Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.
CHARACTERISATION AND AMELIORATION OF LOW pH CONDITIONS IN PYRITIC MINE PITWALL MATERIALS, MARTHA MINE, WAIHI, NEW ZEALAND

A thesis submitted in partial fulfilment of the requirements for the degree of
Doctor of Philosophy in Soil Science
Massey University

Shivaraj Gurung

1998
Abstract

The objective of this thesis was to research the processes associated with the generation of low pH conditions in pitwall rock material at Martha Mine, Waihi, and evaluate the ameliorating effectiveness of some selected acid neutralising materials with an aim to create suitable plant growth media. Approximately 25% of the current pitwall area is affected by pyrite oxidation, resulting in the formation of acid mine drainage (AMD) which limits long-term establishment of vegetation.

The results of this study showed that slope gradient, variable cover material distribution and persistent rill and sheet erosion on the pitwall are some of the physical characteristics restricting plant establishment. Weathered cover materials varied in depth from 5 mm on the upper slopes to > 300 mm in the lower colluvial section of the pitwall. The uneven distribution of pyrite mineralisation has resulted in microenvironments of “acid pockets” in oxidised parts of the pitwall.

The fresh pyritic rock had a near neutral pH while the strongly weathered materials generally had pH < 3.0. Based on the total sulphide S content (2.51%), the fresh rock had a net acid producing potential (NAPP) of 51 kg CaCO₃ t⁻¹. Weathered material still contained significant amounts of sulphide S but because of negative neutralisation potential (NP), it had a higher NAPP of 82 kg CaCO₃ t⁻¹. Kinetic net acid generation (NAG) test revealed that the fresh rock, when exposed, had a lag-period of 22 weeks for the onset of biochemical oxidation. However, the degree of pyrite liberation from the host rock materials is likely to effect the lag-period. The effect of progressive weathering and oxidation was to cause major losses in base cations except for K, which showed an anomalous enrichment, due to incorporation into clays and jarosite-type minerals. Weathering also caused relative enrichment in Ba and As contents of the pitwall materials. Run-off water collected from the bottom of the pitwall had the characteristic AMD composition of low pH and high dissolved metal concentrations.

The spatial variation of pH of the weathered pitwall rock in the study area was in the range 2.0-4.6 while EC varied from 1.9 to 4.3 dS m⁻¹. The study area generally contained high
concentrations of soluble Fe (2506-5758 mg kg\(^{-1}\)), Mn (203-635 mg kg\(^{-1}\)), exchangeable-Al (4.8-10.8 cmol\(_{e}\) kg\(^{-1}\)), \(\text{SO}_4^{2-}\) (1650-3400 mg kg\(^{-1}\)) and acidity (121-668 kg CaCO\(_3\) t\(^{-1}\)). Overall, NAPP distribution varied from 35 to 143 kg CaCO\(_3\) t\(^{-1}\).

A buffer curve lime requirement (LR\(_{Buffer}\)) to raise the pH of the weathered pitwall rock material to 6 (29 kg CaCO\(_3\) t\(^{-1}\)) amounted only to 35% of the acid base accounting (ABA) value of 82 kg CaCO\(_3\) t\(^{-1}\). This suggested that the LR\(_{Buffer}\) only accounted for the acid generated from dissolution of hydroxide precipitates of Fe and Al. It was found that in order to account for the NAPP of the pitwall material, it was important that the lime required to neutralise the potential acidity (LR\(_{NAPP}\)) be added to the LR\(_{Buffer}\) to give the total lime requirement (LR\(_{Total}\)) for long-term control of acid generation.

A 90 days incubation assessment of selected neutralising materials (limestone, LST; dolomite, DOL; reactive phosphate rock, RPR; fluidised bed boiler ash, FBA) indicated that LST, DOL and FBA were similar in attaining the target pH of 6 at a carbonate content equivalent rate (C\(_{ER}\)) of 30 kg CaCO\(_3\) t\(^{-1}\). The RPR did not raise the pH > 4.5 even at C\(_{ER}\) of 50 kg CaCO\(_3\) t\(^{-1}\) but it was equally effective in overall reduction of EC, \(\text{SO}_4^{2-}\), acidity, Fe, Mn and Al in the incubated pitwall rock material. The coarser the grain size, the less reactive the neutralising material was, mainly due to an armouring effect from the Fe and Al hydroxide coatings. While fine-grained material provided quick neutralisation of acid, long-term buffering of the pH may not be possible due to continued generation of acid as more pyrite grains are liberated for oxidation. On the other hand, materials like RPR and coarse LST may provide slow release neutralisation from repetitive dissolution of hydroxide coatings when reacidification occurs.

Results of the column experiments on the assessment of ameliorative effectiveness of neutralising materials on leachate quality and subsurface acidity indicated that although application of amendments significantly raised the pH at 0-60 mm column depth, the leachate pH remained below 2.5 throughout the 12 weeks leaching cycle. The concentrations of EC, \(\text{SO}_4^{2-}\), acidity, Fe, Mn and Al were however, significantly reduced both in the leachate and subsurface column sections. At depth > 60 mm, the leached columns remained acidic irrespective of treatments. Broadcasted and incorporated
methods of application of neutralising material amendments showed similar trends in effectiveness of amelioration. However, the overall ameliorative effectiveness was significantly better with incorporated method of amendments.

Surface application of a shallow depth of topsoil (TS) and incorporation of bactericide ProMac (PM) were found effective in the amelioration of low pH conditions of the pitwall rock material by raising pH and significantly reducing sub-surface concentrations of $\text{SO}_4^{2-}$, acidity, Fe, Mn and Al. The amended columns however, still produced effluent pH of $<2.5$.

The overall results from the study indicated that with detailed on-site characterisation and using laboratory studies to formulate appropriate combinations of neutralising materials, the pyritic pitwall rock materials could be suitably modified for plant growth. In practice, the placement of the amendments on the pitwall remains an engineering challenge.
Acknowledgments

I would like to thank my supervisory panel, Dr. R.B. Stewart (Chief), Professor P.E.H. Gregg, Dr. N.S. Bolan and Dr. C.W. Ross for their constructive advice, interest in the research, encouragement and patience towards completion of this thesis. My special thanks to Professor Paul Gregg for initiating this research.

My gratitude and appreciation for assistance also extends to the following technical staff of the Earth & Soils Science Department:- Messrs Lance D. Currie (Senior Technical Manager), Mike Bretherton, Bob Toes, Ian Furkert, Alton McDonald, Joe Whitten, Ann West, Glenys Wallace and Ross Wallace. I would like to thank Doug Hopcroft at Horticulture and Food Research Institute for assisting with Scanning Microscopy. To the academic staff and to Denise and Marian at the office I say “thank you” for all the help.

Funding for this research was kindly provided by Waihi Gold Mining Company. I wish to thank Keith Brodie (Environmental Manager), Tim Gosling (Mine Manager) and Stewart Miller (EGi.Ltd) for facilitating field studies and for their continued support and keen interest in this mine reclamation research. Kathy Mason (Environmental Officer), thank you for your help in the field and all the documents you provided so readily.

I also acknowledge the fundings from Fertiliser & Lime Research Centre, Helen E. Akers postgraduate scholarship and a grant for XRF analysis at Spectra Chem Analytical, Wellington.

Thanks to all my friends and colleagues in the department who have helped keep my sanity intact. My special thanks to John Morrell, Jim Moir, Shane Cronin & Iris Vogeler, Bret Robinson and Andrew Hammond for inspirational chats and putting up with my antics. Your friendship and companionship will be remembered through the years.

To my family Shanthini, Kesherie, Ishka and Aasha for their love, support and understanding through the student years. Dr & Mrs S. Nissanga and Thilani, thank you for your love and support. Finally, I would like to dedicate this thesis to my parents Ratna Bahadur & Dil Maya Gurung for aspirations fulfilled, obligations neglected.
# TABLE OF CONTENTS

Abstract ................................................................................................................................. i
Acknowledgments.................................................................................................................... iv
Table of Contents................................................................................................................... v
List of Tables.......................................................................................................................... xi
List of Figures ........................................................................................................................ xiii
List of Plates............................................................................................................................ XVI

Chapter 1
Introduction

1.1 Background ....................................................................................................................... 1
1.2 Objectives of this Study ..................................................................................................... 5
1.3 Outline of this Research ................................................................................................... 6

Chapter 2
Literature Review: Mined Land Reclamation

2.1 Introduction ....................................................................................................................... 7
2.2 Acid Mine Drainage (AMD) ............................................................................................. 7
2.3 Sources of AMD ................................................................................................................. 8
2.4 Biochemical Aspects of AMD Formation ........................................................................ 9
   2.4.1 The chemistry of AMD generation from pyrite oxidation ........................................ 10
   2.4.2 Accretion and migration of AMD .............................................................................. 13
   2.4.3 By-products associated with AMD ........................................................................... 15
      2.4.3.1 Metal hydroxides .............................................................................................. 16
      2.4.3.2 Sulphate salts .................................................................................................... 16
      2.4.3.3 Acidity .............................................................................................................. 17
      2.4.3.4 Aluminium ........................................................................................................ 18
   2.4.4 In-situ neutralisation of acidity ................................................................................. 19
2.5 Predictive Techniques for AMD ....................................................................................... 20
   2.5.1 Static tests ................................................................................................................ 21
   2.5.2 Kinetic tests .............................................................................................................. 23
   2.5.3 Evaluation of the predictive techniques ................................................................... 26
2.6 Prevention and Control of AMD ..................................................................................... 29
   2.6.1 Preventive coatings ................................................................................................. 30
   2.6.2 Selective handling ................................................................................................. 30
   2.6.3 Bactericides .......................................................................................................... 31
2.6.4 Oxidant infiltration barriers .......................................................... 31
2.7 Treatment of AMD ........................................................................... 35
  2.7.1 Active treatment systems ............................................................... 35
  2.7.2 Passive treatment systems ............................................................... 37
2.8 Mined Land Reclamation Methods ................................................... 38
  2.8.1 Lime requirement of sulphidic mine wastes .................................... 39
  2.8.2 Alkaline amendments in reclamation ............................................. 39
  2.8.3 Organic amendments ................................................................. 43
  2.8.4 Bactericides ............................................................................. 45
  2.8.5 Reclamation by revegetation ....................................................... 46
2.9 Revegetative Reclamation in New Zealand .......................................... 47
2.10 Summary and Conclusions ............................................................. 49

Chapter 3

Characterisation of Pyritic Pitwall Rock at Martha Mine, Waihi

3.1 Introduction ..................................................................................... 51
3.2 Materials and methods ................................................................. 52
  3.2.1 Site selection and sample collection .............................................. 52
  3.2.2 Grid sampling ......................................................................... 52
  3.2.3 Spatial data analysis ................................................................. 52
  3.2.4 Mineralogical and geochemical studies ...................................... 55
  3.2.5 Analytical methods .................................................................. 56
  3.2.6 Net acid generating (NAG) static test ........................................... 59
  3.2.7 Acid neutralising capacity (ANC) ............................................... 59
  3.2.8 Acid base accounting (ABA) .................................................... 59
  3.2.9 Net acid generating (NAG) kinetic test ....................................... 59
  3.2.10 Column test ........................................................................ 60
3.3 Results and Discussion ................................................................... 62
  3.3.1 Physical and geochemical characteristics of the pitwall rock .......... 62
    3.3.1.1 Physical characteristics ..................................................... 62
    3.3.1.2 Mineralogical properties .................................................. 63
    3.3.1.3 Chemical properties .......................................................... 77
    3.3.1.4 Depth-profile chemistry of the weathered pitwall rock ........... 78
    3.3.1.5 Geochemical Properties ..................................................... 79
    3.3.1.6 Effect of weathering on geochemical properties ................... 81
  3.3.2 Acid generation properties of the pitwall rock ............................... 85
    3.3.2.1 Static net acid generation (NAG) test .................................. 85
    3.3.2.2 Acid base accounting (ABA) .............................................. 85
    3.3.2.3 Kinetic NAG test – Lag period .......................................... 88
| 3.3.2.4 | Column test - rate of acid generation |
| 3.3.3 | Characterisation of pitwall run-off drainage |
| 3.3.4 | Spatial characterisation of the weathered pitwall rock |
| 3.3.4.1 | Geostatistics |
| 3.3.4.2 | Descriptive statistics |
| 3.3.4.3 | Distribution of cover material and moisture content |
| 3.3.4.4 | pH and EC |
| 3.3.4.5 | Exchangeable Al, soluble Fe and Mn |
| 3.3.4.6 | \( SO_4^{2-} \) and Acidity |
| 3.3.4.7 | Total S and NAPP |
| 3.3.4.8 | Distribution of pyrite |
| 3.3.4.9 | Base cations (Ca, Mg, K and Na) |
| 3.4 | Conclusions |

Chapter 4

An Assessment of the Effectiveness of Neutralising Materials in Ameliorating Acidic Pitwall Rock

4.1 | Introduction |
| 4.1.1 | Neutralisation of acid in pyritic mine waste rocks |
| 4.2 | Materials and Methods |
| 4.2.1 | Pitwall rock bulk sample |
| 4.2.2 | Neutralising materials |
| 4.2.3 | Neutralising potential (NP) of the neutralising materials |
| 4.2.4 | Lime requirement of the pitwall rock |
| 4.2.5 | Neutralising material requirements: an incubation study |
| 4.2.6 | Determination of limestone particle size effect on pitwall rock |
| 4.2.7 | Characterisation of hydroxide coating on limestone particles |
| 4.2.8 | Analytical methods |
| 4.3 | Results and Discussion |
| 4.3.1 | Effectiveness of alkaline materials in acid neutralisation |
| 4.3.1.1 | Lime requirement of the pitwall rock |
| 4.3.1.2 | Neutralising material requirements of the pitwall rock |
| 4.3.1.3 | Neutralisation of acidity |
| 4.3.2 | Effect of neutralising materials on chemical properties of the pitwall rock |
| 4.3.2.1 | pH |
| 4.3.2.2 | Electrical conductivity (EC) |
| 4.3.2.3 | Exchangeable Al (\( Al_{exc} \)) |
| 4.3.2.4 | Sulphate (\( SO_4^{2-} \)) |
### Chapter 5

**Effectiveness of Surface Broadcasted Neutralising Materials in Ameliorating Low pH Conditions in Pyritic Pitwall Rock**

5.1 Introduction.................................................................................................................. 153
5.2 Material and Methods.................................................................................................. 156
  5.2.1 Pitwall rock bulk sample ...................................................................................... 156
  5.2.2 Neutralising materials ......................................................................................... 156
  5.2.3 Column set up ...................................................................................................... 156
  5.2.4 Column leaching protocol .................................................................................. 158
  5.2.5 Leachate analysis ................................................................................................ 158
  5.2.6 Column section analysis ..................................................................................... 159
5.3 Results and Discussion ............................................................................................... 159
  5.3.1 Characterisation of the leachate quality ............................................................. 160
    5.3.1.1 Leachate pH .................................................................................................. 160
    5.3.1.2 Leachate EC .................................................................................................. 161
    5.3.1.3 Leachate SO$_4^{2-}$ ...................................................................................... 163
    5.3.1.4 Leachate acidity ........................................................................................... 164
    5.3.1.5 Leachate Fe and Mn .................................................................................... 165
    5.3.1.6 Leachate Al .................................................................................................. 167
    5.3.1.7 Leachate Ca-Mg-K-Na ............................................................................... 168
  5.3.2 Column section chemistry ................................................................................... 170
    5.3.2.1 Column section pH ...................................................................................... 170
    5.3.2.2 Column section EC ...................................................................................... 172
    5.3.2.3 Column section SO$_4^{2-}$ ........................................................................... 173
    5.3.2.4 Column section acidity ............................................................................... 174
    5.3.2.5 Neutralisation of acidity in the pitwall rock column ..................................... 177
    5.3.2.6 Column section Fe and Mn ......................................................................... 180
    5.3.2.7 Column section exchangeable Al (Al$_{exc}$) ................................................. 180
    5.3.2.8 Column section Ca-Mg-K-Na ....................................................................... 181
  5.3.3 Mineralogical composition of leached columns ................................................... 183
Chapter 6

Effectiveness of Depth Incorporated Neutralising Materials in Ameliorating Low pH Conditions in Pyritic Pitwall Rock

6.1 Introduction
6.2 Materials and Methods
   6.2.1 Materials
   6.2.2 Methods
6.3 Results and Discussion
   6.3.1 Effect on chemical properties of the pitwall rock by incorporated neutralising materials
      6.3.1.1 pH and EC
      6.3.1.2 SO$_4^{2-}$ and acidity
      6.3.1.3 Fe, Mn and Al
      6.3.1.4 Base cations (Ca, Mg, K and Na)
   6.3.2 Comparison between broadcasted and incorporated methods of application of neutralising materials
      6.3.2.1 Leachate chemistry
      6.3.2.2 Column section chemistry
      6.3.2.3 Overall effectiveness of amendment methods
6.4 Conclusions

Chapter 7

An Assessment of AMD Inhibitors (Topsoil and ProMac) in Ameliorating Low pH Conditions in Pyritic Pitwall Rock

7.1 Introduction
7.2 Materials and Methods
   7.2.1 Materials
   7.2.2 Methods
7.3 Results and Discussion
   7.3.1 Characterisation of the leachate
      7.3.1.1 Leachate pH
      7.3.1.2 Leachate EC
      7.3.1.3 Leachate SO$_4^{2-}$
      7.3.1.4 Leachate acidity
      7.3.1.5 Leachate Fe and Mn
      7.3.1.6 Leachate Al
   7.3.2 Column section Chemistry
Chapter 7

7.3.2.1 Column section pH ................................................................. 223
7.3.2.2 Column section EC ................................................................. 223
7.3.2.3 Column section \(SO_4^{2-}\) ............................................................... 225
7.3.2.4 Column section acidity .............................................................. 225
7.3.2.5 Column section Fe and Mn ......................................................... 227
7.3.2.6 Column section Al ................................................................. 228
7.3.2.7 Effect of topsoil placement on total Al pool .................................. 229
7.3.3 Effects of combination amendments ............................................. 231
7.3.3.1 Effect of combination treatments on pH and EC ........................... 231
7.3.3.2 Effect of combination treatments on leachate \(SO_4^{2-}\), Fe, Mn and Al 234
7.3.3.3 Effect of combination treatments on column chemistry ............... 235
7.4 Conclusions .................................................................................. 236

Chapter 8

Summary and Conclusions

8.1 Background ................................................................................. 239
8.2 Literature Review ....................................................................... 239
8.3 Characterisation of the Pyritic Pitwall Rock ..................................... 241
8.4 Lime Requirements of the Pitwall Rock ........................................ 244
8.5 Ameliorating Effectiveness of Selected Amendments ....................... 245
8.6 Future Directions ........................................................................ 247

References ....................................................................................... 249
LIST OF TABLES

Table 2.1 ABA procedures ................................................................. 22
Table 2.2 Screening criteria in ABA .................................................. 22
Table 2.3 Comparisons of ABA procedures ....................................... 23
Table 2.4 Reclamation of AMD contaminated mine sites in New Zealand . 48
Table 3.1 Description of the pyritic pitwall rock samples .................... 55
Table 3.2 XRD analysis of major minerals (wt.%) in the pitwall rock .... 64
Table 3.3 Chemical properties of the pitwall rock .............................. 78
Table 3.4 Average composition of the pitwall rock ............................. 82
Table 3.5 NAG test results for the pitwall rock samples ...................... 85
Table 3.6 Acid base accounting (ABA) analysis of pitwall rock .......... 86
Table 3.7 Chemical characteristics of the runoff drainage .................. 96
Table 3.8 Descriptive statistics of spatial characteristics of the pitwall rock (n=47) 101
Table 3.9 Correlation coefficients of the selected parameters ........... 101
Table 3.10 A comparison of pyrite estimation from various methods .... 114
Table 4.1 Selected properties of the bulk pitwall rock ....................... 121
Table 4.2 Properties of the selected neutralising materials ............... 121
Table 4.3 Non-linear regression coefficients for pH-CER curves .......... 128
Table 4.4 Neutralising material required to raise pH>6 in pitwall rock .... 129
Table 4.5 Graded limestone requirement of the pitwall rock to raise pH>6 . 137
Table 4.6 Metal and sulphate analysis of the coated limestone grain .... 144
Table 4.7 Munsells colours after 90 days incubation .......................... 147
Table 5.1 Correlation coefficients (r) of the measured parameters in the leachate . 163
Table 5.2 Average release rates of the concentrations of measured parameters in the leachate from broadcasted pitwall rock column .......... 165
Table 5.3 Correlation coefficients (r) of measured parameters in the column section 173
Table 5.4 Overall comparison of the mean concentrations of chemical properties of the leached pitwall rock columns broadcasted with neutralising materials 173
Table 5.5 Depth-wise base saturation (BS%) in the broadcasted columns .... 183
Table 6.1 Average release rates of the concentrations of measured parameters in the leachate from incorporated columns .................. 192
Table 6.2 Overall comparison of the mean concentrations of chemical properties of the leached pitwall rock columns incorporated with neutralising materials 192
Table 6.3 Overall means comparison of the broadcasted (BC) and incorporated (IC) methods of amendments ........................................... 209
Table 7.1 Selected properties of Waihi topsoil .................................. 214
Table 7.2 Amendments and treatment design .................................... 216
Table 7.3 Average release rates of the concentrations of measured parameters in the leachate from columns treated with various combinations of amendments 221
Table 7.4 Comparison of the mean distribution of selected chemical parameters in leached columns treated with various amendments ........................................ 227

Table 7.5 Average release rates of the concentrations of measured parameters in the leachate from columns treated with various combinations of amendments 234

Table 7.6 Comparison of the mean distribution of selected chemical parameters leached columns treated with various amendments ........................................ 235
LIST OF FIGURES

Figure 1.1 Location map, North Island, New Zealand .............................................. 3
Figure 2.1 A simplified cycle in the generation of AMD ........................................... 13
Figure 3.1 Grid sample locations (PWGS-1, GSC-1..) of the study area in Plate3.1. Contour values represent depth of cover material in mm................................. 53
Figure 3.2 Column test set up (adapted from Miller and Jeffrey, 1995)...................... 61
Figure 3.3 An EDS spectrum of semi-quantitative elemental analysis of the pyrite grain in Plate 3.4 ................................................................................................. 69
Figure 3.4 An EDS spectrum and semi-quantitative elemental analysis of pyrite grain shown in Plate 3.6 ......................................................................................... 73
Figure 3.5 Depth variations of selected chemical properties of the pitwall rock. Horizontal bars represent LSD(5%) .............................................................................. 80
Figure 3.6 Chemical gain-loss diagrams relative to the fresh rock (PWR-1), for the pitwall rock undergoing progressive weathering and oxidation .................... 84
Figure 3.7 Pyrite inclusions and oxidation scenario..................................................... 87
Figure 3.8 NAG test kinetics for (a) fresh PWR-1, (b) freshly weathered PWR-2, (c) moderately weathered PWR-4 and (d) strongly weathered PWR-5..... 89
Figure 3.9 Leachate characteristics of the pitwall rock under laboratory controlled column test. Vertical bars represent LSD(5%) ...................................................... 91
Figure 3.10 Pyritic pitwall showing runoff drainage flow direction and sampling locations (1-8). Contour values represent kriged % pyrite (FeS₂) in the weathered material ............................................................ 95
Figure 3.11 Chemical characteristics of the runoff drainage (a) pH and EC (b) cumulative loading of Fe, SO₄²⁻, Al and Mn ......................................................... 97
Figure 3.12 Distribution of (a) weathered pitwall rock cover depth (CD) and (b) moisture content (MC) of the cover material ...................................................... 103
Figure 3.13 Spatial variations in (a) pH and (b) EC levels in the weathered pitwall cover material ........................................................................................................... 105
Figure 3.14 Distribution of (a) exchangeable Al, (b) soluble Fe and (c) soluble Mn in the weathered pitwall cover material ....................................................... 108
Figure 3.15 Distribution of (a) SO₄²⁻ and (b) acidity in the weathered pitwall cover material ................................................................. 110
Figure 3.16 Spatial distribution of (a) total S content and (b) NAPP of the weathered pitwall rock ........................................................................................................ 112
Figure 3.17 Distribution of pyrite in the weathered pitwall rock material ................. 114
Figure 3.18 Spatial distribution of base cations (a) Ca, (b) Mg, (c) K and (d) Na in the weathered pitwall rock ................................................................. 116
Figure 4.1 (a) NaOH-pH and CaCO₃-pH buffer curves and (b) acidimetric titration curves for solutions containing Fe, Al and pitwall rock sample extract .... 125
Figure 4.2 Response to pH with increasing carbonate content equivalent rate (CER) of neutralising materials ................................................................. 128
Figure 4.3 Reduction in acidity in 90 days incubated pitwall rock (a) with varying CER and (b) overall comparison between neutralising materials.......................... 130

Figure 4.4 Effect on selected chemical properties of the pitwall rock after 90 days incubation with varying CER of neutralising materials. Vertical bars represent LSD(5%). ........................................................................................................ 133

Figure 4.5 Overall effect of neutralising materials on selected chemical properties of the pitwall rock after 90 days incubation. LST, limestone; DOL, dolomite; FBA, fluidised bed boiler ash; RPR, reactive phosphate rock. Vertical bars represent LSD(5%). ............................................................................................................................................. 136

Figure 4.6 Effect on selected chemical properties of the pitwall rock after 90 days incubation with varying CER of different particle size limestone. LSTVF, very fine limestone; LSTF, fine limestone; LSTC, coarse limestone; LSTAR, as received limestone. Vertical bars represent LSD(5%) ........................................................................................................ 139

Figure 4.7 Reduction in acidity in 90 days incubated pitwall rock. (a) With varying CER of graded limestone and (b) overall comparison between the graded limestone.140

Figure 4.8 EDS spectra with accompanying tables of elemental concentrations of hydroxide coated limestone grain incubated for 90 days. Core (limestone), Middle (hydroxide coating) and Outer (pitwall rock front).................... 143

Figure 4.9 Effect of incubation time on selected chemical properties of the pitwall rock treated with neutralising materials at CER = 30 kg CaCO\textsubscript{3} t\textsuperscript{-1}. Vertical bars represent LSD(5%) ........................................................................................................ 146

Figure 5.1 Reconstructed column set up for leaching pitwall rock under glasshouse condition .................................................................................................................................................. 157

Figure 5.2 (a) pH and (b) EC of the leachate from columns broadcasted with neutralising materials. Vertical bars represent LSD(5%)................................. 162

Figure 5.3 Concentrations of (a) SO\textsubscript{4}\textsuperscript{2-}, (b) acidity, (c) Fe, (d) Mn and (e) Al in the leachate from columns broadcasted with neutralising materials. Vertical bars represent LSD(5%)........................................................................................................ 166

Figure 5.4 Concentrations of (a) Ca, (b) Mg, (c) K and (d) Na in the leachate from columns broadcasted with neutralising materials. Vertical bars represent LSD(5%) ............................................................................................................................................. 169

Figure 5.5 (a) pH and (b) EC of the sectioned samples from leached columns. Horizontal bars represent LSD(5%)......................................................................................... 171

Figure 5.6 Distribution of (a) SO\textsubscript{4}\textsuperscript{2-}, (b) acidity, (c) Fe, (d) Mn and (e) Al\textsubscript{ex} in the sectioned samples from leached columns. Horizontal bars represent LSD(5%) ........................................................................................................................................................................ 176

Figure 5.7 A regression plot of overall mean acidity and SO\textsubscript{4}\textsuperscript{2-} values in leachate from control and amended columns. Data points are means of four replicates. 179

Figure 5.8 Distribution of (a) Ca, (b) Mg, (c) K and (d) Na in sectioned samples from leached columns broadcasted with neutralising materials. Horizontal bars represent LSD(5%) ......................................................................................................................................................... 182

Figure 5.9 Distribution of (a) pyrite, (b) gypsum, (c) silica and (d) clay minerals in the leached columns broadcasted with neutralising materials .......... 184
Figure 6.1 (a) pH and (b) EC of the leachate from columns incorporated with neutralising materials. Vertical bars represent LSD(5%) ........................................ 190
Figure 6.2 (a) pH and (b) EC of the sectioned samples from leached columns. Horizontal bars represent interaction LSD(5%) ........................................ 190
Figure 6.3 Distribution of (a) Ca, (b) Mg, (c) K and (d) Na in the sectioned samples from leached columns incorporated with neutralising materials. Horizontal bars represent LSD(5%) ........................................ 198
Figure 6.4 Treatment-wise comparison of leachate chemical properties of the broadcasted and incorporated columns. Vertical bars represent method x treatment interaction LSD(5%) ........................................ 201
Figure 6.5 Week-wise variations in the leachate chemical properties of the broadcasted and incorporated pitwall rock columns. Vertical bars represent LSD(5%) ........................................ 202
Figure 6.6 Treatment-wise comparisons of chemical properties of the broadcasted and incorporated columns. Vertical bars represent LSD(5%) ........................................ 204
Figure 6.7 Comparisons of (a) treatment-wise and (b) depth-wise distributions of exchangeable Al (Al_{exc}) in the broadcasted and incorporated columns ........................................ 205
Figure 6.8 Distribution of chemical parameters in broadcasted and incorporated columns. Horizontal bars represent (LSD5%) ........................................ 207
Figure 7.1 (a) pH and (b) EC of the leachate from columns amended with TS and PM. Vertical bars represent LSD(5%) ........................................ 218
Figure 7.2 Concentrations of (a) SO_{4}^{2-}, (b) acidity, (c) Fe, (d) Mn and Al in the leachate from columns amended with TS, PM and TS+PM. Vertical bars represent LSD(5%) ........................................ 220
Figure 7.3 (a) pH and (b) EC of the sectioned samples from leached columns. Horizontal bars represent LSD(5%) ........................................ 224
Figure 7.4 Distribution of (a) SO_{4}^{2-}, (b) acidity, (c) Fe, (d) Mn and (e) Al_{exc} in the sectioned samples from leached columns. Horizontal bars represent LSD(5%) ........................................ 226
Figure 7.5 Distribution of different forms of Al in topsoil amended columns ........................................ 230
Figure 7.6 Overall effect on (a) leachate pH and (b) column pH by various combinations of treatments ........................................ 232
Figure 7.7 Overall effect on (a) leachate EC and (b) column EC by various combinations of treatments ........................................ 233
Figure 7.8 A conceptual scenario of micro-bench amendment on pyritic pitwall at Martha mine. ........................................ 237
LIST OF PLATES

Plate 1.1 Martha mine and tailings disposal site (1994), Waihi ........................... 3
Plate 3.1 Martha mine (Waihi) shoeing the study area on exposed north face pitwall (1994) .............................................................. 53
Plate 3.2 A section of the pitwall showing (a) Fe-hydroxide coatings and rill erosion pattern and (b) fresh rock in weathered matrix .......................... 65
Plate 3.3 Back-scattered SEM scans of (a) disseminated pyrite crystals and (b) fine grained pyrite lens .......................................................... 67
Plate 3.4 SEM scan of euhedral pyrite grain from fresh rock ......................... 69
Plate 3.5 Forms of pyrite grains (a) sub-rounded pyrite crystals in weathered pitwall rock and (b) flaky calcite grains in fresh rock ................................. 71
Plate 3.6 SEM scan of silica coated pyrite grains in weathered pitwall rock ..... 73
Plate 3.7 SEM scan of pyrite grain with etch holes (a) Magnification x2000 (b) Magnification x20000 .......................................................... 75
Plate 4.1 SEM scan of sectioned 90 days incubated limestone grain. Refer Figure 4.8 for EDS spectra ................................................................. 141
Plate 4.2 Physical effect on pitwall rock incubated with nil (Control), low (10 kg CaCO$_3$ t$^{-1}$), medium (25 kg CaCO$_3$ t$^{-1}$) and high (50 kg CaCO$_3$ t$^{-1}$) rates of neutralising materials. Labels on pitwall rock indicate Munsells colour notations. 149