well known that the properties of the sulfur atoms in many of the species shown in Figure 2.2 are not equivalent (Ames and Willard, 1951). The properties of sulfur in thiosulfate suggest a possible combination of sulfur with sulfite or sulfide with sulfur dioxide, with the effective oxidation state of +2 per sulfur (Suzuki, 1999). The polythionates have two types of sulfur atom – sulphenyl sulfur and sulfonate sulfur.

The rate of the metastable sulfur oxyanions decomposition to thermodynamically stable sulfur ions is often less than predicted. Thiosulfate has been found to be produced under alkaline conditions, during pyrite leaching. No sulfite was detected, implying a kinetic hindrance of further thiosulfate oxidation (Webster, 1984). The fact that thiosulfate has a significant stability under certain conditions makes it useful as a lixiviant for gold. Trithionate is often found to persist in gold leach liquors as a degradation product, even though it is thermodynamically unstable (Lam, 2002, Nicol and O'Malley, 2002, Ji et al., 2001).

An example of an E_h -pH diagram where the stable sulfate ion has been omitted to show the metastable domain of thiosulfate and other species is shown in Figure 2.3. The diagram shows that thiosulfate is 'stable' in a pH range of greater than 6 and redox potential -0.2 V to 0.2 V (SHE), in the absence of other species such as complexing agents. Tetrathionate exhibits metastability at lower pH.

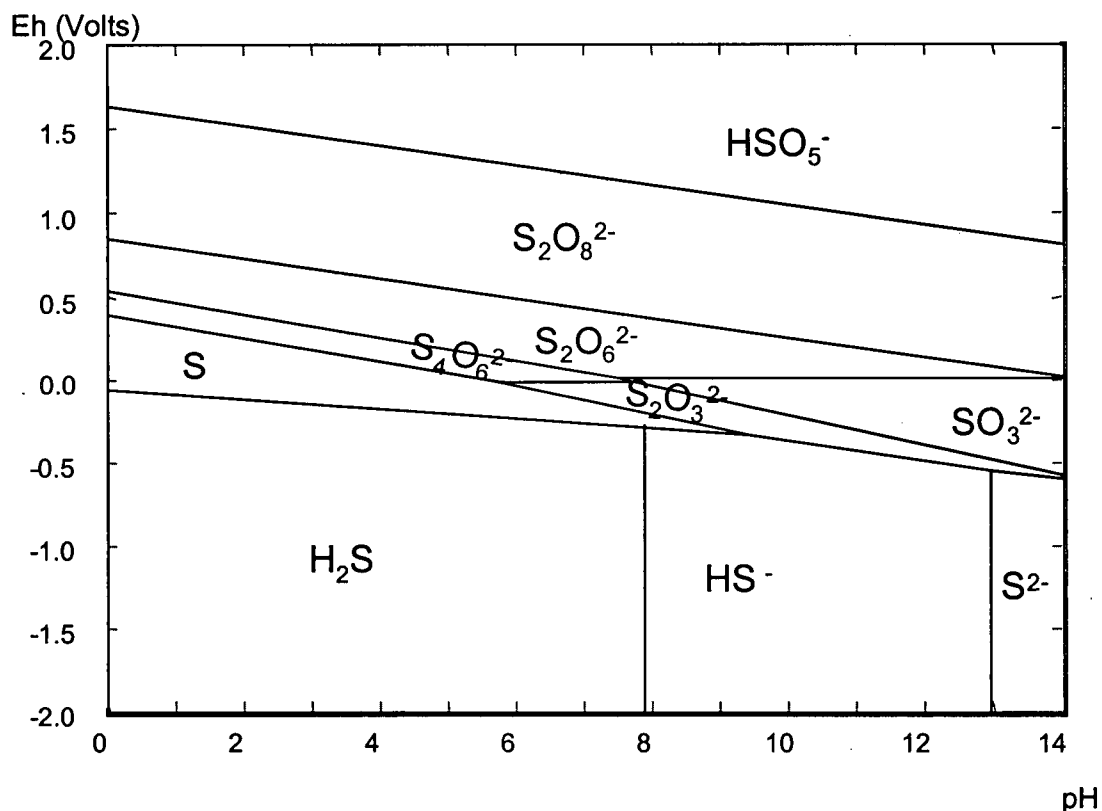


Figure 2.3 : Eh-pH diagram for the metastable aqueous sulfur system with the following species omitted - SO_4^{2-} , HSO_4^- , $\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ (1 M sulfur, 25 °C)

It has been found that sulfite and dithionate ($\text{S}_2\text{O}_6^{2-}$) did not appear in certain gold leach liquors (Aylmore and Muir, 2001b), so these species and other related species were omitted from the E_h -pH diagram, giving the diagram shown in Figure 2.4. In this diagram, trithionate is the most stable polythionate at high E_h and high pH. Based on this diagram, direct formation of trithionate from thiosulfate should be possible, and this has indeed been suggested (see Section 2.5). However, tetrathionate is often reported in gold leach liquors implying that the kinetics of tetrathionate formation are favourable. The presence of oxygen (hence an increase in potential) should favour the formation of trithionate.

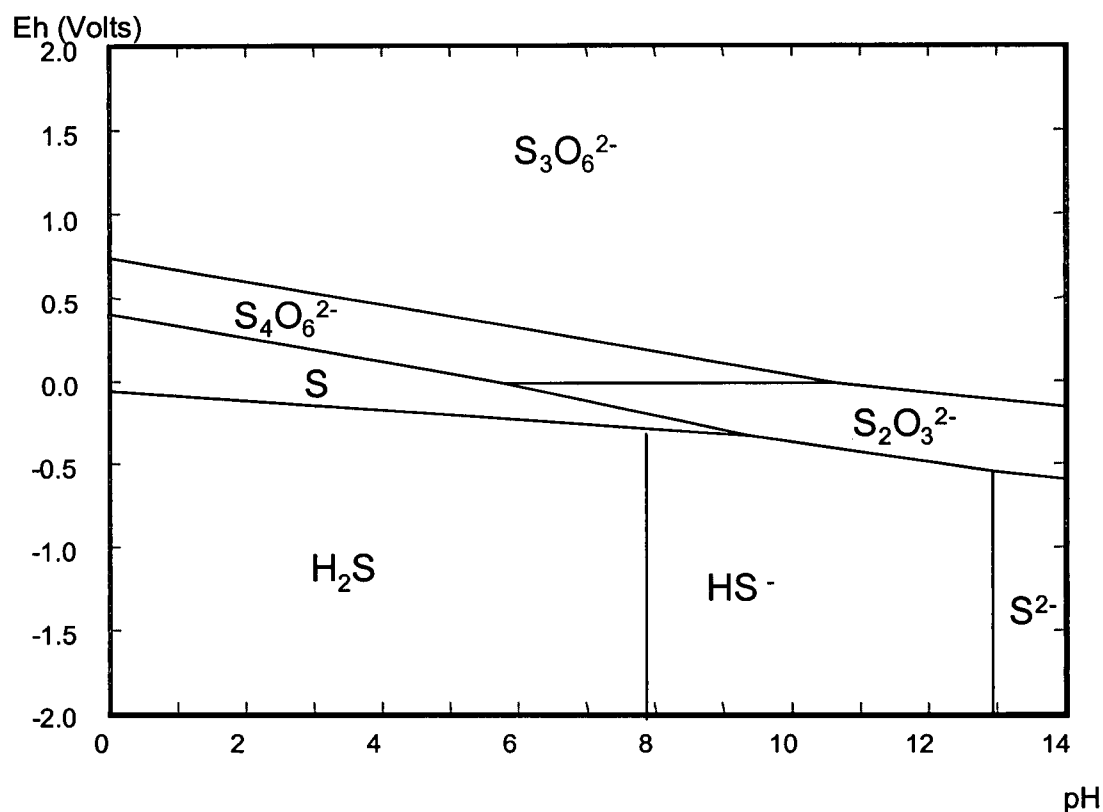


Figure 2.4 : Eh-pH diagram for the metastable aqueous sulfur system with the following species omitted - SO_4^{2-} , HSO_4^- , $\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, SO_3 , SO_3^{2-} , HSO_3^- , $\text{S}_2\text{O}_6^{2-}$, HSO_5^- , $\text{S}_2\text{O}_8^{2-}$.

$\text{S}_2\text{O}_5^{2-}$
(1 M sulfur, 25 °C)

For reference, a selection of Gibbs free energies of formation for species of interest in the gold leaching system is shown in Table 2.1. From these, the standard potentials for a few pertinent thiosulfate oxidation reactions could be calculated (from the relation $\Delta G^\circ = -nFE^\circ$) and are shown in Table 2.2.

Table 2.1 : Selected Gibbs free energies of formation (298 K) for species of interest in the copper – ammoniacal – thiosulfate system (Aylmore and Muir, 2001b)

Species	ΔG° (kJ/mol)	Species	ΔG° (kJ/mol)	Species	ΔG° (kJ/mol)
S	0	Cu	0	Au	0
SO ₃ ²⁻	-486.5	Cu ⁺	50.2	Au ⁺	163.2
SO ₄ ²⁻ *	-742.0	Cu ²⁺	65.0	Au ³⁺	433.5
S ₂ O ₃ ²⁻	-532.2	Cu(S ₂ O ₃) ₃ ⁵⁻	-1624.7	Au(S ₂ O ₃) ₂ ³⁻	-1050.2
S ₂ O ₆ ²⁻	-966.0	Cu(S ₂ O ₃) ₂ ³⁻	-1084.1	Au(NH ₃) ₄ ³⁺	64.4
S ₃ O ₆ ²⁻	-958.0	Cu(S ₂ O ₃) ⁻	-541.0	Au(NH ₃) ₂ ⁺	-41.4
S ₄ O ₆ ²⁻	-1040.4	Cu(NH ₃) ⁺	-10.3		
S ₅ O ₆ ²⁻	-956.0	Cu(NH ₃) ₂ ²⁺	14.5	OH ⁻ *	-157.3
S ₂ O ₄ ²⁻	-600.6	Cu(NH ₃) ₂ ²⁺	-32.3	H ₂ O	-237.2
S ₂ O ₈ ²⁻	-1115.0	Cu(NH ₃) ₃ ²⁺	-73.2	NH ₃	-26.7
		Cu(NH ₃) ₄ ²⁺	-113.0		

* From Weast, 1975.

Table 2.2 : Selected standard oxidation potentials (298 K)

Half Reaction	E ^o _{oxid} (V)
2 S ₂ O ₃ ²⁻ → S ₄ O ₆ ²⁻ + 2 e ⁻	0.12
3 S ₂ O ₃ ²⁻ + 3 H ₂ O → 2 S ₃ O ₆ ²⁻ + 6 H ⁺ + 8 e ⁻	0.51
S ₃ O ₆ ²⁻ + 6 H ₂ O → 3 SO ₄ ²⁻ + 12 H ⁺ + 8 e ⁻	0.20
S ₂ O ₃ ²⁻ + 5 OH ⁻ → 2 SO ₄ ²⁻ + 5 H ⁺ + 2 e ⁻	-0.86

The standard potentials imply that degradation of thiosulfate directly to sulfate should occur readily under the conditions required for gold leaching, and also explain why tetrathionate is likely to be formed, as the standard potentials for these oxidation half reactions are generally lower than those required to leach gold. To form trithionate from thiosulfate requires a higher potential (0.51 V). The data in Table 2.2 highlights the fact that the thermodynamics of the system alone cannot be used as an indicative tool, as kinetically we see the formation and persistence of trithionate, and sulfate is only formed in any significant quantity after long times or as a product of polythionate degradation,

contrary to the predictions of thermodynamics. There appear to be significant kinetic hindrances of trithionate degradation to sulfate in the gold leaching system.

2.4 THIOSULFATE DEGRADATION IN GOLD LEACHING – EXPERIMENTAL OBSERVATIONS

It has been found that thiosulfate degradation in the gold leaching system is often not reported in detail in the literature. Reasons for this could be that much of the reported literature has focussed on gold recovery, or that suitable analytical methods were not available to easily measure thiosulfate consumptions. However, from the literature data available, it has been attempted to compile thiosulfate degradation data in this section to identify the main factors influencing the degradation.

The table in Appendix 2 shows a compilation of thiosulfate consumption data. In many cases, the available data was not completely quantitative or was given as a range. Qualitative information is not included in the appendix but is given in the summary in Table 2.3. The observations in Appendix 2 and in Table 2.3 were for a large range of conditions and in many instances it was not clear why particular conditions were selected. Due to the interdependency of the various parameters and the difficulty in comparing data from different sources with incomplete data sets and different experimental regimes, only general trends are presented.

There was some contradiction in the assessment of how different parameters affect thiosulfate degradation. While it is acknowledged that the concentrations of thiosulfate, ammonia and copper have a significant effect, there is not complete agreement in how these parameters affect the degradation and not much discussion as to how the combination of these species affects degradation. It is generally agreed that an increase in temperature and reaction time, and the presence of ore increases the thiosulfate degradation. The effect of sulfite and sulfate addition has not been clearly established. A more detailed discussion of the chemistry of the thiosulfate degradation inferred in Table 2.3 is given in Section 2.5.

Table 2.3 : Summary of experimental observations for thiosulfate degradation

Parameter	Effect	References	General Comment
Temperature	Inc \Rightarrow increase in degradation	A, B, C, D	Often implied by decrease in gold leaching, assumed to be due to loss of cupric and thiosulfate reagents.
Ammonia concentration	Inc \Rightarrow increase in degradation	C	Ammonia acts as stabiliser for cupric copper, hence it has often been postulated that ammonia inhibits the thiosulfate – copper reaction.
	Inc \Rightarrow decrease in degradation	D, E F G H	
	Optimum required	A	
Copper concentration	Inc \Rightarrow decrease in degradation	G	Postulated that once a certain level of cupric tetraammine is reached, excess cupric oxidizes the leach reagent rather than catalyzing the leach reaction.
	Inc \Rightarrow increase in degradation	C, H, I	
Thiosulfate concentration	Inc \Rightarrow increase in degradation	B, C, H, J	The dependency has been found to vary with other solution parameters e.g. copper concentration.
	Inc \Rightarrow decrease in degradation	G, I	
Ore mineralogy	Presence of sulfides \Rightarrow increase in degradation	K, L, M	Important aspect, but often difficult to quantify and difficult to compare data.
	Ultrafine milling of pyrite \Rightarrow no significant effect	G	
Time	Inc \Rightarrow increase in degradation	G, K	Expected trend as thiosulfate is not a thermodynamically stable species.
Sulfite addition	If present \Rightarrow decrease in degradation	C, N, O	Likely to be highly dependent on ore type, and also known to decrease extent of leaching.
	If present \Rightarrow inconclusive	P	

Table 2.3 (continued) : Summary of experimental observations for thiosulfate degradation

Parameter	Effect	References	General Comment
pH	pH > 11.4 required for minimum degradation	B	Inconclusive.
	Inc pH 8.5 – 10 ⇒ increase in degradation	I	
	Inc pH 9.8 – 11.4 ⇒ decrease in degradation	Q, R	
Oxygen concentration	Inc ⇒ increase in degradation	Q	
Anions (phosphate)	Inc ⇒ decrease in degradation	Q, R	Certain anions said to inhibit thiosulfate coordination with copper (II) ammine complexes

References to Table 2.3

- A Abbruzzese et al., 1995
- B Breuer and Jeffrey, 2000
- C Flett et al., 1983
- D Jeffrey, 2001
- E Aylmore and Muir, 2001a
- F Byerley et al., 1973a
- G Aylmore, 2001
- H Yen et al., 1999
- I Langhans et al., 1992
- J Zipperian and Raghavan, 1988
- K Wan, 1997
- L Xu and Schoonen, 1995
- M Feng and Van Deventer, 2002b
- N Kerley and Bernard, 1981
- O Ji et al., 2001
- P Li et al., 1996
- Q Breuer and Jeffrey, 2003a
- R Breuer and Jeffrey, 2003b

A significant amount of thiosulfate degradation data was given by Aylmore and Muir (2001a). Also reported by them was a comparison of the consumption of copper with time (copper measured by ICP) and thiosulfate (measured by HPLC). (Cupric copper is known to oxidize thiosulfate – see Section 2.5.) This is not reproduced in this summary. However, it is interesting that although copper consumption generally increased as thiosulfate consumption increased, the two reagents were not consumed at a constant ratio. This could imply precipitation of copper or oxidation of thiosulfate by another oxidizing agent such as oxygen, as well as by copper. In other recent work (Breuer and

Jeffrey, 2003a, b) it was also realised that thiosulfate consumption and cupric copper concentration should be considered separately. However, in older work, the thiosulfate degradation was implied by the measured copper concentration (Byerley et al., 1973a) and even though under certain conditions this can give a good approximation, it may not always be entirely appropriate.

A number of effects on thiosulfate degradation were discussed in a silver leaching system (Flett et al., 1983). In leach tests on synthetic argentite, both the thiosulfate and tetrathionate in solution were measured. Although it is commonly accepted or assumed that tetrathionate is the major degradation product of thiosulfate under typical gold and silver leach conditions, it was found that the loss of thiosulfate was slightly higher than the gain in tetrathionate, implying the formation of other sulfur oxyanion species. In many cases only tetrathionate was measured, which could give misleading conclusions.

These observations highlight the importance of appropriate analysis and that some reported results and conclusions are not based on direct analysis.

Very little experimental data on trithionate and tetrathionate production is reported pertaining to gold extraction. It may be that in most reported cases, only the change in thiosulfate concentration was measured, without determining the speciation of sulfur oxyanion degradation products. A few values for trithionate and tetrathionate concentrations observed in gold leach liquors are shown in Table 2.4. While pentathionate has occasionally been noted (qualitatively) in gold leach solutions (De Jong, 2004), it is not a persistent species under these conditions.

Table 2.4 - Literature data for trithionate and tetrathionate production

Leach conditions	$S_2O_3^{2-}$ (mM)	$S_4O_6^{2-}$ (mM)	$S_3O_6^{2-}$ (mM)
0.05 M $S_2O_3^{2-}$ 0.2 M NH_3 20 mg/l each of Pb, Zn, Cu, Ag, Au 48 hrs (Nicol and O'Malley, 2002)			10
Continuous RIP initial 0.05 M $S_2O_3^{2-}$ 0.8 M NH_3 1 mM SO_3^{2-} pH 9.5 (Nicol and O'Malley, 2002)		0.089	0.1
Leach discharge slurry pH 6.9 (Ji et al., 2001)	75	2.3	3
Pregnant leach solution pH 10 (Ji et al., 2001)	70	3.8	7.7

In leach tests at the University of British Columbia (Lam, 2002) at room temperature, using initial solution concentrations of 0.1 – 0.6 M $S_2O_3^{2-}$, 0.16 – 4.7 mM Cu (II) and 0.3 – 0.5 M NH_3 , typical concentrations of the sulfur oxyanions in the leach solutions after 24 to 48 hours were:

$S_2O_3^{2-}$	14 – 567 mM
$S_3O_6^{2-}$	29 – 140 mM
$S_4O_6^{2-}$	0 – 17 mM
SO_4^{2-}	6 – 139 mM

Trithionate in the final leach liquor accounted for 7 – 83 % of the initial thiosulfate added.

The formation of trithionate and tetrathionate in systems resembling gold leaching systems to examine the effect of specific minerals on the thiosulfate degradation kinetics has recently been reported (De Jong, 2004). Various minerals were allowed to react with an ammoniacal thiosulfate solution (0.2 M $(NH_4)_2S_2O_3$ at pH 10) with and without added copper. The author proposed that trithionate was formed by hydrolysis of the tetrathionate produced during thiosulfate degradation rather than directly from thiosulfate

(see Section 2.5). This was not proven as the thiosulfate degradation kinetics were not measured directly in this work due to an unreliable analysis method.

Without added copper, the formation of trithionate increased in the order no mineral ~ hematite ~ galena ~ arsenopyrite < chalcocite < pyrrhotite < pyrite < chalcocite. It is not clear why trithionate formation would be enhanced in the presence of minerals in the absence of copper, but is likely to be a complex effect of surface catalysis, pH, redox potential and possibly the presence of soluble trace elements. The formation of tetrathionate increased in the order no mineral ~ hematite ~ galena ~ arsenopyrite ~ chalcocite < pyrite < pyrrhotite < chalcocite. The authors proposed that certain minerals enhanced the degradation of tetrathionate to trithionate, for example chalcocite.

Where copper was initially present, all the minerals except for chalcocite showed less trithionate formation than the no-mineral condition. The formation of trithionate decreased in the order chalcocite > no mineral ~ hematite > pyrite > arsenopyrite > galena > pyrrhotite ~ chalcocite. The formation of tetrathionate increased in the order chalcocite < no mineral ~ hematite < arsenopyrite < pyrite ~ galena ~ chalcocite < pyrrhotite.

Both with and without initial copper, the presence of chalcocite caused the formation of a significant amount of trithionate. The initial rapid formation of trithionate corresponded to rapid initial copper extraction from the chalcocite. The tetrathionate concentration in this case was very low. Since the author had postulated that trithionate formed from tetrathionate, this observation lead to the suggestion that copper accelerates the decomposition of tetrathionate to trithionate.

To better understand the effects of minerals a more comprehensive sulfur species analysis to include thiosulfate and sulfate would be required.

More fundamental studies investigating the degradation of thiosulfate in the absence of ores are discussed in Section 2.5.

2.5 THIOSULFATE CHEMISTRY AND FUNDAMENTAL STUDIES

Even though the stability of thiosulfate in aqueous solutions is affected by many factors (Dhawale, 1993), thiosulfate in solution, prepared in freshly boiled double distilled water, is very stable stored in air tight bottles (Aylmore and Muir, 2001a). Air oxidation of thiosulfate at normal temperature and pressure is very slow. At pH 7 solutions aerated for 4 months under sterile conditions had less than 10 % change in the thiosalt concentration. There is significant oxidation at higher temperature and air or oxygen pressure, indicating kinetic control. (Rolia and Chakrabarti, 1982).

The degradation of thiosulfate that can be expected in gold leach systems is discussed below.

2.5.1 Oxidative Degradation in Gold Leaching Systems

According to thermodynamics, one would expect that under oxidizing conditions, thiosulfate would eventually be oxidized to sulfate (see Figure 2.1). This is demonstrated in Equation 2.4.



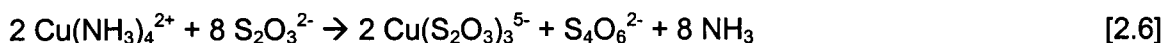
However, a number of metastable oxidation products can be expected. In the gold leaching system, where thiosulfate, copper and ammonia are present, tetrathionate has often been quoted as a primary oxidation product.

Thiosulfate oxidation to tetrathionate by oxygen can be demonstrated by Equation 2.5 (Wan, 1997, Li et al., 1996, Aylmore and Muir, 2001a).



The thiosulfate leach system is complicated by the reduction of copper by thiosulfate (Byerley et al., 1973a, Breuer and Jeffrey, 2000). The reaction of the cupric tetraammine

complex with thiosulfate to form tetrathionate is shown in Equation 2.6 (Aylmore and Muir, 2001a, Breuer and Jeffrey, 2000).



The cupric tetraammine complex is used in the reaction equation rather than simply the cupric ion as it has been often reported that it is the complex that is responsible for reacting with thiosulfate (Lam, 2001, Breuer and Jeffrey, 2000). However, it has also been suggested that $\text{Cu}(\text{NH}_3)_3^{2+}$ rather than $\text{Cu}(\text{NH}_3)_4^{2+}$ oxidizes $\text{S}_2\text{O}_3^{2-}$ to $\text{S}_4\text{O}_6^{2-}$ (Byerley et al., 1973a). This is discussed later in this section. The reaction of thiosulfate with cupric copper is rapid in aqueous solution but slower with ammonia present (Aylmore and Muir, 2001a).

In alkaline solution, the reaction between cupric copper and thiosulfate does not require oxygen (Aylmore and Muir, 2001a). However, oxygen still plays an important role in the overall extent and rate of thiosulfate degradation. In the gold leaching system, oxygen is used to convert cuprous copper to cupric, but depending on the amount of oxygen, some direct oxidation of thiosulfate to tetrathionate and trithionate can also occur. In the presence of oxygen, the redox potential rises and the oxidation of cuprous to cupric is more rapid (as is the oxidation of thiosulfate, where the reaction rate has been quoted to be at least forty times higher in the presence of oxygen (Byerley et al., 1973b)).

Even though in many cited examples, tetrathionate is the main oxidation product referred to (Wan 1997, Muir and Aylmore, 2002), it must be noted that sometimes it has only been assumed that a loss in thiosulfate implies the production of tetrathionate, or sometimes tetrathionate was the only degradation product measured, leading to possible misinterpretation. Trithionate and sulfate have also been reported (Byerley et al., 1973b, Muir and Aylmore, 2002).

Besides copper and oxygen, other oxidants, if present, can also degrade thiosulfate. If iron is present, it can dissolve at pH less than 9.5 and degrade thiosulfate, producing tetrathionate which has no lixiviating action for gold or silver (Aylmore and Muir, 2001a, Perez and Galaviz, 1987). Hence a high pH stabilizes thiosulfate by minimizing iron dissolution (Perez and Galaviz, 1987). Also Ag^+ , Hg^{2+} and cyanide can degrade

thiosulfate (Kelly and Wood, 1994). The addition of the metal ions of Ni, Zn, Pb, Cd, Co and Cr to the gold leaching system all had the effect of decreasing the free thiosulfate concentration, with the largest effect by Cr and least by Ni (Feng and Deventer, 2002a). It was deduced that oxidation (especially for Cr^{6+} and Co^{3+}) as well as complexation (especially for Cd^{2+}) played a role.

Few studies have been done to determine the mechanism or kinetics of thiosulfate degradation, particularly in the gold leaching system. A significant amount of fundamental work was done in the 1970s by Byerley et al. (1973a, 1973b, 1975) and also very recently by Breuer and Jeffrey (2003a, 2003b).

Copper (II) Oxidation of Thiosulfate in Absence of Oxygen

Byerley et al. (1973a) studied the mechanism of thiosulfate degradation by cupric copper in ammonium hydroxide in the absence of oxygen. The mechanism proposed was for a system slightly different to that expected under gold leaching conditions and was primarily related to sulfide leaching in ammonia solutions, where thiosulfate was produced.

When thiosulfate was added to a copper-ammonia system, there was an immediate increase in the absorbance of the solution prior to the commencement of the reaction. But the position of the absorption maximum did not change at this initial time, nor during the reaction. The increase in absorbance was interpreted as an association between the thiosulfate and the copper ammonia complexes. The association was suggested as being at one of the axial positions, therefore giving a strong polarizing effect of cupric copper on thiosulfate. The equatorial square planar structure of the copper complex remained essentially unchanged.

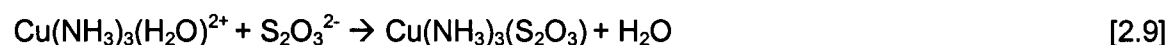
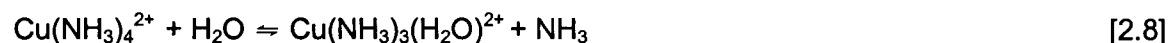
The progress of the reaction was measured by measuring the cupric concentration. Solutions analysed for thiosulfate by iodometric titration and qualitatively for tetrathionate directly after the reaction (when it was observed that all cupric had been consumed) showed that overall one mole of copper (II) was consumed for each mole of thiosulfate, matching the stoichiometry of Equation 2.7.



If higher copper (~0.03 M) or thiosulfate (~0.15 M) concentrations were used, or if the solutions were stored, trithionate and regenerated thiosulfate were produced as products of tetrathionate degradation (Byerley et al., 1973a). Tetrathionate chemistry is discussed later.

At pH > 10, the cupric-ammine complex exists in equilibrium with hydroxo species, so some tri-ammine cupric species co-exist with the tetraammine species. Since the rate of the copper thiosulfate reaction was faster in aqueous solution, it was assumed that the tri-ammine cupric complex was more reactive than the tetraammine complex (Byerley et al., 1973a). Hence, a mechanism suggested from kinetic results implied substitution of thiosulfate into the co-ordination sphere of a copper (II) tri-ammine complex prior to the electron transfer step. An electron transfer from thiosulfate to cupric copper in an intermediate tri-ammine cupric-thiosulfate complex gives cuprous copper and thiosulfate, which dimerises to give tetrathionate.

The mechanism outline is shown in Equations 2.8 to 2.11.



It was determined that the involvement of free radicals in the rate determining step was unlikely as addition of a free radical inhibitor, mannitol, had no effect on the reaction rate (Byerley et al., 1973a).

In Byerley's work plots of $\log [\text{Cu}^{2+}]$ vs time were linear with the same slope, indicating first order dependency, assuming ammonia and thiosulfate concentrations were essentially constant during the reaction. Thiosulfate concentrations up to 0.10 M gave a rate of first order dependence. At higher thiosulfate concentrations (above 0.15 M), the reaction order was higher. There was a linear dependence of the rate on $1/[\text{NH}_3]$ for ammonia concentrations of 0.1 – 1 M.

Under these conditions, the rate of decrease of cupric copper concentration by reaction with thiosulfate in the absence of oxygen was given by Equation 2.12.

$$-d[\text{Cu}^{2+}]/dt = k [\text{Cu}^{2+}][\text{S}_2\text{O}_3^{2-}]/[\text{NH}_3] \quad [2.12]$$

where $k = 8.5 \times 10^{-4} \text{ s}^{-1}$ at 30 °C. The activation energy was 102.5 kJ/mol (based on thermodynamic parameters at 30 °C).

More recent work by Breuer and Jeffrey has developed a further understanding of the system (Breuer and Jeffrey, 2000, 2003b). The main aim for this study of the factors affecting the gold leaching kinetics under anaerobic conditions was to allow for the effect of decreasing copper (II) (and hence cupric to cuprous ratio) to be investigated with a minimal decrease in thiosulfate concentration. All the components except for copper (II) and ammonia were purged with argon, then a concentrated copper (II) – ammonia solution was injected into the vessel. After mixing, a sample was transferred to a sealed UV cell, with no air contact at any time. The general conditions used were 0.1 M sodium thiosulfate, 0.4 M ammonia and 10 mM copper sulfate at 30 °C, pH 11.4. Complete exclusion of air was found to be essential as even trace quantities were shown to increase the copper (II) reduction rate. The cupric ammine complexes absorbing at 605 nm were measured using UV-visible spectrophotometry.

Plots of the cupric ammine complex concentration versus time showed that the relation of $1/[\text{Cu(II)}]$ versus time was fairly linear, while that of $\log[\text{Cu(II)}]$ versus time was not. This would imply that the rate determining step was second order, not first order as suggested by Byerley et al. (1973a). A deviation from linearity at longer times was attributed to further copper (II) reduction by tetrathionate.

The addition of up to 0.8 M sulfate was found to decrease the rate of copper (II) reduction considerably. By changing the experimental procedure to inject a thiosulfate solution into a solution of copper (II), ammonia and sulfate, further information on the mechanism of the action of sulfate ions could be obtained. In this instance, a noticeable induction period occurred, after which the reaction rate increased to reach a similar value to that obtained when a copper (II) – ammonia solution was injected into a thiosulfate – sulfate solution.

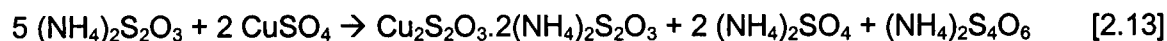
It was noted by Byerley et al. (1973a) and Breuer and Jeffrey (2003b) that in the reaction of thiosulfate with copper (II), it is likely that thiosulfate complexes with the cupric ammine complex at an axial site, based on absorbance measurements. The reaction thus occurs via an inner sphere mechanism. It was postulated that sulfate competes with thiosulfate for co-ordination, hence slowing the copper (II) reduction rate by thiosulfate. Where thiosulfate was added to a copper (II) ammonia sulfate solution, the sulfate was able to co-ordinate before the addition of the thiosulfate, giving an induction period for thiosulfate to replace sulfate before the reaction could occur.

The effect of other anions (chloride and nitrate) and especially phosphate was also to reduce the copper (II) reduction rate, which is consistent with an inner sphere reduction reaction. Phosphate in particular is thought to readily complex with copper (II) at the axial position, inhibiting the substitution of thiosulfate into the inner sphere.

The effect of pH on the reaction mechanism was investigated by using ammonium thiosulfate instead of sodium thiosulfate, with the same concentration of ammonia and same ionic strength. This had the effect of reducing the pH from 11.4 to 9.8. The reaction order of copper (II) reduction at pH 9.8 showed a first order rate limiting step, not second order as found at pH 11.4, which correlates with the observation by Byerley et al. (1973a). The decrease in reaction order from two to one at lower pH could be due to the lack of anions (hydroxide) to compete with thiosulfate for axial coordination. This view was supported experimentally by an observed return to second order kinetics when sulfate was added at pH 9.8.

A rate law was not given in this work. It was suggested that the mechanism was different and more complicated than that suggested by Byerley et al (1973a).

Another mechanism related to the leaching of silver sulfide in the absence of air has been postulated, but with little detail given (Kelly and Wood, 1994). First the reduction of copper by thiosulfate in the bulk solution (Equation 2.13) was postulated, followed by the substitution of copper for silver in the sulfide molecule, within the mineral particle (Equation 2.14).



Copper (II) Oxidation of Thiosulfate in Presence of Oxygen

The reaction between copper ammine solutions and thiosulfate in the presence of oxygen but the absence of ores was studied by Byerley et al (1975). They found that rather than tetrathionate being formed (as suggested above (De Jong, 2004) and as noted when no oxygen was present (Byerley et al., 1973a)), trithionate and sulfate were formed, in ratios varying with the initial thiosulfate concentration and pH. Since both the trithionate and sulfate formed were stable with respect to further oxidation under the conditions tested, it was proposed that the trithionate was not an intermediate to sulfate formation. It was proposed that two reactions were occurring, as in Equations 2.15 and 2.16. Copper does not appear in these equations as it was proposed that copper acted as a catalyst, as discussed later.



The reaction rate was monitored by monitoring the oxygen consumption. The rate of oxygen consumption showed an initial induction period, increasing reaction rate then a linear maximum rate. The initial thiosulfate concentration had a significant influence on the attainment of the maximum rate. Also, the rate of oxygen consumption was virtually identical for a copper (I) or a copper (II) ammonia thiosulfate system, so it was assumed that in the former, copper (I) was rapidly oxidized to copper (II) and then the systems were essentially equivalent.

The initial oxygen consumption region was postulated to involve a build up of a catalytically active copper – oxygen complex, which eventually reached a steady concentration at the maximum reaction rate. It was found that at different parts of the oxygen consumption curve, different yields of trithionate and sulfate were obtained. The

highest yields of trithionate were observed in the initial part of the oxygen consumption curve, and for the highest initial thiosulfate concentrations ($> 0.02 \text{ M}$) and lowest pH values (< 10). Under gold leaching conditions, one would expect a predominantly trithionate product.

At the maximum oxygen consumption rate both trithionate and sulfate were formed concurrently. The rate of sulfate formation was calculated using the total oxygen consumption minus the rate of oxygen consumption for trithionate formation.

The percentage conversion of thiosulfate to trithionate at the end of oxidation is shown in Table 2.5. As the initial thiosulfate concentration increased, the relative yield of trithionate versus sulfate increased. Also as the pH decreased, the yield of trithionate increased. It was also shown that the initial thiosulfate concentration had an effect on the oxygen consumption rate (Byerley et al., 1975). However, in more recent work where the thiosulfate oxidation rate was measured directly, the rate was found to be independent of the thiosulfate concentration (Breuer and Jeffrey, 2003a). It is likely that the oxygen consumption rate is not directly related to thiosulfate oxidation (Breuer and Jeffrey, 2003a).

While Byerley et al. discussed possible mechanisms for the formation of trithionate from thiosulfate, these were postulated to involve $\text{Cu(II)} - \text{oxygen}$ complexes as intermediates. This is not discussed here as it has since been shown that the existence of such complexes is not likely (Breuer and Jeffrey, 2003a). While no rate law was given, it was noted by Byerley et al., that the rate of oxygen consumption was proportional to the copper and oxygen concentrations.

Table 2.5 – Formation of trithionate from thiosulfate in the presence of oxygen
(oxygen pressure 725 mm Hg, 30 °C, [Cu(II)] = 1 mM, [NH₃] = 0.2 M) (Byerley et al.,
1975)

Initial S ₂ O ₃ ²⁻ (mM)	pH	% S converted to S ₃ O ₆ ²⁻
5	11.2	30.6
15	11.2	42.2
25	11.2	50.4
50	11.2	64.1
75	11.2	66.6
100	11.2	75.6
25	11.2	54.0
25	10.0	64.6
25	9.6	81.0
25	9.3	100.0

Breuer and Jeffrey (2003a) investigated the system in a different way. Tests were done in a flow through system, monitoring the copper (II) ammine complexes using UV-visible spectrophotometry. A concentrated copper (II)-ammonia solution was injected into the vessel and after a mixing time the solution was continually pumped through a UV cell. The cell was temperature controlled, and absorbance was measured at 605 nm. The thiosulfate concentration was determined by removing a sample and analysing it using a rotating electrochemical quartz crystal microbalance, by measuring the mass changes to a silver electrode (Breuer et al., 2002). The standard initial reagent concentrations were 0.4 M ammonia, 0.1 M sodium thiosulfate and 10 mM copper sulfate. Where copper (I) was investigated, an ammonia solution was injected into a solution of thiosulfate and copper (I).

Mixtures of copper (II) and thiosulfate, with and without air sparging, showed an initial decrease in copper (II) concentration with time, more so in the presence of air, while the thiosulfate concentration decreased. This result was considered surprising as oxygen readily oxidizes copper (I) to copper (II). Hence it was shown that copper exists as both

copper (I) and copper (II) during the oxidation of thiosulfate. This contrasts with the mechanism by Byerley et al. (1973a) where it was claimed that there was no decrease in copper (II) concentration. In Breuer and Jeffrey's work, since both the rate of thiosulfate oxidation and the rate of copper(II) reduction were increased in the presence of oxygen, an alternative mechanism to Byerley et al.'s was considered necessary.

The oxidation of thiosulfate was slightly faster when the initial copper was present as copper (I), and the initial increase of copper (II) was rapid. This suggested that the reaction products of copper (I) oxidation may be involved in the oxidation of thiosulfate. Thus the mechanisms of the copper (I) oxidation by oxygen were considered.

It is said to be well established that the first steps in copper (I) oxidation by oxygen involve the formation of copper (II) and peroxide, as demonstrated in Equation 2.17.



However, the mechanisms for this process are not clear. The kinetics show that the autooxidation of Cu(I) complexes occurs via inner sphere mechanisms involving di-oxygen adducts formed according to Equation 2.18.

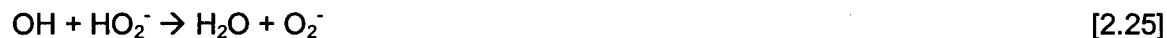
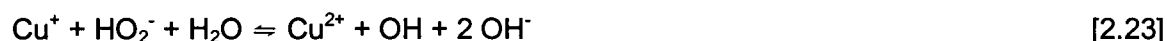
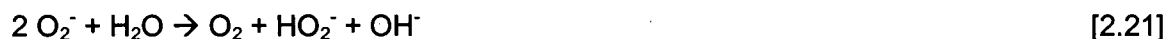


Alternatively this may be viewed as a copper (II) superoxide complex $\text{Cu}^{2+}\text{O}_2^-$. The fact that no superoxide has been identified during copper (I) autooxidation is not surprising given that its reactivity is close to diffusion rates

Tests to investigate the effect of peroxide on thiosulfate oxidation were therefore conducted. Addition of 50 mM hydrogen peroxide to 0.1 M thiosulfate and 0.4 M ammonia (without copper) gave less than 30 % thiosulfate oxidation after 1 hour. However, in the presence of copper (II) a much faster reaction occurred. A rapid reaction also occurred when peroxide was added to a thiosulfate solution containing copper (I) and to a thiosulfate, copper (II) and ammonia leach solution. Hence it was implied that the intermediates of peroxide decomposition by copper oxidize thiosulfate, and not peroxide directly. Peroxide has been considered previously to be involved in the

formation of tetrathionate, for example in the electrolytic oxidation of thiosulfate where peroxide was assumed to be active at the anode (Glasstone and Hickling, 1954).

A reaction scheme was suggested to describe the copper catalysed decomposition of peroxide taking part in thiosulfate oxidation. This is described in Equations 2.19 to 2.26. Two thiosulfate oxidation paths were predicted - the copper(II) thiosulfate reaction catalysed by oxygen, evident by the higher initial rate of copper (II) reduction in the presence of oxygen, and the oxidation of thiosulfate by superoxide or hydroxide radicals as a result of copper (I) oxidation.



The effect of oxygen concentration was investigated by sparging the solution with oxygen, air or a gas mixture containing 1.9 % oxygen in nitrogen. Increased oxygen concentration increased the rate of thiosulfate oxidation and copper (I) oxidation, and associated reactions according to the peroxide reaction scheme. However, the copper (II) to copper (I) ratio was hardly affected. Also the rate of thiosulfate oxidation increased with increased air sparge rate, and it was suggested that the reaction was likely to be limited by the rate of mass transfer of oxygen into solution.

An increase in thiosulfate concentration from 0.05 M to 0.15 M showed similar maximum thiosulfate oxidation rates. However, the corresponding copper (II) concentration profiles showed that increasing the thiosulfate concentration increased the rate of copper (II) reduction and reduced the copper (II) to copper (I) ratio in solution.

A decrease in copper concentration by a factor five decreased the thiosulfate oxidation rate by a factor two. However it also had a significant effect on the solution potential, which decreased as the copper concentration decreased.

The thiosulfate oxidation rate was similar for 0.2 M or 0.4 M ammonia but the initial rate of copper (II) reduction increased with decreasing ammonia.

The effect of pH (at constant ammonia concentration) was shown by comparing reaction rates using ammonium thiosulfate and sodium thiosulfate, with the same ammonia concentration. It was shown (Breuer and Jeffrey, 2003d) that at low pH values, even though the ammonia concentration was constant, copper (II) was much more reactive towards thiosulfate. So it was not surprising that the copper (II) concentration dropped to a lower minimum level at lower pH. Thiosulfate oxidation was also faster at pH 9.8 than 11.4.

The presence of anions was shown to reduce the rate of copper (II) reduction by thiosulfate with phosphate being the most effective. This was shown for the system with or without oxygen present (Breuer and Jeffrey, 2003a, b). This is consistent with the theory of anions competing for coordination at the copper (II) axial sites and thus reducing the rate of copper (II) reduction by thiosulfate involving oxygen.

No kinetic law was given in this case.

Copper (II) Oxidation of Thiosulfate – General Considerations

It was proposed by Byerley et al. (1973a, b, 1975) and Breuer and Jeffrey (2003b) that in the oxidation of thiosulfate by cupric copper, thiosulfate became co-ordinated to the cupric-ammine complex. Senanayake (2004) recently revisited this reaction, using literature data and thermodynamic and kinetic analysis. Based on published stability constants, he considered the species distribution of the cupric – ammonia – thiosulfate – hydroxide system over a range of pH and ammonia and thiosulfate concentrations. Overall, from pH 7 to 12, the species $\text{Cu}(\text{S}_2\text{O}_3)_2^{2-}$, $\text{Cu}(\text{NH}_3)_3^{2+}$, $\text{Cu}(\text{NH}_3)_3\text{OH}^+$ and $\text{Cu}(\text{NH}_3)_4^{2+}$ were predominant. This supports Byerley et al's view that a mixed complex of the type $\text{Cu}(\text{NH}_3)_3(\text{S}_2\text{O}_3)^0$ can be involved in thiosulfate oxidation.

Assuming the general rate law in Equation 2.27, the author determined the reaction orders q , r and l to be 1, -1.1 and 1.2 respectively, based on an analysis of literature data.

$$-d[\text{Cu}^{2+}]/dt = k_{\text{Cu}} [\text{Cu}^{2+}]^q [\text{NH}_3]^r [\text{S}_2\text{O}_3^{2-}]^l \quad [2.27]$$

However, Breuer and Jeffrey (2003b) proposed that the cupric – thiosulfate reaction could be second order with respect to cupric concentration. It was suggested by Senanayake (2004) that the reaction could be either first or second order with one dominating under certain conditions.

Based on work done in the absence of ammonia, Senanayake found that the oxidation of thiosulfate by cupric copper took place via the mixed complex $\text{Cu}(\text{S}_2\text{O}_3)_n(\text{H}_2\text{O})_p^{-2(n-1)}$ and the rate determining step was the decomposition of this complex to products. Hence two scenarios were considered in the presence of ammonia – a first order decomposition and a second order decomposition as the rate determining step.

For the first order scenario, the reaction in Equation 2.28 was considered.



Varying the values of p (2-3) and n (1-2) and comparing the proposed kinetic law with literature data, k_{Cu} was found to be $4 \times 10^{-4} \text{ s}^{-1}$ for $\text{Cu}(\text{NH}_3)_3(\text{S}_2\text{O}_3)^0$ and $\text{Cu}(\text{NH}_3)_2(\text{S}_2\text{O}_3)_2^{2-}$, and $k_{\text{Cu}} = 17 \times 10^{-4} \text{ s}^{-1}$ for $\text{Cu}(\text{NH}_3)_3(\text{S}_2\text{O}_3)_2^{2-}$. These values are similar to that obtained by Byerley et al (1973a).

For the second order scenario, the reaction in Equation 2.29 was considered as the rate determining step.



For this reaction the rate constant k_{Cu} was $0.1 - 0.2 \text{ M}^{-1} \cdot \text{s}^{-1}$ for the decomposition of $\text{Cu}(\text{NH}_3)_3(\text{S}_2\text{O}_3)^0$, $\text{Cu}(\text{NH}_3)_2(\text{S}_2\text{O}_3)_2^{2-}$ and $\text{Cu}(\text{NH}_3)_2(\text{S}_2\text{O}_3)^0$.

Pyrite Catalysed Thiosulfate Oxidation in Presence of Oxygen

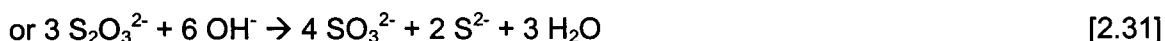
Catalysis by pyrite has also been used to explain thiosulfate oxidation. In the absence of copper, the rate of tetrathionate formation in a thiosulfate leach system was directly proportional to the pyrite surface concentration (Xu and Schoonen, 1995). The dependency on pyrite surface concentration implies a surface mediated reaction mechanism. For pyrite to act as a catalyst, there had to be interaction of thiosulfate, pyrite and oxygen. This was discussed in terms of molecular orbital theory. Since negligible tetrathionate was formed in a system of thiosulfate held under nitrogen, it was assumed that oxygen was the terminal electron acceptor in the oxidation reaction. Also, negligible thiosulfate oxidation to tetrathionate occurred without pyrite present. Since both pyrite and thiosulfate have been found to react slowly with molecular oxygen, it was postulated that a surface complex with interaction between the molecular orbitals of thiosulfate, pyrite and oxygen was required for the reaction to proceed. A mechanism was deduced based on the following three conditions used to determine whether a redox reaction is likely to occur according to molecular orbital theory.

1. The energy of the lowest unoccupied molecular orbital (LUMO) must be less than that of the highest occupied molecular orbital (HOMO) or within 6 eV above that of the HOMO.
2. The symmetries of the HOMO and LUMO must be the same to ensure proper overlap of the orbitals.
3. The electron transfer must yield a stable end product.

The reaction mechanism postulated involved three electron transfer steps. The first transfer was from thiosulfate to an anodic site on pyrite, the second was from an anodic site to a cathodic site on the pyrite surface via its conduction band, and the third was from the cathodic site to the terminal electron acceptor, oxygen (Xu and Schoonen, 1995).

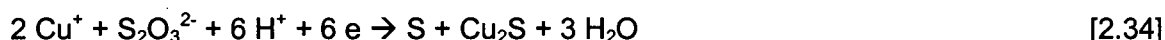
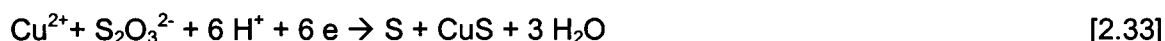
2.5.2 Disproportionation and Reductive Degradation of Thiosulfate

Disproportionation of thiosulfate to sulfur and sulfate, or sulfide and sulfite, is represented in Equations 2.30 and 2.31.



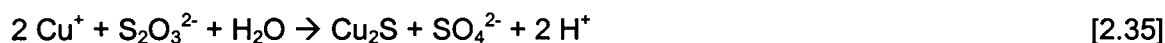
Disproportionation is expected to occur in oxygen deficient or low potential solutions, or where there is a high copper concentration (Aylmore and Muir, 2001a). This type of decomposition of thiosulfate leads to precipitation of elemental sulfur, gold, or copper, gold or silver sulfides (Li et al, 1996). Elemental sulfur and cupric sulfide have been observed experimentally in the gold thiosulfate leach system (Wan, 1997, Aylmore and Muir, 2001a).

Reductive decomposition can be represented by Equations 2.32, or 2.33 and 2.34, in the presence of copper (Li et al, 1996).



Besides the loss of the thiosulfate lixiviant and copper, increasing the operating cost, this reaction may lead to precipitation of silver or block the surface for further leaching (Li et al, 1996).

The pathway for the disproportionation reaction of thiosulfate in the presence of copper has been suggested (Muir and Aylmore, 2002). It was suggested that a fast redox reaction between cupric copper and thiosulfate was followed by slower side reactions of the cuprous produced, forming Cu_2S , as in Equation 2.35.



2.5.3 Thiosulfate Degradation Inhibitors

Based on Equation 2.31, it has been suggested that sulfite inhibits thiosulfate decomposition (Kerley and Bernard, 1981, Hemmati et al, 1989). Sulfite is claimed to prevent the formation of free sulfide (S^{2-}) and hence precipitation of gold or silver (Kerley and Bernard, 1981, Zipperian and Raghavan, 1988). Very low concentrations ($\sim 0.05\%$) of sulfite have been used to stabilise thiosulfate but sulfite addition also lowers the potential, which reduces cupric in solution (Wan, 1997, Aylmore and Muir, 2001a, Ji et al, 2001). Sulfite can also be oxidized by cupric copper or oxygen to sulfate and dithionate, depending on the conditions.

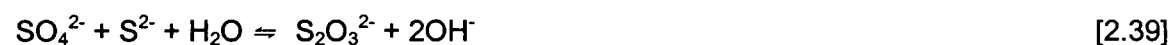
Without sulfite, the following can occur in the presence of the oxides of calcium, as shown in Equation 2.36, and of iron, aluminium, manganese and copper (Kerley and Bernard, 1981).



Sulfite is also known to react with polythionates via the general reaction in Equation 2.37. Generally this reaction equilibrium lies to the right (Foss and Kringlebotn, 1961). Equation 2.38 shows how ammonium sulfite reacts with tetrathionate to produce thiosulfate and sulfate (Flett et al, 1983) thus regenerating thiosulfate. Trithionate, however, is stable in the presence of sulfite (Fleming et al, 2003).



Sulfate has been suggested as alternative to sulfite according to Equation 2.39 (Hu and Gong, 1991).



This is unlikely as sulfate is very stable (Aymore and Muir, 2001a).

Conversion of trithionate and tetrathionate to thiosulfate using sulfide (e.g. NaHS) or polysulfides after removal of gold from the solution has also been suggested (Ji et al, 2001, Fleming et al, 2003). This is demonstrated in Equations 2.40 and 2.41 (Fleming et al, 2003).



Conversion rates of up to 99 % of both trithionate and tetrathionate have been achieved (Ji et al, 2001). Sulfide addition was advocated above sulfite addition as sulfite cannot reduce trithionate at common operating temperatures and pressures and sulfide produces no sulfur containing by-products. Also sparging of a non-oxidising gas such as H_2S or SO_2 has also been used to control the formation of polythionates. Alternative reductants such as hydrogen, fine reactive elemental sulfur and carbon monoxide have also been suggested (Ji et al, 2001). All of these required prior gold removal to ensure no gold losses by precipitation.

Other degradation inhibitors such as phosphate and ethylenediamine tetraacetic acid (EDTA) have also been mentioned briefly (Breuer and Jeffrey, 2003a).

The use of such additives is expected to be limited to tank leaching applications and not to be of particular use in heap leaching (Wan, 1997).

2.6 TRITHIONATE DEGRADATION

The polythionates are well known for the ease with which they undergo heterolytic cleavage in reactions with nucleophilic reagents, usually at a sulfenyl sulfur atom due to the electrophilic character of the divalent sulfur atoms of the chains (Ritter and Krueger 1970). Depending on the properties of the nucleophile, trithionate can undergo nucleophilic attack at either the sulfenyl sulfur atom or the sulfonate sulfur atom. Direct bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$) at the sulfenyl sulfur atom is shown in Figure 2.5 (Ritter and Krueger, 1970). It has been claimed that of the two potential sites for nucleophilic attack, the sulfenyl sulfur atom is much more reactive than the sulfonate

sulfur atom. The sulfonate sulfur atom resists losing its sulfur-oxygen bonds (Ssekalo and Bamuwamye, 1993) and is generally only subject to attack by hydroxide or other hard bases (Ritter and Krueger, 1970). Soft polarizable bases are expected to attack trithionate at the sulfenyl sulfur atom. Hard bases of low polarizability and high electronegativity (e.g. OH⁻, (C₂H₅)₃N) are much less reactive towards trithionate (Ritter and Krueger, 1970).

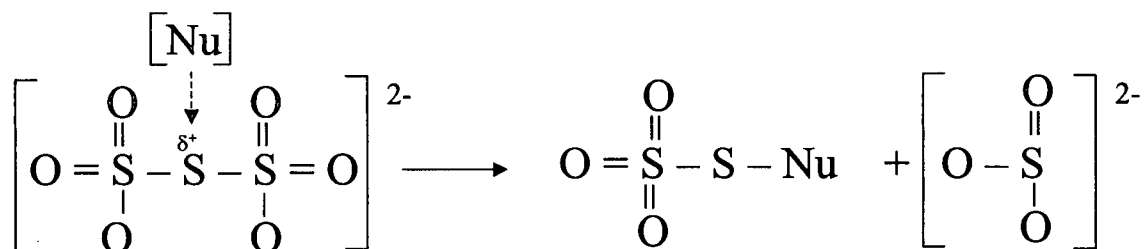
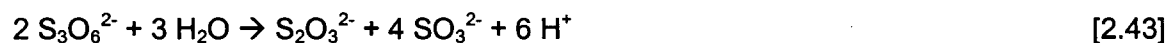


Figure 2.5 - Bimolecular nucleophilic substitution at sulfenyl sulfur of trithionate

Specific examples of nucleophilic substitution reactions relevant to gold leaching are discussed in following sections.

2.6.1 Interaction with Water

Kurtenacker et al (1935) showed that the following two equations held for the decomposition of trithionate in aqueous solutions.



Equation 2.42 was found to occur from pH 5.6 to pH 12 at 50 °C while Equation 2.43 was found to occur at pH 13.4 at 50 °C. While these equations have been well accepted in the literature, the effects, if any, of the species used for pH adjustments (e.g. hydroxide or carbonate ions) were not given any consideration.

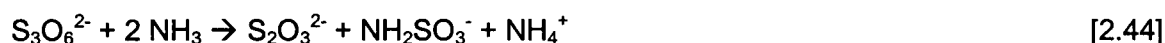
Kinetic testwork on trithionate degradation in water is summarized in Table 2.6.

2.6.2 Interaction with Hydroxide

Based on Kurtenacker et al's findings (1935) the fact that trithionate degradation in water follows a different reaction at high pH (see Equations 2.42 and 2.43) implies that the hydroxide concentration has an effect on the degradation path. In his work, the degradation rate was higher for pH values where Equation 2.43 was valid, than for Equation 2.42. Rolia and Chakrabarti (1982) did not notice any effect of hydroxide concentration, but the highest pH that they used was pH 11 (at 70 °C), lower than that where Equation 2.43 is expected to predominate. It has been suggested that hydroxide would attack trithionate directly at the sulfonate sulfur atom (Ritter and Krueger, 1970).

2.6.3 Interaction with Ammonia

It has been suggested that Equation 2.44 holds for the interaction between trithionate and ammonia (Naito et al, 1975). The presence of sulfamate was not confirmed in these tests. The stoichiometry of the ammonolysis reaction was verified by the authors in anhydrous liquid ammonia, but not published. Previously sulfamate had been measured during the degradation of trithionate at 110 °C at ammonia concentrations of 4 to 8 N (Shieh et al, 1965). Based on this, it was assumed that sulfamate would be a likely reaction product at 40 °C to 80 °C and an ammonia concentration between about 0.5 and 2.75 M. It is not known how likely it is for ammonolysis to occur in aqueous ammonia solutions of low concentration. Kinetic testwork on trithionate degradation in ammonia solutions is summarized in Table 2.7.



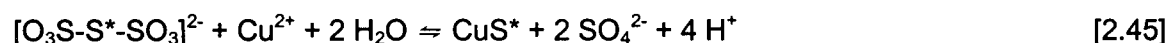
2.6.4 Interaction with Thiosulfate

Exchange reactions are common amongst the sulfur oxyanions. The kinetics of the exchange between trithionate and thiosulfate is summarised in Table 2.8, along with the kinetics of the effect of thiosulfate on trithionate degradation in water and aqueous ammonia solutions. The rate of the exchange reaction between trithionate and thiosulfate was found to increase with the concentration and charge of the positive ions, hence it was proposed that the interaction was between an ionic complex of thiosulfate,

trithionate or both, rather than between free ions (Fava and Pajaro, 1954). As a nucleophile, thiosulfate is expected to interact with trithionate through the sulphenyl sulfur of trithionate.

2.6.5 Interaction with Copper

Cupric copper has been reported to degrade trithionate (Kelly and Wood, 1994). S^* shows a radioactively marked isotope of sulfur to give an indication of the reaction pathway, in Equation 2.45. The conditions for this reaction were not given.



In a study of the reaction between copper (II) and thiosulfate in ammoniacal solutions in the absence of oxygen, it was proposed that the thiosulfate ion became co-ordinated to the copper – ammonia complex before copper reduction (Breuer and Jeffrey, 2003b). Addition of trithionate to this system increased the copper reduction rate, so it was assumed that trithionate can reduce copper but the possible reaction occurring under these conditions was not discussed. Addition of sulfate at the start of the test greatly reduced the reaction rate. It was deduced that the copper – trithionate reaction proceeded via an inner sphere mechanism, where trithionate must first displace sulfate from the copper co-ordination sphere in order to react.

It was claimed that the reactions between cupric copper and trithionate or tetrathionate are faster than thiosulfate. However, we still see significant amounts of trithionate in gold leach solutions. This may be an indication that there is insufficient copper (II) available or that the reaction between copper and trithionate is not as rapid as suggested, or has a more complex dependency on other conditions (e.g. thiosulfate concentration). Also, in recent work investigating the effects of minerals on thiosulfate degradation (De Jong, 2004), the formation rate of trithionate generally increased in the presence of copper, which is contrary to what one would expect if copper reacted faster with trithionate than thiosulfate.

Table 2.6 – Trithionate degradation in water

Ref.	Experimental	Kinetics	Activation energy	Mechanism	Discussion
Naito et al, 1975	Used ethanol / water mixtures to vary $[H_2O]$. $S_3O_6^{2-}$ degradation determined by measuring $[S_2O_3^{2-}]$ and assuming the reaction in Equation 2.42.	$-d[S_3O_6^{2-}]/dt = k_w[H_2O][S_3O_6^{2-}]$ $k_w = 3.56 \times 10^{-6} M^{-1}.min^{-1}$ at 40 °C $k_w = 9.80 \times 10^{-6} M^{-1}.min^{-1}$ at 50 °C $k_w = 7.04 \times 10^{-5} M^{-1}.min^{-1}$ at 70 °C Addition of salts gave an average value of $k_w = 1.08 \times 10^{-6} M^{-1}.min^{-1}$ at 50 °C. This effect was not discussed by the authors.	87.3 kJ/mol (40 – 80 °C)	$S_3O_6^{2-} + H_2O \rightleftharpoons S_3O_6.H_2O^{2-}$ $S_3O_6.H_2O^{2-} \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2 H^+$ 2 nd step rate determining. Water was expected to attack the sulfonate sulfur atom directly.	pH not given – the reaction assumed to be valid may not have been appropriate. Indirect determination of kinetics.
Rolia et al, 1982	Constant pH tests using NaOH addition.	$-d[S_3O_6^{2-}]/dt = k_w[H_2O][S_3O_6^{2-}]$ (assumed) $k_w = 6.78 \times 10^{-5} M^{-1}.min^{-1}$ (70 °C, pH 11)	91.7 kJ/mol (70 – 85 °C)	Assumed Naito's mechanism.	Temperatures higher than gold leaching.
Hofmann-Bang, 1950	Decomposition in sodium acetate, pH 5 – 9. $S_2O_3^{2-}$ measured to infer $S_3O_6^{2-}$ degradation from Equation 2.42.	$-d[S_3O_6^{2-}]/dt = k_w[H_2O][S_3O_6^{2-}]$ (assumed) $k_w = 0.83 \times 10^{-6} M^{-1}.min^{-1}$ at 25 °C $k_w = 4.59 \times 10^{-6} M^{-1}.min^{-1}$ at 40 °C	86.4 kJ/mol (25 – 40 °C)	Not discussed.	Work related to iodine-azide reaction.

Table 2.7 – Trithionate degradation in ammonia

Ref.	Experimental	Kinetics	Activation energy	Mechanism	Discussion
Naito et al, 1975	$S_3O_6^{2-}$ degradation determined by measuring $[S_2O_3^{2-}]$ and assuming the reaction in Equation 2.44. $[NH_3]$ 0.5 – 2.75 M.	$-d[S_3O_6^{2-}]/dt = (k_w[H_2O] + k_a[NH_3])[S_3O_6^{2-}]$ $k_a = 5.18 \times 10^{-5} \text{ M}^{-1} \cdot \text{min}^{-1}$ at 40 °C $k_a = 3.41 \times 10^{-4} \text{ M}^{-1} \cdot \text{min}^{-1}$ at 60 °C	83.5 kJ/mol (40 – 80 °C)	$S_3O_6^{2-} + NH_3 \rightleftharpoons S_3O_6 \cdot NH_3^{2-}$ $S_3O_6 \cdot NH_3^{2-} \rightarrow S_2O_3^{2-} + NH_2SO_3^- + H^+$ 2 nd step rate determining. Ammonolysis reaction proceeds in competition with hydrolysis reaction.	The stoichiometry was not verified under the conditions used. The pH of the ammonolysis tests was not indicated. Indirect determination of kinetics.

Table 2.8 – Trithionate degradation in the presence of thiosulfate

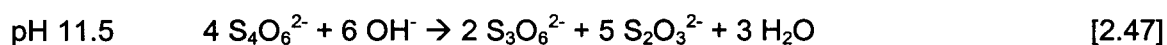
Ref.	Experimental	Kinetics	Activation energy	Mechanism	Discussion
Fava and Pajaro, 1954	Exchange reaction between $S_2O_3^{2-}$ and $S_3O_6^{2-}$ measured using radioactively marked S^* . $O_3S-S-SO_3^{2-} + S^*-SO_3^{2-} \rightleftharpoons O_3S-S^*-SO_3^{2-} + S-SO_3^{2-}$	Rate = $k[S_2O_3][S_3O_6]$ Rate not appreciably affected by pH (7 to 10) or by a 10-fold increase in the surface to volume ratio. k = varied with concentration of inert salts, especially concentration and charge of positive ions.	56 kJ/mol (25 - 51 °C) Independent of the type or concentration of inert salt.	$O_3S-S-SO_3^- + S^*-SO_3^{2-} \rightleftharpoons O_3S-S-S^*-SO_3^- + SO_3^{2-}$ $\rightleftharpoons O_3-S-S^*-SO_3^- + S-SO_3^{2-}$ Proposed that reaction was between trithionate and ionic complex of thiosulfate (due to effect of positive ions).	
Naito et al, 1975	$S_3O_6^{2-}$ degradation determined by measuring $[S_2O_3^{2-}]$ and assuming the reaction in Equation 2.42.	$-d[S_3O_6^{2-}]/dt = (k_w[H_2O] + k_a[NH_3] + k_t[S_2O_3^{2-}])([S_3O_6^{2-}])$ $k_t = 4.15 \times 10^{-3} M^{-1}.min^{-1}$ at 40 °C $k_t = 2.05 \times 10^{-2} M^{-1}.min^{-1}$ at 60 °C	53 kJ/mol (40 – 80 °C)	Thiosulfate essentially behaves as a catalyst. $S_3O_6^{2-} + S_2O_3^{2-} \rightleftharpoons S_3O_6^{2-} \cdot S_2O_3^{2-}$ $S_3O_6^{2-} \cdot S_2O_3^{2-} + H_2O \rightarrow 2 S_2O_3^{2-} + SO_4^{2-} + 2H^+$ 1 st step rate determining.	The mechanism proposed would involve a large transition state – it was not explained why this would be feasible or why the reaction rate would increase.
Rolia et al, 1982	Constant pH tests, pH 5.5 – 8, 85 °C	$S_2O_3^{2-}$ (up to 10 mM) increased $S_3O_6^{2-}$ degradation rate.		Naito et al's mechanism assumed (1975)	

2.7 TETRATHIONATE DEGRADATION

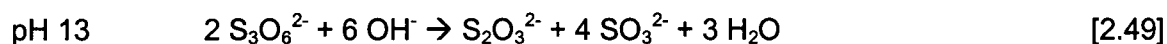
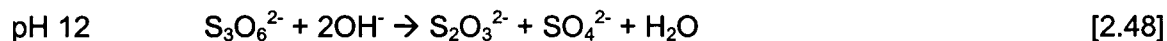
As discussed in the section on trithionate (Section 2.6) the polythionates are well known for their reactions with nucleophilic reagents. This section examines some of the reactions between tetrathionate and other solution components.

2.7.1 Interaction with Hydroxide

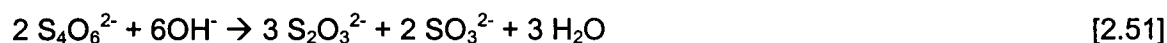
Tetrathionate is known to be unstable in alkaline solutions. Tetrathionate can be decomposed to various products by increasing the pH (Muir and Aylmore, 2002, Rolia and Chakrabarti, 1982, Naito et al, 1970b, Lyons and Nickless, 1968). Degradation of tetrathionate in aqueous ammonia showed the following (Naito et al, 1970b, Smith and Hitchen, 1976).



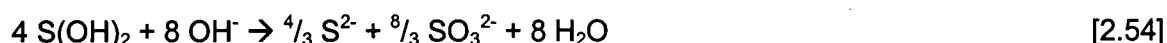
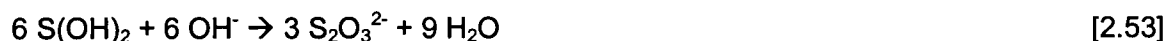
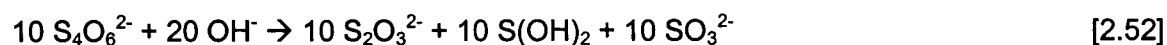
Further decomposition of the trithionate and pentathionate formed is shown in Equations 2.48 to 2.50 (Rolia and Chakrabarti, 1982, Naito et al, 1970b).



Hence, if tetrathionate is aged in strongly alkaline solutions, it will finally form thiosulfate and sulfite (Naito et al, 1970b) as shown in Equation 2.51.



Other reaction schemes for the alkaline decomposition of tetrathionate have also been suggested. Tetrathionate has been claimed to degrade to thiosulfate, sulfite and sulfoxylic acid (S(OH)_2), with further degradation of the sulfoxylic acid to sulfide (Muir and Koh, 1983). The reaction equations are shown below. It would be expected that the sulfide and sulfite in Equation 2.54 would combine to produce thiosulfate.



There have been some studies on the kinetics of tetrathionate decomposition in alkaline systems, with details given in Table 2.9.

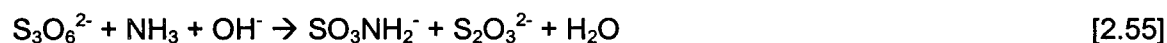
In the absence of ammonia, copper and oxygen, the rate of the alkaline decomposition of tetrathionate was described by Zhang and Dreisinger (2002). No build-up of trithionate was found in this testwork, implying that either trithionate was not a part of the main reaction mechanism or that it decomposed at a similar rate to tetrathionate. The possible catalytic effect of the thiosulfate product on further tetrathionate degradation was not considered.

Rolia and Chakrabarti (1982) did similar work but in the presence of oxygen, and found that while the rate law could be expressed in the same way as that of Zhang and Dreisinger (see Table 2.9), the rate constant was more than 10 times smaller. It was proposed by Zhang and Dreisinger that the presence of oxygen in the work of Rolia et al. and the absence of oxygen in their work was probably the reason for this discrepancy, and that oxidants could possibly retard the rate of tetrathionate degradation. However, similar work by Breuer and Jeffrey (2004) showed that tetrathionate degradation under air-saturated conditions gave no measurable difference in kinetics to tests under nitrogen. Their results were similar to those of Zhang and Dreisinger.

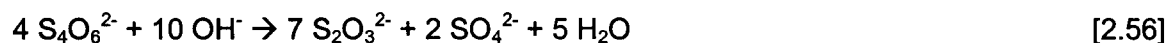
It was suggested that rather than the presence of oxidants being responsible for the difference in kinetics measured by the two previous groups, variations in the ionic strength of the test solutions was responsible (Breuer and Jeffrey, 2004). Increasing the ionic strength was found to have a significant effect on the initial rate of tetrathionate decomposition.

2.7.2 Interaction with Ammonia

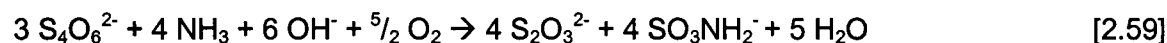
The effect of ammonia on the rate of tetrathionate degradation was measured at 50 to 80 °C by Naito et al (1970b). The ammonia concentration was found to have a significant effect on the rate, with tetrathionate decomposing much faster at higher ammonia concentrations. In addition to the trithionate, thiosulfate and pentathionate formed during the alkaline decomposition of tetrathionate, the formation of sulfamate (SO_3NH_2^-) has also been proposed in the presence of ammonia (without copper). After trithionate was produced by the alkaline degradation of tetrathionate (Equation 2.47), sulfamate was reportedly produced (Equation 2.55) (Naito et al, 1970b, 1975).



The sulfamate yield depended on the ammonia concentration. If the ammonia concentration was less than 2 N, hardly any sulfamate formed. If there was not enough ammonia, the solution became neutral or weakly acidic with the precipitation of sulfur and the formation of higher polythionates. With excess free ammonia, the overall reaction gave sulfamate instead of sulfate. (Equations 2.56 and 2.57)



In the presence of air or oxygen a similar set of equations could be written (Equations 2.58 and 2.59).



Breuer and Jeffrey (2004) found that tetrathionate decomposition in the presence of an ammonium sulfate / ammonia buffer was faster than for a carbonate buffer at the same pH, even though the ionic strength was lower. A similar observation was made for phosphate buffers in comparison with an ammoniacal system. These authors had proposed that an increase in ionic strength would increase the rate of tetrathionate degradation. This observation was not explained.

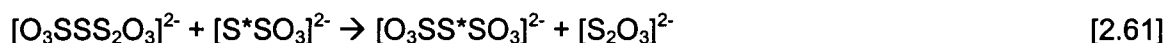
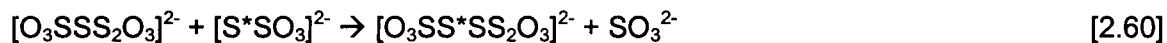
2.7.3 Interaction with Copper

In an investigation of the reaction between thiosulfate and cupric copper in the presence of oxygen (Breuer and Jeffrey, 2003b), the effect of tetrathionate and trithionate on the reaction were also investigated briefly. Addition of tetrathionate increased the copper (II) reduction rate, implying that tetrathionate was also oxidized by copper (II). However, depending on the initial conditions, the tetrathionate concentration was expected to reach a steady state, when its production (by thiosulfate oxidation) and consumption (by copper (II) reduction) were equal. If sulfate was added with tetrathionate to the thiosulfate system, the initial rate of copper (II) reduction was not affected, hence it was concluded that tetrathionate did not need to complex with copper (II) for reduction to occur. Since the addition of sulfate had been found to slow the reaction between copper (II) and thiosulfate (and hence the production of tetrathionate), then the amount of tetrathionate at steady state would be lower in this case. Similarly, if addition of ammonium ions (reduction of pH) increased the copper (II) reduction reaction, the steady state concentration of tetrathionate would be expected to be higher.

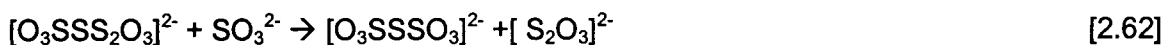
Some solid copper compounds have been said to increase the rate of tetrathionate oxidation. (Chanda and Rempel, 1986) Chalcopyrite, covellite and chalcocite have all been suggested to catalyse oxidation of tetrathionate by air. In the case of cuprous oxide catalysis, only sulfate was formed as a product. No reaction equation was given.

2.7.4 Interaction with Thiosulfate

The displacement reaction between thiosulfate and the polythionates is well known (Foss, 1961, Foss and Kringelbotn, 1961, Fava and Bresadola, 1955). Tetrathionate can undergo nucleophilic attack at the sulfenyl sulfur, with either sulfite or thiosulfate displaced, as in Equations 2.60 and 2.61 (where S* denotes a marked sulfur atom).

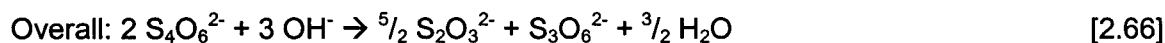
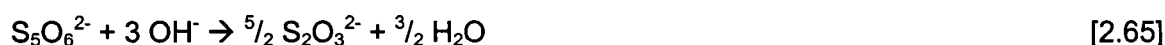


Similarly sulfite can react with tetrathionate, displacing thiosulfate, as in Equation 2.62.



The kinetics of Equation 2.60 were investigated in the presence of formaldehyde as a sulfite acceptor (Foss and Kringelbotn, 1961), at neutral pH. A summary of the kinetics findings is shown in Table 2.9. The positive influence on the rate by positive ions implied that the intermediate complex for the reaction was likely formed not between free ions but ionic complexes of tetrathionate, thiosulfate or both.

The equations above (2.60 and 2.62) can be used to explain the catalytic effect of thiosulfate on tetrathionate degradation. Under non-oxidising conditions, some thiosulfate (about 62.5 %) can be regenerated from the decomposition of tetrathionate to higher or lower polythionates through the formation of trithionate (Aylmore and Muir, 2001a, Marsden and House, 1992). This is highly catalysed by thiosulfate, as represented in Equations 2.63 to 2.66 (Byerley et al, 1973a, Gelves et al, 1996).



The effect of thiosulfate was addressed in a study by Rolia and Chakrabarti (1982) who derived a rate equation for tetrathionate degradation in the absence of ammonia at pH 11. Thiosulfate was found to increase the rate of tetrathionate degradation. The kinetics results are shown in Table 2.9.

However, Breuer and Jeffrey (2004) proposed that the apparent increase in rate when thiosulfate was present was due to the increase in ionic strength that thiosulfate addition would represent rather than the thiosulfate itself.

Table 2.9 – Tetrathionate degradation in neutral to alkaline solutions

Ref.	Experimental	Kinetics	Activation energy	Mechanism	Discussion
Zhang et al, 2002	Alkaline degradation. Absence of oxygen. In bicarbonate/hydroxide or HPO_4 /hydroxide buffer, deaerated with N_2 , under N_2 atmosphere.	$-\text{d}[\text{S}_4\text{O}_6^{2-}]/\text{dt} = k[\text{OH}][\text{S}_4\text{O}_6^{2-}]$ $k = 0.38 \times 10^3 \text{ M}^{-1}.\text{s}^{-1}$ (22 °C, pH 10-11.5)	98.5 kJ/mol (22-40 °C)	Suggested presence of dissolved oxygen and/or copper had a role in mechanism.	pH and temperature dramatically affect degradation rate in alkaline solution.
Rolia et al, 1982	Alkaline degradation in presence of thiosulfate. Constant pH tests using NaOH addition. Oxygen present.	$-\text{d}[\text{S}_4\text{O}_6^{2-}]/\text{dt} = (k_1 + k_2[\text{S}_2\text{O}_3^{2-}])([\text{OH}][\text{S}_4\text{O}_6^{2-}]$ $k_1 = 0.022 \text{ M}^{-1}.\text{s}^{-1}$ $k_2 = 2.77 \text{ M}^{-2}.\text{s}^{-1}$ (25 °C, pH 11)	115.5 kJ/mol (15-45 °C, pH 11)	None given.	Rate constant k_1 10 times smaller than Zhang.
Naito et al, 1970b	Ammoniacal degradation at 50 – 80 °C	None given			In presence of >2M ammonia, sulfamate formed from further degradation of trithionate product.
Foss et al, 1961	Thiosulfate exchange reactions	$-\text{d}[\text{S}_4\text{O}_6^{2-}]/\text{dt} = k[\text{S}_2\text{O}_3^{2-}][\text{S}_4\text{O}_6^{2-}]$ $k = 1.3 \times 10^{-3} \text{ M}^{-1}.\text{s}^{-1}$ (25 °C, $I = 1.15 \text{ M}$)	50.2 kJ/mol (20 – 40 °C, $I = 1.15 \text{ M}$)	$\text{S}_4\text{O}_6^{2-} + \text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_5\text{O}_6^{2-} + \text{SO}_3^{2-}$ via nucleophilic displacement	

2.8 REMOVAL OF POLYTHIONATES FROM SOLUTION

Polythionates are detrimental in gold recovery from thiosulfate leach solutions using adsorbants such as resins. Besides the reactions already discussed to remove polythionates from solution, by hydrolysis, ammonolysis or interchange between various sulfur species, it is possible to remove polythionates in other ways. While many of these methods do not allow for recovery of thiosulfate, this may not be of importance in cases where reduction of thiosulfate consumption is not critical. There is also an environmental concern of discharge of polythionates, as these can produce acid on further oxidation to sulfate under suitable conditions.

A few potential methods are given in Table 2.10. This summary simply gives an indication of the types of processes available and has not been studied in any detail for this review.

Table 2.10 : Potential Methods for Polythionate Removal

Method	Reference	Applicability
Bacterial oxidation	Hansford and Vargas, 2001 De Jong et al, 1997 Sand et al, 1995	A number of bacteria, generally requiring acidic conditions, can oxidize various polythionates to sulfate.
MnO ₂ oxidation	Schippers and Jorgenson, 2001	Oxidation to sulfate.
HOCl oxidation	Horvarth and Nagypal, 2000	Oxidation to sulfate.
Sulfite addition	Kerley and Bernard, 1981 Ji et al, 2001	Reversal to thiosulfate and other lower polythionate.
Sulfide addition	Ji et al, 2001	Reversal to thiosulfate.
Alkaline treatment	Zhang and Dreisinger, 2002	Reversal to thiosulfate and other polythionates.
Cyanide	Nor and Tabatabai, 1975 Koh, 1990 Mizoguchi and Okabe, 1975	Thiosulfate and sulfate produced, and other unwanted products.
Selective resin adsorption	Wassink, 2002	Anion exchange resins can be used to adsorb thiosulfate and polythionates, with selective elution of thiosulfate.

2.9 SUMMARY OF LITERATURE FINDINGS

There is a limited understanding of the degradation of thiosulfate in gold leaching systems. While thiosulfate consumption is usually documented in leach tests, the degradation products are not often identified or quantified. There have been a number of fundamental studies on the degradation of thiosulfate to predominantly trithionate and/or tetrathionate. It seems that one can expect trithionate to form directly when oxygen is present, rather than as a decomposition product of tetrathionate, while tetrathionate is expected in the absence of oxygen. The mechanisms by which these species form and the ways in which the solution conditions affect their rates of formation and their proportions formed relative to other sulfur oxyanions is not understood. However, there is currently a fair amount of research being devoted to the study of thiosulfate degradation under gold leaching conditions. The subsequent behaviour of the thiosulfate degradation products is not well understood.

Tetrathionate has been identified in gold leach solutions, but it is usually quick to degrade under the alkaline conditions used in gold leaching. Thiosulfate catalyses this degradation, and it is postulated that copper can also increase the degradation rate. Tetrathionate is not as persistent as trithionate under many gold leaching conditions.

Trithionate is more persistent in gold leaching solutions but very little is known about this species in the context of gold leaching. Much of the available literature concerning trithionate has not been directly related to gold leaching: the older literature is fundamental in nature and other studies have been published in the context of sulfur oxidation pathways during the ammoniacal treatment of sulfides. To be able to assess thiosulfate degradation in a larger context, it is essential to develop a better understanding of the behaviour of trithionate.

Alleviating the problem of thiosulfate degradation is critical to the success of the thiosulfate leaching process for gold. This review has shown that while the degradation of thiosulfate is not fully understood, there is a fair amount of research currently underway to investigate fundamentals of this degradation process. However, to be able to understand the system in its entirety, it is necessary to understand the behaviour of the other sulfur oxyanions expected to be present, mainly trithionate and tetrathionate.

Of these two species, trithionate often appears to be more persistent in the alkaline solutions used, but very little is understood about this species. The following chapters thus discuss experimental work carried out to better understand the behaviour of trithionate, followed by the integration of the findings with the expected behaviour of thiosulfate and tetrathionate based on literature observations.

2.10 SCOPE AND OBJECTIVES

The specific scope and objectives of this study are outlined below:

- To further the understanding of trithionate solution chemistry under conditions relevant to gold leaching by thiosulfate by experimentally determining the kinetics of trithionate degradation and identifying the effects of various solution conditions on the kinetics.
- To incorporate the findings into a model to predict trithionate degradation kinetics.
- To use literature data and rate equations describing thiosulfate and tetrathionate reactions, as well as the experimentally derived trithionate degradation rate equation to develop a simple kinetic model to determine the expected sulphur oxyanion solution speciation during gold leaching using thiosulfate.
- To evaluate the sensitivity of the model to parameters in the rate equations.
- To evaluate the ability of the model to adequately describe experimental data.
- To identify limitations of the model to determine where further research is required to improve the model.
- To suggest ways in which thiosulfate degradation or the formation of polythionates can be minimised during gold leaching.

3 ANALYTICAL METHODS AND SYNTHESIS

3.1 INTRODUCTION

In this chapter, the analytical methods used in this work are described. Also, the synthesis and characterisation of the sodium trithionate used in the kinetic work and for analytical calibration purposes is described. The experimental procedure for the kinetic testwork is described in Chapter 4.

3.2 ANALYSIS OF SULFUR OXYANIONS – ION CHROMATOGRAPHY

3.2.1 Description of Method

Solution samples were analysed for thiosulfate, trithionate, tetrathionate and sulfate using high performance liquid chromatography (HPLC) using a Dionex Series 600 system. Analysis of thiosulfate, trithionate and tetrathionate involved separation of the species on an OmniPac PAX-100 column, and analysis of the separated species using UV-visible absorption spectrometry at 205 nm. Sulfate was separated from the other sulfur oxyanions using an IonPac AS4A-SC column and measured by conductivity detection. Because the determination of sulfate was by a different method, it was not possible to analyse a single sample for all the species of interest simultaneously. More details of the chromatography methods are given in Appendix 3.

Chromatography requires the use of standard solutions to calibrate the instrument. The preparation and storage of these solutions is discussed in Section 3.2.2. All samples and standards were diluted to the required concentration range (generally less than 20 mg/l) using ultra-pure deionised water and analysed immediately.

Iodometric titration is often used to determine thiosulfate, but it is difficult to determine thiosulfate and the polythionates individually in mixtures. Copper also interferes with this method (Wassink, 2002).

3.2.2 Stability of Standard Solutions

Experimental Work

Calibration standard solutions of sodium thiosulfate (SIGMA, anhydrous, >99% pure), sodium trithionate (synthesised, see Section 3.5) and sodium tetrathionate (SIGMA, dihydrate) were prepared in de-ionised water. The salts were made up to 1000 mg/l solutions of each anion, then diluted to 100 mg/l solutions, and then to 2, 10, 15 and 20 mg/l solutions to be used in calibration. The calibration standards were analysed within two hours of preparation.

To test the stability of standard solutions over longer times and under different storage conditions, 100 mg/l and 10 mg/l solutions of thiosulfate, trithionate and tetrathionate (individually and in combinations) were made up in the same way as the calibration standards. The 100 mg/l solutions were diluted to 10 mg/l immediately before analysis.

Samples of the various 100 mg/l and 10 mg/l solutions were stored in glass bottles at room temperature on the laboratory bench, in the dark, with the head space purged with nitrogen, in the fridge and in the freezer (defrosted at room temperature immediately prior to analysis). Some solutions were also stored in plastic bottles at room temperature on the laboratory bench.

After set times up to about three weeks, the solutions were analyzed for thiosulfate, trithionate and tetrathionate.

Results

Results are general and quantitative. Some instrumental problems were being experienced at the time of this work giving spurious results in cases. The overall trends are summarised in Table 3.1.

Table 3.1 : Summary of observations on stability of standard solutions of thiosulfate,
trithionate and/or tetrathionate

Initial solution concentration	Changes to thiosulfate	Changes to tetrathionate	Changes to trithionate
10 mg/l $S_2O_3^{2-}$	< 10 % degradation over 22 days. Slightly more stable in freezer.	Formed as $S_2O_3^{2-}$ degradation product.	None.
100 mg/l $S_2O_3^{2-}$	< 10 % degradation over 22 days. Similar to 10 mg/l solution.	Seen as $S_2O_3^{2-}$ degradation product	None.
10 mg/l $S_4O_6^{2-}$	Negligible.	< 10 % degradation over 18 days. Freezing enhanced degradation to ~20 % in 18 days.	Negligible except for that formed from $S_4O_6^{2-}$ degradation for frozen sample in 1:1 ratio.
100 mg/l $S_4O_6^{2-}$	Negligible.	< 10 % degradation over 18 days. Freezing more stable than for 10 mg/l solution - ~13 % degradation in 18 days.	Negligible except for that formed from $S_4O_6^{2-}$ degradation for frozen sample in 1:1 ratio.
10 mg/l $S_3O_6^{2-}$	Formed as degradation product corresponding to 1:1 ratio of $S_3O_6^{2-}$ degraded.	Small amount present. An exchange between $S_3O_6^{2-}$ and $S_4O_6^{2-}$ was noted for solutions of $S_3O_6^{2-}$ in water (see Section 3.6).	~ 40 % degradation in 14 days. Stabilised slightly in fridge to give ~20 % degradation in 14 days.
10 mg/l $S_2O_3^{2-}$ 10 mg/l $S_4O_6^{2-}$	Destabilised by presence of $S_4O_6^{2-}$. Typically 30 – 50 % degradation in 22 days. Freezing stabilised.	Increased according to $S_2O_3^{2-}$ degradation. Freezing caused rapid degradation of $S_4O_6^{2-}$ by ~ 60% in 8 days.	Formed from $S_4O_6^{2-}$ degradation in 1:1 ratio for frozen sample.
100 mg/l $S_2O_3^{2-}$ 100 mg/l $S_4O_6^{2-}$	Negligible degradation.	Negligible change except for freezing where ~50 % degraded in 8 days.	Formed from $S_4O_6^{2-}$ degradation in 1:1 ratio for frozen sample.
10 mg/l $S_2O_3^{2-}$ 10 mg/l $S_4O_6^{2-}$ 10 mg/l $S_3O_6^{2-}$	Degradation in similar range as other solutions. Stable on freezing.	Increases except for freezing where ~ 20 % degraded in 1 day.	Degrades at similar rate to $S_3O_6^{2-}$ alone. Increases on freezing from $S_4O_6^{2-}$ degradation in 1:1 ratio.
100 mg/l $S_2O_3^{2-}$ 100 mg/l $S_4O_6^{2-}$ 100 mg/l $S_3O_6^{2-}$	Stable.	Similar to 10 mg/l solution.	Slightly more stable than 10 mg/l solution. Increases on freezing from $S_4O_6^{2-}$ degradation in 1:1 ratio.

In general, the conditions under which the sulfur oxyanion solutions were stored did not significantly affect their stability, with the exception of refrigeration which stabilised trithionate, and freezing which significantly enhanced tetrathionate degradation. In general, the more concentrated solutions were more stable.

It was concluded that calibration standard solutions should be used immediately after preparation for the best accuracy.

3.2.3 Effect of Other Solution Components on Ion Chromatographic Analysis

A number of non-sulfur species expected to be present in the solutions in the kinetic tests were added to solutions of thiosulfate, trithionate and tetrathionate to determine the effect of these components on the ion chromatographic method. Usually it is recommended to use 'matrix matching' of standard solutions used for ion chromatography calibration, however, in this case many of the components tested were known to or suspected to react with the analyte species, so matrix matching could not be used.

Typical test solutions in the kinetic testwork (Chapter 4) were expected to contain 2-7 g/l trithionate, 0.1-0.4 g/l thiosulfate and negligible tetrathionate. Other solution components expected to be present (individually or in combination) were ammonia, ammonium, bicarbonate, carbonate, chloride and potassium (from potassium chloride added). For the purposes of testing the effects of these components on the analysis of the sulfur oxyanions, a solution of 100 mg/l each of thiosulfate, trithionate and tetrathionate was prepared. From this solution a set of solutions of 10 mg/l of each sulfur oxyanion was prepared, containing the components of interest at the concentrations shown in Table 3.2. The concentrations chosen represent typical levels of each component relative to levels expected in the test solutions (taking into account the dilution required for ion chromatography).

Each sample was analysed at least three times since it is recognised that there is some variability in the ion chromatographic method. The mean and standard deviation for each analyte is shown in Table 3.2. The largest difference in measured concentration compared with a standard solution with no extra components added was 2.7 % for

thiosulfate, 1.7 % for trithionate and 2.4 % for tetrathionate. The error expected in preparing the diluted samples was expected to be larger than this, hence it was concluded that the addition of ammonia, ammonium, bicarbonate, carbonate or potassium chloride to the levels indicated in Table 3.2 did not affect the analysis of thiosulfate, trithionate and tetrathionate. The effect of these species on the analysis of sulfate was not tested as sulfate was only measured occasionally and was not used directly in deriving the kinetic results shown in Chapter 5. The effect of copper on analysis was not tested as it is known that cupric copper reacts readily with thiosulfate and that cuprous copper is readily oxidized to cupric in the presence of oxygen.

Table 3.2 : Effect of added species on analysis of sulfur oxyanions

Species added	Concentration of added species (mM)	Mean measured value and standard deviation for nominal 10 mg/l of each of $S_2O_3^{2-}$, $S_3O_6^{2-}$ and $S_4O_6^{2-}$					
		$S_2O_3^{2-}$		$S_3O_6^{2-}$		$S_4O_6^{2-}$	
		mean	σ	mean	σ	mean	σ
None	-	10.0581	0.0169	10.2042	0.0111	10.1115	0.0151
NH ₃	1	10.2037	0.0292	10.3763	0.0670	10.4557	0.1214
NH ₄ ⁺ as (NH ₄) ₂ SO ₄	1	10.0196	0.0469	10.2162	0.0448	9.8734	0.0846
HCO ₃ ⁻ as NaHCO ₃	1.3	10.0502	0.0067	10.1683	0.0287	10.1256	0.0151
CO ₃ ²⁻ as Na ₂ CO ₃	0.9	10.3319	0.0432	10.3315	0.0193	10.2516	0.0929
KCl	1.9	10.0702	0.0224	10.1519	0.0169	10.0504	0.0154

3.3 ANALYSIS OF SULFAMATE

Sulfamate (NH₂SO₃⁻) is a potential species of interest in ammoniacal thiosulfate systems. Two methods were considered to analyse for sulfamate. A titration method used by Sherritt (Liebovitch, 2005) was found to be unsuitable as unreliable results were expected for sulfamate levels below 1 g/l (which is much higher than anticipated levels in the test solutions) and thiosulfate is known to interfere with the determination. It is

suspected that trithionate would also interfere, especially in the solutions of interest where it is expected to be present in excess compared with sulfamate. A chromatographic method using conductivity detection (under the same conditions as that for sulfate determination) was found to be suitable to determine sulfamate and sulfate simultaneously, but in the presence of ammonia the sulfamate peak was obscured. In addition, since the sulfamate concentration in the test solutions was expected to be very low (or even non-existent) the likelihood of being able to optimise the ion chromatographic method to determine sulfamate was considered low.

3.4 ANALYSIS OF TOTAL AMMONIA

A standard distillation method was used to analyse for total ammonia. Sodium hydroxide (1M) was transferred to a round-bottomed flask connected to a condensor with a spray tube. A suitable aliquot of ammonia-containing solution and anti-bumping granules were added to the flask. The flask was heated and the ammonia gas produced was collected in a hydrochloric acid solution (1M HCl). Distillation was continued until the volume in the round-bottomed flask was reduced by about half and no more gas bubbles were observed to be entering the acid solution. The excess acid was titrated against a standard sodium hydroxide solution to determine the total ammonia concentration. The ammonia concentration was determined by subtracting the known ammonium concentration of the original solution from the total ammonia content determined by distillation. Replicate tests involving dilution of a stock ammonia solution followed by analysis of the diluted solution for total ammonia concentration gave up to a 10 % range in results.

3.5 SYNTHESIS OF SODIUM TRITHIONATE

Sodium trithionate is not commercially available, so was synthesised according to a method described by Kelly and Wood (1994). The method involved oxidation of sodium thiosulfate using hydrogen peroxide at low temperature (near 0 °C). A number of batches were synthesized according to the following method, based on Equation 3.1.



Sodium thiosulfate pentahydrate (150 g) was dissolved in 90 ml de-ionised water in a glass beaker. The beaker was placed in a cooling reactor to reduce the temperature to about 1 °C. With continuous stirring, 140 ml 30 % (w/v) hydrogen peroxide was added dropwise (over a few hours), taking care that the temperature remained below 20 °C. Stirring was ceased and the beaker was left at about 0 °C for 1 to 2 hours, allowing for crystallization of sodium sulfate. The sodium sulfate was removed by filtration through a Whatman No. 1 filter paper. The sulfate was washed on the filter with 100 ml ethanol which was allowed to mix with the filtrate. The filtrate was transferred to a beaker at about 3 °C, 250 ml ice-cold ethanol was added and the solution left at 0 – 3 °C for one hour. The resulting precipitate (mostly sulfate) was again removed by filtration, and washed on the filter with 200 ml ice-cold ethanol, which was allowed to mix with the filtrate. The filtrate was transferred to a beaker containing 1 l ice-cold ethanol, and 100 ml ethanol was used to rinse the filtrate from the flask into the beaker. The mixture was stirred thoroughly and left at 0 – 3 °C for 1 - 2 hours. Sodium trithionate formed and was separated by filtration and washed with 50 ml ethanol, 50 ml acetone and dried in a desiccator.

A white crystalline material was produced and stored in a glass bottle in a refrigerator. Storing of such solids at low temperature has been recommended (Miura, 2003).

3.6 CHARACTERISATION OF SODIUM TRITHIONATE

3.6.1 Total Sulfur

The total sulfur content was determined by completely oxidising all the sulfur species to sulfate and analysing sulfate. Complete oxidation of trithionate to sulfate by boiling in peroxide was considered questionable (Tan and Rolia, 1985) and instead Fenton's reagent was used to facilitate oxidation (Druschel, 2003). Fenton's reagent allows for hydroxy radicals to be produced in situ from the reaction of hydrogen peroxide on ferrous ions. Ferrous chloride (1.35 g $\text{FeCl}_2 \cdot x\text{H}_2\text{O}$) was dissolved in hydrochloric acid (50 ml 0.1 M HCl). Any undissolved iron was removed using a syringe filter. A known mass of the sodium trithionate (about 0.2 g) was added to the ferrous solution and hydrogen peroxide (10 ml 30 % (w/v)) was added. The reaction was left to go to completion and

the solution was diluted to 100ml. The diluted solution was then diluted further as appropriate and analysed for sulfate by ion chromatography.

3.6.2 Total Sodium Content

A known mass of sodium trithionate was heated to about 790 °C in a furnace until no more fumes were emitted, and then left at that temperature for another hour. The trithionate was converted to sodium sulfate (Rolia and Chakrabarti, 1982) according to Equation 3.2, and the sodium content determined by the mass change. A correction was made for the quantity of any volatiles and any sodium sulfate present as an impurity in the trithionate.



3.6.3 Volatiles

Thermogravimetric analysis (TGA) was done on two trithionate batches. The sample was heated at 10 °C per minute in an alumina crucible in helium atmosphere to 800 °C. The results are shown graphically for two batches of trithionate in Figures 3.1 and 3.2. The mass drop below 100 °C was likely due to a loss of ethanol adsorbed to the solid. (Ethanol was used extensively in the synthesis.) The mass change at around 250 °C could be due to decomposition of the trithionate.

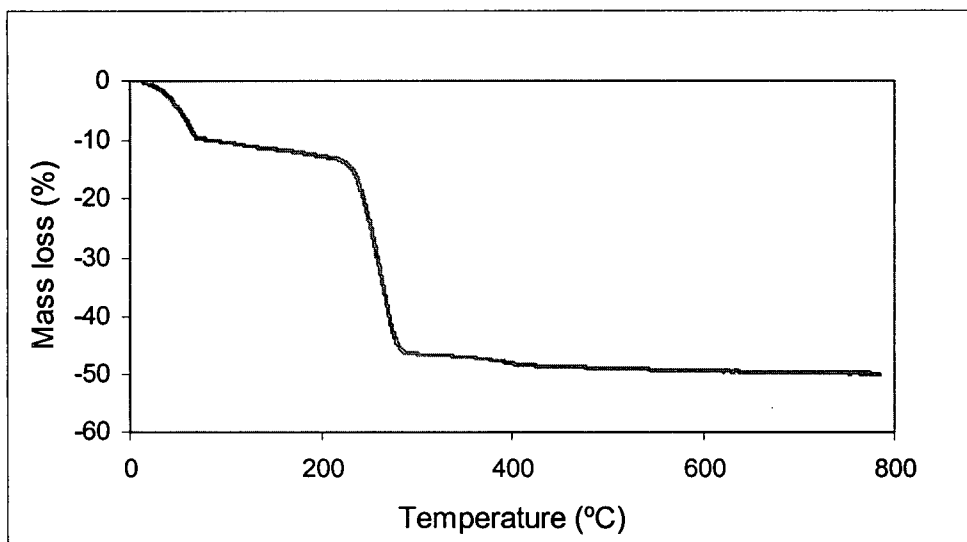


Figure 3.1 : TGA/DTA for sodium trithionate batch 2

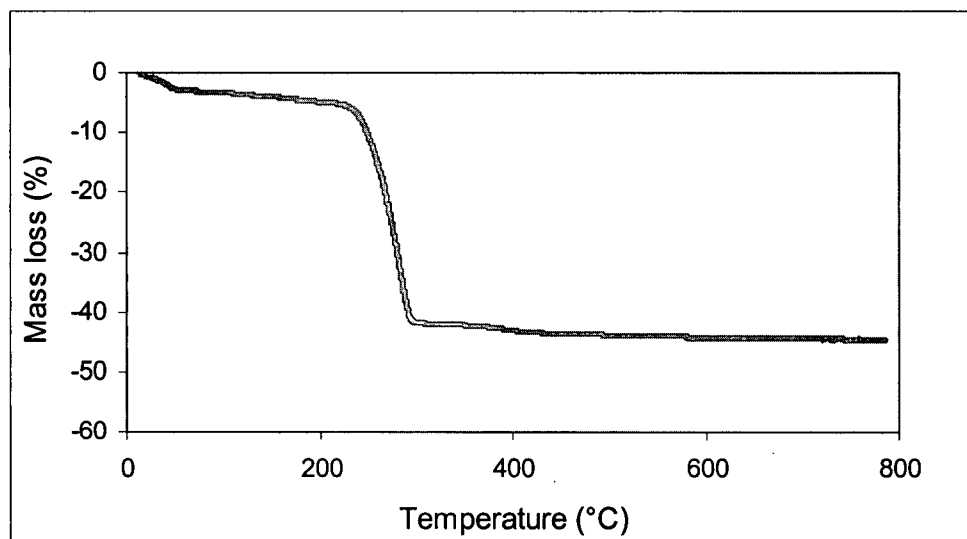


Figure 3.2 : TGA/DTA for sodium trithionate batch 3

3.6.4 Sulfate

A solution of the trithionate was analysed for sulfate by ion chromatography.

3.6.5 Polythionates

A solution of the trithionate was analysed for polythionates by ion chromatography. The solutions were analysed immediately after dilution and were analysed a number of times in succession. The concentration profile with time is shown in Figure 3.3 for solutions prepared using deaerated water and in water without deaeration. Although the measured trithionate concentration was in question here, the values on the graph are still indicated as mg/l trithionate, based on analysis against a mixed trithionate, tetrathionate and thiosulfate standard made using a different batch of trithionate. The actual trithionate concentrations are indicative only. While no thiosulfate was found to be present, the initial analysis at time zero showed a significant concentration of tetrathionate (up to 3 mg/l for an estimated 10 mg/l trithionate concentration). Repeat analyses of the same solution showed a continually dropping tetrathionate concentration and a corresponding increase in the trithionate concentration.

The cause of this phenomenon is not clear. However, it was found that analysing trithionate in alkaline solution (containing 2 mM ammonia for 10 mg/l $S_3O_6^{2-}$, see Figure 3.4) or where thiosulfate and tetrathionate were present (Figure 3.5), this phenomenon did not occur. It is possible that dilute solutions of trithionate in such an unbuffered system (water) were more subject to variations in speciation.

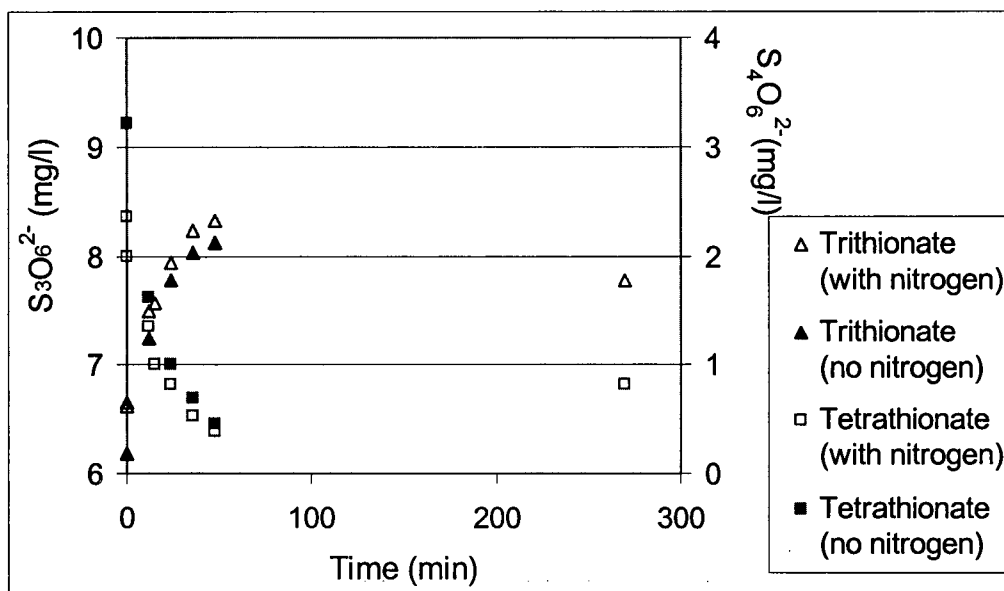


Figure 3.3 : Change of measured trithionate (indicative values only) and tetrathionate concentrations with time with and without using deaerated water in solution preparation

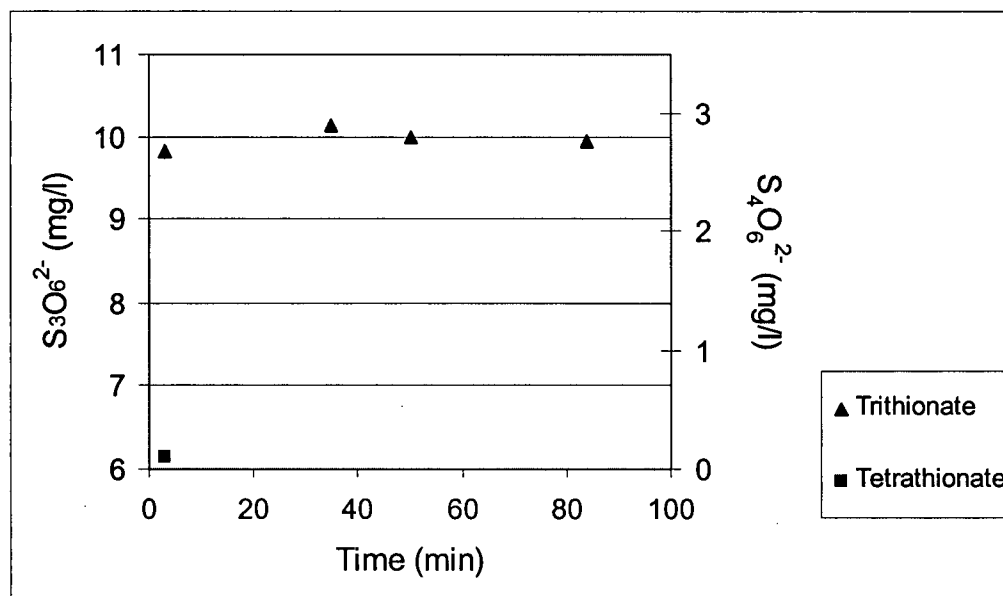


Figure 3.4 : Change of measured trithionate (indicative values only) and tetrathionate concentrations with time in the presence of 2mM NH_4OH

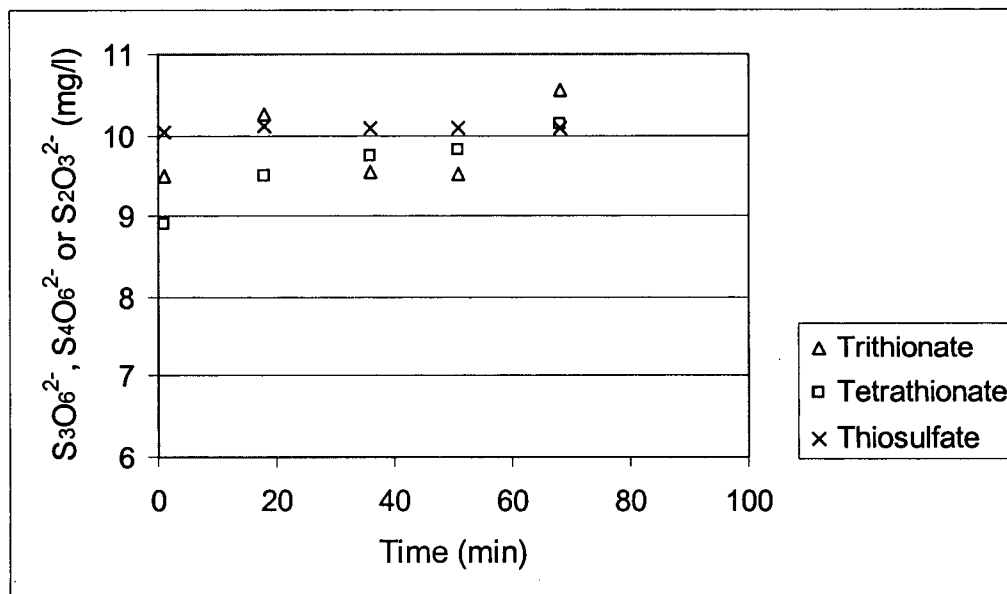


Figure 3.5 : Change of measured trithionate (indicative values only), tetrathionate and thiosulfate concentrations with time in the presence of 10 mg/l $S_2O_3^{2-}$ and 10 mg/l $S_4O_6^{2-}$

3.6.6 Overall Trithionate Purity

Table 3.3 gives comparative data for all the trithionate batches. The purity was calculated as follows: % purity = (total S (%) – sulfate S (%)) x 100 / 40.3

Table 3.3 : Sodium trithionate characterisation

Batch	SO_4^{2-} (%)	Na (%)	S_{TOT} (%)	Volatiles (%)	Purity (based on total S and SO_4^{2-}) (%)
Theoretical	0	19.3	40.3		100
Batch 0	1.34		40.1		98.4
Batch 1	1.69	16.8	36.1		87.2
Batch 2	0.67		36.0	10	88.8
Batch 2a	4.27		39.1		93.4
Batch 3	1.13		40.0	3	98.3
Batch 4					96.0*

* Standardised against Batch 2

3.7 TRACE IMPURITY ANALYSIS OF CHEMICALS USED

Solutions of the main chemicals used in this testwork, namely sodium trithionate (Batch 4), sodium thiosulfate, ammonia and ammonium bicarbonate, were analysed by inductively coupled plasma spectrophotometry to scan for the presence of trace element impurities. The data is shown in Appendix 4.

4 KINETICS OF TRITHIONATE DEGRADATION - METHODOLOGY

4.1 INTRODUCTION

Two standard methods are used to determine reaction kinetics – the integrated rate method and the initial rate method (Brezonik, 1994). Both methods were used in this work to determine the kinetics of trithionate degradation. In this chapter, the basic theory behind each method is summarized, and the experimental methods used to collect the necessary data are described. Example data and the interpretation thereof are given for each method.

4.2 REACTION KINETICS THEORY

For a generic irreversible reaction (Equation 4.1), the rate equation is typically given by Equation 4.2.



$$\text{Rate} = k[A]^a[B]^b \quad [4.2]$$

Elementary reaction kinetics allows for the determination of the reaction orders with respect to the various reactants (a and b in Equation 4.2) and the rate constant (k). In the case of trithionate degradation, Equation 4.2 can be expressed as Equation 4.3.

$$-d[S_3O_6^{2-}]/dt = k_{\text{obs}}[S_3O_6^{2-}]^a \quad [4.3]$$

where k_{obs} is the observed rate constant and is expected to be dependent on various reaction conditions and other reactant concentrations.

The initial rate method involves measuring the rate of a reaction over short times, before any significant changes in concentration of the reactants occur. It is assumed that the reaction rate is constant over the initial time period, i.e. the concentration versus time profile for the reactant (trithionate) is linear.

The reaction order is determined by comparing the initial rates measured at different initial trithionate concentrations. From Equation 4.3, if only the concentration of

trithionate is changing, the reaction order with respect to trithionate can be expressed by Equation 4.4.

$$\text{Reaction order} = \ln(r_1/r_2)/\ln([S_3O_6^{2-}]_1/[S_3O_6^{2-}]_2) \quad [4.4]$$

where r_1 is the initial rate at initial concentration $[S_3O_6^{2-}]_1$ and r_2 is the initial rate at initial concentration $[S_3O_6^{2-}]_2$. A plot of $\ln(r)$ versus $\ln[S_3O_6^{2-}]$ gives the reaction order as the slope.

The rate constant can be determined by plotting the measured initial rate against the initial concentration of trithionate (raised to the power of the reaction order). The gradient of such a plot gives the observed rate constant, according to Equation 4.3.

The integrated rate method involves data collection over longer times. As such, the concentration of reactants and products changes significantly over the duration of the measurements. To account for the continually changing concentrations, an integrated form of Equation 4.3 is used. For a reaction rate first order with respect to the trithionate concentration, the equivalent integrated rate equation is shown in Equation 4.5.

$$\ln [S_3O_6^{2-}]_t = -k_{\text{obs}}t + \ln [S_3O_6^{2-}]_0 \quad [4.5]$$

Thus for a first order dependency, a plot of $\ln [S_3O_6^{2-}]_t$ versus time gives a straight line with the observed rate constant as the slope and $\ln [S_3O_6^{2-}]_0$ (the initial trithionate concentration) as the intercept. Such a plot can be used as a diagnostic tool in determining the reaction order.

The theory for second and higher order reactions is not discussed here, but is readily available in the literature (Brezonik, 1994).

4.3 EXPERIMENTAL METHOD

Sodium trithionate was synthesized according to the method in Chapter 3 for use in these tests. The aim of the experimental programme was to establish the factors influencing trithionate degradation kinetics. The kinetics were examined in simple aqueous solutions with various components present. Most tests were done in a buffer of

ammonium bicarbonate / ammonia, since the buffer pH of this system was maintained between pH 9.3 and 10.3, which is the pH range of interest. An ammonium sulfate / ammonia buffer was also considered, but in that system small concentrations of sulfate produced during the degradation of trithionate could not be accurately measured. The test solutions were made up to the required concentrations using deionised water.

Integrated Rate Method

The ammonium bicarbonate or ammonium sulfate solution was made up (as above) and aqueous ammonia was added to adjust the pH. The amount of ammonia added was not measured. Most tests were done at room temperature unless otherwise stated. In tests where the temperature was controlled, the solutions were brought to the required temperature in a water bath.

For each test, the required mass of sodium trithionate was diluted using the buffer to give a nominal concentration of 8.5 g/l or 4.5 g/l trithionate, and in some cases sodium thiosulfate and/or sodium tetrathionate were added to give 10 g/l thiosulfate and 2 g/l or 10 g/l tetrathionate. These concentrations were selected based on concentrations typically found in gold leach liquors (see Chapter 2). The solutions were transferred to glass vessels and stoppered with rubber stoppers. The ionic strength was not adjusted.

At set times, samples were withdrawn by pipette and diluted for analysis for thiosulfate, trithionate and tetrathionate concentration by ion chromatography. The solutions were also analysed for sulfate level at the termination of the test.

The tests were typically run for 36 to 54 days.

Initial Rate Method

Three or four aliquots (50 ml) of each test solution containing all solution components except sodium trithionate were placed in sealed flasks in a water bath for at least 45 minutes to reach the required temperature. Tests were done at 40 °C unless otherwise stated. Solid sodium trithionate was added to each of three conical flasks and at time zero, one aliquot of test solution was added to each flask and mixed. The amount of

sodium trithionate added was to give nominal concentrations of 2 g/l, 5 g/l and 7 g/l trithionate, based on expected values in gold leach solutions (see Chapter 2). In some cases a 'blank' test was done where trithionate was excluded to determine the pH change in the absence of trithionate. The flasks were sealed with rubber septums and kept at constant temperature in a water bath.

Samples were removed at set times either by removing the rubber septum or by using a syringe to sample through the septum if a significant amount of ammonia was present or if the system was under nitrogen atmosphere. Samples were immediately diluted as appropriate and analysed for trithionate and thiosulfate (and occasionally sulfate) concentration using the ion chromatography methods discussed earlier. Total ammonia was analysed according to the method in Chapter 3. The tests were typically run for 3 to 4 hours.

4.4 DATA ANALYSIS

Integrated Rate Method

The data evaluation for a typical data set obtained using the integrated rate method is explained in this section by example, for a test where 9 g/l $\text{S}_3\text{O}_6^{2-}$ and 10 g/l $\text{S}_2\text{O}_3^{2-}$ were initially present. The data from all tests were treated in a similar way and the findings are summarized in Chapter 5.

The trithionate and thiosulfate concentrations as well as the logarithm of the trithionate concentration are plotted in Figure 4.1. There was a good straight line fit to the $\ln[\text{S}_3\text{O}_6^{2-}]$ versus time data points. Elementary reaction kinetics shows that a relation of this type corresponds to pseudo first order kinetics, shown in Equation 4.5, where k_{obs} is the observed rate constant (Brezonik, 1994). The expected relationships for other reaction orders did not fit the experimental data, so it was deduced that the degradation of trithionate follows first order kinetics. The rate constant was determined by using the best fit curve of this type.

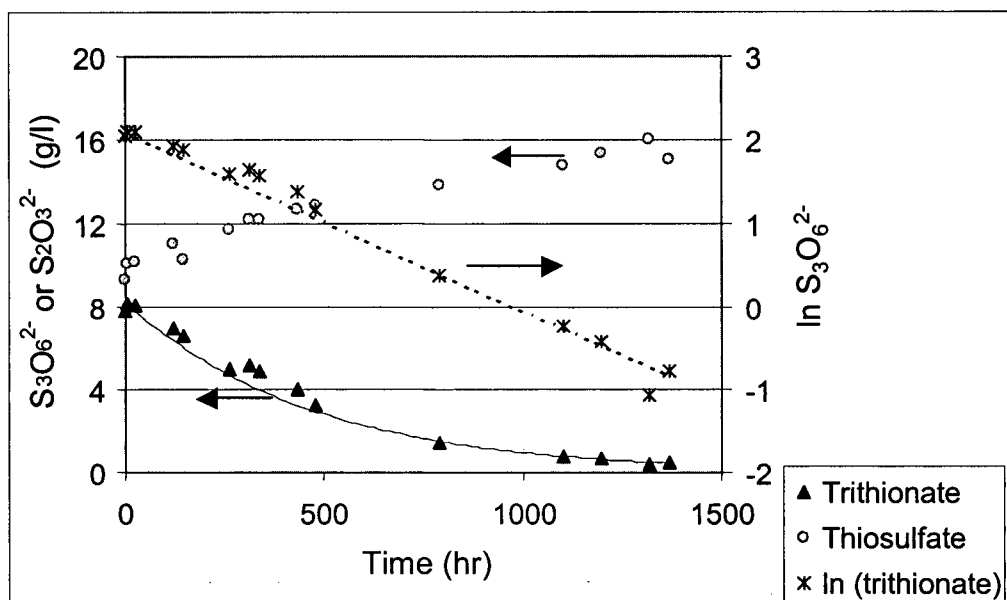


Figure 4.1 : Concentrations of trithionate and thiosulfate with time for an integrated rate method test

(Room temperature, $\text{NH}_4\text{HCO}_3 = 0.03 \text{ M}$, NH_3 added to adjust initial pH to ~ 9.7)

Plotting $[\text{S}_2\text{O}_3^{2-}]$ or $[\text{SO}_4^{2-}]$ against the decrease in trithionate concentration gave the stoichiometric co-efficients of thiosulfate and sulfate in the reaction equation as the gradients. The data was plotted in this manner in Figure 4.2, using experimentally observed concentrations for thiosulfate and sulfate, and using the best-fit exponential equation (from Figure 4.1) to determine the trithionate concentrations.

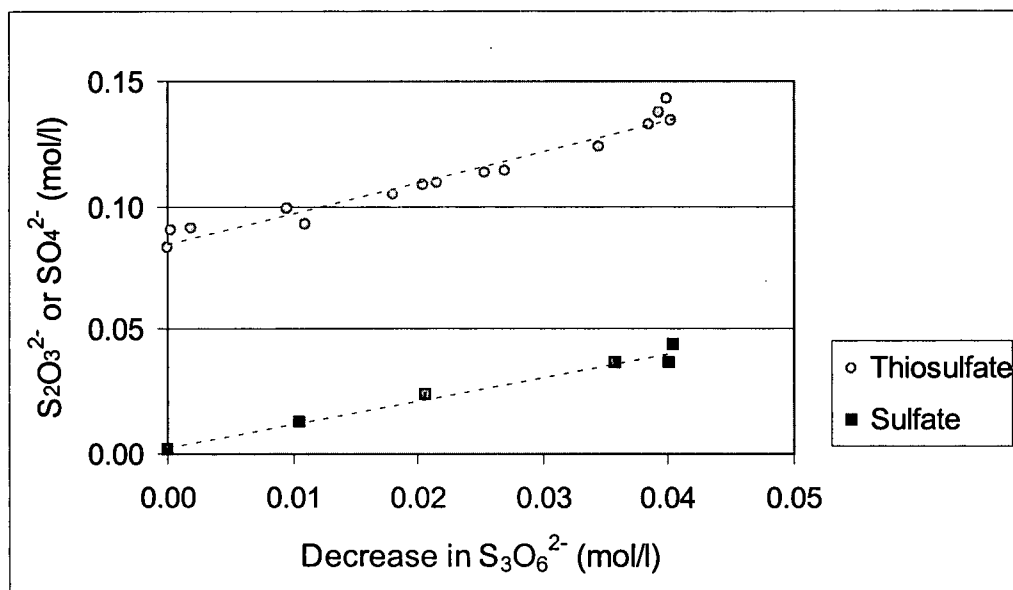


Figure 4.2 : Determination of reaction stoichiometry using the integrated rate method
 (Room temperature, $NH_4HCO_3 = 0.03$ M, NH_3 added to adjust initial pH to ~ 9.7)

Data from the other tests were treated in a similar way. Where tetrathionate was initially added (to simulate a possible recycle solution), the tetrathionate was found to degrade very quickly under the alkaline conditions, causing an initial increase in trithionate and thiosulfate concentrations. In these cases, the best fit of the exponential equation for trithionate degradation excluded the initial data where tetrathionate was still present, and the extrapolated trithionate concentration at time zero was derived from the trithionate concentration at the time when the initial tetrathionate had disappeared.

Initial Rate Method

Typical profiles of trithionate concentration and thiosulfate concentration with time are shown in Figure 4.3 for the initial rate method. A linear decrease in trithionate concentration and a corresponding linear increase in thiosulfate concentration were found, as expected for this method. Over the duration of the test, typically less than 10 % of the trithionate had reacted.

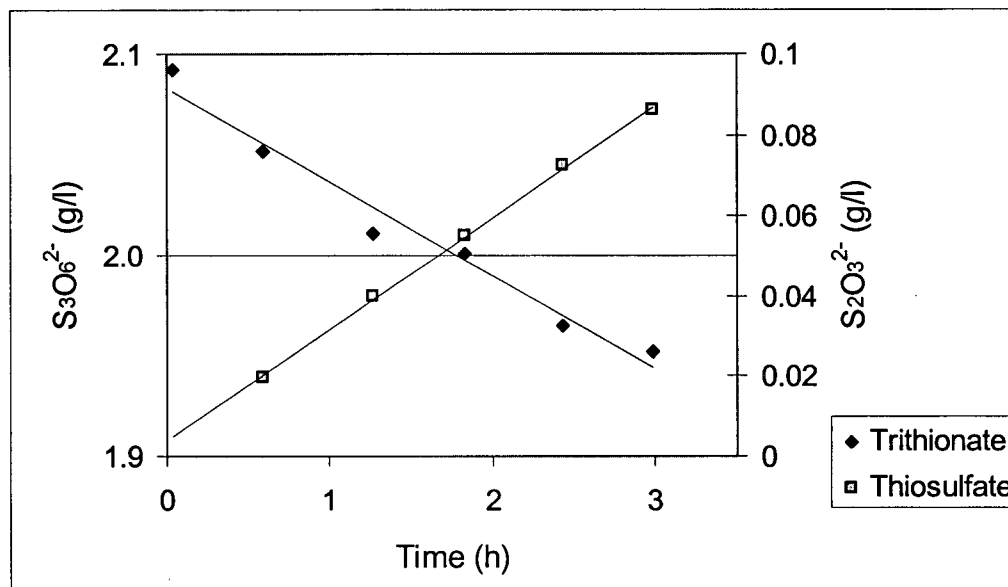


Figure 4.3 : Typical concentration profile for trithionate and thiosulfate using the initial rate method

(40 °C, pH 9.9, 0.05 M NH_4HCO_3 , 0.687 M NH_3 , total ionic strength 1 M)

The reaction order was determined graphically using the relation in Equation 4.4. An example showing this dependency is given in Figure 4.4, where the average slope was 1. The rate equation for the degradation of trithionate can thus be expressed as in Equation 4.6, where the observed rate constant, k_{obs} , is expected to be a function of the concentrations of other solution components affecting the trithionate degradation rate.

$$-d[S_3O_6^{2-}]/dt = k_{obs} [S_3O_6^{2-}] \quad [4.6]$$

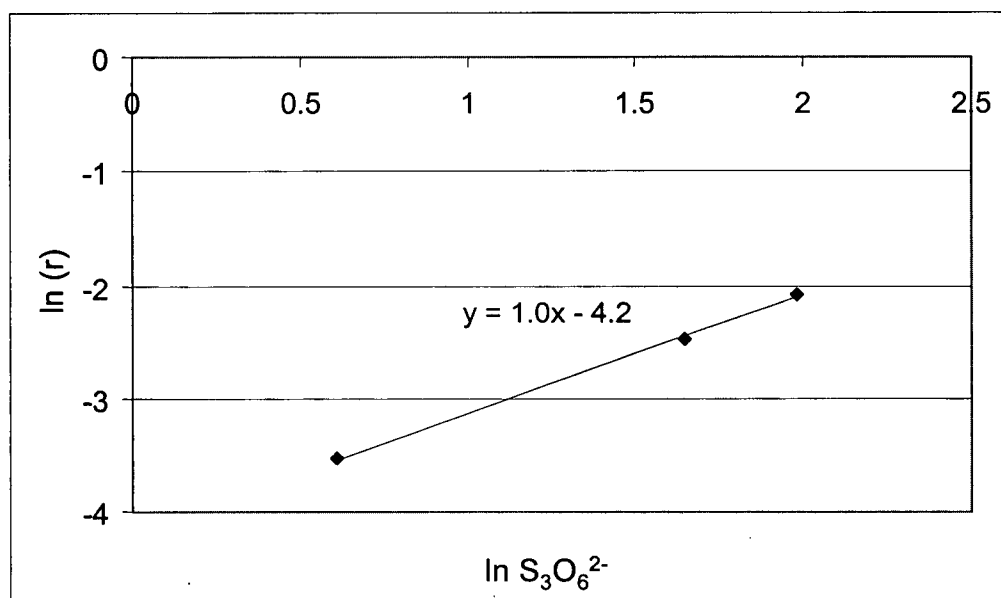


Figure 4.4 : Determination of the reaction order for the rate of trithionate degradation with respect to trithionate

(40 °C, $NH_4HCO_3 = 0.2$ M, initial pH 9.2)

The concentration of trithionate versus time was plotted and using a trendline, the best line fit through the data was determined, giving the initial reaction rate as the slope and the initial trithionate concentration as the intercept. A standard statistical method (Miller and Miller, 1988) to determine the standard deviation in the slope and intercept of a regression line was used to determine the standard deviations of the initial rate and initial trithionate concentration. The initial rate was plotted against the initial trithionate concentration for each test series, usually comprised of three data sets, to determine the average observed rate constant, according to Equation 4.6. To account for experimental variability, the estimated maximum rate (initial rate plus the standard deviation) was plotted against the minimum initial concentration (initial concentration minus the standard deviation), and the minimum rate against the maximum concentration. Regression lines were generated for all three plots, and forced through the origin. The slope of the regression lines represented the average, maximum and minimum observed rate constants. A typical plot to determine the rate constant k is shown in Figure 4.5. In all subsequent figures showing the observed rate constant, the error bars indicate the estimated minimum and maximum rate constants determined in this way.

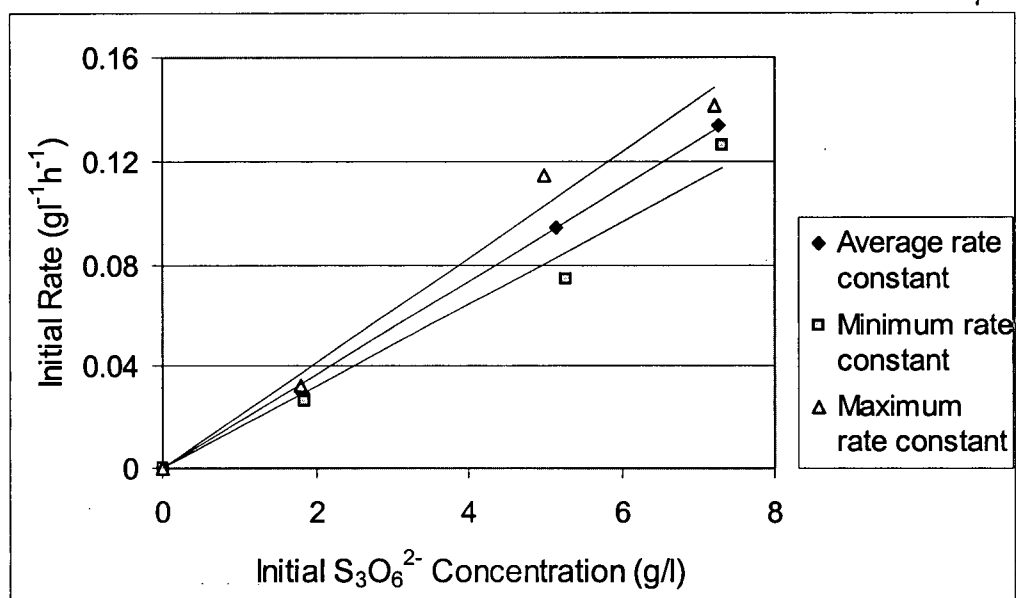


Figure 4.5 : Typical plot of trithionate degradation rate versus initial trithionate concentration to determine the rate constant k_{obs} from the slope
(40 °C, pH 9.9, 0.05 M NH₄HCO₃, 0.687 M NH₃, total ionic strength 1 M)

The reaction stoichiometry was determined in the same way as for the integrated rate method.

5. KINETICS OF TRITHIONATE DEGRADATION – RESULTS

5.1 INTRODUCTION

Both the integrated rate method and the initial rate method were used to investigate the kinetics of trithionate degradation. The experimental methods and the ways in which the data were interpreted using these methods were discussed in Chapter 4. The initial rate method is expected to give more reliable data than the integrated rate method, as by the nature of this method, the reaction conditions are held more constant and the reactions of products are expected to be minimized. However, the integrated rate method is useful to give an indication of the factors expected to be of significance in the trithionate degradation reactions, and also to serve as confirmation of effects noted using the initial rate method. In this chapter, the trithionate degradation kinetics using both methods are discussed together. Most of the results were obtained using the initial rate method and the quantitative conclusions were based primarily on this data. Results from the integrated rate method are indicative and confirmatory.

The aim of this work was to establish the factors influencing trithionate degradation, starting with simply trithionate in aqueous solution and examining solution components systematically to identify individual effects. The effects were manifested in changes to the observed rate constant, k_{obs} , in Equation 5.1.

$$-d[\text{S}_3\text{O}_6^{2-}]/dt = k_{\text{obs}} [\text{S}_3\text{O}_6^{2-}] \quad [5.1]$$

5.2 STOICHIOMETRY

In much of the research reported in the literature, the rate of reaction of various sulfur oxyanions has been deduced based on analysis of thiosulfate and an assumed reaction stoichiometry, rather than direct measurement of the assumed reaction products. In this work, both thiosulfate and trithionate were measured at the same time. One would expect, based on Equation 5.2 (based on prior work, see Chapter 2), that the rate of trithionate degradation would be equal to the rate of thiosulfate production.



For both the initial rate method and the integrated rate method, the ratio of thiosulfate formed to trithionate degraded was measured at 40 °C and at room temperature. In general, a ratio of 1:1, corresponding to Equation 5.2 was found. The limited data for sulfate also gave close to a 1:1 stoichiometric relationship with trithionate, which is also consistent with the reaction in Equation 5.2. Specific cases where a different stoichiometry from Equation 5.2 was observed are discussed separately.

There were anomalies noted in some initial rate tests. In these tests, the trithionate and thiosulfate concentrations were measured, but in most cases, not the sulfate concentration, as a different ion chromatographic method was needed, since sulfate could not be determined simultaneously.

In general it was found that the thiosulfate formation rate was linear except for the initial sampling point. It is possible that slight impurities in the trithionate solution or the necessary re-equilibration of the ion chromatography column when the first sample of the series was injected may have had some influence here. It is relevant to note that especially at the start of the reaction, the concentration of thiosulfate was negligible compared with trithionate, but it was necessary to analyse for both species at the same time using the same dilution factor for analysis. This is not ideal for accurate analysis of the low concentration of thiosulfate. Excluding this initial point, the thiosulfate formation stoichiometry was as expected.

The sulfate formation stoichiometry was also as expected for the limited data available. In addition, the sulfur balances for the measured species of trithionate, thiosulfate and sulfate were typically between 95% and 105%, implying that these species were the only sulfur species present in significant quantities and no other products (e.g. pentathionate) needed consideration.

It has been suggested (Naito et al., 1975) but not proven that sulfamate could form in the presence of ammonia under similar conditions to those tested in this work. If sulfamate was present as a reaction product from trithionate degradation, its concentration would be expected to be trace under the conditions tested here, and it could not be determined in the sample matrix.

5.3 REPRODUCIBILITY

Integrated Rate Method

The concentration profiles for two very similar tests are shown in Figure 5.1. While the test conditions were nominally the same, there was a small difference in the initial trithionate concentration and the tests were done at room temperature at different times, so there were likely also temperature variations. Within these constraints, the results were reproducible – the observed rate constants for the tests were 0.0016 h^{-1} and 0.0017 h^{-1} .

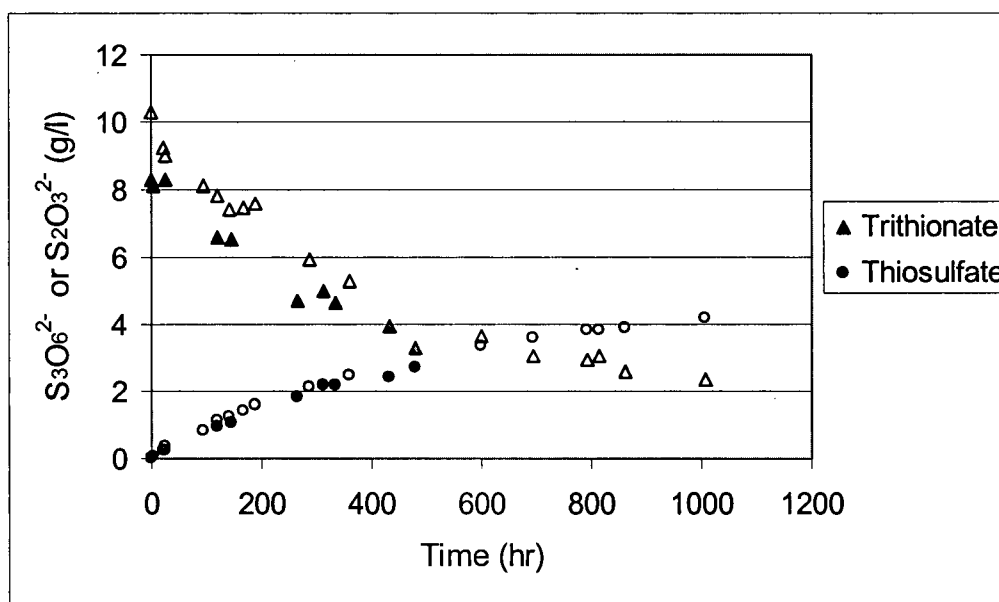


Figure 5.1 : Concentration profiles for trithionate and thiosulfate (room temperature, $\text{NH}_4\text{HCO}_3/\text{NH}_3$ buffer, $[\text{NH}_4^+] = 0.03 \text{ M}$, initial pH 9.7, open symbols represent one test, closed symbols represent a repeated test)

Initial Rate Method

Since two different buffer systems were used predominantly in this work (the ammonia – ammonium bicarbonate system, and the sodium bicarbonate – sodium carbonate system) the reproducibility of the initial rate method was tested for each buffer system at

40 °C. The observed rate constants (and their potential error ranges) are shown in Table 5.1.

For both buffer systems, the potential range in the rate constant measured for each test was significant. This is to be expected since determination of the rate involved measuring small changes of concentration over time, and each rate constant was determined from only four independent data points, as discussed in the methodology section. For this reason, the data is always shown including the potential minimum and maximum values, shown as horizontal bars in all graphs. However, the agreement between tests for each buffer system was well within the error range for observed for each rate constant. Taking into account the appropriate ranges, the initial rate method provided reproducible results for the observed rate constants.

Table 5.1 : Reproducibility in rate constant determination for trithionate degradation for two buffer systems using the initial rate method

Buffer system	Total ionic strength (M)	Buffer contribution to ionic strength (M)	pH	Replicate no.	[NH ₃] (M)	k _{obs} (h ⁻¹)	k _{obs} max (h ⁻¹)	k _{obs} min (h ⁻¹)
Na ₂ CO ₃ / NaHCO ₃	0.5	0.15	8.5	1	0	0.0103	0.0125	0.0084
				2	0	0.0110	0.0129	0.0093
NH ₄ HCO ₃ / NH ₃	1	0.032	10.2	1	0.84	0.0168	0.0181	0.0155
				2	0.89	0.0159	0.0174	0.0144

5.4 WATER

The degradation of trithionate in water was investigated at 40 °C using the initial rate method only. Either sodium perchlorate or potassium chloride was used to adjust the ionic strength (I). Results are shown in Table 5.2. The maximum and minimum rate constants are not shown in this case. Because the reaction rate was very slow and few data points were taken, the calculated deviation of the initial trithionate concentration

was often unrealistically large. However, the observed rate constants were consistent for the four tests carried out.

Table 5.2 : Values for the observed rate constant k_{obs} for trithionate degradation in water using the initial rate method (40 °C)

I adjusted with:	I (M)	k_{obs} (h^{-1})
KCl	0.1	0.010
	1.0	0.012
NaClO ₄	0.1	0.012
	1.0	0.013

The use of KCl or NaClO₄ from 0.1 M to 1.0 M did not have a significant effect. The observed rate constants in water were very similar to those extrapolated from work by Naito et al (1975). Using their rate constant at 40 °C and assuming a water concentration of 55.5 M, a value for k_{obs} of 0.012 h^{-1} was obtained, very close to the values measured here. While it has been proposed that the concentration of water has an influence on the rate (Naito et al., 1975), this was not tested in this work. It was proposed by Naito et al. (1975) that water was expected to attack the sulfonate sulfur atom of trithionate directly. This was discussed in the literature review in Chapter 2.

It is important to note that the natural pH of trithionate in water was around 4.5 (at 40 °C), and decreased with time to around pH 2 after 24 hours at 40 °C. The reactions occurring at these low pH values are not necessarily the same as those at the higher pH values relevant to gold leaching. The overall stoichiometry of thiosulfate formed to trithionate reacted was typically 0.5-0.6 : 1. At neutral and higher pH the stoichiometry is expected to be 1:1 according to Equation 5.2 (Kurtenacker, 1935) but at the low pH values observed here, it is likely that some of the thiosulfate formed was further degraded to elemental sulfur, which was observed in the solutions.

This data shows that trithionate will undergo a slow degradation in aqueous solutions. This inherent instability is common to the polythionates. In summary, the trithionate degradation rate in water at 40 °C can be expressed by Equation 5.3.

$$-d[S_3O_6^{2-}]/dt = 0.012h^{-1} [S_3O_6^{2-}] = k_0 [S_3O_6^{2-}] \quad [5.3]$$

5.5 HYDROXIDE

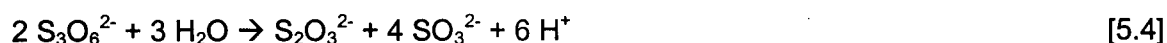
Trithionate degradation in sodium hydroxide solution was investigated using the initial rate method. All tests were done at 40 °C and a total ionic strength of 1 M, adjusted using sodium perchlorate. The results are shown in Table 5.3.

Table 5.3 : Effect of hydroxide concentration on the observed rate constant k_{obs} for trithionate degradation using the initial rate method (40 °C)

[NaOH] (M)	Average initial pH	Ratio $S_2O_3^{2-}$ formed : $S_3O_6^{2-}$ degraded (M:M)	k_{obs} (h^{-1})	k_{obs} min (h^{-1})	k_{obs} max (h^{-1})
0.5	12.62	0.2-0.4	0.729	*	*
0.1	11.96	0.3-0.4	0.143	0.132	0.156
0.01	11.06	0.7-0.8	0.0205	0.0184	0.0224
0.006	10.88	0.8-0.9	0.0146	0.0133	0.0159
0.001	9.76	0.8-0.9	0.0123	0.0098	0.0149

*For the test at 0.5 M NaOH, the reaction rate was very high, so the initial rate method could not be used to determine the observed rate constant. Instead, an exponential fit consistent with first order kinetics was used to derive the rate constant (i.e. the integrated rate method). The error margin was not determined, hence no minimum or maximum value for the rate constant is reported.

At higher hydroxide concentrations (≥ 0.1 M) and corresponding higher pHs (~12 and higher), the degradation of trithionate was very fast. Also the ratio of thiosulfate formed to trithionate reacted corresponds (within error) to literature observations of the reaction of trithionate at high pH according to Equation 5.4 (Kurtenacker, 1935) for reaction at 50 °C and pH 13.4 – 13.7.



In the context of gold leaching, slightly lower pHs are of more interest. The expected trithionate degradation for pH ~6 to ~11 can be expressed by Equation 5.2 and the measured reaction stoichiometry under these conditions supports this. The sulfate concentration was not measured. It should be noted that the tests using 0.001 M NaOH had a significant pH drop of 3 to 6 pH units over the duration of the test. However this did not appear to affect the reaction stoichiometry.

The data for pH values of around 11 and less corresponding to Equation 5.2 were interpreted in the following way. It was shown previously in Section 5.4 that trithionate hydrolyses in water at a rate corresponding to Equation 5.5 at 40 °C.

$$-d[\text{S}_3\text{O}_6^{2-}]/dt = 0.012 \text{ h}^{-1}[\text{S}_3\text{O}_6^{2-}] = k_0 [\text{S}_3\text{O}_6^{2-}] \quad [5.5]$$

It is proposed that the overall observed rate constant in the presence of hydroxide consists of a component for the degradation in water plus a component for degradation influenced by the presence of excess hydroxide. The graph in Figure 5.2 shows a plot of the observed rate constant versus the hydroxide concentration for tests with a hydroxide concentration of $\leq 0.01\text{M}$, including tests in water only. Based on this graph, the observed rate constant can be expressed as Equation 5.6 at 40 °C. The intercept is in agreement with the expected rate constant in water.

$$-d[\text{S}_3\text{O}_6^{2-}]/dt = (0.012\text{h}^{-1} + 0.74\text{M}^{-1}\text{h}^{-1}[\text{OH}^-])[\text{S}_3\text{O}_6^{2-}] = (k_0 + k_1[\text{OH}^-]) [\text{S}_3\text{O}_6^{2-}] \quad [5.6]$$

It is noted from Table 5.3 that the observed stoichiometry of thiosulfate formed to trithionate reacted was slightly lower than one would expect, based on either Equation 5.4 or Equation 5.2. It is possible that part of the thiosulfate formed goes on to react itself. Also it should be noted that the concentration of the thiosulfate in the solutions is very much lower than that of the trithionate, and it is possible for significant analytical errors to occur in this range.

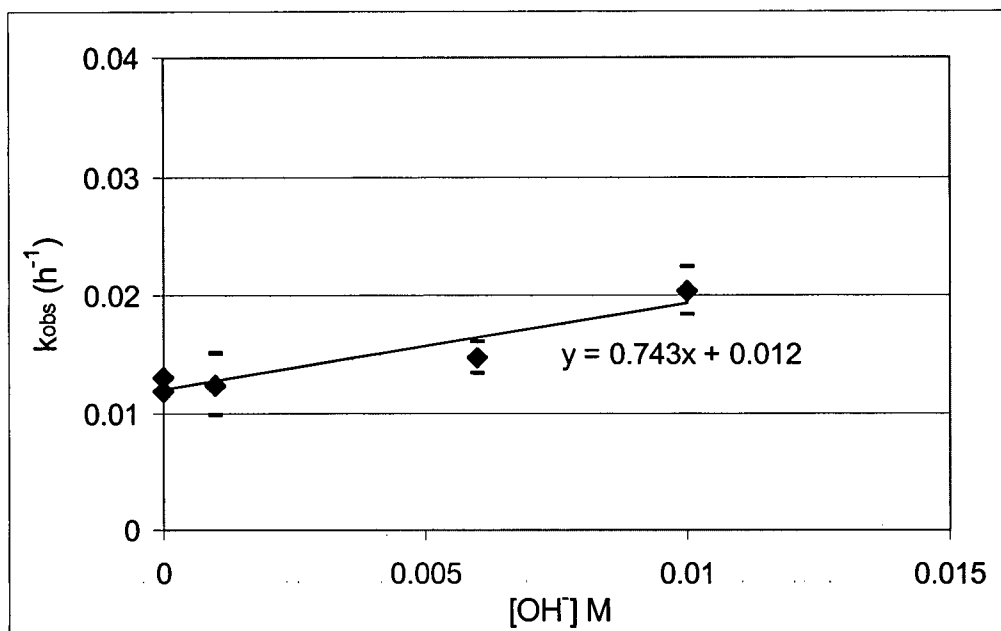


Figure 5.2 : Observed rate constant for trithionate degradation k_{obs} versus $[OH^-]$ for $pH < 11$

In the literature, Rolia and Chakrabarti (1982) claimed that for trithionate degradation between pH 10 and 11 at 70 to 85 °C, the hydroxide concentration did not affect the trithionate degradation rate. However, no results were given to support this assertion, and the conditions used were quite different from those used in this work and of relevance to gold leaching. It has been suggested (Ritter and Krueger, 1970) that hydroxide would attack trithionate directly at the sulfonate sulfur atom as it is a hard base. This was discussed in the literature review in Chapter 2.

5.6 IONIC STRENGTH

It is well known that in aqueous reactions, the ionic strength (I) of the solution can affect the reaction rate (Brezonik, 1994), so it was considered important to investigate the ionic strength in this work. The choice of salt to be used in setting the ionic strength was investigated using the initial rate method. It was shown (Section 5.4) that for a solution of trithionate in water, the presence of variable amounts of KCl or NaClO₄ did not affect the observed trithionate degradation rate constant appreciably. However, in the

presence of ammonia, the choice and concentration of salt had an effect on the rate of degradation.

A series of tests at 40 °C was done in the presence of ammonia, using KCl, NaCl or NaClO₄ to adjust the ionic strength. No ammonium was added and the pH (>10.6) was not adjusted. Results are shown in Table 5.4.

Table 5.4 : Values for the observed rate constant k_{obs} for trithionate degradation in the presence of various salts used to adjust the ionic strength using the initial rate method

I adjusted with:	[NH ₃] (M) (meas)	I (M)	k_{obs} (h ⁻¹)	k_{obs} min (h ⁻¹)	k_{obs} max (h ⁻¹)	Naito et al. est k_{obs} (h ⁻¹)*
KCl	0.15	0.1	0.0166	0.0141	0.0192	0.013
		1.0	0.0232	0.0205	0.0260	0.013
NaClO ₄	0.13	0.1	0.0175	0.0158	0.0192	0.013
		1.0	0.0160	0.0137	0.0185	0.013
KCl	0.39	0.1	0.0116	0.0098	0.0134	0.014
	0.37	0.5	0.0173	0.0161	0.0186	0.014
	0.39	1.0	0.0236	0.0208	0.0264	0.014
NaCl	0.41	1.0	0.0169	0.0142	0.0197	0.014
NaClO ₄	0.49	1.0	0.0171	0.0154	0.0188	0.014

* These observed rate constants were estimated only, as this data was not supplied by Naito et al (1975). Instead they used an estimation of the water concentration (not given) to express k_{obs} in terms of k_w , k_a and k_t for hydrolysis, ammonolysis and the reaction with thiosulfate respectively.

Generally the results obtained gave higher rate constants than those extrapolated from Naito et al's rate equation, introduced in Chapter 2. However, there were a number of differences between the method used by Naito et al. and in this work. At a low ionic strength (0.1 M), the use of KCl gave rate constants similar to solutions containing NaClO₄, but when higher levels of KCl were used, the trithionate degradation rate

increased significantly. NaCl did not have any effect on the rate at an ionic strength of 1M, implying that rather than the chloride anion being responsible for the increased rate when KCl was used, the potassium ion was responsible.

Potassium affected the trithionate degradation rate only in the presence of ammonia. However, in the absence of ammonia (see Section 5.4), the pH was much lower and the reaction stoichiometry was different, so this situation cannot be directly compared with the system of interest, in the presence of ammonia, except to note that potassium does not affect the baseline degradation in water. The influence of positive ions on the reaction rate implies the formation of an activated complex between the positive ion and one of the reactants. In this set of tests, the only species present were sodium trithionate and ammonia, and the species used to set the ionic strength. Since the concentration of sodium did not have any significant effect it would seem that an excess of sodium where the trithionate was already associated with sodium did not provide any competing interaction. However, the addition of potassium, which has a larger ionic radius than sodium, introduced a competing cation for complexation with trithionate. The presence of potassium made the trithionate more amenable to degradation in the presence of ammonia. The exchange reaction between trithionate and thiosulfate has been found to be influenced by the concentration and charge of cations present (Fava and Pajaro, 1954) but it was not evident whether trithionate or thiosulfate was the most likely to form a complex with the positive ion. Since ionic complexes of thiosulfate had been reported previously, it was assumed by Fava and Pajaro (1954) that trithionate reacted with an ionic complex of thiosulfate in this case. The results reported in this thesis imply that trithionate too can form ionic complexes with cations (e.g. MS_3O_6^-). This is discussed further in Chapter 6.

Based on these results, NaClO_4 was used in all further tests to adjust the ionic strength. It is important to realise that in Naito et al.'s work, the use of KCl for ionic strength adjustments may have had a significant influence on the results and was not taken into consideration.

The effect of ionic strength on trithionate degradation was investigated further using sodium perchlorate at slightly lower pH where both ammonia and ammonium were

present. Trithionate solutions in $\text{NH}_4\text{HCO}_3 / \text{NH}_3$ at pH 9 – 9.2 at 40 °C were not affected by ionic strength adjustments up to about 1.8 M, as seen in Figure 5.3.

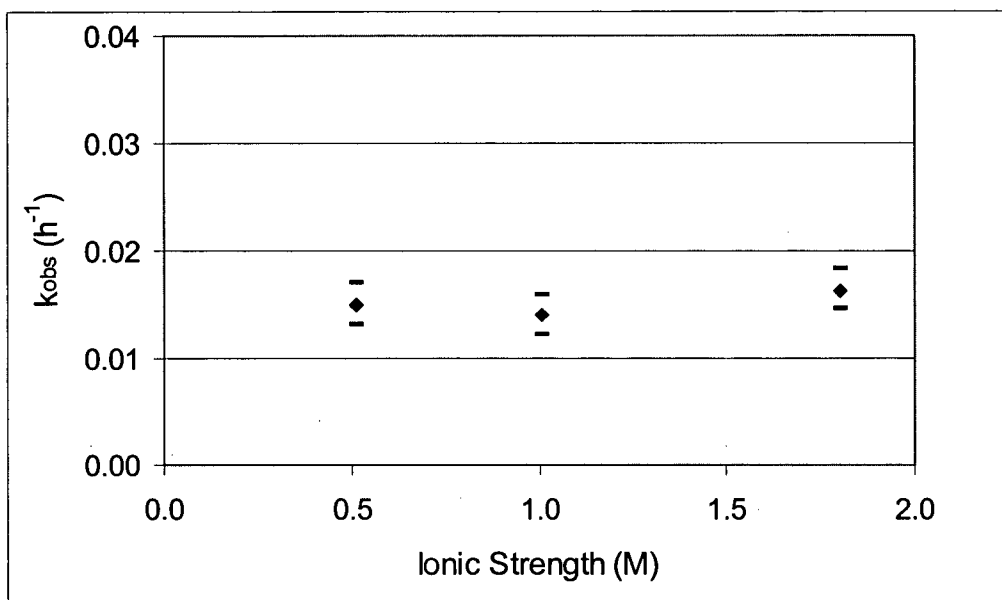


Figure 5.3 : Effect of ionic strength on observed rate constant k_{obs} for trithionate degradation using the initial rate method (0.15 M NH_4HCO_3 at pH 9-9.2 by NH_3 addition, 40 °C)

5.7 CARBONATE AND BICARBONATE

Since most tests were carried out in an ammonium bicarbonate – ammonia buffer system, it was necessary to ensure that the bicarbonate and carbonate ions did not appreciably affect the rate. It had already been established that the concentration of sodium in the form of sodium perchlorate did not affect the trithionate degradation rate (Figure 5.3). The effect of changing the concentration of a sodium bicarbonate / sodium carbonate buffer was investigated using the initial rate method. The results are shown in Figure 5.4 for pH 9.0-9.2 at 40 °C. There appeared to be no influence of the concentration of carbonate / bicarbonate under these conditions. Similar trends have been noted for sodium bicarbonate solutions at pH ~8 (not shown) where increasing the concentration from 0.5 M to 0.7 M bicarbonate had no influence on the rate of trithionate degradation. The use of ammonium bicarbonate was thus deemed acceptable in

investigating the system, particularly to investigate the effect of ammonium concentration.

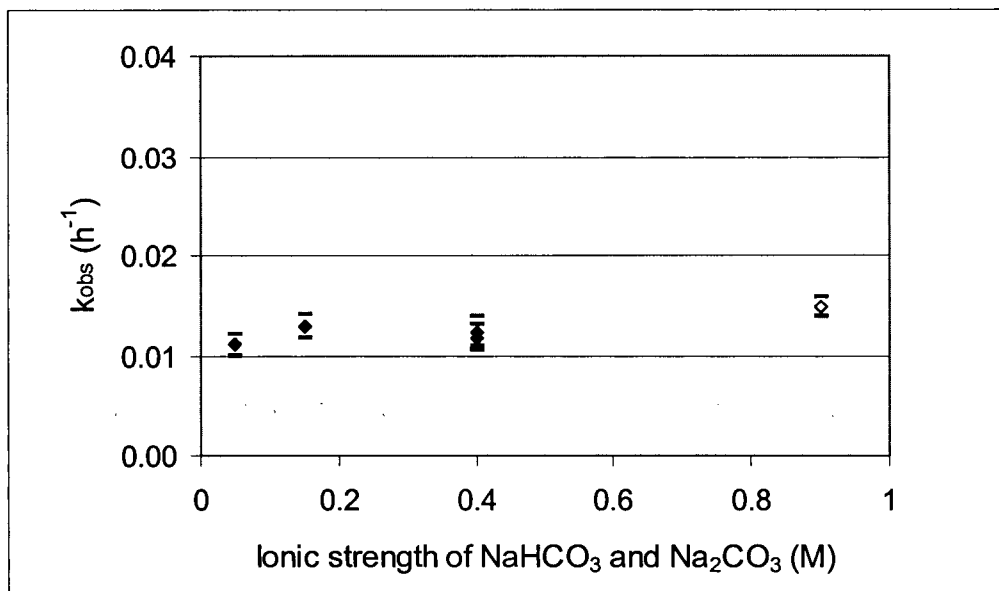


Figure 5.4 : Effect of ionic strength of $NaHCO_3 / Na_2CO_3$ buffer on the observed rate constant k_{obs} for trithionate degradation using the initial rate method (40 °C, pH 9.03 – 9.20, total ionic strength 0.51 M closed symbols, 1 M open symbol)

5.8 AMMONIUM AND AMMONIA

Initial Rate Method

The trithionate degradation rate in solutions of ammonium bicarbonate and ammonium sulfate of various concentrations was determined to find the effect of ammonium concentration on the rate. A plot of the observed rate constant versus the ammonium concentration for the two systems is shown in Figure 5.5.

The observed rate constant increased linearly with ammonium concentration for both systems, but was greater at higher ammonium concentrations in the sulfate medium than the bicarbonate medium. It should be pointed out that in the ammonium bicarbonate system, the pH was fairly stable (around neutral) while in the ammonium sulfate system, the initial pH was 4 to 5, dropping very rapidly throughout the test to as low as pH 1.1.

At pH values as low as this, other factors could come into play and the observed dependency on ammonium concentration was probably not an isolated effect. The data measured in the ammonium bicarbonate system is more suitable to judge the effect of ammonium concentration.

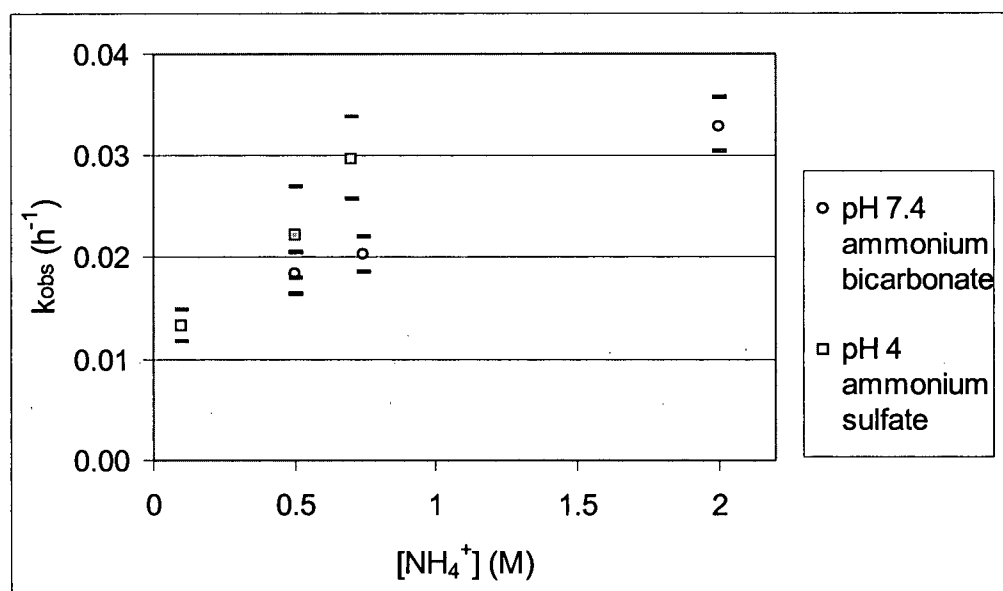


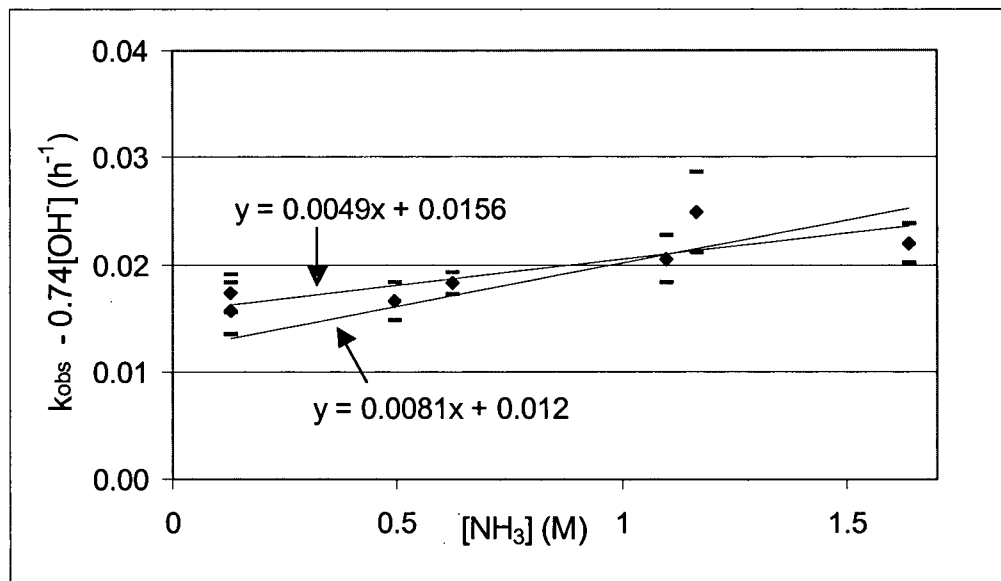
Figure 5.5 : Effect of ammonium concentration on the observed rate constant k_{obs} for trithionate degradation using the initial rate method (40 °C, total ionic strength 1 to 2 M, natural pH)

Taking into consideration the degradation of trithionate in water and the gradient of the ammonium bicarbonate data in Figure 5.5, the extent of the dependency on the ammonium concentration in the bicarbonate system could be expressed as Equation 5.7 at 40 °C. This expression of the rate equation is similar to that for hydroxide solutions, discussed in Section 5.5.

$$-d[S_3O_6^{2-}]/dt = (0.012h^{-1} + 0.01M^{-1}h^{-1}[NH_4^+])[S_3O_6^{2-}] \quad [5.7]$$

The ammonium ion had a very similar effect to the potassium ion, discussed in Section 5.6. These ions have similar radii, with ammonium having a radius of 0.143 nm and potassium having a radius of 0.138 nm (Brodelt and Liou, 1993). This is discussed further in Chapter 6. Since gold leaching by thiosulfate generally takes place in ammoniacal medium, the effect of ammonium was quantified as in Equation 5.7.

The effect of ammonia on the trithionate degradation rate was measured, in the absence of ammonium ions at high pH (>10.5), using the initial rate method. The dependency of the observed rate constant on the ammonia concentration is shown in Figure 5.6. The data in Figure 5.6 shows the observed rate constant adjusted for the effect of hydroxide concentration, as determined in Section 5.5.



$$k_{\text{obs}} = 0.012\text{h}^{-1} + 0.0081\text{M}^{-1}\text{h}^{-1}[\text{NH}_3] + 0.74 \text{ M}^{-1}\text{h}^{-1} [\text{OH}^-] \quad [5.9]$$

A relatively small change in the intercept resulted in a larger variation to the gradient. It should be noted that the results indicating a dependency on ammonia concentration are strongly dependent on the accuracy of the ammonia analysis method. Since the ammonia concentration was found by difference between a total ammonia plus ammonium concentration, and an initial ammonium value, this method is prone to some error.

Naito et al. (1975) assumed that ammonia was involved in a nucleophilic substitution reaction at the sulfonate sulfur atom of trithionate, producing thiosulfate and sulfamate as products. As discussed in the literature review (Chapter 2) the presence of sulfamate was not confirmed by these authors and this deduction was based on reactions known to occur under very different reaction conditions. A suitable method to analyse sulfamate in the presence of trithionate and thiosulfate could not be found (see Chapter 3 on analytical methods) so this assumption could not be confirmed in this work.

Figure 5.7 shows the observed rate constant plotted against the ammonium concentration for both the ammonium bicarbonate / ammonia and the ammonium sulfate / ammonia systems at a constant pH of 9.1 – 9.2 (at 40 °C). Since the pH was constant, an increase in ammonium concentration also implied an increase in ammonia concentration. The data show that the two systems behave fairly similarly, within the error margins for each data point.

It is assumed that the observed rate constant can be interpreted as being representative of the sum of various individual components, including the baseline degradation rate of trithionate in water and an enhanced degradation seen either in the presence of ammonia or ammonium (as noted above). The effect of hydroxide concentration was not included in this case as under these conditions it was expected to contribute to less than 0.1 % of the observed rate constant. The observed rate constant was thus expressed as a sum of its components, as in Equation 5.10.

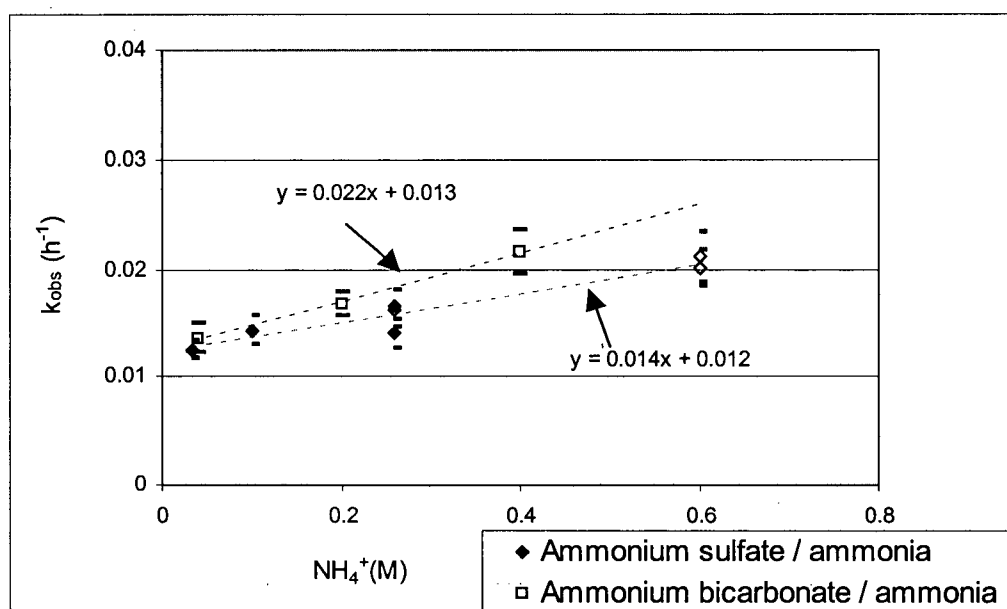


Figure 5.7 : Effect of ammonium concentration on the observed rate constant k_{obs} for trithionate degradation for $(\text{NH}_4)_2\text{SO}_4 / \text{NH}_3$ and $\text{NH}_4\text{HCO}_3 / \text{NH}_3$ buffer systems using the initial rate method

(40 °C, pH 9.13 – 9.19, ionic strength 0.51 M closed symbols, 1 M open symbols)

$$k_{\text{obs}} = 0.012\text{h}^{-1} + k_2[\text{NH}_3] + k_3[\text{NH}_4^+] \quad [5.10]$$

For the data in Figure 5.7, at pH 9.1 to 9.2, the concentration of ammonia was typically 2.1 times greater than that of ammonium, given in Equation 5.11.

$$k_{\text{obs}} = 0.012\text{h}^{-1} + 2.1k_2[\text{NH}_4^+] + k_3[\text{NH}_4^+] \quad [5.11]$$

The slope in Figure 5.7 was thus $2.1k_2 + k_3$. Taking k_3 as $0.01\text{M}^{-1}\text{h}^{-1}$ (see earlier) and k_2 as either $0.0049\text{M}^{-1}\text{h}^{-1}$ (Equation 5.8) or $0.0081\text{M}^{-1}\text{h}^{-1}$ (Equation 5.9), one would expect the slope in Figure 5.7 to be between 0.020 and $0.027 \text{M}^{-1}\text{h}^{-1}$. This is in agreement with the slope obtained for the data obtained in bicarbonate medium ($0.022 \text{M}^{-1}\text{h}^{-1}$).

Integrated Rate Method

Changing the ammonium and ammonia concentration for the standard ammonium bicarbonate / ammonia buffer system as well as for an ammonium sulfate / ammonia buffer system was also investigated at 25 °C using the integrated rate method. Results are shown in Table 5.5.

Table 5.5 : Effect of ammonium concentration on observed rate constant k_{obs} for trithionate degradation
(25 °C, nominally 0.023 M $\text{S}_3\text{O}_6^{2-}$, ammonia added to adjust pH to ~10.3)

Buffer system	$[\text{NH}_4^+]$ (M)	k_{obs} (h^{-1})
$(\text{NH}_4)_2\text{SO}_4$ / NH_3	0.02	0.0022
	0.09	0.0027
NH_4HCO_3 / NH_3	0.03	0.0026
	0.15	0.0034

For either buffer system, increasing the concentration of ammonium (and hence ammonia) increased the observed rate constant. While the effects of ammonia and ammonium were not examined individually using this method, the trends match those found at 40 °C using the initial rate method.

5.9 pH

A number of comparative tests were done at constant pH using the initial rate method. The total ammonia and ammonium concentrations were varied but kept at a constant ratio to maintain the desired pH. The same data is shown in two different ways – as the observed rate constant plotted against the ammonium concentration and against the ammonia concentration. Since it has been shown that the hydroxide concentration influences the reaction rate, the effect of hydroxide ion concentration should be taken into account as the pH varies. However, the value of this contribution was generally negligible, and even at $\text{pH} > 10.5$ was less than 4 % of the observed rate constant, which is less than the level of uncertainty in the measurements. The adjustment was thus not made in the figures.

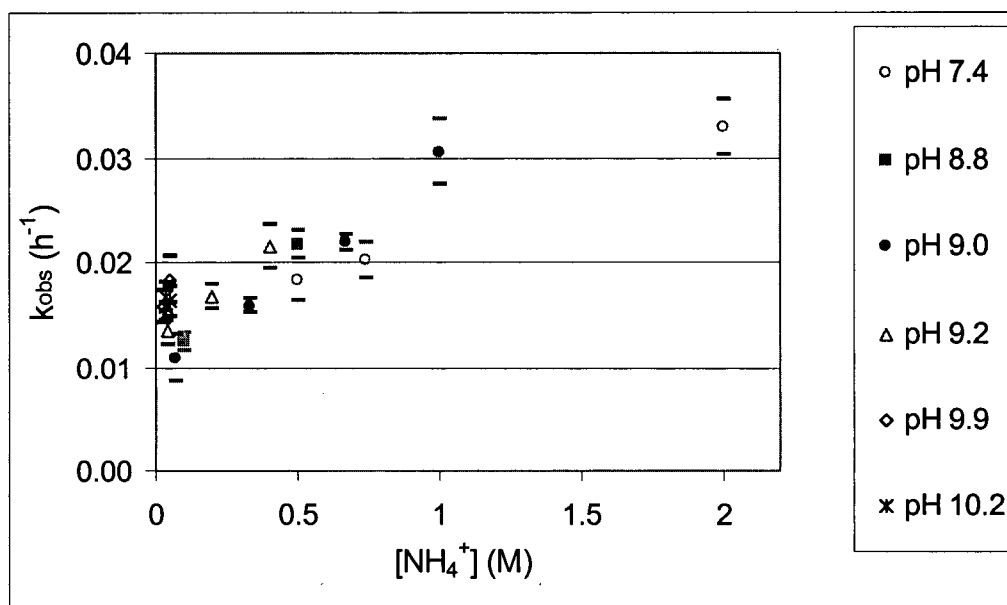


Figure 5.8 : Dependency of the observed rate constant k_{obs} for trithionate degradation on ammonium concentration at various pH (40 °C)

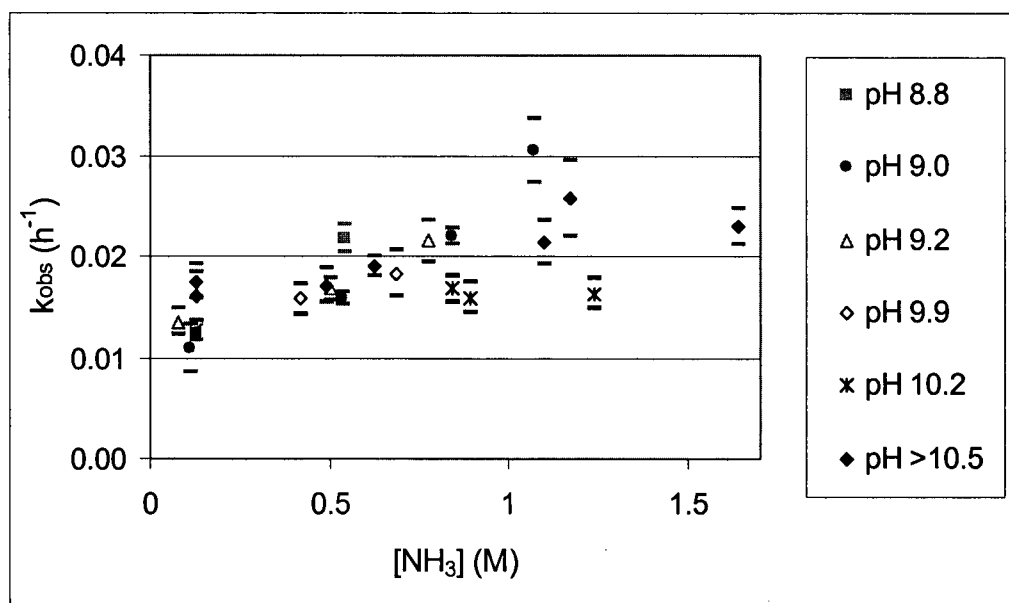


Figure 5.9 : Dependency of the observed rate constant k_{obs} for trithionate degradation on ammonia concentration at various pH (40 °C)

It is difficult to see any variations in the slope of the observed rate constant versus ammonia or ammonium concentrations with pH from Figure 5.8 or 5.9. The same data was therefore plotted in a different way, as sets of data at constant ammonia plus ammonium concentration against the pH, as in Figure 5.10. Since the effect of changing the ionic strength had not been found to be significant when NaClO_4 was used to adjust it, the data in Figure 5.10 represents a range in ionic strengths. Each data series represents a small range of total ammonia concentration as indicated on the graph. Error bars were excluded for clarity. There appears to be a minimum degradation rate around pH 10.

The following general observations were made, taking into consideration that the uncertainty levels for each data point were significant (see Section 5.3):

- For any pH, as the total ammonia plus ammonium increased, the observed rate constant increased.
- There was a minimum in the trithionate degradation rate at around pH 10. At pH values higher than around 10 (at 40 °C), the observed rate constant increased as the pH increased. At pH values lower than around 10 (at 40 °C), the observed rate constant increased as the pH decreased. This effect is attributed to the relative amounts of ammonia and ammonium ions, rather than the pH (hydroxide concentration) directly in this pH range, as discussed in Chapter 6.
- There was a minimum trithionate degradation corresponding to the degradation in water.

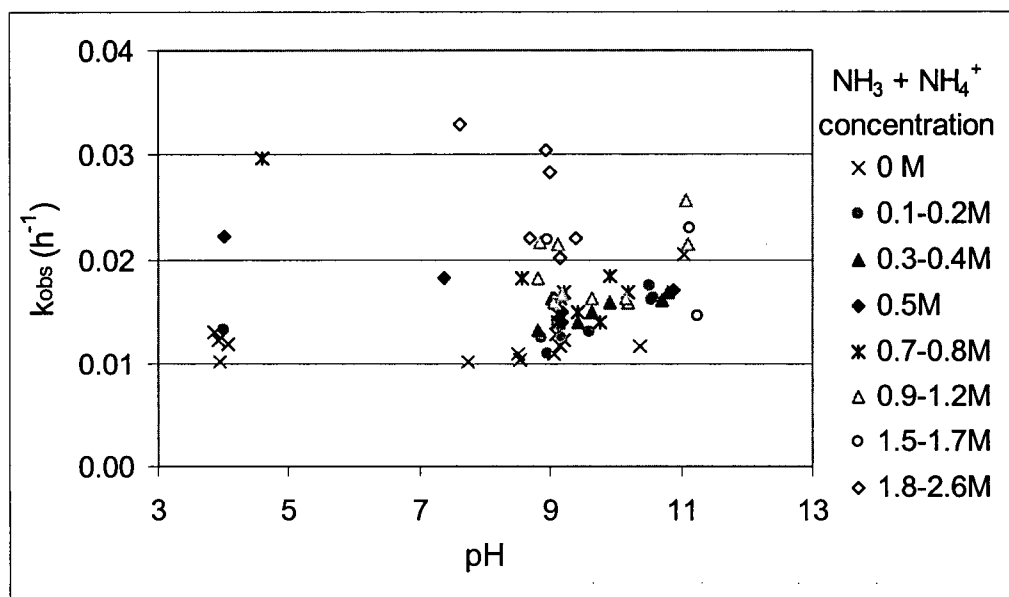


Figure 5.10 : Observed rate constant k_{obs} for trithionate degradation versus pH for a range of ammonia / ammonium concentrations (40 °C, various ionic strength)

The observed rate constant at 25 °C showed very little change with an increase in pH. However, only three data points were available and the magnitude of the observed rate constants were much less than at 40 °C, so it would be much more difficult to notice trends.

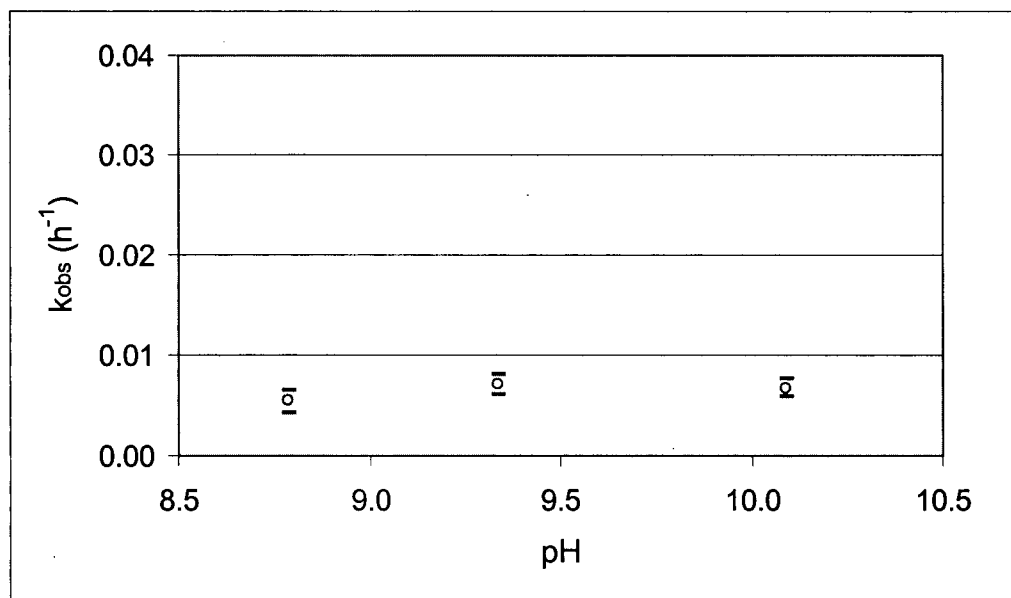


Figure 5.11 : Observed rate constant k_{obs} for trithionate degradation versus pH at 25 °C (Total ionic strength = 1.1 M, 1 M NH_4^+ , ammonium bicarbonate / ammonia system)

In order to investigate pH effects in the absence of complicating effects from ammonia and ammonium, a sodium bicarbonate / sodium carbonate system was used using the initial rate method at 40 °C. It was shown (Section 5.7) that the bicarbonate and carbonate species did not influence the trithionate reaction rate at pH 9-9.2. The bicarbonate to carbonate ratio was varied to investigate the effect of pH without having to introduce ammonia species to the system. The observed rate constant versus pH is shown in Figure 5.12. Because the concentrations of bicarbonate and carbonate did not have an effect, the data shown in Figure 5.12 include data where varying concentrations of bicarbonate/carbonate were used (with the ionic strength from the bicarbonate / carbonate buffer ranging between 0.05 and 0.9 M).

No obvious trend in reaction rate with pH was observed in this pH range. This implies that rather than pH it is the relative concentrations of the ammonium and ammonia which influence the trithionate degradation.

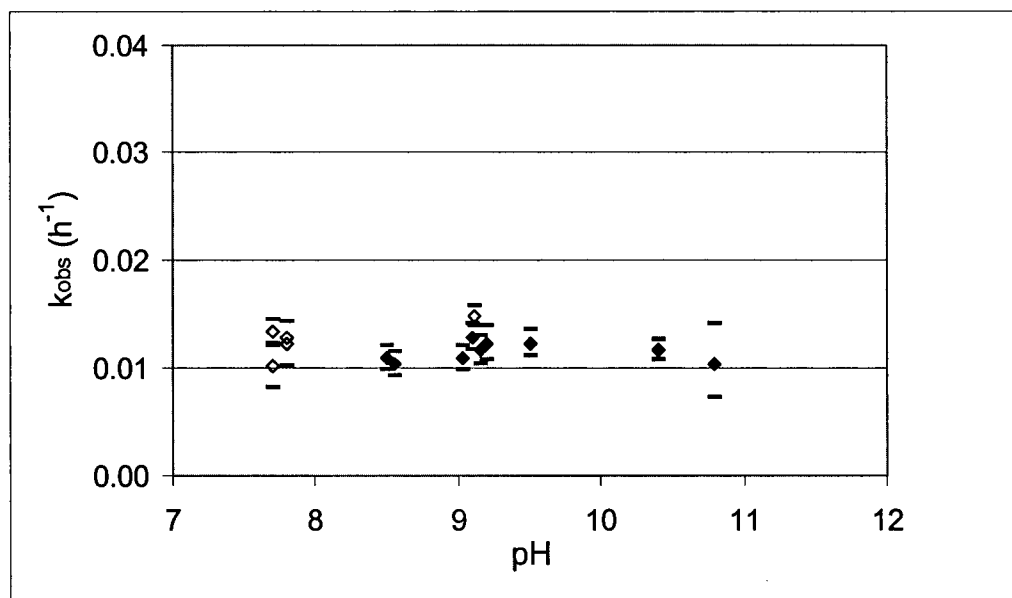


Figure 5.12 : Effect of pH on observed rate constant k_{obs} for trithionate degradation in sodium carbonate/bicarbonate medium
(40 °C, Ionic strength 0.5 M for closed symbols, 1 M for open symbols)

5.10 THIOSULFATE

Initial Rate Method

The effect of thiosulfate on the trithionate degradation rate was investigated in ammoniacal bicarbonate buffer using a range of ammonium concentrations and pH. The tests were done at 40 °C with aqueous ammonia added to adjust the pH to between 9 and 10. Results are shown in Figure 5.13.

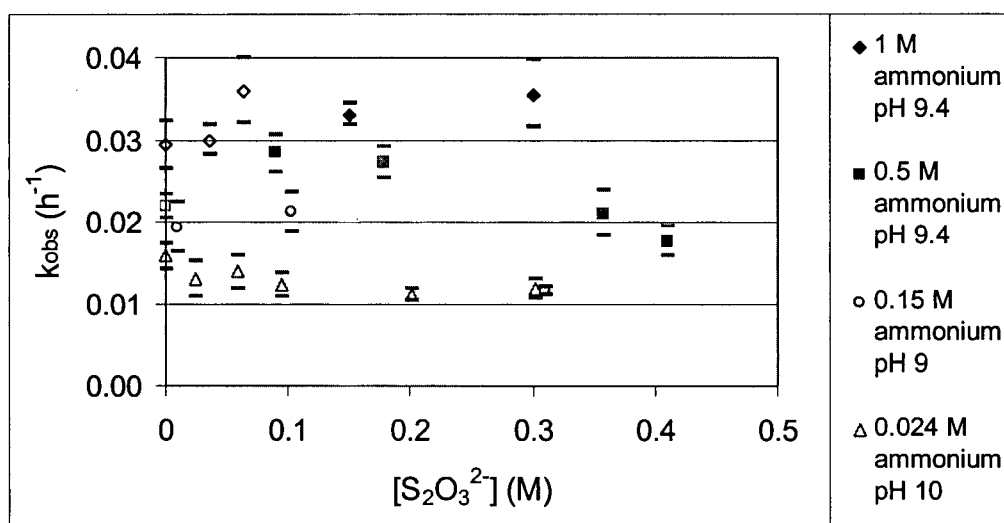


Figure 5.13 : Effect of thiosulfate on the observed rate constant k_{obs} for trithionate degradation using the initial rate method (40 °C)

(Total ionic strength for 1M ammonium tests was 1M (open symbols) or 2 M (closed symbols). Total ionic strength for 0.5 M ammonium tests was 0.6 M (open symbol) or 1.8 M (closed symbols). Total ionic strength for all other data points was 1 M.)

At low ammonium concentration (0.024 M) at pH 10, the addition of thiosulfate had a negligible effect on the trithionate degradation, perhaps causing a slight inhibition of the degradation. However, from the observations of trithionate degradation at different pH, it was found that near pH 10, the trithionate degradation was at a minimum (see Section 5.9). Any effects of thiosulfate may have been minimised at this pH.

At 0.15 M ammonium, pH 9, addition of thiosulfate increased the trithionate degradation rate but caused inhibition at higher levels. Increasing the ammonium concentration to 0.5 M (and the pH to 9.4) showed a similar trend where thiosulfate enhanced the rate at lower levels but inhibited it at higher levels. Similarly, for 1 M ammonium (pH 9.4) addition of thiosulfate increased the trithionate degradation rate. At the levels of thiosulfate tested, no inhibition was noted for this series. Possible reasons for these observations are discussed in Chapter 6.

Integrated Rate Method

The effect of thiosulfate addition at room temperature is shown in Table 5.6 for two sets of tests, using the integrated rate method. It is clear that within the variability of the experimental conditions, thiosulfate at 0.09 M (almost double the initial amount of trithionate and three times the initial ammonium concentration) did not have any significant effect. The reaction stoichiometry was not affected by the presence of initial thiosulfate. However at room temperature, any differences in observed rate constant are expected to be much less than at 40 °C, so it is possible that the effects were simply not measurable at this temperature.

Table 5.6 : Effect of thiosulfate on the observed rate constant k_{obs} for trithionate degradation using the integrated rate method
(room temperature, $[\text{NH}_4\text{HCO}_3] = 0.03\text{M}$, NH_3 added to pH ~9.7)

Initial $\text{S}_3\text{O}_6^{2-}$ (M)	Initial $\text{S}_2\text{O}_3^{2-}$ (M)	k_{obs} (h^{-1})
0.043	0	0.0017
0.041	0.083	0.0021
0.054	0	0.0016
0.053	0.091	0.0017

5.11 OXYGEN EXCLUSION

Initial Rate Method

The effect of limiting the amount of oxygen in solution on the trithionate degradation rate was investigated. Solutions were sparged with nitrogen and a nitrogen-filled glove bag was used during preparation of the test. Samples were removed by syringe through a septum. While this method may not have completely removed all oxygen from the system, the amount of oxygen present would have been significantly limited. The efficiency of oxygen removal was not determined.

The effect of limiting oxygen in solution was investigated in the absence of ammonia for both the low alkaline pH reaction (Equation 5.2) and the high alkaline reaction (Equation 5.4). At high pH (pH ~ 12 at 40 °C) 0.1 M NaOH was used. The results are shown in Table 5.7 where it can be seen that limiting the oxygen in solution gave no significant change in the rate constant or the reaction stoichiometry with respect to thiosulfate under these conditions, implying that dissolved oxygen has no role in this degradation.

Table 5.7 : Effect of limiting dissolved oxygen on the observed rate constant k_{obs} for trithionate degradation in 0.1 M hydroxide solution

Atmosphere	Ave initial pH	Ratio $\text{S}_2\text{O}_3^{2-}$ formed : $\text{S}_3\text{O}_6^{2-}$ decayed	k_{obs} (h^{-1})	$k_{\text{obs min}}$ (h^{-1})	$k_{\text{obs max}}$ (h^{-1})
air	11.96	0.3-0.4	0.143	0.132	0.156
N_2 (O_2 limited)	12.09	0.2-0.4	0.133	0.124	0.141

The effect of nitrogen sparging was also tested at a two different pHs in the ammonia / ammonium bicarbonate medium. Results are shown in Table 5.8, where again there was no significant effect. This is not surprising as the anticipated reaction, shown in Equation 5.2, does not involve oxygen. There is likely to be an effect noted after longer

times, as the thiosulfate produced from trithionate degradation can oxidise slowly in the presence of oxygen.

Table 5.8 : Effect of limiting oxygen on the observed rate constant k_{obs} for trithionate degradation in ammonia / ammonium bicarbonate solution

Atmosphere	$[\text{NH}_4\text{HCO}_3]$ (M)	$[\text{NH}_3]$ (M)	Ave initial pH	k_{obs} (h^{-1})	k_{obs} min (h^{-1})	k_{obs} max (h^{-1})
air	0.5	0	7.4	0.0182	0.0163	0.0203
N_2 (O_2 limited)	0.5	0	7.9	0.0185	0.0178	0.0192
air	0	0.492	10.9	0.0171	0.0154	0.0188
N_2 (O_2 limited)	0	0.625	11.0	0.0190	0.0180	0.0200

Integrated Rate Method

In similar tests using the integrated rate method, the oxygen concentration was limited by using water that had been sparged with nitrogen and filling the test flask head space with nitrogen at the start of the test and at each sampling point. Results for trithionate degradation both in the presence and absence of initial thiosulfate are shown in Table 5.9. Reducing the level of oxygen had no effect on the trithionate degradation, confirming the findings using the initial rate method.

Table 5.9 : Effect of limiting oxygen on the observed rate constant k_{obs} for trithionate degradation using the integrated rate method
(room temperature, $[\text{NH}_4\text{HCO}_3] = 0.03\text{M}$, NH_3 added to pH ~9.7)

Test	Atmosphere	Initial $\text{S}_3\text{O}_6^{2-}$ (M)	Initial $\text{S}_2\text{O}_3^{2-}$ (M)	k_{obs} (h^{-1})
14	air	0.054	0	0.0016
16	nitrogen	0.048	0	0.0016
15	air	0.053	0.091	0.0017
17	nitrogen	0.048	0.089	0.0016

5.12 CUPRIC COPPER

Cupric copper is considered necessary by many to catalyse the thiosulfate leaching of gold, but it is known to enhance the degradation of thiosulfate. It was therefore considered important to establish the effect of copper on trithionate degradation.

Integrated Rate Method

Cupric sulfate (0.0045 M) was added to a trithionate solution (0.049 M) to determine the effect on the trithionate degradation rate. Table 5.10 shows the effect on the observed rate constant and on the reaction stoichiometry.

Table 5.10 : Effect of cupric addition on the observed rate constant k_{obs} for trithionate degradation using the integrated rate method
(room temperature, $\text{NH}_4\text{HCO}_3/\text{NH}_3$ buffer, $[\text{NH}_4^+] = 0.03\text{ M}$, initial pH ~9.7)

Test	Cu^{2+} present (M)	pH after 432 hrs	pH after 600 hrs	k_{obs} (h^{-1})	Stoichiometry	
					$\text{S}_2\text{O}_3^{2-} : \text{S}_3\text{O}_6^{2-}$	$\text{SO}_4^{2-} : \text{S}_3\text{O}_6^{2-}$
14	0	-	9.13	0.0017	0.9	0.9
20	0.0045	8.21	-	0.0018	0	3.3

Even with copper present, the trithionate degradation reaction still followed first order reaction kinetics. Although the rate constant was similar either with or without copper present, the pH drop was much more significant with copper present (based on the limited data available), and no thiosulfate formed. Even though the rate constants were similar, they cannot be directly compared because over these long times different reactions occurred with and without copper present.

Initial Rate Method

The effect of cupric copper (in the form of cupric sulfate) on the trithionate degradation rate in water and in ammonia / ammonium bicarbonate buffer was investigated. Air was not excluded from these tests, as for all other tests except for those reported in Section 5.11, and the temperature was maintained at 40 °C. The results are shown in Table 5.11. It should be noted that in some tests 0.01 M copper was added. The trithionate concentration used in these tests was 0.01 M to 0.04 M, of which only about 10 % is expected to degrade over the duration of the test. Hence the ratio of copper to trithionate was high compared to typical gold leaching conditions. However, the aim was to identify an effect, if any, even in exaggerated form.

Table 5.11 : Effect of cupric copper on the observed rate constant k_{obs} for trithionate degradation

[Cu ²⁺] (M)	[NH ₄ HCO ₃] (M)	Ave initial pH	k_{obs} (h ⁻¹)	k min (h ⁻¹)	k max (h ⁻¹)
0	0	4	0.012	*	*
0.01	0	4	0.027	0.021	0.029
0	0.54	9.4	0.022	0.021	0.023
0.001	0.5	9.7	0.025	0.023	0.026
0.01	0.5	9.6	0.026	0.025	0.027
0	0.02	9.6	0.013	0.011	0.015
0.01	0.02	10.2	0.013	0.012	0.014

* Not determined – see Section 5.4

In water, there was a significant effect of copper on the trithionate degradation rate. Precipitation of copper sulfides was also evident, so this result cannot be directly compared to that in the absence of copper or to higher pH tests where no precipitation was noted.

In the presence of an ammonia / ammonium buffer, copper did not have any significant effect on the observed rate constant. The stoichiometry was the same as in the absence of copper and no precipitation was evident. While the observed rate constant was not affected for the integrated rate method either, a different reaction stoichiometry and precipitation was observed. It may be that in the integrated rate method tests, the much longer test durations were responsible for this. It is possible that over these times, the significant pH drop in combination with the presence of reaction products in the solution could have affected the overall reaction stoichiometry. The initial rate method results are considered to be more reliable.

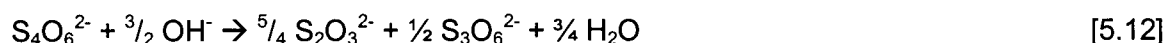
It has been proposed by Jeffrey and his coworkers that trithionate reacts with cupric copper (Breuer and Jeffrey, 2003b). In work focusing on the reaction between cupric copper and thiosulfate, they measured the rate of reduction of cupric copper, inferring from this the thiosulfate degradation rate. On addition of trithionate to the system, the cupric copper was reduced faster, so it was deduced that cupric copper reacts with trithionate in a similar way to with thiosulfate. That observation does not agree with that found in these results.

It was found that for the thiosulfate-copper reaction, the amount of oxygen present is very important (Breuer and Jeffrey, 2003a). In the current tests on trithionate, oxygen was not controlled. It may be necessary to carefully control the levels of dissolved oxygen to notice any effect such as that proposed by Jeffrey et al.

5.13 TETRATHIONATE

The effect of tetrathionate was only examined using the integrated rate method. When tetrathionate was present at the start of a test, it was found to very rapidly degrade to lower than the analysis detection limit, causing a corresponding small increase in the

trithionate and thiosulfate levels. This was expected as tetrathionate is known to degrade rapidly under alkaline conditions, as shown in Equation 5.12.



Besides this small initial effect, the kinetics of trithionate degradation were not affected in any other way by the presence of tetrathionate.

5.14 ELEMENTAL SULFUR, SULFATE AND COPPER POWDER

A few exploratory tests were carried out to investigate the effect of the presence of elemental sulfur (hydrophobic), sulfate and elemental copper on the trithionate degradation rate, using the integrated rate method. Initial conditions of 0.05 M $\text{S}_3\text{O}_6^{2-}$, 0.08 M $\text{S}_2\text{O}_3^{2-}$ and 0.009 M $\text{S}_4\text{O}_6^{2-}$ were used. The change of trithionate concentration with time for each test is shown in Figure 5.14. The observed rate constants corresponding to Figure 5.14 determined from the point when all the tetrathionate had degraded are shown in Table 5.12.

Table 5.12 : Effect of elemental sulfur, sulfate and copper powder on the observed rate constant k_{obs} for trithionate degradation
(room temperature, $[\text{NH}_4\text{HCO}_3] = 0.03\text{M}$, NH_3 added to pH ~9.7,
nominally 0.05 M $\text{S}_3\text{O}_6^{2-}$, 0.08 M $\text{S}_2\text{O}_3^{2-}$, 0.009 M $\text{S}_4\text{O}_6^{2-}$)

Species added	$k_{\text{obs}} (\text{h}^{-1})$
none	0.0021
S (4.95 g/l)	0.0015
SO_4^{2-} (15 g/l)	0.0021
Cu (8 g/l)	0.0010

While the addition of sulfate did not affect the observed rate, elemental sulfur may have slightly retarded the reaction, while metallic copper powder decreased the rate significantly. Where copper powder was used, the copper powder became black, probably due to the formation of sulfides. Insufficient sulfate analyses were available to draw a definitive conclusion regarding the degradation stoichiometry in the presence of

copper powder, but indications are that higher levels of sulfate than expected according to Equation 5.2 were obtained.

These effects were not pursued further in this work, but future work may be warranted.

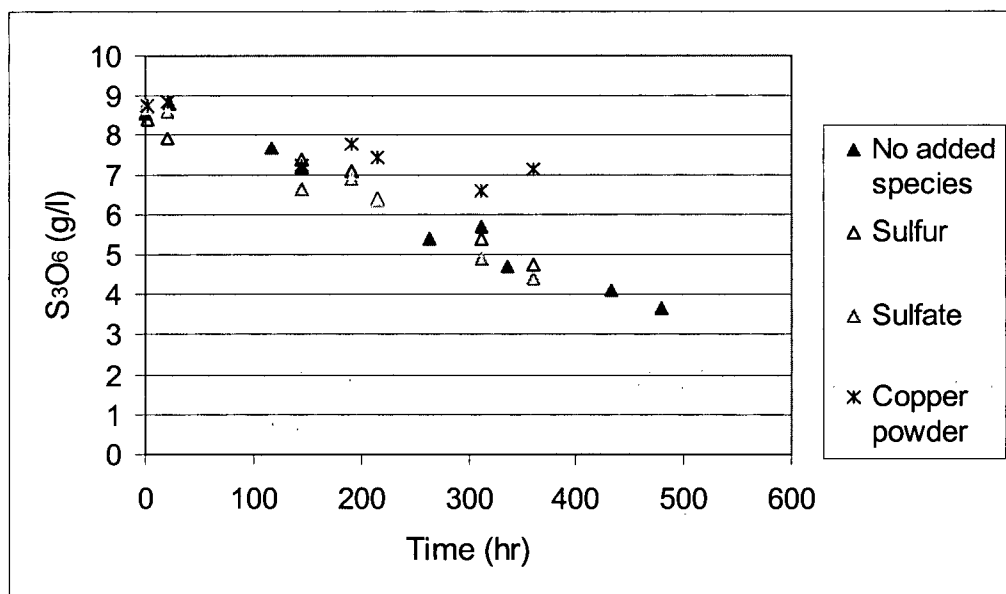


Figure 5.14 : Effect of sulfur, sulfate or copper powder on trithionate concentration profile (room temperature, pH ~ 9.7)

5.15 TEMPERATURE

Initial Rate Method

Most of the kinetic tests were done at 40 °C, to ensure that the reaction rates were high enough for the initial rate method to be used with a reasonable degree of accuracy and to limit the scatter in the data. A few comparative tests were done at 25 °C to quantify the effect of temperature on the degradation rate.

The observed rate constants for tests done in an ammonium bicarbonate / ammonia buffer of ionic strength 1.1 M for three initial pH values at 25 °C and 40 °C are shown in Table 5.13. Based on this data, the activation energies were calculated using the Arrhenius equation. The apparent activation energies ranged between 72.9 and 78.9 kJ/mol between pH 8.8 and 10.1. The perceived increase in activation energy with pH

was within the uncertainty of the measurements of the rate constants. Activation energies calculated under similar conditions in the literature ranged from 81 - 87 kJ/mol for a temperature range of 40 – 80 °C (Naito et al., 1975), to 91.7 kJ/mol measured at 70 – 85 °C (Rolia and Chakrabarti, 1982). This implies the reaction is under chemical reaction control.

Table 5.13 : Effect of temperature on the observed rate constant k_{obs} for trithionate degradation at pH 8.8 – 10.1 (NH_4HCO_3 added to give $I = 1.1 \text{ M}$, variable $[\text{NH}_3]$)

pH	Temperature (°C)	$k_{obs} \text{ (h}^{-1}\text{)}$	Activation energy (kJ/mol)
8.8	25	0.0054	72.9
	40	0.0221	
9.4	25	0.0070	74.2
	40	0.0294	
10.1	25	0.0067	78.9
	40	0.0308	

Integrated Rate Method

The same temperature effect was found in the presence of thiosulfate, using the integrated rate method. The observed rate constants and calculated activation energy are shown in Table 5.14. It is important to note that because of the speed of the reaction, very few data points were measured at 40 °C, so the derivation of the rate constant was not likely to be as accurate as using the initial rate method. Also, for the purposes of the Arrhenius calculation, it was assumed that the room temperature tests were at 22 °C. The estimated activation energy was about 71 kJ/mol.

Table 5.14 : Effect of temperature on the observed rate constant k_{obs} for trithionate degradation using the integrated rate method
 $([\text{NH}_4\text{HCO}_3] = 0.03\text{M}, \text{NH}_3 \text{ added to pH } \sim 9.7)$

Temperature	Initial $\text{S}_3\text{O}_6^{2-}$ (M)	Initial $\text{S}_2\text{O}_3^{2-}$ (M)	k_{obs} (h^{-1})	Estimated E_a (kJ/mol)
RT	0.041	0.083	0.0021	70.6
40 °C	0.047	0.090	0.0110	

6. KINETICS OF THE DEGRADATION OF TRITHIONATE – DISCUSSION AND MODELLING

6.1 QUALITATIVE DISCUSSION

The observed degradation of trithionate in the presence of water or hydroxide ions confirmed the literature. It is likely to proceed via nucleophilic attack at the sulfonate sulfur atom (Naito et al., 1975). An increase in the concentration of hydroxide ions (or pH) increased the trithionate degradation rate, as expected, since hydroxide is known to react directly with trithionate (Equation 6.1).



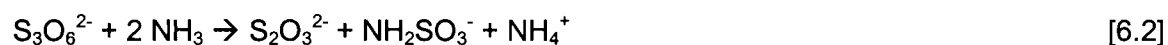
A sodium bicarbonate/carbonate buffer had no effect on the rate, at constant pH (varying concentration) or with varying pH (varying carbonate/bicarbonate ratio) from around pH 7.8 to 11 (at 40 °C). Although the hydroxide concentration increased the rate, this effect was very small at pH values less than 11, so varying the pH in this range did not have much effect. The bicarbonate and carbonate anions were inert in this system. This is not surprising as positive ions, not negative ions, are likely to have an effect on reactions between anions, i.e. trithionate and hydroxide in Equation 6.1.

Increasing the ionic strength using NaClO_4 did not have any effect on the rate of trithionate degradation in the presence of ammonia. However, addition of potassium or ammonium ions generally increased the rate. While no data is available for trithionate, ion pairing of thiosulfate with cations is known. In fact, it has been shown that in the presence of sodium, potassium or ammonium ions, the concentration of the complexed thiosulfate ion (MS_2O_3^-) is the same as or higher than that of the free thiosulfate ion (Senanayake, 2005). This researcher found that there was a linear relationship between the logarithms of the association constants for the species MS_2O_3^- and MSO_4^- for the cations (M^+) Na^+ , K^+ and H^+ . Based on this relationship and the association constant of NH_4SO_4^- , the association constant of $\text{NH}_4\text{S}_2\text{O}_3^-$ was calculated and was found to be similar to that for KS_2O_3^- . The similarity between the behaviour of potassium ions and ammonium ions is likely due to their similar ionic radii.

It has been shown that in the sulfur exchange reaction between thiosulfate and trithionate, an increase in charge and concentration of positive ions increases the reaction rate (Fava and Pajaro, 1954). The authors therefore postulated this reaction to be between ionic complexes of thiosulfate, trithionate or both, rather than between free ions. Since the trithionate degradation rate varied with the concentration of positive ions, it is reasonable to believe that cations influence the reaction, possibly by forming ionic complexes with trithionate.

An increase in sodium ion concentration did not give an increase in the trithionate degradation rate. However, since the trithionate salt was in the sodium form, sufficient sodium was always present to ensure complex ions with sodium, so one would only expect to notice an effect when a competing ion (potassium or ammonium) was introduced. It was interesting that the trithionate degradation rate continued to increase with the ammonium or potassium ion concentrations even when the cation concentration was much higher than the trithionate concentration, and did not reach a maximum over the range of cation concentrations tested. The presence of potassium ions in acidic solutions (the natural pH obtained for a solution of sodium trithionate in water) did not increase the trithionate degradation rate, but the reaction stoichiometry was not necessarily the same as in alkaline systems.

With no ammonium present, an increase in ammonia concentration increased the rate of trithionate degradation. While it could not be proven that the reaction in Equation 6.2 forming sulfamate proceeded, it is possible that this reaction occurred to a small extent, or that the interaction between ammonia and trithionate facilitated the reaction between hydroxide ions and trithionate by altering the electronic properties of the trithionate.



Based on the above discussion, the overall rate of degradation of trithionate is influenced by water, hydroxide and ammonia, and the reaction is enhanced by changing the electronic properties of a complex ion of trithionate by changing the cation type or concentration. It was assumed that the water concentration was constant in this case and that no thiosulfate was originally present. In an ammoniacal medium, which is of most interest to this study, the relative concentrations of ammonia, hydroxide ions and

ammonium ions are shown diagrammatically in Figure 6.1 with varying pH. Since the degradation rate increases with the concentration of each of these species (but to different extents), it is feasible based on the diagram in Figure 6.1 that the overall rate would vary with pH in an ammoniacal system, and there could be a pH of minimum degradation rate. The way in which these qualitative effects can be combined quantitatively is discussed in Section 6.2.

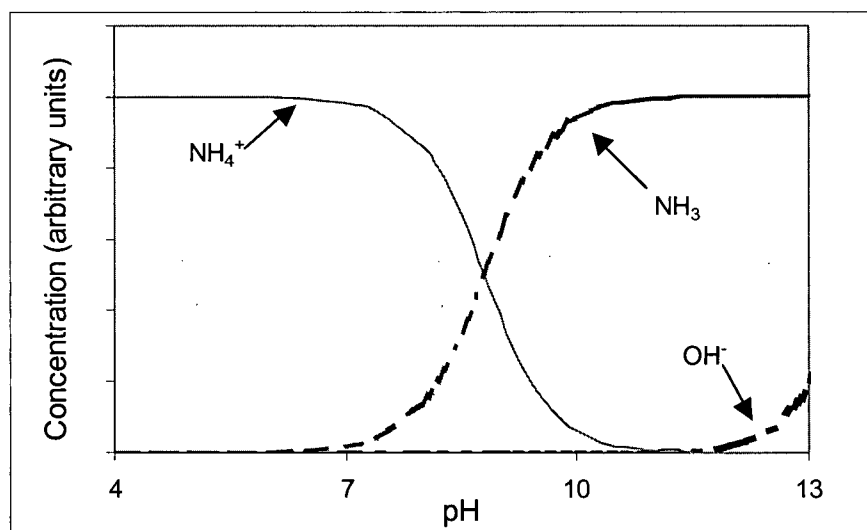


Figure 6.1 : Concentration profiles for ammonia, ammonium ions and hydroxide ions at 40 °C with varying pH, using arbitrary concentration units

It was shown that the effect of thiosulfate on the trithionate degradation rate was dependent on the ammonium concentration. Where the ammonium concentration was higher than the thiosulfate concentration, the trithionate degradation rate generally increased with an increase in thiosulfate concentration. However, as the thiosulfate concentration exceeded the ammonium concentration, the trithionate degradation rate was unaffected or even decreased with a further increase in thiosulfate. Thiosulfate is known to form complex ions, and it has been postulated that the ion $\text{NH}_4\text{S}_2\text{O}_3^-$ exists (Senananyake, 2005). Other reactions have been proposed to occur via thiosulfate complex ions (Fava and Pajaro, 1954, Chandra and Jeffrey, 2004). At high ammonium concentrations, the concentration of the ammonium complex ion is expected to be higher, facilitating the interaction between thiosulfate and trithionate. However, as the thiosulfate concentration becomes comparable with the ammonium ion concentration,

the possibility of free thiosulfate ions (or the sodium complex, since thiosulfate was added as sodium thiosulfate) existing increases. If free or sodium thiosulfate ions do not readily interact with trithionate, one would expect the trithionate degradation rate to plateau with any further increase in thiosulfate concentration. The fact that a further increase in thiosulfate concentration actually decreases the trithionate degradation rate implies a hindrance of the reaction. If thiosulfate interacts via the sulphenyl sulfur atom of trithionate, where it acts to alter the electronic properties of trithionate to facilitate its reaction with hydroxide and ammonia, then it is possible that too much thiosulfate could sterically hinder these reactions.

The effect of thiosulfate on the trithionate degradation rate was not completely in agreement with that found by Naito et al (1975). The range of thiosulfate concentrations tested was based on those to be expected during gold leaching, and were much higher than those used by Naito et al. (typically 0.02 M). The trithionate degradation rate decreased at higher levels of thiosulfate, rather than increasing as expected from Naito et al.'s rate equation. Naito et al. (1975) explained the catalytic effect they observed when thiosulfate was present by proposing that thiosulfate formed a complex with trithionate and the complex reacted with water more rapidly than trithionate alone.

In the presence of ammonia, cupric copper did not affect the reaction rate. In the cases tested, the ammonia was present in a molar ratio of more than 4:1 to cupric copper, so it is expected that a significant amount of the cupric copper was present as the tetraammine complex. The presence of ammonia is known to stabilise cupric copper and hence inhibit the reaction between cupric and thiosulfate. It has been proposed that thiosulfate joins the inner co-ordination sphere of cupric tetraammine for the reaction to proceed (Byerley et al, 1973a, Breuer and Jeffrey, 2000, 2003b). A similar mechanism may be relevant for the interaction between trithionate and copper, but due to steric hindrances, co-ordination of trithionate to cupric tetraammine may not be as favourable (trithionate is larger than thiosulfate). Where copper is not primarily present as the cupric tetraammine complex, there may be an influence on the trithionate degradation rate.

6.2 MODELLING OF TRITHIONATE DEGRADATION

Two types of experimental method were used to investigate the reaction kinetics of the degradation of trithionate: the integrated rate method and the initial rate method. The integrated rate method gave useful information about the system and showed trends consistent with those found using the initial rate method. The analysis which follows is based primarily on results derived from the initial rate method, as in these tests the experimental variables could be better controlled over the short duration of each test.

The effects noted in the testwork on reaction kinetics were combined to derive a mathematical model to express the trithionate degradation rate as a function of the solution conditions.

It was found that the rate of trithionate degradation was first order with respect to the trithionate concentration. The observed rate could thus be expressed by Equation 6.3. The observed rate constant, k_{obs} , was found to depend on other solution conditions and the structure of this dependency was determined by testing one solution variable at a time.

$$-d[\text{S}_3\text{O}_6^{2-}]/dt = k_{\text{obs}} [\text{S}_3\text{O}_6^{2-}] \quad [6.3]$$

For a solution of sodium trithionate in water at 40 °C, the observed rate constant was found to have the magnitude 0.012 h⁻¹ (see Section 5.4). The observed rate constant k_{obs} in Equation 6.3 can thus be expressed as Equation 6.4 under these conditions.

$$k_{\text{obs}} = k_0 = 0.012 \text{ h}^{-1} \quad [6.4]$$

The presence of hydroxide at pH ~11 and less (at 40 °C) increased the trithionate degradation rate. In this case, the dependency of the observed rate constant on the hydroxide concentration could be expressed by Equation 6.5 (see Section 5.5).

$$k_{\text{obs}} = k_1[\text{OH}^-] + k_0 = 0.74 \text{ M}^{-1} \cdot \text{h}^{-1}[\text{OH}^-] + 0.012 \text{ h}^{-1} \quad [6.5]$$

The presence of ammonia and ammonium, which are of importance in the ammoniacal gold leaching system, were found to influence the trithionate degradation rate. Addition of ammonia to the system also increased the pH. In deriving the dependency of the observed rate constant on the ammonia concentration, it was thus necessary to correct for the dependency on the hydroxide concentration determined earlier. In a plot of the corrected rate constant against the ammonia concentration, fixing the intercept as the baseline degradation rate in water, the observed rate constant could be expressed by Equation 6.6. (See Section 5.8)

$$k_{\text{obs}} = k_2[\text{NH}_3] + k_1[\text{OH}^-] + k_0 = 0.0081\text{M}^{-1}.\text{h}^{-1}[\text{NH}_3] + 0.74\text{M}^{-1}.\text{h}^{-1}[\text{OH}^-] + 0.012\text{h}^{-1} \quad [6.6]$$

The equivalent dependency on ammonia concentration derived by Naito et al. expressed in a similar way as Equation 6.6 showed a dependency as in Equation 6.7.

$$k_{\text{obs}} = 0.0031\text{M}^{-1}.\text{h}^{-1}[\text{NH}_3] + 0.012\text{h}^{-1} \quad [6.7]$$

These authors did not state the pH of their work nor did they investigate any effects of hydroxide concentration or pH on the degradation rate. Their ammonia dependency was much less than that obtained in this work. However, the value of the gradient in the plot of the adjusted observed rate constant versus the ammonia concentration was very sensitive to the intercept value selected, and within the error range of each data point, a number of trend lines could be fit to the data. The ammonia dependency was of the same order of magnitude.

The influence of the ammonium ion was to increase the rate of trithionate degradation. The potassium ion gave a very similar effect and the two ions are of a similar size, so it was proposed that the ammonium ion's interaction was based on its association with the trithionate ion (see Section 6.1). At neutral pH in the absence of ammonia, the observed rate constant could be expressed by Equation 6.8. In this case, no correction for hydroxide concentration was necessary as the pH was neutral.

$$k_{\text{obs}} = k_3[\text{NH}_4^+] + k_0 = 0.01\text{M}^{-1}.\text{h}^{-1}[\text{NH}_4^+] + 0.012\text{h}^{-1} \quad [6.8]$$

Other solution components like bicarbonate, carbonate, sulfate and oxygen were shown to have a negligible effect on the trithionate degradation rate.

The interaction between trithionate and thiosulfate was more complex, depending on both the thiosulfate concentration and the ammonium concentration. For the purposes of modelling the trithionate kinetics, the conditions expected to most closely match typical gold leaching conditions were considered. Typical thiosulfate concentrations used in gold leaching are around 0.2 M, and this concentration decreases with time. At the high pHs used in gold leaching, most of the total ammonia present (typically 0.2 – 0.4 M) is expected to be present as ammonia, not ammonium ions, so typically the ammonium ion concentration is expected to be less than 0.2 M. Under these conditions, the effect of thiosulfate on the observed rate constant for trithionate degradation was very small, and for the purposes of modelling trithionate kinetics, the effect of thiosulfate was considered negligible.

No interaction of trithionate with copper was accounted for, as in the presence of sufficient ammonia, cupric copper was found to have no significant effect on the trithionate degradation rate.

The degradation of trithionate was expressed as the sum of various interactions, occurring in parallel. Using the data at 40 °C the various interactions were combined as in Equation 6.9, using Equations 6.5, 6.6 and 6.8.

$$k_{\text{obs}} = k_3[\text{NH}_4^+] + k_2[\text{NH}_3] + k_1[\text{OH}^-] + k_0 \quad [6.9]$$

$$= 0.01\text{M}^{-1}.\text{h}^{-1}[\text{NH}_4^+] + 0.0081\text{M}^{-1}.\text{h}^{-1}[\text{NH}_3] + 0.74\text{M}^{-1}.\text{h}^{-1}[\text{OH}^-] + 0.012\text{h}^{-1}$$

The same approach of parallel interactions was used by Naito et al. (1975) but they only examined the effects of water, ammonia and thiosulfate, and at concentrations that were not specifically relevant to gold leaching.

The data for the measured observed rate constants for the initial rate tests are shown plotted against pH in Figures 6.2 to 6.4 for three representative ranges in total ammonia plus ammonium concentrations. The observed rate constant as calculated by Equation

6.9 is shown superimposed for each. To calculate k_{obs} from Equation 6.9, the pH was converted to $[\text{OH}^-]$, and also used to calculate the ratio of ammonia to ammonium, given the total ammonia plus ammonium and using the pK_a value for ammonia of 8.8 at 40 °C (Dean, 1992).

Qualitatively, the modelled values match the experimental trends, showing a local minimum in degradation rate at pH around 10, but the experimental data shows a lower minimum degradation rate at high ammonia / ammonium concentrations than the model predicts (i.e. the minimum rate is lower). Figure 6.5 shows the calculated rate constant plotted against the observed rate constant for all the data on a logarithmic scale. In some cases the ammonia concentration was not measured but estimated based on the ammonium concentration and pH. This is indicated in Figure 6.5 where the correlation coefficient, R^2 , is equal to 0.6. While the scatter is significant, the gradient is one, showing an overall qualitative match. The typical 10 % error margins in the experimental data are thought to contribute to this scatter significantly.

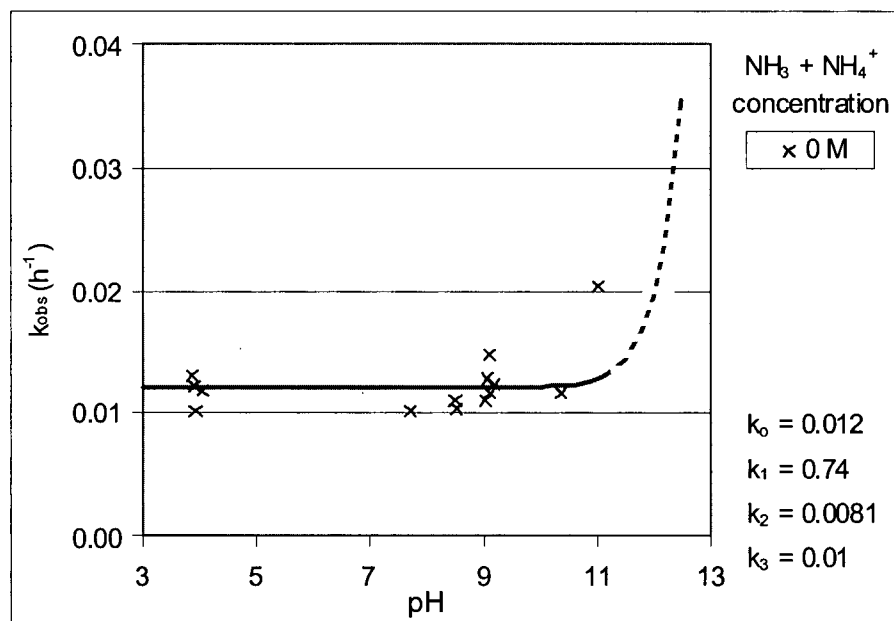


Figure 6.2 : Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0 M against pH, with modelled trend superimposed (using $k_2 = 0.0081 \text{ M}^{-1} \cdot \text{h}^{-1}$)

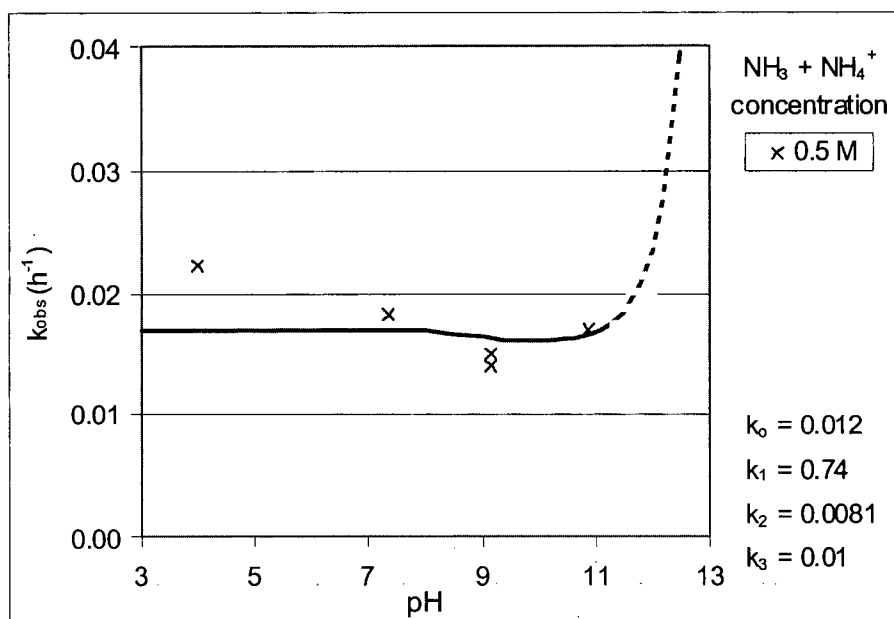


Figure 6.3 : Plot of observed rate constant k_{obs} for trithionate degradation at 40°C for an ammonia + ammonium concentration of 0.5 M against pH, with modelled trend superimposed (using $k_2 = 0.0081 \text{ M}^{-1}.\text{h}^{-1}$)

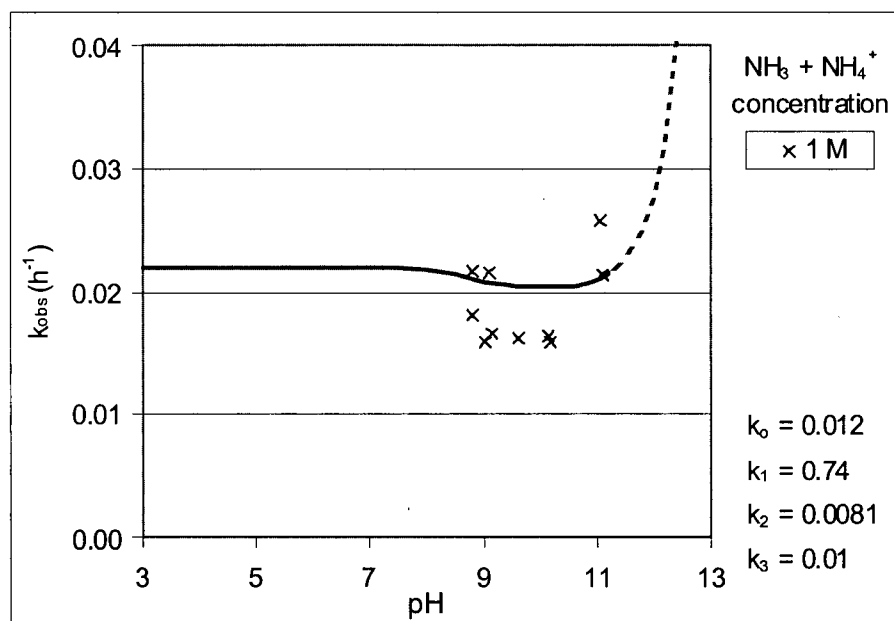


Figure 6.4 : Plot of observed rate constant k_{obs} for trithionate degradation at 40°C for an ammonia + ammonium concentration of 0.9 – 1.2 M against pH, with modelled trend superimposed (using $k_2 = 0.0081 \text{ M}^{-1}.\text{h}^{-1}$)

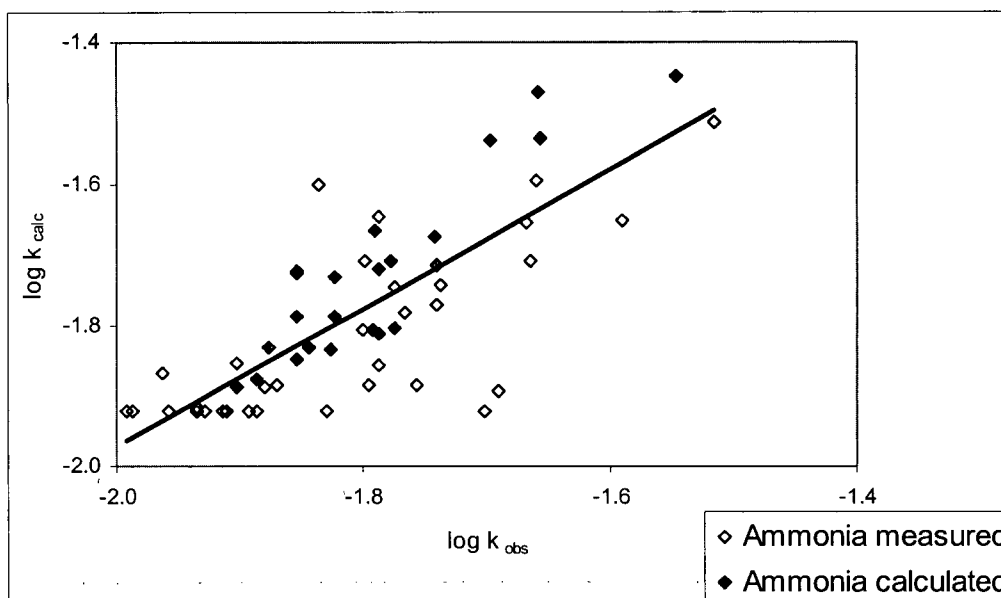


Figure 6.5 : Plot of calculated rate constant k_{calc} versus observed rate constant k_{obs} for trithionate degradation at 40 °C for all data, using $k_2 = 0.0081 \text{ M}^{-1} \cdot \text{h}^{-1}$

If the dependency of the observed rate constant on ammonia (k_2) is changed to $0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$ (as indicated by the best fit line through the ammonia dependency data points, Figure 5.6, Section 5.8), the fit of the model appears better, as is seen for different total ammonia concentrations in Figures 6.6 to 6.12. However, in the plot of the calculated versus the observed rate constant in Figure 6.13, the correlation coefficient R^2 is again 0.6. As discussed earlier, the slope of the line in Figure 5.6 for the ammonia dependency was very sensitive to the chosen intercept and given the error margins for each data point, there were lines of many slopes that were consistent with the data. If we refer back to Equation 5.11 where the dependency of the rate constant on both the ammonia and ammonium concentrations was measured, a value for k_2 of $0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$ was more consistent with the experimental data.

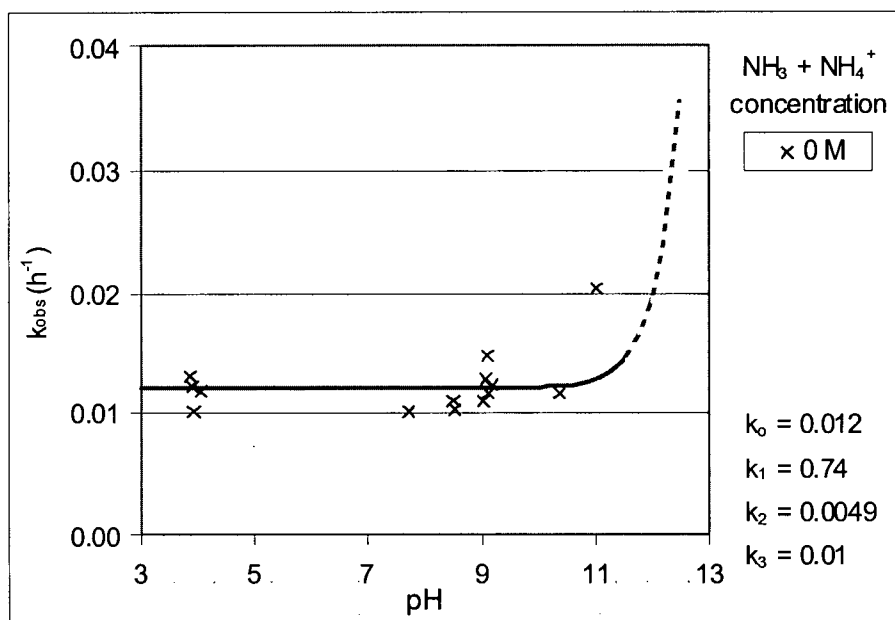


Figure 6.6 : Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1}.\text{h}^{-1}$)

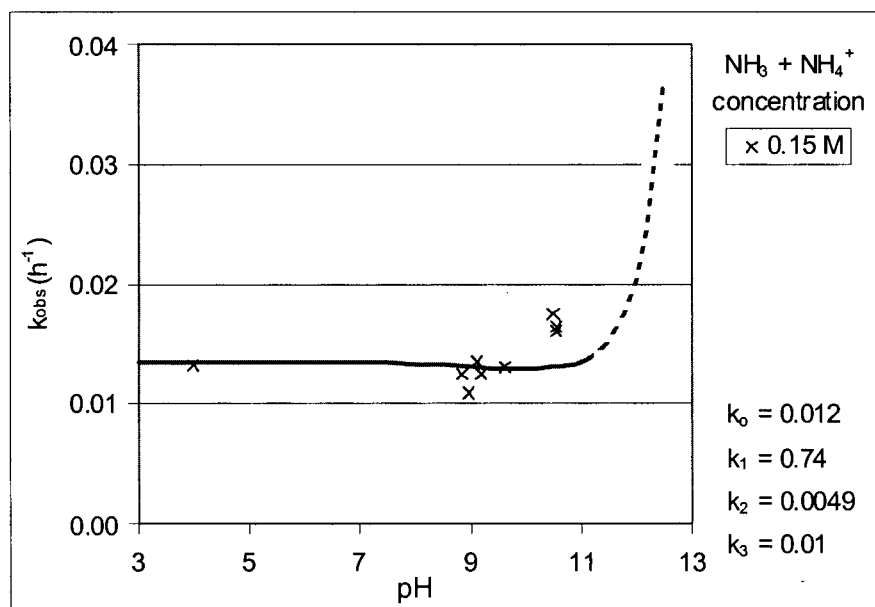


Figure 6.7 : Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.1 – 0.2 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1}.\text{h}^{-1}$)

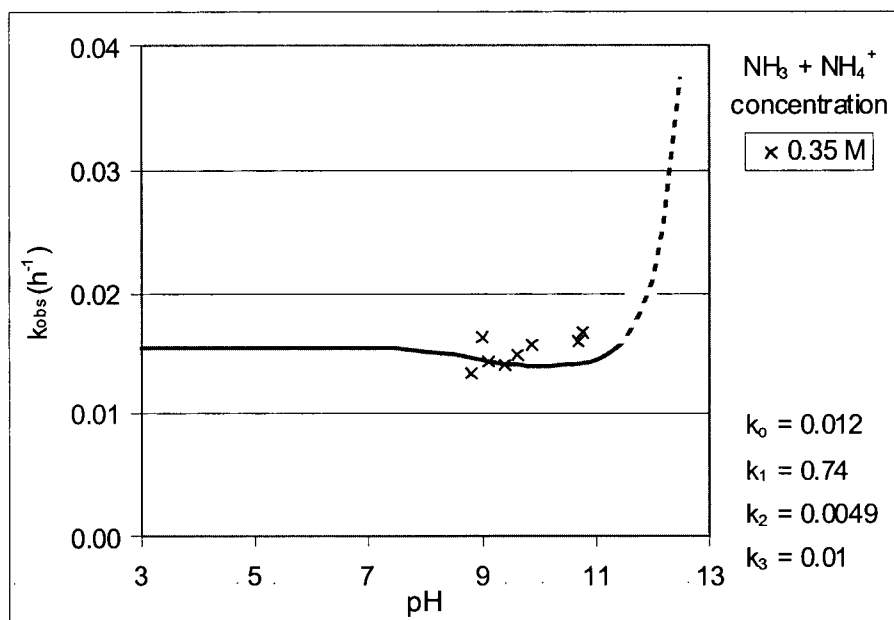


Figure 6.8 : Plot of observed rate constant k_{obs} for trithionate degradation at 40°C for an ammonia + ammonium concentration of $0.3 - 0.4\text{ M}$ against pH, with modelled trend superimposed (using $k_2 = 0.0049\text{ M}^{-1}.\text{h}^{-1}$)

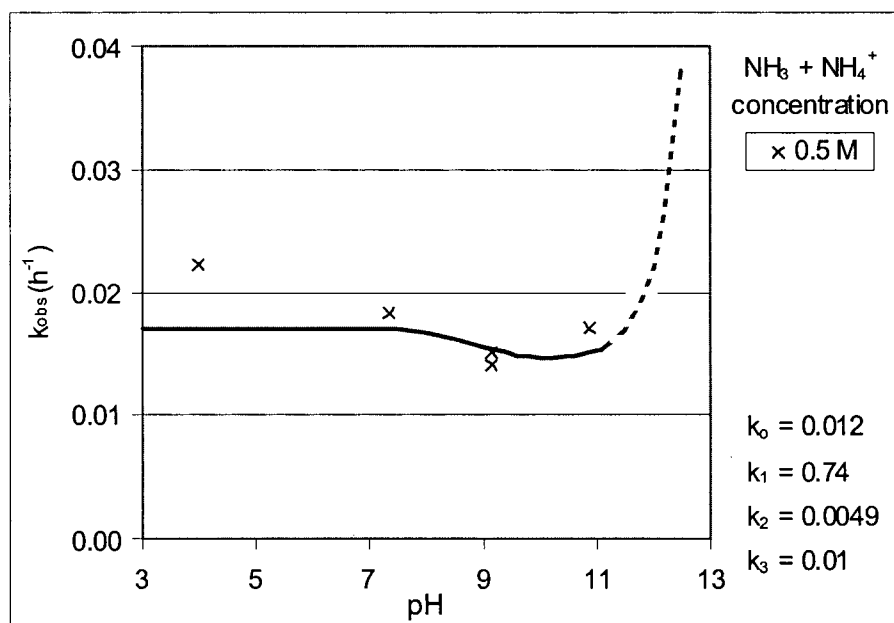


Figure 6.9 : Plot of observed rate constant k_{obs} for trithionate degradation at 40°C for an ammonia + ammonium concentration of 0.5 M against pH, with modelled trend superimposed (using $k_2 = 0.0049\text{ M}^{-1}.\text{h}^{-1}$)

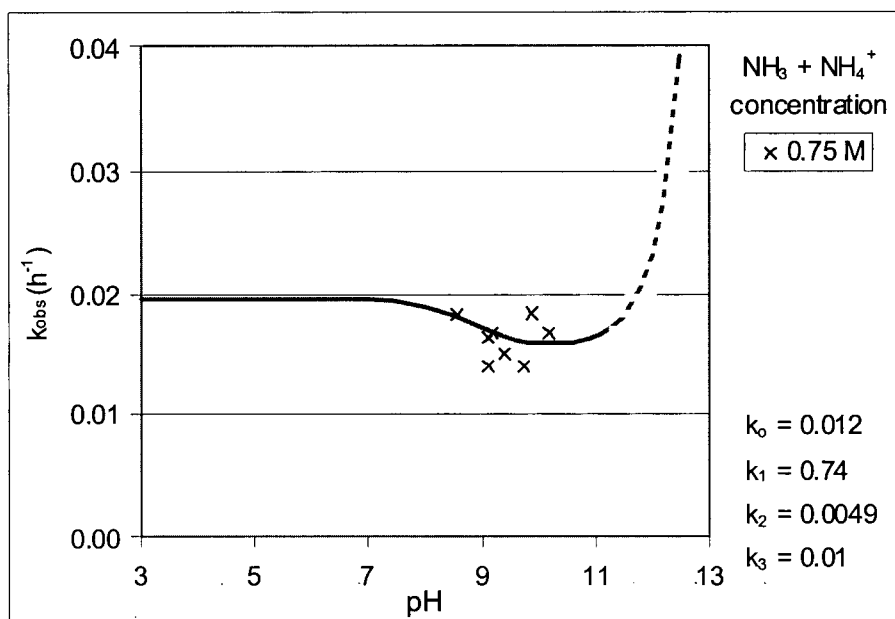


Figure 6.10 : Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.7 – 0.8 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$)

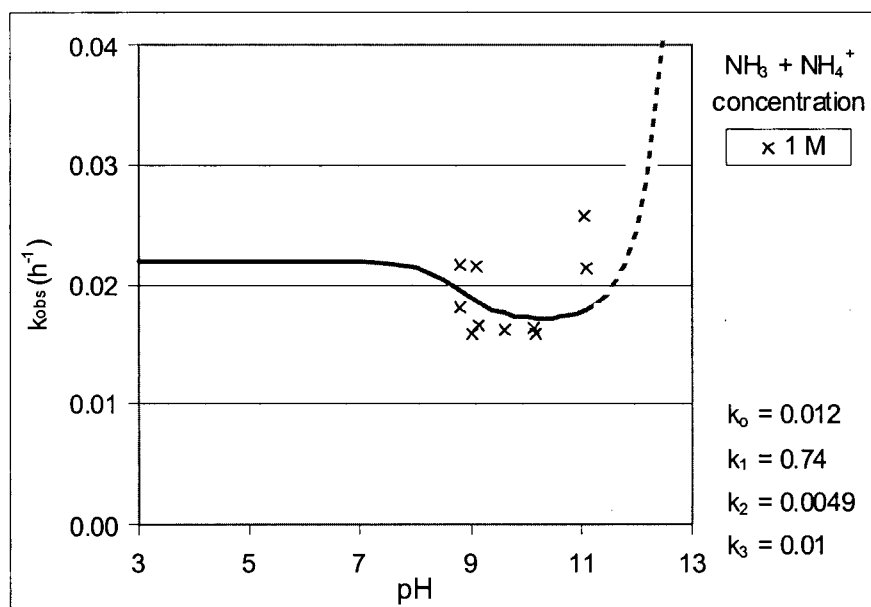


Figure 6.11 : Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 0.9 – 1.2 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$)

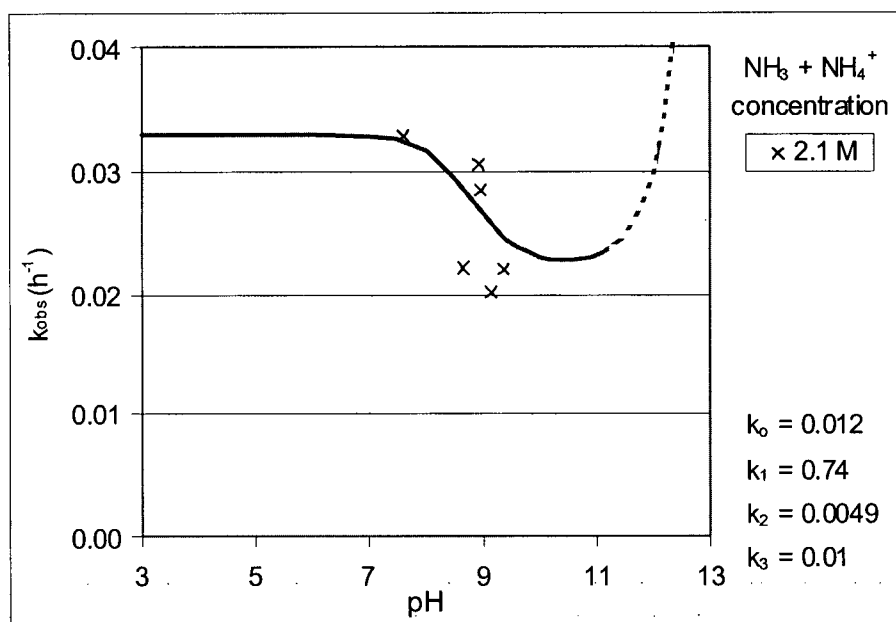


Figure 6.12 : Plot of observed rate constant k_{obs} for trithionate degradation at 40 °C for an ammonia + ammonium concentration of 1.8 – 2.6 M against pH, with modelled trend superimposed (using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$)

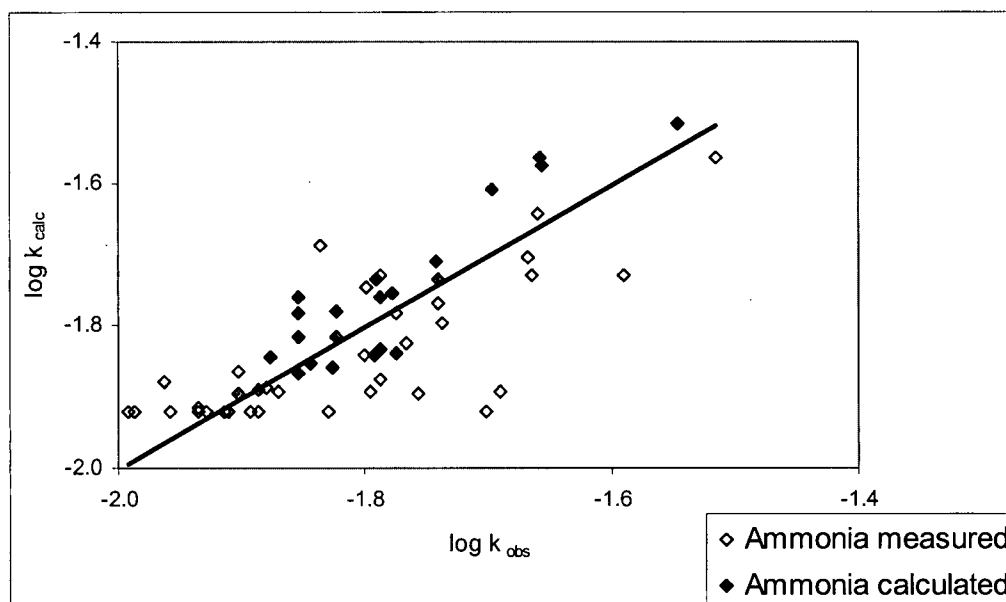


Figure 6.13 : Plot of calculated rate constant k_{calc} versus observed rate constant k_{obs} for trithionate degradation at 40 °C for all data, using $k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$

To summarize, based on the experimental work, the degradation of trithionate to thiosulfate and sulfate at 40 °C could be adequately modelled using the rate equation and parameters expressed in Equation 6.10. The slow reaction of trithionate with water, represented by k_0 , will predominate in typical gold leaching solutions. This rate equation was used in combination with rate equations for other sulfur species to model the overall sulfur speciation expected during thiosulfate degradation during gold leaching. This is discussed in Chapter 7, where it will be shown that although the model for trithionate degradation is prone to a fair amount of variability, this does not affect the overall system speciation to any significant degree.

$$-d[S_3O_6^{2-}]/dt = (k_3[NH_4^+] + k_2[NH_3] + k_1[OH^-] + k_0)[S_3O_6^{2-}] \quad [6.10]$$

where at 40 °C

$$k_0 = 0.012 \text{ h}^{-1}$$

$$k_1 = 0.74 \text{ M}^{-1} \cdot \text{h}^{-1}$$

$$k_2 = 0.0049 \text{ M}^{-1} \cdot \text{h}^{-1}$$

$$k_3 = 0.01 \text{ M}^{-1} \cdot \text{h}^{-1}$$

7 MODELLING OF SULFUR OXYANION SPECIATION DURING THIOSULFATE DEGRADATION

7.1 INTRODUCTION

The degradation of thiosulfate in gold leaching systems, which also involve ammoniacal and copper components, is complex and not fully understood. It has been proposed that thiosulfate can degrade directly to tetrathionate, trithionate or sulfate, but tetrathionate and trithionate themselves undergo further degradation. No published model for this system has been found in the public domain. This chapter shows how a simple model was set up for thiosulfate degradation in the absence of ores and shows the model sensitivity to both the model parameters and experimental conditions. The model was tested against a set of experimental data in the absence of ore and compared with the experimental behaviour in the presence of an ore. Based on this evaluation, the shortcomings and scope of use of the model were identified. The model was used to show some expected effects of changing the solution conditions on thiosulfate degradation.

7.2 MODEL SETUP

Figure 7.1 shows a simplified schematic of some of the possible reaction pathways for thiosulfate in an ammoniacal, copper-containing solution. This schematic was used to set up a basic kinetic model of the system, using rate equations derived from the literature or from experimental work in this thesis (for trithionate). It should be noted that this schematic is not exhaustive but the reactions represented are expected to characterise the system sufficiently well to be able to use the model to identify the factors playing the most significant role in thiosulfate degradation and sulfur oxyanion speciation.

In the schematic the reactions are labelled R1 to R6, with fractions a, b, c and d representing the fraction of thiosulfate at any time reacting through each of the pathways shown. It is recognised that the values for a, b, c and d could change with time, but this was not incorporated into the model.

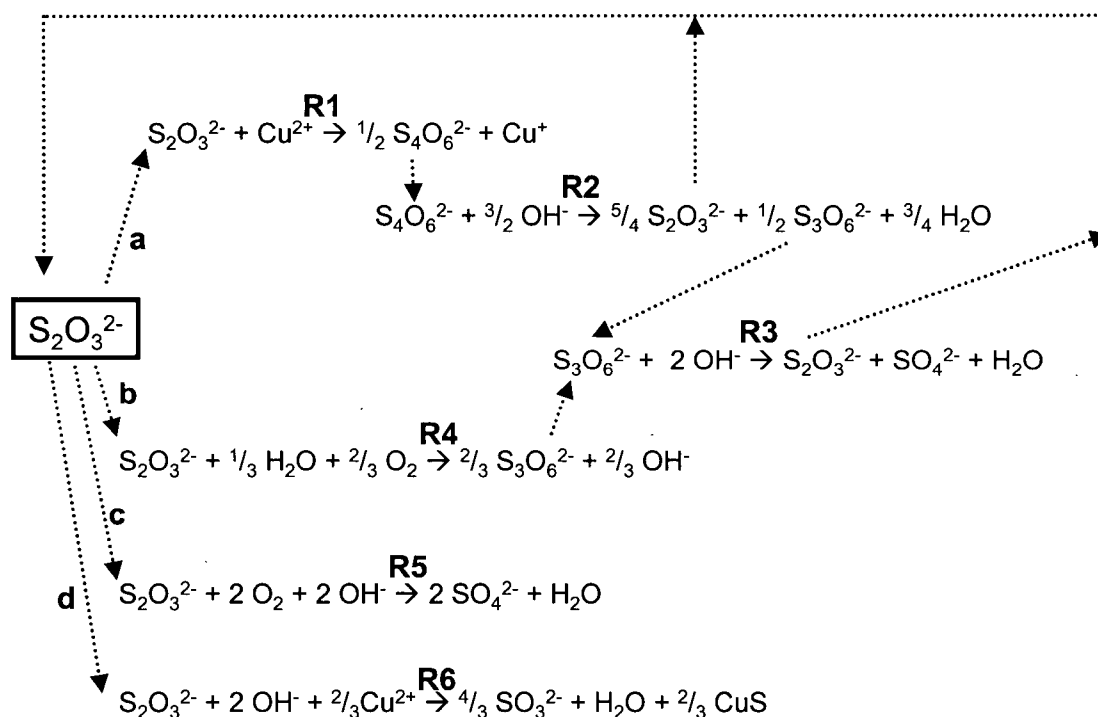


Figure 7.1 : Schematic showing the basis for modelling

The way in which each of reactions R1 to R6 were handled in setting up the model is discussed in turn below.

7.2.1 R1 - Thiosulfate Degradation to Tetrathionate



The rate equation for the reaction between thiosulfate and copper was taken from work by Byerley et al (1973a). The rate of decrease of cupric copper concentration by reaction with thiosulfate in the absence of oxygen was given by Equation 7.2.

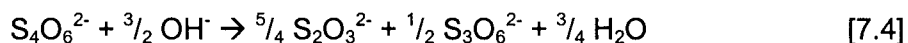
$$-d[\text{Cu}^{2+}]/dt = k_{R1} [\text{Cu}^{2+}][\text{S}_2\text{O}_3^{2-}]/[\text{NH}_3] \quad [7.2]$$

where $k_{R1} = 8.5 \times 10^{-4} \text{ s}^{-1}$ at 30 °C. Using the Arrhenius equation and the activation energy of 102.5 kJ/mol, the rate constant at 25 °C was extrapolated to be $4.2 \times 10^{-4} \text{ s}^{-1}$. Based on the reaction stoichiometry for Reaction R1, the rate of thiosulfate degradation at 25 °C could be expressed by Equation 7.3.

$$-d[S_2O_3^{2-}]/dt = 4.2 \times 10^{-4} [Cu^{2+}][S_2O_3^{2-}]/[NH_3] \text{ M.s}^{-1} \quad [7.3]$$

The rate constant was found to increase up to 40 times in the presence of oxygen, but it is also known that other reactions can occur in the presence of oxygen (e.g. R4 and R5).

7.2.2 R2 - Tetrathionate Degradation



In the absence of ammonia, copper and oxygen, the rate of the alkaline decomposition of tetrathionate was described by Zhang and Dreisinger (2002) in Equation 7.5.

$$-d[S_4O_6^{2-}]/dt = k [S_4O_6^{2-}][OH^-] \quad [7.5]$$

where $k = 1.38 \times 10^3 \text{ M}^{-1}.\text{h}^{-1}$ at 22°C and the activation energy was 98.5 kJ/mol . Hence at 25°C , $k = 5.74 \times 10^{-1} \text{ M}^{-1}.\text{s}^{-1}$.

The effect of copper was not considered by Zhang and Dreisinger in the derivation of this rate equation and copper has been suggested to react with tetrathionate at a significant rate (Breuer and Jeffrey, 2003b). Also, the possible catalytic effect of thiosulfate on the degradation was not considered.

While Naito et al. (1970b) examined the reactions of tetrathionate in ammoniacal systems, no rate equation was derived. The effect of thiosulfate was addressed in a study by Rolia and Chakrabarti (1982) who derived a rate equation for tetrathionate degradation in the absence of ammonia and copper at pH 11. The rate equation in the presence of thiosulfate at 25°C was expressed as Equation 7.6.

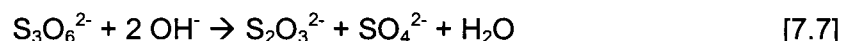
$$-d[S_4O_6^{2-}]/dt = (k_{R2-0} + k_{R2-1}[S_2O_3^{2-}])[S_4O_6^{2-}][OH^-] \quad [7.6]$$

where $k_{R2-0} = 0.022 \text{ M}^{-1}.\text{s}^{-1}$ and $k_{R2-1} = 2.77 \text{ M}^{-2}.\text{s}^{-1}$. The rate constants were determined using the published rate constants at 35°C and the activation energy in the absence of thiosulfate (115.5 kJ/mol).

In the absence of thiosulfate, the rate equation in Equation 7.6 is reduced to Equation 7.5, but it should be noted that the rate constant k_{R2-0} is more than 10 times smaller than that found by Zhang and Dreisinger. It was proposed by Zhang and Dreisinger that the presence of oxygen in the work of Rolia and Chakrabarti and the absence of oxygen in their own work was probably the reason for this discrepancy, and that oxidants could possibly retard the rate of tetrathionate degradation. Breuer and Jeffrey (2004) found that the ionic strength had an effect on tetrathionate degradation and proposed that the difference between the rate constants of Zhang and Dreisinger and Rolia and Chakrabarti was because the solution ionic strengths were different.

Since the modelled system was for thiosulfate degradation in the presence of oxygen and thiosulfate, the rate equation proposed by Rolia and Chakrabarti (Equation 7.6) was used in the model.

7.2.3 R3 – Trithionate Degradation



While limited literature data is available for the degradation of trithionate in ammoniacal solutions, the methodology and conditions used to derive the kinetics were not entirely suitable for gold leaching conditions. The rate equation derived in this thesis (see Chapter 6) was used in modelling the system, as shown in Equation 7.8. The limitations of this rate equation were discussed in Chapter 6. This rate equation is most suitable for pH values where the ammonium to thiosulfate ratio is small, as discussed in Chapters 5 and 6. It should be noted that the rate equation in Equation 7.8 includes the hydrolysis of trithionate, represented by k_0 .

$$-d[S_3O_6^{2-}]/dt = (k_0 + k_1[OH^-] + k_2[NH_3] + k_3[NH_4^+])[S_3O_6^{2-}] \quad [7.8]$$

where at 40 °C

$$k_0 = 3.3 \times 10^{-6} \text{ s}^{-1}$$

$$k_1 = 2.1 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$k_2 = 1.3 \times 10^{-6} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$k_3 = 2.7 \times 10^{-6} \text{ M}^{-1} \cdot \text{s}^{-1}$$

Using the activation energy of 75.3 kJ/mol, the parameters at 25 °C were calculated to

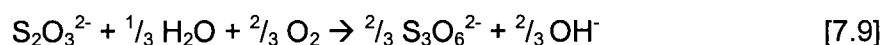
be $k_0 = 1.4 \times 10^{-8} \text{ s}^{-1}$

$$k_1 = 5.8 \times 10^{-5} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$k_2 = 3.1 \times 10^{-7} \text{ M}^{-1} \cdot \text{s}^{-1}$$

$$k_3 = 6.4 \times 10^{-7} \text{ M}^{-1} \cdot \text{s}^{-1}$$

7.2.4 R4 – Thiosulfate Degradation to Trithionate



The degradation of thiosulfate directly to trithionate in the presence of copper amines and oxygen as proposed by Byerley et al. (1975) was discussed in the literature review in Chapter 2. The reaction kinetics of thiosulfate degradation were measured by measuring the oxygen consumption. It was found that under certain conditions, the initial rate of oxygen consumption generally corresponded to the formation of trithionate only, while after longer times when the maximum oxygen consumption was reached, both trithionate and sulfate were formed. Byerley et al. did not deduce a comprehensive rate equation using their data, as the system appeared quite complex. However, for the purposes of this model, the kinetic data for the initial rate of oxygen consumption measured by Byerley et al. was used to derive an approximate rate equation, as follows.

As noted by Byerley et al., the rate of oxygen consumption was found to be proportional to the copper and oxygen concentrations. The dependency on thiosulfate and ammonia concentrations was not straightforward. Assuming that the rate of thiosulfate degradation was equal to the rate of oxygen consumption (as assumed by Byerley et al.) the logarithm of this rate was plotted against the logarithm of ammonia concentration in Figure 7.2 and against the logarithm of the thiosulfate concentration in Figure 7.3.

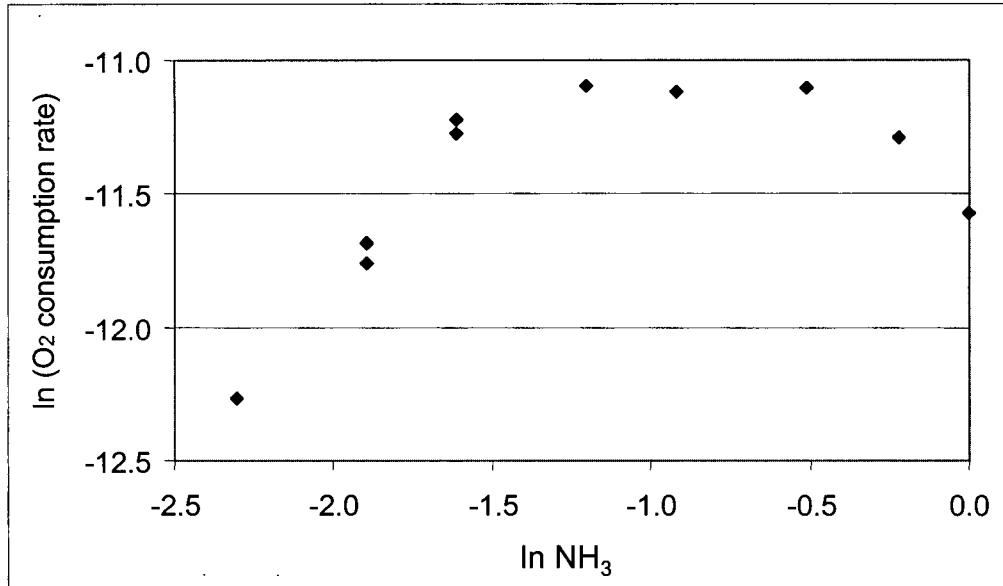


Figure 7.2 : Logarithm of the oxygen consumption rate versus the logarithm of ammonia concentration for thiosulfate degradation to trithionate in the presence of oxygen – Data from Byerley et al (1975)

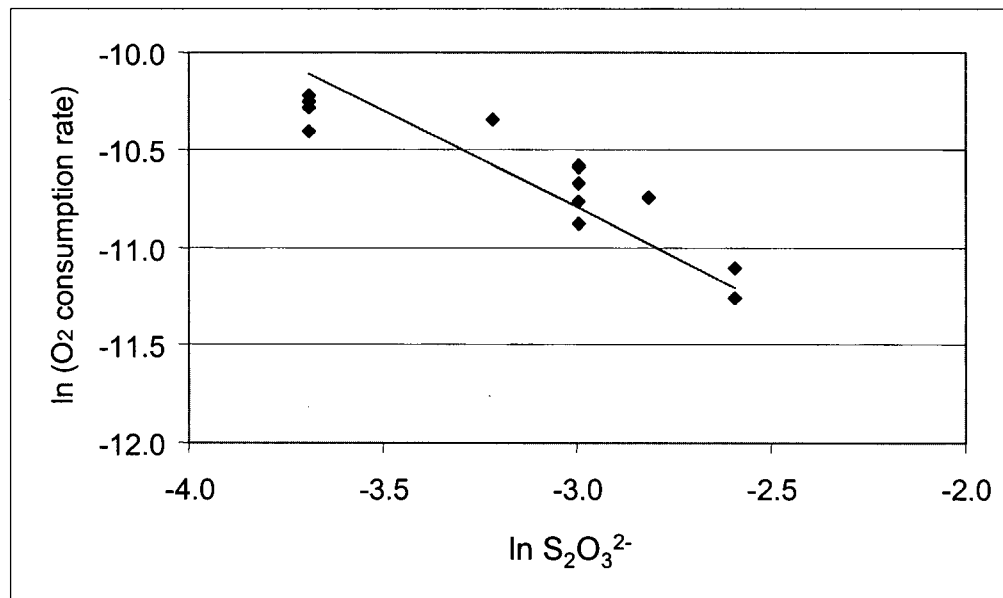


Figure 7.3 : Logarithm of the oxygen consumption rate versus the logarithm of thiosulfate concentration for thiosulfate degradation to trithionate in the presence of oxygen – Data from Byerley et al (1975)

It was found that the rate of oxygen consumption had a reaction order of approximately -1 with respect to thiosulfate (for concentrations greater than 0.025 M) and approximately zero with respect to ammonia (in the range of about 0.2 M to 0.6 M ammonia). The rate was independent of the ammonia concentration for ammonia concentrations where the cupric tetraammine species was expected to be at a maximum concentration relative to the cupric concentrations used in this work, and decreased at higher or lower ammonia concentrations. Therefore Byerley et al. proposed that the cupric tetraammine species is the active cupric species in the formation of trithionate from thiosulfate.

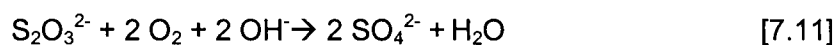
Based on this preliminary evaluation of Byerley et al's data, the overall rate equation was expressed as Equation 7.10.

$$-d[S_2O_3^{2-}]/dt = k_{R4} [Cu^{2+}][O_2]/[S_2O_3^{2-}] \quad [7.10]$$

The rate constant k_{R4} was estimated for each set of data, based on the measured rate and the test conditions, and the average rate constant was found to be $1.03 \pm 0.17 \text{ s}^{-1}$ (at pH 11.2, 30 °C at which most of the data was available). No activation energy was measured but given the limited accuracy of determining the rate using oxygen consumption and of deriving the rate equation shown in Equation 7.10, the rate constant at 25 °C is expected to be of the same order of magnitude as that at 30 °C. Hence using the rate constant estimated at 30 °C was considered sufficiently accurate within these limitations.

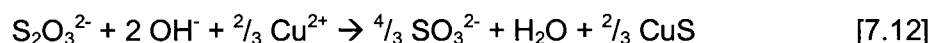
A concern in using this rate equation is the fact that the oxygen consumption rate is not likely to be a direct indicator of the thiosulfate degradation rate. Also, the rate equation and rate constant were derived under very specific conditions which may not always be applicable to thiosulfate leaching conditions.

7.2.5 R5 - Thiosulfate Degradation Directly to Sulfate



It has been found that sulfate can form directly from thiosulfate in the presence of oxygen (Byerley et al, 1975). However, under conditions typical in gold leaching, the proportion of sulfate formed (via Reaction R5) to trithionate formed is expected to be very low, as documented in the literature review in Chapter 2. Since the extent of this reaction is expected to be negligible compared with competing reactions and no rate equation was available, Reaction R5 was excluded from the model.

7.2.6 R6 - Thiosulfate Degradation to Sulfide



While reaction R6 showing the formation of copper sulfide from the reaction between copper and thiosulfate was included in Figure 7.1 for completeness, kinetic data on this reaction was not available. Also during gold leaching, based on mass balances of the sulfur species, sulfide does not appear to be formed in any significant quantities, if at all (Lam, 2002). Hence this reaction was not included in the model.

7.2.7 Incorporation of the Rate Equations into a Model - Method and Constraints

The model was set up in a simple spreadsheet format. The concentration profiles of the various sulfur oxyanion species with time were determined iteratively using time intervals of 0.05 hours over 24 hours. The change in concentration of each of the species thiosulfate, trithionate, tetrathionate and sulfate was determined using the rate equations in Equations 7.3, 7.6, 7.8 and 7.10 and the reaction stoichiometries of Equations 7.1, 7.4, 7.7 and 7.9. These equations accounted for all the sulfur species in the model so the total sulfur present remained constant.

The concentrations of the sulfur oxyanions at time t as a function of the solution conditions, reaction rates and reaction stoichiometry are shown in Equations 7.13 to 7.16.

$$[S_2O_3^{2-}]_t = [S_2O_3^{2-}]_{t-1} + (5/4 r_{2t} + r_{3t} - r_{1t} - r_{4t})\Delta t \quad [7.13]$$

$$[S_4O_6^{2-}]_t = [S_4O_6^{2-}]_{t-1} + (1/2 r_{1t} - r_{2t})\Delta t \quad [7.14]$$

$$[S_3O_6^{2-}]_t = [S_3O_6^{2-}]_{t-1} + (1/2 r_{2t} + 2/3 r_{4t} - r_{3t})\Delta t \quad [7.15]$$

$$[SO_4^{2-}]_t = [SO_4^{2-}]_{t-1} + (r_{3t})\Delta t \quad [7.16]$$

where

$$r_{1t} = ak_{R1} [S_2O_3^{2-}]_{t-1}[Cu]_{t-1}/[NH_3]_{t-1} \quad [7.17]$$

$$r_{2t} = (k_{R2-0} + k_{R2-1}[S_2O_3^{2-}]_{t-1}) [OH^-]_{t-1} [S_4O_6^{2-}]_{t-1} \quad [7.18]$$

$$r_{3t} = (k_0 + k_1[OH^-]_{t-1} + k_2[NH_3]_{t-1} + k_3[NH_4^+]_{t-1})[S_3O_6^{2-}]_{t-1} \quad [7.19]$$

$$r_{4t} = bk_{R4} [Cu]_{t-1}[O_2]_{t-1}/[S_2O_3^{2-}]_{t-1} \quad [7.20]$$

Standard values for the rate constants in Equations 7.17 to 7.20 and initial conditions are discussed in Section 7.3.

The model was subject to the following constraints:

- The only chemical reactions assumed to be occurring were those shown in Figure 7.1 as discussed above.
- It was assumed that any cuprous copper formed was immediately re-oxidised to cupric, so that the cupric concentration remained constant.
- It was assumed that the solutions contained 10 mg/l dissolved oxygen.
- The ammonia concentration, pH and dissolved oxygen concentration were assumed to remain constant.
- The pH was used to calculate the hydroxide ion concentration and the ratio of ammonia to ammonium given the total ammonia concentration.
- The effects of ore were ignored.
- The effects of other anions (e.g. sulfate) were ignored.

7.3 MODEL SENSITIVITY TO MODEL PARAMETERS

The model output is dependent on the form of the rate equations, the values of the rate constants and the solution conditions. Before testing the validity of the model against

experimental data, the sensitivity of the model to changing the model parameters was investigated. It was anticipated that the model as set up in Section 7.2 may not always be suitable to describe experimental observations during gold leaching as the conditions under which the various model rate equations were derived were not always related to gold leaching. By identifying the effects of the various parameters, a better understanding of possible shortcomings of the model in describing experimental situations could be gained.

In this section, the forms of the rate equations were not changed, but the qualitative effects of changing the rate constants for each rate equation (see Table 7.1) and also of varying the proportion of thiosulfate reacting to form tetrathionate versus trithionate (Reaction R1 versus Reaction R4) were investigated. As a standard condition, the rate constants discussed in Section 7.2 were used, and it was assumed that 80 % of the thiosulfate reacted to form tetrathionate via Reaction R1 and 20 % reacted to form trithionate via Reaction R4. These percentages were selected simply as examples, and are consistent with the observation (see later in Section 7.4) that a greater percentage of thiosulfate appears to react via Reaction R1 to form tetrathionate.

Table 7.1 : Model parameters used to test model sensitivity

Parameter	Standard value	Range tested
a (proportion of thiosulfate reacting via R1 to form tetrathionate)	80 %	0 – 100 %
b (proportion of thiosulfate reacting via R4 to form trithionate)	20 %	0 – 100 %
k_{R1}	$4.2 \times 10^{-4} \text{ s}^{-1}$	$4.2 \times 10^{-4} \text{ s}^{-1} \times 10$
k_{R2-0}	$0.022 \text{ M}^{-1} \cdot \text{s}^{-1}$	$0.022 \text{ M}^{-1} \cdot \text{s}^{-1} \times 10$
k_{R2-1}	$2.77 \text{ M}^{-2} \cdot \text{s}^{-1}$	$2.77 \text{ M}^{-2} \cdot \text{s}^{-1} \times 10$
k_0	$1.4 \times 10^{-8} \text{ s}^{-1}$	$1.4 \times 10^{-8} \text{ s}^{-1} \times 10$
k_1	$5.8 \times 10^{-5} \text{ M}^{-1} \cdot \text{s}^{-1}$	$5.8 \times 10^{-5} \text{ M}^{-1} \cdot \text{s}^{-1} \times 10$
k_2	$3.1 \times 10^{-7} \text{ M}^{-1} \cdot \text{s}^{-1}$	$3.1 \times 10^{-7} \text{ M}^{-1} \cdot \text{s}^{-1} \times 10$
k_3	$6.4 \times 10^{-7} \text{ M}^{-1} \cdot \text{s}^{-1}$	$6.4 \times 10^{-7} \text{ M}^{-1} \cdot \text{s}^{-1} \times 10$
k_{R4}	1.03 s^{-1}	$1.03 \text{ s}^{-1} \times 10$

The solution conditions in Table 7.2 were selected as standard conditions for the purposes of this evaluation.

Table 7.2 : Standard experimental parameters used in modelling

Leach conditions	Standard value
Temperature	25 °C
$[S_2O_3^{2-}]_0$	0.2 M
$[NH_3]_{tot}$	0.4 M
$[Cu^{2+}]$	30 mg/l
pH	10
DO ₂	10 mg/l

7.3.1 Proportion of Thiosulfate Forming Tetrathionate versus Trithionate

The proportion of thiosulfate reacting directly to form tetrathionate (Reaction R1) versus that reacting directly to form trithionate (Reaction R4) (i.e. a and b in Table 7.2) was considered. In Figure 7.4 it is assumed that thiosulfate does not form trithionate directly, only tetrathionate (i.e. a = 100%) while in Figure 7.5, only trithionate is formed (i.e. b = 100%). Two intermediate combinations of these two reaction paths are shown in Figures 7.6 and 7.7.

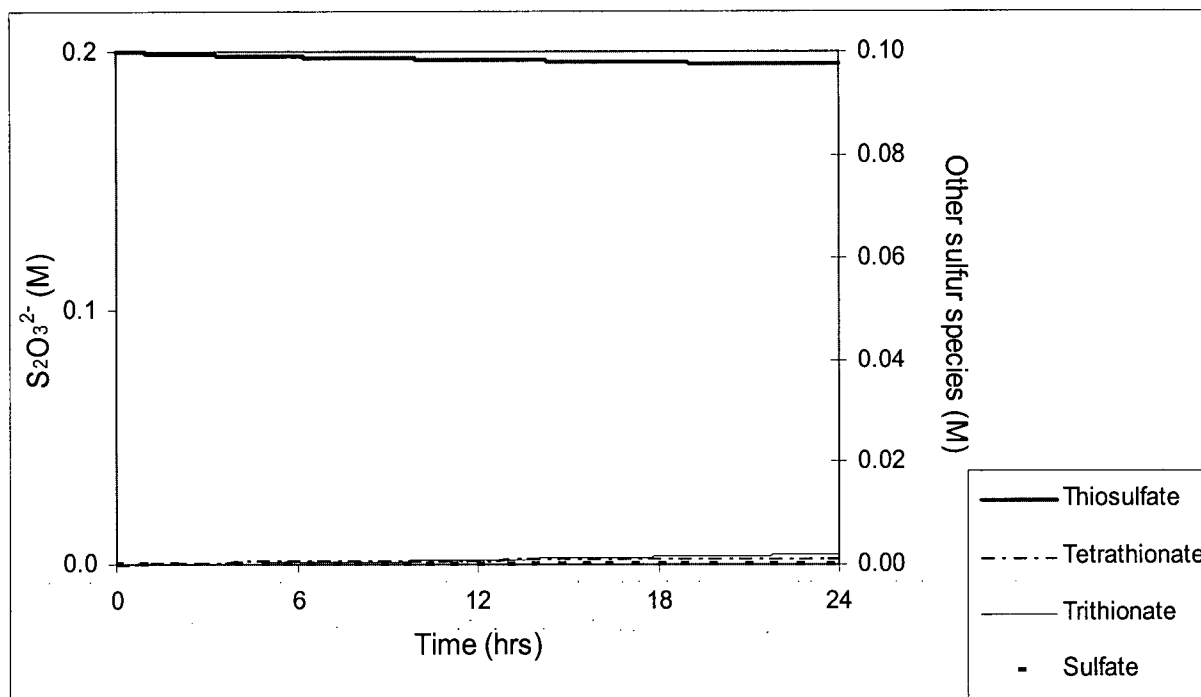


Figure 7.4 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation

- Assumed all thiosulfate degradation is via Reaction R1 ($a = 100\%$, $b = 0\%$).
- Initial conditions: $0.2\text{ M } S_2O_3^{2-}$, $0.4\text{ M } NH_3$, $30\text{ mg/l } Cu^{2+}$, pH 10, 25°C .

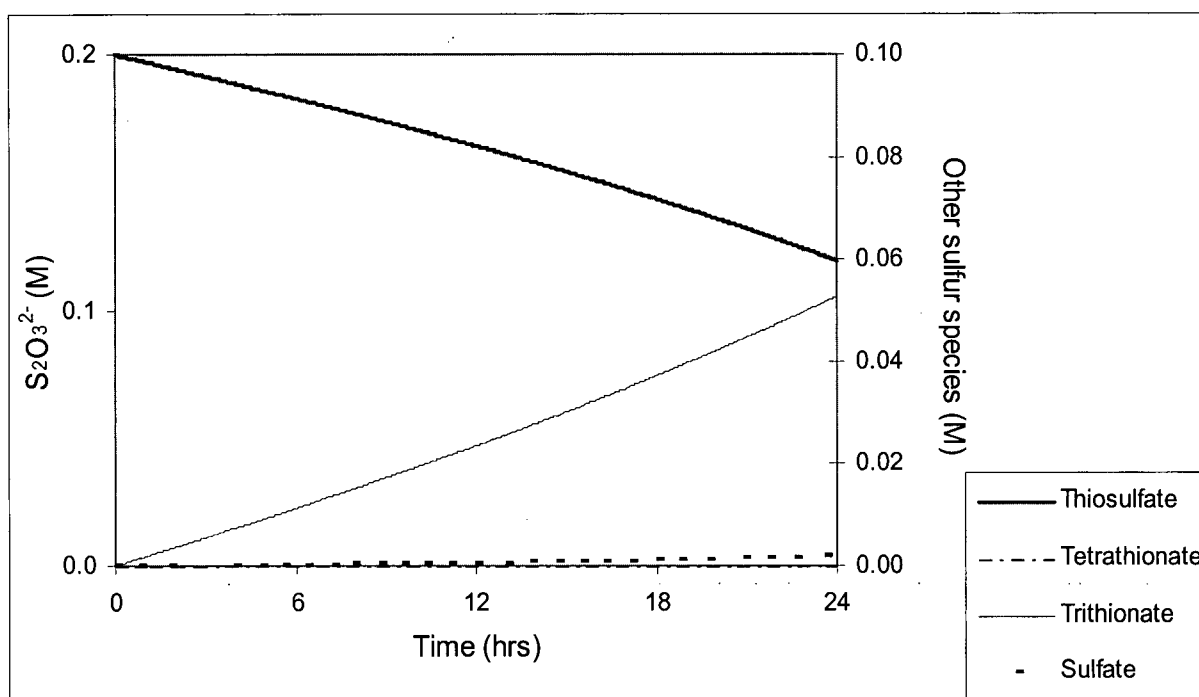


Figure 7.5 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation

- Assumed all thiosulfate degradation is via Reaction R4 ($a = 0 \%$, $b = 100 \%$).
- Initial conditions: $0.2 \text{ M S}_2\text{O}_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 10, 25°C .

Figures 7.4 and 7.5 show the extremes of the model with respect to the thiosulfate degradation pathway. From this it is obvious that the model output is very sensitive to the ratio of thiosulfate assumed to react to form tetrathionate versus the thiosulfate that forms trithionate directly. Qualitatively, where Reaction R1 to tetrathionate is favoured, the thiosulfate degradation curve is concave. While this is not immediately clear from Figure 7.4, it is apparent if the thiosulfate concentration axis is changed. Where Reaction R4 to trithionate is favoured, the thiosulfate degradation curve is convex and the trithionate formation curve is much more concave. These observations were used to assess the model against experimental data in Section 7.4.

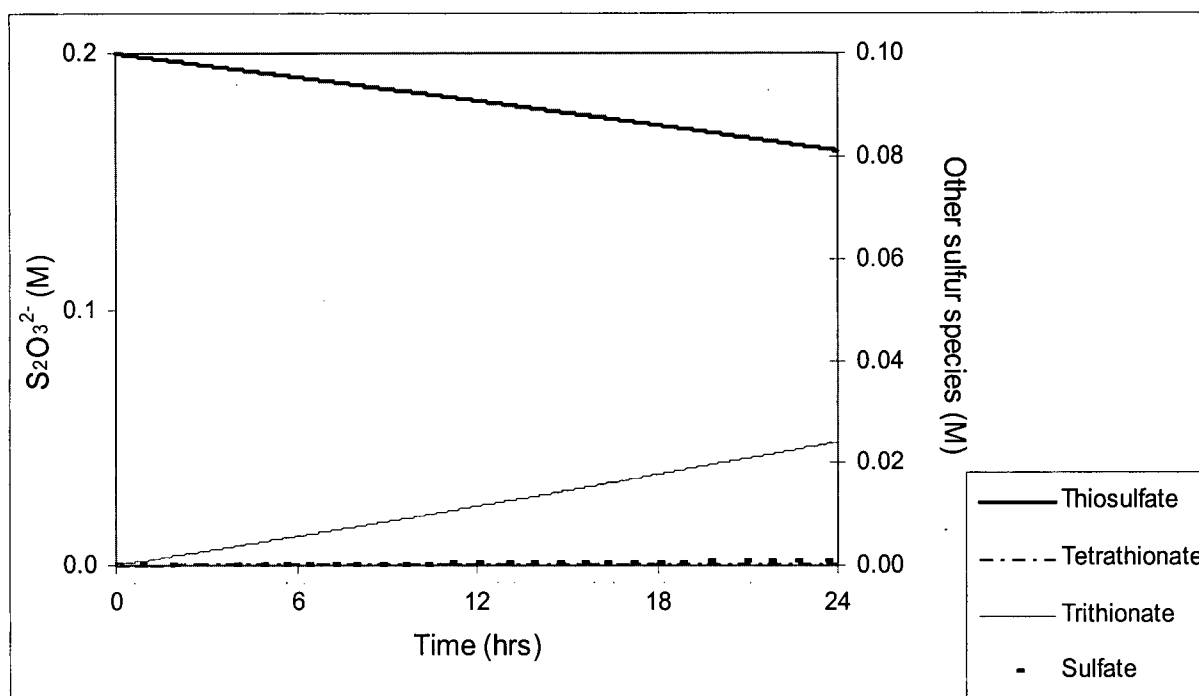


Figure 7.6 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation

- Assumed thiosulfate degradation is via both Reaction R1 and Reaction R4 (**a = 50 %**, **b = 50 %**).
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 10, 25 °C.

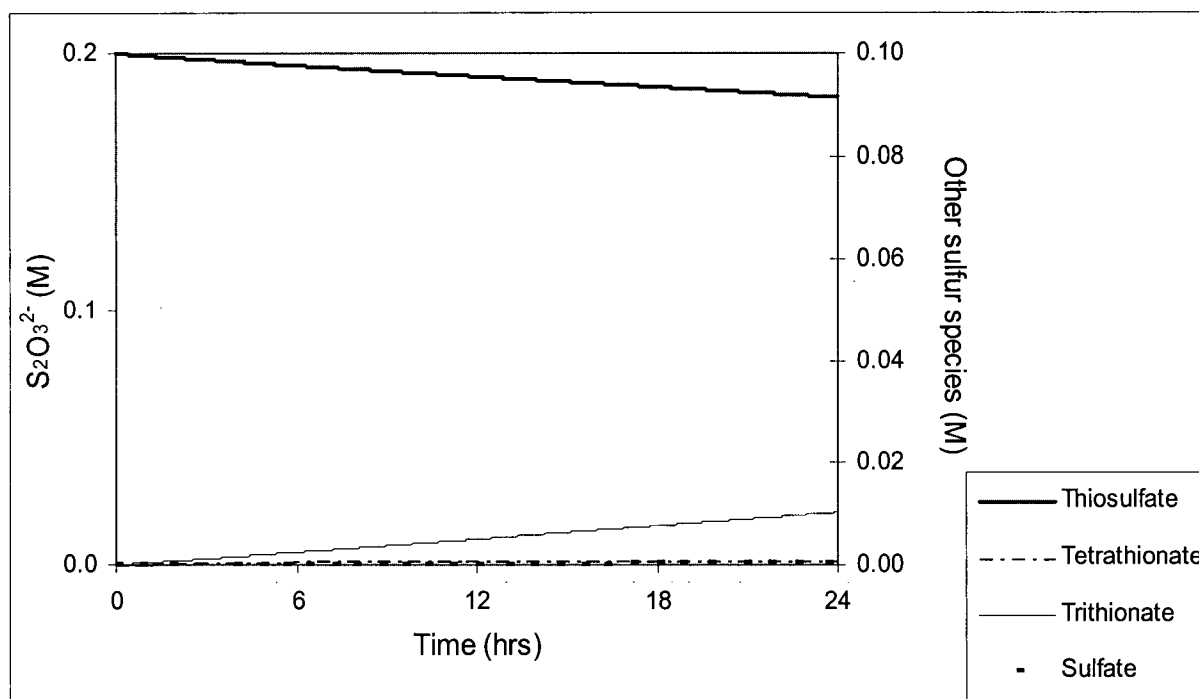


Figure 7.7 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation

- Assumed thiosulfate degradation is via both Reaction R1 and Reaction R4 (**a = 80 %**, **b = 20 %**).
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 10, 25 °C.

For the purposes of demonstrating the sensitivity of the model to other parameters, it was assumed that around 80 % of the thiosulfate reacts via Reaction R1 and 20 % reacts via Reaction R2, simply as an example. All other figures showing the sensitivity of the model to the model parameters can be compared to Figure 7.7.

7.3.2 Rate of Reaction R1 – Thiosulfate Degradation to Tetrathionate

The rate constant for Reaction R1, k_{R1} , was increased by a factor of 10 and the model output is shown in Figure 7.8. When compared with Figure 7.7, it can be seen that increasing the value of k_{R1} has a significant effect on the model output, increasing the rate of thiosulfate degradation, the rate of trithionate formation, and the tetrathionate concentration. The standard value for k_{R1} shown in Table 7.1 was derived in the

absence of oxygen and it is known that the rate of this reaction can increase up to 40 times in the presence of oxygen (Byerley et al, 1973b).

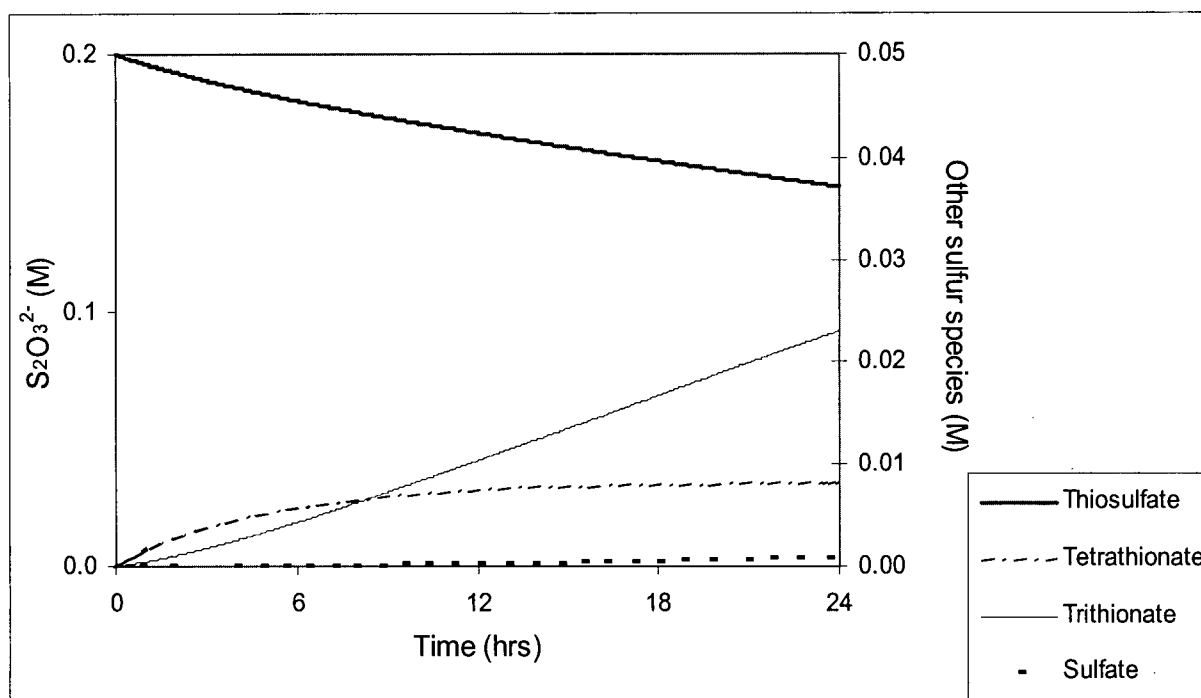


Figure 7.8 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation
- k_{R1} increased by a factor 10

- Assumed thiosulfate degradation is via both Reaction R1 and Reaction R4 ($a = 80\%$, $b = 20\%$).
- Initial conditions: $0.2\text{ M S}_2\text{O}_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , $\text{pH } 10$, 25°C .

7.3.3 Rate of Reaction R4 – Thiosulfate Degradation to Trithionate

The rate constant for Reaction R4, k_{R4} , was increased by a factor of 10 and the model output is shown in Figure 7.9. This has a tremendous effect on the output, giving very rapid thiosulfate degradation and trithionate formation, accentuating the convex nature of the thiosulfate degradation curve and concave nature of the trithionate formation curve. Very little tetrathionate is formed. Note that the dashed line for the thiosulfate concentration profile after about 16 hours indicates that the rapid decline of thiosulfate to zero concentration may not be reliable and is a manifestation of the inverse dependency of the thiosulfate degradation rate on the thiosulfate concentration (Equation 7.10). The

rate constant describing this reaction was increased by a factor of 10 in Figure 7.9, which is much higher than would be expected based on comparison with experimental data (see Section 7.4).

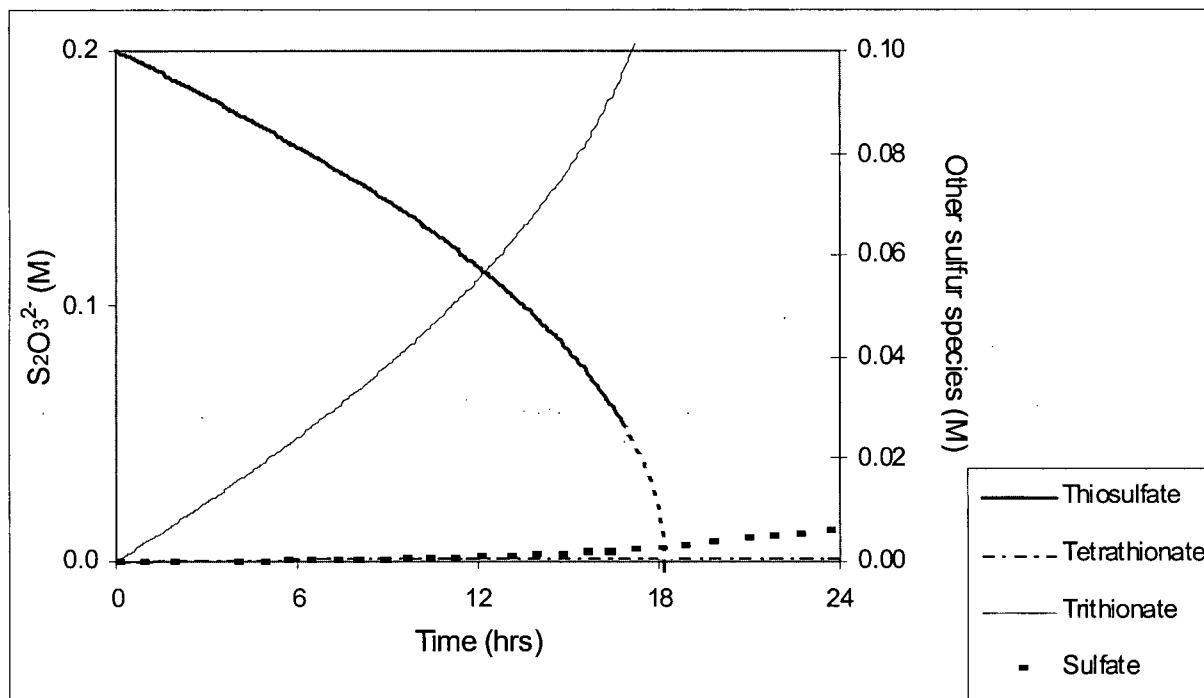


Figure 7.9 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation
- k_{R4} increased by a factor 10

- Assumed thiosulfate degradation is via both Reaction R1 and Reaction R4 ($a = 80\%$, $b = 20\%$).
- Initial conditions: $0.2\text{ M S}_2\text{O}_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 10, $25\text{ }^\circ\text{C}$.

7.3.4 Rate of Reaction R2 – Tetrathionate Degradation

The rate constants for Reaction R2, k_{R2-0} and k_{R2-1} , were increased by a factor of 10 (separately) and the model output for each situation is shown in Figures 7.10 and 7.11. The scale has been changed to show the differences in tetrathionate concentration more clearly. While adjusting the value of k_{R2-0} did not have much effect, the tetrathionate concentration decreased significantly by increasing k_{R2-1} .

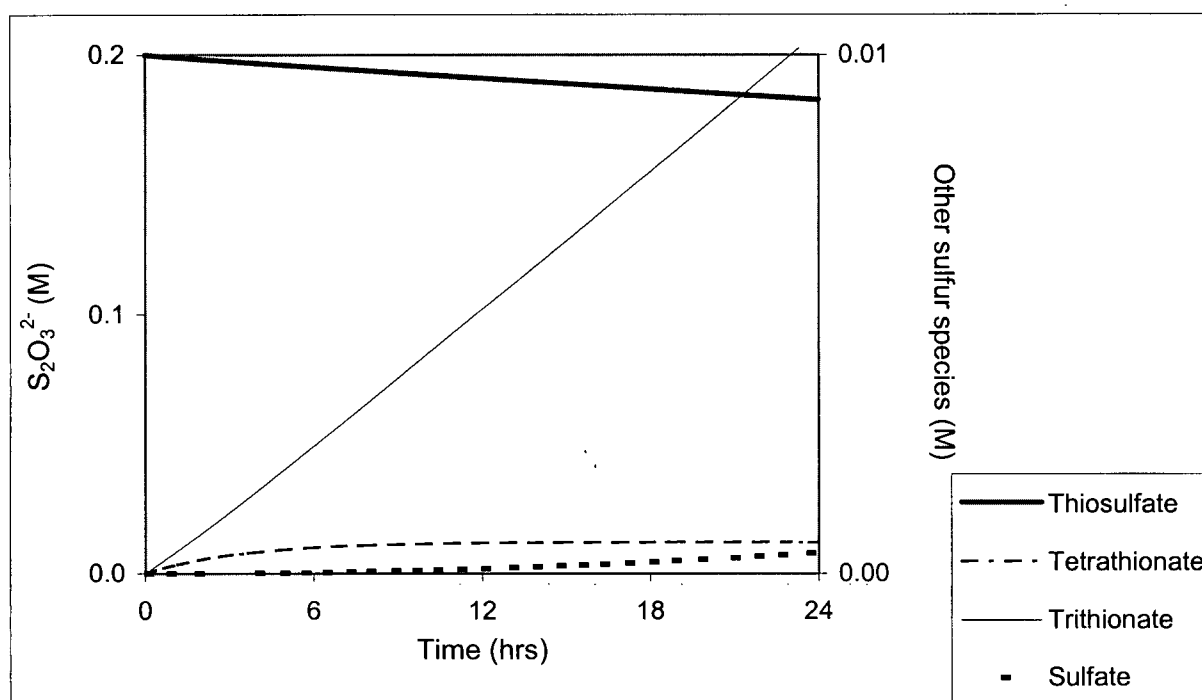


Figure 7.10 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation - k_{R2-0} increased by a factor 10

- Assumed thiosulfate degradation is via both Reaction R1 and Reaction R4 ($a = 80\%$, $b = 20\%$).
- Initial conditions: $0.2\text{ M S}_2\text{O}_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 10, 25°C .

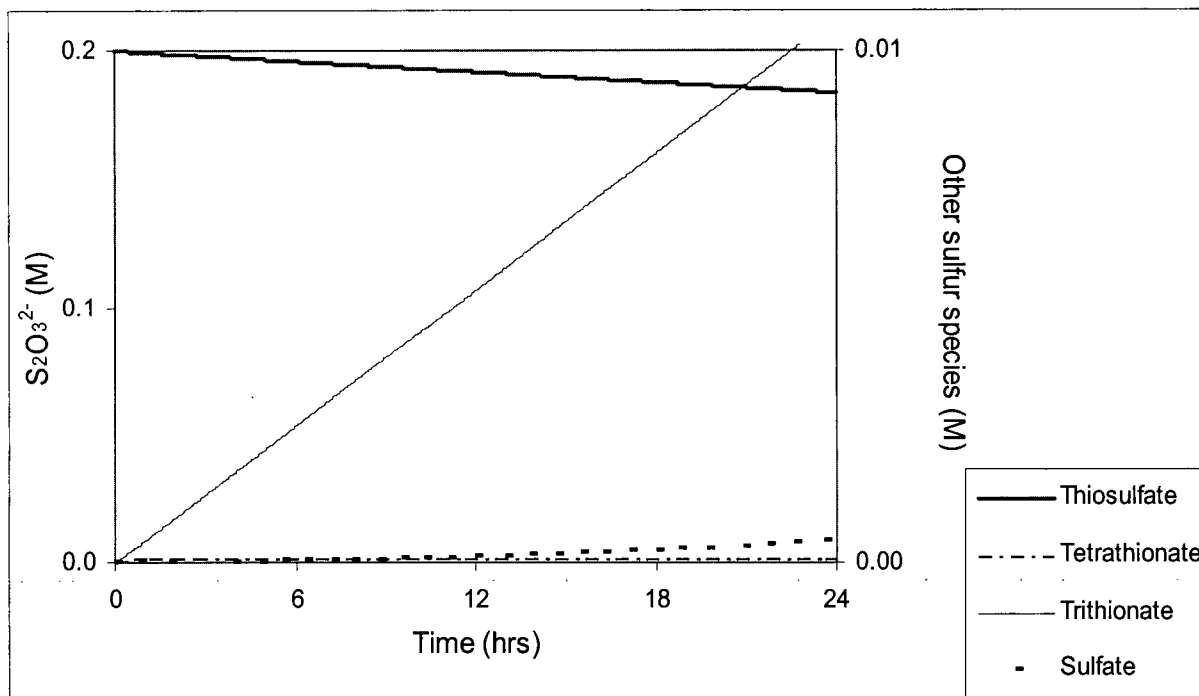


Figure 7.11 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation - k_{R2-1} increased by a factor 10

- Assumed thiosulfate degradation is via both Reaction R1 and Reaction R4 ($a = 80\%$, $b = 20\%$).
- Initial conditions: $0.2\text{ M S}_2\text{O}_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 10, 25°C .

7.3.5 Rate of Reaction R3 – Trithionate Degradation

The rate constants for Reaction R3, k_0 , k_1 , k_2 and k_3 , were all increased by a factor of 10, and the model output is shown in Figure 7.12. Increasing the rate of trithionate degradation had the overall effect of lowering the rate of trithionate formation, and the formation of sulfate was enhanced. The trithionate concentration curve became more convex.

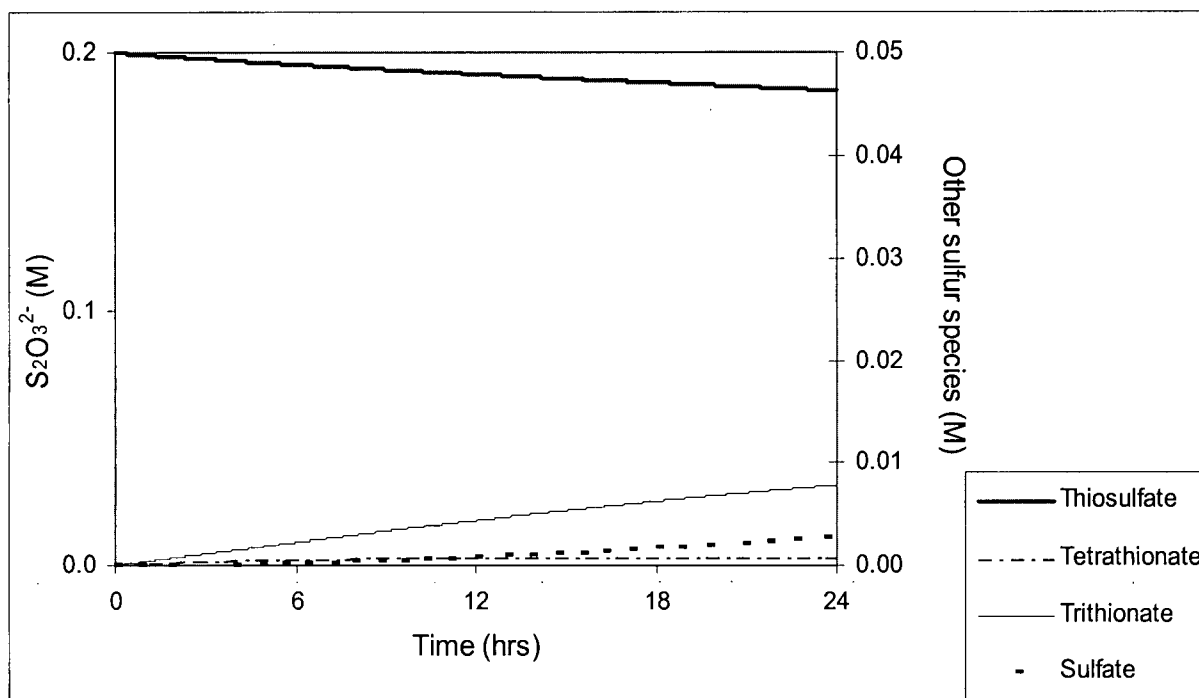


Figure 7.12 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation - k_0 , k_1 , k_2 and k_3 increased by a factor 10

- Assumed thiosulfate degradation is via both Reaction R1 and Reaction R4 ($a = 80\%$, $b = 20\%$).
- Initial conditions: $0.2\text{ M S}_2\text{O}_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , $\text{pH } 10$, 25°C .

7.3.6 Summary – Effect of Model Parameters

The percentage of thiosulfate reacting to form tetrathionate versus that reacting to form trithionate had a significant impact on the model output, as did the magnitude of the rate constants for these reactions. Where tetrathionate formation was favoured, the thiosulfate concentration profile was more concave, while where trithionate formation was favoured it was convex. Changing the rate constants for tetrathionate degradation had a significant effect on the tetrathionate concentration, also affecting the thiosulfate and trithionate concentrations slightly, as these species are products of that degradation. The rate of degradation of trithionate affected the trithionate concentration, as well as having an impact on the thiosulfate and sulfate concentrations. Increasing the rate of trithionate degradation caused the trithionate concentration profile to become more convex. Overall, the model was most sensitive to the rate of degradation of thiosulfate to

tetrathionate and/or trithionate. A comparison of the model output with experimental data (Section 7.4) was used to better estimate these model parameters.

7.4 COMPARISON OF MODEL OUTPUT WITH EXPERIMENTAL RESULTS IN THE ABSENCE OF ORE

The aim of this section was to determine whether the model qualitatively and quantitatively was able to describe experimental data in the absence of ore, and to identify shortcomings in the model.

7.4.1 Experiments

A few experiments were carried out to provide a data set against which to test the model. A solution containing ammonia and copper (added as cupric sulfate) was made up and the pH adjusted using sulphuric acid (to pH 9 or 10). The solution was transferred to a beaker in a water jacket and brought to 25 °C. An aliquot of sodium thiosulfate solution was added so that the final solution would have the required concentration of thiosulfate (0.2 M), copper (30 or 100 mg/l) and ammonia (0.3 – 0.4 M). The headspace above the solution was purged with oxygen and the beaker sealed with plastic film. The solution was stirred using a magnetic stirrer and kept at 25 °C. The test conditions are shown in Table 7.3. Samples were removed periodically by syringe connected to a tube extending into the solution and diluted as required for analysis for thiosulfate, trithionate and tetrathionate concentrations by ion chromatography, as discussed in Chapter 3. Sulfate was not measured as it could not be determined at the same time as the other sulfur oxyanions and storing of the sample for later analysis of sulfate was not considered due to the sometimes rapid change in solution concentrations. Therefore no sulfur balance could be carried out. The total ammonia concentration was analysed by titration, as discussed in Chapter 3.

Table 7.3 : Experimental conditions used in tests for model validation

Test	Initial thiosulfate (M)	Copper (mg/l)	Total ammonia (M)	pH
1	0.2	0	0.42	10
2a	0.2	32	0.42	10
2b	0.2	32	0.38	10
3	0.2	30	0.33	9
4	0.2	30	0.40	9
5	0.2	101	0.30	10

The solution was kept under oxygen since the model assumed that there was sufficient oxygen present so that all cuprous copper was re-oxidised to cupric copper. In a more elaborate model, it would be necessary to take copper speciation into consideration. Assuming that only thiosulfate was likely to react with cupric copper (and not any trithionate or tetrathionate that formed), the maximum oxygen requirement to maintain all the copper in the cupric form could be determined based on the total thiosulfate concentration. According to Equation 7.1, each mole of thiosulfate oxidized requires one mole of cupric copper. Hence for 100 ml 0.2 M thiosulfate solutions, 20 mmol cupric copper would be required for complete oxidation of thiosulfate to tetrathionate. Even with low levels of copper present (30 – 100 mg/l) continual replenishment of the cupric could facilitate this. The amount of oxygen required to oxidise 20 mmol of cuprous copper is 5 mmol. Based on the standard gas volumes at atmospheric pressure, this is equivalent to about 112 ml oxygen. The headspace in the vessel used was approximately 160 ml, allowing for sufficient oxygen to be present so as not be limiting.

7.4.2 Validation Method

While the forms of the rate equations were not changed, the magnitude of the rate constants and the proportion of thiosulfate reacting to form tetrathionate or trithionate (i.e. a or b in Figure 7.1) were adjusted to fit experimental data to identify shortcomings of the model. Because the change of thiosulfate concentration was given by the appropriate rate equation multiplied by the percentage of thiosulfate reacting either via Reaction R1 or R4, the product of this percentage and the appropriate rate constant for

each of these reactions was considered as a single parameter in this evaluation. Hence the following four parameters were adjusted as necessary to attempt to find a good fit of the model to the experimental data:

$a \times k_{R1}$ for Reaction R1, where $a = 1$ for the standard case

k_{R2-0} and k_{R2-1} (adjusted together by the same factor as k_{R2}) for Reaction R2

k_0 , k_1 , k_2 and k_3 (adjusted together by the same factor as k_{R3}) for Reaction R3

$b \times k_{R4}$ for Reaction R4, where $b = 1$ for the standard case

These parameters were multiplied by a factor as necessary to give the best fit. Hence a factor for ak_{R1} of 10 would imply that the percentage of thiosulfate reacting via Reaction R1 multiplied by the rate constant would be 10 times higher than if all the thiosulfate reacted via Reaction R1 ($a = 1$) and the rate constant k_{R1} was its standard value as in Table 7.1. This method cannot distinguish whether an overall increase of 10 times (for ak_{R1}) is due to a 10 fold increase in the rate constant only, for example, or a 20 fold increase in the rate constant but with only 50 % of the thiosulfate reacting via this reaction.

Two approaches were considered in comparing the experimental data to the model output. In the first approach, it was attempted to use a mathematical method to adjust the model parameters to obtain the best fit. The sum of the squares of the errors between the experimental data points and the modelled values was minimised by adjusting the model parameters. However, this approach gave a large variation in the best fit model parameters, giving what appeared to be meaningless scenarios at times. Also the final outcome of the adjusted parameters was strongly dependent on the starting values selected. The concentrations of thiosulfate and trithionate found experimentally were generally higher than those of tetrathionate and sulfate. Hence minimising the sum of the squares of errors for all species could be easily biased depending on which species were present in higher concentrations and on whether the absolute or relative errors were used.

The second approach used visual inspection and adjustment of parameters and gave more realistic results. This method used what was learnt in examining the sensitivity of the model to the model parameters in Section 7.3 and the parameters were adjusted based on the expected shortcomings of parts of the model and a visual best fit. The

concave and convex natures of the concentration profiles were used to estimate whether the system was biased towards thiosulfate degradation to tetrathionate or trithionate, and the magnitudes of the rate constants were adjusted to allow for an improved model fit to match both the measured concentrations and the qualitative shape of the concentration profiles. The results obtained were more realistic and consistent using this approach.

The five sets of test results are first considered separately and the overall findings are summarised thereafter. In all figures, the model output is shown by continuous lines while experimental data is shown as individual data points. Since no experimental data for sulfate concentrations were available, the modelled sulfate concentrations are not shown.

7.4.3 Test 1 – No Copper

The graph in Figure 7.13 shows the model output and experimental data points for a test with no copper present. Over the duration of the test there was no significant thiosulfate degradation. The model assumes that copper is present. These results show that it is appropriate to require copper in the model to have any significant thiosulfate degradation, for these conditions and test duration.

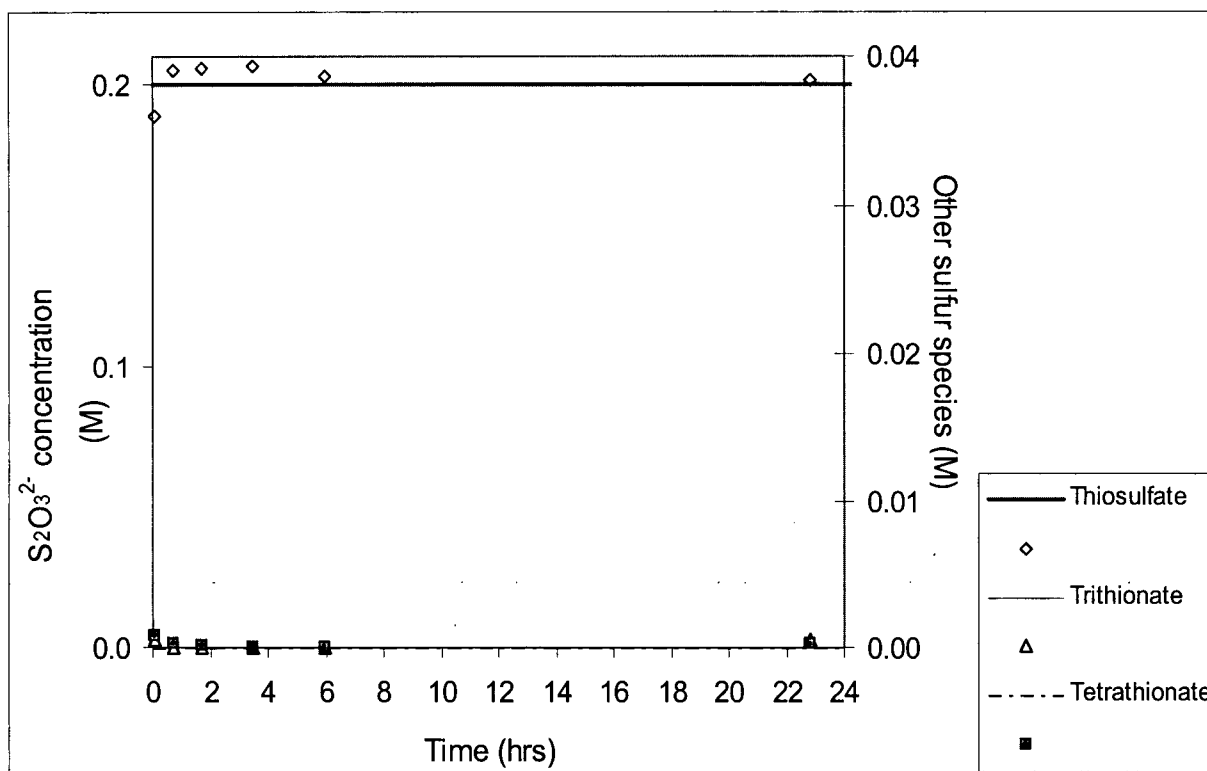


Figure 7.13 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.42 M NH_3 , 0 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space

7.4.4 Tests 2a and 2b – Low Copper, pH 10

The following conditions were used in Test 2 (a and b): Cu^{2+} (added as $CuSO_4$) – 32 mg/l, NH_3 (total) – 0.38 - 0.42 M, pH 10. The graph in Figure 7.14 shows the test data. The thiosulfate concentration curve is concave while the trithionate concentration curve is convex. The initial data point for the thiosulfate concentration is lower than expected, probably due to poor mixing. The tetrathionate concentration reaches a maximum within the first 2 hours of reaction then slowly degrades. Based on these qualitative trends and the qualitative behaviour of the model, it is reasonable to assume that most of the thiosulfate reacts via reaction R1 to form tetrathionate. The model output assuming that all thiosulfate reacts via this pathway and none reacts to form trithionate directly is also shown in Figure 7.14. In Figure 7.14, the model predicts much slower thiosulfate

degradation than observed experimentally and correspondingly much slower trithionate and tetrathionate formation.

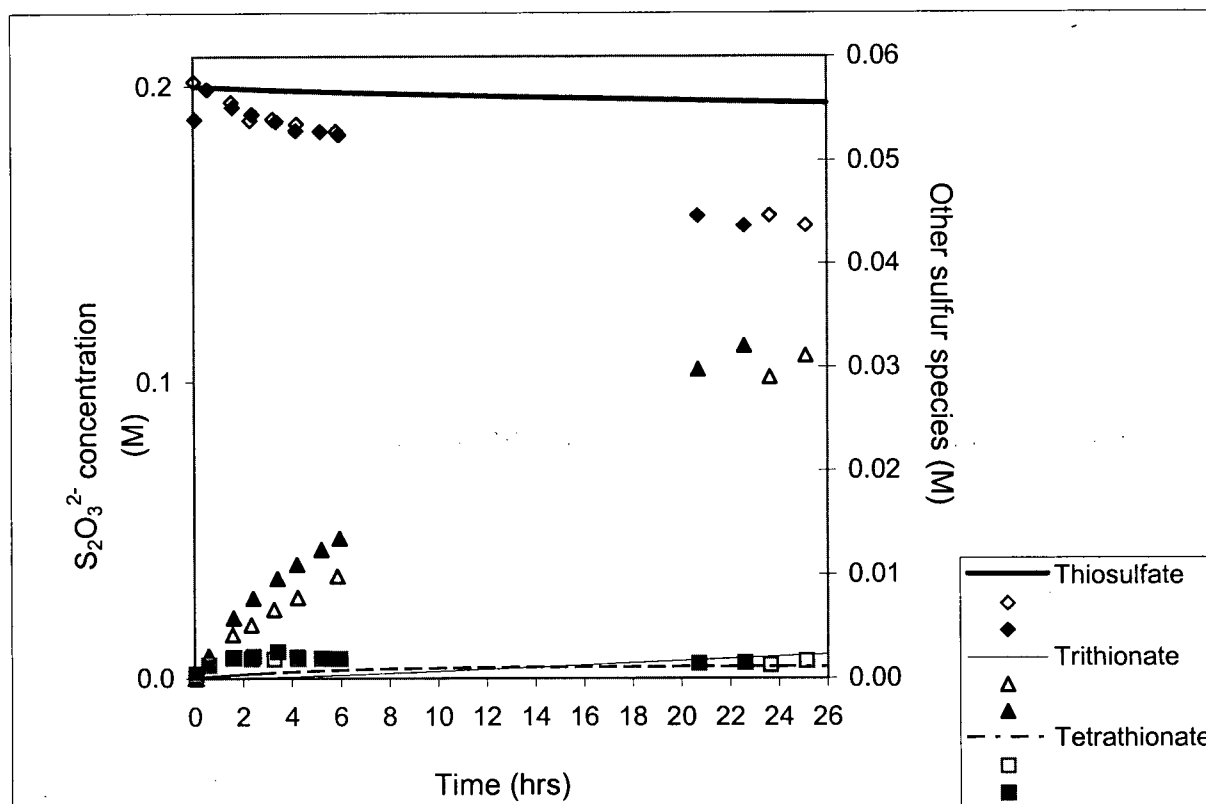


Figure 7.14 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 1 \times$, $k_{R2} - 1 \times$, $k_{R3} - 1 \times$, $bk_{R4} - 0 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.42 M NH_3 (closed symbols) or 0.38 M NH_3 (open symbols), 32 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space.
- Assumed that all thiosulfate reacts via reaction R1.

Multiplying the rate of thiosulfate degradation via Reaction R1 (ak_{R1}) by a factor of 10 allowed a much better fit to the thiosulfate degradation data. It is known that this reaction proceeds much faster in the presence of oxygen than in its absence (for which the rate equation was derived), so increasing the rate is justifiable. This effect is shown in Figure 7.15. However, although the thiosulfate data was adequately described by the

model, the tetrathionate concentration predicted was too high, and the trithionate concentration too low.

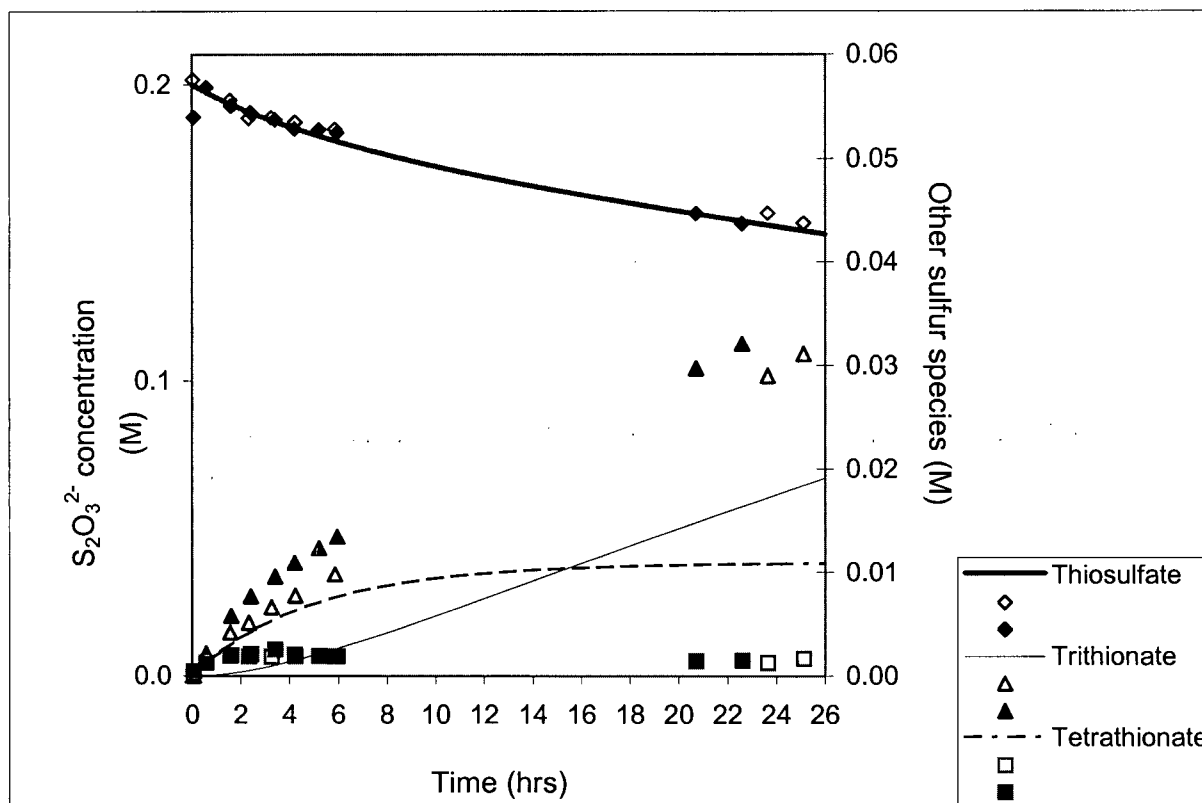


Figure 7.15 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} = 10 \times$, $k_{R2} = 1 \times$, $k_{R3} = 1 \times$, $bk_{R4} = 0 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.42 M NH_3 (closed symbols) or 0.38 M NH_3 (open symbols), 32 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space
- Assumed that all thiosulfate reacts via reaction R1.

The rate of tetrathionate degradation predicted by the model was too low. However, increasing the rate of tetrathionate degradation would affect the net thiosulfate concentration, as thiosulfate is a product of tetrathionate degradation. Hence, increasing the rate of tetrathionate degradation would also require a further increase of the thiosulfate degradation rate to maintain a good fit for the thiosulfate data. Figure 7.16 shows the model output where the tetrathionate degradation rate (k_{R2}) is increased by a factor of 8 and the thiosulfate degradation rate to tetrathionate (ak_{R1}) is increased by a

factor of 14. This produces a better fit in general, however, the trithionate concentration curve is not quite convex enough to fit the experimental data.

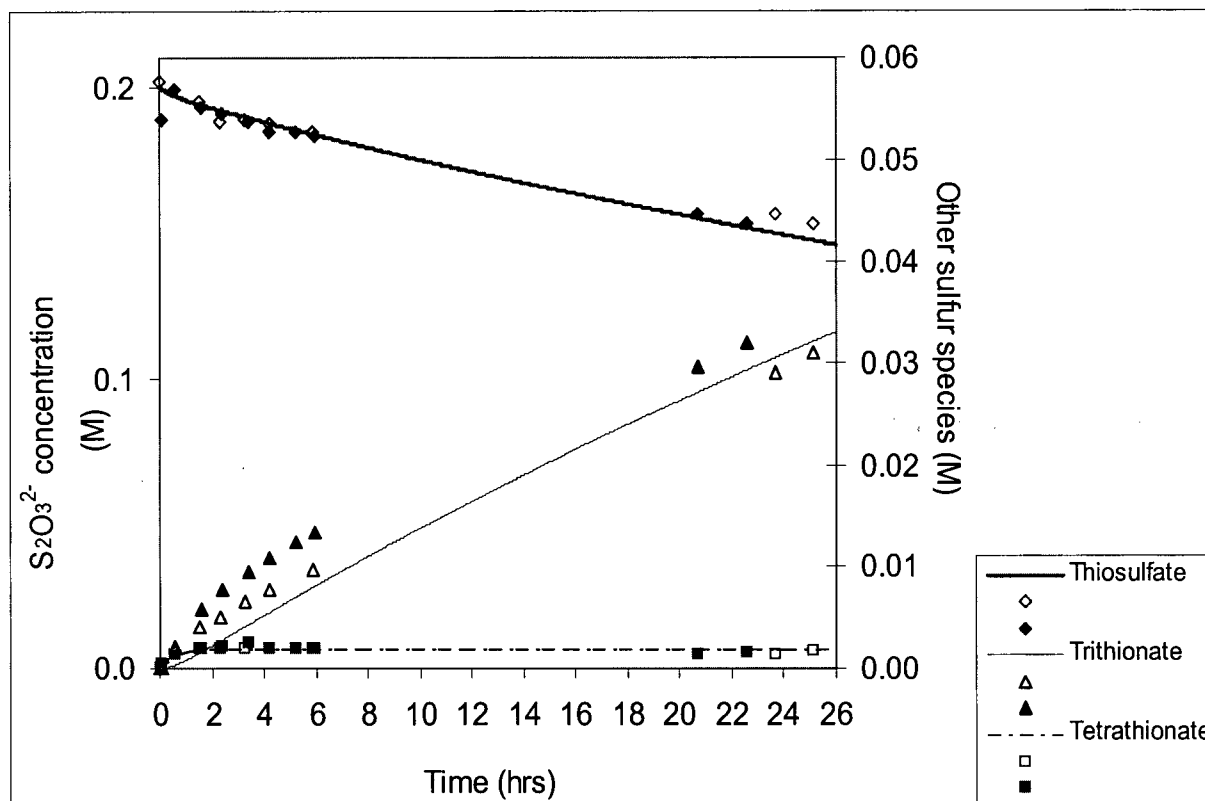


Figure 7.16 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 14 \times$, $k_{R2} - 8 \times$, $k_{R3} - 1 \times$, $bk_{R4} - 0 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.42 M NH_3 (closed symbols) or 0.38 M NH_3 (open symbols), 32 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space
- Assumed that all thiosulfate reacts via reaction R1.

It was shown in determining the model sensitivity to the model parameters that increasing the rate of trithionate degradation would give a more convex trithionate concentration profile. Thiosulfate is produced during the degradation of trithionate, so increasing the trithionate degradation rate would required an increase in the rate of thiosulfate degradation to ensure a satisfactory fit remains for the thiosulfate data. Also, since it has been shown that trithionate forms from thiosulfate in the presence of copper

and oxygen, it is not realistic to assume that no thiosulfate reacts via Reaction R4. Allowing for a small fraction of thiosulfate to react via this route ($bk_{R4} = 0.05$) enhances the model fit slightly. In Figure 7.17, the model output is shown where the rate of thiosulfate degradation is increased by a factor of 15, the rate of tetrathionate degradation is increased by a factor of 8, the rate of trithionate degradation is increased by a factor of 5, and some reaction of thiosulfate to trithionate is allowed. This produces a slightly more satisfactory fit to the experimental data than in Figure 7.16.

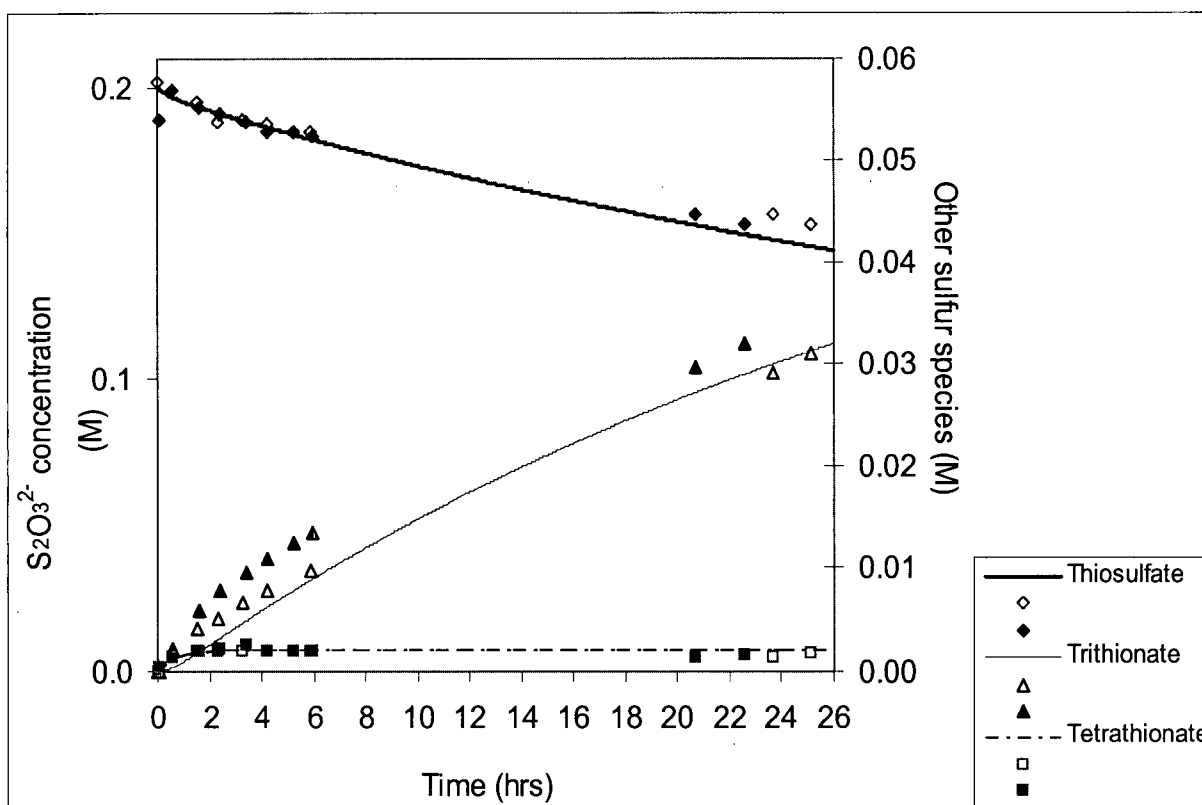


Figure 7.17 : Modelled versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.05 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.42 M NH_3 (closed symbols) or 0.38 M NH_3 (open symbols), 32 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space
- Assumed that thiosulfate reacts via reaction R1 and R4.

7.4.5 Test 3 - Low Copper, pH 9, Low Ammonia

The following conditions were used in Test 3: Cu^{2+} (added as CuSO_4) – 30 mg/l, NH_3 (total) – 0.33 M, pH 9. The graph in Figure 7.18 shows that the thiosulfate concentration curve is concave while the trithionate concentration curve is convex, but less so than for Test 2 at higher pH. The overall thiosulfate degradation was less and less trithionate was formed. The maximum tetrathionate concentration reached was higher than that at higher pH. The model output shown in Figure 7.18 assumes that the thiosulfate reacts only via Reaction R1 to form tetrathionate, based on the qualitative trends of the data. While the thiosulfate degradation predicted adequately fits the data, especially at shorter times, the tetrathionate concentrations predicted were too high while the trithionate concentrations were too low, as was found in Test 2. Increasing the tetrathionate degradation rate provided a better fit, as shown in Figure 7.19.

However, the trithionate concentration curve in Figure 7.19 was concave instead of convex. To alter the shape of the trithionate concentration curve, the rate of trithionate degradation could be increased. Increasing the rate of trithionate degradation in this case would improve the shape of the modelled trithionate profile, but the values would be too low compared with experimental data. To increase the trithionate concentration, the reaction of thiosulfate degradation to trithionate was assigned a non-zero value. Figure 7.20 shows the model output where it is assumed that part of the thiosulfate reacts via Reaction R4 to form trithionate, and also that the trithionate degradation rate is 5 times higher than predicted by the original model. The fit to the experimental data is much improved.

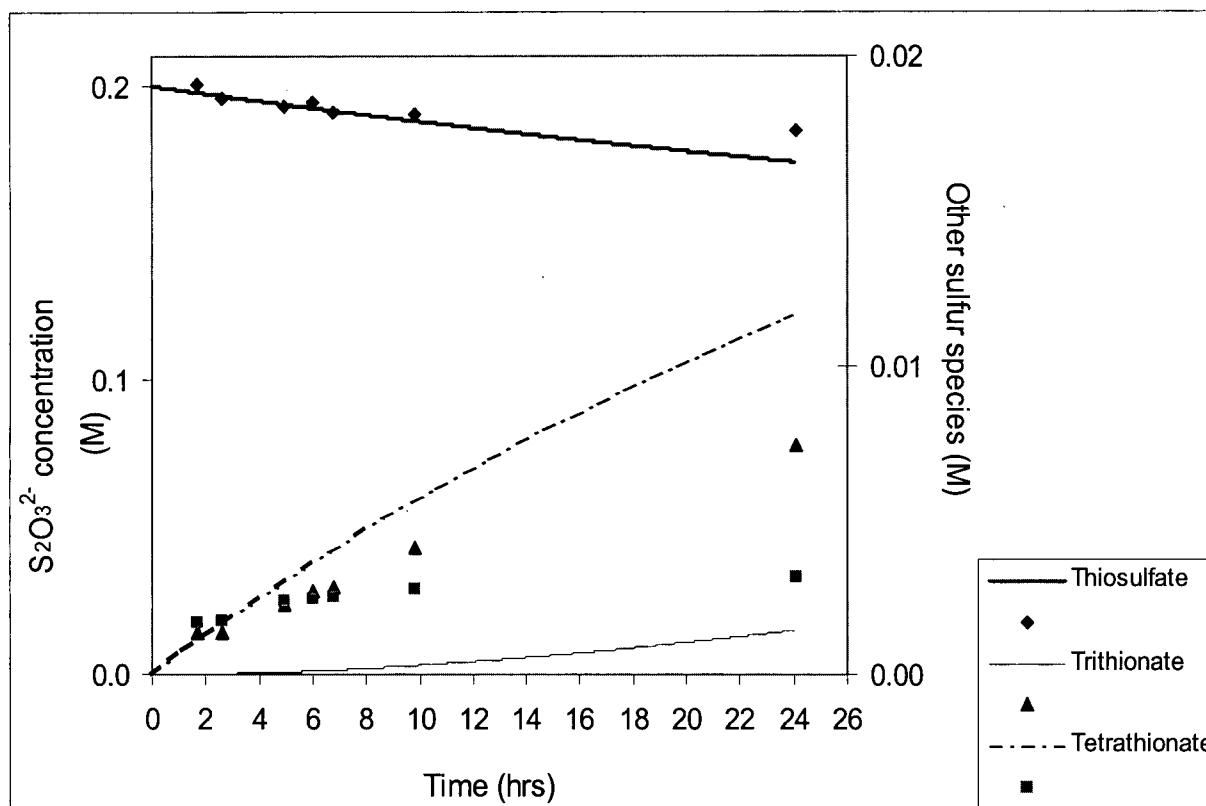


Figure 7.18 : Model output versus experimental data for sulfur oxyanion speciation
during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 1 \times$, $k_{R2} - 1 \times$, $k_{R3} - 1 \times$, $bk_{R4} - 0 \times$.
- Initial conditions: $0.2 \text{ M S}_2\text{O}_3^{2-}$, 0.33 M NH_3 , 30 mg/l Cu^{2+} , pH 9, 25°C , sealed vessel with O_2 in head space
- Assumed that all thiosulfate reacts via reaction R1.

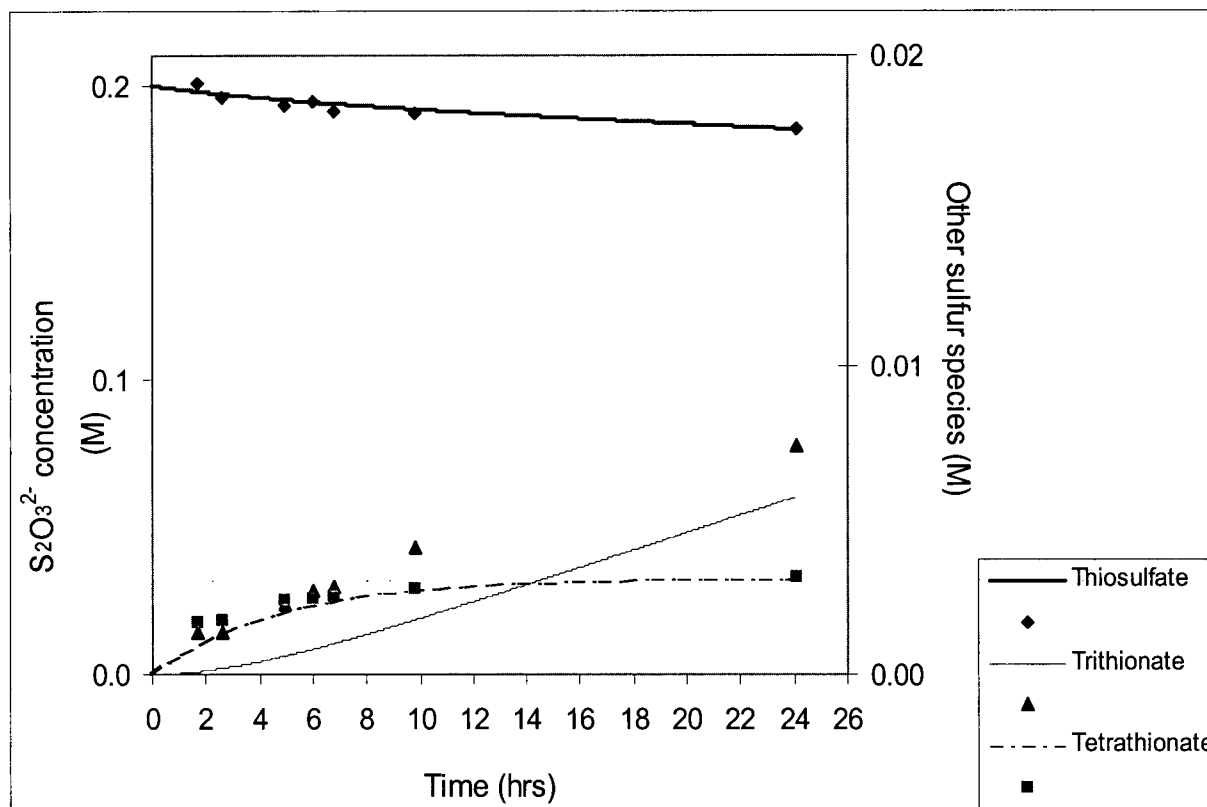


Figure 7.19 : Model output versus experimental data for sulfur oxyanion speciation
during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} = 1 \times$, $k_{R2} = 10 \times$, $k_{R3} = 1 \times$, $bk_{R4} = 0 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.33 M NH_3 , 30 mg/l Cu^{2+} , pH 9, 25 °C, sealed vessel with O_2 in head space.
- Assumed that all thiosulfate reacts via reaction R1.

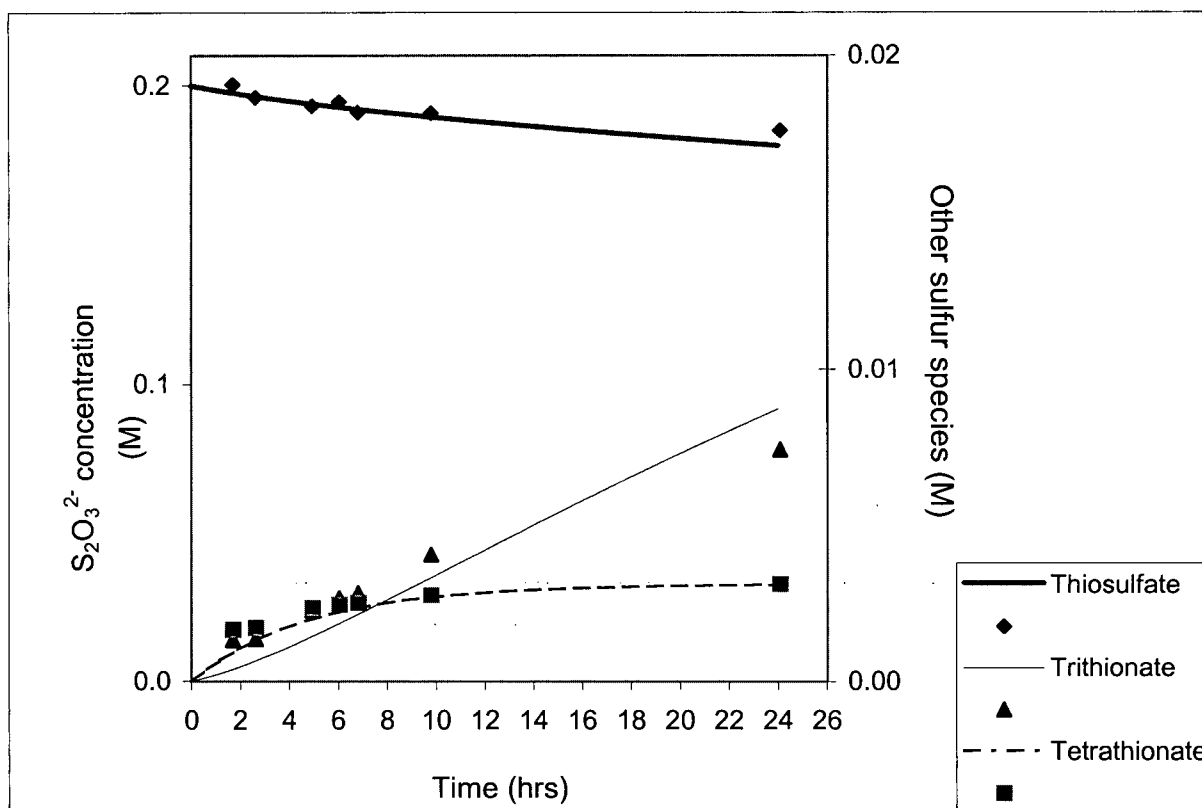


Figure 7.20 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 1 \times$, $k_{R2} - 10 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.1 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.33 M NH_3 , 30 mg/l Cu^{2+} , pH 9, 25 °C, sealed vessel with O_2 in head space.
- Assumed that all thiosulfate reacts via reaction R1.

7.4.6 Test 4 – Low Copper, pH 9, Higher Ammonia

Test 4 was very similar to Test 3, except that the ammonia concentration was higher at 0.40 M. The following conditions were used in Test 4: Cu^{2+} (added as $CuSO_4$) – 30 mg/l, NH_3 (total) – 0.40 M, pH 9. Fitting of the model required similar adjustments as for Test 3, and a satisfactory fit is shown in Figure 7.21.

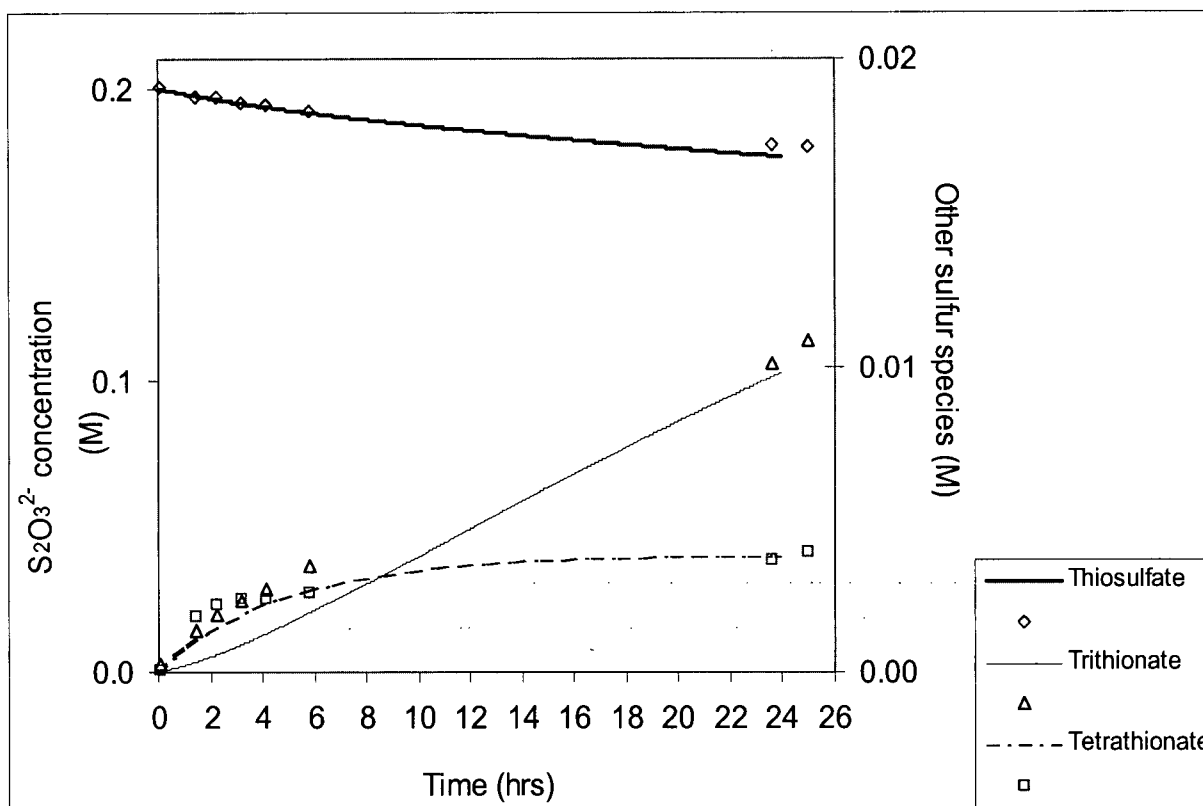


Figure 7.21 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 1.5 \times$, $k_{R2} - 10 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.1 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.40 M NH_3 , 30 mg/l Cu^{2+} , pH 9, 25 °C, sealed vessel with O_2 in head space
- Assumed that all thiosulfate reacts via reaction R1.

7.4.7 Test 5 – High Copper, pH 10

The following conditions were used in Test 5: Cu^{2+} (added as $CuSO_4$) – 101 mg/l, NH_3 (total) – 0.30 M, pH 10. As shown in Figure 7.22, the thiosulfate concentration curve is initially concave while the trithionate concentration curve is initially convex. The higher copper concentration caused a much more rapid thiosulfate degradation and trithionate production than in Test 2. The tetrathionate reached a maximum concentration then degraded much more rapidly than for Test 2 at lower copper concentration. Based on

the basic shape of the curves, it was first assumed that no thiosulfate reacted via Reaction R4 to form trithionate directly. As in the previous examples, it was necessary to increase the rate of thiosulfate degradation to tetrathionate and of tetrathionate degradation to improve the model fit. This model output is shown in Figure 7.22. While the model fit was adequate at shorter times, it did not describe the data at longer times.

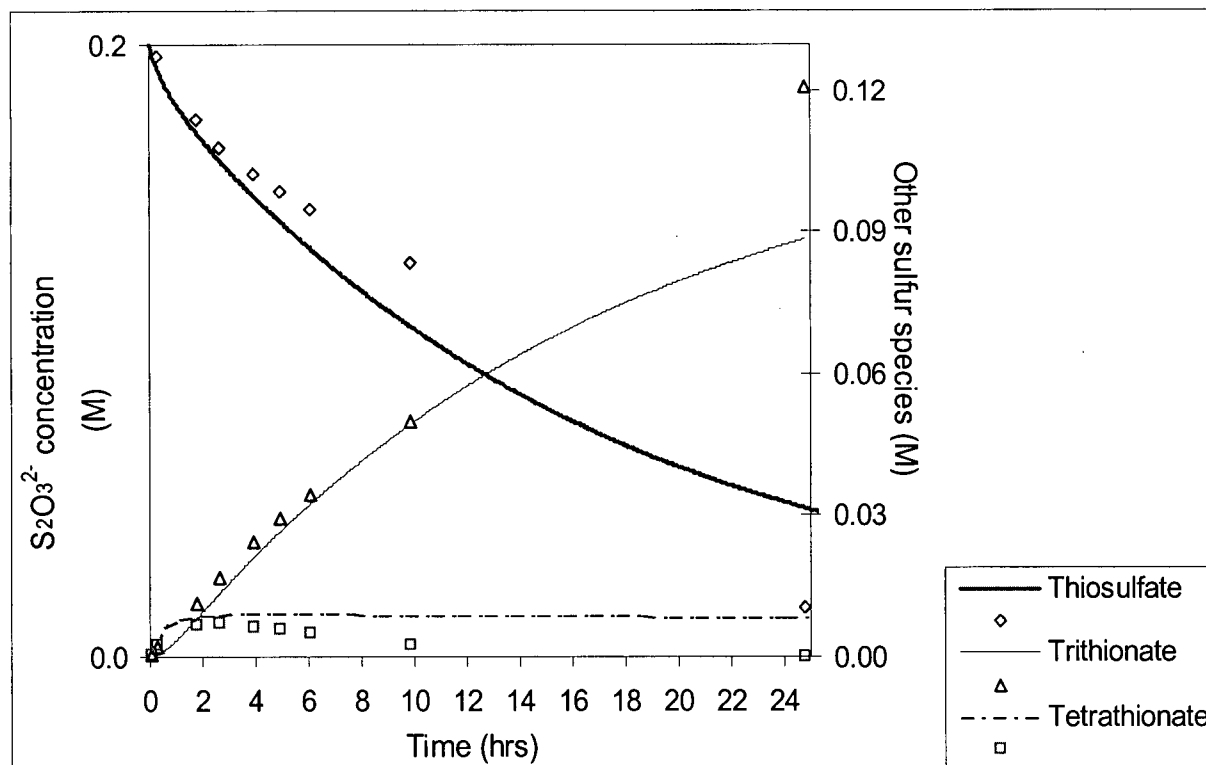


Figure 7.22 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} = 16 \times$, $k_{R2} = 8 \times$, $k_{R3} = 1 \times$, $bk_{R4} = 0 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.30 M NH_3 , 101 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space
- Assumed that all thiosulfate reacts via reaction R1.

A more linear trend for both thiosulfate concentration and trithionate concentration was required. Allowing for thiosulfate degradation via both Reaction R1 and Reaction R4 was found to give this type of trend. Figure 7.23 shows the model output where this is taken into account.

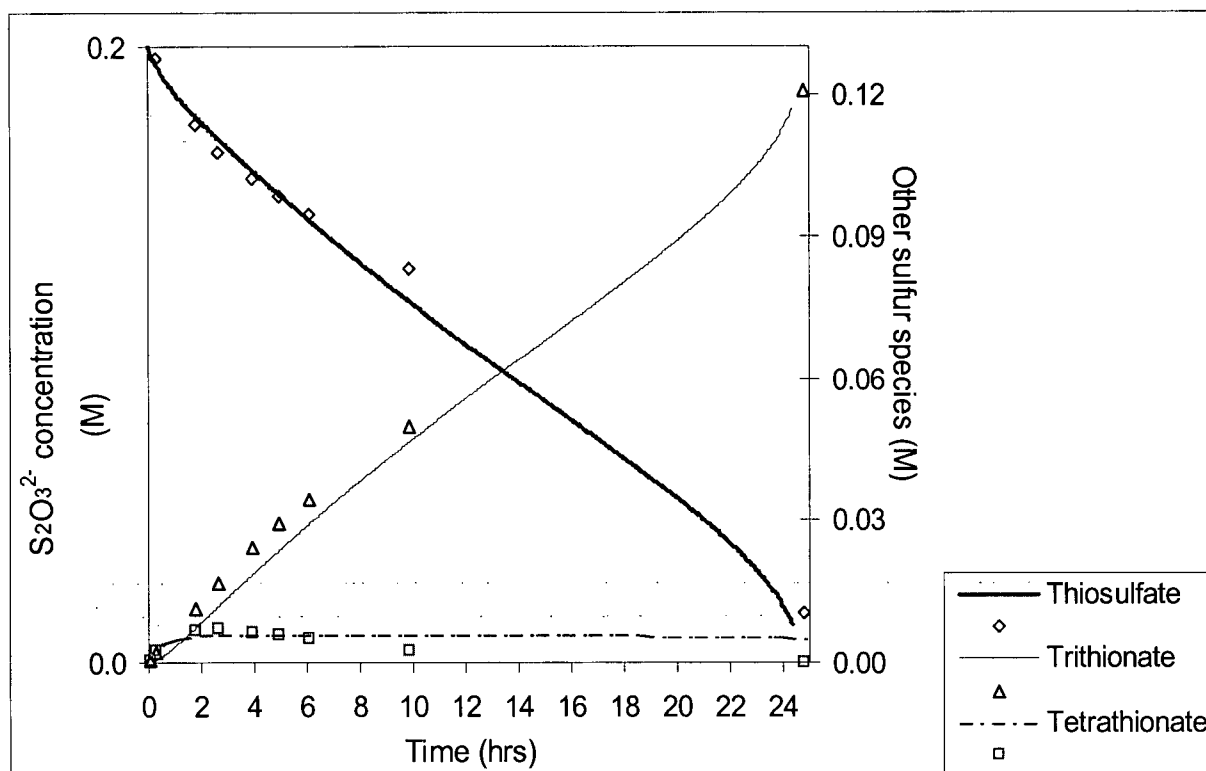


Figure 7.23 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 12x$, $k_{R2} - 8x$, $k_{R3} - 1x$, $bk_{R4} - 0.15x$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.30 M NH_3 , 101 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space.
- Assumed that all thiosulfate reacts via reaction R1.

Similar output is obtainable where the rate of trithionate degradation is increased 5 fold to be consistent with that required for Tests 2, 3 and 4. This is shown in Figure 7.24.

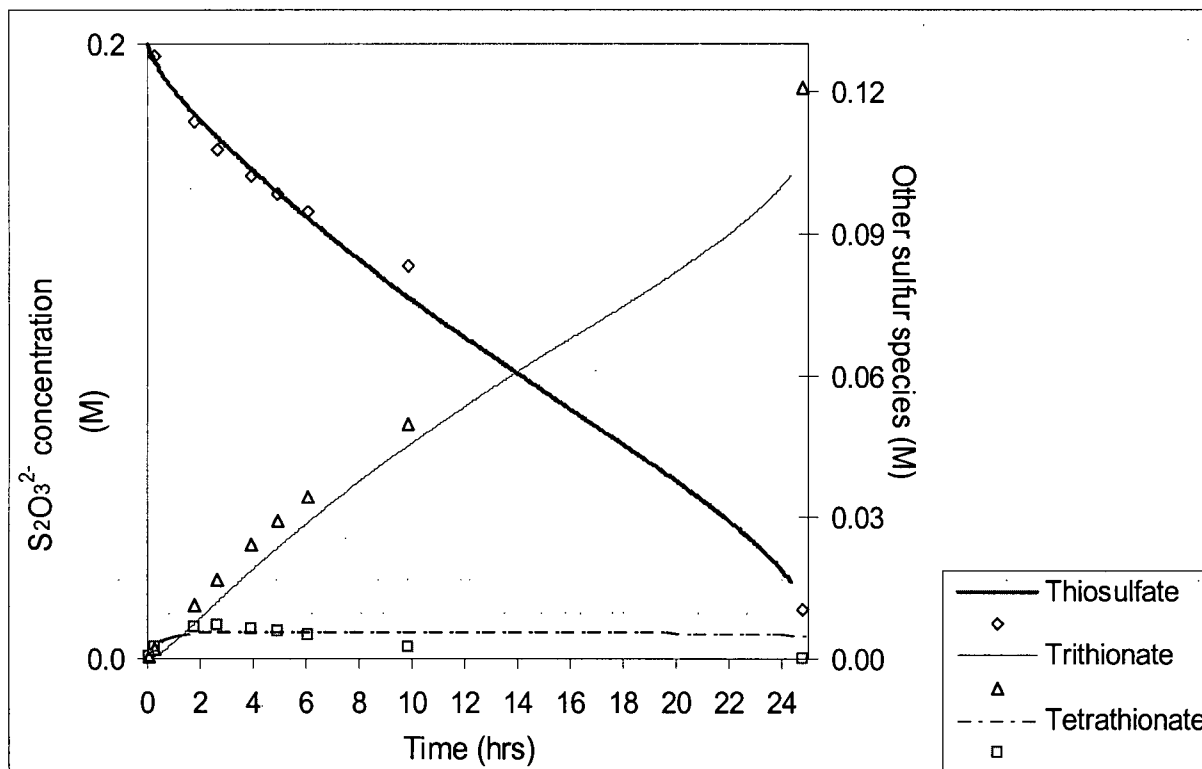


Figure 7.24 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 12 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.17 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.30 M NH_3 , 101 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space
- Assumed that thiosulfate reacts via reaction R1 and R4.

7.4.8 Summary

While adjustments to the model were based only on visual inspection, the extent of such adjustments required to give a better fit to the experimental data give useful insight into the shortcomings of the model. Examples of adjustments found to improve the agreement between the model and experimental data are shown in Table 7.4. It should be noted that these model parameter adjustments are not unique.

Table 7.4 : Adjustment of model parameters found to give improved agreement between model output and experimental data

Test	[Cu] (mg/l)	[NH ₃] (M)	pH	Multiplication factor for ak_{R1}	Multiplication factor for k_{R2} (k_{R2-1} and k_{R2-2})	Multiplication factor for k_{R3} (k_0 , k_1 , k_2 and k_3)	Multiplication factor for bk_{R4}
2a, 2b	32	0.38- 0.42	10	15	8	5	0.05
3	30	0.33	9	1.5	10	5	0.10
4	30	0.40	9	1.0	10	5	0.10
5	101	0.30	10	12	8	5	0.17

The following conclusions can be drawn from this validation of the model:

The model can be used to qualitatively describe the degradation of thiosulfate and the subsequent formation and degradation of polythionates in ammoniacal systems containing copper in a very general manner. Both the model and experimental results show that as thiosulfate degrades, both tetrathionate and trithionate are formed initially. The tetrathionate itself degrades at an appreciable rate, so the tetrathionate concentration reaches a maximum, varying with the pH and copper concentration, before degrading to very low levels. The trithionate concentration continually increases over the time frame of interest (24 hours).

However, the model in its standard form is not adequate to quantitatively describe the degradation of thiosulfate and the speciation of the sulfur oxyanions. The model can be made to fit the experimental data by multiplying each of the applicable rate equations by a factor, however, the value of each factor is not consistent for all the conditions tested, as can be seen in Table 7.4. Even using the best fit factors, the model does not predict the tetrathionate degradation seen after the maximum concentration of tetrathionate is reached, and the trithionate concentrations predicted in the early stages of the tests are not high enough compared with the experimental data.

The tetrathionate degradation rate predicted by the model was lower than that seen experimentally. Increasing the tetrathionate degradation rate constants by a consistent factor of about 8 to 10 was beneficial in allowing the model to better describe the experimental observations. In the section discussing the model setup (Section 7.2), it was mentioned that Zhang and Dreisinger (2002) found that the rate constant corresponding to k_{R2-0} for the degradation of tetrathionate in alkaline solutions in the absence of thiosulfate was 10 times higher than that found by Rolia and Chakrabarti (1982), whose rate equation was used for this analysis. However, Rolia and Chakrabarti also included a much stronger dependency on the thiosulfate concentration. Using Zhang and Dreisinger's rate equation for tetrathionate degradation instead of Rolia and Chakrabarti's would not have allowed for a better fit of the model to the experimental data since the rate constant for the thiosulfate dependence (k_{R2-1}) was of much more significance. It is possible that tetrathionate reacts with cupric copper and that this could enhance the reaction rate. The tetrathionate concentration profile predicted by the model shows an increase in tetrathionate concentration to a maximum concentration with very little further degradation over the time frame tested. However, especially for Test 5 in the presence of higher copper concentration, the tetrathionate concentration decreased much more rapidly than predicted by the model after reaching a maximum. This degradation is expected to be a function of the copper concentration and is not accounted for in the model. It has also been proposed that the ionic strength affects the tetrathionate degradation rate (Breuer and Jeffrey, 2004). Given that the tetrathionate concentration is generally low, the rate equation describing tetrathionate degradation is adequate under the conditions tested when the rate constant is increased by a factor of 8 to 10.

To allow for an improved model fit, the rate of trithionate degradation was increased consistently by a factor of 5. This implies that the rate equation derived in this work predicts trithionate degradation rates that are too low. It is thought that either the presence of copper or of thiosulfate could be the reason for this. In the rate equation derived for trithionate degradation, copper and thiosulfate concentrations were assumed to have no significant effect on the rate (see Chapter 6). However, there were certain conditions for which thiosulfate increased the trithionate degradation rate, and the effect of copper was not comprehensively tested, and not tested in the presence of excess oxygen. Since the factor required to increase the trithionate degradation rate was the

same for both copper concentrations tested, it is more likely that the observed effect was due to the role of thiosulfate.

The degradation of thiosulfate was the most important in determining the model output. Not only could the percentage of thiosulfate reacting via two routes to form either tetrathionate or trithionate be varied, but the rate constants for the rate equations describing these two reactions could be varied. The overall factors giving a satisfactory model fit shown in Table 7.4 were not consistent across all tests. For the degradation of thiosulfate to tetrathionate (Reaction R1), there was some consistency between the tests at pH 9 and those at pH 10, but the degradation rate was higher at higher pH (or higher free ammonia concentration). The copper concentration did not have any notable effect (as seen in a comparison of Tests 2a and 2b, and Test 5).

However, for the degradation of thiosulfate to trithionate (Reaction R4), a comparison of the factors required for the tests at pH 10 at different copper concentrations show that the presence of copper does influence the best fit factor. This factor increased with an increase in copper concentration, by a similar factor. This could imply a stronger dependency on the copper concentration than used in the model. Comparing Tests 2a and 2b with Test 4 shows an increase in the best fit factor with a decrease in pH, implying either a dependence of the degradation rate on the pH or indirectly on the free ammonia concentration.

It is likely that the percentage of thiosulfate reacting to form tetrathionate versus trithionate changes with time. This was not accounted for in the model and may account for the under-prediction of trithionate concentration for the initial times in the model. Since the formation of trithionate from thiosulfate depends on the concentration of dissolved oxygen, the availability of oxygen is expected to influence the relative rates of formation of trithionate and tetrathionate from thiosulfate.

Although the rates of degradation for tetrathionate and trithionate had a significant influence on the model output, the rates of thiosulfate degradation either to tetrathionate or to trithionate were the determining factors in the model output. This exercise has highlighted how the way in which thiosulfate is assumed to degrade has the greatest impact on the predicted solution speciation. The deficiencies in the rate equations used

for these reactions have also been highlighted. There is a need to better account for the effect of copper concentration, perhaps by using the active copper species, possibly cupric tetraammine, in the rate equations rather than the total cupric concentration. There is also a possible effect of pH or free ammonia concentration that is not adequately addressed.

The inadequacy of the rate equations describing thiosulfate degradation suggests a serious shortcoming in the model, as the model outcome is very sensitive to these rate equations. A better understanding is required of how thiosulfate degrades to trithionate and tetrathionate.

7.5 COMPARISON OF EXPERIMENTAL RESULTS WITH AND WITHOUT ORE

Limited comparable data was available where ores were leached in thiosulfate solutions. A series of leach tests was carried out by Lam (2002) on an ore provided by Placer Dome. The ore was relatively free of copper with the coarse gold removed by gravity separation. Results of an analysis of the ore are shown in Table 7.5. Sub samples of the ore were analysed at different laboratories at different times, and sample variability may be the reason for the apparently wide range in sulfide concentrations.

Table 7.5 : Assay results for ore from Placer Dome used in leach tests

Species	Concentration
Au	1.14 – 1.20 g/t
Cu	0.004 – 0.006 %
Fe	3.84 %
S (total)	0.52 – 0.58 %
S as SO_4^{2-}	< 0.01 %
S^0	<0.01 %
S^{2-}	0.07 – 0.51 %
C (total)	1.62 %
C (organic)	0.47 %

The tests were done at 30 % solids at room temperature in a sealed vessel with oxygen in the headspace and oxygen was replenished after sampling. The pH was adjusted manually. The test duration was typically 24 hours during which four samples were removed for analysis of thiosulfate, trithionate, tetrathionate and sulfate concentrations. The analysis of thiosulfate, trithionate and tetrathionate was immediate, but sulfate analyses were generally carried out at least four hours after sampling and therefore these values are not included in this analysis. A maximum gold leaching of about 80 % was achieved (compared with 75 - 88 % gold extraction during cyanidation), but it was found that gold could not be leached efficiently or completely without sufficient thiosulfate or cupric tetraammine present.

Two such leach tests were compared with the tests in the absence of ore – Test 2a and Test 5 respectively. No data was available for a test comparable with Tests 3 or 4. The results from the leach tests are superimposed on the data from the solution-only tests and the model predictions, using the standard model with the parameters adjusted as in Table 7.4. Test 2 and the corresponding leach test for 30 mg/l copper are shown in Figure 7.25, and Test 4 and the corresponding leach test for 100 mg/l copper are shown in Figure 7.26.

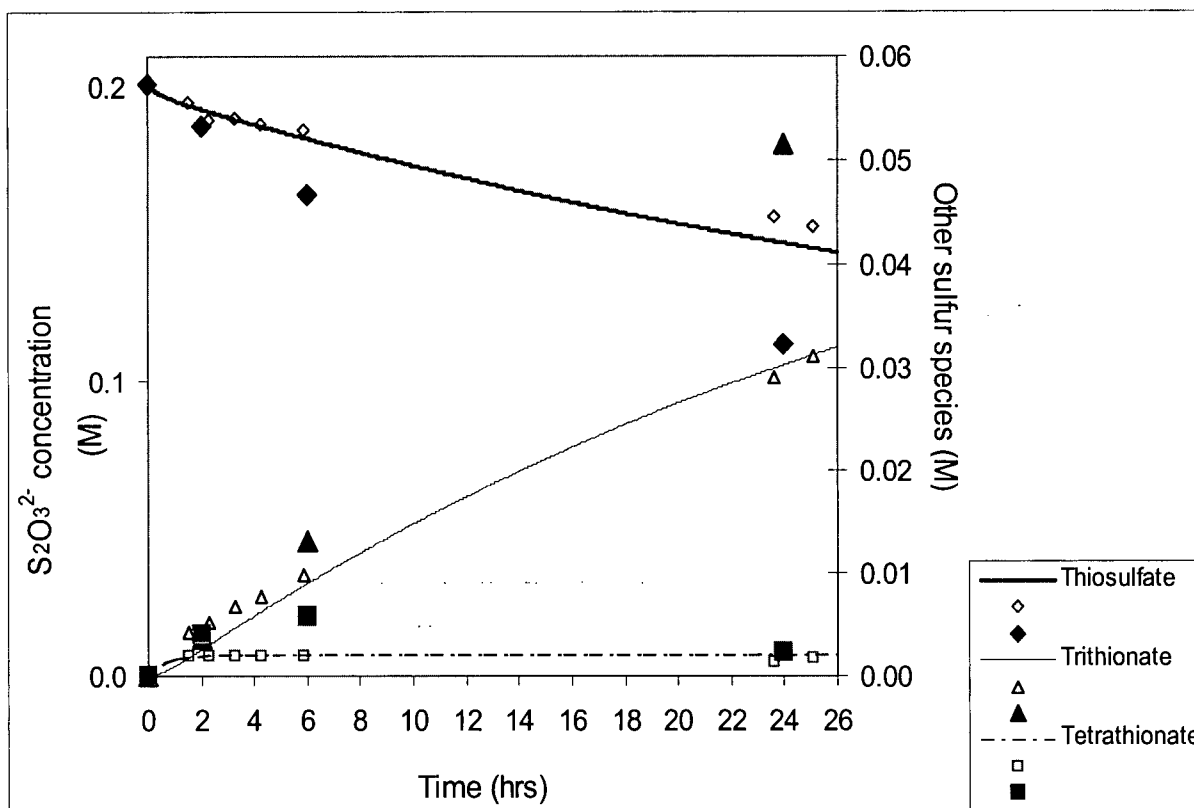


Figure 7.25 : Model output versus experimental data for sulfur oxyanion speciation
during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.05 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.4-0.42 M NH_3 , 30-32 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space
- Assumed that thiosulfate reacts via reaction R1 and R4.

(Lines represent modelled trends. Open symbols represent experimental values in the absence of ore, closed symbols represent experimental values in the presence of ore.)

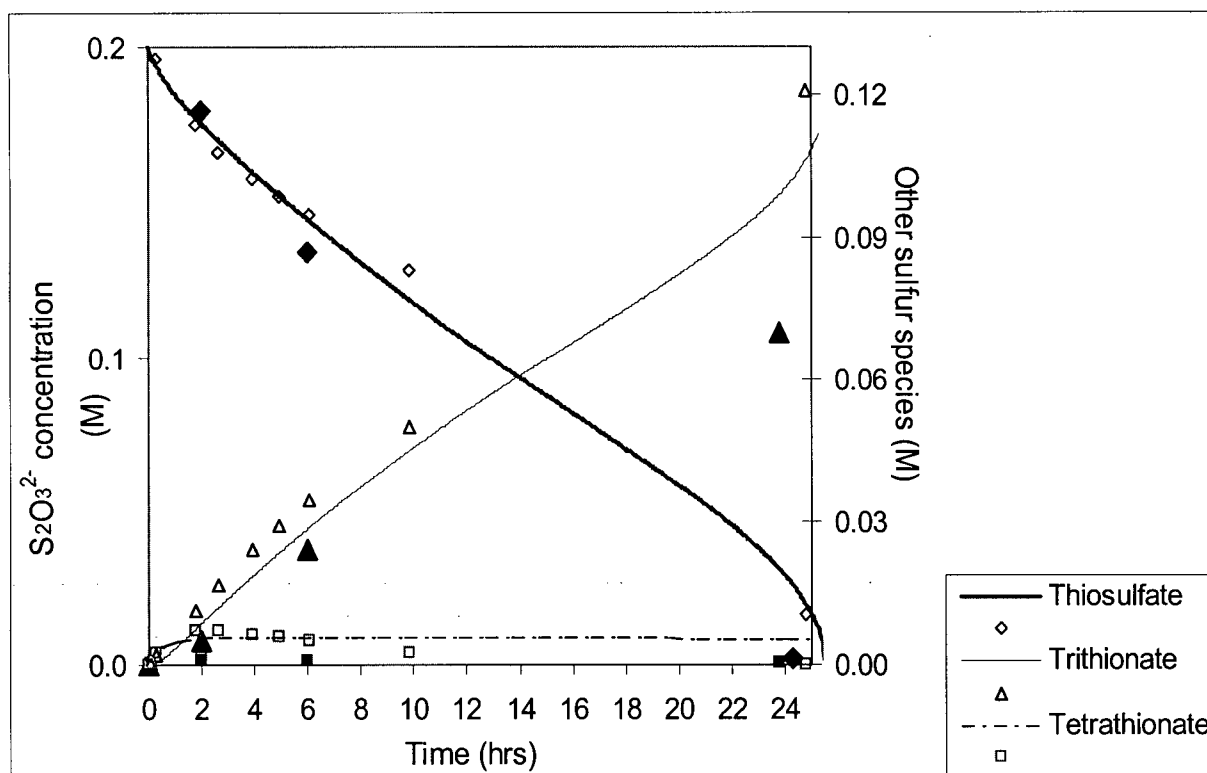


Figure 7.26 : Model output versus experimental data for sulfur oxyanion speciation during thiosulfate degradation

- Model parameters adjusted by the following factors: $ak_{R1} - 12 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.17 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.3 – 0.4 M NH_3 , 100 - 101 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space
- Assumed that thiosulfate reacts via reaction R1 and R4.

(Lines represent modelled trends. Open symbols represent experimental values in the absence of ore, closed symbols represent experimental values in the presence of ore.)

For both leach tests, the thiosulfate degradation was faster in the presence of ore than in the solution only tests. The presence of ore is likely to enhance the degradation of thiosulfate, and there have been some limited investigations into the effects of ore on thiosulfate degradation (Wan, 1997, Xu and Schoonen, 1995, De Jong, 2004). For the test at 30 mg/l copper, more trithionate was produced than in the absence of ore, while for the 100 mg/l copper test, less trithionate was produced. There could be an effect of ore on the trithionate degradation rate.

The differences between tests in the presence and absence of ore show that it is necessary to test the effects of ores on the various sulfur oxyanion reactions to be able to fully understand the system.

7.6 SCOPE OF USE OF MODEL

Based on the discussion in Section 7.4.7 on the shortcomings of the model in predicting thiosulfate degradation and the subsequent sulfur oxyanion speciation in the absence of ores, and the observed difference in solution chemistry in the presence of ore (Section 7.5), the scope of use of the model in its current form is somewhat limited and cannot be considered quantitative. However, the model does show that our understanding of the thiosulfate degradation pathways in particular is limited, highlighting the need for further work in this area. The model can be used to estimate general trends in sulfur oxyanion speciation during thiosulfate degradation, provided that the model parameters are adjusted according to the empirical factors given in Table 7.4. While the model was not optimised for solutions containing ores and there is a difference in results when ores are present, the general trends are similar. Even though the model is in need of significant refining, involving much testwork, since the qualitative trends it predicts are similar to those seen experimentally, the model is useful to identify factors which have a significant influence on the sulfur oxyanion speciation. The impact of solution conditions on the thiosulfate degradation and sulfur oxyanion speciation as predicted by the model is discussed in Section 7.7.

7.7 IMPACT OF SOLUTION CONDITONS

The model was used to predict the sulfur oxyanion speciation for changing solution conditions. The effects of copper concentration, ammonia concentration, pH, dissolved oxygen concentration, initial thiosulfate concentration and solution recycle on the model output were examined. Each of these parameters was varied in turn and input into the model. Because the best-fit model parameters in Table 7.4 varied with the experimental conditions, three scenarios were modelled for each of the solution parameters tested, using the best-fit model parameters and solution conditions for Test 2, Test 4 and Test 5. The solution speciation after 24 hours predicted by the model was plotted against the parameter being tested.

This evaluation shows how the model could be used to highlight potential concerns regarding thiosulfate degradation during gold leaching, and how solution conditions can be optimised to minimise thiosulfate degradation.

7.7.1 Copper Concentration

The copper concentration was increased from 10 mg/l to 90-120 mg/l for the three model scenarios based on Tests 2, 4 and 5. In all cases, increasing the copper concentration increased the thiosulfate degradation rate as expected, since thiosulfate degradation to both tetrathionate and trithionate has a rate dependent on the copper concentration. According to the model, neither trithionate degradation nor tetrathionate degradation are affected by copper, so the overall rate of formation of these species increased with an increase in copper concentration.

The concentrations of thiosulfate and trithionate after 24 hours, as well as the molar ratio of trithionate to thiosulfate are shown in Figures 7.27, 7.28 and 7.29 for the three model scenarios corresponding to Tests 2, 4 and 5 respectively. The tetrathionate concentration was found to vary much more with the pH than with the copper concentration, and since the tetrathionate concentrations were generally much lower than the other species, they are not shown in this evaluation. In all cases, the trithionate to thiosulfate ratio increased with an increase in copper concentration, with the extent of this increase increasing with copper concentration as well. Limiting the copper concentration is essential to limit thiosulfate degradation, but since copper is required to facilitate gold leaching, the system needs to be optimised for both leaching and thiosulfate degradation.

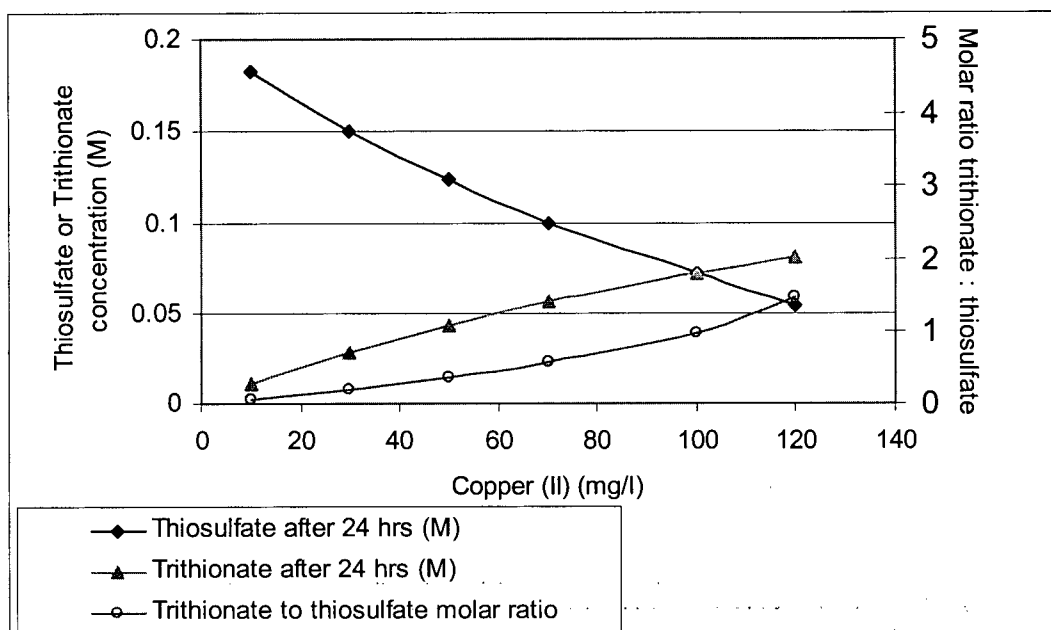


Figure 7.27 : Modelled thiosulfate and trithionate concentrations after 24 hours at varying copper concentrations

- Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.05 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.4 M NH_3 , pH 10, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

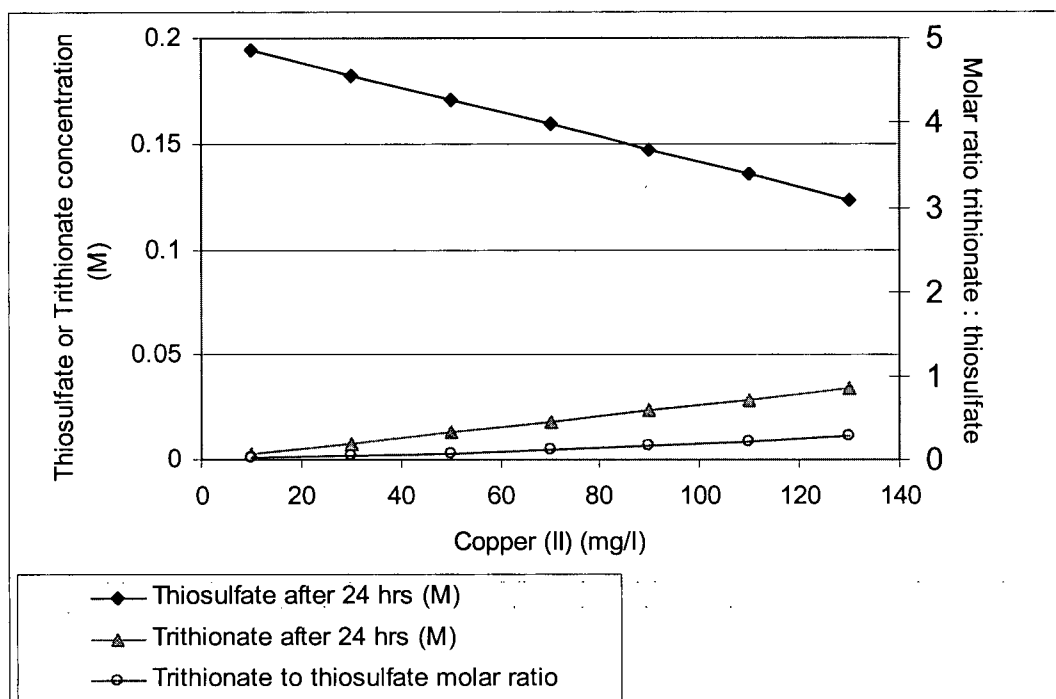


Figure 7.28 : Modelled thiosulfate and trithionate concentrations after 24 hours at varying copper concentrations

- Model parameters adjusted by the following factors: $ak_{R1} - 1x$, $k_{R2} - 10x$, $k_{R3} - 5x$, $bk_{R4} - 0.10x$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.4 M NH_3 , pH 9, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

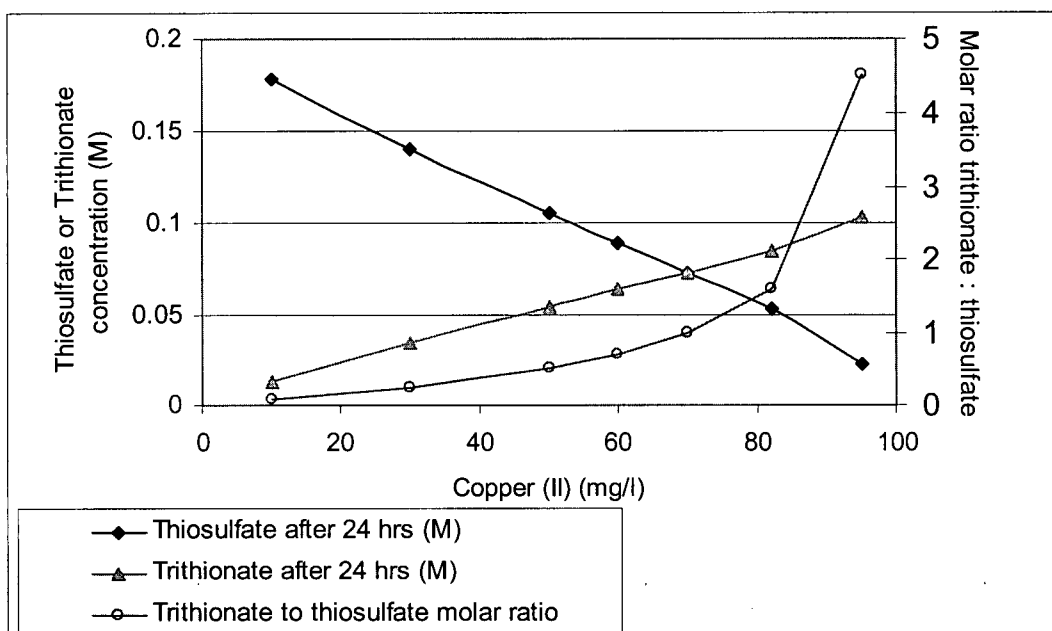


Figure 7.29 : Modelled thiosulfate and trithionate concentrations after 24 hours at varying copper concentrations

- Model parameters adjusted by the following factors: $ak_{R1} - 12 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.17 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.3 M NH_3 , pH 10, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

7.7.2 Total Ammonia Concentration

The effect of the ammonia concentration on the thiosulfate and trithionate concentrations modelled after 24 hours is shown in Figures 7.30, 7.31 and 7.32 for the three model scenarios. While there are quantitative differences depending on which model parameters were used, in all cases the model shows that it is beneficial to increase the ammonia concentration to limit thiosulfate degradation and the ratio of trithionate to thiosulfate. It is known that free copper reacts very rapidly with thiosulfate and that ammonia retards this reaction as expressed in the rate equation for Reaction R1 in Equation 7.3. The optimal ammonia concentration will depend on the other solution conditions (copper concentration and pH). It should be noted that the rate equation for Reaction R4 (thiosulfate degradation to trithionate) was derived under conditions of

about 0.2 to 0.6 M ammonia. At higher ammonia concentrations, the rate of thiosulfate degradation to trithionate was dependent on an inverse of the ammonia concentration (see Figure 7.2), so the trends noted in Figure 7.30, 7.31 and 7.32 would be even more pronounced.

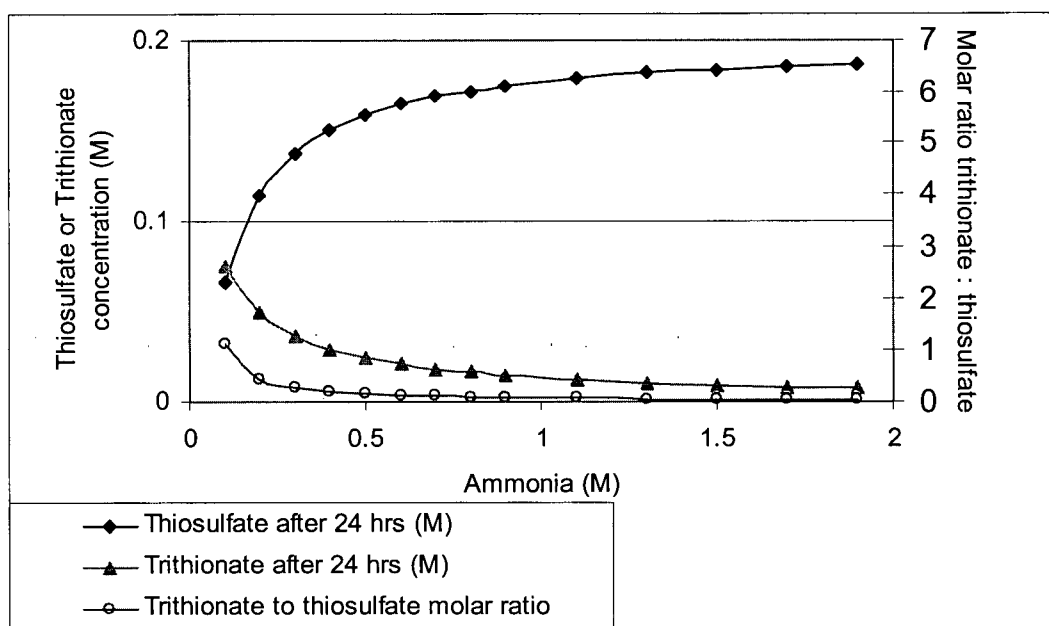


Figure 7.30: Modelled thiosulfate and trithionate concentrations after 24 hours at varying ammonia concentrations

- Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.05 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 30 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

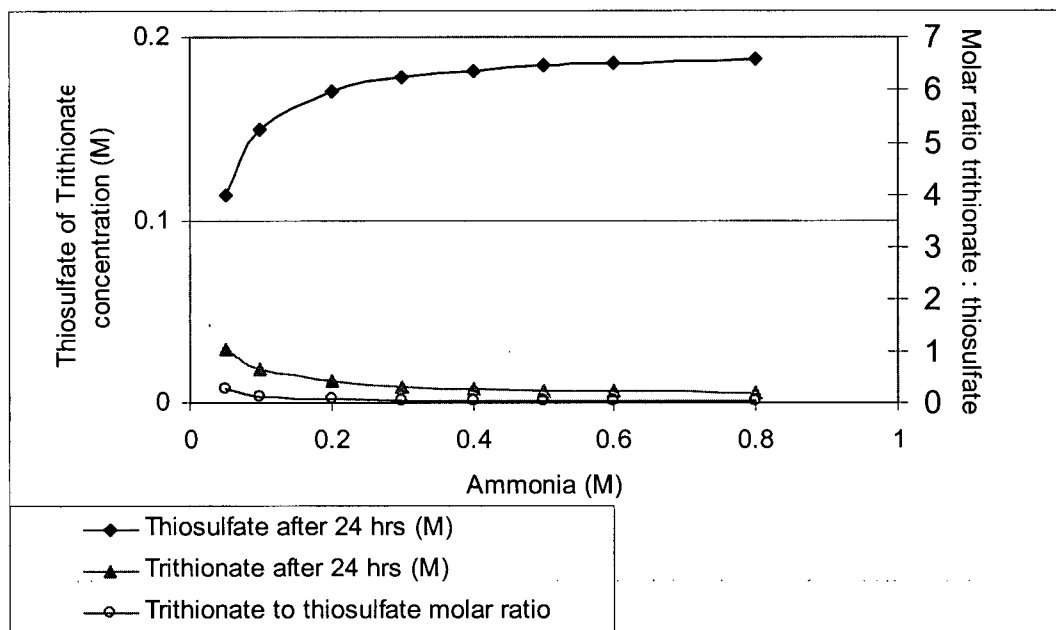


Figure 7.31 Modelled thiosulfate and trithionate concentrations after 24 hours at varying ammonia concentrations

- Model parameters adjusted by the following factors: $ak_{R1} - 1 \times$, $k_{R2} - 10 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.10 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 30 mg/l Cu^{2+} , pH 9, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

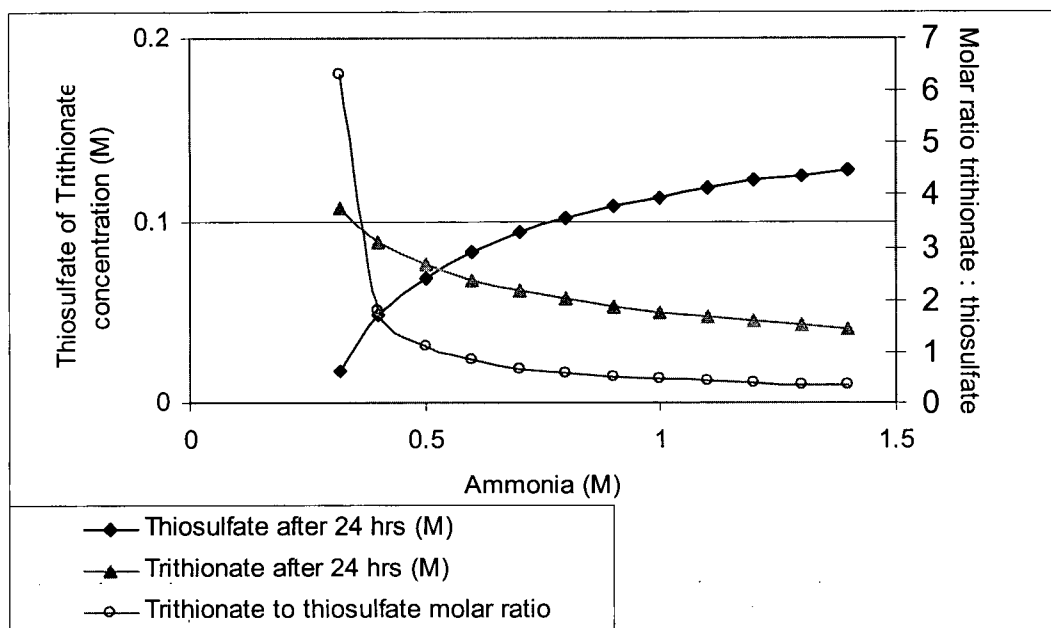


Figure 7.32: Modelled thiosulfate and trithionate concentrations after 24 hours at varying ammonia concentrations

- Model parameters adjusted by the following factors: $ak_{R1} - 12 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.17 \times$.
- Initial conditions: $0.2 \text{ M S}_2\text{O}_3^{2-}$, 100 mg/l Cu^{2+} , pH 10, 25°C , sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

7.7.3 pH

The effect of the pH on the thiosulfate, trithionate and tetrathionate concentrations modelled after 24 hours is shown in Figures 7.33 and 7.34 for two model scenarios, corresponding to Tests 2 and 4 respectively. Data is not shown corresponding to the Test 5 scenario since at pH values less than 10, all the thiosulfate was predicted to have degraded in less than 24 hours. The main impact of changing pH was to change the tetrathionate concentration, with greater tetrathionate concentrations being reached at lower pH values. It was shown that for either scenario, the trithionate concentration was not affected much by a change in pH, but the overall polythionate to thiosulfate ratio was higher at lower pH due to the presence of tetrathionate. The fact that the model gave an increased thiosulfate degradation rate at lower pH is due mainly to the changes in free

ammonia concentration with pH for a given total ammonia concentration. The variability in the best-fit model parameters for Test 2 and for Test 4 (at different pH values) may be due to the way in which ammonia is taken into consideration in the rate equations or because pH is not directly included in the rate equations for thiosulfate degradation. This highlights a shortcoming in the model.

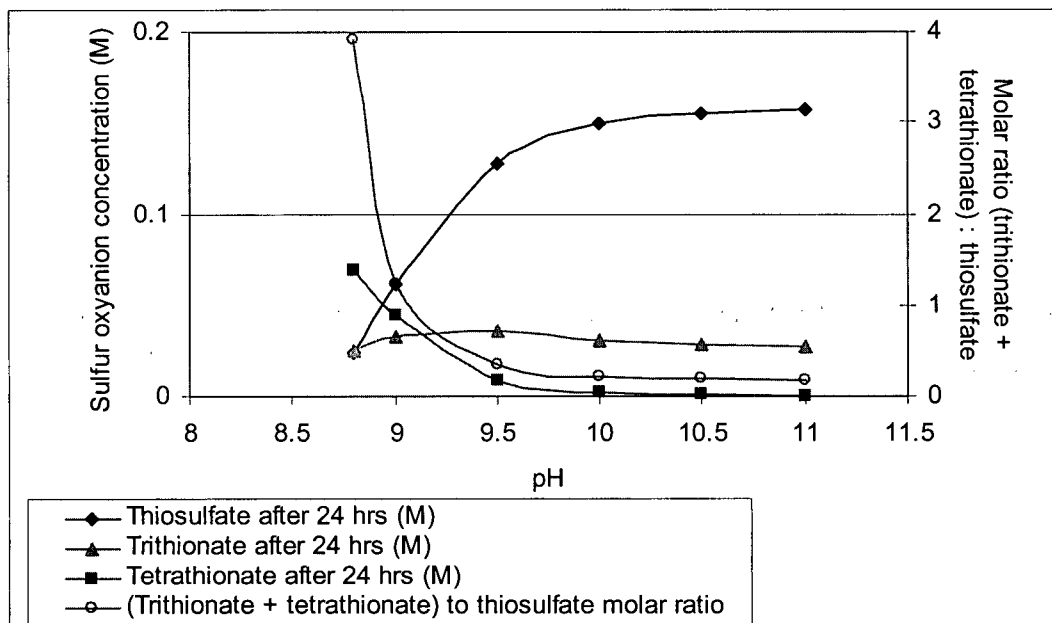


Figure 7.33: Modelled thiosulfate and trithionate concentrations after 24 hours at varying pH

- Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.05 \times$.
- Initial conditions: $0.2 \text{ M S}_2\text{O}_3^{2-}$, 30 mg/l Cu^{2+} , 0.4 M NH_3 , 25°C , sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

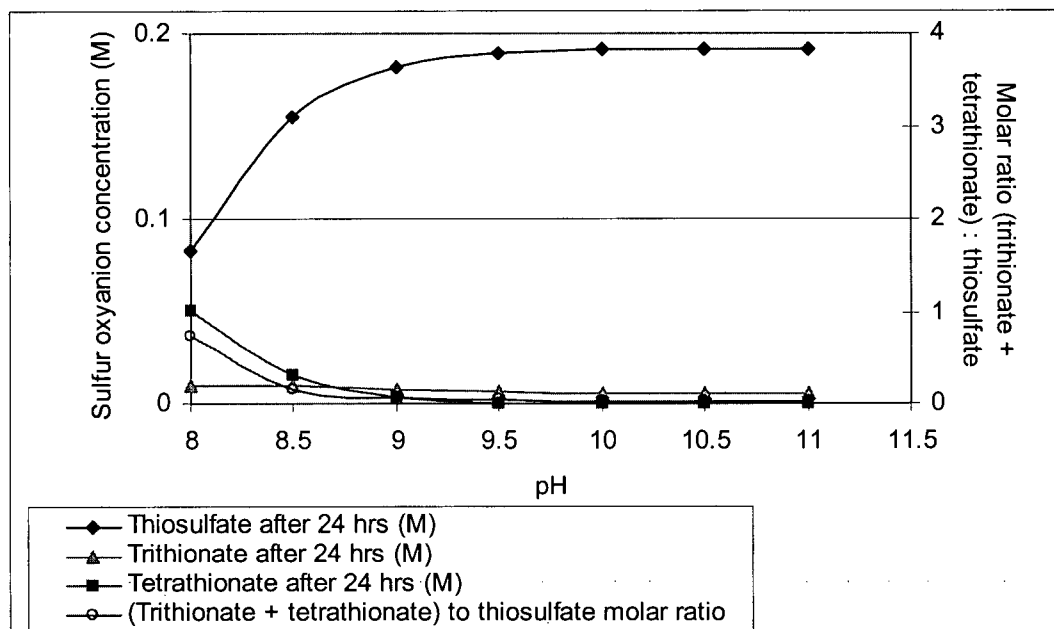


Figure 7.34: Modelled thiosulfate and trithionate concentrations after 24 hours at varying pH

- Model parameters adjusted by the following factors: $ak_{R1} - 1 \times$, $k_{R2} - 10 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.10 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 30 mg/l Cu^{2+} , 0.4 M NH_3 , 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

7.7.4 Dissolved Oxygen

According to the model, only the degradation of thiosulfate to trithionate is affected by the dissolved oxygen concentration. As seen in Table 7.4, this reaction seemed to occur to the greatest extent under conditions corresponding to Test 5 (high copper concentration). The model was tested using the best fit conditions for this test varying the dissolved oxygen concentration. With 20 mg/l dissolved oxygen, 0.2 M thiosulfate degraded completely within 22 hours, producing 0.118 M trithionate. With 2 mg/l dissolved oxygen, 0.2 M thiosulfate took 25 hours to completely degrade, producing 0.113 M trithionate. The level of dissolved oxygen did not lead to a significant difference in the time taken for complete thiosulfate degradation nor the solution speciation. However, it is possible that the dissolved oxygen concentration could have had an effect

on other reactions, particularly the degradation of thiosulfate to tetrathionate, but this was not taken into account in the model.

7.7.5 Thiosulfate Concentration

The graphs in Figure 7.35, 7.36 and 7.37 show how the concentrations of thiosulfate and trithionate at 24 hours are affected by the initial thiosulfate concentration, and the effect on the ratio of trithionate to thiosulfate after 24 hours, for the three different model scenarios. From these graphs it is clear that if the initial thiosulfate concentration is too low, the relative amount of trithionate formed is very large. At higher initial thiosulfate concentrations, even though the magnitude of the trithionate concentration formed is higher, so is the remaining thiosulfate concentration.

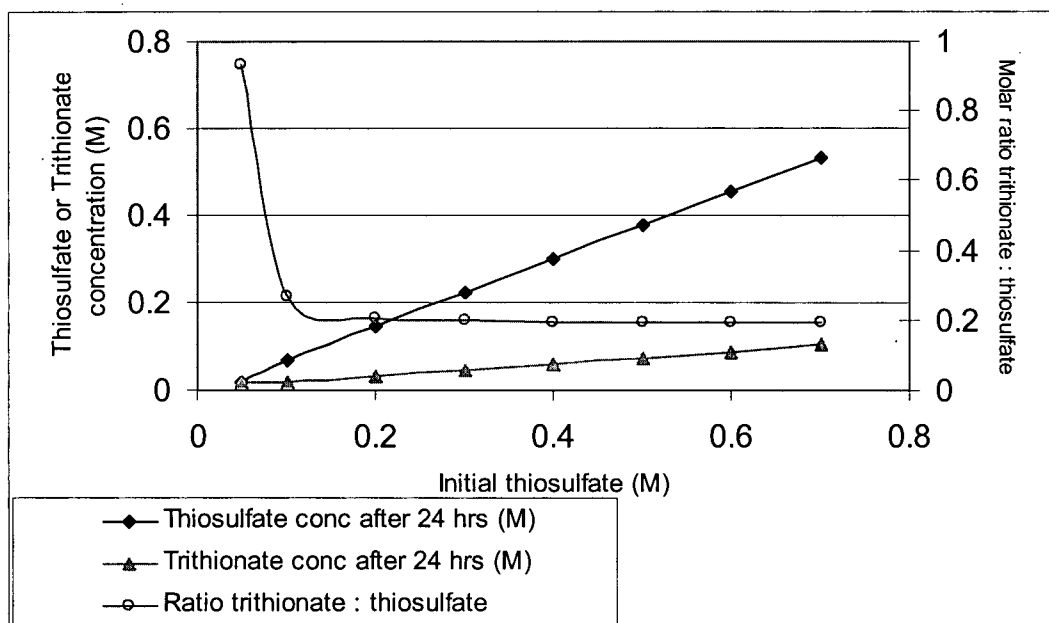


Figure 7.35 : Modelled thiosulfate and trithionate concentrations after 24 hours at varying initial thiosulfate concentrations

- Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.05 \times$.
- Initial conditions: 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

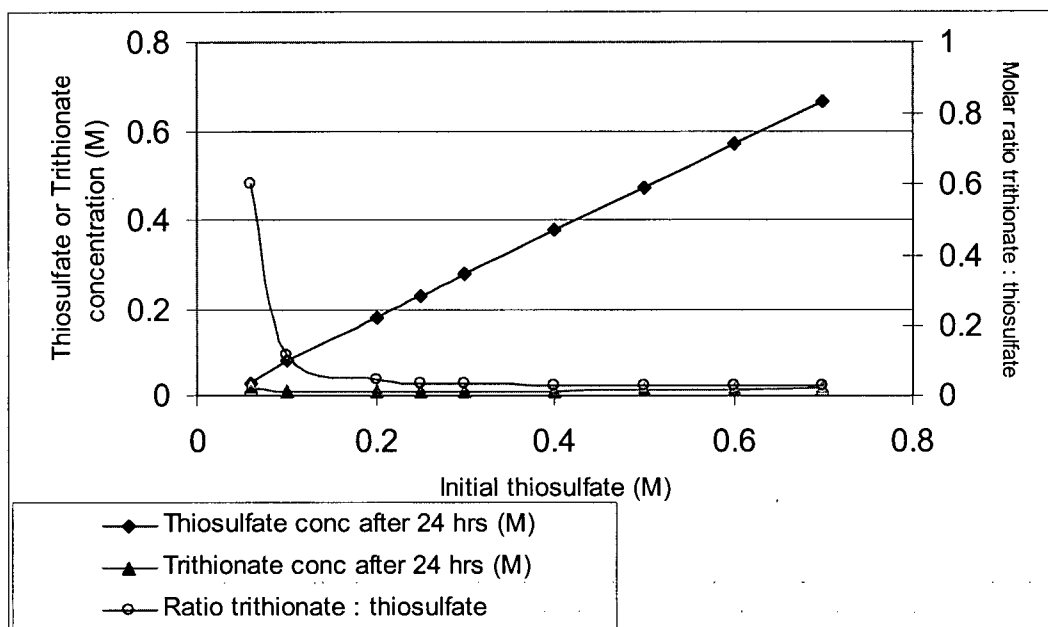


Figure 7.36 : Modelled thiosulfate and trithionate concentrations after 24 hours at varying initial thiosulfate concentrations

- Model parameters adjusted by the following factors: $ak_{R1} - 1 \times$, $k_{R2} - 10 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.10 \times$.
- Initial conditions: 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 9, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

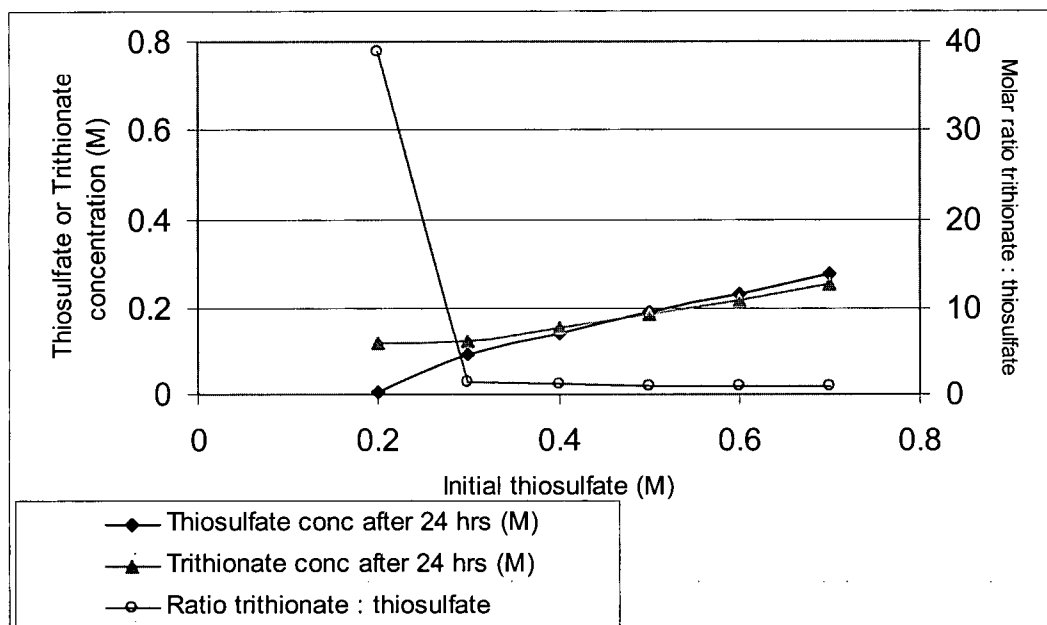


Figure 7.37 : Modelled thiosulfate and trithionate concentrations after 24 hours at varying initial thiosulfate concentrations

- Model parameters adjusted by the following factors: $ak_{R1} - 12 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.17 \times$.
- Initial conditions: 0.3 M NH_3 , 100 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

This effect is enhanced in Figure 7.37, which gives the model scenario corresponding to the high copper situation of Test 5. In this case, the reaction of thiosulfate degradation to trithionate plays a significant role, and the rate equation for this reaction involves an inverse dependency on the thiosulfate concentration. Lower thiosulfate concentrations will thus give more rapid degradation after longer times, as was seen in Figure 7.24.

The effect of recycling the solution with and without replenishing the thiosulfate concentration was investigated using the model. The graph in Figure 7.38 shows the model output over 7 days, assuming recycling of the leach solution with no adjustment to the reagent concentrations. Conditions and model best-fit parameters corresponding to Test 2 were used, according to Table 7.4. In Figure 7.39, the effects of replenishing the

thiosulfate concentration to its initial concentration every 24 hours are shown. The findings are summarised in Table 7.6, along with a comparison to a situation with no recycling where it was assumed that fresh leach solution was used every 24 hours.

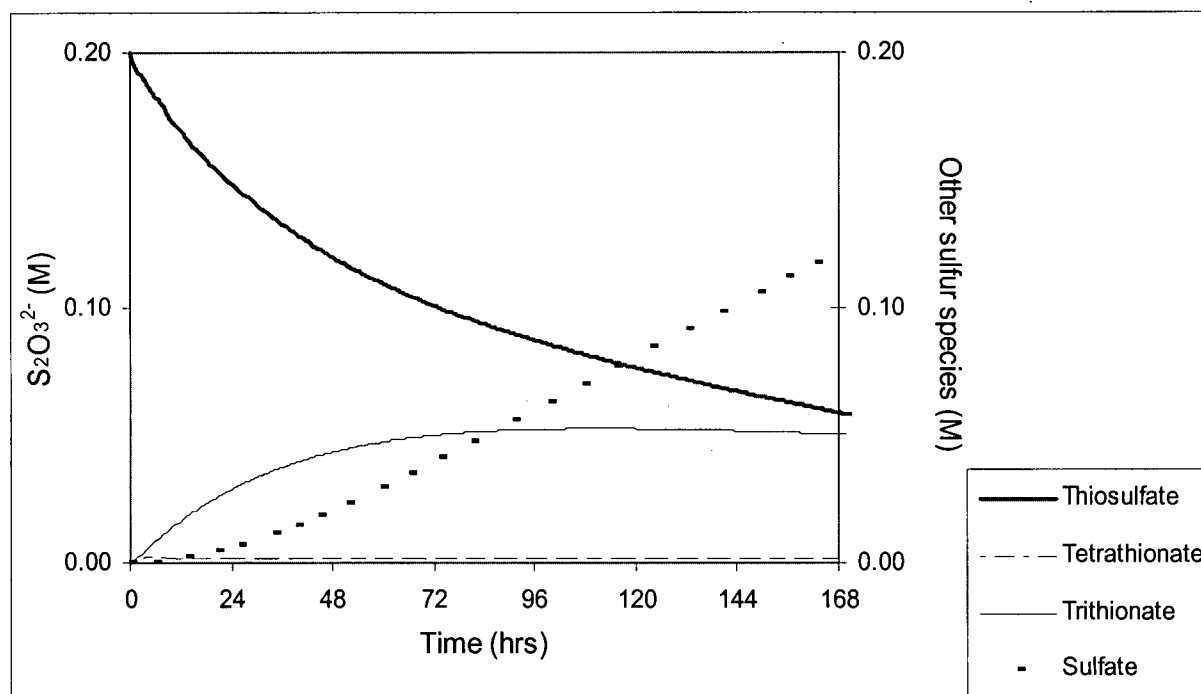


Figure 7.38 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation over 7 days

- Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.05 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

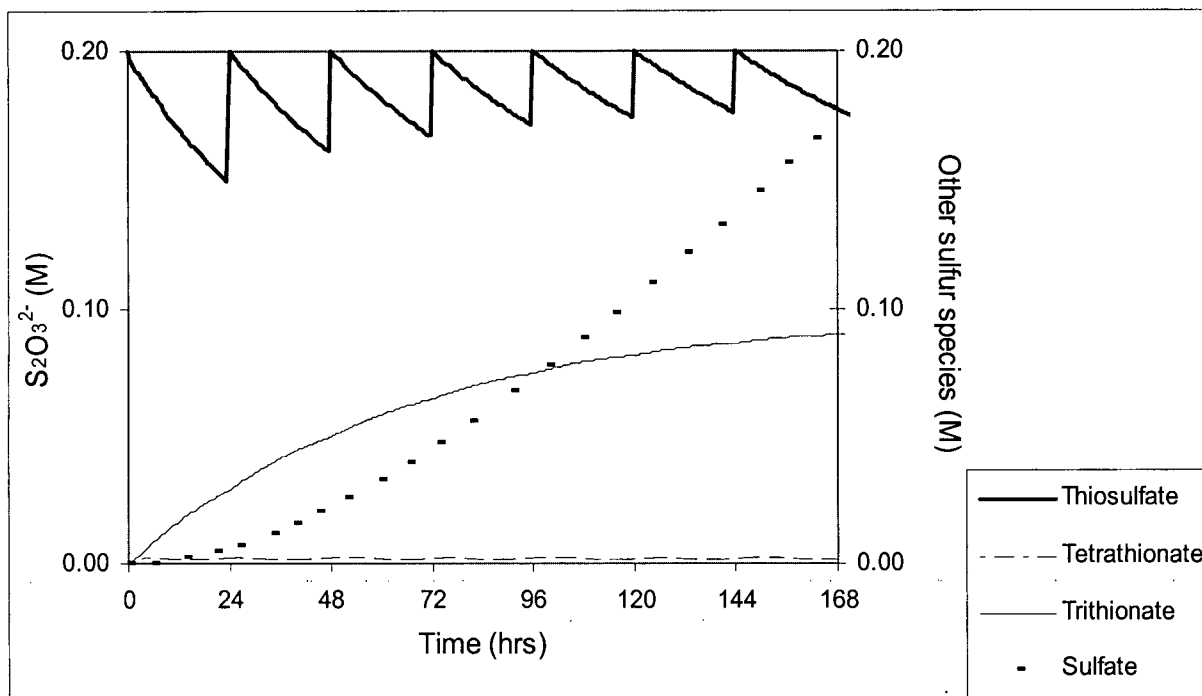


Figure 7.39 : Modelled output for sulfur oxyanion speciation during thiosulfate degradation with thiosulfate replenished every 24 hours

- Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.05 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.4 M NH_3 , 30 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space.
- Assumed that thiosulfate reacts via reaction R1 and R4.

Table 7.6 : Effect of recycling on thiosulfate consumption and solution speciation (Initial conditions 0.2 M $S_2O_3^{2-}$, 30 mg/l Cu, 0.4 M NH_3 , 25 °C, pH 10, with model parameters set as in Table 7.2 for Test 2)

Condition	Total $S_2O_3^{2-}$ consumed (M)	Solution concentration after 7 days (M)			
		$S_2O_3^{2-}$	$S_4O_6^{2-}$	$S_3O_6^{2-}$	SO_4^{2-}
No recycle – 7 x 24 hr leaches, each with fresh thiosulfate-only leach solution	0.357	0.149	0.002	0.0287	0.006
Recycle – 7 day recycle with no additional reagent addition	0.141	0.059	0.002	0.0503	0.122
Recycle with reagent replenishment – 7 days recycle with thiosulfate concentration replenished every 24 hrs	0.224	0.177	0.002	0.0897	0.174

The total thiosulfate consumption was the highest where there was no solution recycle. However, the thiosulfate to polythionate ratio in the solution after each 24 hour leach was the highest, so this scenario could be favoured in situations where resin recovery of gold is used and the polythionate concentration is ideally kept as low as possible. Solution recycle with replenishment of the thiosulfate reagent every 24 hours gave higher thiosulfate consumption and higher trithionate concentration in the final solution after 7 days recycling than where the solution was recycled with no thiosulfate replenishment. However, the final ratio of polythionates to thiosulfate was lower than where no reagent addition occurred.

Similarly, the thiosulfate consumption for a higher copper scenario corresponding to Test 5 with and without recycling is shown in Table 7.7. In this case, the thiosulfate reagent was completely depleted after 24 hours, so only two situations were considered. In the first, it was assumed that there was no recycling and that fresh leach solution was used every 24 hours. In the second case it was assumed that the thiosulfate reagent was replenished to its initial concentration every 24 hours.

Table 7.7 : Effect of recycling on thiosulfate consumption and solution speciation (Initial conditions 0.2 M $S_2O_3^{2-}$, 100 mg/l Cu, 0.3 M NH_3 , 25 °C, pH 10, with model parameters set as in Table 7.2 for Test 5)

Condition	Total $S_2O_3^{2-}$ consumed (M)	Solution concentration after 7 days (M)			
		$S_2O_3^{2-}$	$S_4O_6^{2-}$	$S_3O_6^{2-}$	SO_4^{2-}
No recycle – 7 x 24 hr leaches, each with fresh thiosulfate-only leach solution	1.4	0	0.006	0.1104	0.019
Recycle with reagent replenishment – 7 days recycle with thiosulfate concentration replenished every 24 hrs	0.81	0.117	0.007	0.3297	0.624

In this case, the thiosulfate consumption was again decreased by recycling with replenishment of thiosulfate compared with no recycling at all.

The effect of recycling on gold leaching needs to be taken into consideration as well.

8. CONCLUSIONS

A review of the literature showed that while there is a significant amount of literature on gold leaching in ammoniacal thiosulfate solutions, the topic of thiosulfate degradation during leaching has not been given the attention it deserves, especially since thiosulfate degradation is one of the major concerns in the thiosulfate leaching process. Where thiosulfate degradation has been discussed, often the reagent consumption is given without reference to which degradation products have been formed, or their quantities. The two most common metastable thiosulfate degradation products are trithionate and tetrathionate, with trithionate being particularly persistent in gold leach solutions. It was found in the review that little was known about this species, particularly in the context of gold leaching. Therefore, in this work, the reactions of trithionate in solution were investigated experimentally, and the kinetics of trithionate degradation were derived. The rate equation derived was used in a model of the overall thiosulfate degradation system.

The reaction stoichiometry of trithionate degradation in alkaline solutions was found to match that of Equation 8.1.



Based on the quantitative experimental observations, the rate of degradation of trithionate in aqueous ammoniacal solutions could be expressed by Equation 8.2.

$$-d[\text{S}_3\text{O}_6^{2-}]/dt = (k_3[\text{NH}_4^+] + k_2[\text{NH}_3] + k_1[\text{OH}^-] + k_0)[\text{S}_3\text{O}_6^{2-}] \quad [8.2]$$

where at 40 °C

$$\begin{aligned} k_0 &= 0.012 \text{ h}^{-1} \\ k_1 &= 0.74 \text{ M}^{-1}.\text{h}^{-1} \\ k_2 &= 0.0049 \text{ M}^{-1}.\text{h}^{-1} \\ k_3 &= 0.01 \text{ M}^{-1}.\text{h}^{-1} \end{aligned}$$

The degradation of trithionate in water, represented by k_0 in Equation 8.2, was in agreement with that found by others. An increase in hydroxide concentration increased the trithionate degradation rate.

The presence of ammonia was found to increase the rate of trithionate degradation to a small extent. It has been suggested previously that in the presence of ammonia, sulfamate forms instead of sulfate as one of the reaction products. While this has not been proven either by previous researchers under the conditions relevant here, or in this work, it is possible that even if ammonia itself does not react to form sulfamate, it could still interact with trithionate and facilitate the latter's degradation by hydroxide, for example.

Potassium and ammonium ions were found to increase the rate of trithionate degradation. The similar effect of these ions was likely due to their similar size and equal charge. This effect of positive ions on the rate implied the formation of a positive complex between the positive ions and trithionate, possibly of the form KS_3O_6^- or $\text{NH}_4\text{S}_3\text{O}_6^-$, which altered the electronic properties of the trithionate to enhance its degradation. Such ionic complexes have been reported previously for thiosulfate.

The effect of pH (hydroxide ions) was only significant at high pH values where the hydroxide ion concentration was high. However, the effects of ammonia and ammonium ions gave an apparent pH effect. As the pH increased, for a given total ammonia plus ammonium concentration, the rate of trithionate degradation decreased slightly to around pH 9, then decreased faster to around pH 10 where the rate reached a minimum. Upon further increase of the pH the rate increased rapidly, due to the increase in both hydroxide and ammonia concentration.

Thiosulfate was found to affect the trithionate degradation rate in different ways, depending on the ammonium concentration. The presence of lower concentrations of thiosulfate catalysed the reaction while excess thiosulfate inhibited it. The amount of thiosulfate required to see these effects was dependent on the ammonium ion concentration. It is known that thiosulfate can form complex ions with monovalent cations. Interaction of thiosulfate with trithionate at the sulfonyl sulfur atom of trithionate is likely to cause the catalytic effect on trithionate degradation, as thiosulfate and trithionate are known to undergo an exchange reaction, involving bond breaking and reforming. However, too high a thiosulfate concentration may sterically hinder the

association of trithionate with other species like hydroxide and ammonia, giving the observed inhibitory effect.

Limiting the amount of oxygen in solution had no influence on the trithionate degradation rate. This is to be expected based on the reaction stoichiometry of Equation 8.1.

Cupric copper was not found to have any significant effect on the rate of trithionate degradation under the conditions tested. It is possible that there could be an effect noted under a different experimental regime.

The activation energy for the trithionate degradation reaction in the presence of ammonia and ammonium was found to be about 75 kJ/mol between 25 and 40 °C.

A model was set up to integrate the observed trithionate degradation rate equation (Equation 8.2) into the overall thiosulfate degradation scheme in gold leaching systems. Rate equations based on literature findings were used in conjunction with the experimental findings reported in this thesis. The model was evaluated against experimental results for thiosulfate degradation and subsequent solution speciation in the absence of ores.

The model parameters were adjusted to obtain a best fit to the experimental data. It was found that the best-fit parameters varied with the experimental conditions, indicating inadequacies not only in the initial values of the model parameters but in the form of the rate equations used to set up the model.

The main objective of the model was to improve the understanding of the sensitivity of the solution speciation to the various reaction pathways involved, to highlight shortcomings in our understanding of sulphur oxyanion speciation during thiosulfate degradation. The model in its standard form was not able to quantitatively describe the system.

The graph in Figure 8.1 shows typical qualitative output for the model matched by experimental data. The thiosulfate concentration rapidly decreases and there is an initial increase in tetrathionate concentration. However at the alkaline pH values used in gold

leaching, the tetrathionate rapidly degrades, resulting in a slow decrease in the tetrathionate concentration. This results in the formation of trithionate. Trithionate is also formed directly from thiosulfate degradation.

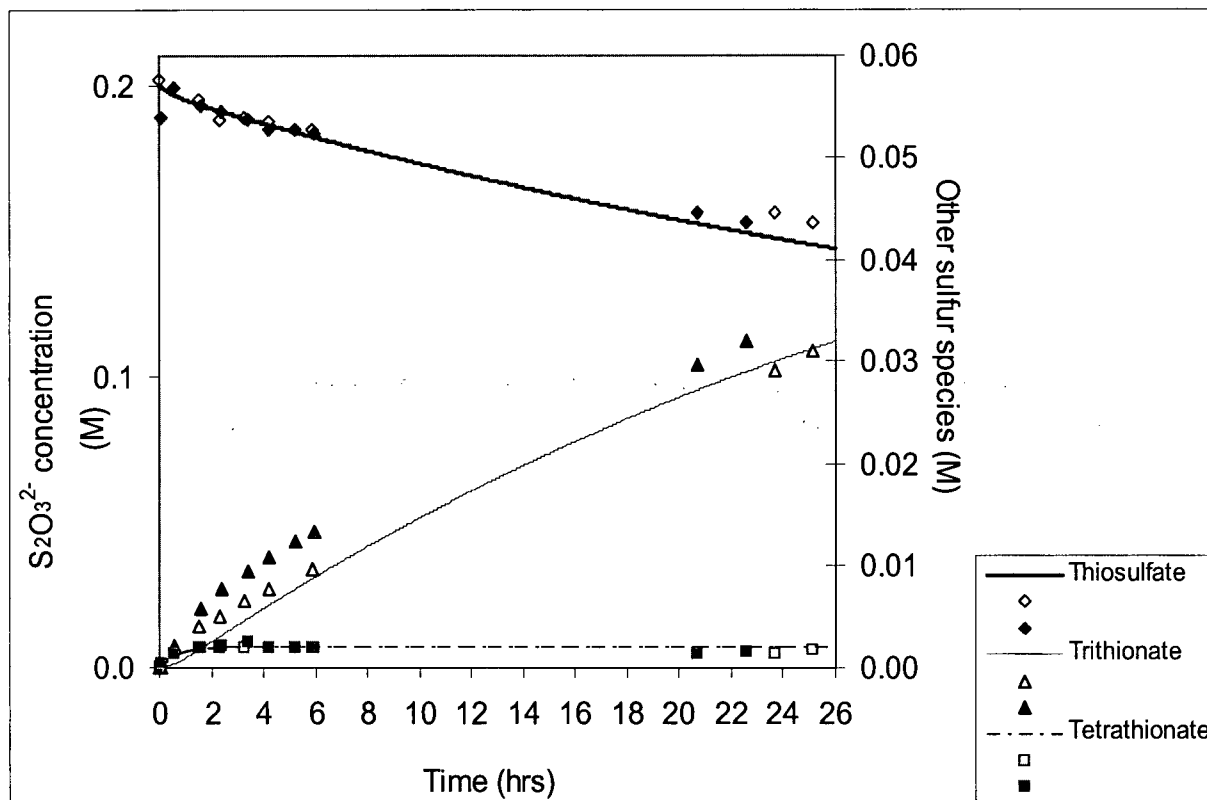


Figure 8.1 : Typical model output against experimental data

- Model parameters adjusted by the following factors: $ak_{R1} - 15 \times$, $k_{R2} - 8 \times$, $k_{R3} - 5 \times$, $bk_{R4} - 0.05 \times$.
- Initial conditions: 0.2 M $S_2O_3^{2-}$, 0.42 M NH_3 (closed symbols) or 0.38 M NH_3 (open symbols), 32 mg/l Cu^{2+} , pH 10, 25 °C, sealed vessel with O_2 in head space

The model had the following shortcomings:

Tetrathionate concentration profile: The tetrathionate concentration predicted by the model was too high. Increasing the rate of tetrathionate degradation by a constant factor across a range of experimental conditions gave a much more satisfactory fit, but the model was not able to predict the decrease in tetrathionate concentration which occurred

after its maximum concentration had been reached. It is thought that the presence of copper was responsible for this behaviour and copper was not taken into consideration in modelling tetrathionate degradation. Even with these shortcomings, given that the tetrathionate concentration was very low, it could be adequately predicted by the model if the tetrathionate degradation rate was increased by a factor of 8-10.

Trithionate concentration profile: In general, the trithionate concentrations predicted by the model at longer times were too high. Increasing the rate of trithionate degradation by a constant factor for the range of experimental conditions used improved the fit. The rate of trithionate degradation modelled in this work did not take into account the effect of thiosulfate concentration, as it was expected to be negligible, as discussed in Chapter 5. However, after longer times where less thiosulfate was available, conditions for thiosulfate catalysis of trithionate degradation could have become more favourable. Even increasing the trithionate degradation rate by a constant factor did not give a perfect fit to the experimental data. This is expected to be due to inadequacies in the prediction of trithionate formation from thiosulfate.

Thiosulfate concentration profile: While the thiosulfate concentration profile could be predicted using the model, it was necessary to adjust the rates of thiosulfate degradation to both tetrathionate and trithionate, and the extent of these adjustments varied with the experimental conditions. The modelled thiosulfate degradation had the most significant effect on the solution speciation. But variation of the thiosulfate degradation rate with copper concentration and pH were not adequately addressed.

The main limiting factor in the model is finding the best way to include the thiosulfate degradation reactions. The rate equations used were derived from experimental data that utilised non-reliable techniques, and the data was open to interpretation to derive the kinetics. There is currently a significant amount of work being done in this area, and hopefully there will soon be a better fundamental understanding of this process. In particular, the role of cupric copper (in its various forms), dissolved oxygen and ores/minerals needs to be included.

There are two ways to limit thiosulfate consumption – either thiosulfate degradation can be inhibited, or thiosulfate can be regenerated from its degradation products. The

problem with regeneration is that for commercial reasons, gold must first be removed from the solution. It is also possible to regenerate part of the thiosulfate from tetrathionate and trithionate degradation, but part of the initial thiosulfate is then lost to sulfate. The favoured route will vary depending on the extent of degradation under the leach conditions used, the economics of the process and the proposed process for gold recovery from solution. The complete removal of trithionate even at the expense of forming some sulfate may be generally more favourable than sacrificing gold leaching to minimise trithionate formation in the first place.

Based on the model output under a number of conditions, decreasing the cupric concentration and increasing the ammonia concentration should help to minimise thiosulfate degradation. Solution recycle can also be used to minimise thiosulfate degradation but often results in a build up of trithionate. Limiting the reaction time would also be useful. If the aim is to form the least amount of trithionate possible, it is better to encourage the degradation of thiosulfate to tetrathionate and allow for tetrathionate degradation to trithionate and to inhibit the direct degradation of thiosulfate to trithionate. The tetrathionate route generates less trithionate per mole of thiosulfate and also the degradation of tetrathionate allows for the partial regeneration of thiosulfate. Limiting the amount of oxygen or increasing the amount of initial thiosulfate may encourage this. Both degradation pathways are directly related to the copper concentration, so limiting the copper concentration would be beneficial, as long as gold leaching is not inhibited. An increase in cupric concentration leads to more rapid thiosulfate degradation and more rapid formation of tetrathionate and trithionate. An increase in the ammonia concentration slows the rate of thiosulfate degradation, and less tetrathionate and trithionate are formed. Ammonia is known to complex with cupric copper, inhibiting the reaction between cupric copper and thiosulfate. Careful manipulation of the cupric and ammonia concentrations will have a significant impact on the stability of thiosulfate. A decrease in pH reduces the rate of tetrathionate degradation, in turn reducing the formation rate of trithionate, but also reducing the regeneration rate of thiosulfate.

However, even if leaching conditions are adjusted to minimise thiosulfate degradation, it is inevitable that trithionate will form. Rather than minimising trithionate formation, another option could be to remove trithionate from the leach solutions by its degradation. However, compared to the other reactions involved, the degradation of trithionate is

extremely slow under typical leach conditions. A large increase in pH or ammonia concentration will increase the trithionate degradation rate, but probably not sufficiently to have any major impact on the solution speciation. The effect of other cations in the system on trithionate degradation are not known – it is possible that certain cations will increase the degradation rate, while others may cause precipitation of trithionate. Similarly the degradation rate may be slowed down by the presence of certain components (e.g. metallic copper). The effect of ores and of elements solubilised from ores during gold leaching on the degradation rate of thiosulfate and the degradation products needs investigation. A more suitable focus for minimising trithionate in solution would be to investigate ways to selectively remove trithionate from solution.

9. RECOMMENDATIONS

This investigation has led to an improved understanding of the behaviour of trithionate in gold leach solutions and the model of the thiosulfate degradation system is a first step in developing a useful assessment method for thiosulfate degradation and solution speciation under gold leaching conditions. Further research is required in the following areas:

Trithionate degradation

- To confirm the effect of positive ions on trithionate degradation, a larger range of ions should be tested, e.g. Li^+ , Cs^+ , Ca^{2+} , Mg^{2+} , Au^+ and Ag^+ .
- More detail on the effect of copper and particularly the various complexes of copper on trithionate degradation is required.
- The role of dissolved oxygen should be investigated in the presence of copper.
- The effect of gold, silver and ores on trithionate degradation should be tested.

Modelling

- The model output was most sensitive to the parameters for the thiosulfate degradation rate. To be able to predict the rate of thiosulfate degradation and the reaction products, it is essential to fully understand this sub-process. There is currently a significant amount of work being carried out on in this area (Breuer and Jeffrey, various references). In particular the role of copper (or its complexes) and oxygen are considered important, and once better understood, the effect of using heterogeneous systems and ores should also be included.
- The effect of ores on not only thiosulfate degradation but on trithionate and tetrathionate degradation needs to be included in the model. Certain ore/mineral types will likely have a significant effect on these species.
- The sulfate concentrations predicted by the model should be validated against experimental data.

- Reasons for why the tetrathionate degradation rate and trithionate degradation rate predicted by the model are too low need further investigation. In particular, the effect of various copper species and the presence of thiosulfate are expected to be of importance.

Gold leaching

- The sulfur degradation products should always be determined during gold leaching if we are to be able to fully understand thiosulfate degradation.
- To minimise thiosulfate degradation, copper and oxygen required for gold oxidation should be minimised, and the ammonia concentration should be maximised, without inhibiting gold leaching. Solution recycling should be optimised based on the specific process requirements to either minimise thiosulfate degradation or minimise the polythionate to thiosulfate ratio. The leaching time should be limited.
- Depending on the temperature dependence of the gold leaching kinetics, it may be possible to select an optimum temperature to maximise gold leaching while minimising thiosulfate degradation.
- This work has not addressed the usefulness of using other species (e.g. EDTA) to inhibit the reaction between thiosulfate and cupric copper. There is scope for an investigation of this type, but the effects of the additives on gold leaching and on downstream processing and waste management issues must be included.
- Ways to selectively remove trithionate (and tetrathionate) from gold leach solutions possibly by high pH treatment, using resins and/or bioreduction should be investigated further, as these polythionates are always likely to be present.

10. REFERENCES

Abbruzzese C., Fornari P., Massida R., Veglio F., Ubaldini S. (1995) 'Thiosulphate leaching for gold hydrometallurgy', *Hydrometallurgy*, 39, 265-276.

Ames D.P., Willard J.E. (1951) 'The kinetics of the exchange of sulfur between thiosulfate and sulfite', *Journal of the American Chemical Society*, 73, 164-172.

Aylmore M.G. (2001) 'Treatment of a refractory gold-copper sulfide concentrate by copper ammoniacal thiosulfate leaching', *Minerals Engineering* 14 (6), 615-637.

Aylmore M.G, Muir D.M. (2001a) 'Thiosulfate leaching of gold – a review', *Minerals Engineering*, 14, 135-174.

Aylmore M.G., Muir D.M. (2001b) 'Thermodynamic analysis of gold leaching by ammoniacal thiosulfate using Eh/pH speciation diagrams', *Minerals and Metallurgical Processing*, 18 (4), 221-227.

Berezowsky R.M., Gormely L.S. (1978) 'Recovery of precious metals from metal sulfides', US patent 4 070 182, 24 January 1978.

Breuer P.L., Jeffrey M.I. (2000) 'Thiosulphate leaching kinetics of gold in the presence of copper and ammonia', *Minerals Engineering*, 13 (10-11), 1071-1081.

Breuer P.L., Jeffrey M.I., Tan E.H.K., Bott A.W. (2002) 'The electrochemical quartz crystal microbalance as a sensor in the gold thiosulfate leaching process', *Journal of Applied Electrochemistry*, 32, 1167-1174.

Breuer P.L., Jeffrey M.I. (2003a) 'Copper catalysed oxidation of thiosulfate by oxygen in gold leach solutions', *Minerals Engineering*, 16, 21-30.

Breuer P.L., Jeffrey M.I. (2003b) 'The reduction of copper (II) and the oxidation of thiosulfate and oxysulfur anions in gold leaching solutions', *Hydrometallurgy*, 70, 163-173.

Breuer P.L., Jeffrey M.I. (2003c) 'A review of the chemistry, electrochemistry and kinetics of the gold thiosulfate leaching process', *Hydrometallurgy 2003 – Fifth Int Conf*, Vol. 1: Leaching and solution purification, 139-154.

Breuer P.L., Jeffrey M.I. (2003d) Unpublished work, personal communication, January 2003.

Breuer P.L., Jeffrey M.I. (2004) 'The effect of ionic strength and buffer choice on the decomposition of tetrathionate in alkaline solutions', *Hydrometallurgy*, 72 (3-4), 335-338.

Brezonik P.L. (1994) 'Chemical Kinetics and Process Dynamics in Aquatic Systems', CRC Press.

Brodbeck J.S., Liou C.C. (1993) 'New frontiers in host-guest chemistry: the gas phase', *Pure and Applied Chemistry*, 65 (3), 409-414.

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

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

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

Chanda M., Rempel G.L. (1986) 'Cuprous oxide catalysed air oxidation of thiosulfate and tetrathionate', *Applied Catalysis*, 23, 101-110.

Chandra .I., Jeffrey M.I. (2003) 'Can a thiosulfate leaching process be developed which does not require copper and ammonia?', Hydrometallurgy 2003 – Fifth Int Conf, Vol. 1: Leaching and solution purification, 69-182.

Chandra I., Jeffrey M.I. (2004) 'An electrochemical study of the effect of additives and electrolyte on the dissolution of gold in thiosulfate solutions', Hydrometallurgy, 73, 305-312.

Chu C.K., Breuer P.L., Jeffrey M.I. (2003) 'The impact of thiosulfate oxidation products on the oxidation of gold in ammonia thiosulfate solutions', Minerals Engineering, 16, 265-271.

Dean J.A. (1992) 'Lange's Handbook of Chemistry', 14th Edition, Published McGraw-Hill Inc.

De Jong G.A.H., Hazeu W., Bos P. (1997) 'Polythionate degradation by tetrathionate hydrolase of *Thiobacillus ferrooxidans*', Microbiology UK, 143 (2), 499-504.

De Jong S.V.Z. (2004) "The effect of mineralogy on the ammoniacal thiosulphate extraction of gold", Ph.D. Thesis, University of Melbourne.

Dhawale S.W. (1993) 'Thiosulfate: an interesting sulfur oxoanion that is useful in both medicine and industry-but is implicated in corrosion', Journal of Chemical Education., 70, 12-14.

Druschel G. (2003) University of Vermont, personal communication.

EMJ. (2004) 'Gold producers endorse cyanide code', Engineering and Mining Journal, July 2004, 38.

Fava A., Bresadola S. (1955) 'Kinetics of the catalytic rearrangement of tetrathionate', Journal of the American Chemical Society, 77, 5792-5794.

Fava A., Pajaro G. (1954) 'Cinetique de l'echange isotopique thiosulfate-trithionate', Journal of Chemical Physics, 51, 594-599.

Feng D., Van Deventer J.S.J. (2002a) 'The role of heavy metal ions in gold dissolution in the ammoniacal thiosulfate system', Hydrometallurgy, 64, 231-246.

Feng D., Van Deventer J.S.J. (2002b) 'Leaching behaviour of sulphides in ammoniacal thiosulfate systems', Hydrometallurgy, 63, 189-200.

Fleming C., Wells J., Thomas K.G. (2000) 'Process for recovering gold from thiosulfate leach solutions and slurries with ion exchange resin', US Patent 6 344 068, 4 April.

Fleming C.A., McMullen J., Thomas K.G., Wells J.A. (2003) 'Recent advances in the development of an alternative to the cyanidation process: thiosulphate leaching and resin in pulp', Minerals and Metallurgical Processing, 20(1), 1-9.

Flett D.S., Derry R., Wilson J.C. (1983) 'Chemical study of thiosulphate leaching of silver sulphide', Transaction of the Institution of Mining and Metallurgy, 92, 216-223.

Foss O., Kringlebotn I. (1961) 'Displacement of sulphite groups of polythionates by thiosulphate', Acta Chemica Scandinavica. 15 (7), 1608-1609.

Foss O. (1961) 'Thiosulfate catalysis on rearrangements of higher polythionates', Acta Chemica Scandinavica., 15, 1610-1611.

Gelves G.A., Arias V.A., Pedraza J.E. (1996) 'Recovering of refractory gold using ammonium thiosulfate solutions', Clean Technology for the Mining Industry, ed. MA Sanchez, F Vergara, SH Castro, University of Concepcion, Concepcion, Chile, 477-487.

Glasstone, Hickling. (1954) Journal of the Chemical Society, 1932, p2345, p2800 and 1933, p 829, cited in Partington JR, 'General and Inorganic Chemistry for University Students', 2nd edition, Macmillan and Co Ltd., London, p726.

Hansford G.S., Vargas T. (2001) 'Chemical and electrochemical basis of bioleaching process', *Hydrometallurgy* 59 (2-3), 135-145.

Hemmati M., Hendrix J.L., Nelson J.H., Milosavljevic E.B. (1989) 'Study of the thiosulphate leaching of gold from carbonaceous ore and the quantitative determination of thiosulphate in the leached solution', *Extraction Metallurgy '89 Symposium*, Inst. Min. Metall., London UK, 665-678.

Hofman-Bang N. (1950) 'The iodine-azide reaction. V. The catalytic effect of trithionate ions and their decomposition in aqueous solution', *Acta Chemica Scandinavica*, 4, 1005-1013.

Horvath A.K., Nagypal I. (2000) 'Kinetics and mechanism of the reaction between hypochlorous acid and tetrathionate ion', *International Journal of Chemical Kinetics*, 32 (7), 395-402.

Hu J., Gong Q. (1991) 'Substitute sulfate for sulfite during extraction of gold by thiosulfate solution'. *Randol Gold Forum*, Cairns, Pub. Randol International Ltd, 126-132.

Jeffrey M.I. (2001) 'Kinetic aspects of gold and silver leaching in ammonia-thiosulphate solutions', *Hydrometallurgy*, 60, 7-16.

Ji J., Fleming C.A., West-Sells P.G., Hackl R.P. (2001) 'Method for thiosulfate leaching of precious metal-containing materials', *International Patent Application PCT WO 01/88212 A2*, 22 November 2001.

Ji J., Fleming C., West-Sells P.G., Hackl R.P. (2003) 'A novel thiosulfate system for leaching gold', *Proceedings Hydrometallurgy 2003*, Ed. C. A. Young et al, TMS, Warrendale, p241.

Kelly D.P., Wood A.P. (1994) 'Synthesis and determination of thiosulfate and polythionates', *Methods in Enzymology*, 243, 475-501.

Kerley J., Bernard J. (1981) 'Recovery of precious metals from difficult ores', US Patent 4 269 622, 26 May 1981.

Koh T. (1990) 'Analytical chemistry of polythionates and thiosulfate – a review', *Analytical Sciences*, 6, 3-14.

Kurtenacker A., Mutschin A., Stastny F.Z. (1935) 'Über die selbstersetzung von polythionatlosungen', *Zeitschrift für Anorganische und Allgemeine Chemie*, 224, 399-419.

Lam A.E. (2001) 'The thiosulfate leaching of gold: introduction to phase III', Project report, University of British Columbia, October 2001.

Lam A.E. (2002) 'The thiosulfate leaching of gold: A continuing investigation', Project report, University of British Columbia, December 2002.

Langhans J.W., Lei K.P.V., Carnahan T.G. (1992) 'Copper-catalysed thiosulfate leaching of low-grade gold ores', *Hydrometallurgy*, 29, 191-203.

Li J., Miller J.D., Wan R.Y. (1996) 'Important solution chemistry factors that influence the copper-catalyzed ammonium thiosulfate leaching of gold', 125th SME Annual Meeting, Phoenix, Arizona.

Liebovitch M. (2005) Sheritt Metals, personal communication.

Lyons D., Nickless G. (1968) 'The lower oxy-acids of sulfur' in *Inorganic Sulfur Chemistry*, ed. G Nickless, Elsevier Publishing Co., 509-532.

Marsden J., House I. (1992) 'The Chemistry of Gold Extraction', Pub. Ellis Horwood Ltd.

Miller J.C., Miller J.N. (1988) 'Statistics for Analytical Chemistry', Second Edition, Ellis Horwood Series in Analytical Chemistry, Pub. Ellis Horwood Ltd.

Mining Magazine. (2004) 'Cyanide management', September 2004, 34-35.

Mizoguchi T., Okabe T. (1975) 'The chemical behavior of low valence sulfur compounds. IX. Photometric determination of thiosulfate, trithionate and tetrathionate in mixture', Bulletin of the Chemical Society of Japan, 48 (6), 1799-1805.

Molleman E. (1998) 'The treatment of copper-gold ores by ammonium thiosulfate leaching', MASc Thesis, Department of Metals and Materials Engineering, University of British Columbia.

Muir D.M., Aylmore M.G. (2002) 'Thiosulphate as an alternative to cyanide for gold processing – issues and impediments', Green Processing Conference, Aus IMM, Cairns, May 2002, draft copy, no page numbers given.

Miura Y. (2003) Department of Chemistry, Tokai University, Personal communication, May 2003.

Miura Y., Koh T. (1983) 'Spectroscopic determination of tetrathionate by means of its alkaline decomposition', Nippon Kagaku Kaishi, 11, 1597-1601.

Naito K., Yoshida M., Sheih M.C., Okabe T. (1970a) 'The chemical behaviour of low valence sulfur compounds. III. Production of ammonium sulfamate by the oxidation of ammonium thiosulfate', Bulletin of the Chemical Society of Japan, 43, 1365-1372.

Naito K., Shieh M.C., Okabe T. (1970b) 'The chemical behaviour of low valence sulfur compounds. V. Decomposition and oxidation of tetrathionate in aqueous ammonia solution', Bulletin of the Chemical Society of Japan, 43, 1372-1376.

Naito K., Hayata H., Mochizuki M. (1975) 'The reactions of polythionates. Kinetics of the cleavage of trithionate ion in aqueous solutions', Inorganic and Nuclear Chemistry, 37, 1453-1457.

Nicol M.J., O'Malley G. (2002) 'Recovering gold from thiosulfate leach pulps via ion exchange', JOM, 54 (10), 44-46.

Nor Y.M., Tabatabai M.A. (1975) 'Colorimetric determination of microgram quantities of thiosulfate and tetrathionate', *Analytical letters*, 8 (8), 537-547.

Perez A.E., Galaviz H.D. (1987) 'Method for recovery of precious metals from difficult ores with copper-ammonium thiosulfate', US Patent 4 654 078, 31 March 1987.

Ritter R.D., Krueger J.H. (1970) 'Nucleophilic substitution at sulfur. Kinetics of displacement reactions involving trithionate ion', *Journal of the American Chemical Society*, 92.(8), 2316-2321.

Roine A. (1994) 'Outokumpu HSC Chemistry for Windows' software version 5.0.

Rolia E., Chakrabarti C.L. (1982) 'Kinetics of decomposition of tetrathionate, trithionate and thiosulfate in alkaline media', *Environmental Science and Technology*, 16, 852-857.

Sand W., Gerke R., Hallmann R. (1995) 'Sulfur chemistry, biofilm, and the (in)direct attack mechanism – a critical evaluation of bacterial leaching', *Applied Microbiology and Biotechnology*, 43 (6), 961-966.

Schippers A., Jorgensen B.B. (2001) 'Oxidation of pyrite and iron sulfide by manganese dioxide in marine sediments', *Geochimica et Cosmochimica Acta*, 65 (6), 915-922.

Senanayake G. (2004) 'Analysis of reaction kinetics, speciation and mechanism of gold leaching and thiosulfate oxidation by ammoniacal copper (II) solutions', *Hydrometallurgy*, 75, 55-75.

Senanayake G. (2005) 'Kinetic model for anodic oxidation of gold in thiosulfate media based on the adsorption of MS_2O_3^- ion-pair', *Hydrometallurgy*, 76, 233-238.

Shieh M.C., Otsubo H., Okabe T. (1965) 'The chemical behaviour of low valence sulfur compounds. I. Oxidation of elemental sulfur with compressed oxygen in aqueous ammonia solution', *Bulletin of the Chemical Society of Japan*, 38 (10), 1596-1600.

Smith C.W., Hitchen A. (1976) 'Aqueous solution chemistry of polythionates and thiosulphate: a review of formation and degradation pathways.', CANMET Mineral Sciences Laboratories Report MRP/MSL 76-223 (LS).

Ssekalo H., Bamuwanye M. (1993) 'Mechanisms of interactions involving formation and rupture of S-S bonds in inorganic sulphur oxo-derivative systems', *Research on Chemical Intermediates*, 19 (6), 565-600.

Suzuki I. (1999) 'Oxidation of inorganic sulfur compounds: chemical and enzymatic reactions', *Canadian Journal of Microbiology*, 45, 97-105.

Tan K.G., Rolia E. (1985) 'Chemical oxidation methods for the treatment of thiosalt-containing mill effluents', *Canadian Metallurgical Quarterly*, 24 (4), 303-310.

Wan R.Y. (1997) 'Importance of solution chemistry for thiosulphate leaching of gold', *Proceedings of World Gold '97*, Singapore, Soc. Mining Metallurgy and Exploration, Littleton, 1997, 159-162.

Wassink B. (2002) University of British Columbia, personal communication.

Weast R. (1975) (Ed.) 'CRC Handbook of Chemistry and Physics', 56th Edition, Pub. CRC Press.

Webster J.G. (1984) 'Thiosulphate complexing of gold and silver during the oxidation of a sulphide-bearing carbonate lode system, upper ridges mine, PNG', Aus IMM Perth and Kalgoorlie branches, Regional Conference on Gold Mining, Metallurgy and Geology, Pub. Aus IMM.

West-Sells P.G., Ji J., Hackl R.P. (2003) 'A process for counteracting the effect of tetrathionate on resin gold adsorption from thiosulfate leachates', *Proceedings of Hydrometallurgy 2003*, Ed. C.A. Young et al, TMS, Warrendale, 245-256.

Williamson M.A., Rimstidt J.D. (1992) 'Correlation between structure and thermodynamic properties of aqueous sulfur species', *Geochimica et Cosmochimica Acta*, 56, 3867-3880.

Xu Y., Schoonen A.A. (1995) 'The stability of thiosulfate in the presence of pyrite in low-temperature aqueous solutions', *Geochimica et Cosmochimica Acta*, 59 (22), 4605-4622.

Yen W.T., Guo H., Deschenes G. (1999) 'Development in percolation leaching with ammonium thiosulfate for gold extraction of a mild refractory ore', 10th Annual EPD Congress, San Diego, Ed. B. Mishra, Minerals, Metals and Materials Society, 441-455.

Zhang H.G., Dreisinger D.B. (2002) 'The kinetics for the decomposition of tetrathionate in alkaline solutions', *Hydrometallurgy*, 66 (1-30), 59-65.

Zipperian D., Raghavan S. (1988) 'Gold and silver extraction by ammoniacal thiosulfate leaching from a rhyolite ore', *Hydrometallurgy*, 19, 361-375.

Appendix 1 : Thermodynamic Values used to construct Eh-pH Diagrams

(Taken from best available values from HSC Chemistry for Windows, Roine, 1994)

Species	ΔH kJ/mol	S J/mol/K
S	0	32.070
S^{2-}	33.095	-14.602
SO_3	-395.765	256.772
SO_3^{2-}	-635.550	-29.288
SO_4^{2-}	-909.602	18.828
$S_2O_3^{2-}$	-648.520	66.944
$S_2O_4^{2-}$	-753.538	92.048
$S_2O_5^{2-}$	-970.688	104.600
$S_2O_6^{2-}$	-1173.194	125.520
$S_2O_8^{2-}$	-1344.763	244.346
$S_3O_6^{2-}$	-1167.336	138.072
$S_4O_6^{2-}$	-1224.238	257.316
$S_5O_6^{2-}$	-1175.704	167.360
$S_6O_6^{2-}$	-1381.000	321.323
HS^-	-16.108	68.199
HSO_3^-	-626.219	139.746
HSO_4^-	-889.100	125.520
HSO_5^{2-}	-775.63	212.129

Ref	Ore	Set up	Temp (°C)	Time (hrs)	Initial $S_2O_3^{2-}$ (M)	$S_2O_3^{2-}$ salt	SO_4^{2-} etc	NH_3 (M)	Cu^{2+} conc (mM)	pH	E (mV SHE)	g ore / l solution	Au leached (%)	$S_2O_3^{2-}$ consumed kg/ton	$S_2O_3^{2-}$ consumed %	$S_2O_3^{2-}$ analysis
A	Au ore, quartz, muscovite, 90 % <74 μm	Stirred tank	25, 40, 60	3	0.125 – 2	Na	0	1 – 8	30-60	8.5 – 10.5		40 % solids	~80		40-50%	Iodometric titration
B	Quartz	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		42	3%	Iodometric titration with acetic acid added to eliminate Cu – NH_3 complex effect.
	Pyrite	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		392	28%	
	Arsenopyrite	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		252	18%	
	Chalcopyrite	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		168	12%	
	pyrrhotite	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		140	10%	
C	Untreated pyrite conc	Stirred tank	RT?	96	0.4	Na	0	4	50	10.2	80-180	417		61	57%	Immediate HPLC
				96	0.5			4	50					52	39%	
				24	0.8			4	50					30	14%	
				96	0.8									56	26%	
				24	0.8			1.5	50					39	18%	
				96										128	59%	
				24	0.8			3	50					99	46%	
				96										115	54%	
				24	0.8			4	12.5					90	42%	
				96										166	77%	
				24	0.8			4	50					22	10%	
				96										99	46%	
				24	0.8			4	37.5					41	19%	
				96										137	64%	
				24	0.8			4	62.5					40	19%	
				96										80	37%	

Ref	Ore	Set up	Temp (°C)	Time (hrs)	Initial $S_2O_3^{2-}$ (M)	$S_2O_3^{2-}$ salt	SO_3^{2-} etc	NH_3 (M)	Cu^{2+} conc (mM)	pH	E (mV SHE)	g ore / l solution	Au leached (%)	$S_2O_3^{2-}$ consumed kg/ton	$S_2O_3^{2-}$ consumed %	$S_2O_3^{2-}$ analysis
A	Au ore, quartz, muscovite, 90 % <74 μm	Stirred tank	25, 40, 60	3	0.125 – 2	Na	0	1 – 8	30-60	8.5 – 10.5		40 % solids	~80		40-50%	Iodometric titration
B	Quartz	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		42	3%	Iodometric titration with acetic acid added to eliminate Cu – NH_3 complex effect.
	Pyrite	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		392	28%	
	Arsenopyrite	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		252	18%	
	Chalcopyrite	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		168	12%	
	pyrrhotite	Stirred tank	25	24	0.25	NH_4	0.25 M SO_4^{2-}	1	6	With NH_4OH		20		140	10%	
C	Untreated pyrite conc	Stirred tank	RT?	96	0.4	Na	0	4	50	10.2	80-180	417		61	57%	Immediate HPLC
				96	0.5			4	50					52	39%	
				24	0.8			4	50					30	14%	
				96	0.8									56	26%	
				24	0.8			1.5	50					39	18%	
				96										128	59%	
				24	0.8			3	50					99	46%	
				96										115	54%	
				24	0.8			4	12.5					90	42%	
				96										166	77%	
				24	0.8			4	50					22	10%	
				96										99	46%	
				24	0.8			4	37.5					41	19%	
				96										137	64%	
				24	0.8			4	62.5					40	19%	
				96										80	37%	

Ref	Ore	Set up	Temp (°C)	Time (hrs)	Initial $S_2O_3^{2-}$ (M)	$S_2O_3^{2-}$ salt	SO_3^{2-} etc	NH_3 (M)	Cu^{2+} conc (mM)	pH	E (mV SHE)	g ore / l solution	Au leached (%)	$S_2O_3^{2-}$ consumed kg/ton	$S_2O_3^{2-}$ consumed %	$S_2O_3^{2-}$ analysis
D	Synthetic Ag_2S	in air	~20	24	0.072	NH_4	0		16			9.92	Ag 86.7	192	43%	IX, also for $S_4O_6^{2-}$
		in air	~20	24	0.073	NH_4	0		15			9.92	Ag 81.7	164	36%	
		in N_2	~20	24	0.073	NH_4	0		15			9.92	Ag 85.3	114	25%	
		in air	~20	24	0.073	NH_4	3.5 mM SO_3		15			9.92	Ag 66.4	114	25%	
		in N_2	~20	24	0.073	NH_4	3.5 mM SO_3		15			9.92	Ag 70.3	68	15%	
		in air	~20	24	0.073	NH_4	14 mM SO_3		15			9.92	Ag 50.7	68	15%	
		in N_2	~20	24	0.073	NH_4	14 mM SO_3		15			9.92	Ag 44.7	25	5%	
E	Low grade oxidized Au ore	Bottle roll	ambient	48	0.2	Na	0-0.0125 M not specified		1				83	0.40		IC for $S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-}
		Bottle roll	ambient	94	0.2	Na	0-0.0125 M not specified		1				90	1.71		
		Bottle roll	ambient	94	0.125	Na	0-0.0125 M not specified		1				85.8	3.60		
		Bottle roll	ambient	94	0.05	Na	0-0.0125 M not specified		1				<11	4.61		

Ref	Ore	Set up	Temp (°C)	Time (hrs)	Initial $S_2O_3^{2-}$ (M)	$S_2O_3^{2-}$ salt	SO_3^{2-} etc	NH_3 (M)	Cu^{2+} conc (mM)	pH	E (mV SHE)	g ore / l solution	Au leached (%)	$S_2O_3^{2-}$ consumed kg/ton	$S_2O_3^{2-}$ consumed %	$S_2O_3^{2-}$ analysis
E	Rhyolite and andesite breccia matrix, 80 % < 200 mesh, Mn	Stirred tank	25	28	0.15	NH_4			~31	8.5		40 % solids		8	32%	Iodometric titration
		Stirred tank	25	28	0.23	NH_4			~31	8.5		40 % solids		12	32%	
		Stirred tank	25	28	0.38	NH_4			~31	8.5		40 % solids		15	23%	
		Stirred tank	25	28	0.15	NH_4			~31	9.5		40 % solids		13	52%	
		Stirred tank	25	28	0.23	NH_4			~31	9.5		40 % solids		21	55%	
		Stirred tank	25	28	0.38	NH_4			~31	9.5		40 % solids		33	52%	
		Stirred tank	25	28	0.12	NH_4			~31	10		40 % solids		9	36%	
		Stirred tank	25	28	0.23	NH_4			~31	10		40 % solids		19	50%	
		Stirred tank	25	28	0.38	NH_4			~31	10		40 % solids		35	55%	
F	Mn ore, 2.1 % Mn, difficult to leach	See text			18 %?	NH_4	3% $(NH_4)_2 SO_3$	2 % NH_4OH	~ 4 g/l				86.7	3.6		
G	Sulfide gold flotation conc with Cu, 90% - 200 mesh	Stirred tank	60	0.5	0.14	NH_4	0.8 M $(NH_4)_2 SO_4$	4	47	10.2		500		2.2	7%	unspecified
		Stirred tank	60	1	0.14	NH_4	0.8 M $(NH_4)_2 SO_4$	4	47	10.2		500		2.2	7%	
		Stirred tank	60	1.5	0.14	NH_4	0.8 M $(NH_4)_2 SO_4$	4	47	10.2		500		0.0	0%	
		Stirred tank	60	2	0.14	NH_4	0.8 M $(NH_4)_2 SO_4$	4	47	10.2		500		6.6	21%	

Ref	Ore	Set up	Temp (°C)	Time (hrs)	Initial $S_2O_3^{2-}$ (M)	$S_2O_3^{2-}$ salt	SO_3^{2-} etc	NH_3 (M)	Cu^{2+} conc (mM)	pH	E (mV SHE)	g ore / l solution	Au leached (%)	$S_2O_3^{2-}$ consumed kg/ton	$S_2O_3^{2-}$ consumed %	$S_2O_3^{2-}$ analysis
H	Refractory gold ore	Bottle roll	RT	24	0.5	NH_4	-	6	50	10.2		45 % solids	72	52.0		Iodometric titration
H	Refractory gold ore	Column	RT	50 d	0.1	NH_4	-	3	30	10.2		3000	45	15.5		
		Column	RT	50 d	0.3	NH_4	-	3	30	10.2		3000	64.2	27.5		
		Column	RT	50 d	0.5	NH_4	-	3	30	10.2		3000	64.9	30.3		
		Column	RT	50 d	1	NH_4	-	3	30	10.2		3000	71.9	36.8		
		Column	RT	50 d	0.3 maintained	NH_4	-	1	50	10.2		3000	57	35.8		
		Column	RT	50 d	0.3 maintained	NH_4	-	3	50	10.2		3000	60.7	30.4		
		Column	RT	50 d	0.3 maintained	NH_4	-	6	50	10.2		3000	71.7	28.1		
		Column	RT	50 d	0.3 maintained	NH_4	-	3	50	10.2		3000	67.7	27.5		
		Column	RT	50 d	0.3 maintained	NH_4	-	3	50	10.2		3000	60.7	30.5		
		Column	RT	50 d	0.3 maintained	NH_4	-	3	50	10.2		3000	56.7	35.8		
		Column	RT	50 d	0.5	NH_4	-	3	30	10.2		830		38.6		
		Column	RT	50 d	0.5	NH_4	-	3	30	10.2		5000		15.9		

References for Appendix 2

- | | | | |
|---|------------------------------|---|--------------------------|
| A | Abbruzzese et al, 1995 | E | Langhans et al, 1992 |
| B | Fend and Van Deventer, 2002b | F | Kerley and Bernard, 1981 |
| C | Aylmore, 2001 | G | Cao et al, 1992 |
| D | Flett et al, 1983 | H | Yen et al, 1999 |

Appendix 3 : Determination of Sulfur Oxyanions by Ion Chromatography

(modified from a method by Lakefield Research Ltd)

Analysis of thiosulfate, trithionate and tetrathionate

Reagent Preparation

Calibration standards

Prepare 1000 mg/l thiosulfate solution by dissolving the required amount of sodium thiosulfate anhydrous in ultrapure de-ionised water.

Prepare 1000 mg/l trithionate solution by dissolving the required amount of sodium trithionate in ultrapure de-ionised water.

Prepare 1000 mg/l tetrathionate solution by dissolving the required amount of sodium tetrathionate in ultrapure de-ionised water.

From these standards, prepare calibration standards containing 2, 10, 15 and 20 mg/l thiosulfate, trithionate and tetrathionate.

Calibration standards should be prepared immediately prior to use.

Eluant – Sodium perchlorate (0.038 M) with 10 % methanol

Dissolve 10.675 g $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (HPLC grade) in water and add 200 ml methanol (HPLC grade). Dilute to 2 litres using ultrapure de-ionised water. Filter the solution through a 0.22 μm filter.

Procedure

Set up the ion chromatograph according to the manufacturers instructions, using an OmniPac PAX 100 guard column and an OmniPac PAX 100 analytical column.

Pump the eluant through the system at 1 ml/min.

Monitor the absorbance at 205 nm using a UV-visible absorption detector.

Allow the instrument to equilibrate so that the absorbance measured is constant (typically 2 hours).

Inject the 2 mg/l calibration standard solution, followed by the 10 mg/l, 15 mg/l and 20 mg/l standard solution.

Check that the calibration curve is linear and then proceed to analyse the sample solutions, which must be diluted to within the calibration range immediately prior to analysis.

Typical retention times are about 2 minutes for thiosulfate, 6 minutes for trithionate and 10 minutes for tetrathionate, depending on the condition of the columns.

Analysis of sulfate

Reagent Preparation

Calibration standards

Prepare 1000 mg/l sulfate solution by dissolving the required amount of sodium sulfate in ultrapure de-ionised water.

From this standard solution, prepare calibration standards containing 2, 10, 15 and 20 mg/l sulfate.

Eluant – Sodium carbonate (1.8 mM) – sodium bicarbonate (1.7 mM) with 10 % methanol

Dissolve 0.382 g Na_2CO_3 and 0.286 g NaHCO_3 in water and add 200 ml methanol (HPLC grade). Dilute to 2 litres using ultrapure de-ionised water. Filter the solution through a 0.22 μm filter.

Procedure

Set up the ion chromatograph according to the manufacturers instructions, using an IonPac AG4A-SC guard column and an IonPac AS4A-SC analytical column.

Pump the eluant through the system at 2 ml/min.

Set the suppressor current at 27 mA.

Monitor the conductivity using a conductivity detector.

Allow the instrument to equilibrate so that the conductivity measured is constant (typically 2 hours).

Inject the 2 mg/l calibration standard solution, followed by the 10 mg/l, 15 mg/l and 20 mg/l standard solution.

Check that the calibration curve is linear and then proceed to analyse the sample solutions, which must be diluted to within the calibration range immediately prior to analysis.

Typical retention times are about 8 minutes for sulfate, depending on the condition of the columns.

Appendix 4 – Chemical Impurity Analysis

Impurity Analysis for a solution of Ammonium Bicarbonate

Solution of 37.6 g/l NH_4HCO_3

Element	Concentration (mg/l)
Al	<0.2
Sb	0.3
As	0.3
Ba	<0.01
Bi	<0.1
Cd	<0.01
Ca	0.1
Cr	<0.01
Co	<0.01
Cu	<0.01
Fe	<0.03
La	<0.05
Pb	<0.05
Mg	<0.1
Mn	<0.01
Hg	<0.05
Mo	<0.02
Ni	2.28
P	<0.1
K	<2
Sc	0.02
Ag	<0.02
Na	7
Sr	<0.01
Tl	<0.2
Ti	<0.1
W	<0.1
V	<0.01
Zn	<0.01
Zr	<0.01

Impurity Analysis for a solution of Ammonium Hydroxide
Solution of 0.5 M NH₃

Element	Concentration (mg/l)
Al	<0.2
Sb	0.1
As	1.2
Ba	<0.01
Bi	<0.1
Cd	<0.01
Ca	1
Cr	<0.01
Co	0.06
Cu	0.23
Fe	<0.03
La	0.09
Pb	<0.05
Mg	2.3
Mn	<0.01
Hg	<0.05
Mo	<0.02
Ni	1.54
P	<0.1
K	<2
Sc	<0.01
Ag	<0.02
Na	48
Sr	<0.01
Tl	<0.2
Ti	<0.1
W	<0.1
V	<0.01
Zn	<0.01
Zr	<0.01

Impurity Analysis for a solution of Sodium ThiosulfateSolution of 1.5 g/l $\text{Na}_2\text{S}_2\text{O}_3$

Element	Concentration (mg/l)
Al	<0.2
Sb	<0.1
As	<0.2
Ba	<0.01
Bi	<0.1
Cd	<0.01
Ca	0.5
Cr	<0.01
Co	0.09
Cu	<0.01
Fe	<0.03
La	0.22
Pb	0.31
Mg	1.2
Mn	<0.01
Hg	<0.05
Mo	<0.02
Ni	<0.02
P	0.9
K	20
Sc	<0.01
Ag	<0.02
Na	529
Sr	<0.01
Tl	<0.2
Ti	<0.1
W	<0.1
V	<0.01
Zn	<0.01
Zr	<0.01

Impurity Analysis for a solution of Sodium TrithionateSolution of 1.3 g/l $\text{Na}_2\text{S}_2\text{O}_3$ Batch 4

Element	Concentration (mg/l)
Al	<0.2
Sb	<0.1
As	<0.2
Ba	<0.01
Bi	<0.1
Cd	<0.01
Ca	0.8
Cr	<0.01
Co	0.11
Cu	<0.01
Fe	<0.03
La	0.18
Pb	0.34
Mg	1
Mn	<0.01
Hg	<0.05
Mo	<0.02
Ni	<0.02
P	<0.1
K	20
Sc	<0.01
Ag	<0.02
Na	316
Sr	<0.01
Tl	<0.2
Ti	<0.1
W	<0.1
V	<0.01
Zn	<0.01
Zr	0.04