



THE KINETICS OF PYRITE AND ELEMENTAL SULFUR REACTIONS DURING NITRIC ACID PRE-OXIDATION OF REFRACTORY GOLD ORES

Thesis submitted for the degree of Doctor of Philosophy

by

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ABSTRACT

Refractory gold deposits are of increasing interest to the mining industry in Australia and overseas. Nitric acid technology for the pre-oxidation of sulfides in such refractory deposits has shown kinetic advantages. Developers of the "Redox" nitric acid process have cited cost advantages to the low temperature process variant, but have also encountered difficulties from elemental sulfur formed during the process. The focus of the present work is to investigate the fundamental kinetics of the pyrite-nitric acid system. Particular attention is paid to the formation and oxidation of elemental sulfur.

Predictive work was undertaken using linear potential-sweep voltammetry. It was shown that the proportion of elemental sulfur formed in 0.22 M nitric acid is independent of temperature but decreases with increasing Eh. Leach tests confirmed the temperature independence. Leach tests were unable to confirm that elemental sulfur would be eliminated at Eh - 1.4 volts SHE. This inability was due to limits of Eh imposed by the nitric acid system itself and also due to difficulties in measuring Eh of hot strongly acidic solutions. Predicted pyrite oxidation rates of $91 \times 10^{-8} \text{ g cm}^{-2}\text{sec}^{-1}$ at 1.20 volts were confirmed by leach tests rates at similar conditions.

Leach tests of pyrite in nitric acid enabled quantification and analysis of seventeen variables and observed phenomena. The data fit a first-order model well, particularly once observed lag period effects were deleted. Lag periods effects were the main differences between pyrites from different sources. These effects are thought to be predominantly caused by rapidly-forming surface layers on pyrite. First-order rate constants from 0.003 min^{-1} to 1.10 min^{-1} were found. However, most tests were in the range considered to be industrially realistic, giving rate constants around 0.1 min^{-1} . The proportion of elemental sulfur which forms from pyrite is higher than expected from the literature, being about twenty percent under conditions typical of the majority of the tests (2.6 M HNO_3). Once formed, this elemental sulfur oxidises slowly compared to the pyrite, with a typical first-order rate constant being 0.007 min^{-1} . Further, the elemental sulfur oxidation rate is an order of magnitude less sensitive to the test variables than the pyrite oxidation rate.

The variation in the oxidation rates of both pyrite and elemental sulfur with experimental conditions accounts for apparently conflicting reports, for both pyrite oxidation rates and elemental sulfur found, in the literature. The present study evaluates more variables than any study found in the literature for pyrite oxidation. The use of nitric acid and elemental sulfur focus goes beyond anything reported.

The independent variables tested proved unable to eliminate elemental sulfur formation, although there is scope for further investigation of silver ion addition, or higher Eh systems. Once formed, elemental sulfur, if it is to be oxidised completely, dictates reaction retention time for the low-temperature "Redox" variant. If less than three percent of elemental sulfur were to be required from a high-sulfide feed, elemental sulfur would dictate unrealistic retention times. This confirms developers' expedient preference for the more expensive high temperature process variant.

Pre-oxidation and cyanidation tests on four refractory gold-bearing materials confirmed the technical capabilities of nitric acid leaching. Gold recoveries were improved from 48-68% to an average of 93%. Reductions of around 2 kg of cyanide and base per tonne of ore were also shown for most materials.

Remaining unrecovered gold could be partially due to elemental sulfur remaining after the pre-oxidation step. This, and other avenues for further investigations, are enumerated in the thesis.

TABLE OF CONTENTS

Declaration

Acknowledgments

Abstract

| | Page |
|---|-------------|
| Chapter 1: Introduction | |
| 1.1 Reasons for the study | 1 |
| 1.2 Refractory gold ores | 1 |
| 1.3 Specific aims | 2 |
| 1.4 Scope | 2 |
| 1.5 Limitations | 3 |
| 1.6 Summary of Introduction | 4 |
| Chapter 2: Background to Study | |
| 2.1 Chapter content | 5 |
| 2.2 Refractory gold ore | |
| 2.2.1 Practical definition | 5 |
| 2.2.2 Importance | 6 |
| 2.2.3 Causes of refractory behaviour | 6 |
| 2.2.4 Treatment alternatives | 7 |
| 2.2.5 Generalized Flowsheet for Pre-oxidation | 8 |
| 2.2.6 Broader Engineering considerations | 9 |
| 2.3 Nitric acid processes for pre-oxidation | |
| 2.3.1 Preamble | 9 |
| 2.3.2 Brief overview of process chemistry | 10 |
| 2.3.3 Early research | 11 |
| 2.3.4 The "Nitrox" process | 14 |
| 2.3.5 The "Redox" process | 15 |
| 2.3.6 Experimental conditions investigated | 18 |
| 2.3.7 Value of present testwork | 18 |
| 2.4 Elemental Sulfur | |
| 2.4.1 Problems caused during refractory gold processing | 19 |
| 2.4.2 Observations during development testwork | 20 |
| 2.4.3 Pertinent properties | 21 |
| 2.5 Summary | 22 |
| 2.6 References | 24 |
| Chapter 3: Autoclave and Cyanidation Tests | |
| 3.1 Philosophy | 28 |
| 3.2 Scope of Testwork | |
| 3.2.1 Refractory gold-bearing materials tested | 28 |
| 3.2.2 Pre-oxidation and cyanide tests | 29 |

| | Page |
|--|-------------|
| 3.3 Experimental Method | |
| 3.3.1 Rolling bottle cyanidation | 30 |
| 3.3.2 Autoclave pre-oxidation tests | 31 |
| 3.4 Summarised Experimental Results | |
| 3.4.1 Example of individual tests | 32 |
| 3.4.2 Parameters of feed materials | 35 |
| 3.4.3 Effect of nitric acid pre-oxidation on gold cyanidation parameters | 37 |
| 3.4.4 Metal deppartment | 38 |
| 3.4.5 Elemental sulfur in pre-oxidation and cyanidation tests | 39 |
| 3.5 Discussion of Results | |
| 3.5.1 Typical individual tests | 40 |
| 3.5.2 Parameters of feed materials | 41 |
| 3.5.3 Effects of pre-oxidation with nitric acid | 41 |
| 3.5.4 Effects on metal depportments | 42 |
| 3.5.5 Findings concerning elemental sulfur | 43 |
| 3.6 Chapter Summary | 45 |
| 3.7 References | 47 |
| Chapter 4: Electrochemistry | |
| 4.1 Philosophy | 48 |
| 4.2 Literature Review | |
| 4.2.1 Linear potential sweep voltammetry | 50 |
| 4.2.2 Related general electrochemical observations | 51 |
| 4.2.3 Elemental sulfur to sulfate ratio | 53 |
| 4.2.4 Nature of the oxidising pyrite surface | 56 |
| 4.3 Experimental Method (General) | |
| 4.3.1 Equipment | 57 |
| 4.3.2 Electrode fabrication | 58 |
| 4.3.3 Electrode polishing | 59 |
| 4.4 Duplication Experiments | |
| 4.4.1 Equipment calibration | 60 |
| 4.4.2 Hamilton and Woods Experiments | 62 |
| 4.5 Ranging Experiments - HNO₃ - H₂SO₄ | |
| 4.5.1 Purpose | 65 |
| 4.5.2 Wide potential-limit experiements | 65 |
| 4.5.3 Higher sensitivty tests | 67 |
| 4.6 Main Test Series | |
| 4.6.1 Experimental Method | 69 |
| 4.6.2 Typical Voltammetric Scan | 70 |
| 4.6.3 Typical Calculations | 71 |
| 4.6.4 Main Test series - Results and Discussion | 74 |
| 4.6.5 Relation to pre-oxidation | 80 |
| 4.7 Summary of Electrochemical Findings | 81 |
| 4.8 References | 83 |

Chapter 5: Pyrite Leach Tests

| | | |
|------------|--|-----------|
| 5.1 | Philosophy | 85 |
| 5.2 | Literature Review | |
| 5.2.1 | Introduction | 88 |
| 5.2.2 | Thermodynamics and metastable sulfur | 88 |
| 5.2.3 | Kinetics of pyrite oxidation | 92 |
| 5.2.4 | Experimental conditions suggested by the literature | 96 |
| 5.2.5 | Section summary | 101 |
| 5.3 | Experimental Method | |
| 5.3.1 | Preparation and analysis of solids | 102 |
| 5.3.2 | Test apparatus and method for main test series | 104 |
| 5.3.3 | Test apparatus and method for attritioning series | 107 |
| 5.3.4 | Liquid assays | 108 |
| 5.3.5 | Sample calculations | 108 |
| 5.4 | Typical Leach Test Results and Discussion | |
| 5.4.1 | Note on grouping of tests | 112 |
| 5.4.2 | Elemental Sulfur formation from pyrite | |
| 5.4.3 | Typical leach test - results | 113 |
| 5.4.4 | Typical leach test - discussion | 114 |
| 5.4.5 | Section summary | 116 |
| 5.5 | Classical Variables - Results and Discussion | |
| 5.5.1 | Stirring rate | 116 |
| 5.5.2 | Temperature | 118 |
| 5.5.3 | Particle size | 120 |
| 5.5.4 | Nitric Acid Concentration | 121 |
| 5.5.5 | Section Summary | 122 |
| 5.6 | Experimental Consistency - Results and Discussion | |
| 5.6.1 | Leach Test method | 123 |
| 5.6.2 | Aging of pyrite samples | 124 |
| 5.6.3 | Sulfur gap | 127 |
| 5.6.4 | Section summary | 128 |
| 5.7 | Industrial Variables - Results and Discussion | |
| 5.7.1 | Sulfuric Acid concentration | 129 |
| 5.7.2 | Ferric Ion concentration | 130 |
| 5.7.3 | Chloride Ion concentration | 132 |
| 5.7.4 | Pulp density | 134 |
| 5.7.5 | Blend of feed sizes | 136 |
| 5.7.6 | Section Summary | 137 |
| 5.8 | Additional Factors - Results and Discussion | |
| 5.8.1 | Attritioning | 138 |
| 5.8.2 | The effect of Eh | 141 |
| 5.8.3 | Addition of Silver ion | 144 |
| 5.8.4 | Additive effect of variables | 146 |
| 5.8.5 | Lag time in pyrite dissolution | 147 |
| 5.8.6 | Pyrite source effects | 149 |
| 5.8.7 | Section summary | 149 |

| | | |
|--|---|------------|
| 5.9 | Mathematical Analysis of Leach Tests | |
| 5.9.1 | Preamble | 150 |
| 5.9.2 | Summary of kinetic data | 151 |
| 5.9.3 | First-order kinetics versus shrinking core model | 159 |
| 5.9.4 | Lag period consideration | 162 |
| 5.9.5 | Variation of pyrite with source | 164 |
| 5.9.6 | Calculation of activation energies | 165 |
| 5.9.7 | Oxidation rate of elemental sulfur | 166 |
| 5.9.8 | Section Summary (Mathematical Analysis) | 177 |
| 5.10 | Relation of Leach Test Findings to the Literature, Electrochemical Results and Refractory Gold Ore Treatment | |
| 5.10.1 | Relation to the literature | 180 |
| 5.10.2 | Relation to the electrochemical findings | 182 |
| 5.10.3 | Relation to refractory gold ore treatment | 185 |
| 5.11 | Chapter Summary | 189 |
| 5.12 | References | 192 |
| Chapter 6: Conclusions and Recommendations | | |
| 6.1 | Preamble - Review of Chapters, Main Findings | 194 |
| 6.2 | Specific Findings New to this Study | 199 |
| 6.3 | General Patterns Found | 201 |
| 6.4 | Recommendations | 202 |
| 6.5 | Summary | 205 |
| | Nomenclature | 206 |
| | Figures | 208 |
| | Tables | 212 |
| Appendix: | Supporting Information | |
| | SEM and XRay Testwork | |

Detailed raw data for Chapters 3, 4 and 5 may be found in the "Supplementary Volume – Raw Experimental Data" (141 pages). Copies of this volume are kept in the libraries of the University of South Australia and the University of Adelaide