APPLICATION OF ELECTROCHEMICAL KINETICS TO
ELUCIDATE THE LEACHING MECHANISM IN THE BIO-
OXIDATION OF A SYNTHETIC NICKEL SULPHIDE

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fulfilment of the requirements for the degree Master of
Science in Engineering

Johannesburg, 1986
I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

[Signature]

10th day of DECEMBER 1986
Abstract

The importance of the direct and indirect mechanisms in the bacterial leaching of a synthetic nickel sulphide is investigated using an electrochemical leaching model. Sterile controls runs, in which only ferric leaching took place, are compared with runs in the presence of an active, adapted bacterial culture.

The direct mechanism occurs when bacteria attach to the sulphide mineral and catalyze the oxidation of the mineral, presumably with enzymes (biological catalysts). No evidence was found of the direct mechanism, in fact ferric leaching appeared to be inhibited as the bacterial presence increased due to growth. Considering evidence obtained by the fitting of the electrochemical model, it is tentatively suggested that leaching of the mineral is largely due to chemical ferric leaching, with the leaching role of bacteria restricted to re-oxidizing the resulting ferrous ions. Whether this is the case for other minerals remains to be established.
Acknowledgements

I firstly wish to thank the Council for Mineral Technology for financing this research. Furthermore, I am indebted to all those Mintek staff who have provided me with so much assistance: Mike Dry for his helpful suggestions; the High Temperature Group from the Mineralogy Division guiding me in the manufacture of nickel sulphide; the Pyrometallurgy Division for the use of their furnaces; the scientists from the Mineral and Processing Division who have been of help; the Analytical Division for performing numerous assays; the Mineralogy Division for examining residues; the staff from the Ore Dressing Division for the help they provided, and to my academic supervisor, Dr Bernie Verbaan, for his support.

I do not know how this work could have been conducted without help from all these people. Thank you!
# CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Declaration</td>
</tr>
<tr>
<td>Abstract</td>
</tr>
<tr>
<td>Acknowledgements</td>
</tr>
<tr>
<td>Contents</td>
</tr>
<tr>
<td>List of Figures</td>
</tr>
<tr>
<td>List of Tables</td>
</tr>
<tr>
<td>List of Symbols</td>
</tr>
</tbody>
</table>

## 1. INTRODUCTION

1.1. BACKGROUND ON BACTERIAL LEACHING 1

1.2. THE BIOLEACH PROCESS

   1.2.1. BIOLEACHING BY DIRECT MECHANISM 2

   1.2.2. BIOLEACHING BY INDIRECT MECHANISM 3

   1.2.3. RELATIVE IMPORTANCE OF DIRECT AND INDIRECT MECHANISMS 4

   1.2.4. MODELLING DEVELOPMENTS IN BIOLEACHING 5

1.3. BACTERIAL BY-PRODUCTS 7

1.4. GALVANIC INTERACTIONS 8

1.5. OBJECTIVE AND SCOPE OF THE PRESENT STUDY 9

## 2. THEORETICAL ANALYSIS AND MODELLING

2.1. REDOX POTENTIAL AND pH PREDICTION 13

2.2. ELECTROCHEMICAL MODEL FOR PREDICTION OF LEACH RATE OF NICKEL SULPHIDE 18

2.3. DETERMINATION OF ELECTROCHEMICAL MODEL CONSTANTS FOR NICKEL SULPHIDE SYSTEM 22

2.4. PREDICTING LEACH RATE OF NICKEL SULPHIDE FOR VARYING REDOX POTENTIALS 26
3. EXPERIMENTAL

3.1. NICKEL SULPHIDE MINERAL UTILIZED 28
3.2. AQUEOUS MEDIA UTILIZED 30
3.3. APPARATUS 31
3.4. ANALYTICAL METHODS 34
3.5. RESIDUE ANALYSIS 36
3.6. PROCEDURES

3.6.1. DETERMINATION OF EFFECTS OF NUTRIENTS, OXYGEN AND BACTERIA ON REDOX POTENTIAL IN ABSENCE OF NICKEL SULPHIDE 37
3.6.2. DETERMINATION OF ELECTROCHEMICAL MODEL CONSTANTS OF NICKEL SULPHIDE SYSTEM IN ABSENCE OF BACTERIA 38
3.6.3. DETERMINATION OF BIOLEACHING CHARACTERISTICS OF NICKEL SULPHIDE 39
3.6.4. DEDUCTION OF EFFECT OF HYDROGEN PEROXIDE ON LEACHING OF NICKEL SULPHIDE IN ABSENCE OF BACTERIA 42

4. RESULTS

4.1. EFFECTS OF AERATION, NUTRIENTS AND BACTERIA ON REDOX POTENTIAL IN ABSENCE OF NICKEL SULPHIDE 44
4.2. EFFECT OF REDOX POTENTIAL ON NICKEL SULPHIDE LEACHING IN ABSENCE OF BACTERIA 47
4.3. LEACHING CHARACTERISTICS OF NICKEL SULPHIDE IN PRESENCE AND ABSENCE OF BACTERIA

4.3.1. CHANGE IN REDOX POTENTIALS DURING LEACHING 50
4.3.2. EXTRACTION OF NICKEL DURING LEACHING 52
4.3.3. CHANGE IN IRON CONCENTRATIONS DURING LEACHING 55
4.3.4. CHANGE IN AMMONIUM AND POTASSIUM CONCENTRATIONS DURING LEACHING 57
4.3.5. ACID CONSUMPTIONS DURING LEACHING 61
4.3.6. ANALYSIS OF SOLID RESIDUES ARISING FROM LEACHING 63
4.4. NICKEL SULPHIDE LEACHING CHARACTERISTICS WITHOUT HYDROGEN PEROXIDE ADDITION IN ABSENCE OF BACTERIA 68

5. MATHEMATICAL MODELLING OF EXPERIMENTAL RESULTS
5.1. MODELLING OF REDOX POTENTIAL AND pH IN ABSENCE AND PRESENCE OF NICKEL SULPHIDE 69
5.2. ESTIMATION OF ELECTROCHEMICAL MODEL CONSTANTS FOR NICKEL SULPHIDE LEACHING 74
5.3. MODELLING LEACHING OF NICKEL SULPHIDE IN PRESENCE AND ABSENCE OF BACTERIA 77

6. DISCUSSION AND CONCLUSIONS 84

7. RECOMMENDATIONS 87
APPENDIX

A.1. ADDITIONAL LITERATURE AND DISCUSSIONS
   A.1.1. NATURE AND REQUIREMENTS OF Thiobacillus ferrooxidans 89
   A.1.2. OXIDATION OF FERROUS IONS BY BACTERIA 97
   A.1.3. DISCUSSION OF SOME OF THE LITERATURE ON IMPORTANCE OF DIRECT AND INDIRECT MECHANISM 101

A.2. EXPERIMENTAL DETAILS
   A.2.1. NICKEL SULPHIDE PREPARATION AND CHARACTERIZATION
      A.2.1.1. PRECIPITATION OF NICKEL SULPHIDE 107
      A.2.1.2. MELTING AND RECRYSTALLIZATION OF NICKEL SULPHIDE 111
      A.2.1.3. SIZING OF NICKEL SULPHIDE 116
   A.2.2. DECIDING ON AN AQUEOUS MEDIUM FOR USE IN LEACHING TESTS 128
   A.2.3. DEVELOPMENT AND MAINTENANCE OF CULTURE
      A.2.3.1. FERROUS IRON BACTERIAL CULTURE 133
      A.2.3.2. NICKEL SULPHIDE BACTERIAL CULTURE 133
   A.2.4. FURTHER DETAILS ON LEACHING TESTS
      A.2.4.1. SEMI-ASCEPTIC TECHNIQUE IN TESTS 135
      A.2.4.2. WASHING AND ACID LEACHING OF TYPE C SAMPLES 136
      A.2.4.3. COUNTING OF BACTERIA IN TYPE C TESTS 140
   A.2.5. ELECTRODE MAINTENANCE AND CALIBRATIONS 141
A.3. EXPERIMENTAL DATA

A.3.1. READINGS IN DETERMINATION OF EFFECTS OF NUTRIENTS, OXYGEN AND BACTERIA ON REDOX POTENTIAL IN ABSENCE OF NICKEL SULPHIDE 144

A.3.2. READINGS IN DETERMINATION OF ELECTROCHEMICAL MODEL CONSTANTS OF NICKEL SULPHIDE SYSTEM IN ABSENCE OF BACTERIA 149

A.3.3. READINGS IN DETERMINATION OF BIOLEACH CHARACTERISTICS OF NICKEL SULPHIDE 150

A.3.4. READINGS IN DEDUCTION OF EFFECT OF HYDROGEN PEROXIDE ON CHEMICAL LEACHING OF NICKEL SULPHIDE IN ABSENCE OF BACTERIA 171

A.3.5. GRAPHICAL REPRESENTATION OF DATA OF TWO SETS OF PARALLEL TESTS OF TYPE C 173

A.4. MODELLING OF REDOX POTENTIAL AND pH IN ABSENCE OF NICKEL SULPHIDE 184

A.5. COMPUTER PROGRAMS

A.5.1. REDOX POTENTIAL AND pH PREDICTION 193

A.5.2. DETERMINATION OF ELECTROCHEMICAL MODEL CONSTANTS 199

A.5.3. PREDICTION OF EXTRACTION IN STERILE LEACHING 203

A.6. COMPUTER PRINTOUTS

A.6.1. CALCULATED REDOX POTENTIAL AND pH VALUES 206

A.6.2. ELECTROCHEMICAL MODEL CONSTANTS 214

A.6.3. EXTRACTION IN STERILE LEACHING 216

REFERENCES (ix) 219
List of Figures

Figure (page)

3.1. Schematic Representation of Apparatus Used in Main Experiments. (32)

3.2. Photograph of Apparatus Used to Determine Bioleaching Behaviour of Ni$_3$S$_2$, Showing the Parallel Inoculated and Sterile Control Systems. (33)

4.1. Effects of Aeration and Nutrients on Redox Potential in Absence of Ni$_3$S$_2$. (45)

4.2. Effect of Presence of Bacteria on Redox Potential in Absence of Ni$_3$S$_2$. (46)

4.3. Effect of Redox Potential on Leaching of Ni$_3$S$_2$ in Absence of Bacteria. (48)

4.4. Test C.5, Variation of Redox Potential (vs SCE @ 37°C) with Time in Bioleaching of Ni$_3$S$_2$ and Parallel Sterile Control. (51)

4.5. Test C.5, Nickel Recoveries vs Time in Bioleaching of Ni$_3$S$_2$ and Parallel Sterile Control. (53)

4.6. Tests C.1 to C.5, Nickel Concentrations vs Time in Bioleachings of Ni$_3$S$_2$ and Parallel Sterile Controls. (54)

4.7. Test C.5, Iron Balance in Bioleaching of Ni$_3$S$_2$. (56)
List of Figures (Continued...)

Figure (page)

4.8. Test C.4, Ammonium Consumption in Bioleaching of Ni$_3$S$_2$. (59)

4.9. Test C.5, Ammonium Consumption in Bioleaching of Ni$_3$S$_2$. (60)

4.10. Test C.5, Acid Consumptions (200 g/l 98% H$_2$SO$_4$) in Bioleaching of Ni$_3$S$_2$ and Parallel Sterile Control. (62)

4.11. Test C.5, Residue of Parallel Sterile Control of Ni$_3$S$_2$ Leaching at 70% Ni Extraction. (65)

4.12. Test C.5, Residue of Bioleaching of Ni$_3$S$_2$ at 70% Ni Extraction. (66)

4.13. Test C.5, Residue of Bioleaching of Ni$_3$S$_2$ at 55% Ni Extraction. (67)


5.1. Modelling Redox Potential and pH Levels in Tests of Type A by Multiplying the Literature Value of K(3) by 160. (71)
List of Figures (Continued...)

Figure (page)

5.2. Test C.5, Modelling of Redox Potential in Bioleaching of Ni₃S₂ and Parallel Sterile Control by Multiplying the Literature Value of K(3) by 160. (73)

5.3. Linear Regression of Data from Tests of Type B, in Order to Obtain Values for the Electrochemical Model Constants k₁ and k₂ for a Shape Factor of 10. (75)

5.4. Comparing Data from Tests of Type B with the Graph Obtained Using the Trial-and-Error Electrochemical Constants k₁ and k₂ ("Model 2"). (78)

5.5. Test C.5, Modelling of Nickel Extraction in Bioleaching of Ni₃S₂ and Parallel Sterile Control Using the Two Sets of Electrochemical Model Constants. (80)

5.6. Tests D.1 and D.2, Modelling of Nickel Extraction in Leaching of Ni₃S₂ in Absence of Bacteria and Without Hydrogen Peroxide Addition Using the Two Sets of Electrochemical Model Constants. (81)

A.1. Apparatus Used in the Large Scale Precipitation of Nickel Sulphide from a Concentrated Nickel Sulphate Solution by Bubbling Hydrogen Sulphide Through the Solution. (108)
List of Figures (Continued...)

Figure (page)

A.2. Screening Masses of Pulverized Nickel Sulphide Recorded in Various Size Fractions with time. (118)

A.3. Comparison of Screening and Malvern Results of Pulverized Nickel Sulphide. (121)

A.4. Malvern Sizing of +45 -53 Micron Screening Fraction, Compared With a Distribution Resulting from a Hypothetical Two Dimensional Ellipse of Size 49(min) by 98(max) Microns. (123)

A.5. Procedure Used to Separate Supernatant of Samples and to Wash Solid Residues. (137)

A.6. Acid Leaching With HCl and Washing of Residues. (139)

A.7. Test C.4, Variation of Redox Potential (vs SCE @ 37°C) with Time in Bioleaching of Ni₃S₂ and Parallel Sterile Control. (174)

A.8. Test C.5, Variation of Redox Potential (vs SCE @ 37°C) with Time on Bioleaching of Ni₃S₂ and Parallel Sterile Control. (174)

A.9. Test C.4, Nickel Recoveries vs Time in Bioleaching of Ni₃S₂ and Parallel Sterile Control. (175)
List of Figures (Continued...)

Figure (page)

A.10. Test C.5, Nickel Recoveries vs Time in
Bioleaching of Ni$_3$S$_2$ and Parallel Sterile Control. (175)

A.11. Test C.4, Iron Balance in Sterile Leaching of
Ni$_3$S$_2$. (176)

A.12. Test C.4, Iron Balance in Bioleaching of Ni$_3$S$_2$. (176)

A.13. Test C.5, Iron Balance in Sterile Leaching of
Ni$_3$S$_2$. (177)

A.14. Test C.5, Iron Balance in Bioleaching of Ni$_3$S$_2$. (177)

A.15. Test C.4, Ammonium Balance in Sterile Leaching of
Ni$_3$S$_2$. (178)

A.16. Test C.5, Ammonium Balance in Sterile Leaching of
Ni$_3$S$_2$. (178)

A.17. Test C.4, Ammonium Consumption in Bioleaching of
Ni$_3$S$_2$. (179)

A.18. Test C.5, Ammonium Consumption in Bioleaching of
Ni$_3$S$_2$. (179)
List of Figures (Continued...)

Figure (page)

A.19. Test C.4, Ammonium Balance in Bioleaching of Ni₃S₂. (180)

A.20. Test C.5, Ammonium Balance in Bioleaching of Ni₃S₂. (180)

A.21. Test C.4, Other Concentrations in Sterile Leaching of Ni₃S₂. (181)

A.22. Test C.4, Other Concentrations in Bioleaching of Ni₃S₂. (181)

A.23. Test C.5, Other Concentrations in Sterile Leaching of Ni₃S₂. (182)

A.24. Test C.5, Other Concentrations in Bioleaching of Ni₃S₂. (182)

A.25. Test C.4, Acid Consumptions (200 g/l 98% H₂SO₄) in Bioleaching of Ni₃S₂ and Parallel Sterile Control. (183)

A.26. Test C.5, Acid Consumptions (200 g/l 98% H₂SO₄) in Bioleaching of Ni₃S₂ and Parallel Sterile Control. (183)
List of Figures (Continued...)

Figure (page)

A.27. Modelling Redox Potential and pH Levels in Tests of Type A, Using Equilibrium Data from the Literature (Table A.46). (186)

A.28. Modelling Redox Potential and pH Levels in Tests of Type A, but Changing a Single Hydroxide Equilibrium Constant at a Time from its Literature Value (Table A.46). (187)

A.29. Multiplying $K(3)$ by Various Amounts to Find the Value of $K(3)$ Which Gives the Smallest Average Error in Prediction of Redox Potentials Recorded in Tests A. ($K(6) = 0$) (189)

A.30. Modelling Redox Potential and pH Levels in Tests of Type A by Multiplying the Literature Value of $K(3)$ (Table A.46) by 160. (190)

A.31. Tests A, Major Ferric Species Obtained When Modelling With $K(3) = 9.04 \times 10^{13}$ and $K(6) = 0$. (192)

A.32. Tests A, Major Ferrous Species Obtained When Modelling With $K(3) = 9.04 \times 10^{13}$ and $K(6) = 0$. (192)
List of Tables

Table (page)

1.1. Categories of Experiments, with Descriptions and Aims (11)

1.2. Location of Material Relevant to Types of Experiments (12)

3.1. 9K Medium: amounts per litre (30)

5.1. Equilibrium Constant Values @ 37°C of Complexes Used in Calculation of Redox Potential and pH Levels in Solutions of Experiments of Type A (70)

A.1. Nutritional Requirements of *Thiobacillus ferrooxidans*, Values are Given in Parts Per Million (93)

A.2. Timé Course of Precipitation of NiS by Bubbling Hydrogen Sulphide Through a Concentrated Nickel Sulphate Solution (109)

A.3. Recrystallization of NiS on Small Scale in Alumina Crucibles. All Tests Were Performed Under an Argon Atmosphere. (113)

A.4. Recrystallization of 1 kg Batch of NiS Precipitate in an Induction Furnace Under an Argon Atmosphere. (114)

A.5. Screening Masses of Pulverized Nickel Sulphide Recorded in Various Size Fractions with time. (116)
List of Tables (Continued...)

Table (page)

A.6. Size Distribution Obtained by Screening for 120 minutes. (117)

A.7. Malvern Size Analysis of Three Different Samples of Sulphide Using a Coarse Lens, Showing Reproducibility of Results. (119)

A.8. Malvern Size Analysis of Two Samples of the -38 Micron Screening Fraction, Using a Medium Lens. (120)

A.9. Malvern Size Analysis of the 45 to 53 Micron Screening Fraction, Using a Medium Lens. Values Obtained are the Average of Three Determinations on the Same Sample. (124)

A.10. Size Distribution Used in Modelling. Malvern Results up to 38 Microns, Screening Results for the Remainder. (125)

A.11. 9K Medium: Amounts per Litre (128)

A.12. Time Course Data in Shake Flasks Used to Determine the Effect of Diluting 9K Nutrients and Using Lower pH Levels. (Concentrations in g/l, 30 ml Samples Taken on Days 7, 12, and 17) (131)
List of Tables (Continued...)

Table (page)

A.13. Results of shake flask tests to determine the effect of pH and 100 x dilution of the 9K nutrients on the extraction of nickel. (132)

A.14. Determination of Effect of Aeration only on Redox Potential in Absence of Nickel Sulphide. (Test A.1.) (144)

A.15. Determination of Redox Potential Without Nutrients in Absence of Nickel Sulphide. Solution is Purged With Nitrogen. (Test A.2.) (145)

A.16. Determination of Effect of a Combination of Nutrients and Aeration on Redox Potential in Absence of Nickel Sulphide. (Test A.3.) (146)

A.17. Determination of Effect of Nutrients on Redox Potential in Absence of Nickel Sulphide. Solution is Purged with Nitrogen. (Test A.4.) (147)

A.18. Determination of Effect of a Combination of Nutrients, Aeration and Presence of Bacteria on Redox Potential in Absence of Nickel Sulphide. (Test A.5.) (148)

List of Tables (Continued.. )

Table (page)

A.20. Test C.1, Time Course Data in Determination of Bioleach Characteristics of Nickel Sulphide. (150)

A.21. Test C.1, Sterile Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm.) (152)

A.22. Test C.1, Inoculated Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm, Bugs = (no of bacteria in solution)/ (cm⁻³ x 10⁸).) (152)

A.23. Test C.2, Time Course Data in Determination of Bioleach Characteristics of Nickel Sulphide. (153)

A.24. Test C.2, Sterile Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm.) (154)

A.25. Test C.2, Inoculated Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm, Bugs = (no of bacteria in solution)/ (cm⁻³ x 10⁸)) (154)

A.26. Test C.3, Time Course Data in Determination of Bioleach Characteristics of Nickel Sulphide. (155)
List of Tables (Continued...)

Table (page)

A.27. Test C.3, Sterile Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm.) (156)

A.28. Test C.3, Inoculated Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm, Bugs = (no of bacteria in solution)/ (cm\(^{-3}\) x 10\(^8\))) (156)

A.29. Test C.4, Time Course Data in Determination of Bioleach Characteristics of Nickel Sulphide. (157)

A.30. Test C.4, Example of Sampling Data for Sterile Control in Determination of Bioleach Characteristics of Nickel Sulphide. Sampling Procedure is Discussed in the Appendix Figures A.5 and A.6. (159)

A.31. Test C.4, Example of Sampling Data for Inoculated System in Determination of Bioleach Characteristics of Nickel Sulphide. Sampling Procedure is Discussed in the Appendix Figures A.5 and A.6 page 150. (160)

A.32 Test C.4, Sterile Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm.) (161)
List of Tables (Continued...)

Table (page)

A.33. Test C.4, Inoculated Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm, Bugs = (no of bacteria in solution)/ (cm^{-3} x 10^8)) (161)

A.34. Test C.4, Sterile HCl Extract Data (see Appendix A.2.4.2) in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm.) (162)

A.35. Test C.4, Inoculated HCl Extract Data (see Appendix A.2.4.2) in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm.) (162)

A.36. Test C.5, Time Course Data in Determination of Bioleach Characteristics of Nickel Sulphide. (163)

A.37. Test C.5, Example of Sampling Data for Sterile Control in Determination of Bioleach Characteristics of Nickel Sulphide. Sampling Procedure is Discussed in the Appendix Figures A.5 and A.6. (165)

A.38. Test C.5, Example of Sampling Data for Inoculated System in Determination of Bioleach Characteristics of Nickel Sulphide. Sampling Procedure is Discussed in the Appendix Figures A.5 and A.6. (166)
List of Tables (Continued...)

Table (page)

A.39. Test C.5, Sterile Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm.) (167)

A.40. Test C.5, Inoculated Supernatant Data in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm, Bugs = (no of bacteria in solution)/ (cm\(^{-3}\) x 10^8)) (168)

A.41. Test C.5, Sterile HCl Extract Data (see Appendix A.2.4.2) in Determination of Bioleach Characteristics of Nickel Sulphide. (169)

A.42. Test C.5, Inoculated HCl Extract Data (see Appendix A.2.4.2) in Determination of Bioleach Characteristics of Nickel Sulphide. (Values in ppm.) (169)

A.43. Tests C.4 and C.5, Ammonium Balances for Inoculated Systems in Determination of Bioleach Characteristics of Nickel Sulphide. (170)

A.44. Test D.1, Data for Deduction of Effect of Hydrogen Peroxide on Chemical Leaching of Nickel sulphide. (10 g Solid in 1.5 Litre, 5 ml 98% H\(_2\)SO\(_4\) / l initially) (171)
List of Tables (Continued...)

Table (page)

A.45. Test D.2, Data for Deduction of Effect of Hydrogen Peroxide on Chemical Leaching of Nickel sulphide. (10 g Solid in 1.5 Litre, 5 ml 98% H₂SO₄ / l initially) (172)

A.46. Equilibrium Constant Values @ 37°C of Complexes Used in Initial Calculation of Redox Potential and pH Levels in Solutions of Experiments of Type A (185)
List of Symbols

<table>
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<td>Density of mineral</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>Symbol</td>
<td>Quantity</td>
<td>Units</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>$k_1$</td>
<td>Rate Constant</td>
<td>mol hr$^{-1}$</td>
</tr>
<tr>
<td>$M$</td>
<td>Moles in a Size Range</td>
<td>-</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of particles in a Size Range</td>
<td>-</td>
</tr>
<tr>
<td>$k_3$</td>
<td>Modelling Constant</td>
<td>Mol hr$^{-1}$</td>
</tr>
<tr>
<td>$k_4$</td>
<td>Modelling Constant</td>
<td>mV hr$^{-1}$</td>
</tr>
<tr>
<td>$k_5$</td>
<td>Modelling Constant</td>
<td>mV</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

In Section 1.1, background on organisms associated with bioleaching is presented. Literature on the bioleaching process is presented in Section 1.2. In Section 1.3 certain by-products of bacterial leaching processes are described, and the importance of galvanic effects is discussed in Section 1.4.

In Section 1.5 the objective and scope of the dissertation is presented. Two tables are provided to act as a guide to the various sections of the work.

1.1. BACKGROUND ON BACTERIAL LEACHING

In 1947 Colmer and Hinkle\(^1\) described a bacterium which was able to oxidize reduced ferrous and sulphur compounds. The bacterium was given the name \textit{Thiobacillus ferrooxidans}, the generic name "Thiobacillus" referring to the sulphur oxidizing capability, and the epithet "ferrooxidans" indicating ferrous iron oxidation capability.

This organism features prominently in bacterial leaching processes, and is well adapted to acidic inorganic environments. More details on the nature of the organism and its growth requirements are supplied in Appendix A.1.1.
1.2. THE BIOLEACHING PROCESS

Two mechanisms operative in bacterial leaching have been presented in the literature: the direct and the indirect mechanisms. These are discussed in Sections 1.2.1 and 1.2.2 respectively. Comments from the literature on the relative importance of the mechanisms are provided in Section 1.2.3. In Section 1.2.4 some recent modelling developments are presented.

1.2.1. BIOLEACHING BY DIRECT MECHANISM

The direct mechanism refers to the situation in which the bacteria directly oxidize the sulphide entity of a mineral to sulphate, thereby simultaneously dissolving the metal moiety. Usually the bacteria are visualized to be in direct contact with the mineral sulphides being oxidized.

Tributsch and Tributsch and Bennett ascribed direct leaching of a mineral by bacteria to a kind of "molecular carrier" produced by the organism, which was thought to remove -SH groups from the sulphide surfaces. The resulting compound was then visualized to be reabsorbed into the cell, where the sulphide ion was oxidized. Tuovinen and Kelly, however, found it likely that sulphide minerals should at least enter the peripheral membranes of the bacterial cells. Lundgren and Tanoha felt that the cell envelope, which forms the exterior of the bacteria, contained the necessary enzymes (biological catalysts) for sulphide oxidation.
Southwood and Southwood\(^6\) observed tunneling in the bioleaching of pyrite. They suggested this to be partly due to direct action by bacteria, which attached preferentially to irregularities in the crystal structure of the sulphide.

Torma, Legault, Kougiomoutzakis and Quellet\(^7\), Torma and Sakaguchi\(^8\), and Tributsch and Bennett\(^3\) found that there was a correlation between the solubility product of a given sulphide and the bacterial activity associated with it (a high solubility product resulted in more bacterial activity). Tributsch and Bennett\(^3\) found one exception to this general trend: Sulphides having p-type conducting characteristics showed bacterial activity more enhanced than that expected by the mentioned general trend. They ascribed this to the large number of holes in the valence band, which are equivalent to a large number of broken bonds. In the presence of a \(S^2^-\) acceptor, e.g. the molecular carrier postulated by the authors, the dissolution of the sulphide is accelerated.

It is clear that the direct mechanism could be of importance in bacterial leaching. The extent to which this mechanism operates seems to depend on the type of mineral being leached. Conditions in the leach could also have an influence.

1.2.2. BIOLEACHING BY INDIRECT MECHANISM

In the indirect mechanism ferric ions, known to be good oxidizing agents of metal sulphides, dissolve the metal moiety by oxidizing the sulphide ions in the mineral to
sulphur. Ferric ions are simultaneously reduced to their ferrous state. The ferrous ions formed may be oxidized back to their ferric state by bacteria (in this process bacteria obtain energy for growth, etc.). Thus a cycle is formed, and this process, where bacteria do not directly attack the mineral sulphide, is known as the indirect mechanism. Some viewpoints on the oxidation of ferrous ions by bacteria are presented in Appendix A.1.2.

Dry\(^9\) leached a sulphide matte which consisted mainly of triolite (FeS), and Verbaan and Crundwell\(^{10}\) leached a sphalerite concentrate. These authors found that the leaching behaviour in acidic iron sulphate solutions could be explained by an electrochemical mechanism.

1.2.3. RELATIVE IMPORTANCE OF DIRECT AND INDIRECT MECHANISMS

Tributch and Bennett\(^3\) postulated that if suitable oxidizing agents are present, e.g. ferric ions, electrons may be extracted from the valence band of the mineral. This means that more broken bonds are formed in the sulphide lattice, leading to enhanced leaching. It is thought that this could imply that the indirect and direct mechanisms might interact: The action of the ferric ions, creating holes, could facilitate the direct attack of bacteria on the mineral. It is not known whether this conceptual combined effect would be equal to the sum of the two effects working individually.

Duncan, Landesman and Walden\(^{11}\) bacterially leached chalcopyrite and pyrite minerals, and used selective