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**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
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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 $\text{pH} < 3.0$. Based on the total sulphide S content (2.51%), the fresh rock had a net acid producing potential (NAPP) of $51 \text{ kg CaCO}_3 \text{ t}^{-1}$. Weathered material still contained significant amounts of sulphide S but because of negative neutralisation potential (NP), it had a higher NAPP of $82 \text{ kg CaCO}_3 \text{ t}^{-1}$. 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_c kg⁻¹), SO₄²⁻ (1650-3400 mg kg⁻¹) and acidity (121-668 kg CaCO₃ t⁻¹). Overall, NAPP distribution varied from 35 to 143 kg CaCO₃ t⁻¹.

A buffer curve lime requirement (LR_{Buffer}) to raise the pH of the weathered pitwall rock material to 6 (29 kg CaCO₃ t⁻¹) amounted only to 35% of the acid base accounting (ABA) value of 82 kg CaCO₃ 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 CaCO₃ t⁻¹. The RPR did not raise the pH > 4.5 even at C_{ER} of 50 kg CaCO₃ t⁻¹ but it was equally effective in overall reduction of EC, SO₄²⁻, 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, SO₄²⁻, 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 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.

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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 <i>In-situ</i> 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 <i>Physical characteristics</i>	62
3.3.1.2 <i>Mineralogical properties</i>	63
3.3.1.3 <i>Chemical properties</i>	77
3.3.1.4 <i>Depth-profile chemistry of the weathered pitwall rock</i>	78
3.3.1.5 <i>Geochemical Properties</i>	79
3.3.1.6 <i>Effect of weathering on geochemical properties</i>	81
3.3.2 Acid generation properties of the pitwall rock.....	85
3.3.2.1 <i>Static net acid generation (NAG) test</i>	85
3.3.2.2 <i>Acid base accounting (ABA)</i>	85
3.3.2.3 <i>Kinetic NAG test – Lag period</i>	88

3.3.2.4 Column test - rate of acid generation.....	90
3.3.3 Characterisation of pitwall run-off drainage	94
3.3.4 Spatial characterisation of the weathered pitwall rock.....	98
3.3.4.1 Geostatistics	98
3.3.4.2 Descriptive statistics	99
3.3.4.3 Distribution of cover material and moisture content.....	102
3.3.4.4 pH and EC.....	104
3.3.4.5 Exchangeable Al, soluble Fe and Mn.....	106
3.3.4.6 SO_4^{2-} and Acidity.....	109
3.3.4.7 Total S and NAPP.....	111
3.3.4.8 Distribution of pyrite	113
3.3.4.9 Base cations (Ca, Mg, K and Na).....	115
3.4 Conclusions.....	117

Chapter 4

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

4.1 Introduction	119
4.1.1 Neutralisation of acid in pyritic mine waste rocks	119
4.2 Materials and Methods.....	120
4.2.1 Pitwall rock bulk sample	120
4.2.2 Neutralising materials	120
4.2.3 Neutralising potential (NP) of the neutralising materials.....	121
4.2.4 Lime requirement of the pitwall rock	122
4.2.5 Neutralising material requirements: an incubation study.....	122
4.2.6 Determination of limestone particle size effect on pitwall rock	122
4.2.7 Characterisation of hydroxide coating on limestone particles	123
4.2.8 Analytical methods	123
4.3 Results and Discussion	123
4.3.1 Effectiveness of alkaline materials in acid neutralisation	123
4.3.1.1 Lime requirement of the pitwall rock	123
4.3.1.2 Neutralising material requirements of the pitwall rock.....	126
4.3.1.3 Neutralisation of acidity	129
4.3.2 Effect of neutralising materials on chemical properties of the pitwall rock	131
4.3.2.1 pH	131
4.3.2.2 Electrical conductivity (EC)	131
4.3.2.3 Exchangeable Al (Al_{exc})	132
4.3.2.4 Sulphate (SO_4^{2-}).....	134

4.3.2.5 <i>Fe and Mn</i>	134
4.3.2.6 <i>Overall neutralising effectiveness of alkaline materials</i>	135
4.3.3 Neutralising effect of limestone particles on pitwall rock	137
4.3.3.1 <i>Lime requirement based on limestone particle size</i>	137
4.3.3.2 <i>Limestone particle size effect on chemical properties</i>	137
4.3.3.3 <i>Characterisation of the hydroxide coating</i>	141
4.3.3.4 <i>Quantification of elements in the hydroxide coating</i>	144
4.3.4 Effect of incubation time on pitwall rock chemical properties.....	145
4.3.5 Effect of incubation on physical properties of the pitwall	147
4.4 Conclusions.....	148

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

5.4 Conclusions.....	185
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Chapter 6

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

6.1 Introduction	187
6.2 Materials and Methods.....	188
6.2.1 Materials.....	188
6.2.2 Methods.....	188
6.3 Results and Discussion	188
6.3.1 Effect on chemical properties of the pitwall rock by incorporated neutralising materials.....	189
6.3.1.1 pH and EC.....	189
6.3.1.2 SO ₄ ²⁻ and acidity	191
6.3.1.3 Fe, Mn and Al	195
6.3.1.4 Base cations (Ca, Mg, K and Na).....	196
6.3.2 Comparison between broadcasted and incorporated methods of application of neutralising materials.....	199
6.3.2.1 Leachate chemistry`	199
6.3.2.2 Column section chemistry	203
6.3.2.3 Overall effectiveness of amendment methods`	208
6.4 Conclusions.....	209

Chapter 7

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

7.1 Introduction.....	213
7.2 Materials and Methods.....	214
7.2.1 Materials.....	214
7.2.2 Methods.....	215
7.3 Results and Discussion	216
7.3.1 Characterisation of the leachate.....	217
7.3.1.1 Leachate pH	217
7.3.1.2 Leachate EC	219
7.3.1.3 Leachate SO ₄ ²⁻	219
7.3.1.4 Leachate acidity	221
7.3.1.5 Leachate Fe and Mn`	222
7.3.1.6 Leachate Al	223
7.3.2 Column section Chemistry	223

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-C _{ER} 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 Plate 3.1. Contour values represent depth of cover material	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 (FeS_2) in the weathered material.	95
Figure 3.11 Chemical characteristics of the runoff drainage (a) pH and EC (b) cumulative loading of Fe , SO_4^{2-} , 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) SO_4^{2-} 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 CaCO_3 -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 (C_{ER}) of neutralising materials	128

Figure 4.3 Reduction in acidity in 90 days incubated pitwall rock (a) with varying C_{ER} 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 C_{ER} 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 C_{ER} of different particle size limestone. LST _{VF} , very fine limestone; LST _F , fine limestone; LST _C , coarse limestone; LST _{AR} , as received limestone. Vertical bars represent LSD(5%)	139
Figure 4.7 Reduction in acidity in 90 days incubated pitwall rock. (a) With varying C_{ER} 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 $C_{ER} = 30 \text{ kg CaCO}_3 \text{ t}^{-1}$. 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_4^{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_4^{2-} , (b) acidity, (c) Fe, (d) Mn and (e) Al_{exc} 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_4^{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

Chapter 1

Introduction

1.1 Background

Waihi Gold Company (WGC) operates the Martha Mine located within the northern perimeter of Waihi township on the southern end of the Coromandel Peninsula (Figure 1.1 & Plate 1.1). The Martha Mine is one of the previously worked epithermal gold-silver deposits in the Hauraki goldfield and was reopened in 1988 as a result of resurgence in gold prices and technological advances in ore processing methods. The ore is extracted by open pit mining and is processed by the carbon-in-pulp process. The current annual production rate is 0.85 Mt of ore and 3.5 Mt of waste rock with an average ore grade of 3.1 g t⁻¹ gold and 24 g t⁻¹ silver (Brodie et al., 1996). The total production of precious metals during the period 1988-1996 was 645,000 oz gold and over 3 millions oz of silver respectively (Gregg et al., 1998). An estimated 11 million tonnes of gold-silver bearing ore and 25 million tonnes of overburden is expected to be mined during the lifetime of the current mining operation. The waste rock is disposed at a site about 2.3 km away from the mine, where it is used as an embankment to store tailings from the processing plant.

Since the mine is located in close proximity to the Waihi township and the disposal site is on pastoral land, the mining licence required that stringent environmental controls were implemented from the onset of mining. Under the current licensing agreement, the final land use of the disposal site is to be pastoral farming and the post-mining option for the pit is a recreational lake. The WGC is also required to revegetate the pitwall above the projected final lake level, primarily for aesthetic reasons as well as to prevent erosion (WGC, 1985; Gregg and Stewart, 1996).

A preliminary study undertaken by Widdowson et al. (1984) indicated that although the oxidised waste rock showed potential as a plant growth medium, the unoxidised rock, which contained significant amounts of pyrite mineralisation, was highly unsuitable due to its poor texture, formation of excessive amounts of dissolved aluminium and salt content when oxidised. Onsite baseline studies and environmental impact assessments of the mine site (WGC, 1985; Miller, 1986) showed that pyrite exposed in some areas of the

pit had the potential to generate acid when oxidised, resulting in acid mine drainage (AMD).

Open pit mining of base metal deposits generally exposes large volume of sulphidic rocks to weathering and oxidation processes and is often regarded as an unsightly visual impact on the local landscape. With an annual average rainfall of 2300 mm and dry spells in summer, the local climatic conditions at Waihi provide a high erosion index, resulting in acidic runoff from pitwalls and surface precipitation of metal salts respectively. Such characteristics pose serious limitations to revegetation of the pyritic pitwalls. Pre-mining and on-going geochemical characterisation of the waste rock generated from open pit mining have indicated that approximately 40% of the waste rock is classified as a potentially acid generating type (WGC, 1985; Brodie et al., 1996). In terms of pitwall area, about 25% of the current pit slopes contain pyritic host rock (andesite) undergoing varying degrees of oxidation and weathering processes. Acid generation from oxidation of pyrite exposed on parts of the pitwall has created a highly acidic pitwall rock material with serious limitations to plant growth.

Past revegetation efforts on the pitwall have had mixed success. Whilst the non-pyritic sections of the pitwall have been successfully revegetated by hydroseeding with grass seed mixture, the pyritic areas of the pitwall have failed to sustain any form of vegetation (Gregg and Stewart, 1996). Large surface area exposed on steep pit slope (43°), low pH conditions created by accelerated pyrite oxidation and mobilisation of oxidation by-products are considered primary factors restricting plant growth on the pitwall.

Mining is a disruptive activity, especially so when it involves open-pit mining methods. The environmental impact of mining is now a global issue and the struggle to remediate AMD contamination is a challenging problem. Acid mine drainage poses a significant threat to the environment and a liability for sulphide mine operations, if not properly managed. Many countries in the world are bringing out newer legislation with stricter guidelines for environmentally responsible mining (so much so that in New Zealand, in an effort to project the country as a “clean green image”, there is even stricter Resource Management Act (1991) to control the mining agencies activities).

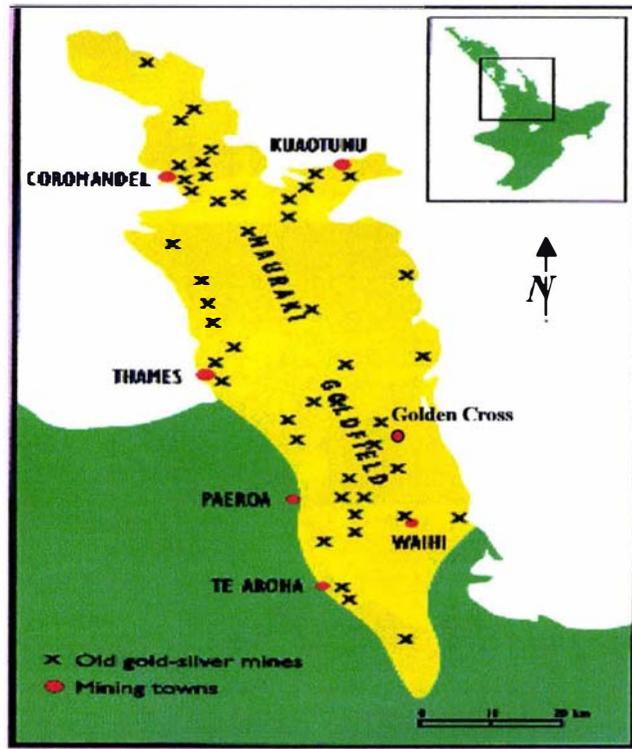


Figure 1.1 Location map, North Island, New Zealand.

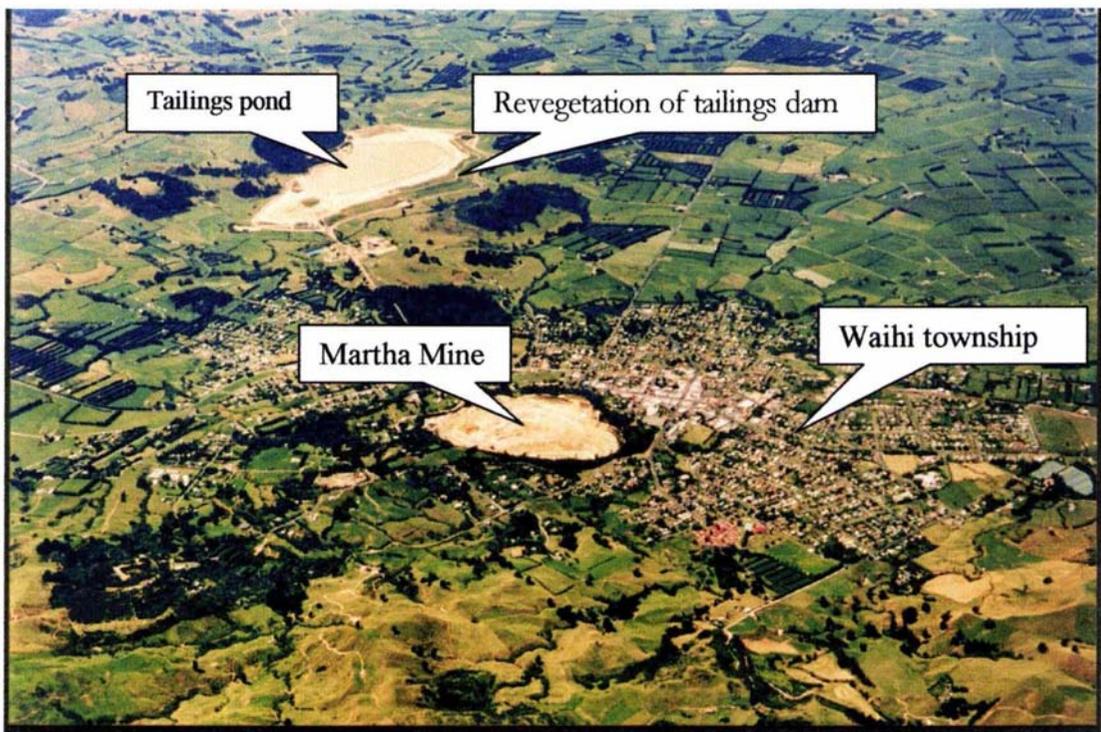


Plate 1.1 Martha Mine and tailings disposal site (1994), Waihi.

Most of the research on mine environments focuses on the development and testing of better tools for prediction and treatment of AMD problems with particular emphasis put on the generation, migration, and ultimate fate of mining-related contaminants in the environment. The development of a “safety-proof” treatment technology and remediation program however, represents the “holy grail” of much of the current research on mine waste. A “tug of war” exists between the regulators, reclamation experts, the environmentalists and mine operators. Regulators are faced with the overall problem of contamination of the environment from mining activity, mine operators envision the liability and expenditure of scarce resources, the “reclaimers” want expensive undertakings to rehabilitate the disturbed site, while the environmentalists want to close down the mine. Amidst these tensions lies the underlying fact that something must be done to reclaim the disturbed land to avoid the legacy of an abandoned mine, of which the Tui Mine at Te Aroha is a classic example (Morrell, 1997).

The process of erosion and chemical evolution that develop into AMD conditions can have serious impacts on mine development and mine site rehabilitation. Pyritic pitwalls are dynamic environments where steep slope gradients facilitate rapid weathering and erosion, resulting in continued exposure and oxidation of pyrite and migration of AMD. Many of the current reclamation and remediation techniques have been used with a varying degree of success to rehabilitate mine wastes, coal mine spoils and tailings disposal sites. There is, however, an apparent lack of attention directed towards reclamation of mine pitwalls and therefore this area warrants further research in terms of how low pH conditions are generated and the applicability of amendments for vegetative establishment.

1.2 Objectives of this Study

Past attempts to revegetate the pyritic pitwall at Martha mine have indicated that long-term sustenance of vegetative growth is limited by the low pH conditions created by AMD. The general objective of this study was to highlight the importance of site knowledge for the reclamation of acid generating mine pitwalls with an aim to study the generation of low pH conditions limiting plant growth and to investigate the ameliorative effectiveness of some selected amendments.

The specific objectives were directed towards:

- Detailed geochemical characterisation of the pyritic pitwall rock material
- Spatial distribution of the geochemical properties on the pitwall.
- Assessment of the lime requirements to neutralise of pyritic pitwall rock.
- Kinetic evaluation of the ameliorative effectiveness of selected amendments.

1.3 Outline of this Research

This thesis comprises eight chapters. Following introduction of this study in Chapter 1, a literature review of acid generation processes and the remediation of materials resulting from weathering and oxidation of sulphides in hard rock mining activities is presented in Chapter 2. The results of the characterisation of the pitwall rock materials are presented in Chapter 3 and include mineralogical studies, geochemical analysis, static and kinetic predictive tests and spatial distribution of the geochemical properties limiting revegetation on the pitwall. An incubation study to evaluate the liming requirements of the pitwall rock material and effectiveness of selected neutralising materials to ameliorate low pH is presented in Chapter 4. This is followed by kinetic evaluation of the comparative effects of these neutralising materials on leachate and subsurface chemistry of the pitwall rock under broadcasted and incorporated methods of amendments, in Chapters 5 and 6. An investigation of the effects of topsoil as cover material and application of a commercial bactericide to reduce acid generation are presented in Chapter 7. A general summary and implications of this research are presented in Chapter 8.

Chapter 2

Literature Review: Mined Land Reclamation

2.1 introduction

This chapter outlines an overview of the problems associated with reclamation of sulphidic mine waste materials applicable to pitwall revegetation. The significance of the processes leading to acid mine drainage (AMD) and its impact on the substrate environment is highlighted. The critical role of predictive techniques in optimising the prevention, control and treatment of AMD is examined. Established, innovative and pre-commercial amendment methods are reviewed with particular reference to alkaline materials used in AMD mitigation and their effective performance. Reclamation practices pertinent to revegetation of pitwall are reviewed and conclusions are drawn with implications for the direction of this research.

2.2 Acid Mine Drainage (AMD)

Acid mine drainage (AMD¹) from both active and abandoned mine sites is a major environmental issue for the mining industry in environmentally concerned regions of the world (Caruccio, 1975; Ritcey, 1989; Gray and Sullivan, 1995; Taylor, 1997). The term AMD is used to describe any seepage, leachate or drainage affected by the oxidation products of sulphide minerals when exposed to air and water. Both chemical reactions and biological activities are recognised as responsible for generating AMD (Kleinmann and Crerar, 1979; Nordstrom, 1982). The AMD is typically characterised by low pH and high levels of dissolved metal salts, as well as high concentrations of acidity, sulphate, iron and other metals (Caruccio, 1975). Once the AMD process begins it is difficult to control, often accelerates and is likely to persist for decades or centuries. In the absence of neutralising materials (carbonate minerals such as calcite or dolomite), the AMD may contain toxic levels of metals such as Fe, Al, Mn, Cu, Pb, Zn, Cd etc. which can cause serious environmental problems in soil and water systems (Sengupta, 1994)

¹ In Australia and Pacific regions AMD is the standard term used to refer to problems associated with the development of acidic drainage at sulphide-rich rock surfaces exposed by mining and other industrial activities and involves a complex combination of chemical and biological reactions. The same phenomenon is described as acid rock drainage (ARD) in North America (Murray et al., 1995).

Regulations in many countries have developed ways to address the issue of AMD at the permitting stage rather than as an afterthought. There are signs that some operators, working in partnership with regulatory authorities and other stakeholders, are developing proactive methodologies based in part upon improvements in predictive techniques (Taylor et al., 1997). Many of the currently practised preventive measures, however, still require extensive field validation before they can be prescribed as standard techniques in the environmental management of AMD. Since it is now a recognised fact that AMD generation is a site-specific phenomenon, effective control and treatment measures have been directed towards fulfilling the problem on site rather than to providing universal solutions.

2.3 Sources of AMD

There are five major sources of AMD, namely drainage from underground workings; run-off and discharges from open pits; waste rock dumps; tailings and ore stockpiles. The sources may be locally significant, for example spent heap-leach piles, stockpiles of segregated sulphides and natural seeps and springs in areas of sulphidic mineralisation. In general terms, potential sources of AMD in mining activities are well understood and widely documented (Bloomfield, 1972; Dent, 1986; Doyle, 1990; Brodie et al., 1991; Broughton and Robertson, 1992; Bhole, 1994; Durkin and Herrmann, 1996; Robertson, 1996).

Abandoned underground workings can result in the release of high concentrations of metal salts into the aqueous environment as the water table rebounds and the workings flood. These metal salts accumulate when the mine is pumped "dry" and in-place sulphides are exposed to oxygen and moisture. AMD generation may continue even after flooding if there is a persistent source of dissolved oxygen.

Open pit mining can expose very large areas of sulphide-bearing rock to air and water. Failure to control water flow into open pit slopes can result in large volumes of AMD. As oxidation of the sulphides proceeds, fresh sulphides may be exposed by spalling of the rock face, resulting in the constant renewal of the AMD source (Kuyucak et al., 1991; Morin and Hutt, 1995).

Waste rock has become a more significant threat as open pit mining has replaced underground mining, particularly in developed countries, and the volumes produced have increased (Morin, 1990). The highly permeable coarse nature of the waste rock facilitates rapid oxidation of sulphides after disposal. During extended dry periods, dumps may build-up "stored" acid products and salts through evaporation and supersaturation processes which are then released in the form of highly contaminated AMD during the next significant precipitation event (USEPA, 1994).

Tailings often have a high sulphide content (mainly in the form of rejected pyrite, marcasite and pyrrhotite) and are much finer than waste rock. Although tailings have a much higher specific surface area than waste rock, the uniform and fine particle size leads to a much lower permeability than that seen in waste rock piles. Therefore, the increased surface area available for oxidation and leaching reactions is balanced by reduced contact with oxygen due to saturation by a relatively static water body. Consequently, tailings often generate AMD more slowly than coarser, but more permeable, waste rock (Filipek et al, 1996).

2.4 Biochemical Aspects of AMD Formation

Numerous workers have studied the reaction kinetics of pyrite oxidation (Singer and Stumm, 1970; Walsh and Mitchell, 1972; Kleinmann and Crerar 1979; Nordstrom, 1982; Williams et al., 1982; Dent, 1986; Caruccio et al., 1988; Ritcey, 1989; Evangelou and Zhang, 1995). In simplicity, acid generation involves a complex combination of organic and inorganic processes and reactions. This happens when reactive sulphide rock (eg. pyrite) is initially exposed to air and water. The extent and duration of acid generation depend on the intrinsic geochemical characteristics of the sulphidic rocks.

The generation of acid in the oxidation of pyrite is considered to involve abiotic and biotic processes under aerobic environments. The former is catalysed by ferric iron (Fe^{3+}) while the latter is catalysed by acidophilic bacteria, chiefly *Thiobacillus ferrooxidans*. The role of bacteria in AMD generation from oxidation of pyrite has been recognised and studied by many workers (Kleinmann and Crerar, 1979; Williams et al., 1982; Bruynesteyn & Hackl, 1984). Both abiotic and biotic processes are considered pH and temperature dependent. The net generation of acidity in any sulphidic substrate will

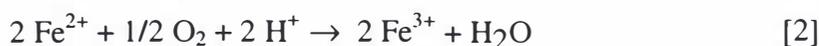
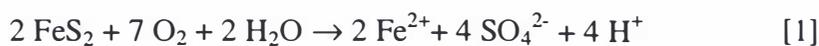
ultimately depend on the host rock mineralogy, bio-geochemical and environmental factors. The pyrite crystal morphology and degree of liberation of grains are important factors affecting oxidation rates (Mills, 1996).

Generation and migration of AMD are complex subjects and intimately linked with the nature of the ore body, host rock mineralogy and local and regional hydrology and hydrogeology. The occurrence of AMD does not necessarily lead to its migration as there are a number of chemical processes that prevent the movement of AMD away from its source (Doyle, 1990; Sengupta, 1994; Gray and Sullivan, 1995; Sherlock et al., 1995; Howell et al., 1996). The main points of AMD forming processes are summarised briefly below.

2.4.1 The chemistry of acid generation from pyrite oxidation

The dominant sulphide mineral involved in the development of AMD in sulphidic mine waste rocks are commonly pyrite (FeS_2), marcasite (FeS_2) and pyrrhotite (FeS). Other sulphide minerals such as chalcopyrite (CuFeS_2), Chalcocite (Cu_2S), covellite (CuS), pentlandite [$(\text{Fe},\text{Ni})_8\text{S}_9$], arsenopyrite (FeAsS), stibnite (Sb_2S_3), molybdenite (MoS_2), sphalerite (ZnS) and galena (PbS) are also likely to make a secondary contribution to sulphide oxidation and contribute towards acid generation (Jambor and Blowes, 1994; MVTI, 1994; Mills, 1997), although PbS , ZnS and bornite (Cu_5FeS_4) are considered non-acid generating (Bruynesteyn and Hackl, 1984; Kwong, 1995). These non-pyritic sulphide minerals are however, likely to be subjected to direct chemical attack by Fe^{3+} generated from oxidation of associated pyrite minerals or indirect oxidation by thiobacilli resulting in the generation of significant amount of acid (MVTI, 1994; Kwong, 1995).

The biochemistry of pyrite oxidation and its products have been studied in detail and described by many workers (Harnsen, 1954; Le Roux et al., 1974; Nordstrom, 1982; Backes et al., 1986; Chander and Briceno, 1988; Caruccio et al., 1990; Arora et al., 1992; Evangelou and Zhang, 1995; Ciminelli and Osseoasare, 1995; Taylor and Thornber, 1995; Bronswijk and Groenenberg, 1996). The basic chemistry of AMD generation from oxidation of pyrite is summarised in the following equations.



Ferrous iron (Fe^{2+}) is initially released by the oxidation of FeS_2 (Eqn.1). After the sequence has been initiated, a cycle is established in which Fe^{2+} is oxidised by oxygen to Fe^{3+} (Eqn.2). FeS_2 is subsequently oxidised by Fe^{3+} , generating additional Fe^{2+} and acid (Eqn.3). Certain conditions can cause rapid oxidation and hydrolysis of Fe^{3+} , resulting in generation of further acidity (Eqn.4). The forward reaction in Eqn.4 depends on the rate of production of Fe^{3+} in Eqn. 2 and the reaction in Eqn. 2 is therefore the rate limiting step in the generation of acid in sulphidic ores (Nordstrom, 1982). The principal products of the overall pyrite oxidation are therefore, ferric oxyhydroxide and sulphuric acid (Eqn.5). The rate controlling factor in pyrite oxidation is thus the availability of Fe^{3+} ion or the products of its hydrolysis and secondary reactions, $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{SO}_4)_3$. The hydrolysis of the soluble hydrous metal sulphates formed during the oxidation reactions and formation of ferric oxyhydroxides will result in the net production of acidity (Backes et al., 1986; Caruccio et al., 1988).

Pyrite oxidation in the absence of Fe^{3+} is relatively slow (Eqn.1). The rate of abiotic oxidation of Fe^{2+} to Fe^{3+} (Eqn.2) is also slow in acidic environments. However, the presence of certain catalysing bacteria (eg: *Thiobacillus ferrooxidans*) can increase the rate of Fe^{2+} oxidation by as much as a factor of 10^6 (Singer and Stumm, 1970; Kleinmann and Crerar, 1979; Evangelou and Zhang, 1995), pushing Eqn. 2 to the right. The bacteria *Thiobacillus ferrooxidans* is considered to be the most important organism involved in the biochemical oxidation of sulphide minerals (LeRoux et al., 1974; Williams et al., 1982; Bruynesteyn and Hackl, 1984). Biologically catalysed oxidation of pyrite leads to the production of ferrous iron, sulphate and hydrogen ions.

Most of the H^+ generated from the oxidation of pyrite is spent on the subsequent oxidation of Fe^{2+} to Fe^{3+} . Catalytic oxidation of pyrite predominantly occurs at $\text{pH} < 4$ because Fe^{3+} is only soluble and *Thiobacillus ferrooxidans* activity is optimum under

these acidic conditions (Dent, 1986). Both pH and temperature control the biological oxidation rate: the optimum pH range being 1.5-3.5 and temperature range of 30-35°C (Roman and Benner, 1973; Caruccio et al., 1988; Ritcey, 1989). The pH also has a significant effect on the oxidation rate of ferrous ion. For example, Hutchison and Ellison (1989) indicate that at pH 7, the oxidation of Fe^{2+} to Fe^{3+} happens within minutes while it takes about 300 days at pH 4.5 and about 1000 days at pH 3.5 (Roman and Benner, 1973).

Acid formation occurs due to hydrolysis of ferric sulphate (Nordstrom, 1982). Ferric ions produced by the oxidation of pyrite usually either precipitate as ferric oxyhydroxides if the pH is sufficiently high, or serve to oxidise other metal ions and become reduced again to supply additional substrate for microbial growth. The rate of pyrite oxidation by bacteria depends on the amount and form of pyrite, pyrite activity, O_2 and CO_2 availability, pH, temperature and presence of inhibiting compounds (Le Roux et al., 1974; Nordstrom, 1982; Ritcey, 1989).

The Fe^{3+} generated is a very strong oxidant, and will readily attack pyrite (generating acidity and Fe^{2+}) and oxidise other metal sulphides (releasing the metals into the acid aqueous phase) while itself being regenerated by biotic and abiotic reactions. The dissolution of non-pyritic minerals can be accelerated by galvanic interactions causing preferential dissolution in acid solutions (Doyle, 1990; Kwong, 1995), possibly enhanced by the presence of certain bacteria which continuously oxidise the layer of elemental sulphur formed on the pyrite surface that would otherwise prevent galvanic action (Gray and Sullivan, 1995). Sulphate concentrations can often also rise to high levels. Because of these reinforcing "feedback" loops, AMD generation is considered autocatalytic. Once the process has started, it can be very difficult to halt (Doyle, 1990) indicating the importance of taking preventative measures. An overall generalised acid production cycle for pyritic mine waste is shown in Figure 2.1.

AMD generation depends primarily on the abundance or ratio of acid producing sulphide minerals to acid neutralising alkaline minerals. The presence or absence of alkaline material is generally regarded as the most critical element in determining AMD characteristics (Caruccio et al., 1988). The degree of acidity and concentration and

speciation of dissolved contaminants varies according to a number of site-specific factors, but typical contaminants include Fe, Mn, Al, Cu, Pb, Zn, Cd, As, SO_4^{2-} and Cl (Herr et al., 1996). Less common dissolved components may also be present, depending on localised and regional mineralogy. Dissolved concentrations can range from below the limits of detection up to thousands or tens-of-thousands of milligrams per litre while pH can vary from near neutrality down to one and below.

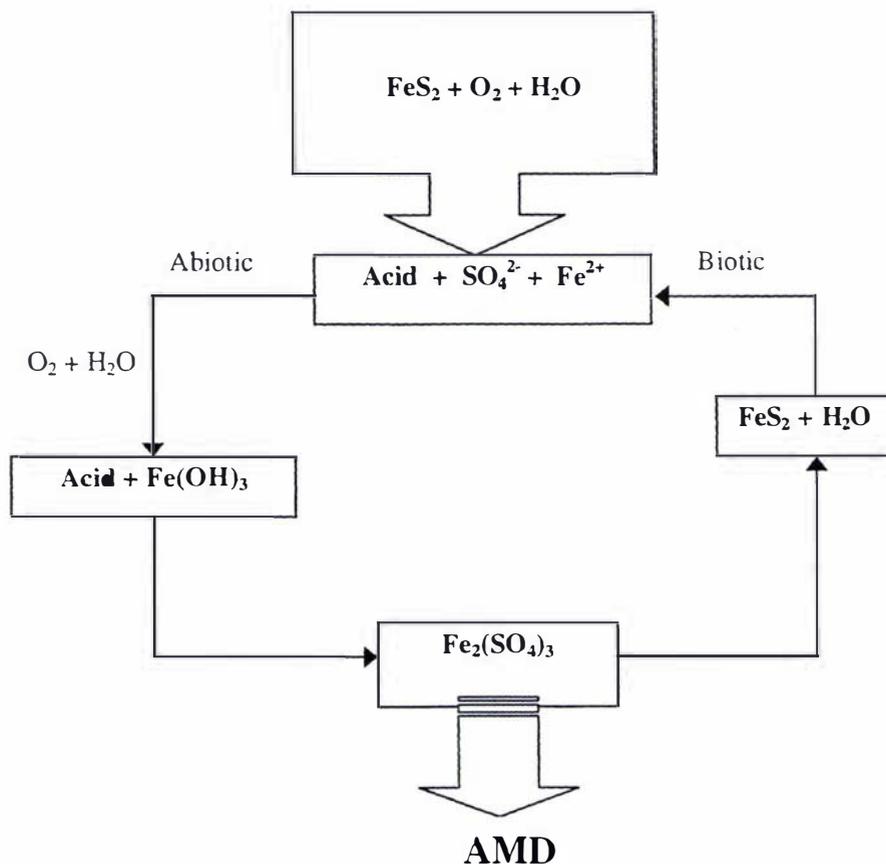


Figure 2.1 A simplified cycle in the generation of AMD

2.4.2 Accretion and migration of AMD

The processes that occur in the accretion and migration of AMD are controlled by both physical and chemical factors. Local environmental conditions no doubt play an important role in the accretion and migration of AMD. The degree of liberation of pyrite grains, the amount of rainfall infiltration, sulphide rock permeability, availability of pore water pressure and migration mechanism of AMD (surface flow, capillary flow, discrete seepage) are important physical characteristics.

The migration and fate of many of the dissolved metals and metalloids present in AMD is significantly affected by adsorption by, or co-precipitation with, the various iron compounds that may form under favourable conditions. In general, the iron species that precipitates is determined by the iron concentration, redox potential, pH, concentration of complexing anions such as carbonate, sulphate and sulphide and partial pressure of CO_2 and O_2 (Schwertmann and Taylor, 1989). For example, Fe^{3+} is rapidly hydrolysed, even at relatively low pH, to form iron oxyhydroxides (ochre). These ochres can contain significant concentrations of metals through co-precipitation and adsorption (Bloomfield, 1972; Howell et al, 1996;). Similarly, aluminium hydroxide can play an important role in the adsorption and precipitation of other metals. In relatively dry environments, various iron sulphates may crystallise; if Fe^{2+} is oxidised to Fe^{3+} , basic sulphates and oxyhydroxides may form. In low pH, high sulphate environments, jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) may form while at higher pH and lower sulphate concentrations, iron oxide species such as goethite and hydroxides may precipitate (Herbert, 1995). These minerals have a large capacity to adsorb non-ferrous metals and metalloids, and will also remove metals from solution by co-precipitation processes. Such reactions are considered capable of preventing the dispersion of dissolved contaminants (Sullivan and Yelton, 1988).

The other main chemical control on AMD accretion is the neutralising effect of minerals such as carbonates and silicates. However, even if the host rock contains significant quantities of acid-neutralising minerals, the rate of acid generation may exceed that of neutralisation, leading to AMD accretion. The rate of neutralisation is influenced by pH, the partial pressure of CO_2 , temperature, mineral composition and structure, redox conditions and the presence of impurity ions in the neutralising mineral's lattice (Sherlock et al, 1995). The most important factor in determining the extent of AMD is not the pH, but the total acidity (Erickson and Hedin, 1988). Total acidity is a measure of the excess amount of H^+ over other ions present in the solution. This takes into account the neutralisation of the acid by other materials present. Usually, however, a high acidity is accompanied by a low pH in the AMD. Consequently, a low pH has detrimental effects on the bicarbonate buffering system.

The concentrations and mobility of metal ions in AMD are important aspects in the assessment of the environmental impact of mining base metal sulphide deposits. Metal

concentrations mobilised in soil and water exert a strong influence on vegetation since plant uptake of heavy metals is considered a function of element speciation (Dunn, 1989). The distinction between “total” metal and “available metal is critical to the understanding of potential contamination/pollution problems. Although total metal concentrations in various forms can have little impact on the environment, bioavailability of dissolved metals in phytotoxic levels can be a limiting factor to plant growth (Lindsay and Norvell, 1978; Luo and Rimmer, 1995).

A clear understanding of the accretion of AMD, its migration and metal loading can be a powerful tool in planning preventative or control measures. Natural processes such as attenuation and neutralisation by alkaline minerals present can go some way toward mitigating the impacts of AMD. Long-term preventative measures and effective treatment prescriptions adapted to site-specific criteria accordingly may be viable options for mitigating low pH environment created by AMD.

2.4.3 By-products associated with AMD

Pyrite oxidation and its oxidation by-products are as much environmental problems as AMD itself. Sulphide oxidation and migration of its by-products have been studied mainly on coal overburden using complex geochemical and numerical models (Vanberk and Wisotzky, 1995; Wunderly, et al., 1996). However, the overall products of pyrite oxidation would be similar for hard rock mine waste materials as well. The primary reaction products resulting from biochemical oxidation of pyrite are H^+ , Fe^{2+} , Fe^{3+} , SO_4^{2-} and $Fe(OH)_3$. The $Fe(OH)_3$ remains in solution as long as the pH of the AMD is <4 . At this pH, most of the metals ions (Fe, Mn, Al, Cu, Zn, Pb, As etc.) remain mobilised in AMD (Nordstrom, 1982; Wunderly et al., 1996). If the pH of the AMD is increased by contact with carbonate minerals (if present) or entry into water system of higher pH, a number of secondary products (metal hydroxides and sulphate salts) can form under surficial conditions resulting in considerable build up of reserve acidity (Wunderly et al., 1995).

2.4.3.1 Metal hydroxides

When the pH AMD increases to >4 , metallic ions such as Fe^{3+} , Al^{3+} , Cu^{2+} , Zn^{2+} , Pb^{2+} and As^{3+} will react with hydroxyl ions to eventually form hydroxides as precipitates by the general reaction:- $M^{n+} + nOH^- \leftrightarrow M(OH)_n$ where M = metal ion, OH^- = hydroxyl

ion and $M(OH)_n$ = metal hydroxides, n = oxidation state. Fe-oxyhydroxides [(FeO.OH) and $Fe(OH)_3$] precipitate directly by oxidation of dissolved Fe^{2+} (Backes et al., 1986; Dent, 1986). These highly insoluble amorphous Fe-oxyhydroxide gels often precipitate as rusty-brown or yellowish surface expression in areas of intense sulphide mineral oxidation or as “ochre” in pore fillings (Tucker et al., 1987; Taylor and Thornber, 1995). The formation of ironstone (ferricrete) from cementing of unconsolidated surficial material by oxyhydroxides in fracture zones and slope surfaces of weathering iron sulphides is generally indicative of natural AMD (Taylor and Thornber, 1995).

2.4.3.2 Sulphate salts

Associated with the acid environment are elevated levels of soluble salts which solubilise during wet periods and severely affect plant growth on the reclaimed mine waste. In the presence of carbonate minerals such as calcite ($CaCO_3$) and dolomite ($CaMgCO_3$), the sulphate salt most commonly formed is gypsum ($CaSO_4 \cdot 2H_2O$), which may precipitate copiously on surface during dry periods. Unlike iron, which remains immobilised in the waste rock substrate, most of the soluble sulphate salt is leached with the AMD and only a fraction of sulphate may be retained as gypsum, jarosite [$(KFe_3(SO_4)_2(OH)_6$], alunite [$(KAl_3(SO_4)_2(OH)_6$] and mallardite ($MnSO_4 \cdot 7H_2O$) (Kerth and Wiggering, 1990; Herbert, 1995; Wiggering, 1977).

Under very low pH ($pH < 3.7$) and strongly oxidising environments ($Eh > 400$ mV), characteristic pale yellow deposits of minerals in the iron and aluminium jarosite-natrojarosite range [$(K,Na)(Fe,Al)_3(SO_4)_2(OH)_6$] commonly precipitate as pore fillings and coatings on exposed surfaces (Kwong and Huang, 1979; Dent, 1986). Jarosite is unstable at higher pH where it is hydrolysed to iron oxide (goethite), releasing further acidity (Bloomfield, 1972). Thus neutralisation with alkaline amendments is likely to effect dissolution of jarosite and formation of Fe-hydroxide. Since the precipitation of iron hydroxide leads to formation of free acidity, jarosite acts as a storage sink for the acidity formed by pyrite oxidation and weathering (van Breeman, 1973; Kerth and Wiggering, 1990). The formation of efflorescence minerals such as jarosite ($KFe(SO_4)_2 \cdot 2Fe(OH)_3$) and melanterite ($FeSO_4 \cdot 7H_2O$), which usually occur as surface encrustation during dry periods, will through hydrolysis result in the release of acidity to the ambient AMD (Eqns. 6 and 7). This is considered to be the reason why in the

presence of jarosite, mine waste dumps remain acidic long after the cessation of pyrite oxidation (Dent, 1986; Kwong and Ferguson, 1997).



Accumulation of acid in pyritic waste materials also facilitates rapid chemical degradation, leading to progressive decomposition of clay minerals and extreme acidification of the spoil can have a detrimental impact on the wider environment through salinisation and contamination of ground waters.

2.4.3.3 Acidity

Acidity is the base-neutralising capacity of the solution, which results from H^+ , Al^{3+} , Fe^{3+} , Fe^{2+} , Mn^{2+} , and other hydrolyzable cations in a sample (Hedin et al., 1994; Cravotta, 1995; Hedin and Erickson, 1998). In polymetallic base metal deposits, Cu^{2+} , Zn^{2+} and Pb^{2+} can also contribute significantly to total acidity of the material (Skousen, 1995). Acidity data is therefore useful in defining AMD, which commonly contains substantial quantities of Fe^{2+} , Mn^{2+} and Al^{3+} (and other hydrolyzable cations), the oxidation and hydrolysis of which can have significant affect on pH of the mine drainage. Oxidation and hydrolysis of Mn^{2+} is known to occur at circumneutral pH 6-7 and therefore can contribute significant acidity even in AMD with neutral pH (Hem, 1963). In fact, $\text{Fe}(\text{OH})_3$ can be directly involved in the heterogeneous adsorption and oxidation of Mn^{2+} to MnO_2 . Hedin et al.(1994) have indicated that in the absence of acid neutralising materials, a theoretical total acidity of the mine drainage containing significant amount of Fe^{2+} , Mn^{2+} and Al^{3+} can be calculated from the equation:

$$\text{Acidity (mg CaCO}_3 \text{ L}^{-1}) = [50 * (2 * \text{Fe}/56) + (2 * \text{Mn}/55) + (3 * \text{Al}/27) + 10^3 * (10^{\text{exp-pH}})]$$

(Metal concentrations are in mg L⁻¹, converted to cmol_c kg⁻¹)

Thus, the emerging AMD containing abundant Fe^{2+} and Mn^{2+} can have pH ~6, but it may also have significant acidity. Alternatively, if the AMD contains low concentrations of dissolved metals (hence low acidity), a very low pH does not necessarily mean high acidity. In other words, just knowing the pH of the AMD does not really tell you much about the inherent acidity of the solution. This has important

implications for treatment and amendment of low pH conditions in oxidising pyritic materials. For example, a material with a pH of 2, but very low metal concentrations may be neutralised more readily than a material with a pH of 5 and high metal concentrations. Acidity determination is, therefore, very important for assessing the buffering capacity of the material.

2.4.3.4 Aluminium

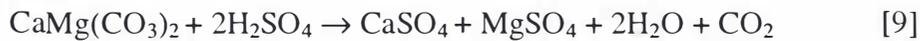
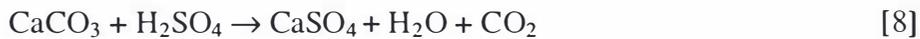
Dissolution of aluminium (Al) in acid soils is one of the most pronounced soil chemical effects of AMD. Because of its toxicity to plants, the chemical behaviour of Al has been a major research topic for decades of agronomic and environmental studies (Mulder et al., 1989). Low pH conditions promote solubility of Al and result in the concentration of phytotoxic levels of Al in the soil solution (Conyers, 1990; Aitkin, 1992; Helyar et al., 1993). The distribution of aluminium in acid soil materials is dependent on the forms of inorganic and organic anionic ligands present and the relative competition between Al and other cations for ligands. There is increasing evidence that the phytotoxicity of aluminium is reduced in the presence of inorganic and organic complexing anions (Bloom and McBride, 1979; Kwong and Huang, 1979; Young and Bache, 1985; Hue et al., 1986; Gurung et al., 1996). Possible inorganic ligands with tendencies to form polymeric complexes with solution Al are OH, SO₄, F, Si(OH)₄ and H₂PO₄ (Ritchie, 1989) and these ligands have been found to detoxify Al (Helyar, 1978; Blamey et al., 1983, Alva et al., 1986, Cameron et al., 1986). Soluble Al-hydroxy phosphate polymers were found at a pH region of 4.1-4.8 and at P concentrations <25 μM (Blamey et al., 1983). At pH values <5.5, silicate ions are found to form stable complexes with Al-hydroxy polymers (Luciuk and Huang, 1974). The Al-hydroxy silicates are considered a major cause of the Al and pH buffering in acid soils (Bloom and McBride, 1979). The effect of Al adsorption on pH depends on the type of clay mineral present and the OH:Al ratio in the solution. Thus removal of hydrolysed Al species from solution would induce further hydrolysis of Al and therefore a lowering of pH is expected (Bache, 1974).

Manganese (Mn) in soil is considered to behave similarly to Al in that it may be adsorbed onto the surface of hydrous oxides, clay particles and organic matter, or exist as discrete Mn compounds. However, it differs from Al because it exists in more than one oxidation state under conditions naturally found in soils. In very acid soils,

however, Mn^{2+} may be the dominant species and competes with other cations for exchange sites (Walker and Barber, 1960; Salcedo et al., 1979).

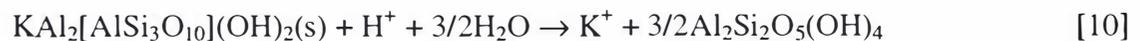
2.4.4 *In-situ* neutralisation of acidity

In sulphidic deposits, acid generating minerals such as pyrite often occur in close association with acid neutralising minerals such as calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] that normally occur as late stage mineralisation. The acid produced from pyrite oxidation is neutralised, in-situ, by dissolution of these basic minerals if in contact with the migrating AMD, resulting in precipitation of sulphate salts (Eqns. 8 & 9). These chemical reactions must also be examined to fully understand the processes occurring and to be able to predict the chemistry of solutions resulting from the combination of oxidation and neutralisation processes (Blowes et al., 1994; Morin et al., 1995)

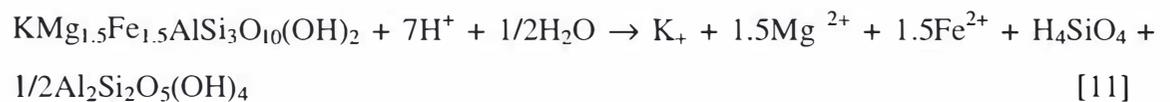


Silicate minerals such as plagioclase feldspars also have the potential to neutralise acid under specific pH conditions (Ritchie, 1994; Mills, 1997), by the dissolution reactions listed below (Eqns.10-14). In acidic conditions, the silicate minerals rapidly decompose clay products as well as releasing significant amount of Al^{3+} and K^+ in the soil solution. The dissolution of $Fe(OH)_3$ is also considered acid consuming reaction (Eqn.15).

Muscovite dissolution



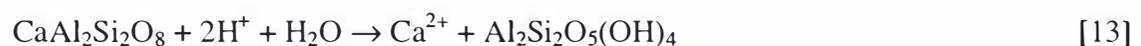
Biotite dissolution



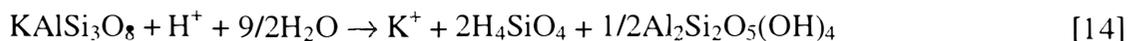
Albite dissolution



Anorthite dissolution



K-feldspar dissolution



Iron oxyhydroxide dissolution



The *in-situ* neutralisation processes described above highlights the fact that mineralogy of the pyritic rocks is a key factor in defining the composition of the AMD and emphasises the importance of mineralogical characterisation. The amelioration of AMD in pyritic materials is primarily based on the neutralisation of the acid as it occurs naturally *in-situ* conditions.

2.5 Predictive Techniques for AMD

The ability to predict acid generation from mine waste materials is an important step in the process of preventing AMD. This allows the appropriate control measures to be taken to prevent/mitigate the formation of AMD. Predictive tests specifically designed for coal mine waste have been used for decades and significant advances in predictive techniques applied to hard rock metal mine waste have been made in the last 5 to 10 years (Sobek et al., 1987; Skousen et al., 1990; Miller et al, 1994). The prediction of acid producing potential (APP) of materials begins with an understanding of the geology and geochemical properties of the rock type encountered during the mining process (Miller and Murray, 1988). Several laboratory and field test procedures to assess or predict the generations of AMD are in use or have been proposed. These include: geochemical static tests, geochemical kinetic tests, mineralogical and petrologic studies (Jambor and Blowes, 1994; Kwong and Ferguson, 1997), mathematical and geochemical modelling (Ritcey, 1989; Sengupta, 1994; White et al., 1994) and remote sensing (Paterson and Stanton-Gray, 1995).

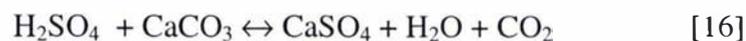
Geochemical static and kinetic tests form the most commonly used techniques currently used for prediction of acid generation from mine waste rock materials. To be useful, the techniques must firstly predict whether a particular mine waste will generate acid at some time and, if so, the rate at which it will occur and secondly, it should predict the characteristics of the drainage leaving the mine waste, from both controlled and

uncontrolled sites. The current static and kinetic testing procedures used are described below (sections 2.5.1 & 2.5.2 respectively) and their merits evaluated in section 2.5.3.

2.5.1 Static tests

The static test is generally the first step in the analysis of acid generation potential. It is based on an acid-base accounting (ABA) procedure whereby the acid neutralising capacity (ANC) and acid producing potential (APP) of the samples are determined, and the difference, net acid producing potential (NAPP) is calculated. It serves as a screening process to categorise materials into potentially acid generating, potentially non-acid generating and uncertain groups. There are several different static test procedures, all serving the basic requirements of ABA (Table 2.1)

ABA remains the most widely used screening test procedure for AMD prediction. It is based on the total sulphide S content and acid neutralising capacity (ANC) of a sample. The APP of the material is estimated stoichiometrically by assuming ideal oxidation of pyrite (Eqn.5) and the equivalent CaCO_3 required to neutralise the potential acidity produced from the oxidation of 1 mole of pyrite (Eqn.16).



According to the equation 5, one mole of pyrite contains 64 g of pyritic S which will theoretically produce 4 moles of acidity (H^+), equivalent to 2 moles of CaCO_3 or 200 g CaCO_3 equivalent acidity i.e. 1 g S will potentially produce acidity equivalent to 3.125 g CaCO_3 . A sample containing 1 % pyritic S (sulphide-S), therefore, will have an APP of 31.25 kg $\text{CaCO}_3 \text{ t}^{-1}$. The ABA of a sample is calculated according to the following relationship: $\text{APP (kg CaCO}_3 \text{ t}^{-1}) = \text{Total sulphide-S (\%)} \times 31.25$.

The ANC ($\text{kg CaCO}_3 \text{ t}^{-1}$) of the pyritic material is determined by chemically digesting a pulverised sample with dilute acid (HCl) and the solution back-titrated to a predetermined endpoint (pH 7 or 8.3) with a standard base (NaOH) to determine the amount of acid consumed by the material. The ANC value is subtracted from the APP to derive NAPP where: $\text{NAPP (kg CaCO}_3 \text{ t}^{-1}) = \text{APP} - \text{ANC}$. Lime requirement for sulphidic mine waste is generally based on this NAPP value.

Table 2.1 ABA procedures

PROCEDURE	Reference
Sobek Neutralisation Potential Method and Peroxide Siderite Correction for Sobek Method	<i>Sobek et al.(1978); Skousen et al. (1997).</i>
BCRI Initial Test	<i>Duncan & Bruynesteyn (1979).</i>
BCRI Confirmation Test	<i>Bruynesteyn & Hackl (1984).</i>
Coastech Research Modified Biological Oxidation Test	<i>Lawrence & Sadeghbari (1986). Lawrence et al.(1989).</i>
Lapakko Neutralisation Potential	<i>Lapakko (1994).</i>
Modified Sobek Neutralising Potential Method	<i>Coastech Research (1991); Lawrence & Wang (1997).</i>
Static Net Acid Generation (NAG)	<i>Lawrence (1990); Miller (1996); Miller et al.(1997).</i>
Paste pH	<i>Sobek et al.(1978); Price (1997).</i>

Alternatively, the NAG test procedure based on the accelerated oxidation of a sample by H_2O_2 , and measuring the resultant pH, predicts the acid generating nature of the material if the pH of the solution (NAGpH) is < 4 (Miller & Jeffrey, 1995). However, the ratio ANC:APP is now more often used to determine the potential for AMD generation, with incorporation of a factor-of-safety into the ratio to reduce risks arising from unknown parameters. For example, Placer Dome Inc. uses the following ANC:APP ratios (Table 2.2) to screen samples (Robertson and Ferguson, 1995).

Table 2.2 Screening criteria in ABA

ANC/APP	< 1	Likely to generate AMD unless sulphides are unreactive
ANC/APP	1-2	Possible AMD generation if neutralising minerals are preferentially depleted, coated or otherwise unreactive
ANC/APP	> 2	AMD generation not expected

A still higher ANC:APP ratio may be warranted to cover the situation where the dissolution rate of acid neutralising minerals is generally low compared with the rate of pyrite oxidation. If an apparently "safe" ANC:APP ratio overestimates the neutralisation

capacity or rate, then there can be severe environmental and ultimately cost implications in terms of both site operation and closure (Sherlock et al, 1995).

In the Australasia and Pacific regions, both NAPP and NAG test procedures are commonly used as initial screening and monitoring tools for predicting acid generation from mine waste. Currently both the North American and the Australian terminology and units expressing the results of ABA testing are in use. Both procedures give the desired end results, as compared in Table 2.3 below (Murray et al., 1995).

Table 2.3 Comparisons of ABA procedures

Australia	North America
Acid Producing Potential (APP)	Acid Potential (AP)
Acid Neutralising Capacity (ANC)	Neutralisation Potential (NP)
Net Acid Producing Potential (NAPP) (NAPP = APP - ANC)	Net Neutralisation Potential (NNP) (NNP = NP - AP)
Result Interpretation:	
Potential AMD, NAPP = positive (+ve)	Potential ARD, NNP = negative (-ve)
Standard units kg H ₂ SO ₄ t ⁻¹	Standard units, kg (t) CaCO ₃ t ⁻¹

Note: 1 kg H₂SO₄ t⁻¹ = 0.98 kg CaCO₃ t⁻¹

2.5.2 Kinetic tests

For materials where the potential for acid generation is uncertain, kinetic test work is performed to attempt to define acid generation characteristics. In kinetic test procedures, the acid generation (and metal mobilisation and transport) characteristics of a sample are measured with respect to time. Kinetic test procedures include humidity cells (Sobek et al, 1978; Sullivan and Sobek, 1982; ASTM, 1996; Price, 1997; Soregaroli and Lawrenc, 1997), column tests (Sturey et al., 1982; Price, 1997), soxhlet reactors (Sullivan and Sobek, 1982), Shake Flasks (Bruyensteyn and Hackl, 1984), field lysimeters and test plots (Eger and Lapakko, 1981) and barrel tests (Kalin et al. 1995). Miller and Jeffrey (1995) suggested that the static net acid generation test (NAG) procedure could also be considered as a kinetic test as the data generated provide information on the kinetics of the reaction from the short-term simulation of the weathering process. A development stage procedure, "Minewall" is also being tested for

determining the kinetic AMD characteristics of *in-situ* rock such as pitwalls and the rock surfaces of adits, stopes and other underground workings (MEND, 1995).

Currently there has been little standardisation of kinetic testwork procedures with regard to sample preparation, cell or column design and operation or data reporting. Most kinetics tests involve weathering of samples under laboratory controlled conditions to simulate time dependent chemical changes in the mine waste and determine the potential to generate net acidity, the rates of sulphide oxidation and neutralisation and the quality of the leachate/drainage. The most commonly used laboratory scale kinetics test procedures are humidity cells and columns.

Humidity cells are typically laboratory units in which samples are subjected to accelerated weathering by cyclic permeation of dry and humid air followed by flushing with water (Caruccio et al., 1990; ASTM, 1996). The test usually determines if a given sample will generate acidity but not when the material will produce acidity since the cells undergo accelerated oxidation of sulphide minerals (Price, 1997). The accelerated rate of oxidation processes will thus result in an accelerated rate of generation of oxidation products as dissolved metals and/or precipitated metal compounds. The humidity cell tests are not designed to provide leachates that are similar to the actual leachate produced in field conditions and therefore are not intended to simulate site-specific leaching conditions (ASTM, 1996; Guard, 1997). The humidity cell tests were originally developed for coal overburden in which the lag period is shorter and then run for only 10 weeks. For hard rock materials, the lag periods are longer and a 10 week period is not adequate to give accurate results (Miller and Jeffrey, 1995).

Column testwork is generally conducted to simulate the leaching effects of precipitation infiltration into, and drainage from, material exposed to the atmosphere. The aim is to monitor leachate quality with time by cyclic flushing with water to simulate seasonal variations at site. Unlike humidity cells, there is no standard testwork procedure and the operation can be highly site or material specific with regard to material particle size range, sample mass, water infiltration rate and degree of oxygenation (Sturey et al., 1982; Mills, 1995). The column is operated without aggressive flushing so that oxidation product may accumulate at particle surfaces in addition to being removed in

leachate. This behaviour parallels field conditions and, as a result, leachate analyses from column testworks are a better indicator of expected water quality than leachate analyses from humidity cells—particularly if column infiltration rate is varied to simulate site conditions (Mills, 1995; 1996).

There is no standardisation of column testwork procedures, allowing considerable flexibility, which permits column operation to be highly site or material specific with regard to material particle size range, sample mass, water infiltration rate and degree of oxygenation. Column tests also allow treatments to be tested and compared which is major advantage over humidity cells (Miller and Jeffrey, 1995). Column tests are intended to simulate natural conditions and are simple to construct, operate and monitor. Various environmental factors can be assessed, as can the influence of various control measures such as cover systems. However, the kinetics of reaction may not be distinguishable from rate limiting transport phenomena and bacterial populations may differ from those found under field conditions. Column tests, on the other hand can become water saturated and interpretations of the results become difficult (Lawrence, 1991; Miller and Jeffrey, 1995; Perkins et al., 1995).

Kinetic tests generally only attempt to predict what will happen in the early stages of acid generation processes (Miller and Murray, 1988; Sherlock et al, 1995) and the data interpretation and modelling is complex irrespective of the nature of the tests carried out. Irrespective of the different types of kinetic tests, the overall objective of the tests is to provide data on the rate of acid generation and acid neutralisation under laboratory controlled conditions. In most kinetic tests water is commonly added to a sample, the mixture is allowed to incubate for a certain period to allow acid-base reactions, and samples of leachate or extracts are collected and analysed. The tests are required to run for a long time to generate overall acid generation information. The major parameters measured in kinetic tests are trends in pH, sulphate, acidity or alkalinity and metals. The pH identifies the stage of the acid generating process, sulphate production relates to rates of sulphide oxidation, acidity/alkalinity give an indication of the rate of acid generation/neutralisation and metal levels evaluate metal solubility and leaching behaviour.

2.5.3 Evaluation of the predictive techniques

Although data generated from predictive techniques give a base for planning preventive, corrective and remedial measures, so far they have been found to have restricted application as universal predictive tool. Sherlock et al (1995) considered that predictive techniques must be applied on a site-specific basis and take into account the mineralogy of the waste material. For example, minerals present, percent sulphides and their distribution within the rock mass and along joints and other discontinuities and the likely durability of the waste rock are likely to effect the predictive test results (MEND, 1991; Orava and Swider, 1996). Moreover, predictive techniques alone do not account for the build-up of metal salts that may occur after disposal but prior to final reclamation. The tests also fail to incorporate an assessment of the coating of sulphide phases with unreactive coatings that may occur naturally (Pratt et al, 1996).

Most of these tests also force oxidation or neutralisation reactions that may never occur in the real situation. Acid generation (and neutralisation) are time dependent phenomenon, and until someone develops a test that takes into account time dependency, there will never be an "exact" predictor. For example a test that indicates the presence of neutralisers, inherent or added does not mean that the net result will be no acid. That depends on the reactivity and kinetics. If the acid is generated faster than it can be neutralised, the net result will be an acid effluent regardless of how much neutraliser is available.

Short-term static tests, which are conducted to determine the acid generating or acid consuming potential, will usually provide only an indirect assessment of the net acid generating potential. A longer-term kinetic test, which allows reactions to occur, will provide a more comprehensive assessment. However, even a kinetic test may not predict the net acid generating potential accurately because the ongoing sulphide oxidation will continue to produce acid and acid consumption by the alkalinity present in the system may be dominant only in the beginning. Conversely, the alkalinity in the system could overcome and exhaust the supply of sulphide bearing rock present. It is therefore clear that both the static and kinetic tests must be designed to suit the mineralogy of the waste rock being tested. Both acid generating and acid consuming reaction rates in the

oxidation of pyrite and reactions with carbonate and silicate minerals must be considered for predictive acid generation tests.

The issue of appropriate NP/AP ratios is a key area of debate among the regulatory agencies and the mining industry. To date there is no comprehensive compilation of case histories of mine sites with significant ABA data, NP/AP ratios and AMD problems. The NP/AP ratio is the most significant of the variables which regulatory agencies are attempting to use as a prescriptive measure. Ferguson and Morin (1991) and Cravotta et al. (1990) suggested that NP/AP criterion separating potentially acid generating and non-acid generating samples could be about 2:1. However, in the data base presented by them, no sample with NP/AP >1 produced acidic leachate in 166 laboratory leaching tests. There is also no field evidence of NP/AP>1 producing AMD. The NP/AP ratio may be considered as a safety factor with a higher safety factor probably required for mines in wet climates where carbonate minerals may be preferentially leached from the mine waste relative to the oxidation of the contained sulphide minerals.

The first interpretative use published for ABA was an estimate of $\text{NNP} > 5 \text{ kg CaCO}_3 \text{ t}^{-1}$ producing alkaline conditions (Sobek et al., 1978). This screening criteria was selected based on soil quality and plant growth media considerations, not mine drainage prediction. ABA later began to be applied to coal mine drainage prediction, beginning in the late 1970's. At this time it became apparent that ABA interpretation depended on whether the end use was mine drainage prediction or mine spoil/growth media suitability. ABA is still used for both purposes today and two sets of interpretative frameworks have developed.

Several researchers have suggested that the standard ABA procedures may in fact substantially underestimate the neutralising material requirement of the potentially acid generating materials (Cravotta et al., 1990; Brady and Cravotta, 1992; Brady et al., 1994). It has been suggested that the currently used value of 3.125 g CaCO_3 equivalent to neutralise acidity from oxidation of 1 g S should in fact be 6.25 g CaCO_3 to assure a neutral AMD (Cravotta et al., 1990; Brady et al., 1994). Field studies conducted by Brady et al. (1994) found that the alkaline material requirement calculated from ABA

analysis using sulphide-S to CaCO_3 ratio of 3.125 was inadequate for controlling AMD. Only when the ratio was doubled to 6.25, was there an overall net alkalinity of water at 11 of 12 coal mine sites studied. Perry and Brady (1995) showed that material with an $\text{NP} > 21$ generally produced alkaline drainage whereas $\text{NP} < 10$ produced acidic drainage. The APP on the other hand, is considered adequate in predicting AMD only in materials that contained insignificant amount of carbonates ($< 1\% \text{CaCO}_3$), in which case a relationship between total sulphide-S and acidity could be defined (Perry and Brady, 1995). Other studies have shown that factors other than mine waste characteristics may be involved in the generation of AMD (DiPretoro and Rauch, 1988; Erikson and Hedin, 1988). They found that there was poor correlation among APP, NP and NNP from ABA and net alkalinity from drainage water. O'Hagan and Caruccio (1986) found that addition of CaCO_3 at 5% by weight to a coal refuse containing 1% S produced alkaline drainage whereas Lapakko (1988) indicated that $\text{CaCO}_3 > 3\%$ was needed to neutralise an overburden material with 1.17% S.

The discussions above indicate that there are still discrepancies in the use of ABA as screening tool in predicting AMD. It is also evident from their results that lime requirement assessed from ABA analysis did not always produce neutral drainage from waste rock dumpsites. There was a need for further studies on the rate, application and placement of alkaline materials in mine waste and mine sites with potential to generate AMD. There appears to be no universal set of threshold numbers for defining cut-offs on ABA. Instead, the data tend to group themselves in ranges (Brady et al., 1990; Cravotta et al., 1990; DiPretoro and Rauch, 1988). However, ABA testing procedures are firmly entrenched in the mining industry and it is likely to stay in use because it is familiar to industry, consultants and regulators, and it is low cost and has rapid turnaround time.

As with the static tests, kinetic tests are also subject to queries about their accuracy in predicting real situation AMD conditions. Kinetic tests (humidity cells, columns and soxhlets) not only produce a unique leachate but also modify the sample and a significant variation in the accuracy of the results was observed (Bradham and Caruccio, 1990). No data is yet available from weathering tests which were run long enough to see the sulphate generation rate begin to taper off. Most weathering test

results are assessed as "acid or not acid" producing. In other words, there is not anything particularly kinetic about the data analysis. While static and kinetic tests and the associated models are far from perfect in their capacity to predict the generation or migration of AMD, they do allow for a more systematic approach to understanding the potential problems.

2.6 Prevention and Control of AMD

Various physical, chemical and biological control measures have been used to prevent, minimise and treat AMD. Basically there are two types of prevention and control, the first relates to the generation of AMD, while the second relates to its *in-situ* mobilisation and subsequent migration. Both are inter-related in as much as certain approaches to preventing and controlling generation can reduce migration and *vice versa* (Mills, 1996).

Methods proposed for the prevention and control of AMD generation include treatment of sulphide surfaces via the formation of inert surface "coatings", the use of bactericides, the segregation of the principal AMD generating waste fraction and control of oxygen and/or water infiltration of the sulphide-bearing material. Currently, waste segregation and prevention or control of water/oxygen infiltration dominate, with the other methods having only limited application at full-scale. Certain approaches such as inert surface coatings are considered unproven at present but worthy of further research. In addition to the use of engineered covers, the most common approaches to preventing or controlling the migration of AMD are the re-routing of water away from the source or the use of sub-surface seals and barriers to impede the movement of contaminated groundwater (Filipek et al, 1996). The greater the control achieved, the smaller the volume of AMD that is likely to require treatment. Just as waste minimisation is typically more cost-effective than waste management, prevention or minimisation of AMD is generally considered a cheaper option than long-term treatment (Filipek et al, 1996). The principle involved in the prevention and control of AMD from mining activities has been centred on removal and abatement of one or more of the essential components in the acid generation process. These components are the sulphide mineral, bacteria, air and water. The prevention and control procedures currently practised to abate acid generation are described in the following sections.

2.6.1 Preventive coatings

Several techniques have been experimented within recent years, which inhibit pyrite and pyrrhotite oxidation using inert coatings. Most of the studies centre around coating of isolated sulphide mineral grains with coating agents such as iron phosphate (Evangelou and Huang, 1992, Fytas et al. 1994, Evangelou, 1994, Georgopolou et al. 1995), acetyl acetone, humic acid, oxalic acid, sodium silicate and lignin (Maki et al. 1995; Mitchell and Atkinson, 1995). Cathodic protection of the weathering sulphide ore body has also been attempted (Shelp et al., 1995). Preventive coating experiments have been done mainly on separated grains of pyrite crystals and their use in the field is impractical, because of different forms and types of pyrite present in the waste rock. Attempts were also made by Ahmed (1994) to form pyrrhotite hard pans on tailings surfaces to prevent atmospheric oxidation of pyrrhotite. The method involved electrochemical treatment of FeS rich tailings with ferrous solution to form an oxyhydrate (goethite) matrix.

A recent advance has seen research on the use of fatty acid amines, which suppress bacterial activity and chemical oxidation through a process of hydrophobic coatings (Nyavor et al., 1996). Treatment with the amine makes the pyrite highly hydrophobic and the pyrite surface consequently repels oxidising ions (i.e.: Fe^{3+}). It is, however, unclear whether the effect of the hydrophobicity prevents the bacteria from contacting the pyrite surface.

While some of these techniques have prevented further oxidation of pyrite minerals, their applicability to the field situation is not proven as yet. Further research is necessary to detail the economic costs and technical constraints of larger-scale applications, but this approach does look promising, possibly as a means of treating segregated high-sulphide wastes prior to disposal.

2.6.2 Selective handling

Partitioning of wastes into sulphide-rich and sulphide-depleted fractions offers the chance to expand waste management options in the control and prevention of AMD. In theory, the low-volume, sulphide-rich fraction can be disposed of at a highly engineered disposal site or at least isolated as buried "cells" within the bulk waste while the high volume sulphide-depleted fraction can be disposed of as an inert waste. Blending of

acid-generating and non-acid generating wastes can also be used to prevent or control AMD. However, as the latter waste is often exempt from permitting due to its inert nature, blending can sometimes result in the permitting of a much larger volume. This approach may, therefore, be environmentally attractive, but constrained by operator's reticence to extend or further complicate the permitting process.

Several mineral processing techniques are available for separating acid-generating sulphides. Methods include gravity separation (e.g. centrifugal concentrator, shaking table, spiral concentrator), flotation, magnetic separation and cyclone classification. The segregated pyrite can be substituted for elemental sulphur in the production of sulphuric acid. Research also shows that pyrite may have some use in the removal of dissolved arsenic species by adsorption (Humber, 1995).

2.6.3 Bactericides

Bactericides normally contain anionic surfactants that destroy the greasy outer cell membrane coating of the bacteria *Thiobacillus ferrooxidans*. The greasy film coating normally protects the bacteria from the surrounding acid environment and once it is destroyed, the bacteria can not survive in the acid conditions (MVTI, 1994; Sanda, 1989). ProMac System, comprising commercial short-term and long-term slow release bactericides have been widely used in the treatment of AMD (Rastogi et al., 1986; MVTI, 1994; Sengupta, 1994). Alternative bactericides such as sodium dodecylbenzene sulfonate (SDS), sodium laurel sulfate (SLS) and thiol-blocking agents have also been suggested for the inhibition of *Thiobacillus* bacteria (Sengupta, 1994; Stichbury et al, 1995).

2.6.4 Oxidant infiltration barriers

Seals, grouting, cover layers, interception trenches and sub-surface barriers have been used to prevent infiltration of oxidants (air and water) to control AMD generation (Nicholson et al., 1989; Schueck et al., 1994; Tremblay, 1994; Stogran and Wiseman, 1995; Scheetz et al., 1995; Foote, 1996; McCloskey, 1996; Mueller et al., 1996). Sealing mine openings, tunnels and adits can prevent the infiltration of water into, and the migration of AMD out of underground workings. Preventing the movement of water through such workings can minimise sulphide oxidation even if the workings are flooded, as static water will quickly become anoxic as oxygen is consumed by chemical

and biological reactions. Cementitious grouts can also be applied to mine adit and pitwalls to prevent the infiltration of oxygenated water (Scheetz et al, 1995). Interception trenches for directing AMD to passive treatment systems have also been successfully used to prevent the migration of AMD (Mueller et al, 1996).

Although waste rock dump and pitwall geometry can be important in defining surface area exposure and air infiltration rates (USEPA, 1994; Rastogi et al, 1995), engineered covers are effective at controlling oxygen and water infiltration and can be classified as oxygen barriers, oxygen consumers or reaction inhibitors (MEND, 1994a). Pitwalls generally have steep gradients and therefore placement of amendments becomes impractical. Often heavy engineering of the acid generating pitwall area is required to implement stabilised placement of suitable cover system (Watson, 1995). Engineered cover systems often include layers that promote lateral rather than vertical movement of water, as well as providing a substrate for vegetation and protective layers between the geofabric and the waste to reduce the risk of physical damage to plant root systems.

Synthetic geofabrics such as polyvinyl chloride (PVC) and high density polyethylene (HDPE), have been used to prevent and control water and oxygen infiltration into AMD generating wastes (Nicholson et al., 1989; Ritcey, 1989; Sengupta, 1994; Jones and Wong, 1994). Geofabrics are expensive but if applied properly (i.e. to avoid punctures and rips) they are likely to have useful working lives in excess of 100 years (Filipek et al, 1996). **Clays** and clay mixtures such as kaolin amorphous derivatives (KAD) and sand-bentonite mixture have often been used as oxidant infiltration barriers because of their minimal permeability when compacted and relatively low cost (Yanful and Shikatani, 1995; Mackinnon et al., 1997). However, there is a danger that if the clay cover dries, deep cracks can occur, allowing the rapid ingress of water and oxygen. Moreover, compacted clays provide poor growing media for plants.

Organic covers consisting of sewage sludge, papermill sludge, topsoil and wood bark have also been found to be effective in reducing oxygen infiltration in sulphidic mine wastes and tailings ponds (Pierce et al., 1994; Tremblay, 1994; Stogran and Wiseman, 1995). Surface application of organic materials not only provides a physical barrier to oxygen and moisture but also provides leachate rich in soluble organic compounds that

encourage the activity of sulphate reducing bacteria (Pierce et al., 1994). The placement of a biologically active organic layer on top of tailings has been suggested as a means of reducing oxygen diffusion and to confine metal contaminants (Ritchie, 1997). Oxygen infiltration into the tailings is controlled by its consumption in the organic layer (e.g. via conversion to carbon dioxide and water), while metal diffusion into the water can be further controlled by inoculation of the organic layer with sulphate-reducing bacteria capable of precipitating the metals as sulphides (Nicholson et al., 1989).

Organic ligands leached from decomposing organic matter are found to be effective in reducing phytotoxic levels of Al by readily complexing with the exchangeable Al (Hargrove and Thomas, 1981; Young and Bache, 1985; Hue et al., 1986; Hern et al., 1988; Shuk-Ching and McColl, 1990; Gurung et al., 1996). One potential drawback to this approach has been highlighted by recent research which has shown that ferric oxyhydroxides present in weathered tailings dissolve when in contact with organic acids originating from carbon-rich oxygen consuming covers (Ribet et al., 1995). The dissolution of the oxyhydroxide phase can result in the release of adsorbed or co-precipitated non-ferrous metals into the aqueous phase.

Although reclamation of mine waste materials by municipal sludge application has been shown to be beneficial to plant growth by providing a growth medium and nutrient reserves (Dinauer et al., 1977; Gemmell, 1981; Sopper, 1992), there are serious environmental problems associated with such organic-based amendments (Sopper, 1992; LRNL, 1993). Composted organic sludge materials commonly contain high concentrations of heavy metals such as Cd, Cu, Mo, Mn, Pb and Zn (Forstner, 1991) which can be hazardous contaminants in soils, water and plants. Surface applications of sludge materials can mobilise heavy metals through reductive dissolution as well as mobilising nitrate into the ground water system (Voos and Sabey, 1987; Sopper, 1992; Ribet et al., 1995). Field and laboratory studies have shown that surface applied sewage sludge to promote revegetation at reclaimed mines resulted in increased down gradient concentrations of sulphate and acidity, indicating that superficially applied sludge was not an effective barrier to O₂ entering into underlying zones (Cravotta, 1997). Laboratory leaching tests also indicated that sewage sludge additions produced significant increases

in microbial pyrite oxidation and that only when CaCO_3 was added was there a reduction in bacterial oxidation of pyrite (Cravotta and Trahan, 1996; Cravotta, 1997).

Composite cover system consisting of layers of non-acid generating geologic materials has been developed with an aim to establish vegetation as well as isolating sulphidic waste materials (Harris and Richie, 1988; Aachib et al., 1994; Bell et al., 1995). Composite soil covers are often up to 1 m thick and they can be applied only on low gradient rehabilitation sites. Such a cover system has been used in the rehabilitation of Rum Jungle mine site in Australia (Ryan, 1987; Harries and Richie, 1988; Bennett et al., 1989; Sengupta, 1994). On-going monitoring of the effectiveness of the composite cover system at Rum Jungle has shown significant reduction in metal loading in the AMD from the rehabilitated dump sites (Bennett et al., 1987; Sengupta., 1994).

Relevant research and modelling work has been published on soil covers which limit oxygen influx to tailings and their subsequent effect on oxidation of pyrite/ pyrrhotite. For example, Nicholson et al. (1989) demonstrated that, in addition to a fine particle size of the cover material, maintenance of high moisture content is essential to minimise diffusion of oxygen. Furthermore, although erosion and stability are important considerations with respect to slope, one must also consider that the slopes are influx zones for oxygenated air entering the pitwall (Murray, 1997). Buoyant air, heated by pyrite oxidation tends to rise, drawing fresh air into the slopes. Accordingly, convective airflow may develop within the sloughed pitwall rock, maintaining oxidation despite burial of the acid-forming material. In order to inhibit continued oxidation, the slopes need low-permeability or oxygen-consumptive covers (Guo and Cravotta, 1996).

Sub-aqueous disposal of reactive waste rocks by flooding of open pits or dumping into natural lakes or impoundments has been practised by many mining operations, although such practices require a thorough understanding of local and regional hydrology and hydrogeology (Fraser and Robertson, 1994; Dave and Vivyyurka, 1994; St-Arnaud, 1994; Filipek et al, 1996). In Canada, the recommended method of preventing AMD is to dispose of sulphide waste rocks and tailings deposits sub-aqueously (MEND, 1991; Pederson et al., 1994). While this is feasible in areas of high precipitation, low temperature and abundance of lakes, it cannot be considered in areas of low

precipitation and lack of fresh water lakes. Disposal of sulphidic waste into sea water has also been practice by mining operators in Norway (Sengupta, 1994) and in Papua New Guinea, river disposal of tailings has been practised for some time at the Pogera Gold and Ok Tedi copper mines (Harries, 1997).

Sub-aqueous disposal controls acid generation from sulphidic wastes by limiting the diffusion rate of oxygen through the water cover (Filipek et al., 1996). However, research over a three-year period at the Noranda Technology Centre has shown that although water covers can reduce the rate of acid generation by 99.7% (Payant et al, 1995), the concentration of metals in the surface water can still exceed regulatory limits (Aubé et al, 1995). The efficacy of subaqueous disposal and the environmental impact on the aquatic life are yet to be fully assessed.

Other barrier methods such as deliberate construction of *hardpan* (using electrochemical methods), which consist of a cementitious iron oxyhydrate matrix, may also help control infiltration by water and thus reduce or prevent the generation of AMD (Ahmed, 1995).

2.7 Treatment of AMD

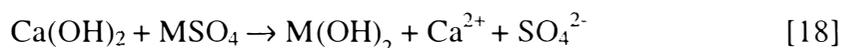
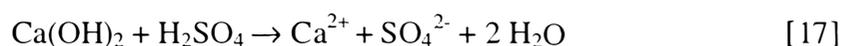
There are number of overlapping approaches to the treatment of AMD, which are nominally categorised here as active, passive and active-passive hybrid systems. In the recent past, research into the use of ion exchange resins and natural and synthetic zeolites to treat AMD have also shown promising results (Zamzow et al., 1989; Schultze et al., 1994; Mondale et al., 1995; Riveros, 1995). The most common methods employed in the treatment of AMD are through chemical and biological processes. The chemical treatment processes include complexation, oxidation and reduction principles (Cohen, 1996). Although all of these methods show promising inhibitive properties in chemical sense, they are not all found to be practical under field conditions.

2.7.1 Active treatment systems

Active treatment systems basically involve neutralisation of AMD with lime and precipitation of metals as hydroxides. There are numerous studies carried out on the variations of this technique but the ultimate process involves the addition of base to neutralise acid (Bell et al. 1982; Skousen et al., 1990; Boling and Kobylinski, 1992;

Bhole, 1994; Kuyucak et al., 1995; Murdock et al., 1995; Taylor et al., 1997). Liming materials commonly used in neutralisation techniques are hydrated lime [$\text{Ca}(\text{OH})_2$], sodium bicarbonate (NaHCO_3) and sodium hydroxide (NaOH) (Bell et al., 1982; Skousen et al., 1990). Agricultural limestone and phosphate rocks have also been used to treat AMD (Hill and Willmouth, 1970; Renton et al., 1988; Hart et al., 1990; Spotts and Dollhopf, 1990; Fyson et al., 1994; Kalin et al., 1997).

In conventional lime treatment, there are five basic steps following collection of the AMD:- (i) equalisation to minimise variations in water quality; (ii) aeration to oxidise Fe^{2+} to the less soluble Fe^{3+} , (iii) neutralisation to increase pH to precipitate metals as hydroxides, (iv) sedimentation to separate water and solids and (v) sludge disposal (Bell et al., 1982; Bhole, 1994; Murdock et al., 1995; Taylor et al., 1997). Lime is normally introduced into the system as a 5-20% (by weight) water-based slurry, although it is sometimes applied as a dry powder when the water volume to be treated is low. The principal reactions are summarised in Equations 17 to 19 where M represents dissolved metals (Fe, Zn, Cu, Zn, Mn, Al etc.). Detailed analysis of the reactions between lime and acidic metal contaminated AMD is explained in Marchant (1987).



Major drawbacks of the lime treatment system are the large volume of potentially toxic sludge produced (which must be physically removed) and a relatively high pH required to remove metals such as Mn. Some metal hydroxides such as $\text{Fe}(\text{OH})_3$ $\text{Al}(\text{OH})_3$ may re-dissolve in the highly alkaline solutions required to complete metal precipitation, necessitating a multi-stage treatment to reduce all metals to acceptable concentrations. Sludges derived from the liming of AMD are chemically unstable and will partially redissolve if exposed to a sufficiently acidic environment (Kuyucak et al, 1995; Murdock et al., 1995).

To address some of these drawbacks, a number of refinements to standard liming treatments have been developed in recent years. Two such examples include the High

Density Sludge (HDS) process and the patented Noranda Technology Centre (NTC) process which are being applied increasingly within the mining industry. The HDS process produces a more compact and higher density sludge (Murdock et al, 1995) and is carried out in aerated reactors. Part of the settled sludge is recycled to the beginning of the process, where it is mixed with the lime slurry. The NTC process uses pH controlled reactors in which sludge density and settling rates are improved relative to the HDS process (Kuyucak, 1995; Kuyucak et al, 1995).

However, the benefit of such lime treatment is a proven technology with well documented and understood mechanisms of metal removal and acid neutralisation. Despite the commercial availability of processes such as HDS and NTC, increasingly stringent legislation is likely to drive mine operators to look beyond the use of lime to avoid incurring growing disposal costs, and to avoid the possibility of future liability and litigation. One alternative to which serious consideration has been given is the use of passive treatment systems.

2.7.2 Passive treatment systems

Passive treatment systems encompass a number of discrete neutralisation processes and they are described by numerous researchers (Faulkner and Skousen, 1984; Holm and Elmore, 1986; Howard et al., 1989; Kleinmann and Hedin, 1993; Hedin et al., 1994; Gusek and Wildeman, 1995; Cambridge, 1995; Cohen, 1996; Gazea et al., 1996; Robbins et al., 1996). These include anoxic ponds (AP), limestone ponds (LSP), anoxic limestone drains (ALD), alkalinity producing system (APS), Reverse alkalinity producing system (RAPS), open limestone channels (OLC), aerobic and anaerobic wetlands (Faulkner and Skousen, 1984). Porous reactive alkaline walls have also been proposed as a means of treating sub-surface AMD *in-situ* (Blowes et al, 1995; Waybrant et al, 1995). This approach has only been attempted on a limited scale, although the preliminary results appear promising in terms of both economic and technical performance (Blowes et al, 1995). Passive treatment systems have demonstrated substantial mitigation in AMD quality in some cases, while in other situations, less dramatic results has been obtained (Brodie and Hedin, 1994; Falkner and Skousen, 1996; Skousen, 1995). High concentration of Fe and Al in the AMD often precipitate as hydroxide when in contact with the alkaline treatment systems, causing an "armouring

effect" on the limestone, thereby reducing the generation of further alkalinity and impeding flow through the drain (Filipek et al, 1996; Robbins et al., 1996).

The use of sulphate-reducing bacteria in open pits or underground workings has been suggested as a means of treating AMD *in-situ* (Kuyucak and St.-Germain, 1994). This approach might be suitable for low load scenarios, where a suitable organic substrate for bacterial growth is locally and cheaply available. However, efficiency might be compromised by a single addition if the substrate is so deep that mass-transfer is detrimentally affected. The operational temperature at depth is also an issue as this will influence bacterial activity.

Constructed or engineered aerobic and anaerobic wetlands are passive treatment systems which attempt to duplicate natural systems and use chemical and biological processes to reduce dissolved metal concentrations and neutralise acidity (Holm and Elmore, 1986). Compared with conventional active chemical treatment by liming, passive methods generally require more land area, but use cheaper materials to support the chemical and biological processes, and require less operational attention and maintenance (Cambridge, 1995). However, wetlands are not "walk-away" solutions but, rather, low maintenance, low energy systems designed to treat effluent AMD and are not suitable treatment options for *in-situ* neutralisation of AMD.

2.8 Mined Land Reclamation Methods

Reclamation and revegetation of sulphidic mine waste rock materials have become a challenging practical problem for the mining industry worldwide. The acid produced in the mine waste substrate solubilises toxic quantities of heavy metals and reaches elevated levels of salinity, making reclamation difficult, if not impossible, without physiochemical modification of the material. Amendment of the sulphidic waste with alkaline materials have been commonly practised to ameliorate acidic conditions for establishment of vegetation (Pulford, 1991; Dollhopf, 1992). Alkaline addition to acid producing sites during surface mining and reclamation has shown variable success in ameliorating low pH conditions (Brady et al., 1990; Ziemkiewicz and Skousen, 1995). Several studies have been conducted on the efficacy of alkaline amendments to ameliorate acidity problems in reclaimed coal mine sites (Costigan et al., 1984;

Bhumbla et al., 1990; Brady et al., 1990; Cravotta et al., 1990; Evans and Rose, 1995). The type of alkaline materials and the method of applications have been important factors both in terms of economy and effectiveness.

2.8.1 Lime requirement of sulphidic mine wastes

For many years lime requirement determinations of acid agricultural soils have been made by quick-test buffer methods involving buffer mixtures (Shoemaker et al., 1961; McLean et al., 1966; McLean, 1982). Recently, methods have been developed which predict lime requirements from measurements of soil pH, organic matter, extractable Al and clay content of the soil (Oates and Kamprath, 1983; Bailey et al., 1989; Aitkin, 1992). While these methods appear to accommodate acid agricultural soils, they have been found to be inappropriate for mine wastes that generate continuous acidity from pyrite oxidation.

In the mining industry, lime requirements for acidic overburden and mine waste dumps are commonly determined from standard ABA procedures (Sobek et al., 1978). The liming rate assessed from ABA analysis, however, is found to vary considerably and does not always bring the expected results in long-term neutralisation of acidity and prevention of mobilisation of heavy metals (Costigan et al., 1982; Brady et al., 1990; Cravotta et al., 1990; Skousen et al., 1997). Site specific variations in the sulphide content of the mine wastes make it difficult to specify a standard rate of lime requirement (Sorensen et al., 1980). Large amounts of liming materials are therefore, commonly required for long-term amelioration of acidic conditions in sulphidic waste rock materials. Even then, reacidification can occur when the added neutralising materials are exhausted or “armoured” by oxyhydroxides (Hill and Willmouth, 1970; Costigan et al., 1982).

2.8.2 Alkaline amendments in reclamation

Large quantities of alkaline materials such as *limestone* or lime products (CaO, Ca(OH)₂, fly ash, lime kiln dust) *dolomite* and alkaline shale are often used in mine reclamation to control acidity. There have been several studies carried out on the effectiveness of alkaline addition to sulphidic mine waste rock in ameliorating low pH conditions and creating suitable growing media for plant growth (Sorensen et al, 1980; Costigan et al., 1982; Hoving and Hood, 1984; Stiller et al., 1984; Joost et al., 1987;

Sullivan and Yelton, 1988; Brady et al., 1990; Meek, 1994; Skousen and Larew; 1994). Although alkaline materials are effective in short-term neutralisation of acid and aid in the initial establishment of plant growth, long-term sustenance of the ameliorative effectiveness has not been successful. Several factors such as local climatic conditions and site-specific nature of the waste rock can affect the dissolution of various types of alkaline materials in highly acidic materials (Sorenson et al., 1980; Costigan et al., 1981).

The effect of limestone grain size on its solubility and neutralisation of substrate acidity in acidic agricultural soils has been studied in detail (Albrecht, 1946; Meyer & Garth, 1952; Elphick, 1955; Gemmell, 1981; Costigan et al., 1984). All of these authors have shown that limestone solubility in acidic soils is affected by its effective grain size, carbonate content and the amount of dissolved metals (especially Fe and Al) in pore solutions. In highly acidic mine waste materials, the liming agents were found to react vigorously and often the rate applied was insufficient to counterbalance the acid released from oxidation of pyrite. Alternatively, the armouring effects by precipitated metal hydroxides on the coarser limestone particles rendered it ineffective in neutralising acid (Gemmell, 1981; Costigan et al., 1982, 1984).

When large quantities of limestone are applied to acidic colliery spoils, Costigan et al. (1984) have observed that coarser grained limestone reacts more slowly than fine grades although it has no significantly different effect on the plant growth compared with that of fine grade limestone. Their study also indicated that depth incorporation did not raise subsurface pH significantly from that of equal rates of surface application and that the long-term neutralisation effect was only evident from particle size < 3 mm.

Leaching experiments using lime kiln flue dust amendments on pyritic shale, have shown that it significantly reduce acidity, SO_4 , Fe, Mn, Al and Mg by up to 85% compared to a control despite still producing acidic effluent from the test cells (Evan and Rose, 1995). Their study also showed that alkaline amendments produced leachate pH that remained <3 even at the highest rate of application (171% of that required to neutralise APP of $31.25 \text{ kg CaCO}_3 \text{ t}^{-1}$ at 1% S). They found that the amount of lime needed to prevent AMD could not be predicted from the calculated rates based on ABA

analysis because of site specific nature of the sulphidic waste rock and the environmental conditions.

Agronomic effectiveness and environmental impact of fly ashes used to reclaim pyritic acid mine spoils have been investigated in the laboratory and field (Bhumbla et al., 1990; Bhumbla, 1992). Application of fly ash decreased bulk density, increased moisture retention capacity of spoils and reduced toxic levels of Fe, Mn and Al in soils by buffering soil pH at 6.5, and retarding pyrite oxidation.

Fluidised bed boiler bed ash (FBA) generated from fossil fuel-fired boilers has been much investigated for use as a liming material in acid agricultural soils because of its high alkalinity (Stenhouwer et al., 1995; Wang et al., 1994). Because FBA contains both lime and gypsum, it has been shown to ameliorate both surface and subsurface acidity (Sumner et al., 1986; Wang et al., 1994). Its use as AMD ameliorant in reclamation of coal mine spoils has been investigated by several workers (Siddle et al., 1979; Dick et al., 1994; Stehouwer et al., 1995). Similar other by-products such as fluidised bed combustion ash (FBC), fluidised bed waste (FBW) and flu gas desulphurisation sludge (FGD) have been investigated as possible ameliorants for AMD in coal mine waste (Bhumbla, 1992). Since FBA is a waste product, its use in large quantities in reclamation of coal refuse serves as a viable alternative for its disposal.

Greenhouse column leaching of pyritic mine spoil has shown that FBA applied at the rate of 30 to 60 g kg⁻¹ mine spoil, was effective in neutralising acidity, increasing leachate pH, Ca, Mg and reducing concentrations of Fe, Mn and Al (Stehouwer et al., 1995). However, their results also indicated that EC and SO₄²⁻ increased with increasing rates of FBA applications. Other workers (Balla and Edwards, 1995; Reichert and Norton, 1996) have explored the possible use of FBA to improve the physical properties of acid agricultural soils (increase water infiltration, reduce surface sealing and erosion control. A major drawback in using FBA as amendment is that it is compositionally similar to portland cement. When applied at a high rate, it can form a cementitious crust (which can impede water infiltration and plant root growth) from the reaction of CaO with aluminosilicate minerals (Korcak, 1988; Dick et al. 1994; Dawson et al, 1995; Stehouwer et al. 1995).

Several studies have been done on the use of *phosphate rock* as a potential AMD ameliorant (Stiller et al., 1986; Renton et al., 1988; Sencindiver and Bhumla, 1989; Spotts and Dollhopf, 1990; Hart and Stiller, 1991; Evangelou et al., 1992; Fyson et al., 1994; Kalin et al., 1997). Laboratory studies have shown that precipitation of iron phosphate on pyrite surfaces has an armouring effect that prevents further oxidation (Evangelou, 1994, Huang and Evangelou, 1995). Other studies have reported that pyritic waste amended with natural phosphate rock can induce significant reductions in acidity, Fe, Mn and Al (Kalin et al., 1997; Fyson et al., 1994).

Natural phosphate rocks such as North Carolina reactive phosphate rock (RPR) which contains about 11.7% free CaCO_3 and 13.1% P has been shown in the laboratory and field studies to be a potential ameliorative material in acid agricultural soils (Bolan et al. 1988; Loganathan et al., 1995). The theoretical liming value from complete dissolution of RPR is equivalent to 600 kg CaCO_3 . For every tonne of RPR dissolved, the estimated liming value is 419 kg CaCO_3 from dissolution of P plus 117 kg CaCO_3 from free CaCO_3 to give a total 536 kg CaCO_3 (Bolan, 1995).

In pyritic mine waste devoid of Ca and P, phosphate rock is considered an effective liming material in reducing substrate acidity, providing Ca and P as well as inhibiting further chemical oxidation of pyrite by coating with Fe-PO_4 compound (Pulford and Duncan, 1975; Backes et al., 1987). The PO_4^- formed from dissolution of RPR combines with Fe to form Fe-PO_4 which has been shown in laboratory studies to armour the pyrite surface from further attack by oxidising agents (Evangelou and Huang, 1992; Georgoupoulou et al., 1995). Phosphate rock not only reduces soil acidity but also reduces phytotoxic Al concentrations and leads to a significant increase in the effective cation exchange capacity of the soils (Loganathan et al., 1995).

The use of natural phosphate rock to reduce AMD from pyritic waste rock and colliery spoil has also been studied by several workers (Backes et al., 1987; Sencindiver and Bhumla, 1989; Hart et al., 1990; Hart and Stiller, 1991; Kalin et al., 1995). Laboratory experiments by Hart et al., (1990) and Hart and Stiller (1991) have shown that application of natural phosphate to acid generating coal waste was an effective

ameliorant. In a drum test trial of pyritic mine waste rock using a natural phosphate rock amendment, Kalin et al. (1995) have shown that phosphate rock applied at 115 kg t^{-1} waste rock significantly reduced cumulative acidity (74%) over 989 days of monitoring. They found that mixing phosphate rock with the waste rock was more effective in reducing acidity than placement on the surface.

A long term field experiment on the effect of alkaline amendments on mine waste rock piles has shown that over an 11 year period limestone addition had no effect on the rate of sulphate production from pyrite oxidation although leachate pH remained above neutral (Ziemkiewicz and Meek, 1994). A similar effect on sulphate generation was indicated for phosphate amended piles but there was a significant drop in leachate pH from near neutral to $\text{pH} < 4$ over an 11 year period. In both limestone and phosphate amendments, the high rates of application (2.4% limestone and 0.3% phosphate by mass) generally resulted in acidic leachate, indicating possible armouring effects on the limestone and phosphate grains from metal precipitates. In the same field experiment, they also showed that application of bactericide (sodium lauryl sulphate) had no effect on the rate of pyrite oxidation and the pH and sulphate fluxes in the leachate were similar to the lowest rates (0.5% limestone and 0.15% phosphate by mass) of alkaline addition. The concluding results from their 11 year monitoring of the leachate characteristics from alkaline and bactericide amended test piles were that pyrite oxidation was not affected by these amendments and independent of leachate pH.

This review on alkaline amendments indicates that various alkaline materials can be used to mitigate acidic conditions in sulphidic mine wastes, albeit with varying degree of success. Given favourable conditions and with appropriate rates of application, alkaline materials are an important chemical additive in modifying mine wastes to create suitable plant growth media in reclamation practices (Johnson et al., 1977). This ameliorative approach is one of the frequently used methods to establish vegetation on mine wastes.

2.8.3 Organic amendments

The potential use of organic and inorganic cover materials to inhibit the oxidation of pyrite and thereby mitigate acid mine drainage (AMD) have been investigated by

several workers (Nicholson et al., 1989; Daniel and Koerner, 1993; Guo et al., 1994; Bell et al., 1995; Stogran and Wiseman, 1995; Swanson et al., 1995; Guo and Cravotta, 1996; Miller, 1997). As most mine waste materials are devoid of organic matter, many researchers have tested several organic matter sources (chiefly municipal sludge, peat, wood-wastes, papermill sludge and topsoil materials) as amendments in land reclamation (Pulford, 1991; Gregg et al., 1998). An extensive review of the organic materials as amendments in land reclamation can be found in LRNL (1993) and comparisons of various amendments in several research papers (Haghiri and Sutton, 1982; Hoitink et al., 1982; Bennett et al., 1984;; Voos and Sabey, 1987; Pichtel et al., 1994). Organic wastes such as municipal sludge (Halderson and Zenz; 1978; Joost, et al., 1987; Sopper, 1992), organic compost (Pierce et al., 1994) and papermill sludge (Hoitink et al., 1982) are some of the waste materials commonly used in the reclamation of lands disturbed by mining.

The use of municipal sludge in reclamation and revegetation of disturbed land has been extensively investigated by the above authors, especially Halderson and Zenz (1978). The results to date are encouraging and show that stabilised municipal sludge, if applied properly according to guidelines used, can be used to revegetate mined lands in an environmentally safe manner with no major adverse effects on the vegetation, soil, or groundwater quality. Field and laboratory studies conducted by Cravotta (1997) using surface applied sewage sludge to promote revegetation at two reclaimed mines in western Pennsylvania showed that concentrations of sulphate and acidity increased down gradient and that surficially applied sludge was not an effective barrier to O₂ entering into underlying zones. Laboratory leaching tests also indicated that sewage sludge additions produced a small increase in microbial pyrite oxidation and that highest oxidation rates resulted when sewage sludge was added. The lowest oxidation rates resulted when CaCO₃ was added, indicating promotion of bacterial oxidation of sulphides under sewage treated conditions (Cravotta, 1997). Pichtel et al. (1994) indicated that sewage sludge, papermill sludge, and topsoil amendments were superior to fly ash in maintaining forage crops on pyritic mine spoils. Their conclusion was that both sewage sludge and papermill sludge amendments were equivalent to limed topsoil for successful reclamation of toxic mine spoils.

In open-cast strip mining, large volumes of topsoil are available for use in reclamation. The reclamation practice in New Zealand is to replace topsoil to at least the original depth where applicable (Gregg et al., 1998). In acidic mine waste materials with poor chemical and physical properties suitable for plant growth, use of topsoil or surrogate soil material becomes a necessity to provide an uncompacted growing medium. What depth of topsoil to use is limited by the configuration of the reclamation site, topsoil availability and the local climatic conditions. Current reclamation trial work at Martha mine site (see Plate 1, Chapter 1), has demonstrated that depth of topsoil was not a critical factor in the land being returned to pasture under Waihi's local annual average rainfall regime of 2100 mm (Gregg and Stewart, 1990).

2.8.4 Bactericides

Several studies have investigated the use of bactericides in the control of acid mine drainage and in land reclamation (Rastogi et al., 1986; Watzlaf, 1988; MVTI, 1994; Parisi et al., 1994; Splittorf and Rastogi, 1995). Bactericide agents such as sodium lauryl sulphate (SLS) have been shown to effectively kill *Thiobacillus ferrooxidans* (Kleinmann and Erickson, 1983). Field trial results after the application of 514 L ha⁻¹ of 30% SLS solution has been reported to reduce acid production by 60% to 90% over a period of 4 to 5 months (Erickson et al., 1985). Although bactericide agents such as ProMac have been used for controlling acid generation from bacterial oxidation of sulphidic mine wastes, their application in mine reclamation and revegetation have been trialled only recently (Watzlaf, 1988a; Parisi et al., 1994; MVTI, 1995). Column leaching studies on ProMac-amended mine wastes have been shown to effectively reduce acidity and sulphates in the column leachate by 85% and 73% respectively (Parisi et al., 1994). In some reclamation trials, use of ProMac-based slow-release capsules have been shown to reduce acidity and aluminium by up to 98% and 95% respectively (MVTI, 1989). However, in sulphidic materials that are partially oxidised and already colonised by *Thiobacilli*, Watzlaf (1988) indicated that bactericides might not be effective in suppressing bacterial activity.

Although bactericides can temporarily disrupt the activity of acidophilic bacteria, recolonisation of the local environment is likely once the bactericides become depleted (Filipek *et al.*, 1996). Most bactericides are surface-applied as spray or in powder form.

On steep mine pitwall slopes, the effectiveness of bactericides by such methods of application may be affected by high losses due to erosion and runoff leaching. Slow-release formulations are commercially available that reduce acid generation up to 10 years (Sanda, 1989). Ideally, this is long enough to establish stable soil and vegetative covers that prevent further acidification.

2.8.5 Reclamation by revegetation

The primary purpose of establishment of vegetation on barren mine sites has been to control against erosion from wind and water and stabilise slope surfaces as well as providing an aesthetic appearance to the site (Sengupta, 1994). A more obligatory purpose is that many countries with active mining operations have promulgated stringent, specific, and detailed rules and regulations concerning mined land reclamation. Therefore, the issue of environmentally responsible mining is not whether a mine site will be reclaimed, but rather, the manner in which reclamation is accomplished (Todd and Struhsacker, 1997). In its most basic form, mined land reclamation is a “green is good” and “grow grass” proposition.

Revegetation of metalliferous mine sites and coal spoils have had varying degrees of success mainly because the ameliorative approaches used to establish plant growth have not been perfected as yet. Several approaches to revegetation have been practised in mine sites contaminated by AMD. Most mine waste dump sites and abandoned pits have steep slopes which require heavy engineering modification prior to placement of stabilised amendments (Jeffrey et al., 1974; Johnson et al., 1977; Sencindiver and Bhumbla 1989, Sengupta, 1994; Dick et al., 1994).

Alkaline materials such as limestone, dolomite and fluidised bed boiler ash are the most commonly used amendments for pH modification to suit establishment of vegetation (Joost et al., 1987; Pulford, 1991). A variety of organic waste materials and industrial by-products have found increasing use in reclamation of mined land (Hoitink et al., 1982; Joost et al., 1987; Pulford, 1991, Sopper, 1992; LRNL, 1993; Shelp et al., 1994).

In mine waste material devoid of plant growth media, an engineered soil cover not only aids in vegetation establishment but also serves as oxidant infiltration barrier for

sulphide oxidation (Cairney, 1987; Bell et al., 1995; Swanson et al., 1995). Design and performance of soil cover in terms of thickness and stability has been site specific so far (Hoving and Hood, 1984; Barton-Bridge and Robertson, 1989). In plant growth trials conducted at Martha mine site on oxidised mine waste, Gregg et al. (1990) indicated that topsoil depth was not a critical factor in the reclamation of land being returned to pasture. While this may be true for pasture grass that requires a minimum rooting depth for propagation, establishment of higher order plant species (shrubs and native plants) may not be possible on slopes that restrict placement of amendments.

Bioengineering (synonymous with biotechnical erosion control, biostabilisation or soil-bioengineering) is an alternative approach to revegetation on steep slopes areas prone to intense erosion. Bioengineering is a method of construction using live plants alone or combined with dead or inorganic materials, to produce living functional systems to provide erosion protection for hillslopes, stream banks and lakeshores (Gray and Laiser, 1982; Franti, 1997). There are a number of bioengineering techniques available for erosion control and these include:- (i) contour wattling, (ii) brush layering, (iii) trench packing (iv) brush matting (v) prevegetated mats (vi) interplanting rip rap and (vii) staking. Often a combination of these methods are used depending upon site-specific requirements (Franti, 1997). These methods are, however, designed for plant establishment on non-sulphidic material where low pH conditions are not a limitation for plant establishment. Methods such as brush layering (construction of micro-trenches on slopes and using live branches and soil cover to create a series of reinforced benches) and prevegetated mats (live plants grown on a movable mat of organic material) may be suitable for application to pyritic pitwalls, provided AMD is controlled with suitable amendments.

2.9 Revegetative Reclamation in New Zealand

In New Zealand, the 1991 Resource management Act (RMA) imposes resource consent that require a mining company to “*promote the sustainable management of natural and physical resources, which underpins the environmental requirement to reclaim land disturbed by mining operations*” (Gregg et al., 1998). Compared to USA, UK, Canada and Australia, revegetative reclamation practices for mined land in New Zealand is only a few decades old. This is mainly due to the fact that compared to many other countries,

New Zealand has been little impacted by mining activities. Since the advent of active mining in New Zealand in the early 1850s, only < 0.02% of the country's land surface is estimated to be disturbed by some form of mining activities (Gregg et al., 1998). While there are several active and abandoned mine sites in New Zealand, lack of mine survey data make it difficult to estimate the number affected by AMD. This author believes that many coal mines in New Zealand would experience some degree of AMD from dumpsites because of the fact that coal seams often contain pyrite mineralisation. The prominent mines sites in New Zealand that are affected by AMD and need some form of remediation measures for successful reclamation are listed in Table 2.4. Reviews of land reclamation by revegetation on alluvial gold mine, aggregate mine and coal mines occur in Morrell (1997) and Gregg et al. (1998). Many mines in New Zealand are located on pasture lands, and therefore, restoration to pasture is the norm in the reclamation practices.

Table 2.4 Reclamation of AMD contaminated mine sites in New Zealand.

Mine sites	Reclamation
Martha Mine, Waihi. Open pit mining of gold-silver ore. Dominant sulphide mineral- FeS ₂ .	Oxidised waste and tailings revegetated with pasture grass. Lime, organic compost and fertilisers used as amendments (Gregg & Stewart, 1990, Gregg et al., 1995; Gregg et al., 1998; Mason et al., 1995). Pitwall hydroseeded with grass and legume mixture. Successful on areas containing weathered oxidised rock material. Plant growth failed to establish on pyritic areas of the pitwall (Mason, 1996; Gregg et al., 1998).
Golden Cross Mine, Waihi. Open pit/underground mining of gold-silver ore. Dominant sulphide- FeS ₂	Small scale revegetation with exotic grasses and native plants (Bokich, 1995)
Tui Mine, Te Aroha. Underground base-metal mining. Dominant sulphides- PbS, ZnS, CuS and FeS ₂	None. Over 20 years of abandonment, natural vegetation colonisation on the acidic tailings dam has not occurred. Glasshouse plant growth trials have indicated that the tailings material has the potential for revegetation with suitable metal tolerant plant species and lime and organic based amendments (Morrell et al., 1995).
Macraes Flat Mine, Eastern Otago. Open pit gold mining. Dominant sulphides- FeS ₂ .	Significant areas revegetated with pastoral grass. Arid conditions help minimise AMD from sulphide oxidation (Gregg, 1997).

2.10 Summary and Conclusions

Acid mine drainage from mines containing sulphidic ores and its preventive and control measures are a major environmental issue in the mining industry. The understanding of AMD, its prediction and treatment are the subject of a substantial research effort by government, the mining industry, universities and research establishments with input from the general public and environmental groups. Increasing worldwide awareness of the environmental impacts of mining activities has directed government agencies to lay down strict guidelines for reclamation and rehabilitation of mined lands. So much so that in New Zealand, in an effort to project the country as having a “clean green image”, there are even stricter Resource Management Act criteria that control the mining agencies activities.

Acid generation from pyrite oxidation is the principle cause of AMD. The understanding of the biochemistry of pyrite oxidation and the resulting by-products has lead to significant advances in AMD mitigation technology. The nature of pyrite oxidation itself is *site-specific* and dependent upon a number of factors including host rock mineralogy, weathering conditions, forms and distribution of pyrite and local climatic conditions. AMD generation depends primarily on the abundance or ratio of acid producing sulphide minerals to acid neutralising alkaline minerals. The presence or absence of acid- neutralising material is generally regarded as the most critical factor in determining the intensity and migration of AMD in the mine waste rocks.

Predictive techniques employed in the assessment of AMD do not have standardised applications as yet mainly because acid generation in mine sites is *site-specific*. Appropriate predictive testing along with waste characterisation and scientific interpretation of the data are essential if proper AMD prevention and management practices are to be developed, disseminated and sustained. Despite the uncertainties in ABA screening criteria, the ABA method of evaluating acid generating potential of sulphidic mine waste materials has become mandatory requirement of regulatory guidelines in mining industry.

Liming, organic waste application and less commonly bactericides, have so far been the common amendment materials in the vegetative reclamation of mine sites. However,

these amendments have had varying successes in alleviating low pH conditions created by AMD mainly because of difficulties in assessing the lime requirement of sulphidic waste rocks. Because acid generation from pyrite oxidation is a continual process, the ABA method of estimating the liming requirement of sulphidic waste rock has been inadequate for providing long-term pH modification suitable for sustaining plant growth.

There is an apparent lack of kinetic data on comparative effectiveness of alkaline materials (limestone, dolomite, reactive phosphate rock, fluidised bed boiler ash etc.) in *in-situ* amelioration of AMD conditions in weathered pyritic waste rock materials. The *site specific* characteristics of the AMD necessitates investigative evaluations of the ameliorating effectiveness of amendments in creating suitable plant growth media.

It is evident from this review that the major emphasis has been placed on investigations regarding mechanisms and probable technologies (e.g. phosphate coatings, cover materials, collection and treatment with lime additions and bactericides) for prevention and control of AMD primarily arising from coal refuse, mill tailings and waste rock piles. Many of the procedures and techniques discussed in the review are site specific in nature and often expensive to implement in field scale. Very little research has been undertaken to investigate the *in-situ* characterisation and mitigation of AMD conditions on active mine pitwalls like that of Martha mine at Waihi, although many of the waste rock characterisation procedures and preventive measures can equally be applied to pitwall rock materials.

Chapter 3

Characterisation of Pyritic Pitwall Rock at Martha Mine, Waihi

3.1 Introduction

Pyritic pitwall rock surfaces are significant sources of AMD and metal contaminants. The primary step in the prediction and control of AMD has been the identification of source material and characterisation of sites affected by AMD. The sites of concern have generally been the sulphidic waste rock dumps from hard rock and coal mining and the control-treatment efforts are generally centred on the resultant AMD prior to discharge into a natural drainage system. Much of the effort to mitigate AMD in the past has been directed at both management of waste rock and effluent streams but little has been directed towards mitigating AMD problems at source (mine pit). A literature review of AMD revealed that virtually no attention has been directed towards AMD generation and mitigation in open pit mines and pitwalls.

Low pH conditions resulting from oxidation of pyrite in parts of the pitwall rock exposed on the north face pitwall of Martha mine has been a major obstacle to revegetation. Amelioration of such low pH conditions for plant growth will involve combinations of control, prevention and treatment of AMD. The primary step in the mitigation of AMD effects at any mine site must, therefore, involve detailed characterisation of the mineralogical and geochemical properties of the pitwall rock, and identifying the AMD products that are likely to cause limitation to plant growth.

The objectives of this part of the study were thus to examine the site specific geochemical characteristics of part of the pyritic rock exposed on the pitwall at Martha mine and map spatial distributions of selected chemical properties. Such a characterisation is an important primary investigative step in defining the factors preventing establishment of plant growth and providing prescriptive design for control and remediation of sites affected by AMD.

3.2 Materials and Methods

3.2.1 Site selection and sample collection

The study area is located on the north face of the Martha Mine pitwall and covers a slope area of 1200 m² (Plate 3.1). This area of the pitwall contained pyritic andesite undergoing progressive weathering and a varying degree of pyrite oxidation, resulting in low pH conditions. The area had been hydroseeded with grass in an earlier unsuccessful attempt to revegetate the pitwall. Representative samples of the pitwall rock used to study the geochemical characteristics of the pitwall are described in Table 3.1. About 10 kg of each representative samples were collected from the north facing pitwall in November 1995. Duplicate samples were oven dried and ground to ≤ 2 mm and < 150 μ m fractions for chemical and elemental analysis respectively. The samples were stored in sealed containers to prevent further oxidation.

3.2.2 Grid sampling

The grid samples for spatial characterisations of weathered material were collected from the north face of the pitwall (Plate 3.1 and Figure 3.1). A 40 m x 30 m surface on the pit slope was measured and sampled at a major grid interval of 5 m. Grid sampling was also done at 2.5 m intervals along the down-slope profiles. At the time of sampling (November 1995) the cover depth of weathered materials on the study area (Figure 3.1) varied from 0 mm on hard rock surfaces to 600 mm in post-blast cavities and in colluvial materials deposited along the bottom of the pitwall. The pitwall surface had a closely spaced, parallel rill erosion pattern from surface runoff and patches of reddish-brown coatings of Fe-hydroxides (Plate 3.2). Pit slope angle was 43⁰ with a total slope length of 30 m.

Where possible core samples at each grid site were taken down to the depth of the hard rock surface. About two kilogram samples (47 samples) were collected from each of the grid points. Sampling locations and the grid plan is shown in Figure 3.1. The samples were air-dried and ground to ≤ 2 mm and ≤ 150 μ m fractions for chemical and total elemental analysis respectively.

3.2.3 Spatial data analysis

Spatial distribution maps of the selected chemical properties of the pitwall rock within a 40 m x 30 slope area were obtained by the geostatistical method of kriging. Kriging is a geostatistical interpolation technique based on the theory of rationalised variables with a

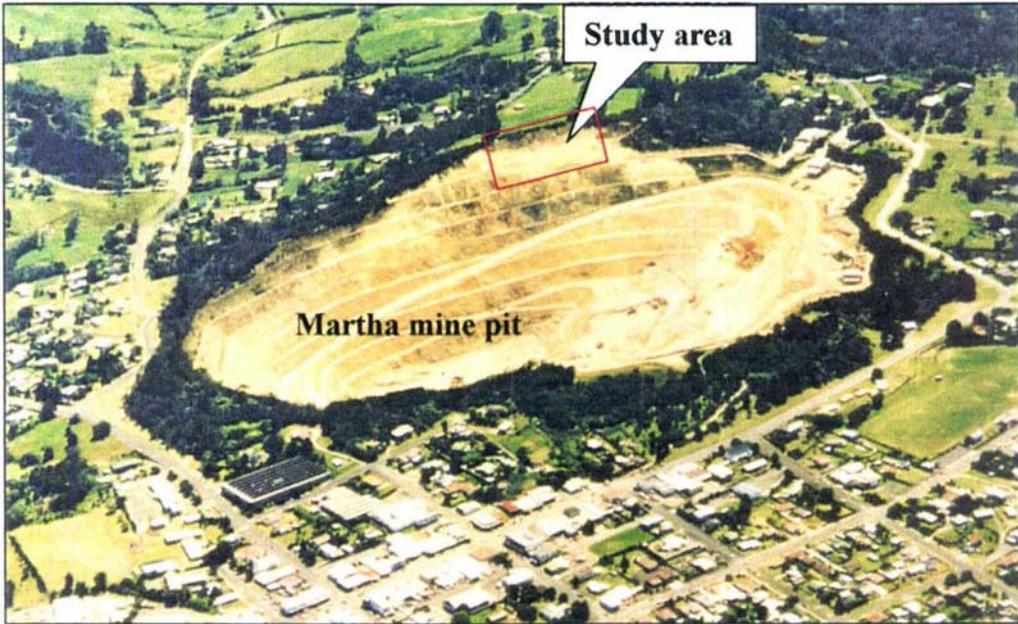


Plate 3.1 Martha mine showing the study area on exposed north face pitwall (1994).

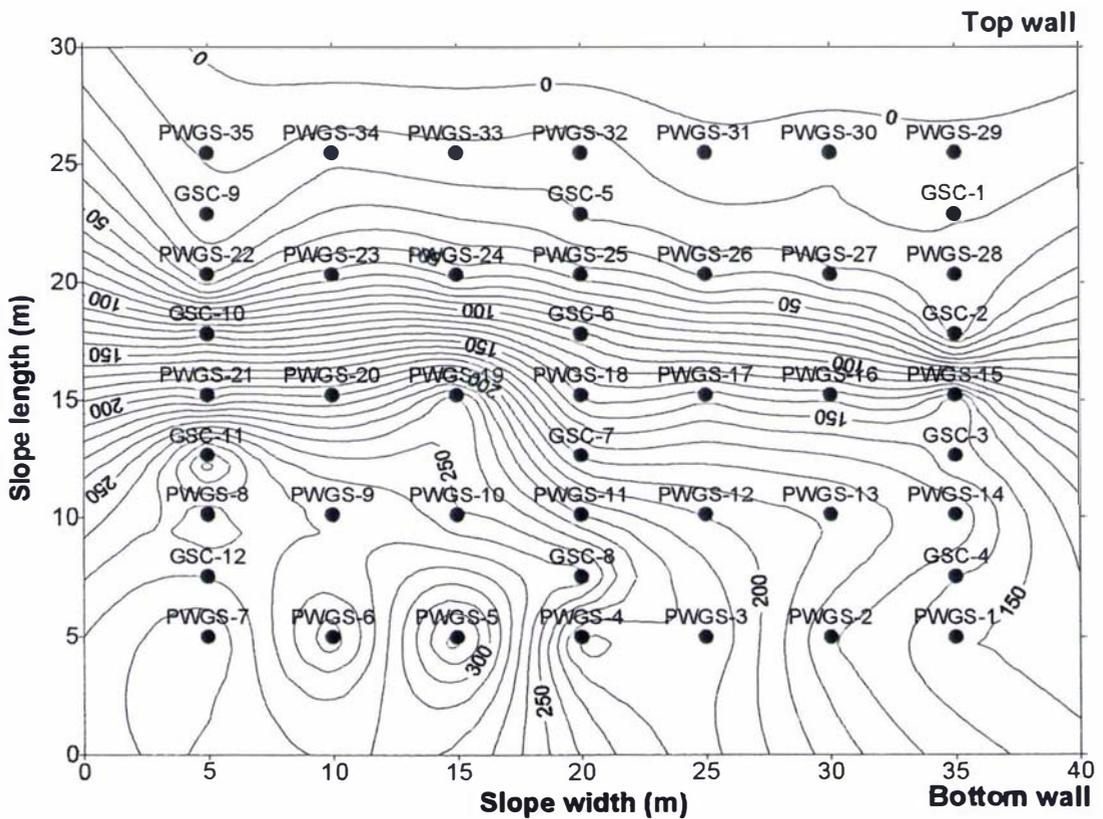


Figure 3.1 Grid sample locations (PWGS-1, GSC-1..) of the study area in Plate 3.1. Contour values represent depth of cover material in mm.

spatial distribution of values (Webster and Burges, 1984; Berndtsson et al., 1993). Surfer for Windows software (Keckler, 1994) was used to generate contour and 3D surface maps. Data kriging was performed using a linear semi-variogram model.

3.2.4 Mineralogical and geochemical studies

Petrographic examination of the samples described in Table 3.1 were conducted by transmitted and reflected light microscopy on polished thin sections and grain mounts respectively. Scanning electron microscopy (SEM) examination and energy dispersion spectroscopy (EDS) analysis of the representative samples were made with a Cambridge Stereoscan 250 Mark 3 Scanning Electron Microscope, with an attached Link E5431 EDS detector.

Table 3.1 Description of the pyritic pitwall rock samples.

Sample No.	Description
PWR-1	Light bluish-grey, hard, massive fresh pyritic andesite
PWR-2	Freshly weathered, bluish-grey, pyritic andesite containing disseminated pyrite crystals and lenses of pyrite
PWR-3	Freshly weathered dark blue pyritic rock with disseminated pyrite mineralisation
PWR-4	Light bluish-grey, moderately weathered pyritic andesite containing disseminated pyrite crystals and lenses of pyrite
PWR-5	Light grey, strongly weathered pyritic rock forming loose cover material on the pitwall surface

Samples were collected from north face pitwall during November 1995.

Determination of major oxides and trace elements was carried out using a Siemens SR303AS wavelength dispersive fluorescence spectrometer (XRF). Samples for the major oxides were prepared by fusion with lithium tetraborate/metaborate flux and cast into solid solution glass discs. Trace elements were determined on 40 mm diameter pressed powder samples with 10% wax added as a binder. Relative masses of the main minerals were also determined semi-quantitatively by X-ray diffraction analysis (XRD) using a Philips PW1710 instrument.

3.2.5 Analytical methods

The analytical procedures outlined below apply throughout the thesis and will be referred to frequently.

pH in water

The pH was measured in a suspension containing sample to deionised water ratio of 1:2.5 (10 g air-dried ≤ 2 mm waste rock to 25 ml deionised water). The stirred sample mixture was left to stand overnight and stirred again 30 minutes prior to pH measurement. A Radiometer PHM83 Autocal pH meter fitted with a Radiometer GK2401C combined glass/reference electrode was used to measure pH. The method for measuring pH is outlined in Blakemore et al. (1987). *Leachate pH* was measured in about 25 ml solution.

Electrical conductivity (EC)

The methods for extraction of soluble salts and EC measurement is described in detail by Metson (1956) and is outlined in Blakemore et al. (1987). The EC was measured in a solution extracted from 1:5 sample to deionised water ratio. A 10 g air-dried (≤ 2 mm) sample was mixed with 50 ml deionised water in a 100 ml beaker, stirred well, allowed to stand 1 hour and agitated for 5 minutes prior to filtering through Whatman filter paper No.1. A Portable Conductivity Meter HI8633 (HANNA Instruments) was used to measure EC (dS m^{-1}) at 25°C solution temperature. A reference 0.01 M KCl solution was used to standardise the EC reading at 35°C.

The EC ratings in dS m^{-1}) are: >2.0 = very high, $0.8-2.0$ = high, $0.4-0.8$ = medium, $0.15-0.4$ = low and <0.15 = very low. *Total soluble salts (%) = EC (dS m^{-1}) x 0.35*. (Blakemore et al., 1987). *Leachate EC* was measured in 30 ml solution.

Base cations (Ca, Mg, K and Na)

Exchangeable bases were determined by the Silver Thiourea (AgTU) method of Pleysier and Juo (1980) as outlined in Blakemore et al. (1987). Standard CEC methods using 1 M ammonium acetate (pH~7.0) and high electrolyte concentrations can result in hydrolysis or salt adsorption and is considered to overestimate CEC for variable-charge soils (Gillman, 1979). The single extraction AgTU method for measuring exchangeable cations and effective cation exchange capacity (ECEC) uses an unbuffered 0.1 M solution. The AgTU complex is considered an efficient exchanger of cations on clay surfaces (Gillman,

1979) and the method has been used in a wide range of New Zealand soils (Searle, 1986). A 0.8 g air-dried ($2 \leq \text{mm}$) sample was mixed with 40 ml 0.01 M AgTU in a 50 ml polypropylene centrifuge tube and shaken overnight (~16 hrs) on a end-over-end shaker and centrifuged @2000 rpm for 10 min and filtered through Whatman filter paper No.41. The concentration of bases in the extract was measured by atomic absorption/emission spectrometry (AAS/AES). The $ECEC (\text{cmol}_c \text{ kg}^{-1}) = \sum \text{bases} + \text{exchangeable Al} (\text{Al}_{\text{exc}})$ and the base saturation ($BS\%$) = $\sum \text{bases} / ECEC$.

KCl-extractable exchangeable Al (Al_{exc})

Exchangeable Al was extracted with 1 M KCl solution according to method outlined in Blakemore et al., (1987) with a minor modification in the extraction procedure. 5.0 g air-dried ($\leq 2\text{mm}$) sample was mixed with 25 ml 1 M KCl in a 50 ml polypropylene centrifuge tube and shaken overnight (~16 hrs) on a end-over-end shaker and centrifuged @2500 rpm for 5 min and filtered through Whatman filter No.42. The Al_{exc} in the extract was measured by AAS using a N_2O /acetylene flame. Dissolved Al concentrations in the leachate and runoff drainage water were measured by AAS in 0.1 M HCl matrix.

Total Sulphur (S)

Total S was determined by using the sodium bicarbonate/silver oxide ($\text{NaHCO}_3/\text{AgO}$) fusion method of Steinbergs et al. (1962). The method involves ashing of 0.25 g of sample ($< 150 \mu\text{m}$) with 0.5 g of $\text{NaHCO}_3/\text{AgO}$ mixture at 550°C for 3 hours. The ashed sample is solubilised in 5 M HCl and an appropriate dilution carried out before determining the concentration of total S by the turbidimetric method using an auto-analyser as described in Blakemore et al. (1987).

Sulphate sulphur (SO_4^{2-})

Adsorbed sulphate concentrations in the sample was determined as per method of Searle (1979) outlined in Blakemore et al. (1987). The method basically involves displacement of SO_4^{2-} by HPO_4^{2-} ion and measuring the displaced SO_4^{2-} . 5.0 g of air-dried ($\leq 2 \text{ mm}$) sample was extracted with 25 ml 0.01 M calcium di-hydrogen phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] solution in a 50 ml polypropylene centrifuge tube. The mixture was shaken for 0.5 hour on an end-over-end shaker, centrifuged @9000 rpm for 5 min and filtered through Whatman filter No.41. The SO_4^{2-} in the extract was measured turbidimetrically in an auto-analyser. Leachate and runoff drainage water SO_4^{2-} was

measured in a 5 ml aliquot with appropriate dilutions. *Sulphide S* in the sample was obtained by subtracting SO_4^{2-} from the total S (organic S is assumed negligible in the pitwall rock).

Determination of Fe and Mn

Concentrated HNO_3 and dilute HCl are commonly used in extracting total and soluble plant available metals in soils (Viets and Boawn, 1965; Smith and Bradshaw, 1979). In a comparison of chelating agents for extracting for metals from diverse soil materials, Norvell (1984) observed that 0.1 M HCl was severe enough to extract most metals particularly Fe, Mn and Al. Dilute HCl is commonly used for extracting plant available heavy metals.

The original method of Viets and Bowen (1965) was used to extract soluble forms of Fe and Mn in the sample. 5.0 g sample was mixed with 25 ml 0.1 M HCl in a 50 ml centrifuge tube and shaken overnight in an end-over-end shaker. The mixture was centrifuged @9000 rpm for 5 min and metals in the extract were measured by AAS. Dissolved Fe and Mn in the leachate and drainage water were measured by AAS in 0.1 M HCl matrix.

Total Fe and Al was extracted with 25% HNO_3 according to the method outlined in Smith and Bradshaw, (1979). 0.5 g air-dried ($< 150 \mu\text{m}$) sample was digested with 25 ml 25% HNO_3 in a 200 ml digestion tube @100°C. The digest was centrifuged @9000 rpm for 5 min, filtered and diluted before measuring the concentration of Fe by AAS. *Pyritic Fe* in the sample was obtained by subtracting 0.1 M HCl-extractable Fe from total Fe.

Acidity

Acidity was measured in 1:5 pitwall rock to deionised water extract. 10 g sample was mixed thoroughly in 50 ml deionised water and left to stand overnight (~16 hr). The solution mixture was filtered through Whatman filter paper No.41. A 10 ml aliquot was diluted with 20 ml deionised water and titrated with 0.1 M NaOH to pH 8.3 using a Mettler DL21 Autotitrator. Acidity in the leachate was measured with the same dilution ratio. The amount of NaOH consumed was converted to kg CaCO_3 equivalent.

3.2.6 Net acid generation (NAG) static test

Static NAG tests were carried out according to the method outlined by Miller and Jeffrey (1995), where 2.5 g of pulverised ($\leq 150 \mu\text{m}$) sample was treated with 250 ml 15 % H_2O_2 (pH stabilised to 5.5 with 0.1 M NaOH) in a 500 ml beaker under a fume-hood. The beaker was kept covered with a watch glass until vigorous reaction stopped. The sample was heated on a hot plate for 2 hours and cooled to room temperature before measuring the pH (NAGpH) in the residual solution. The sample was then made up to 250 ml with deionised water and titrated with standardised 0.5 M NaOH to pH 7. The net acid generation (NAG) by the sample was calculated as:

$$\text{NAG (kg CaCO}_3 \text{ t}^{-1}) = \frac{50 \times [\text{volume NaOH, ml}] \times [\text{molarity of NaOH}]}{\text{weight of the sample (g)}}$$

3.2.7 Acid neutralising capacity (ANC)

The neutralisation potential (NP) method from Sobek et al. (1978) was adapted for determination of ANC. It involved treating 2 g of sample with 20 ml of 0.1 M HCl in 250 ml flasks, heating nearly to boiling with periodical swirling until no gas evolution was observed. The sample was made up to 125 ml with deionised water, boiled for 1 minute, then cooled to room temperature. The treated samples were back-titrated with standard 0.5 M NaOH to pH 7. The ANC was calculated as the amount of HCl consumed by the sample and converted to equivalent CaCO_3 .

$$\text{ANC (kg CaCO}_3 \text{ t}^{-1}) = \frac{50 \times [\text{volume HCl consumed, ml}] \times [\text{molarity of HCl}]}{\text{weight of the sample (g)}}$$

3.2.8 Acid base accounting (ABA)

The net acid producing potential (NAPP) of the sample was derived from total sulphide-S analysis as per standard acid base accounting analysis (ABA) procedures described in section 2.5.1 (Chapter 2).

3.2.9 Net acid generation (NAG) kinetic test

The NAG kinetic test was carried out according to the procedure described by Miller (1996). Although this method is still in its development stage, it has been routinely used

by Environmental Geochemistry International Pty. Ltd. to determine the real time kinetics of sulphide oxidation and the onset of acid generation, termed a 'lag-period'. The NAG test kinetic result is compared with the column test data to estimate the approximate lag-period. The NAG test reaction time (X) to reach pH 4 is used to extrapolate the lag-period (Y) from the linear regression equation of the form: $Y = 2.4 * X + 0.60$ ($R^2 = 0.88$) obtained by Miller (1996) from static and kinetic data of 18 different waste rock samples classified as potentially acid forming.

In this test, 2.5 g of pulverised pitwall rock sample ($< 150 \mu\text{m}$) was oxidised with 15% H_2O_2 , following the procedure for the NAG static test. Temperature and pH of the test samples were monitored at 2 minute intervals until the reaction was complete. The temperature and pH were plotted against time for extrapolation of approximate time taken for complete oxidation of sulphide mineral.

3.2.10 Column test

Column test for kinetic evaluation of the acid generation by fresh rock (PWR-1) and freshly weathered/partially-oxidised rock (PWR-3) was done according to the modified method of Miller and Jeffrey (1995). Although the test is still in its development stages, such a real time kinetic test can give an approximate indication of the time (lag-period) involved in the oxidation of pyrite present in a sample. Samples PWR-1 and PWR-3 were used in the column test in order to compare the rate of release of sulphate and acid produced between fresh and partially oxidised samples of pitwall rock. The column test set up for evaluating acid generation and leachate chemistry is shown in Figure 3.2. One kilogram of representative sample (nominal size $\leq 4 \text{ mm}$) was packed in the column and initially leached with 200 ml of deionised water over a two-day period. The leachate collected was labelled week-1. Subsequent leaching was done with 100 ml of water on a 7 days cycle. During the 7 days non-leaching period the column surface was kept at a temperature of $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$ with an overhead heat lamp to simulate a dry period and to provide an optimum temperature for *Thiobacillus ferrooxidans* activity. Bacterial activity is considered to be most active at this temperature range (Carrucio et al., 1988). The leaching was carried out in duplicate for 10 weeks. Leachate pH, EC, SO_4^{2-} and acidity were monitored weekly.

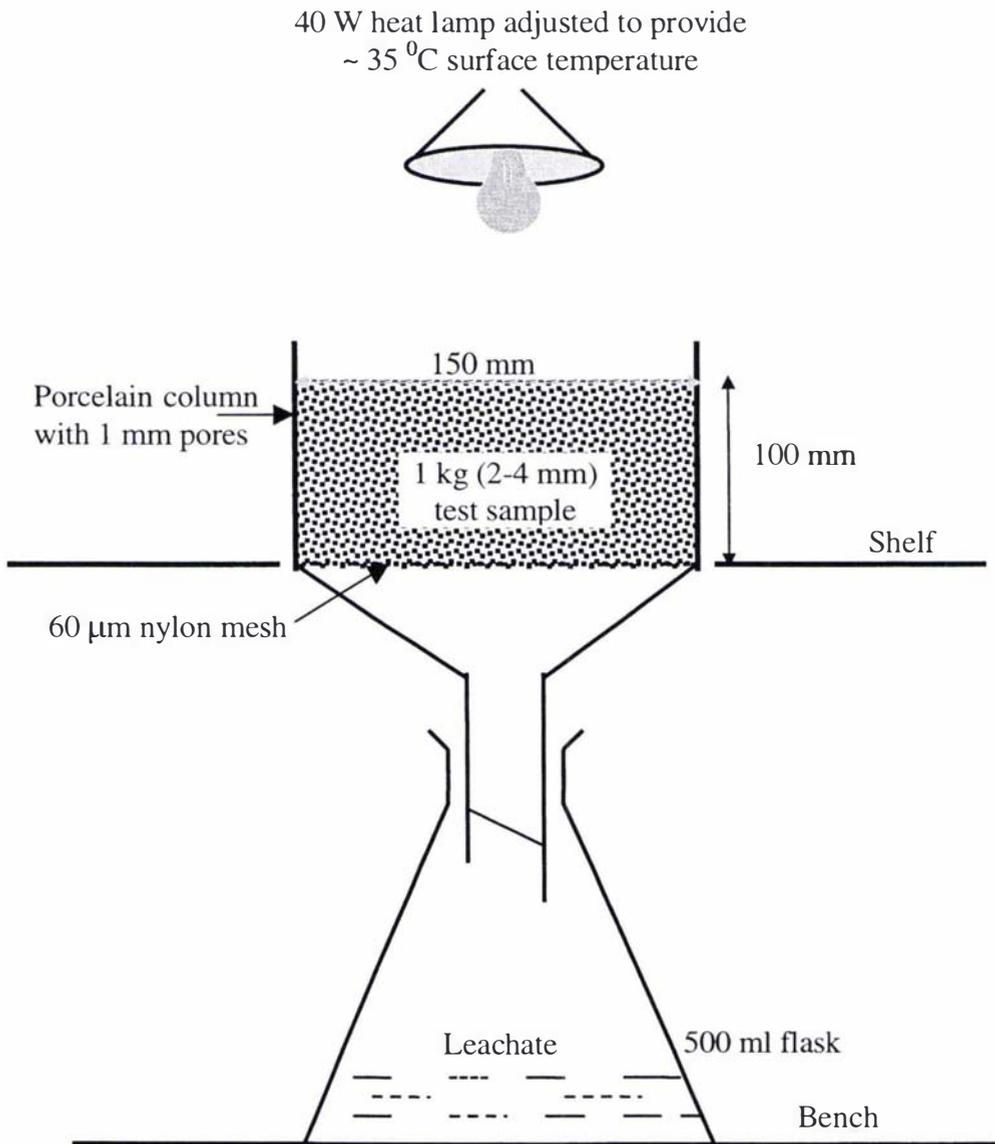


Figure 3.2 Column test set up (adapted from Miller and Jeffrey, 1995)

3.3 Results and Discussion

3.3.1 Physical and geochemical characteristics of the pitwall rock

3.3.1.1 *Physical characteristics*

At the time of field sampling (December 1994 and November 1995), the pitwall consisted of waste rock materials undergoing various degrees of physiochemical weathering. The weathered rock material generally appeared light-grey in colour with numerous patches of reddish-brown Fe-hydroxide coatings (Plate 3.2a). Freshly weathered wall rock generally appeared light bluish-grey whereas the fresh pyritic rock appeared dark blue. Cobble sized fresh pyritic rock commonly occurs embedded within the finer grained, light-grey weathered material (Plate 3.2b). The pitwall rock as a whole appeared highly fractured and the fractures were commonly filled with limonitic clay material. Disseminated grains and lenses of pyrite and occasional fine-grained quartz and calcite veins were observed in some hard, fresh rock.

Weathering was found to be more intense in areas where pyrite vein mineralisation was most abundant. Due to the steep gradient of the pit slope (43°), most of the weathered, loose material had gravity-sloughed towards the bottom of the pitwall to form a colluvial deposit. Rill and sheet erosion of the weathered and oxidised loose rock materials facilitated rapid down-slope migration of the weathered materials and pyrite oxidation products.

Grain-size analysis of the weathered rock materials indicated that it contained 2% clay (≤ 0.06 mm), 35% fines (0.06 - 2 mm) and 63% coarse materials (2 - 100 mm). Bulk density varied from 1.23 to 1.6 Mg m^{-3} with a mean of 1.4 Mg m^{-3} . The field moisture content of the weathered pitwall rock varied from 4.3 to 16.3% by weight (mean 9.3%). The water content (field capacity) of the weathered pitwall rock was 14.2% by weight at -10 KPa. Pore water content of the pitwall rock samples (≤ 4 mm fractions), determined by saturating a 1 kg column of sample with distilled water and oven drying at 105 $^{\circ}\text{C}$, was 47% by weight.

3.3.1.2 Mineralogical properties

Petrographic examination of fresh pyritic rock samples showed that pyrite commonly occurred as fine-grained, disseminated euhedral crystals and as lenses. Colloform bands of very fine-grained pyrite were also observed. Some pyrite grains showed scoured surface striations and circular cavities which may have been remnants of fluid inclusions or etch marks caused by bacterial activity. No framboidal forms of pyrite were observed in the thin sections.

An average of 11 liberated or partially liberated grains up to 0.5 mm size were identified in 10 g sample (≤ 2 mm) of the fresh rock (PWR-1) under reflected light. In the strongly weathered material (PWR-5), the average number of liberated pyrite grains was 5 in 10 g sample (≤ 2 mm). Most pyrite grains appeared euhedral, except in some weathered samples where some of the pyrite grains showed rounded edges which were due to the effect of weathering and oxidation.

SEM and EDS examinations of the fresh rock samples highlighted the disseminated and lensoid forms of pyrite mineralisation observed under the petrographic microscope (Plate 3.3a & b). The pyrite grains in the lenses (Plate 3.3b) were very fine-grained (<40 μm). Observation of fresh pyrite crystals under SEM scans showed that they have a perfect euhedral form (Plate 3.4). An EDS analysis of the grains indicated that the crystals were stoichiometrically pure pyrite (Fe : S ratio of 1 : 2) as indicated by the EDS spectrum and elemental analysis (Figure 3.3). Exposed pyrite crystals in weathered rocks showed moderately rounded crystals (Plate 3.5a). Fresh rock also contained rhombohedral crystals of calcite as vein fillings with perfect 010 cleavage surfaces, giving them a flaky appearance (Plate 3.5b). No framboidal forms of pyrite were observed in the samples, consistent with their abiotic origin.

In strongly weathered samples, clusters of pyrite crystals were entirely coated with a thin film of highly siliceous material (Plate 3.6). An EDS analysis of the coated pyrite grains (Figure 3.4) indicated that the presence of a significant amount of Si (16.4%), Al (1.0%) and K (1.8%). It is possible that under very acidic conditions, decomposition of silica and clay minerals may form precipitates that selectively coat the pyrite grain. Possible

evidence of bacterial oxidation of pyrite was observed in SEM scans of some pyrite grains where characteristic etch pits were observed (Plate 3.7), which are considered to result from bacterial activity (Mustin et al., 1992). Similar etch pits were also reported in pyrite from Tui mine tailings by Morrell et al.(1996).

XRD analysis of the rock samples (Table 3.2) indicated that the fresh rocks (PWR-1) contained up to 12% by weight CaCO_3 . Pyrite content was greater in the rocks containing both vein as well as disseminated pyrite mineralisation. A trend of increasing quartz content with increasing degree of weathering was observed. Feldspars remained resistant to weathering except in strongly weathered rocks (PWR-5). Clay content (mostly chlorite, illite and vermiculite) generally increased with progressive weathering and was highest in the strongly weathered sample.

Table 3.2 XRD analysis of major minerals (wt. %) in the pitwall rock

	PWR-1	PWR-2	PWR-3	PWR-4	PWR-5
Quartz (SiO_2)	50	60	60	67	70
Pyrite (FeS_2)	10	16	6.8	14	4.3
Calcite (CaCO_3)	12	1.3	0	0	0
Gypsum (CaSO_4)	0	0	0	0	2.5
Feldspars	25	20	20	30	0
Clays *	11	15	13	15	17

* About 60% kaolinite, minor illite and chlorite.

Strongly weathered samples contained <5% pyrite compared with >10% pyrite in fresh to moderately weathered rocks. With progressive weathering, the reduction in rock grain-size resulted in more liberation of the entrapped pyrite and hence a lower content of pyrite was expected in more weathered rocks, due to loss from oxidation and dissolution. The strongly weathered samples also contained 2.5% gypsum, indicating that salt precipitation is a common phenomenon during weathering of pyritic pitwall rock under dry environmental conditions.

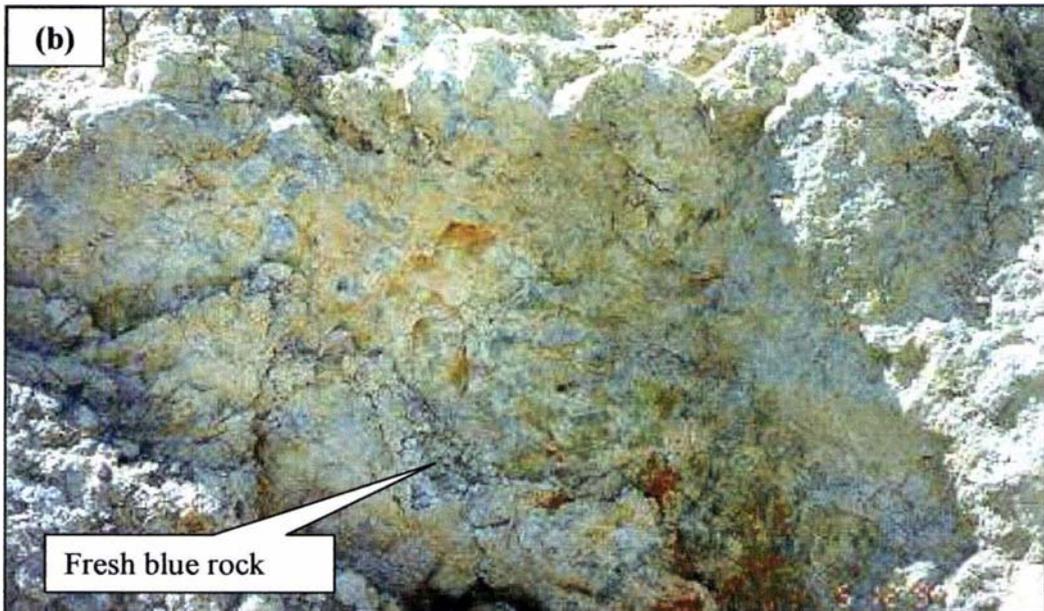
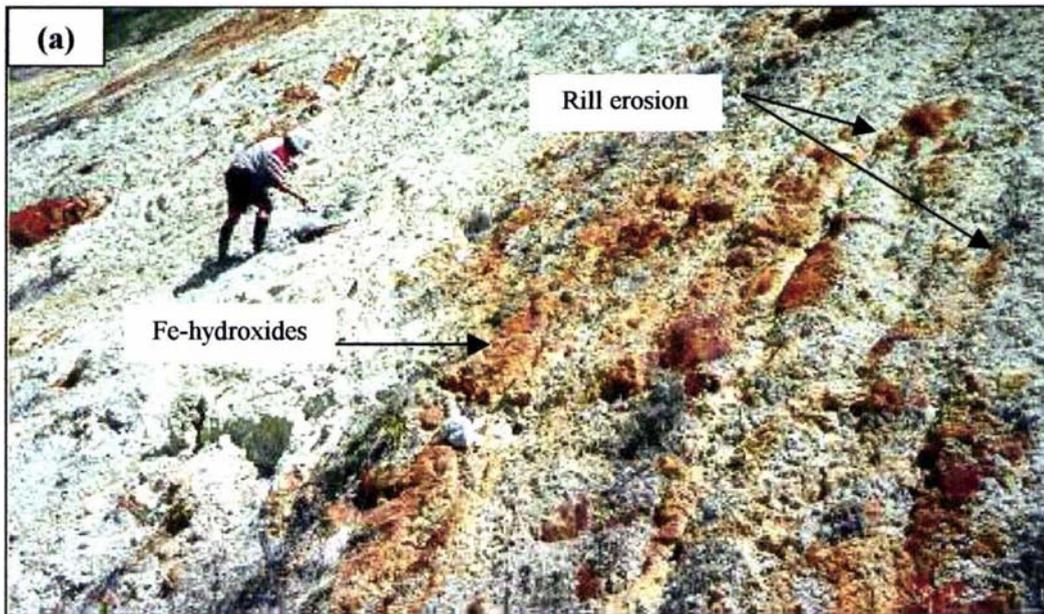


Plate 3.2 A section of the pitwall showing (a) Fe-hydroxide coatings and rill erosion pattern and (b) fresh (blue) rock in weathered matrix.

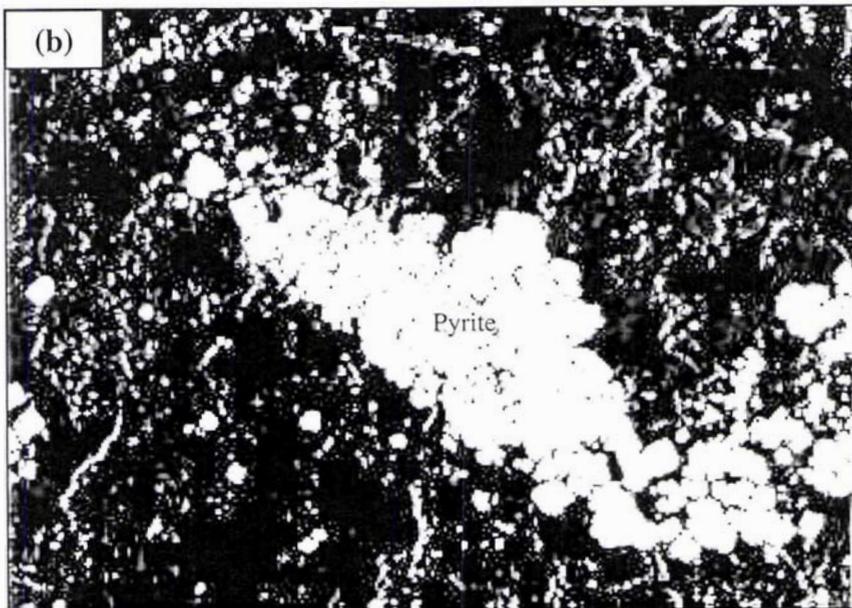
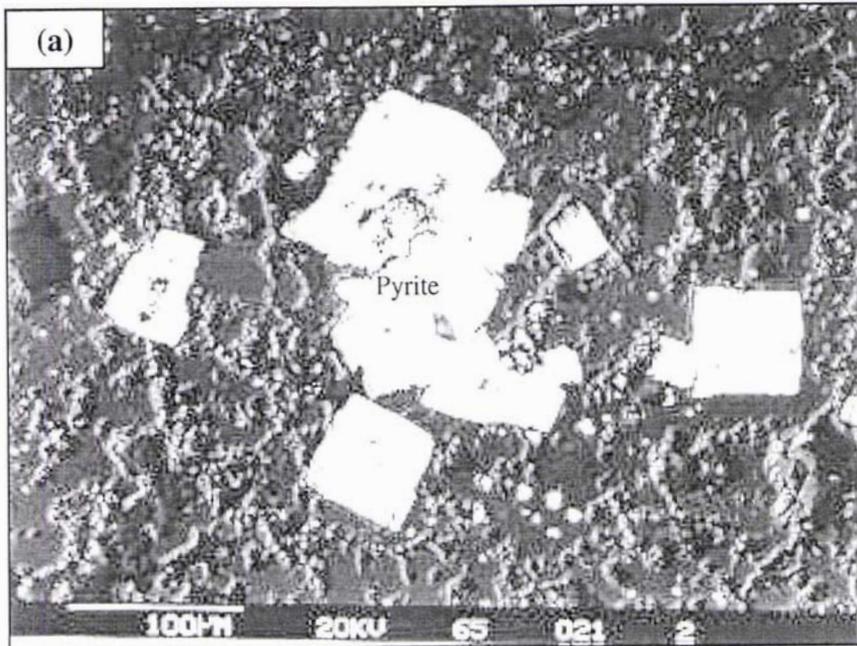


Plate 3.3 Back-scattered SEM scan of (a) disseminated pyrite crystals and (b) fine grained pyrite lens.

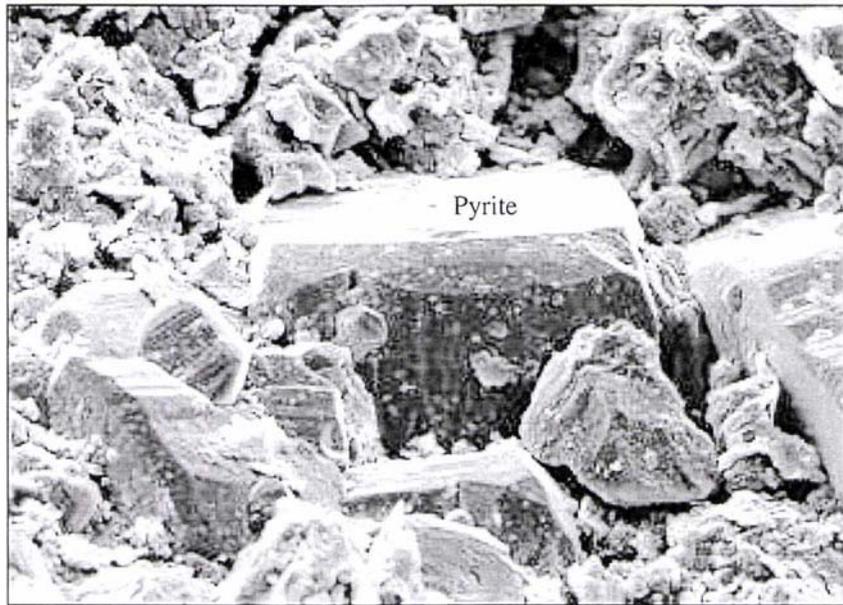


Plate 3.4 SEM scan of euhedral pyrite grain from fresh rock

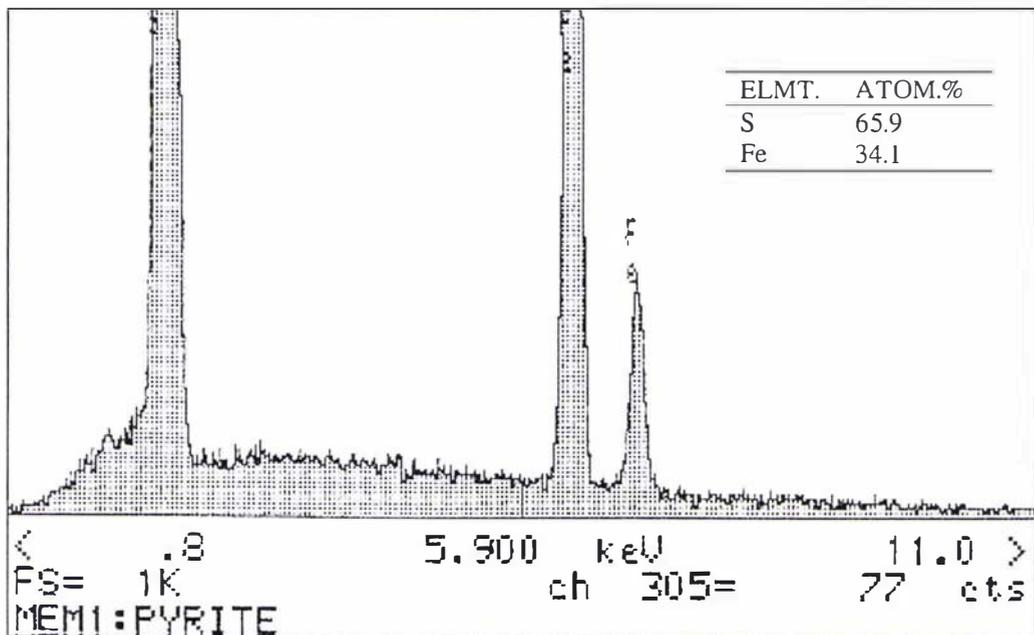
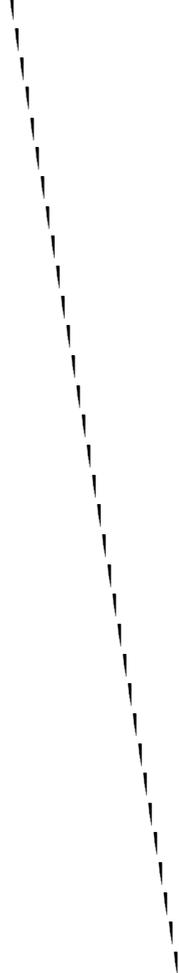


Figure 3.3 EDS spectrum of semi-quantitative elemental analysis of the pyrite grain in Plate 3.4.



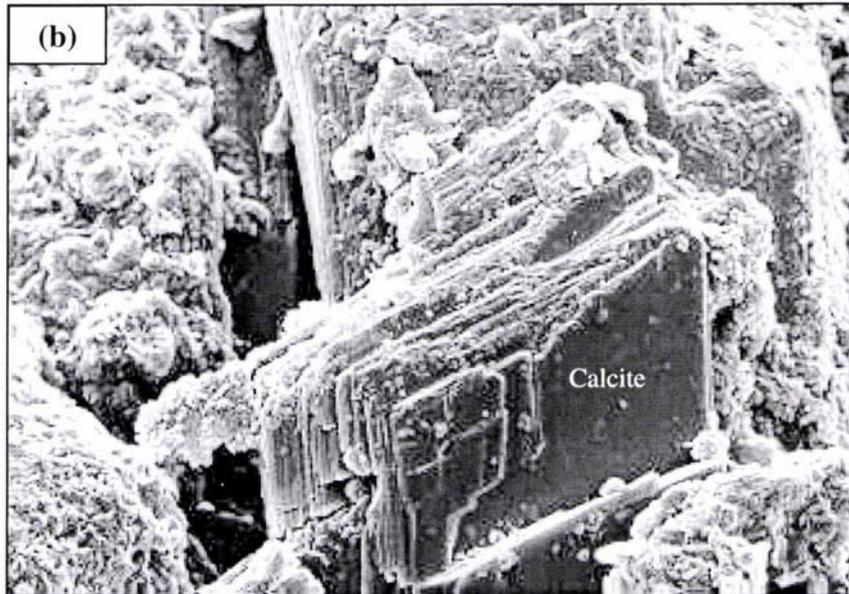
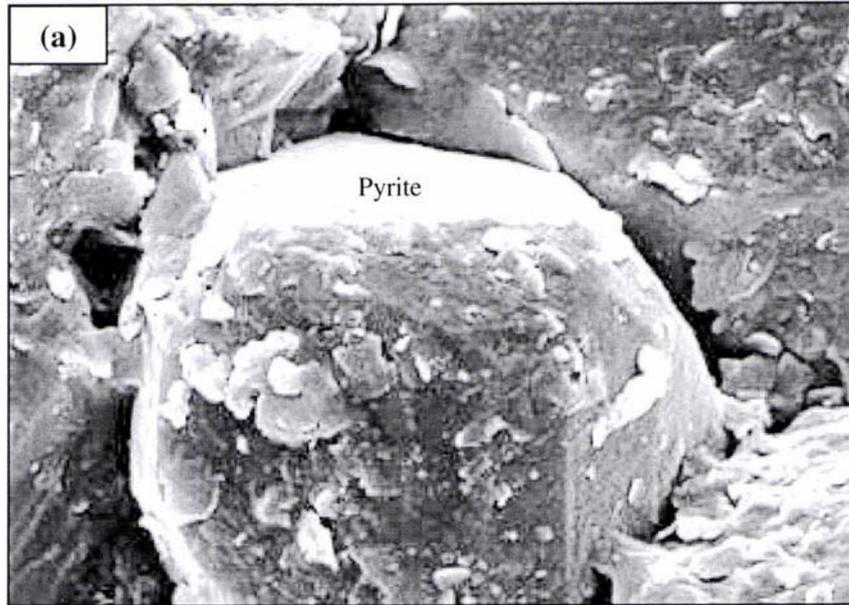


Plate 3.5 Forms of pyrite grains (a) sub-rounded pyrite crystals in weathered pitwall rock and (b) flaky calcite grains in fresh rock.

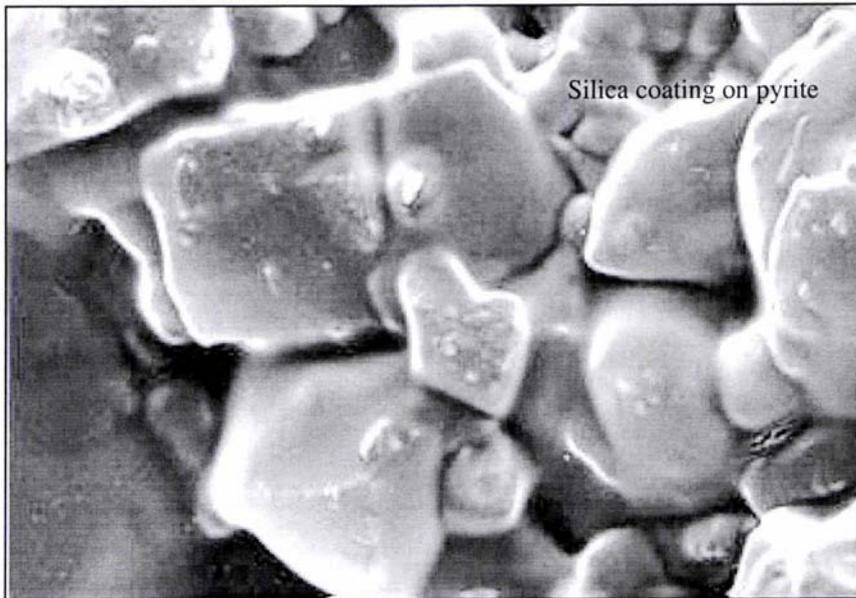


Plate 3.6 Silica coated pyrite grains in weathered pitwall rock.

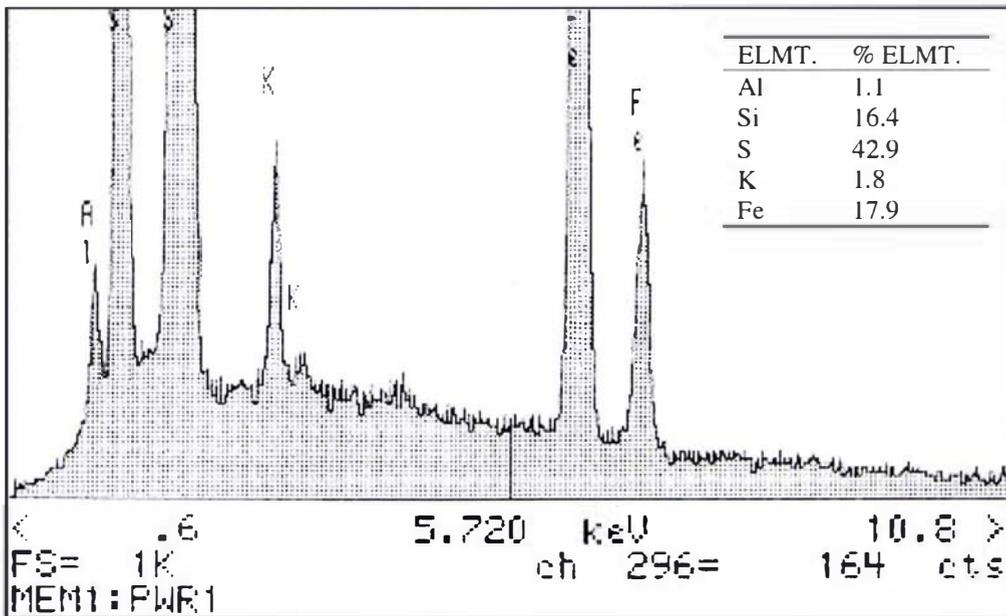


Figure 3.4 EDS spectrum and quantitative elemental analysis of pyrite grain shown in Plate 3.6.

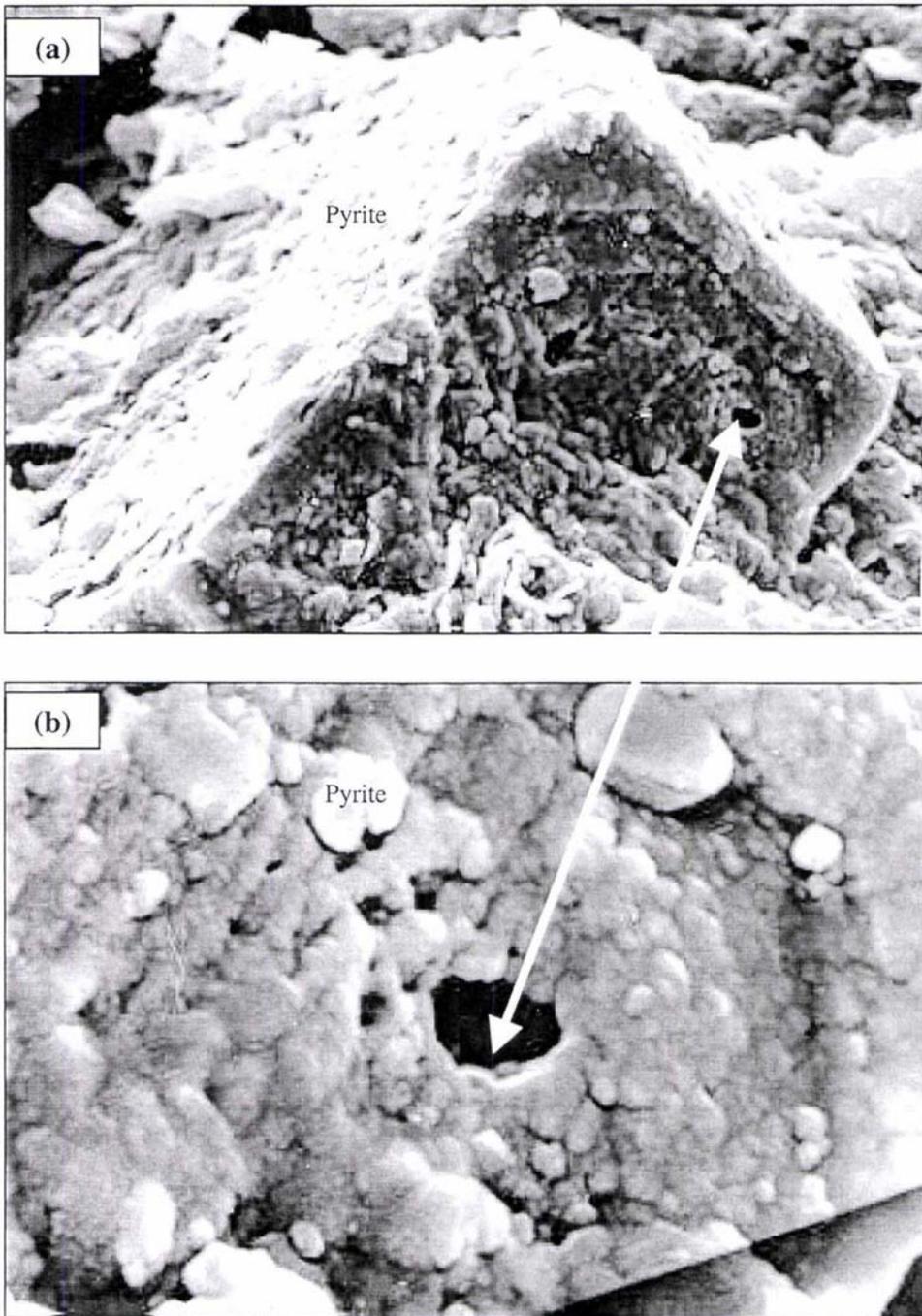


Plate 3.7 Pyrite grains with etch holes (a) Magnification x2000 (b) Magnification x20000.

3.3.1.3 Chemical properties

Chemical characteristics of the pitwall rock showed that, with progressive weathering and oxidation, there were gross chemical changes in the composition of the rocks (Table 3.3). Mean chemical properties of the pitwall rock samples listed in Table 3.3 showed that the fresh sample (PWR-1) and the freshly weathered sample (PWR-2) had a near neutral pH of 7.3 and slightly acid pH of 5.9 respectively. With increasing degrees of weathering there was a corresponding decrease in pH, the strongly weathered rock sample (PWR-5) having a pH as low as 1.8 with a mean of 2.1 ± 0.4 . Fresh and freshly weathered rocks had an $EC < 2 \text{ dS m}^{-1}$ whereas moderately to strongly weathered samples in colluvial deposits had an $EC > 2 \text{ dS m}^{-1}$ because of increase in SO_4^{2-} levels.

There was a general increase in SO_4^{2-} , soluble Fe, Mn and exchangeable Al (Al_{exc}) from fresh to weathered pitwall rock. The increase in Al_{exc} from fresh to weathered rock samples is mainly due to contribution from decomposition of aluminosilicate minerals and increasing mobilisation with decreasing pH. Soluble Fe and SO_4^{2-} in the samples ranged from as low as 477 mg kg^{-1} and 460 mg kg^{-1} to 4100 mg kg^{-1} and 7440 mg kg^{-1} from fresh to strongly weathered pitwall rock, respectively. Total S was highest in the samples containing pyrite lenses as well as disseminated pyrite mineralisation (PWR-2, PWR-3 and PWR-4). The total Fe was highest (4.6%) in PWR-1, remaining constant in all other samples.

Generally, the pitwall rock had very low concentrations of base cations. The effective cation exchange capacity (ECEC) was in the medium range for all the samples although there was nearly a two-fold increase in ECEC from fresh to strongly weathered sample mostly due to the effect of increase in Al_{exc} . The base saturation (BS%) however, was very high in the fresh rock and decreased gradually with increased weathering, as a result of leaching of base cations. An apparent increase in exchangeable Ca in PWR-5 and Mg in PWR-2 and PWR-4 was possibly due to release of these elements from decomposition of feldspars and ferromagnesian minerals in acidic conditions. Exchangeable K^+ and Na^+ remained constantly low in all the samples in spite of the differing degrees of weathering and oxidation.

Table 3.3 Chemical properties of the pitwall rock.

Parameters	Units	PWR-1	PWR-2	PWR-3	PWR-4	PWR-5
pH (H ₂ O)		7.3	5.9	4.7	4.2	2.1
EC	dS m ⁻¹	0.1	1.3	0.3	2.8	3.8
SO ₄ ²⁻	mg kg ⁻¹	460	680	960	3200	7440
Total S	%	2.6	3.5	2.5	4.0	3.4
Soluble Fe	mg kg ⁻¹	477	398	2970	3050	4100
Total Fe	%	4.6	3.2	3.6	4.1	3.8
Soluble Mn	mg kg ⁻¹	215	271	295	357	328
Exchangeable Al	cmol _c kg ⁻¹	2.1	6.1	5.4	10.6	14.9
Ca	cmol _c kg ⁻¹	7.7	4.7	2.4	1.9	5.3
Mg	cmol _c kg ⁻¹	2.5	2.4	3.3	5.4	1.3
K	cmol _c kg ⁻¹	0.3	0.6	0.9	0.4	0.7
Na	cmol _c kg ⁻¹	0.4	0.3	0.4	0.2	0.2
ECEC	cmol _c kg ⁻¹	13.0	14.1	12.4	18.5	22.4
Base saturation	%	84	57	56	43	33

3.3.1.4 Depth-profile chemistry of the weathered pitwall rock

Selected chemical properties (pH, EC, SO₄²⁻, Al and Mn) of the strongly weathered 60 cm of sloughed pitwall rock material (grid site PWGS-5, Figure 3.2) were measured at 10 cm depth intervals in order to determine whether stratification of pyrite oxidation products occurred. Results of the analyses of the selected chemical properties are presented in Figure 3.5. Vertical profiling of pH variation showed that there was a significant change in pH from the surface to a depth of 40 cm (Figure 3.5a). The mean profile pH was 2.5 ± 0.2 .

The EC varied from 9.2 dS m⁻¹ at surface to 5.7 dS m⁻¹ at 60 cm depth with a profile mean of 7.2 ± 1.4 dS m⁻¹. A significantly higher EC at the surface than at depth (Figure 3.5b), indicated evidence of sulphate salt formation on the surface during the dry period existing at the time of sampling. Formation of sulphate salts such as epsomite (MgSO₄·7H₂O), alunite [(KAl₃(SO₄)₂(OH)₆] and minor gypsum (CaSO₄·2H₂O) on the surface of the pitwall rock were observed both in field and laboratory (section 3.3.2.4) studies.

The mean SO₄²⁻ in the 60 cm depth profile was 4950 ± 649 mg kg⁻¹ and varied significantly within the depth profile (Figure 3.5c). The high and low SO₄²⁻ levels within the depth profile are likely to be due to distribution of oxidisable liberated grains of pyrite and subsequent formation of sulphate salts with the cations released from weathering and

oxidation processes. The maxima in the depth profile could also be due to increased activity of *T. ferrooxidans* under optimum conditions.

Al_{exc} remained at $7.1 \pm 0.8 \text{ cmol}_c \text{ kg}^{-1}$ and showed a significant increase at depth except at a median sampling depth of 35 cm (Figure 3.5d). Soluble Mn showed an initial increase at median depth of 15 cm but otherwise remained more or less constant throughout the profile depth at an average of $467 \pm 20 \text{ mg kg}^{-1}$ (Figure 3.5e).

Acidity showed a very similar trend to that of SO_4^{2-} and varied significantly within the depth profile (Figure 3.5f). The high and low acidity values within the depth profile were consistent with the trends in SO_4^{2-} levels in the column sections. Step-wise multiple regression of the measured chemical properties of the depth profile showed that as expected, there was a positive correlation ($R^2 = 0.93$) between acid production and SO_4^{2-} release. However, SO_4^{2-} versus EC showed a negative correlation ($R^2 = 0.82$) in the depth profile, contrary to the expected positive trend. This could be due to periodic flushing of the salt by infiltrating runoff water and gypsum formation under dry conditions prevailing at the time of sampling.

Because of the coarse texture and high porosity of the weathered rock material, moisture and oxygen readily diffuse through to greater depth to facilitate biochemical and abiotic pyrite oxidation and hence acid generation. This characteristic of the weathered pitwall rock has an important implication to remediation measures for revegetation. Any amendments for amelioration of low pH conditions in the pitwall rock must take into consideration the subsurface distribution of pyrite oxidation products (acidity, EC and SO_4^{2-}) especially in relation to amendment application and selection of suitable plant species to be grown under site specific conditions.

3.3.1.5 Geochemical properties

Table 3.4 is a summary of the average major oxide and trace element concentrations present in the pitwall rock samples characterised in this study. The pyritic rocks showed chemical compositions typical of the Coromandel Group andesitic rocks (Brathwaite and Christie, 1996). Weathered pitwall rock generally had higher SiO_2 contents, with highest

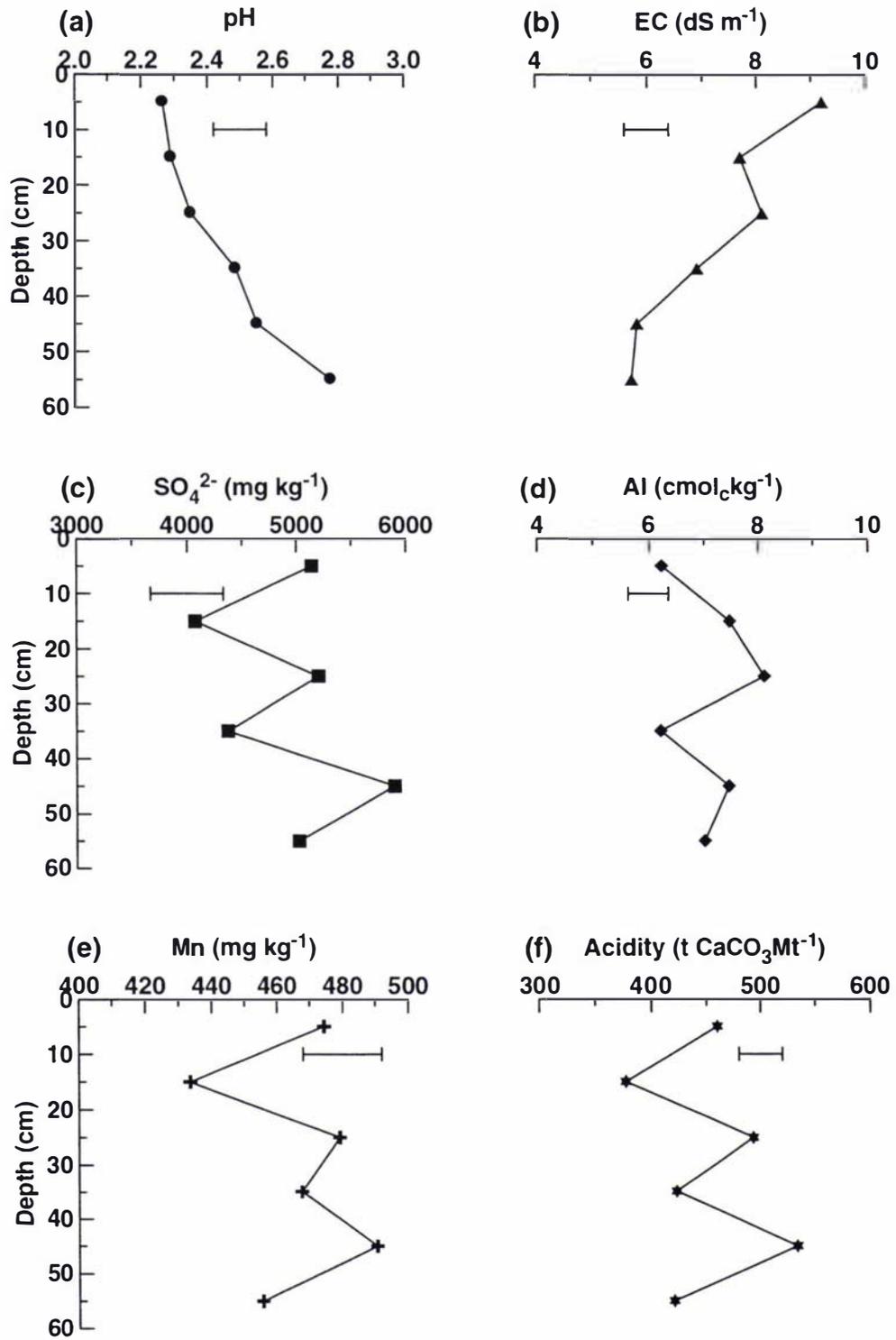


Figure 3.5 Depth variations of selected chemical properties of the pitwall rock. Horizontal bars represent LSD(%).

SiO₂ (70%) being in PWR-3, indicating a possible residual effect of weathering. Fe₂O₃ was highest (6%) in the fresh rock but was generally 1% less in the weathered rocks. Both CaO and MgO showed decreasing trends with increasing degree of weathering while Na₂O was mostly enriched in PWR-4. Water content (L.O.I.) was highest in the strongly weathered PWR-5. An anomalously high K₂O content in PWR-3 and PWR-4 may have been initial residual enrichment of K-bearing feldspar minerals resistant to dissolution under conditions of light weathering. Except for slight decreases in PWR-3, both Al₂O₃ and TiO₂ remained immobile to weathering.

The trace element compositions of the pitwall rock indicated a nearly two-fold increase in Ba in weathered samples (531 mg kg⁻¹) from that of the fresh pyritic rock (PWR-1), indicating that it is strongly immobilised by SO₄²⁻ to form BaSO₄. Over most of the Eh-pH field of water, Ba is immobile as BaSO₄ and is fixed in soils and rocks materials (Sullivan and Yelton, 1988; Larocque and Rasmussen, 1998). A strong linear regression coefficient of R² = 0.98 between SO₄²⁻ and Ba supports the above observation. Trace amounts of heavy metals (Cu, Zn, Pb, Cr and Co) were mobilised into AMD solution and removed as indicated by the decreasing levels of metals with increasing degree of weathering. Arsenic (As) increased with progressive weathering from 2 mg kg⁻¹ in PWR-1 to 10 mg kg⁻¹ in PWR-5 as a result of oxidation of arsenopyrite (FeAsS) and subsequent accumulation in the weathered rocks as insoluble As(SO₄)₂ complex. Strontium (Sr) was unusually high (210 mg kg⁻¹) in PWR-1, but the level dropped to < 100 mg kg⁻¹ in rocks undergoing progressive weathering, indicating that it is highly mobile in the acidic environment. The higher Sr in the fresh PWR-1 may have resulted from substitution of Sr for Ca. Rubidium (Rb) concentrations were very high (>200 mg kg⁻¹) in moderately weathered rocks whereas fresh and strongly weathered rocks contained 10 mg kg⁻¹ and 98 mg kg⁻¹ respectively. The Rb/Sr ratios for the pitwall rocks were thus 1.0 (PWR-1): 0.005 (PWR-2): 0.014 (PWR-3): 0.019 (PWR-4): 0.009 (PWR-5) from fresh to strongly weathered rocks.

3.3.1.6 Effect of weathering on geochemical properties

The major changes in mineralogical compositions of the rocks under surficial weathering are described by either changes in volume or mass of the rock with respect to constant mass/volume of resistant oxides such as Al₂O₃ and TiO₂. The most commonly used

Table 3.4 Average composition of the pitwall rocks

Oxides, %	PWR-1	PWR-2	PWR-3	PWR-4	PWR-5
SiO ₂	57.95	62.41	69.46	67.21	65.34
TiO ₂	0.65	0.69	0.58	0.60	0.78
Al ₂ O ₃	15.35	16.52	13.70	14.13	15.87
Fe ₂ O ₃	5.91	4.80	4.09	4.48	4.12
MnO	0.13	0.09	0.02	0.14	0.02
MgO	4.84	3.54	0.75	1.29	2.90
CaO	7.31	2.11	0.89	1.07	0.99
Na ₂ O	1.80	0.16	0.22	1.67	0.13
K ₂ O	0.26	2.01	6.26	5.32	1.53
P ₂ O ₅	0.19	0.16	0.13	0.17	0.14
L.O.I.	5.42	5.25	3.87	4.08	8.17
SUM	99.79	97.70	99.94	100.13	99.97

Trace elements, mg kg⁻¹					
As	2	4	8	7	10
Ba	265	368	588	534	470
Ce	25	23	23	19	14
Co	22	24	22	12	10
Cr	317	156	115	193	289
Cu	28	29	31	26	13
Ga	15	17	16	15	17
La	17	17	21	14	7
Nb	6	6	6	7	6
Ni	86	36	25	39	28
Pb	4	5	6	8	1
Rb	10	226	313	227	98
Sc	10	20	18	17	22
Sr	210	23	90	94	18
Th	6	10	11	8	5
U	3	3	5	4	4
V	139	144	106	108	148
Y	18	15	11	13	9
Zn	74	61	67	59	34
Zr	100	113	101	99	116

method has been the calculation of gains-losses from chemical analysis either in weight (%) or volume (%) basis. Gresens (1967) originally considered compositional-volume relations in metasomatised rocks to determine compositional changes during alteration. Grant (1986) later modified the same principle and he termed it the isocon method. Other workers (Mountain and Williams-Johns, 1995; Huston, 1993) used the isocon methods to represent mass transfer of elements in metasomatic and hydrothermal alteration processes. In this study, simple gain-loss diagrams were used to represent compositional changes in the mass of the oxides (%) in the pitwall rock during progressive weathering, relative to constant mass of Al_2O_3 . Based on the constant mass of Al_2O_3 , the change in mass (ΔM) of the oxides can be represented in simplified Gresens's equation:

$$\text{Change in mass of oxides } (\Delta M) = \frac{\text{Wt. \% } Al_2O_3(F)}{\text{Wt. \% } Al_2O_3(W)} \times \frac{\text{Wt. \% Oxide } (W)}{\text{Wt. \% Oxide } (F)}$$

Where F , fresh rock composition; W , weathered rock composition.

Major gains and losses of oxides calculated from Table 3.3 and presented diagrammatically in Figure 3.6, showed that the progressive weathering of the pitwall was accompanied by a consistent addition of Si and K, and general depletions in Ca, Mg, Na, P, Fe and Mn. The apparent gain in K in PWR-3 and PWR-4 could be the result of acid leaching of Ca and Na and residual incorporation of K in the formation of the clay mineral illite [$KAl_2(AlSi_3)O_{10}(OH)_2$] from weathering of potassium feldspars ($KAlSi_3O_8$) under acidic environments. Gains in K may also reflect a pre-weathering enrichment of K-rich minerals such as sericite and potassic feldspars. The re-precipitation of minerals such as alunite [$(KAl_3(SiO_4)_2(OH)_6$] and jarosite [$(KFe_3(SO_4)_2(OH)_6$] during dry periods could also elevate the K content temporarily as would in the transformation of feldspars to a potassic phase. Most of the Fe^{2+} oxidised to Fe^{3+} would initially be precipitated as ferric hydroxide [$(Fe(OH)_3$] and release acid in the process. Similar gains in Si and K and losses in Ca, Na and Fe were also suggested by Huston (1993) as typical in alteration of pyritic volcanic rocks.

The losses in base cations Ca, Mg and Na showed the expected trend of preferential leaching during progressive weathering of the pitwall rock. Losses in base cations

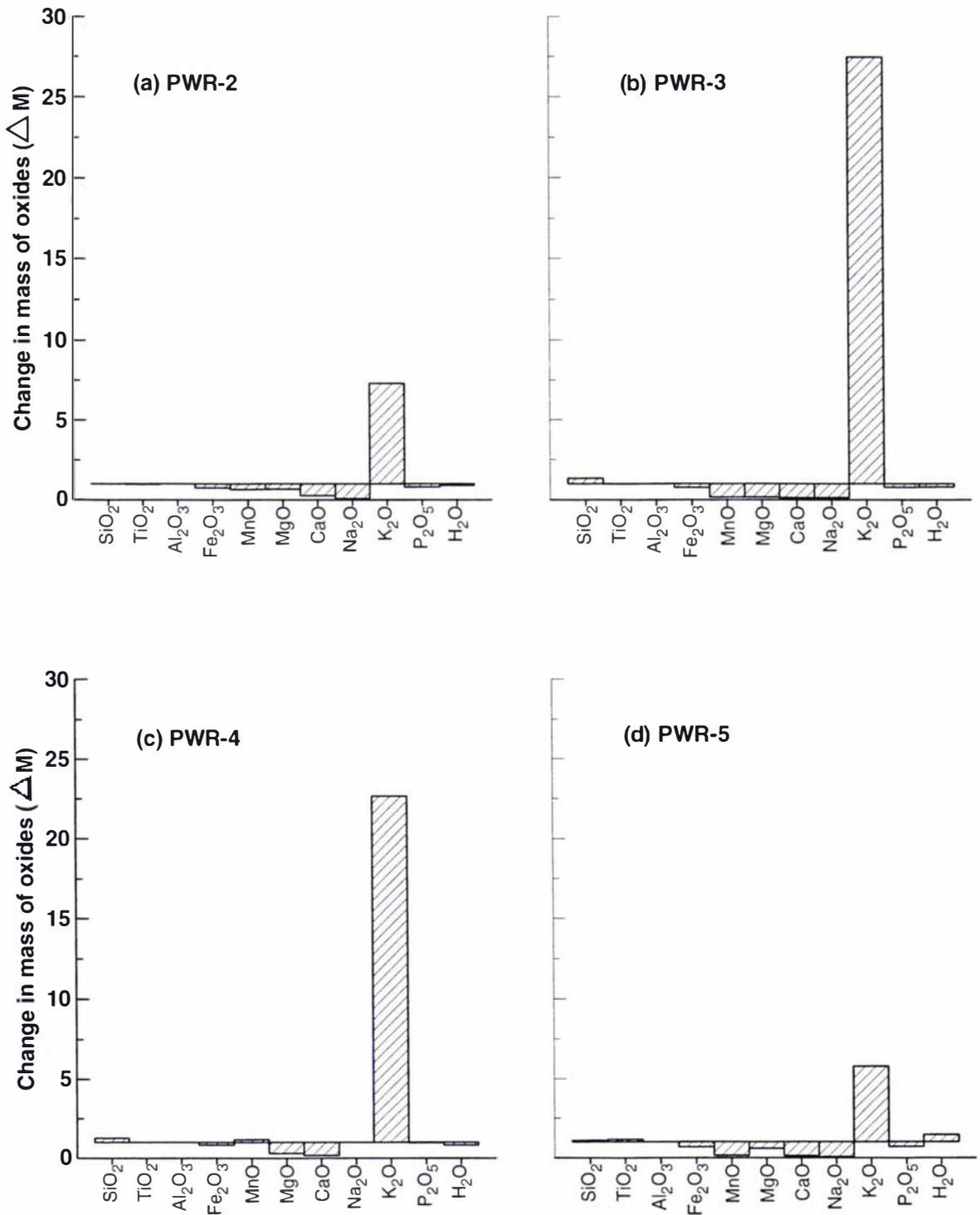


Figure 3.6 Chemical gain-loss diagrams relative to the fresh rock (PWR-1), for the pitwall rock undergoing progressive weathering and oxidation.

generally increased with increasing intensity of weathering. Greatest amounts of depletion were in PWR-3 and PWR-5. Most of the Mn was also depleted with increasing degree of weathering except for PWR-4, which showed a gain compared to the fresh rock. With progressive weathering and partial oxidation, the overall trend in the distribution of major oxides showed general depletion in major cations except for K, which showed an anomalous enrichment possibly in clays and as a substituted ion in jarosite type minerals.

3.3.2 Acid generation properties of the pitwall rock

3.3.2.1 Static net acid generation (NAG) test

When the pitwall rock samples were treated with unstabilised 15% H₂O₂ solution, the most vigorous reaction was observed in the freshly weathered (PWR-2) and moderately weathered (PWR-4) pitwall rocks. These samples contained pyrite lenses as well as disseminated crystals, which contributed to a higher amount of liberated pyrite grains and resulted in greater reactivity with the oxidant. The average time taken for the reaction to be completed until no effervescence was observed was 44 minutes. Results of the NAG test on the pitwall rock samples showed that they are potentially acid generating types, as indicated by their NAGpH < 3 (Table 3.5). Sulphidic materials with NAGpH < 4 are considered to be potentially of acid forming type (Miller and Jeffrey, 1995). The resultant acidity obtained from titration of the test solution to pH 7 showed that samples containing pyrite lenses as well as disseminated crystals, that are undergoing a moderate degree of weathering had potential to produce higher acidity than samples with disseminated pyrite crystals alone. Lower net acid generation in PWR-1 reflected the presence of some carbonate minerals in the sample (Table 3.2, 3.3 and 3.4).

Table 3.5 NAG test results for the pitwall rock samples.

	PWR-1	PWR-2	PWR-3	PWR-4	PWR-5
NAGpH	2.98 ± 0.33	2.11 ± 0.24	1.95 ± 0.23	2.03 ± 0.14	2.08 ± 0.22
NAG, kg CaCO ₃ t ⁻¹	42 ± 3	52 ± 8	44 ± 3	68 ± 7	52 ± 4

3.3.2.2 Acid base accounting (ABA)

Analysis of the sulphur forms present in the pitwall rock indicated that samples with pyrite vein mineralisation generally contained higher amounts of sulphide S than the samples that only contained disseminated pyrite crystals. The acid base analysis (ABA) of the pitwall rock samples is given in Table 3.6. The result of the ABA analysis indicated

that all the samples, irrespective of weathering, showed positive net acid producing potentials (NAPP), indicating that all of the pyritic rocks in the pitwall are potentially acid generating types. $NAPP > 0$ is considered potentially acid forming material in ABA analysis.

Table 3.6 Acid base accounting (ABA) analysis of pitwall rock

Sample	Paste pH	Sulphur forms, %			ABA, kg CaCO ₃ t ⁻¹		
		Total	Sulphate	Sulphide	APP	ANC	NAPP
PWR-1	7.3	2.56	0.046	2.51	78	27	51
PWR-2	6.9	3.54	0.068	3.47	108	-1	108
PWR-3	4.7	2.54	0.096	2.44	76	-5.8	76
PWR-4	4.2	4.02	0.320	3.70	116	-3	116
PWR-5	2.1	3.36	0.744	2.62	82	-8	82

Organic S is assumed to be negligible. Negative acid neutralisation capacity (ANC) values indicate nil ANC, in which case $NAPP = APP$ where APP is acid producing potential ($= \text{total sulphide-S} * 31.25$).

The APP values obtained from ABA analysis were generally higher than the NAG test values but there was a positive correlation between the NAG and APP data from the five samples of pitwall rocks ($NAG = 2.27 * APP + 32.14$, $R^2 = 0.81$). The NAPP values in Table 3.6 indicated that the fresh sample containing an ANC of 27 kg CaCO₃ t⁻¹ resulted in much lower NAPP than the progressively weathered samples. It is likely that the higher NAPP in the weathered samples is due to residual concentration of pyrite. Although pyrite grains and veins that are directly exposed undergo rapid oxidation to produce a very low pH in weathered pitwall rock, a significant amount of disseminated pyrite grains will not be immediately oxidised in the host rock and will form an unoxidised pyrite concentrate as weathering progresses. This is reflected in the significant pyrite content in the weathered samples (Table 3.2) and high total sulphide-S content (Table 3.6), indicating that moderately to strongly weathered pyritic rock will still have the potential to generate acidity more readily than the fresh rock.

It is important to consider the effect pyrite grain liberation during weathering has on the NAPP under field conditions. Even with an advanced degree of weathering and oxidation, fine-grained pyrite crystals may remain encapsulated and unoxidised in coarse grained fractions of the pitwall rock. Thus, only the pyrite grains that are directly or partially

exposed by weathering are likely to be involved in acid generation under field conditions (Figure 3.7).

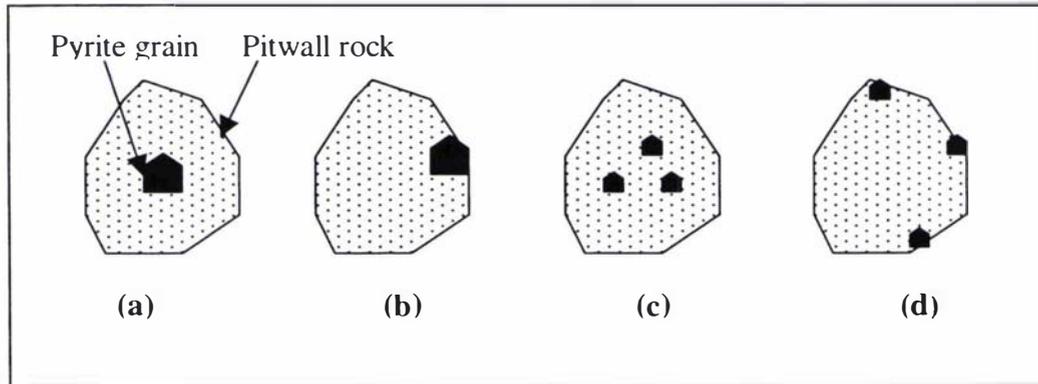


Figure 3.7 Pyrite inclusions and oxidation scenario.

Grains (b) and (d) are available for oxidation while grains (a) and (c) will remain inert until exposed by rock weathering. Thus the amount of acid generated and the intensity of AMD in the substrate will depend on the textural relationships between the pyrite mineral and the host rocks under given conditions of atmospheric exposure and weathering intensity. Where pyrite presence is dominated by vein mineralisation, one may find anomalously high AMD compositions. Even if the rock appears to be strongly weathered/oxidised it may contain 'entombed' pyrite grains which may eventually produce acid.

The above scenario can have important implications for the prediction of AMD and in kinetic testwork. The degree to which individual pyrite grains are susceptible to oxidation depends largely on the distribution of the mineral grains, nature of mineralisation and, therefore, the size of the sample involved. The ABA test assumes that the small sample used in the test is representative of an uniformly mineralised strata. However, this is not always the case and unless the ABA test is performed on large bulk sample, the NAPP properties of the sample will not be properly assessed. Field observation indicated that pyrite mineralisation in the pitwall at Martha mine is not uniformly distributed. This necessitated the detailed spatial delineation of the AMD properties of the pitwall rock discussed later in section 3.3.

3.3.2.3 Kinetic NAG test - Lag-period

Although standard ABA techniques have been widely used as screening tools to identify potentially acid producing sulphidic waste rocks, there is still an uncertainty in the prediction of AMD generation. In order to establish the real time pH-temperature dependent kinetics involved in pyrite oxidation and acid generation, a kinetic NAG test was performed on fresh and progressively weathered samples. The method of Miller (1996) was adopted for this test. The results of the NAG test kinetics (Figure 3.8) showed that fresh samples took approximately 80 minutes before vigorous reaction started while partially oxidised/weathered samples (PWR-2, PWR-4, PWR-5) took comparatively much less time; 30, 20 and 20 minutes respectively. Studies by Miller and Jeffrey (1995) and Miller (1996) have attempted to correlate NAG test kinetic data with that of conventional column test results of potentially acid forming mine wastes materials. They indicated that the time taken (minutes) for the pH of the NAG test solution to decrease by 1 unit from the starting value (X) is directly related to the time taken (weeks) to reach pH 4 in the column weathering test (Y) and obtained a linear regression equation of the form: $Y = 2.40 * X + 0.60$ ($R^2 = 0.88$) for 18 samples classified as potentially acid forming by the NAPP and static NAG test results. Based on this equation, the fresh PWR-1 gave a lag-period of 22 weeks ($X = 9$ minutes) while progressively weathered PWR-2, PWR-4 and PWR-5 had much shorter lag-periods of 13 weeks ($X = 5$ minutes), 13 weeks ($X = 5$ minutes) and 7 weeks ($X = 3$ minutes) respectively. The result for PWR-3 was similar to PWR-2 and therefore not included in this discussion. The lag-period of 22 weeks for fresh rock to generate acid is above the upper range of field lag-period (15-20 weeks) indicated by Miller (1986) and Brodie et al. (1996) in their on-site prediction of AMD from fresh unoxidised waste rock from borehole cores. Miller (1986) also indicated that about 20 to 30 weeks time period was taken for bacterially catalysed oxidation to take place in the unoxidised waste rock.

Under the local environmental conditions of Waihi (dry periods in summer and wet winters, and an annual average rainfall of 2500 mm), the pitwall affected by pyrite mineralisation will remain continuously acidic due to varying lag-periods of the pitwall rocks. The nature of pyrite mineralisation and amount of pyrite grains liberated during progressive weathering of the pitwall rock directly control acid generation in the pitwall. Although the fresh rock showed longer lag-period (22 weeks), once weathering

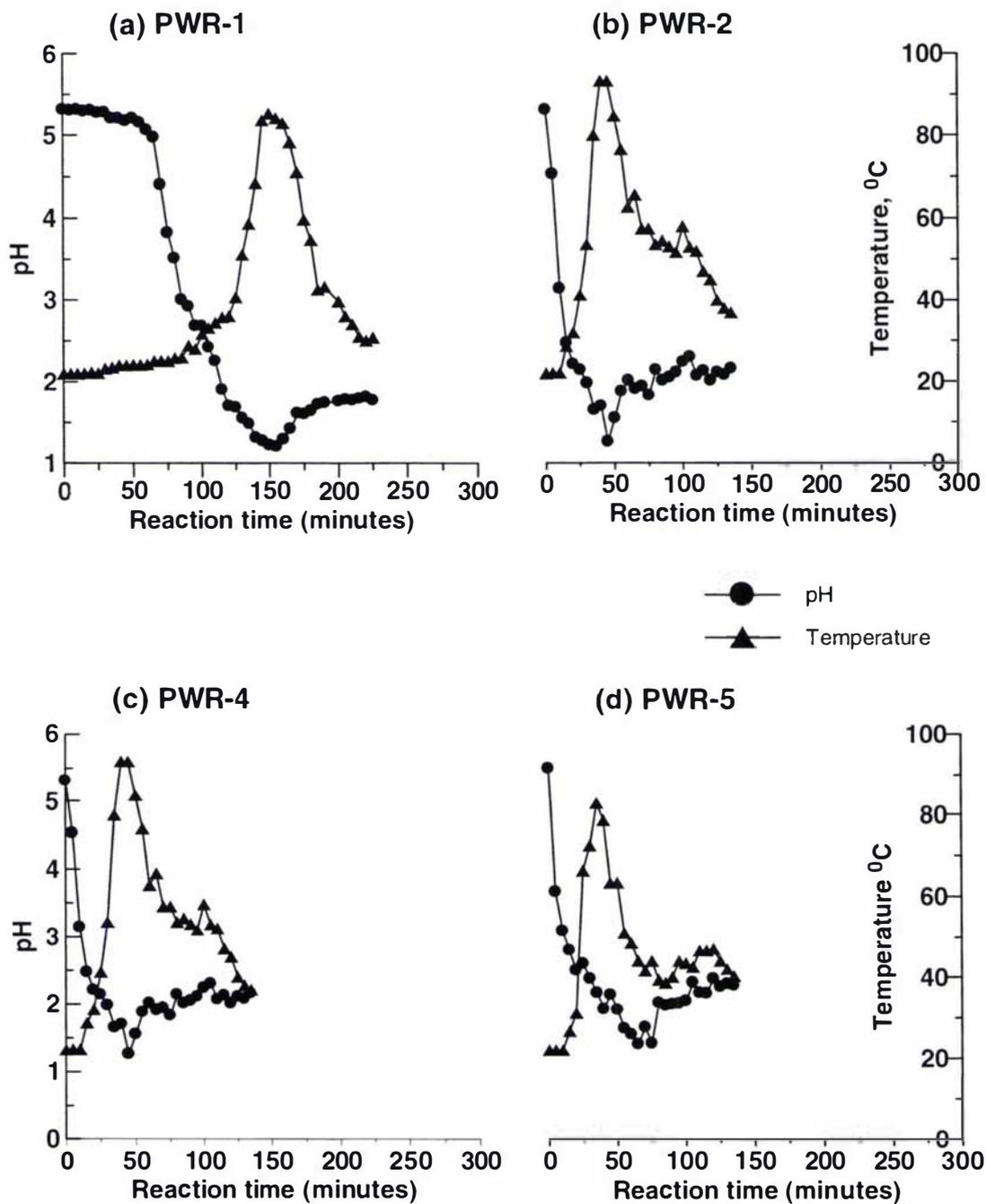


Figure 3.8 NAG test kinetics for (a) fresh PWR-1, (b) freshly weathered PWR-2, (c) moderately weathered PWR-4 and (d) strongly weathered PWR-5.

commences the lag-period is significantly reduced and the rate of AMD generation will be rapidly increased.

3.3.2.4 Column test - rate of acid generation

Leaching studies are concerned with the kinetics of mineral dissolution. Thus, a basic understanding of the leaching of constituents from the pitwall rock is required in order to quantify the rate of release of the pyrite oxidation products. The objective of the kinetic test was to provide real time data on the rate of acid generation/neutralisation under laboratory controlled conditions so that quantitative information on leachate characteristics could give some indication of likely AMD contaminants under field conditions. Such information not only complements the static test results but also provides an assessment of treatment options for remedial measures.

Kinetic column tests involve repetitive oxidation during leaching cycles on a sample and are frequently used for predicting acid generation and neutralisation. The kinetic NAG test (section 3.3.2.3) indicated a widely varying lag-period of 22, 13 and 7 weeks for fresh to strongly weathered pitwall rocks respectively; they gave no indications of the amount of acid generated and the characteristics of the AMD. In this study, a column test was conducted on the fresh (PWR-1) and freshly weathered (PWR-3) rock samples for a 10 week period. These two samples were selected so that a comparison could be made of leachate quality and rate of acid generation between fresh and freshly weathered rocks.

Results of 10 weeks of column leaching showed that in the freshly weathered sample (PWR-3) there was a steady decrease in pH up to week 7 (Figure 3.9a). The lowest pH reached was 2.3 at week 7 after which it remained constant. The largest drop in pH occurred in weeks 4 to 7. There was no significant drop in pH of the leachate in fresh rock (PWR-1) columns, even after 10 weeks of leaching. It is possible that in the fresh rock, only chemical oxidation of pyrite may have been taking place, which is insignificant compared with the rate of oxidation due to bacteria.

Leachate EC in the PWR-3 remained in the mean range of 2 to 3 dS m⁻¹, except for a sudden increase to about 4 dS m⁻¹ at week 7 (Figure 3.9b). This was in response to the sudden drop in pH and increase in SO₄²⁻ released as a result of possible bacterial oxidation

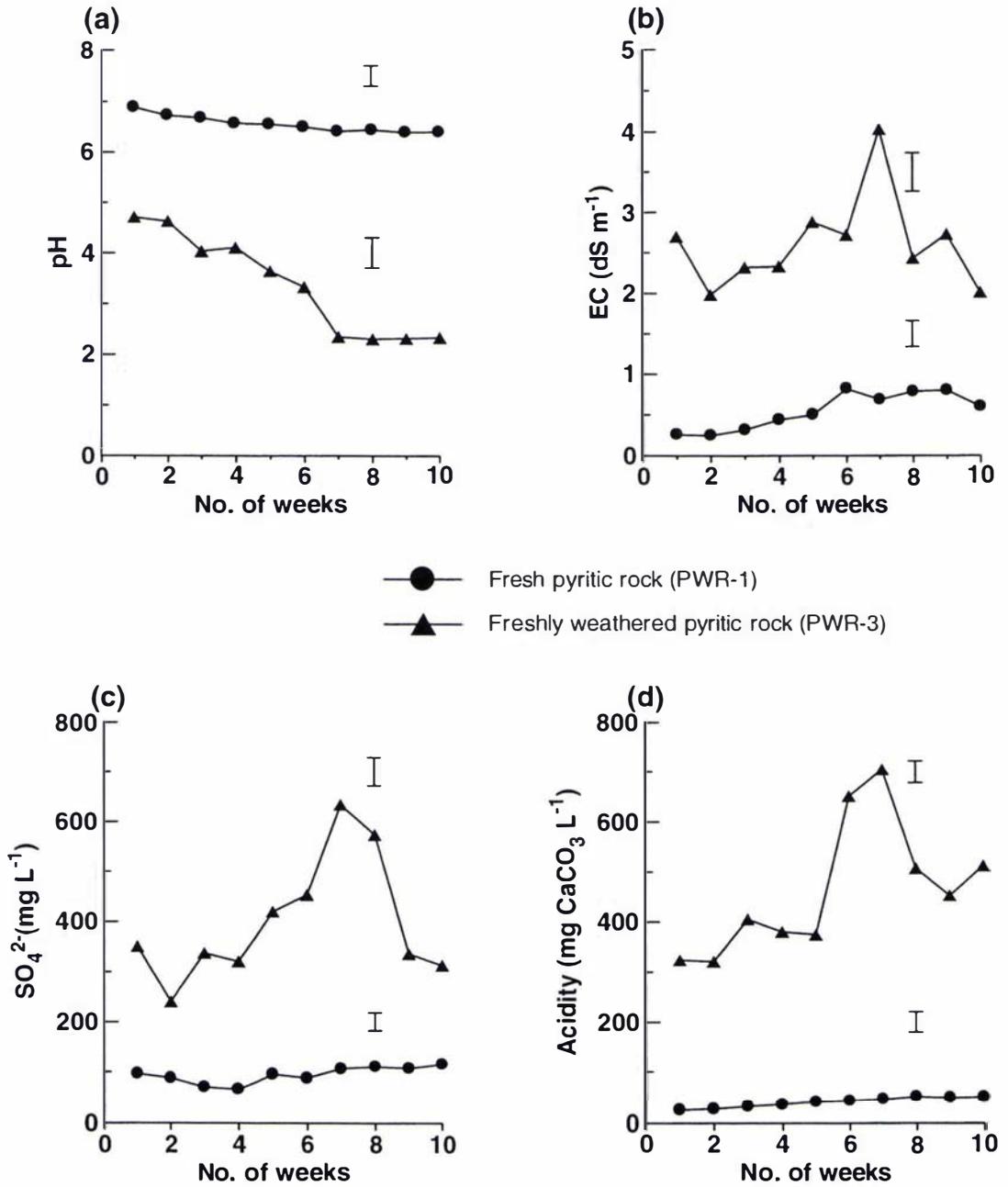


Figure 3.9 Leachate characteristics of the pitwall rock under laboratory controlled kinetic column test. Vertical bars represent LSD(5%).

of pyrite. In contrast, the slight increase in the EC levels in the leachate fresh sample from week-6 onwards was insignificant.

Sulphate-S (SO_4^{2-}) level in the column leachate from freshly weathered rock (PWR-3) reached a maximum (634 mg L^{-1}) at week 7, after which there was a sudden drop to a level below 400 mg L^{-1} at week 8 (Figure 3.9c). The increase in SO_4^{2-} production from week 5 to week 7 indicated that bacterial oxidation of pyrite began to be effective only when the pH decreased to < 3.5 (Figure 3.8a) in spite of the optimum surface temperature of 35°C . The sudden drop in leachate SO_4^{2-} after week-8 also indicated that the amount of free pyrite (grains b & c in Figure 3.7) available for oxidation by *T. ferrooxidans* was only sufficient to support bacterial activity for about 3 weeks. In comparison, there was no indication of pyrite oxidation in the fresh samples, although some amount of chemical oxidation may have been taking place.

Total acidity in the leachate from freshly weathered samples increased to a peak of $704 \text{ mg CaCO}_3 \text{ L}^{-1}$ at week 7 (Figure 3.8d) after which it decreased to levels $< 500 \text{ mg CaCO}_3 \text{ L}^{-1}$. Acid generation in the weathered samples appeared to be directly proportional to SO_4^{2-} production during week-3 to week-7 but the overall correlation was poor ($R^2 = 0.55$). This may be due to neutralisation of some of the acid by dissolution of silicate and carbonate minerals present.

Although there were some variations in SO_4^{2-} production and acid generation, there were steady increases in the cumulative levels of EC, SO_4^{2-} and acidity over the 10 week period of leaching. The linear trends in cumulative amounts of the measured parameters in the PWR-3 leachate over the 10 weeks were highly significant (Eqns. 3, 4 & 5). Since fresh rock remained inert throughout the leaching period, only trends in the cumulative amounts of the EC, SO_4^{2-} and acidity in the PWR-3 leachate are considered.

$$\text{EC} = 2.73 * \text{week} - 0.87 \quad (R^2 = 0.99) \quad [3]$$

$$\text{SO}_4^{2-} = 431 * \text{week} - 309 \quad (R^2 = 0.98) \quad [4]$$

$$\text{Acidity} = 497 * \text{week} - 406 \quad (R^2 = 0.99) \quad [5]$$

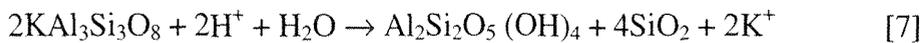
The rate of acid generation is commonly measured in terms of rate of SO_4^{2-} production and in simple terms, the amount of SO_4^{2-} in the column leachate is a measure of the amount of acid generated. Over the 10 weeks period, the cumulative amount of SO_4^{2-} produced was 3977 mg L^{-1} and the rate of SO_4^{2-} release was $398 \text{ mg L}^{-1} \text{ week}^{-1}$. The corresponding release of acid in the leachate was $463 \text{ mg CaCO}_3 \text{ L}^{-1} \text{ week}^{-1}$. The column test results indicated that the onset of acid generation started in week 5, as reflected in the significant increases in SO_4^{2-} and acidity. This corresponded to a lag-period of 5 weeks for freshly weathered sample compared to a lag-period of 13 weeks predicted from the NAG test kinetics. This indicated that under leaching conditions, assumed to be simulative of field conditions, acid generation in the pyritic pitwall rock at Martha mine is predicted to take a much shorter period to start once weathering commences.

The PWR-3 sample had a pyrite content of 4.6% (based on the total sulphide-S content of 2.4%). This meant that only 1.6 % of the total pyrite was being oxidised per week in the column. Assuming the same average rate of SO_4^{2-} release (398 mg L^{-1}), it would take approximately 63 weeks for the PWR-3 to completely oxidise, all factors (grain liberation, environmental conditions etc.) being favourable.

The ideal oxidation of pyrite produces 2 moles of acidity (equivalent to 100 mg CaCO_3 ; given that 1 mole H^+ is equivalent to 0.5 mole CaCO_3) for every mole of SO_4^{2-} produced (96 mg SO_4^{2-}) according to Eqn. 6.



This molar ratio of 2:1 (acidity to SO_4^{2-} weight ratio 100/96) should theoretically give a weight equivalent acidity versus SO_4^{2-} slope ratio of 1.04. A regression plot of acidity versus SO_4^{2-} for the column test on PWR-3 gave a linear relationship of the form: $\text{Acidity} = 0.79 * X + 150$ ($R^2 = 0.55$) with a slope of 0.79. This slope is clearly less than the ideal slope of 1.04 expected for stoichiometric oxidation of pyrite, indicating that about 25% ($(1.04 - 0.79 / 1.04 * 100)$) of the acid produced is unaccounted for. It is possible that the acid produced is being neutralised by dissolution of silicate minerals or transformation of K-feldspars to kaolinite (Eqn. 7).



The lower slope ratio of 0.79 may also be due to incomplete rinsing of the interstitial SO_4^{2-} , thus giving lower concentration in the leachate. The molar ratio of 2:1 for acidity to SO_4^{2-} is based on the ideal conditions of pyrite oxidation and thus may also not be applicable to samples that have variable pyrite content and liberated pyrite grains. Both SO_4^{2-} and acidity levels in the column test leachate should be accounted for in order to give a reliable value for the rate of pyrite oxidation and hence acid generation.

In sample PWR-3 columns, clusters of mushroom-shaped salt crystals were observed on the surface a day after the leaching. These crystals continued to form throughout the test period, although fewer crystals were observed towards the end. An XRD analysis of the crystals indicated that they consisted mainly of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), alunite [$(\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6)$] and minor gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). This indicated that in pyritic materials that have low neutralisation potential, preferential precipitation of Mg, Al, Fe and possibly Mn sulphate salts are likely to occur during dry conditions. These observations suggest that under field conditions, a dry spell after a rain event may result in high concentrations of salt in pore waters, leading to salt precipitation, which may be detrimental to plant growth.

Column tests on fresh rock (PWR-1) and freshly weathered rock (PWR-3) indicated that only PWR-3 was susceptible to biochemical oxidation and acid generation over a 10 week period. Sample PWR-1 remained inert over this period, indicating that under column test leaching conditions (section 3.2.2.2.2) fresh rock may remain unoxidised over a long period (lag-period > 23 weeks) until exposed to oxidants and bacterial activity. Even though the column test was run for twice the length of time suggested in the standard method of Miller and Jeffery (1995), the fresh rock continued to produce neutral AMD and may continue to do so until lag-period of over 22 weeks is completed.

3.3.3 Characterisation of pitwall runoff drainage

In order to assess the pitwall runoff drainage characteristics, drainage water from the bottom of the pitwall was collected after one brief rainfall event in November 1995. Drain water samples were collected at 8 locations (10 m intervals) along the base length of the

pitwall up to the manhole point (Figure 3.9). Drainage water pH was measured in the field with a portable pH meter as well as in the laboratory in collected samples. There were no differences between field and laboratory pH measurements. EC was measured in filtered, undiluted solution. The drainage water samples were analysed for SO_4^{2-} , Fe, Mn and Al and the results presented in Table 3.7 and Figure 3.10.

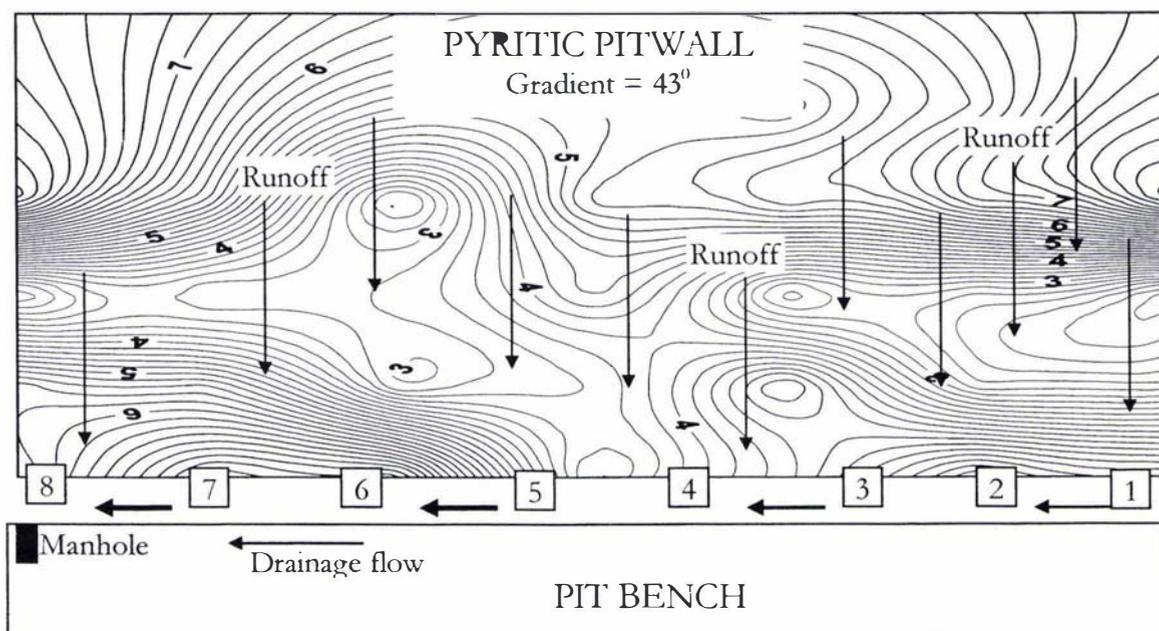


Figure 3.10 Pyritic pitwall showing runoff drainage flow direction and sampling locations (1- 8). Contour values represent kriged % pyrite (FeS_2) in the weathered material.

The results of the analysis showed that the runoff drainage from the exposed pyritic pitwall was highly acidic and contained elevated levels of soluble salts, as reflected in high EC (Figure 3.11a). The runoff drainage water was found to be extremely acid all along the 70 m flow. Away from location 1 the pH increased slightly and reached a maximum of 3.12 at location 8 as a result of progressive dilution downstream. Runoff drainage EC ranged in value from a high of 3.7 dS m^{-1} at sampling location 1 to < 2.0 at downstream location 8.

Soluble metal (Fe, Mn and Al) loading and SO_4^{2-} were generally higher at location 1 and decreased in concentration with increasing distance towards downstream location 8. Total soluble Fe and SO_4^{2-} ranged in value from 17040 mg L^{-1} and 8300 mg L^{-1} at location 1 to 1750 mg L^{-1} and 891 mg L^{-1} respectively towards downstream location 8. A similar trend was also shown by the soluble Al, which ranged from 8220 mg L^{-1} to 264 mg L^{-1} from

location 1 to downstream location 8. Soluble Mn loading was also highest at source and decreased gradually downstream.

Table 3.7 Chemical characteristics of the runoff drainage[#]

Loc.	Distance (m)	pH	EC dS m ⁻¹	SO ₄ ²⁻	Fe, mg L ⁻¹	Mn	Al
1	0	2.44	3.68	8300	17040	495	7940
2	10	2.83	2.77	6800	13400	423	5400
3	20	2.85	2.74	4680	8200	383	3940
4	30	2.80	2.27	4190	7100	381	3550
5	40	2.86	2.10	2900	4200	364	2980
6	50	2.88	2.12	3200	3700	323	3150
7	60	2.92	2.14	2660	2300	248	1770
8	70	3.12	1.81	2100	1600	140	1690

[#] Sample collected during short rainfall in November 1995.

The gradual decrease in the concentrations of SO₄²⁻, Fe, Al and Mn indicated that either there was mass dilution or mass adsorption on sediments of these species downstream. However, the drainage also contained a high sediment loading and as a result selective adsorption/precipitation of metal ions are likely to effect the downstream concentration.

The cumulative loading of Fe, Mn, Al and SO₄²⁻ in the runoff drainage water are shown in Figure 3.10b. The maximum cumulative loading of SO₄²⁻, Fe, Mn and Al at 70 m distance were 34830 mg L⁻¹, 57540 mg L⁻¹, 2757 mg L⁻¹ and 34020 mg L⁻¹ respectively. Although the cumulative loading of these elements indicated toxic levels, the extent of exponential reduction due to dilution with increasing distant and with increasing volume of flow is going to be major factor in affecting the final drainage water quality. Overall, the cumulative concentrations of SO₄²⁻, Fe, Al and Mn followed a logarithmic trend with distance (x) away from source of the drainage as explained by the following equations.

$$\text{SO}_4^{2-} = 12884 * \text{Log}(x) + 6878, R^2 = 0.99 \quad [8]$$

$$\text{Fe} = 20047 * \text{Log}(x) + 17041, R^2 = 0.99 \quad [9]$$

$$\text{Al} = 11106 * \text{Log}(x) + 6442, R^2 = 0.98 \quad [10]$$

$$\text{Mn} = 1143 * \text{Log}(x) + 259, R^2 = 0.96 \quad [11]$$

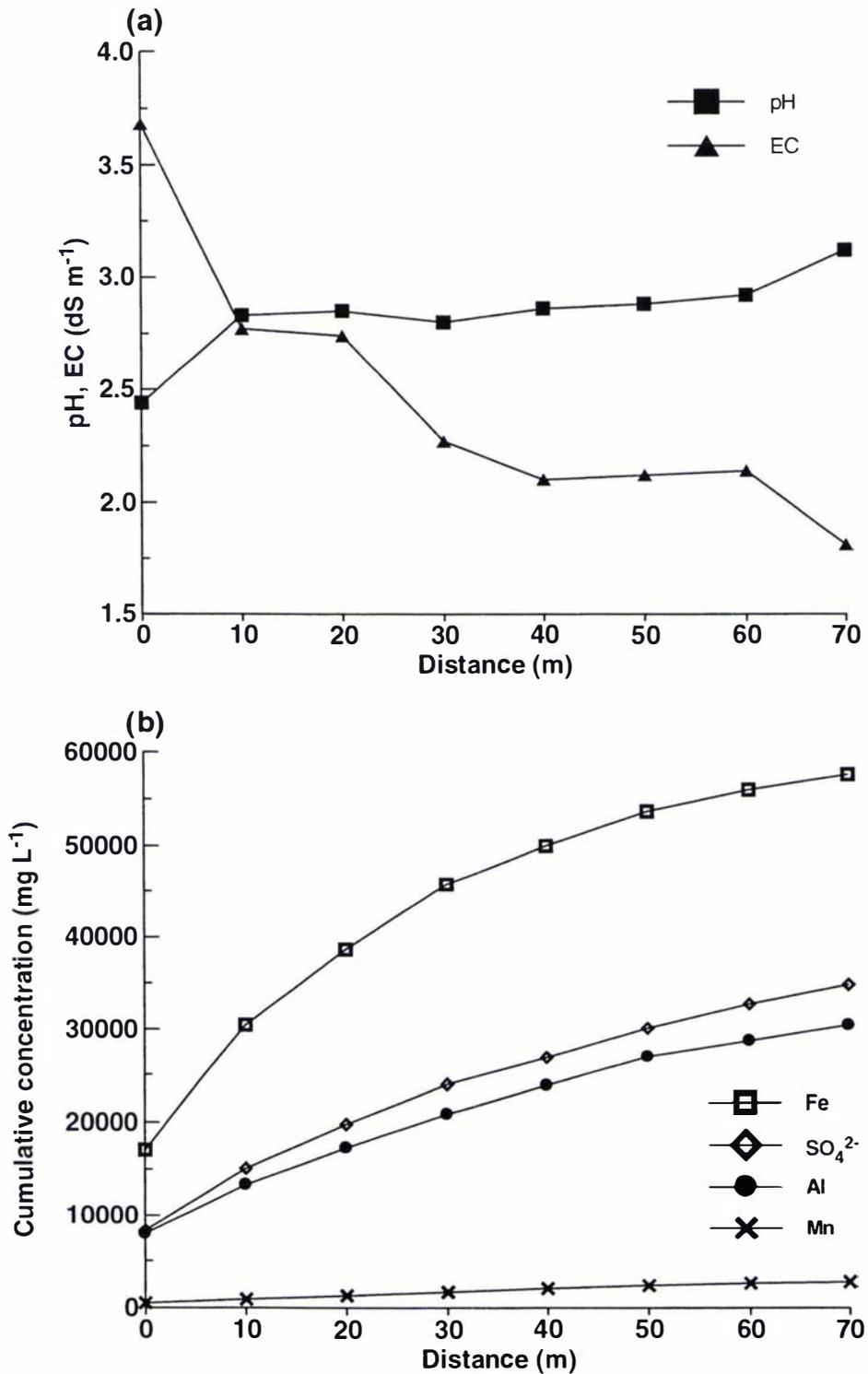


Figure 3.11 Chemical characteristics of the run-off drainage. (a) pH and EC (b) cumulative loading of Fe, SO₄²⁻, Al and Mn.

The rainfall event had occurred for a brief period (1.5 hours) after a spell of dry weather. The runoff water thus had the effect of flushing accumulated salts. The rapid dissolution of salts, formed during dry periods by surface evaporation is the likely cause of elevated levels of metal ions at source. Salt formation during dry periods [(mainly alunite: $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, epsomite: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and jarosite: $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$] was evident in column tests. Although metal and salt loadings in the drainage water are likely to decrease with distance and flow volume, the intensity and frequency of rainfall are going to be important factors affecting loading capacity of the drainage. The pitwall is prone to drying out under low rainfall conditions, resulting in the precipitation of metal salts on the surface. During rainfall events, periodic flushes of AMD pollutants can be expected and may temporarily exceed toxic levels for some metals.

The runoff drainage also contained a significant sediment loading. Although not reflected in the water analysis, large amounts of metal ions will be transported in the fine sediments as adsorbed species. With eventual increase in pH, these adsorbed metal species will desorb and co-precipitate with Fe as hydroxide sludge on drainage beds.

3.3.4 Spatial characterisation of the weathered pitwall rock

3.3.4.1 Geostatistics

Spatial properties of the parameters listed in Table 3.8 were investigated by use of geostatistical procedures. Estimates for the mean spatial values of the pitwall rock properties within a small rectangular block have been obtained by kriging using a linear semi-variogram model. Kriging is a geostatistical procedure based on the concept of regionalised variables and used to study spatial characteristics (Webster and Burgess, 1984). The method has been traditionally used for geochemical distribution of elements at a regional scale but in recent years it has found use in characterising spatial variability of soil chemical properties and crop yields (Bahri et al., 1993; Berndtsson et al., 1993; Persicani, 1995). Webster and Burgess (1984) have shown that data kriging can also be applied to small areas ($< 10000 \text{ m}^2$) with regular grid spacing and that minimum variance was observed when the *sampling interval* = *block length* / \sqrt{n} (Where n = sample size). In this study, the pitwall block size was 40 m x 30 m and therefore a sampling grid interval of ≤ 5 m and sample size of 47 was sufficient to provide values with standard errors $\pm 10\%$ of the mean.

The mean spatial value, $z(A)$, of the pitwall rock property, z , in a small rectangular shaped area A , is estimated from the observed values, $z(x_i)$ measured at grid points x_i where $i = 1$ to n . Thus,

$$z(A) = \sum_{i=1}^n w_i z(x_i), \text{ } w_i = 1 \text{ to } n \text{ are weights.}$$

Kriging is the procedure for finding the weights w_i and using them in the estimation of regionalised variables using a semi-variogram model. The semi-variogram, $\gamma(h)$, is a measure of the variance of the estimation of the sample value z at a location $(x+h)$ using the sample value measured at location (x) and is defined as (Berndtsson et al., 1993, Webster and Burgess, 1984):

$$\gamma(h) = \frac{1}{2} E\{[Z(x) - Z(x+h)]^2\}$$

where E is the expected value (mean) of $\gamma(h)$.

In the simplest case, the semi-variogram is linear and isotropic, at least over small distances (Webster and Burgess, 1984). Regression fits for $\gamma(h)$ for all the variables over a 40 m distance gave a linear relationship with regression coefficients (R^2) greater than 0.60 for most of the variables described in the spatial distributions. For a small area (1200 m²), sampled at grid interval of < 5 m, the variogram fits for 47 samples along the 40 m profile were sufficient to perform data kriging within a search radius of 18 m and standard error of < 10%.

3.3.4.2 Descriptive statistics

Descriptive statistics for the selected parameters of the pitwall used in the geostatistical analysis are shown in Table 3.8. The data showed that, in most cases, there was a wide variation in measured parameters. Weathered pitwall rock cover depth varied from a minimum of 5 mm on the top end of the pitwall to up to 330 mm towards the bottom end of the pitwall where colluvial deposition was highest. In some areas of the pitwall not covered by the grid, up to 600 mm of cover depth was observed. Moisture content ranged from 9.3 in upper slopes to 16.3% in lower parts of the pitwall where cover material was thickest. The pH was generally lowest in strongly weathered parts of the pitwall and ranged from 2.9 to a maximum of 4.3. The highest deviations from the mean ($n=47$) were

in cover depth, SO_4^{2-} , soluble Fe, soluble Mn, acidity and NAPP. The variations in Ca and Mg were relative to dissolution of carbonates and enrichment from dissolution of alkali feldspars. The distribution of pyrite also showed a wide variation, pyrite content ranging from 2.1 to 8.1%. While variability in cover depth is controlled by the physical aspects of the slope and local climatic conditions, variability in chemical parameters were most likely to be controlled by the reactive elements in the cover depth and mobilisation of these elements by AMD.

The degree of spatial interdependence of measured variables within the cover depth of the pitwall rock is reflected in the correlation coefficients shown in Table 3.9. Correlation coefficients, $r > 0.40$ were statistically significant at the probability level of $p < 0.005$. As expected, the moisture content in the cover depth is highly dependent on the depth of weathered cover material. Both cover depth and moisture content were significantly correlated ($p = 0.001$) with EC, Al, SO_4^{2-} , Fe, Mn, acidity and K.

At the same probability level, pH showed negative correlation with EC, Al and acidity indicating that the low pH conditions in the cover depth are buffered by mainly solubilised Al, and SO_4^{2-} salts of the metal ions. Acidity in the cover depth was found to be directly controlled by cover depth, moisture content, pH, EC, Al, SO_4^{2-} , Fe and Mn. It is interesting to note that K had a strong correlation with cover depth, moisture content, EC, Al, SO_4^{2-} , Fe, Mn and acidity. A large fraction of K released during weathering is probably retained in the cover depth as metal salt complexes with Al, Fe and Mn. The high linear correlation between Fe, Al and Mn is indicative that these elements coexist as hydroxide complexes as well SO_4^{2-} salts.

Magnesium content in the cover depth is proportional to the buffer acidity. Most of Mg would be derived from breakdown of ferromagnesian minerals with increasing acidity of the substrate. The strong correlation ($r = 0.71$) between FeS_2 and NAPP is expected since both are dependent on the total Fe and S content of the pitwall rock material.

Table 3.8 Descriptive statistics of spatial characteristics of the pitwall rock (n = 47).

Parameters	Unit	Mean	Median	SD	Min.	Max.
CD	Mm	137	150	102	5	330
MC	%	9.3	9.2	3.0	4.3	16.3
pH		2.9	2.8	0.6	2.0	4.6
EC	dS m ⁻¹	3.2	3.3	0.6	1.9	4.3
Exch. Al	cmol _c kg ⁻¹	7.4	7.3	1.5	4.8	10.8
Total Al	%	1.8	1.8	0.5	1.1	3.4
Total S	%	2.7	2.5	0.8	1.4	4.8
SO ₄ ²⁻	mg kg ⁻¹	2467	2500	453	1650	3400
Total Fe	%	2.7	2.7	0.6	1.5	4.1
Soluble Fe	mg kg ⁻¹	4084	4138	881	2506	5758
Soluble Mn	mg kg ⁻¹	342	323	102	203	635
Acidity	kg CaCO ₃ t ⁻¹	402	420	116	121	668
FeS ₂	%	5.0	5.1	1.4	2.1	8.1
NP	kg CaCO ₃ t ⁻¹	-10.5	-9.9	3.2	-19.4	-5.4
NAPP	kg CaCO ₃ t ⁻¹	74.4	68.0	24.4	35.4	143.0
Ca	cmol _c kg ⁻¹	4.4	4.1	1.8	1.8	9.5
Mg	cmol _c kg ⁻¹	1.8	1.6	0.6	0.8	3.2
K	cmol _c kg ⁻¹	0.6	0.6	0.2	0.3	1.0
Na	cmol _c kg ⁻¹	0.2	0.2	0.1	0.1	0.5

SD, standard deviation; CD, cover depth; MC, moisture content; EC, electrical conductivity, NP, neutralisation potential; NAPP net acid producing potential.

Table 3.9 Correlation coefficients of the selected parameters

	CD	MC	pH	EC	Al	SO ₄ ²⁻	Fe	Mn	Acidity	Ca	Mg	K	FeS ₂
MC	<u>0.83</u>												
pH	-0.38	-0.36											
EC	<u>0.74</u>	<u>0.72</u>	<u>-0.44</u>										
Al	<u>0.69</u>	<u>0.65</u>	<u>-0.44</u>	<u>0.57</u>									
SO ₄ ²⁻	<u>0.43</u>	0.36	-0.33	0.34	0.21								
Fe	<u>0.76</u>	<u>0.68</u>	-0.38	<u>0.72</u>	<u>0.61</u>	0.34							
Mn	<u>0.65</u>	<u>0.66</u>	-0.28	<u>0.51</u>	<u>0.57</u>	<u>0.41</u>	<u>0.44</u>						
Acidity	<u>0.61</u>	<u>0.53</u>	<u>-0.51</u>	<u>0.51</u>	<u>0.55</u>	<u>0.50</u>	<u>0.50</u>	<u>0.44</u>					
Ca	-0.07	-0.01	0.01	-0.03	0.01	0.20	0.08	-0.14	0.06				
Mg	0.37	0.22	-0.09	0.22	0.27	0.16	0.29	0.27	<u>0.41</u>	0.03			
K	<u>0.72</u>	<u>0.62</u>	-0.22	<u>0.56</u>	<u>0.56</u>	<u>0.41</u>	<u>0.49</u>	<u>0.60</u>	<u>0.43</u>	-0.26	0.22		
FeS ₂	-0.26	-0.31	0.19	-0.18	-0.20	0.05	-0.22	-0.11	-0.03	<u>0.43</u>	-0.13	-0.35	
NAPP	-0.27	-0.24	0.07	-0.02	-0.21	0.16	-0.12	-0.09	0.04	<u>0.49</u>	0.05	<u>-0.42</u>	<u>0.71</u>

Underlined coefficients are statistically significant at 5% significance level (n=47).

CD, cover depth, MC, moisture content

3.3.4.3 Distribution of cover material and moisture content

The distribution of weathered pitwall rock cover material and moisture content within the grid block are shown in Figures 3.12a and 3.12b respectively. Most of the cover material had accumulated at the bottom half of the pitwall as a 400 mm thick band of colluvial material deposited from erosion and gravity sliding. The cut and fill volume calculation approximated by trapezoidal rule (Golden Software Inc., 1994) gave a positive volume of 160 m³ of weathered cover material at the time of sampling. Taking 1.4 Mg m⁻³ as a mean bulk density of the material, the 1200 m² pitwall, contained 224 Mt of weathered cover material at the time of sampling. The volume calculated from a mean cover depth of 137 mm (Table 3.8) was 164 m³ (40 m x 30 m x 0.137 m), which gave 230 Mt of pitwall cover material. The kriged cover depth variability in the pitwall is thus well within the 10% standard error margin.

The moisture content of the cover material was directly related to the thickness of the cover material. This direct relationship is reflected in the high correlation coefficient of 0.83 between the moisture content and cover depth (Table 3.9). The pitwall cover material had a very low mean moisture content of 9.3% (with values ranging from 4.3 to 16.3 %) and was much lower than the field capacity value of about 14% for the bulk sample from maximum depth of colluvial deposition (600 mm). The high macroporosity of the cover material and the time of sampling (during a dry period) would have resulted in such low moisture contents. Towards the top half of the pitwall, where mean depth of weathered cover material was <100 mm, moisture content was generally < 5% whereas lower half of the pitwall had a mean moisture content of 15% (Figure 3.12).

Although, the lower half of the pitwall contained sufficient depth of weathered pitwall material to support plant root systems to a depth of about 300 mm, high macroporosity, very low moisture content and surface encrustation with salts during dry periods are likely to be the major physical constraints to plant growth.

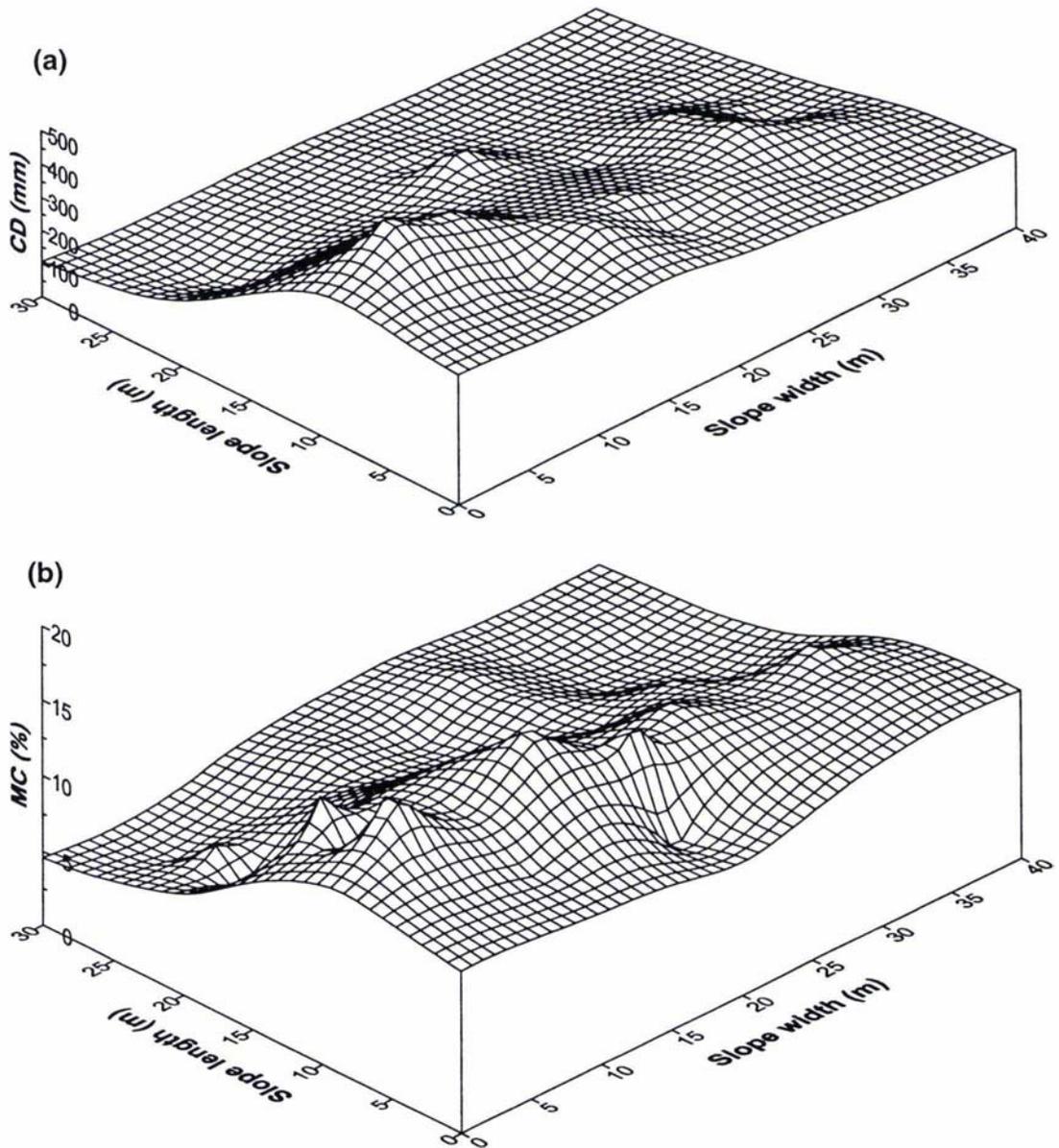


Figure 3.12 Distribution of (a) weathered pitwall rock cover depth (CD) and (b) moisture content (MC) of the cover material.

3.3.4.4 pH and EC

The spatial representation of the pH in the weathered pitwall rock is shown in Figure 3.13a. Generally, the lower half and the top left quadrant of the pitwall had pH < 3.0. The top right quadrant of the pitwall and certain areas in the lower half had peak pH of >3.5. Overall, the entire grid surface had a mean pH of 3.3 with a variance of 2.0 to 4.6. The high and low zones of pH were a result of varying degrees of weathering, dissolution of calcite and oxidation of liberated pyrite. The residence time of the weathered materials on the pitwall slope surface may influence the development of low pH micro-environments since static conditions give rise to a favourable environment for oxidants to oxidise liberated pyrite grains and for bacterial activity. Thus, the lower part of the pitwall with thickest colluvial deposit provided a stable environment for AMD generation, as indicated by generally low pH of < 3.0.

Electrical conductivity (EC) showed a very uneven spatial distribution throughout the gridded pitwall surface (Figure 3.13b). Except for the top left quadrant which had EC < 2.5 dS m⁻¹, the rest of the pitwall area had EC > 3dS m⁻¹. There were distinct high and low areas of EC levels indicating that salt levels are primarily determined by the distribution of SO₄²⁻ and buffer acidity. The mean EC was 3.2 dS m⁻¹, equivalent to 1.1% total soluble salt (total soluble salt = EC x 0.35) over an area of 1200 m². Salt levels in the weathered cover material are likely to vary seasonally. Since the grid samples were collected during a dry period, the distribution of soluble salt is likely to be less during a wet period when most of the precipitated salts will be transported down slope by the runoff water and enter the runoff drainage along the base of the pitwall.

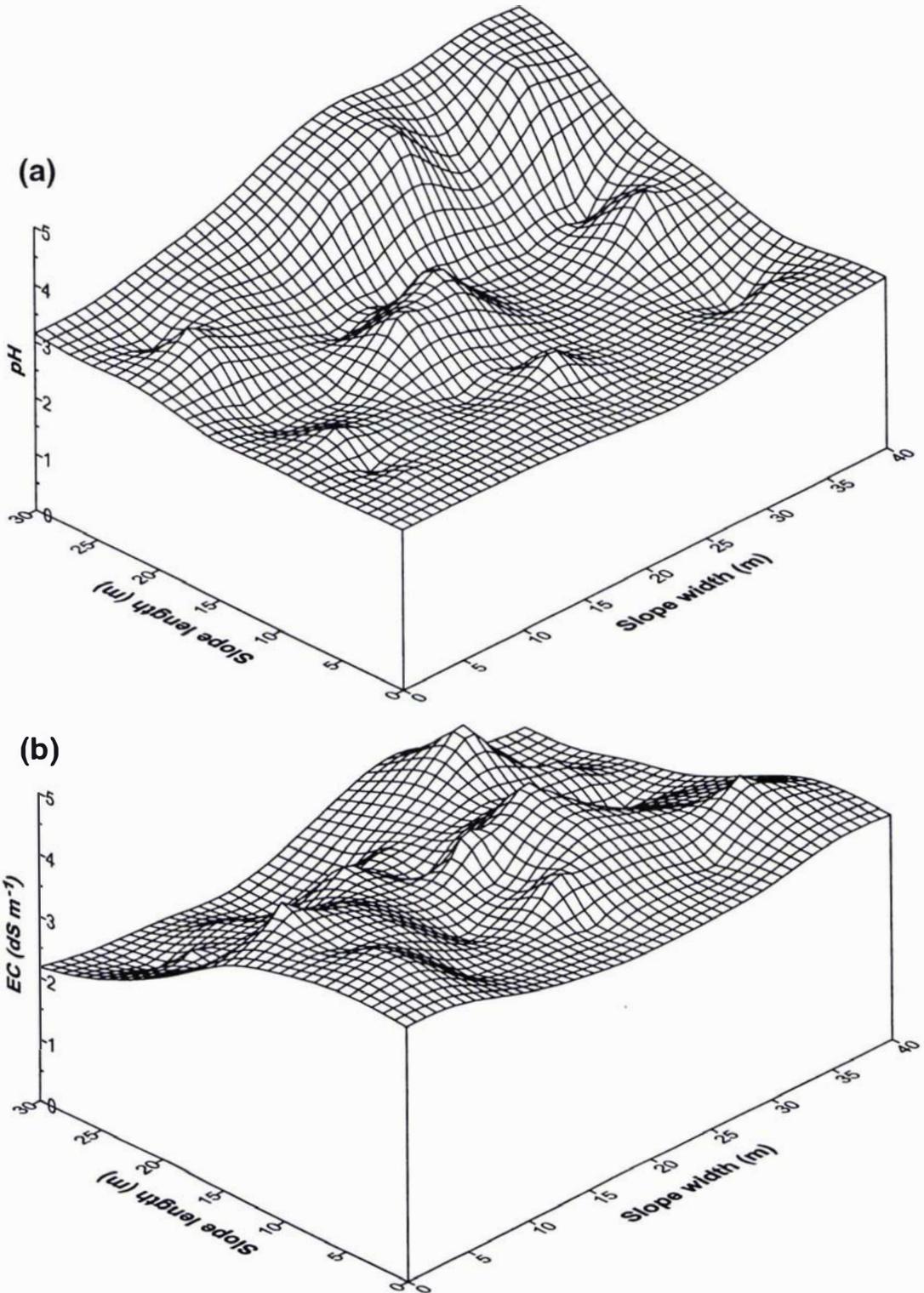


Figure 3.13 Spatial variations in (a) pH and (b) EC in the weathered pitwall cover material.

3.3.4.5 Exchangeable Al, soluble Fe and Mn

The level of exchangeable Al (Al_{exc}) in the weathered pitwall rock generally increased gradually down the slope of the pitwall (Figure 3.14a). Higher Al_{exc} levels were observed in lower parts of the pitwall where high acidity and accumulation of clay minerals facilitated greater mobilisation of Al species in pore water solution. The mean Al_{exc} content in the pitwall rock was $7.4 \text{ cmol}_c \text{ kg}^{-1}$ and ranged in value from 4.8 to $10.8 \text{ cmol}_c \text{ kg}^{-1}$ in an area of 1200 m^2 . At the time of grid sampling, the 1200 m^2 area of pitwall contained 149 kg of Al_{exc} .

The Al_{exc} has been identified as one of the main factors restricting the plant growth potential of unoxidised pitwall rock (Widdowson et al., 1984; Mason, 1996) as well as oxidised waste rock (Gregg and Stewart, 1990; Gurung et al., 1996) from Waihi mine. Aluminium phytotoxicity under low pH conditions has been well documented by several workers, notably Foy (1971), Hargrove and Thomas (1981) and Barcello et al (1996). Exchangeable Al $> 100 \text{ mg kg}^{-1}$ ($1.1 \text{ cmol}_c \text{ kg}^{-1}$) is considered a critical toxicity level for plant growth (Cameron et al., 1986; Percival et al., 1994; Barcelo et al., 1996). Although Al phytotoxicity in acid soils can be alleviated by the standard practice of liming (Shoemaker et al., 1961; Oats and Kamprath, 1983; Hern et al., 1988; Conyers, 1990; Slattery et al., 1995), phosphate addition (Alva et al., 1988; Loganathan et al., 1995) and organic matter complexation (Hargrove and Thomas, 1981; Hue et al., 1986, Young and Bache, 1985; Tan and Binger, 1986), the long-term amelioration of Al in the pitwall rock will no doubt depend on the control of AMD and alleviation of low pH environment. Soluble Al along with Fe and Mn are considered the major cations involved in keeping waste rock buffered at low pH (Luciuk and Huang, 1974; Huang, 1988; Sue et al., 1995). At $\text{pH} < 3.5$, the depletion of solution Al in pitwall rock by formation of salts like alunite with SO_4^{2-} , Al-hydroxy compounds and by leaching is going to be minimal in comparison with Al on exchange sites in the pitwall material.

The overall mean distribution of soluble Fe was 4084 mg kg^{-1} and ranged in value from 2506 to 5758 mg kg^{-1} . Soluble Fe distribution showed a broad band across the middle of the pitwall (Figure 3.14b). A large fraction of the soluble Fe in the weathered pitwall rock would be precipitated as hydroxide coatings (Plate 3.2), jarosite and copiapite during dry periods while dissolution of these precipitates during wet periods will release further

acidity in the system, resulting in very acidic AMD. Under acidic conditions, jarosite is probably precipitated in inter-granular spaces. Like Al, soluble Fe is also largely responsible for keeping the pitwall rock buffered at low pH. Although, from plant the growth point of view, soluble Fe is not a major toxicity concern, its involvement in the formation of jarosite at low pH can lead to storage of acid which is released during subsequent rainfall events.

The distribution of soluble Mn in the pitwall rock was generally higher towards the down-slope on the pitwall (Figure 3.14c). The mean distribution was 342 mg kg^{-1} and range was from 203 to 635 mg kg^{-1} . Because Mn is highly mobile, the distribution of Mn in the pitwall rock will largely depend on the distribution of amount of cover material and its moisture content. The dependence of Mn mobility on moisture content of soil has been suggested by Christensen et al. (1950). Because Mn exists in up to six oxidation states, its chemistry and mobility in acid soils is considered to be controlled by mainly the Eh-pH environment (Watzlaf, 1988b; Ritchie, 1989; Willet et al., 1992).

Soluble Mn is known to be toxic to both plant and aquatic biota (Helyar, 1978). The major concern about high levels of mobilised Mn in the pitwall rock AMD will be its entry into the drainage system. Liming has been shown to reduce the availability of Mn to plants (Sanchez and Kamprath, 1959; White, 1970). Its affinity to adsorption by soil aggregates has been shown to result in longer residence times (Ritchie, 1989).

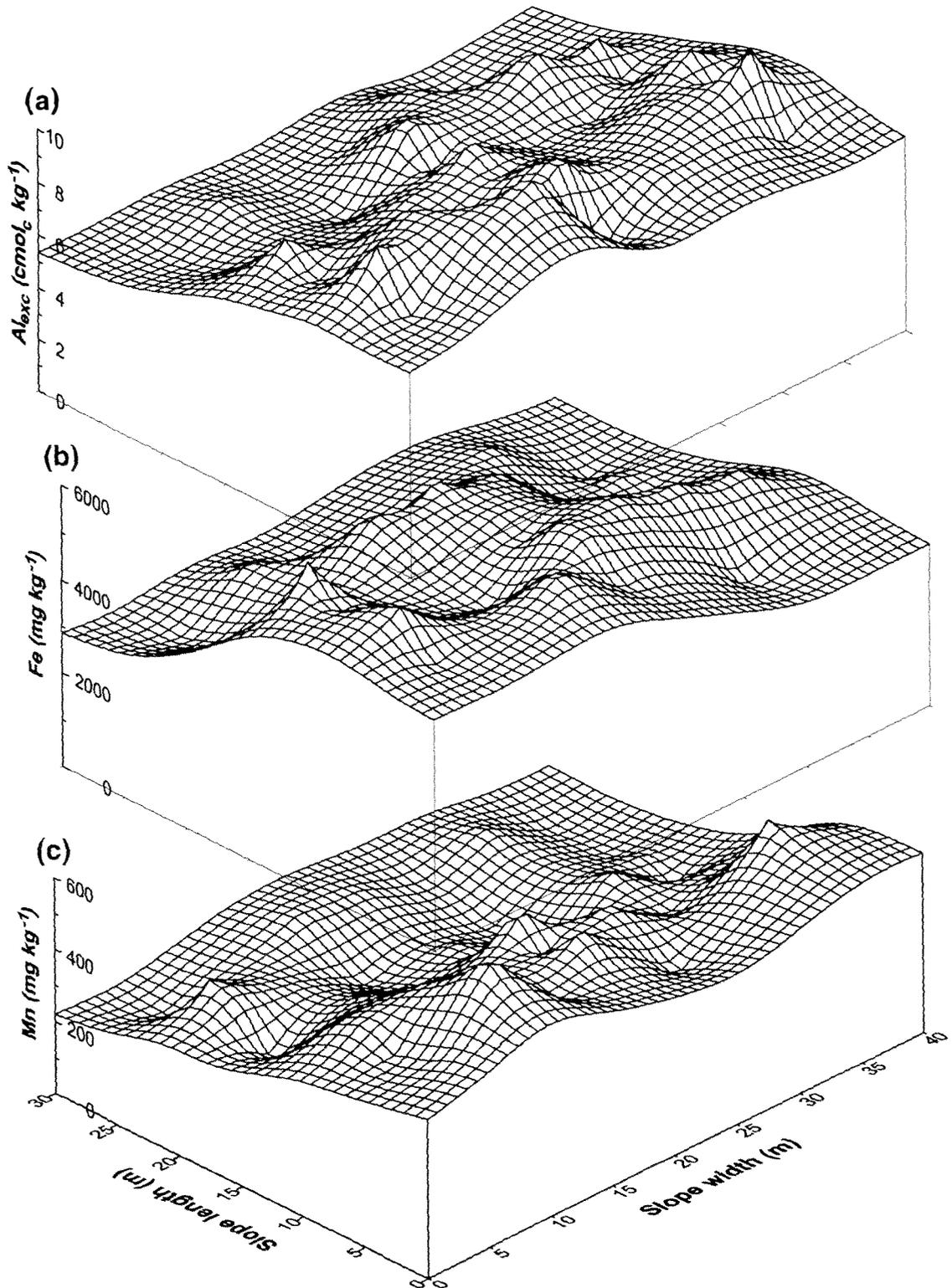


Figure 3.14 Distribution of (a) exchangeable Al (Al_{exc}), (b) Fe and (c) Mn in the weathered pitwall cover material.

3.3.4.6 SO_4^{2-} and Acidity

The distribution of SO_4^{2-} in the weathered pitwall cover material was spatially dependent and remained high throughout the pitwall area under study (Figure 3.15a). The mean distribution of SO_4^{2-} content was 2467 mg kg^{-1} although the top 5 m band width of the pitwall had a SO_4^{2-} content $< 2000 \text{ mg kg}^{-1}$. As with EC, there were areas of high and low SO_4^{2-} content and at any one time the SO_4^{2-} level in the pitwall cover material was dependent on the level of dissolved metals and acidity. However, at probability level $p < 0.003$, only Mn, K, acidity and cover depth were significantly correlated with the SO_4^{2-} content.

This may indicate that both Fe and Al were either highly mobilised under very acidic conditions or they may have formed interstitial and surface precipitates of hydroxides ($Fe(OH)_3$, $Al(OH)_3$) and stable salt complexes such as jarosite and alunite. The high correlation of Mn and K with SO_4^{2-} suggest that these elements exist mainly as sulphate complexes in the pitwall cover material.

Acidity levels in the pitwall cover material were $> 300 \text{ kg CaCO}_3 \text{ t}^{-1}$ throughout the grid area with the maximum being towards the lower areas of the pitwall (Figure 3.14b). The mean acidity level in the pitwall rock was $402 \text{ kg CaCO}_3 \text{ t}^{-1}$ and ranged from 121 to $668 \text{ kg CaCO}_3 \text{ t}^{-1}$. This corresponds to an equivalent of 90 t $CaCO_3$ equivalent acidity in the 1200 m^2 of pitwall having a mean cover depth of 137 mm at any one time. In terms of acid neutralisation, carbonate equivalent of 90 t of liming material will be required for an area of 1200 m^2 of pitwall. The level of acidity in the pit cover material was positively correlated at probability level $p = 0.002$ with cover depth, MC, EC, Al, SO_4^{2-} , Fe and Mn (Table 3.7b), and is consistent with low pH level of the pitwall surface (negative correlation).

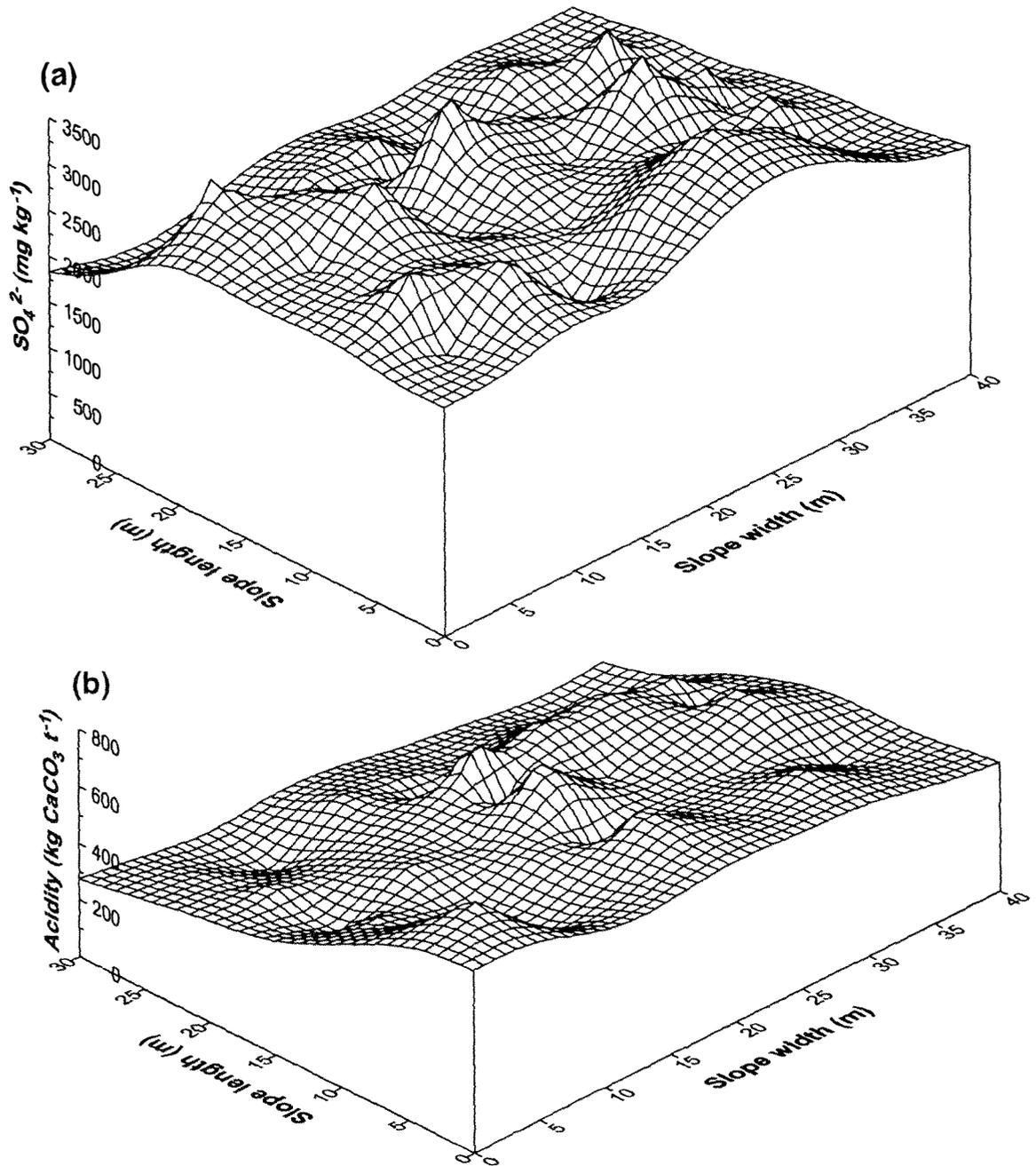


Figure 3.15 Distribution of (a) SO_4^{2-} and (b) acidity in the weathered pitwall cover material.

3.3.4.7 Total S and NAPP

Total S distribution in the weathered pitwall rock showed distinct topographical highs and lows in the 3-D surface plots (Figure 3.16a). The high total S areas corresponds to less weathered pitwall rock in which pyrite oxidation has not reached to advanced stage whereas the low areas contain significant amount of solubilised SO_4^{2-} (Figure 3.15a). The mean total S content over the 1200 m² grid area was 2.7% and ranged from 1.4 to 4.8%. This mean value was much higher than the value of 1.5% estimated for the pyritic waste by (Miller, 1986). However, Miller's data was from borehole composite fresh rock samples and therefore likely to show lower value from that of the weathered pitwall rocks in which liberated pyrite may form localised concentrations.

The distribution of NAPP characteristics of the pitwall rock is shown in Figure 3.15b. The mean NAPP in the weathered pitwall rock was 74.4 kg $\text{CaCO}_3 \text{ t}^{-1}$ and ranged from 35 to 143 kg $\text{CaCO}_3 \text{ t}^{-1}$. Since the NAPP values were derived from total S content, their distribution in the pitwall closely resembles the total S distribution. The NAPP values were significantly correlated with the Ca distribution ($r=0.49$, $p=0.002$) indicating possible acid neutralisation reactions of silicate minerals. On the other hand NAPP showed a negative correlation ($r= -0.42$) with K distribution, supporting the idea that K released from decomposition of primary K-bearing minerals may have gone in to formation of potash salts such as jarosite in acidic conditions.

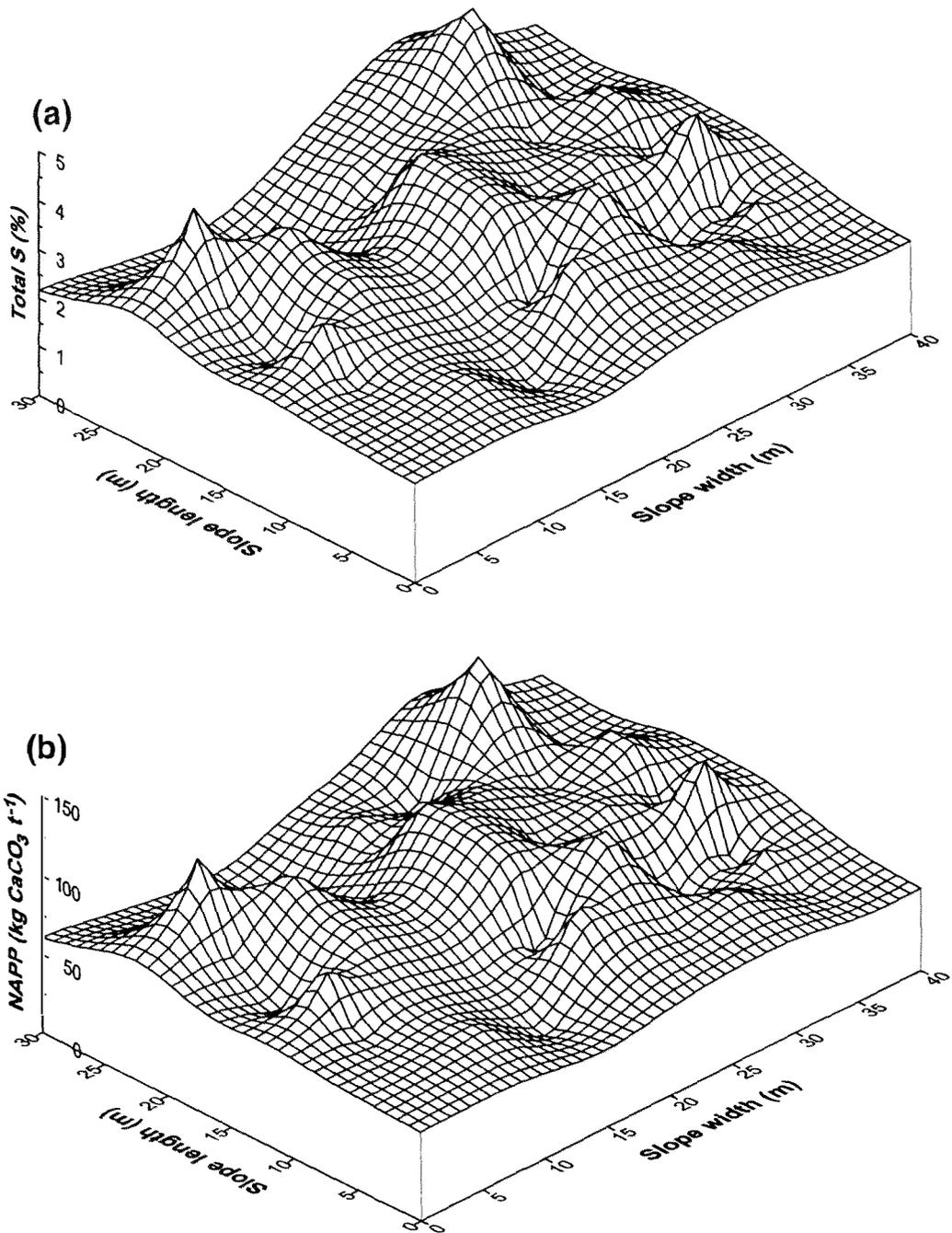


Figure 3.16 Spatial distribution of (a) total S content and (b) NAPP of the weathered pitwall rock.

3.3.4.8 Distribution of pyrite

Pyrite content was estimated stoichiometrically from the molar ratio of total Fe content in FeS_2 (where $\text{FeS}_2, \% = [\text{Fe}, \%] / 56 * 120$), assuming all the Fe is in the form of FeS_2 . The pyrite distribution showed an uneven pattern in the measured section of the pitwall (Figure 3.17). The mean pyrite content over the 1200 m² pitwall area was 5% and ranged from 2.1 to 8.1%. The distribution of cover depth and moisture content was not related to the distribution of pyrite in the weathered pitwall rock. Generally, the upper part of the pitwall appeared to contain a higher amount of pyrite. Weathered rock grain size and degree of liberation of pyrite during weathering may have greater control on distribution of pyrite content rather than the chemical control. Based on the mean spatial pyrite content of 5%, the 1200 m² of pitwall with 137 mm mean depth, contained about 11 t of pyrite.

A comparison of the pyrite contents estimated from various methods showed a wide variability in the pyrite contents (Table 3.10). The XRD and XRF analysis gave the highest mean values of 10.2 % \pm 4.8 % and 10.0 % \pm 1.6 respectively whereas pyrite content estimated from total S and total Fe were lower by about 20%. The pyrite content estimated from total S and total Fe gave similar values. The higher amounts of pyrite contents estimated from XRF and XRD analyses may be explained by the fact that a large part of total Fe consists of oxidised Fe^{3+} existing as dimorphs of pyrite. On the other hand, lower pyrite contents estimated from total S and Fe may reflect the incomplete extractions of S and Fe by bicarbonate digestion and 25% HCl extraction methods respectively.

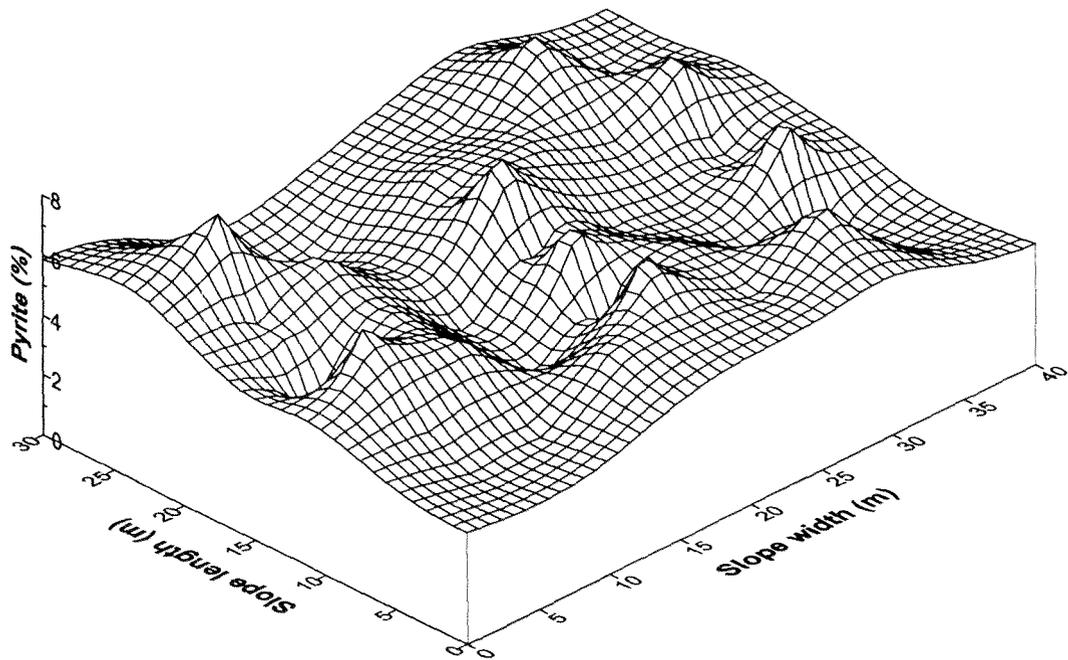


Figure 3.17 Distribution of pyrite in the weathered pitwall rock material.

Table 3.10 A comparison of pyrite estimation from various methods.

Method	Pyrite content (%)					Mean \pm SD
	PWR-1	PWR-2	PWR-3	PWR-4	PWR-5	
Total S	4.8	6.6	4.8	7.5	6.3	6.0 \pm 1.2
Total Fe	8.6	6.0	6.8	7.7	7.1	7.2 \pm 1.0
XRF [#]	12.6	8.6	10.3	9.6	8.8	10.0 \pm 1.6
XRD	10	16	6.8	14	4.3	10.2 \pm 4.8

[#] derived from weight % Fe_2O_3

3.3.4.9 Base cations (Ca, Mg, K and Na)

The distribution of base cations in the weathered pitwall rock followed a broad band of high and low concentration areas with Ca and Na showing a general depletion towards lower pitwall slopes (Figure 3.18). Both Mg and K showed relative enrichment towards lower slope areas of the pitwall. The trends in the distribution of the cations closely followed the high area trends of cover depth, moisture content (Figure 3.12a & b), SO_4^{2-} (Figure 3.15a), and the low pH zones (Figure 3.13a). The mean Ca, Mg, K and Na distributions were $4.4 \text{ cmol}_c \text{ kg}^{-1}$, $1.8 \text{ cmol}_c \text{ kg}^{-1}$, $0.6 \text{ cmol}_c \text{ kg}^{-1}$ and $0.2 \text{ cmol}_c \text{ kg}^{-1}$ respectively.

The distribution of Ca showed localised highs, indicative of possible calcite vein dissolution in these areas (Figure 3.18a). The mean Ca distribution was $4.4 \text{ cmol}_c \text{ kg}^{-1}$ (880 mg kg^{-1}) and ranged in value from 1.8 to $9.5 \text{ cmol}_c \text{ kg}^{-1}$. Both Mg and K tended to be higher towards lower slope areas where as Na was generally higher towards upper slope (Figure 3.18 b, c and d).

Most of the cations are the products of chemical weathering of the pitwall rock and as such would be expected to concentrate in the down-slope areas of the pitwall. Although most of the cations would be leached and lost into solution during progressive weathering of the pitwall rock, because of elevated levels of SO_4^{2-} in the sediment, some will be retained in the sediment as metastable sulphate salts, notably gypsum and hydrated MgSO_4 salts. Most of the K may be retained as weathering residual clays as well as incorporation into jarosite under low pH conditions. Exchangeable Ca and Na showed no spatial dependence with other parameters. The Mg content appeared to be spatially dependent ($r=0.41$, $p=0.002$) with the distribution of acidity in the pitwall rock. Exchangeable K distribution was also found spatially related with cover depth, moisture content, EC, Al, SO_4^{2-} , Mn and acidity.

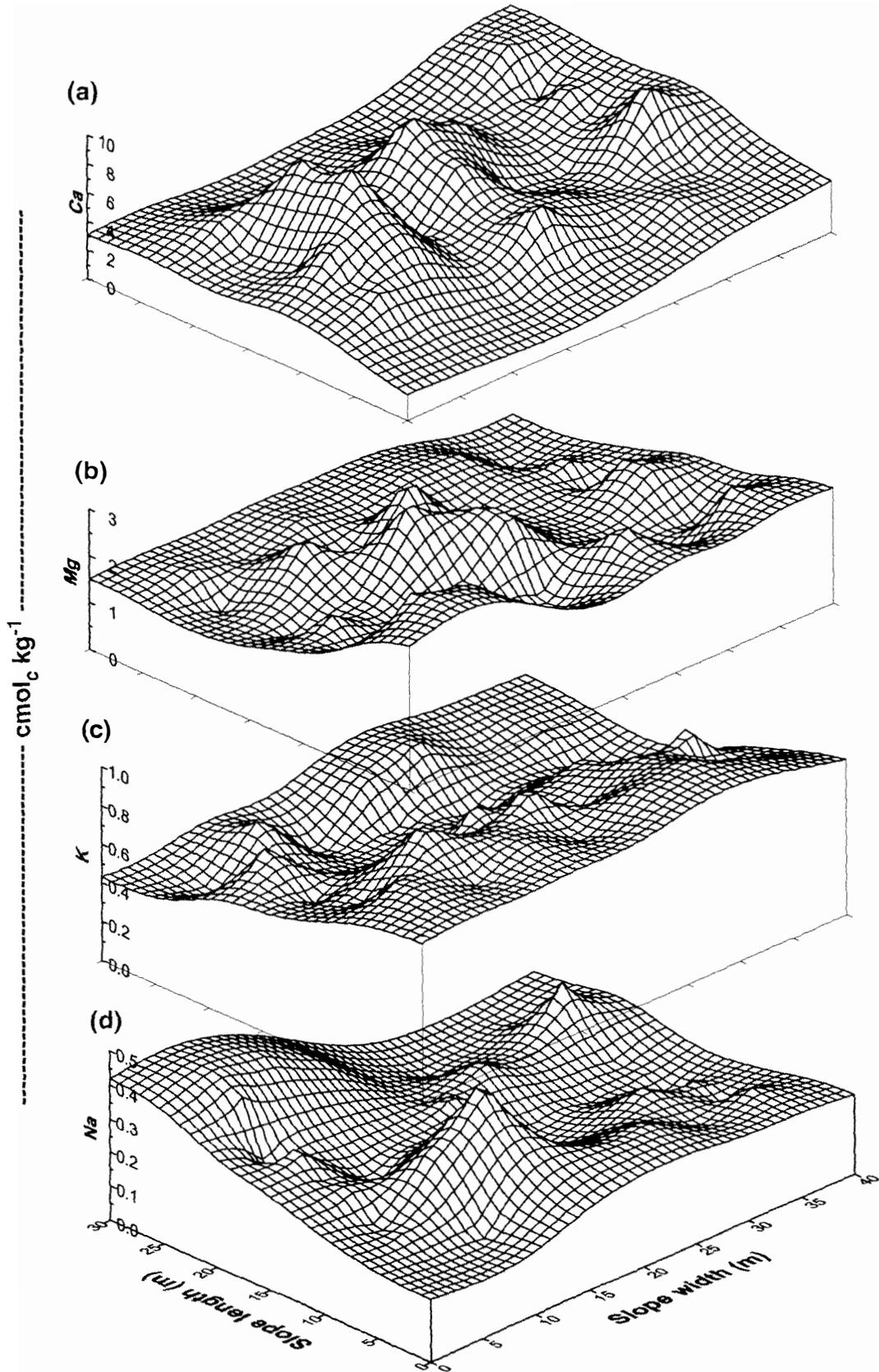


Figure 3.18 Spatial distribution of base cations (a) Ca, (b) Mg, (c) K and (d) Na in the weathered pitwall rock.

3.4 Conclusions

Spatial and geochemical characterisations of the pitwall rock undergoing various degrees of weathering showed that AMD has resulted in the creation of extremely low pH conditions with elevated levels of SO_4^{2-} , Fe, Mn and Al. Both physical (slope gradient, insufficient cover material and low moisture content) and chemical (H^+ , Al^{3+} and soluble salts) characteristics of the weathered pitwall rock are going to be major factors limiting plant growth potential of the pitwall rock. Progressive weathering of the pitwall rock resulted in depletion of base cations except for K, which showed relative enrichment due to formation of clays and jarosite type minerals.

ABA analysis indicated that irrespective of the degree of weathering, the pitwall rock showed a positive net acid producing potential (NAPP) and that the NAPP values were proportional to the amount of pyrite contained in the representative samples. Fresh pitwall rock had a NAGpH < 3 and NAPP of $51 \text{ kg CaCO}_3 \text{ t}^{-1}$ while strongly weathered samples showed a higher NAPP value of $82 \text{ kg CaCO}_3 \text{ t}^{-1}$, a possible effect of mass residual enrichment of unoxidised pyrite during weathering. Although pyrite grains and veins that are directly exposed undergo rapid oxidation to produce a very low pH in weathered pitwall rock, a significant amount of disseminated pyrite grains may not be immediately oxidised in the host rock and is likely to form an unoxidised pyrite concentrate as weathering progresses. Even with an advanced degree of weathering and oxidation, fine-grained pyrite crystals may remain 'entombed' in coarse-grained fractions of the pitwall rock and may thus eventually produce acid. A strongly weathered pyritic rock will therefore, still have the potential to generate acidity.

Mineralogical properties of the pitwall rock have a major control on AMD. Acid generation in the pitwall rock is time dependent as well as dependent on intensity of weathering and liberation of pyrite grains. Kinetic evaluation (NAG test) indicated that the pitwall rock has an estimated lag-period of 22 weeks prior to onset of acid generation from biochemical oxidation of pyrite. Since oxidative processes in acid generation involves micro-sites around pyrite grains, the nature and form of pyrite mineralisation has an important implication on the acid generating properties of the pitwall rock.

Low pH conditions were found to persist up to 60 cm depth in weathered pitwall rock. The levels of EC, SO_4^{2-} , Fe, Mn and Al were variable within the depth profile and the cause in variations are most likely to be due to distribution of liberated pyrite grains and favourable oxidation conditions. Runoff drainage from AMD-contaminated pitwall generally had very low pH and contained elevated levels of Fe, Mn, Al and SO_4^{2-} .

There was a definite spatial relationship in the distribution of pyrite oxidation products (Fe, SO_4^{2-} and acidity) in the weathered pitwall rock over an area of 1200 m². Cover material and moisture content were both positively correlated with the spatial distribution of pyrite oxidation products in the pitwall. Variations in the distributions of metals, salts and base cations indicated that the pitwall contained highly variable microenvironments, largely controlled by the distribution of pyrite and degree of liberation of pyrite grains during weathering of the pitwall rock.

The upper slope area of the pitwall generally had higher pH (>3), lower EC, SO_4^{2-} , acidity, Fe, Mn and exchangeable Al. This attribute of the pitwall rock may have been due to the less weathered materials at the upper pit slope area. While lower pit slope area contained thicker deposition of cover material for suitable amendments to be applied, the upper surface generally had lesser degree of AMD effects. Provided suitable depth of cover material can be retained on the slope surface by engineering modifications, the pitwall rock can be amended with acid neutralising materials, which are evaluated in Chapters 4, 5 and 6.

Any attempts to revegetate the pitwall must, therefore, overcome toxicity from H^+ and Al^{3+} species plus possible heavy metal and soluble salt effects. Both chemical and biological oxidation of pyrite must be controlled long enough for the establishment of suitable plant species and pH must be raised to provide a less hostile environment. Because mine pitwall slopes are often too steep for stabilised application of amendments, revegetation techniques have to be a combination of engineering, chemical and biological modifications along with the selection of plant material adapted to cope with the adverse physical and chemical conditions.

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

Acid mine drainage (AMD) from sulphidic mine waste rock dumps and open pits is a major concern in the rehabilitation of both active and abandoned mines associated with sulphide bearing ores. Numerous methods of acid neutralisation have been used with varying degree of success to abate AMD in pyritic coal refuge and mine waste rock dumpsites. Large amounts of limestone are commonly used for presumed long-term control of acid generation and reclamation of sulphidic mine wastes (Costigan et al., 1982, 1984; Pulford et al., 1984; Pulford, 1991; Dollhopf, 1992). Although liming initially helps establish plants, the rapid depletion of the neutralising material in a continually acid producing media may result in plant die-back. The relatively slow reactivity of coarse-grained limestone and the armouring effect from Fe-hydroxides may also result in reacidification (Gemmell, 1981; Costigan et al., 1984). While problems of reacidification may arise from underestimating the lime requirement, overliming with high rates of limestone can have a negative impact on plant growth due to Ca induced deficiency in plant available nutrients such as P, Mg and Cu (Costigan et al., 1982; Brady et al., 1990; Pulford, 1991).

Characterisation of the weathered pyritic pitwall rock material in Chapter 3 showed that low pH conditions resulting from oxidation of pyrite and associated high levels of SO_4^{2-} , Al, acidity and soluble salts are some of the chemical characteristics of the pitwall rock limiting plant growth. Geochemical characterisation showed that acid generation is active on the pitwall and the spatial distribution of low pH micro-environments is primarily controlled by the degree of pyrite oxidation and distribution of the weathered cover material. Metastable salts such as epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), alunite ($\text{KAl}_3(\text{SO}_4)_2$) and jarosite [$(\text{KFe}_3(\text{SO}_4)_2(\text{OH})_2$)] have been identified as common minerals likely to be formed at the surface during dry periods. The dissolution of salts like jarosite and

hydrolysis of Fe and Al during wet period may often result in the formation of free acidity, and thus keeping the pitwall rock buffered at a low pH at all times.

Neutralisation of strongly buffered acidic pyritic rocks therefore, requires consideration of both active and potential acidity to prevent reacidification as a result of continued oxidation of pyrite. An assessment of the effectiveness of various neutralising materials in reducing pitwall rock acidity and toxic elemental concentration is thus a primary step in ameliorating the low pH condition on the pitwall.

The primary objective of the incubation study reported in this section was to assess the ameliorating properties of selected neutralising materials added to partially oxidised pyritic pitwall rock. A second objective was to investigate the acid neutralising effectiveness of limestone particle size in partially oxidised pyritic rock material.

4.2 Materials and Methods

4.2.1 Pitwall rock bulk sample

Approximately 500 kg bulk sample of weathered pyritic pitwall rock was collected from a single location on the north face pitwall at Martha mine (Grid location PWGS-5, Figure 3.1). The bulk sample was air-dried and crushed to nominal 4 mm size prior to making into duplicate subsamples by coning and quartering. In this incubation study, the sample was further crushed to ≤ 2 mm fractions. The chemical properties of the pitwall rock bulk sample used in the incubation study are given in Table 4.1.

4.2.2 Neutralising materials

Limestone (LST) used in this study was obtained from a Te Kuiti limestone quarry (MacDonalds). The as-received limestone (LST_{AR}) had approximately 55% fines (≤ 2 mm). Slaked, fluidised bed boiler ash (FBA) was obtained from the Te Awamutu Milk Powder factory operated by the NZ Dairy Company. Reactive phosphate rock (RPR) used was North Carolina phosphate rock and dolomite (DOL) was commercial dolomite dust. Pure calcium carbonate used was of laboratory analytical grade. The physical and chemical characteristics of the neutralising materials are given in Table 4.2.

Table 4.1 Selected properties of the bulk pitwall rock

Properties	Units	Amount
pH (1:2.5 w/v soil to water)		2.1
Electrical conductivity (EC)	dS m ⁻¹	3.8
Total Fe (25% HNO ₃ -extractable)	%	3.7
Soluble Fe (0.1 M HCl-extractable)	mg kg ⁻¹	4100
Soluble Mn, (0.1 M HCl-extractable)	mg kg ⁻¹	328
Total S	%	3.36
Sulphate-S (SO ₄ ²⁻)	mg kg ⁻¹	7440
Acid producing potential (APP)	kg CaCO ₃ t ⁻¹	82
Acid neutralising capacity (ANC)	kg CaCO ₃ t ⁻¹	-8.0
Net acid producing potential (NAPP)	kg CaCO ₃ t ⁻¹	82
Exchangeable Al (Al _{exc})	cmol _c kg ⁻¹	14.9
Ca ²⁺	cmol _c kg ⁻¹	5.3
Mg ²⁺	cmol _c kg ⁻¹	1.3
K ⁺	cmol _c kg ⁻¹	0.7
Na ⁺	cmol _c kg ⁻¹	0.2
Base saturation (BS)	%	33
Olsen-P	mg kg ⁻¹	8.6
Moisture content	%	15
Bulk density	Mg m ⁻³	1.4

Table 4.2 Properties of selected neutralising materials.

Neutralising materials	Particle size (mm)	Equivalent, CaCO ₃ (%)	Neutralisation potential (NP) (kg CaCO ₃ t ⁻¹)
Limestone (LST)	≤ 0.5	95	1010
Dolomite (DOL)	≤ 0.5	114	1135
Fluidised bed boiler ash (FBA)	≤ 2.0	42	438
Reactive phosphate rock (RPR)	≤ 2.0	27	689

For RPR, ANC includes 419 t CaCO₃ from dissolution of RPR

4.2.3 Neutralisation potential (NP) of the neutralising materials

The NP of the neutralising materials was determined by treating a 0.5 g sample with 50 ml of 0.5 M HCl, heating nearly to boiling and swirling periodically until no gas (CO₂) evolution was observed. The samples were made up to 125 ml with distilled water, boiled for one minute, and cooled to room temperature. The treated sample was then back titrated with standard 0.5 M NaOH to pH 7 using a Mettler DL21 Autotitrator. The NP was calculated as the amount of HCl consumed by the sample and converted to units of kg CaCO₃ t⁻¹ material.

$$\text{NP (kg CaCO}_3 \text{ t}^{-1}) = \frac{50 \times [\text{volume HCl consumed, ml}] \times [\text{molarity of HCl}]}{\text{weight of the sample (g)}}$$

4.2.4 Lime requirement of the pitwall rock

The lime requirement of the pitwall rock bulk sample used in this study was determined by equilibrating the pitwall rock with both 1 M NaOH and pure CaCO₃ and obtaining their respective buffer curves. For the NaOH-pH buffer curve, 20 g of pitwall rock was incubated with 0 to 20 ml of 1M NaOH (with step-wise increments of 2 ml) for two weeks. The pure CaCO₃-pH buffer curve was obtained by incubating 200 g of pitwall rock with 10 rates of 0 to 10 g of CaCO₃ (equivalent to 0 to 50 kg CaCO₃ t⁻¹) for 60 days @ 20 °C and 80% moisture content.

Acidimetric titration was done in 10 g : 50 ml (pitwall rock to deionised water ratio) equilibrated overnight and titrated with 0.5 M NaOH to pH 8.2 using a Mettler DL21 Autotitrator. Titration curves for Al and Fe were obtained by titrating solutions containing 1000 mg L⁻¹ Al(NO₃)₃ and 400 mg L⁻¹ Fe(NO₃)₃ respectively.

4.2.5 Neutralising material requirements: an incubation study

Air dried pitwall rock bulk samples (200 g) were weighed into the plastic bags and mixed with varying CaCO₃ equivalent rates (C_{ER}) of the four neutralising materials used and incubated at 20 °C for 90 days. Moisture levels at 80% field capacity were maintained throughout the incubation period. The C_{ER} of neutralising materials added were in the range 0 to 50 kg CaCO₃ t⁻¹ with increment of 5 kg CaCO₃ t⁻¹.

The incubation experiment was a complete factorial design with 10 different C_{ER} of neutralising materials replicated 4 times. SAS for Windows software was used to perform relevant statistical analyses to test significant differences between treatment effect and C_{ER} effect.

4.2.6 Determination of limestone particle size effect on pitwall rock

A second set of incubation experiments was conducted to study the effective neutralisation properties of different particle sizes of limestone. Very fine limestone (LST_{VF}, < 0.5 mm), fine limestone (LST_F, 0.5-2 mm), coarse limestone (LST_C, 2-4 mm)

and as received limestone from quarry (LST_{AR} , $55\% \leq 2 \text{ mm}$) were incubated with bulk pitwall rock samples as per the method described above.

4.2.7 Characterisation of hydroxide coating on limestone particles

Various sizes (2 mm, 4 mm and 8 mm) of limestone grains were also incubated with pitwall rock for 90 days in order to quantify the amount of Fe, Al and SO_4^{2-} in their associated coatings. The coated grains were dissolved in 1 M HCl, filtered and the Fe, Al and S in the solution analysed by atomic absorption spectrometry (AAS) and sulphate Auto-Analyser respectively.

An 8 mm limestone grain incubated for 90 days was impregnated with epoxy resin, cut in half, polished and the surface carbon coated for scanning electron microscopy (SEM)/energy dispersion spectrometry (EDS) probe analysis for semi-quantitative elemental analysis.

4.2.8 Analytical methods

Chemical parameters were measured on air-dried samples after 45 and 90 days incubation. pH, electrical conductivity (EC), exchangeable Al (Al_{exc}), SO_4^{2-} , Fe, Mn and acidity were determined according to methods outlined in section 3.2.4 (Chapter 3).

4.3 Results and Discussion

4.3.1 Effectiveness of neutralising materials in acid neutralisation

4.3.1.1 Lime requirement of the pitwall rock

The NaOH and $CaCO_3$ equilibrated buffer curves for the pitwall rock used in this study indicated that a large amount of base was required to neutralise acidity because of the substantial buffer exerted by Fe and Al at pH range 2.0 to 4.5 (Figure 4.1a). The pitwall rock used in this study contained 4100 mg kg^{-1} soluble Fe, and exchangeable Al up to $15 \text{ cmol}_c \text{ kg}^{-1}$ (1350 mg kg^{-1}). At the pH range of the pitwall rock (2.0-4.5), a large amount of the base added was buffered by the precipitation of Fe and Al hydroxides. This is shown by the acidimetric titration of pitwall rock extract and solutions containing approximately equivalent concentrations of Fe and Al (Figure 4.1b). The horizontal section of the curves indicates the formation of metal hydroxides.

The increase in pH with incremental C_{ER} followed a sigmoidal logistic equation of the form shown below with accompanying table of respective regression coefficients.

$$y = y_0 + \frac{a}{1 + \left(\frac{x}{x_0}\right)^b}$$

	y_0	x_0	a	b	R^2
CaCO ₃ -pH	2.7	27	5.1	-12.0	0.99
NaOH-pH	2.3	557	8.9	-8.2	0.99

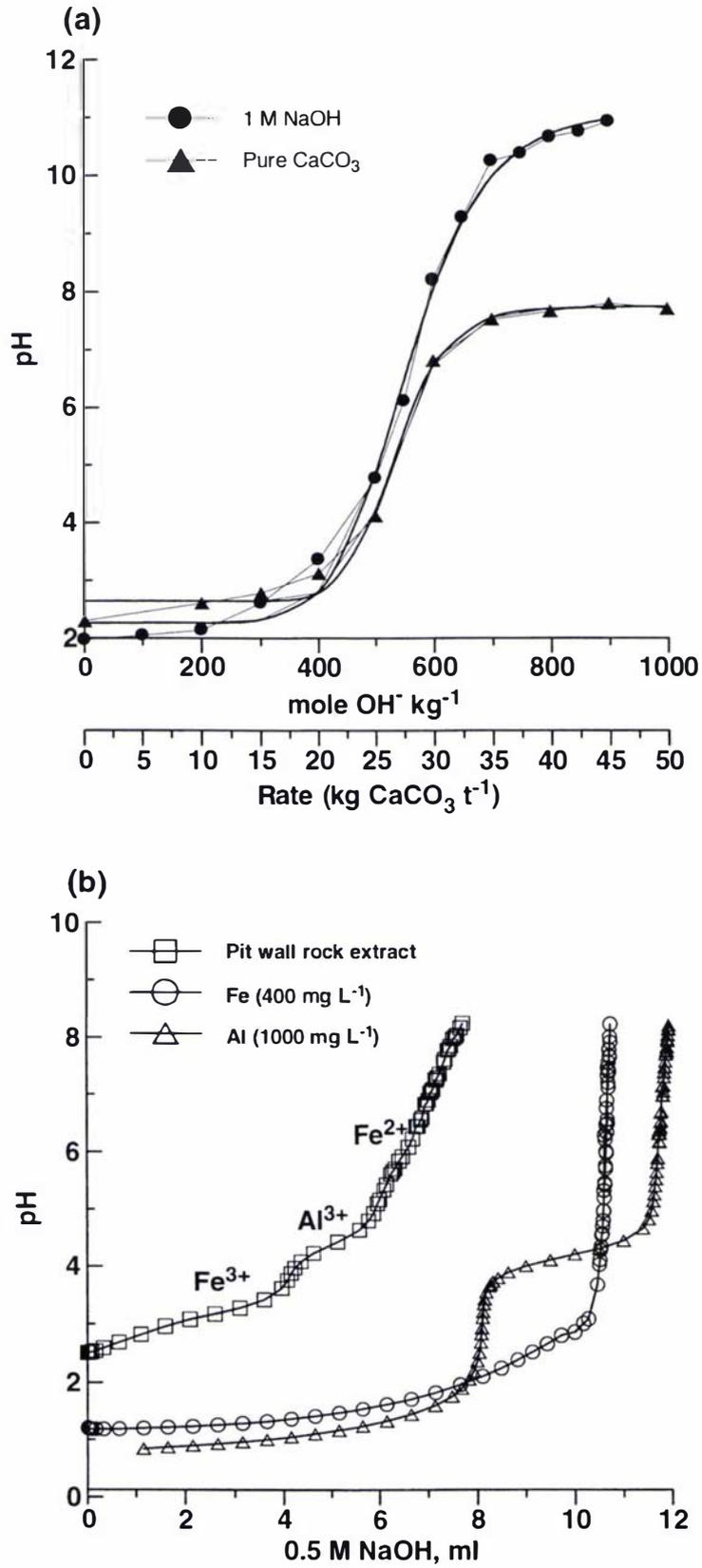
Where y = target pH, y_0 = initial pH, x_0 = minimum C_{ER} to overcome buffer requirement, x = C_{ER} required to reach target pH, a and b are regression coefficients.

The lime requirement predicted from the NaOH-pH and CaCO₃-pH buffer curves described above indicated that buffer lime requirements (LR_{Buffer}) of 29 kg CaCO₃ t⁻¹ pitwall rock was required to raise the pH > 6.0 (Figure 4.1a). This LR_{Buffer} however, only takes into account the neutralisation of active acidity and does not therefore assess the lime required to neutralise the acid generated from further oxidation of pyrite disseminated in larger fractions of the pitwall rock. The LR_{Buffer} therefore, grossly underestimated the lime requirement based on theoretical NAPP value of 82 kg CaCO₃ t⁻¹ pitwall rock determined by ABA. In order to account for the potential acid generation from pyrite oxidation, it is important that the lime required to neutralise the potential acidity (LR_{NAPP}) be included in the LR_{Buffer} to give “total lime requirement” (LR_{Total}). This LR_{Total} would thus be the true lime requirement for long-term control of acid generation in pitwall rock undergoing progressive weathering and oxidation.

The LR_{Total} of the pitwall rock that takes into account the neutralisation of both the active and potential acidity from further oxidation of unoxidised pyrite is thus :

$$\begin{aligned} LR_{Total} &= LR_{Buffer} + LR_{NAPP} \\ &= 29 \text{ kg CaCO}_3 \text{ t}^{-1} + 82 \text{ kg CaCO}_3 \text{ t}^{-1} \\ &= 111 \text{ kg CaCO}_3 \text{ t}^{-1} \text{ pitwall rock} \end{aligned}$$

The direct establishment of vegetation on the pyritic pitwall is entirely dependent upon acid neutralisation for both pH control and for reducing toxic levels of soluble metals. The assurance of long-term revegetation success demands that amelioration of low pH conditions be maintained for several years. Since it is impractical for subsurface



incorporation of liming materials into the reclaimed area on a regular basis, the LR_{Total} has to be met in a single treatment before the establishment of vegetation. However, application of large amounts of agricultural limestone may cause excess alkalinity, adversely affect the availability of phosphorus and trace elements and increase salinity of the pitwall rock by mass precipitation of metal sulphate salts. On the other hand, armouring effects of oxyhydroxides on the liming material may suppress its reactivity and thus provide a long-term slow release carbonate reserve to maintain pH at levels favourable to plant growth conditions.

Acidimetric titrations (Figure 4.1b) showed that a large part of the buffer lime requirement was induced by the co-precipitation of Fe and Al hydroxides and that only a small fraction of the lime requirement will be generated by the H^+ in the solution. This study showed that acidimetric titration of the pitwall rock not only determined the Fe-Al induced acidity but also the active acidity due to H^+ protonation. Such a titration curve may therefore be used to predict the neutralisation requirement of the pitwall rock active acidity. The pH range in which the pitwall rock is buffered is closely similar to the NaOH and $CaCO_3$ buffer range. From the acidimetric titration curve (Figure 4.1b), the amount of OH^- consumed to pH 6 was approximately $300 \text{ mmol } OH^- \text{ kg}^{-1}$ pitwall rock, which is equivalent to $30 \text{ kg } CaCO_3 \text{ t}^{-1}$. This value is similar to that obtained from NaOH and $CaCO_3$ buffer curves.

4.3.1.2 Neutralising material requirements of the pitwall rock

The rise in pH of the 90 days-incubated pitwall rock with increasing C_{ER} of neutralising materials followed a sigmoidal type log function (Figure 4.2) similar to that for buffer curves in Figure 4.1a. The respective regression coefficients for the equation are given in Table 4.3.

The comparative neutralising material requirements to raise pH >6 in 90 days incubated pitwall rock predicted from the above equation are presented in Table 4.4. Both LST and DOL were applied as fine materials ($\leq 0.5 \text{ mm}$) and may have therefore been completely dissolved to provide a quick pH response. Larger fractions ($\geq 2 \text{ mm}$) of these materials may not be as effective in neutralising pitwall rock acidity, as indicated by the limestone particle size effect (section 4.3.3.3). On the other hand, incorporation

of large amount of FBA may create highly alkaline conditions in the pitwall rock and this is likely to affect plant growth, causing an imbalance in the Ca/Mg ratio and phytotoxic salt concentrations.

The mean pH buffer curves presented in Figure 4.2 after 90 days of incubation showed that LST, DOL and FBA were comparable to pure CaCO_3 at same C_{ER} level of application in raising the pH to > 6. At a lower C_{ER} , however, DOL was significantly ($p=0.05$) more effective in acid neutralisation due to its higher neutralisation value but the trend was reversed at $C_{\text{ER}} > 30 \text{ kg CaCO}_3 \text{ t}^{-1}$. There was no further significant increase in pH at $C_{\text{ER}} > 30 \text{ kg CaCO}_3 \text{ t}^{-1}$ for LST, DOL and FBA. On the other hand, although RPR significantly ($p = 0.05$) raised the pH to 4.2 from a control pH value of 2.3, it was unable to raise the pH to 6.0, even at the highest C_{ER} of $50 \text{ kg CaCO}_3 \text{ t}^{-1}$.

The incubation experiment showed that although RPR had a higher theoretical NP value than FBA, it was ineffective in neutralising pitwall rock acidity. The theoretical liming value from complete dissolution of North Carolina RPR (1 kg of P dissolved from RPR has an estimated liming value of 3.2 kg CaCO_3) is estimated to be $536 \text{ kg CaCO}_3 \text{ t}^{-1}$ based on 13.1% P and 11.7% CaCO_3 (Bolan, 1995). It is likely that only the carbonate fraction of the RPR was responsible for neutralising the pitwall rock acidity. Acid neutralisation through dissolution of RPR and adsorption of H_2PO_4^- to Fe and Al hydroxides through ligand exchange processes and subsequent release of OH^- may thus be negligible. However, formation of Fe and Al phosphate compounds may reduce the activities of these ions in the acid solution.

Incorporation of RPR to neutralise pitwall rock acidity may have the beneficial effect of providing a slow release, long-term acid neutralisation effect as well as reducing the oxidant (Fe^{3+}) level and raising the P content of the pitwall rock. Furthermore, laboratory studies have shown that FePO_4 coating of pyrite grains can effectively control further oxidation of pyrite (Evangelou, 1994 & 1995; Fytas et al., 1994; Georgopoulou et al., 1995 & 1996). However, application of RPR at a very high rate (LR_{Total} of 630 t ha^{-1}) on the pitwall is unlikely to be cost effective viable option (at a current price of $\text{NZ\$}200 \text{ t}^{-1}$).

Table 4.3 Non-linear regression coefficients for pH-C_{ER} curves

	y ₀	x ₀	a	b	R ²
LST	2.43	27	5.26	-5.12	0.99
DOL	2.69	20	4.33	-6.03	0.99
FBA	2.41	26	5.21	-7.16	0.99
RPR	2.44	40	3.11	-2.26	0.99

Where y = target pH, y₀ = initial pH, x₀ = minimum C_{ER} to overcome buffer requirement, x = C_{ER} required to reach target pH, a and b are regression coefficients.

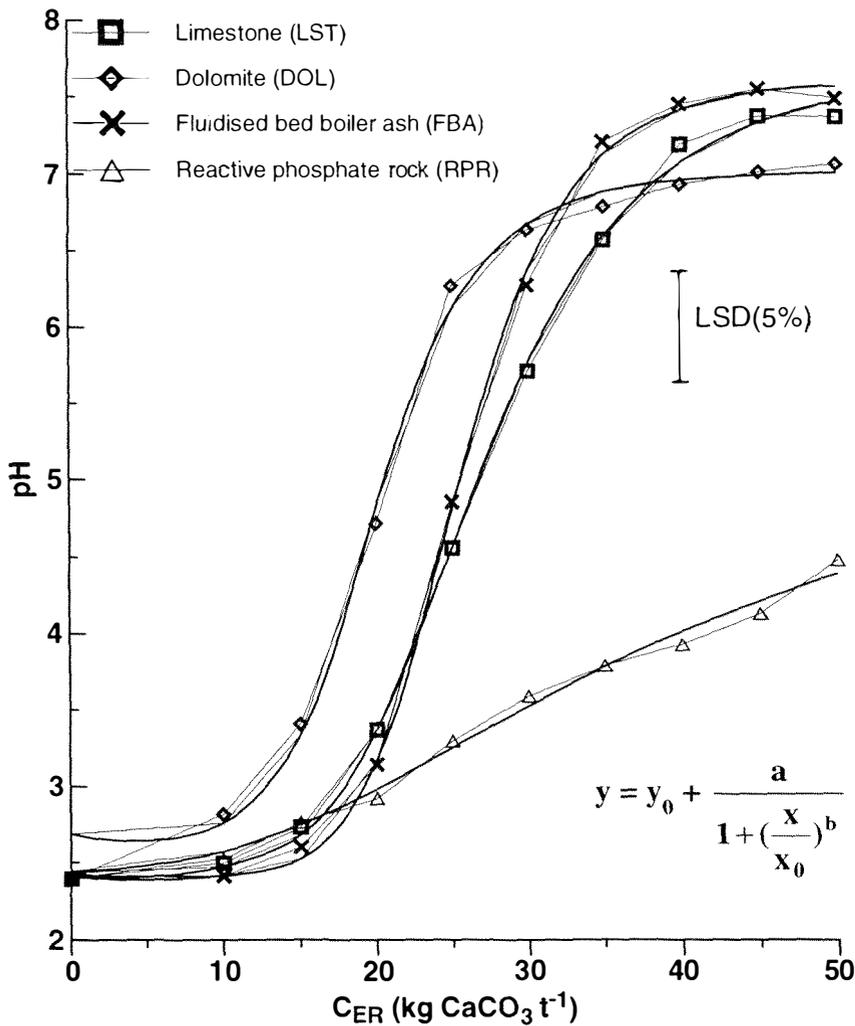


Figure 4.2 Response to pH with increasing carbonate content equivalent rate (C_{ER}) of neutralising materials.

Table 4.4 Neutralising material required to raise pH>6 in pitwall rock.

Neutralising materials	LR _{Buffer} (C _{ER}) kg CaCO ₃ t ⁻¹	CaCO ₃ equivalent (%)	Actual rate kg t ⁻¹	LR _{Total} kg t ⁻¹
CaCO ₃	29	100	29	111
LST	32	95	34	120
DOL	25	114	22	94
FBA	30	42	71	266
RPR*	88	27	326	630

* Extrapolated rate ($\text{pH} = 0.04 * C_{\text{ER}} + 2.22$, $R^2 = 0.97$). Actual rate is based on the CaCO₃ (%) equivalent of the neutralising materials (Table 4.2). $\text{LR}_{\text{Total}} = \text{LR}_{\text{Buffer}} + \text{LR}_{\text{NAPP}}$ (equivalent).

4.3.1.3 Neutralisation of acidity

Overall, there was a significant ($p=0.05$) reduction in acidity in the pitwall rock material treated with neutralising materials compared with that of the control with nil treatment. The effectiveness of neutralising materials in reducing acidity in 90 days-incubated pitwall rock is shown in Figure 4.3a. Acidity in the pitwall rock was reduced to $\leq 50 \text{ kg CaCO}_3 \text{ t}^{-1}$ at $C_{\text{ER}} = 30 \text{ kg CaCO}_3 \text{ t}^{-1}$ for all the treatments except for RPR treated pitwall rock in which it remained above $75 \text{ kg CaCO}_3 \text{ t}^{-1}$ at the same C_{ER} . However, at $C_{\text{ER}} \geq 40 \text{ kg CaCO}_3 \text{ t}^{-1}$ all the amendments gave similar values. At a C_{ER} of $30 \text{ kg CaCO}_3 \text{ t}^{-1}$, the overall reduction in acidity in the 90 days incubated pitwall rock was 85%. The rate of decrease in acidity of the pitwall rock was more rapid with DOL and FBA than with either LST or RPR at low rates ($C_{\text{ER}} < 20 \text{ kg CaCO}_3 \text{ t}^{-1}$) of neutralising materials. In the case of RPR, some of the phosphate released during dissolution may be used up in the formation of Fe-PO₄ and Al-PO₄ compounds and therefore the total neutralisation potential would be much less than the theoretical value of $689 \text{ kg CaCO}_3 \text{ t}^{-1}$.

The net neutralisation of acid will depend on the rate of dissolution of the carbonate fractions of the neutralising materials (LST, DOL, FBA and RPR). Gypsum and portlandite in FBA are far more soluble and faster reacting than either LST or RPR and hence the greater reduction in acidity. The overall comparison of the effectiveness of neutralising materials in the reduction of pitwall rock acidity showed that at $C_{\text{ER}} > 30 \text{ kg CaCO}_3 \text{ t}^{-1}$, all the neutralising materials were equally effective in reducing the acidity of the 90 days incubated pitwall rock. (Figure 4.3b).

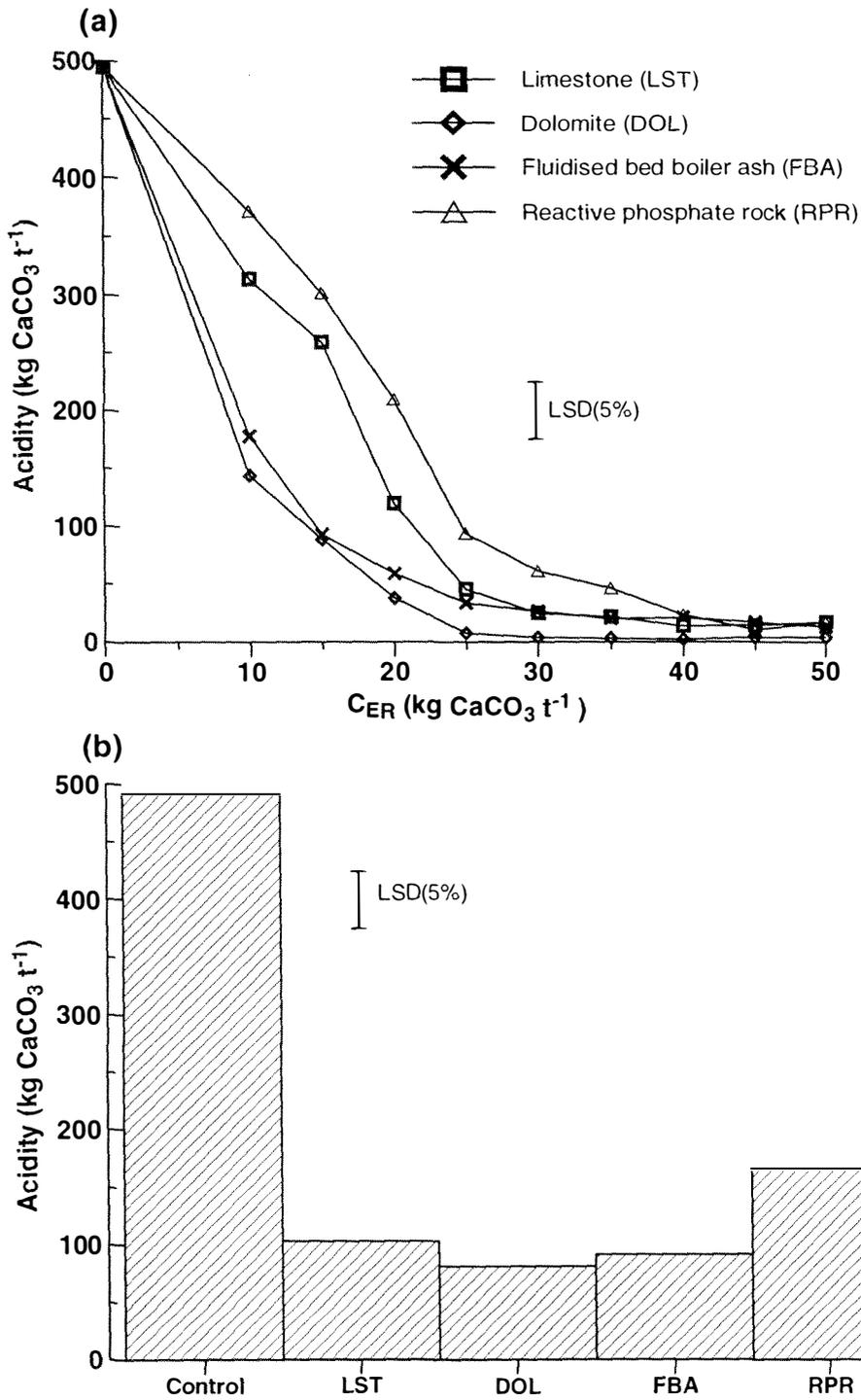


Figure 4.3 Reduction in acidity in 90 days incubated pitwall rock (a) with varying C_{ER} and (b) overall comparison between neutralising materials.

4.3.2 Effect of neutralising materials on chemical properties of the pitwall rock

4.3.2.1 pH

The response of pH with increasing rates of application of neutralising materials was similar for LST and FBA and both required C_{ER} of about $20 \text{ kg CaCO}_3 \text{ t}^{-1}$ to satisfy the buffering exerted by co-precipitation of Fe and Al at $\text{pH} < 3.5$ (Figure 4.2). In contrast, DOL required only half as much C_{ER} to satisfy the buffer. The rate of increase in pH was significantly ($p = 0.05$) greater for DOL compared with other treatments. At $C_{ER} > 30 \text{ kg CaCO}_3 \text{ t}^{-1}$, the neutralising effects of LST, DOL and FBA was restricted and there was no further increase in pH. Even with highly alkaline FBA, the pH did not rise above 7.3 at higher rates of application. This may be due to excessive precipitation of Fe hydroxide, which could reduce the reactivity of these neutralising materials. The pH in RPR treated pitwall rock increased linearly ($\text{pH} = 0.04 * C_{ER} + 2.22$, $R^2 = 0.97$) and the maximum pH reached was 4.3 at the highest rate of application ($50 \text{ kg CaCO}_3 \text{ t}^{-1}$). The regression coefficients in Table 4.3 suggest that application of RPR at $C_{ER} > 50 \text{ kg CaCO}_3 \text{ t}^{-1}$, may not result in a significant increase in pH.

4.3.2.2 Electrical conductivity (EC)

The pitwall rock initially maintained a very high level of EC (3.6 dS m^{-1}), equivalent to a total dissolved salts content of 1.3%. Although 90 days incubation of the pitwall rock with neutralising materials significantly reduced the EC to $< 2.5 \text{ dS m}^{-1}$ at $C_{ER} 30 \text{ kg CaCO}_3 \text{ t}^{-1}$, it was not possible to reduce the EC levels to $< 2 \text{ dS m}^{-1}$, even at the highest C_{ER} of $50 \text{ kg CaCO}_3 \text{ t}^{-1}$ (Figure 4.4a). The EC in FBA treated pitwall rock was significantly ($p=0.05$) higher than the LST treated pitwall rock at $C_{ER} > 30 \text{ kg CaCO}_3 \text{ t}^{-1}$. There was no significant difference in the reduction of EC among LST, DOL and RPR. Since FBA contains both gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and portlandite ($\text{Ca}(\text{OH})_2$), the solubilised gypsum would have contributed to elevated levels of EC in the pitwall rock for this treatment.

There was a linear decrease in EC with increasing rates as indicated in the regression equations 1- 4. The lower regression correlations for DOL and FBA were due to higher solubilities of these neutralising materials and precipitation of Mg^{2+} and Ca^{2+} with SO_4^{2-} to form MgSO_4 and CaSO_4 respectively.

$$\text{LST, EC} = -0.03 * C_{\text{ER}} + 3.35, R^2 = 0.95 \quad [1]$$

$$\text{DOL, EC} = -0.02 * C_{\text{ER}} + 3.31, R^2 = 0.88 \quad [2]$$

$$\text{FBA, EC} = -0.02 * C_{\text{ER}} + 3.52, R^2 = 0.89 \quad [3]$$

$$\text{RPR, EC} = -0.02 * C_{\text{ER}} + 3.38, R^2 = 0.95 \quad [4]$$

In pitwall rock which contains elevated levels of SO_4^{2-} , Fe and Al, a large part of the applied neutralising materials will be consumed in satisfying the large buffering demand by the formation of Fe and Al hydroxides. Formation of gypsum with the increasing amount of Ca^{2+} will initially consume acid but it may have the undesirable effect of raising the salt concentration, as indicated by the slow decrease in EC levels (Figure 4.4a).

4.3.2.3 Exchangeable Al (Al_{exc})

Incubation with neutralising materials caused a sharp decrease in Al_{exc} content of the pitwall rock and there was no significant difference between the treatments (Figure 4.4b). There was however, a significant ($p=0.05$) reduction in Al_{exc} from a control value of $14 \text{ cmol}_c \text{ kg}^{-1}$ to less than $2 \text{ cmol}_c \text{ kg}^{-1}$ in the treated pitwall rock after 90 days of incubation period at a C_{ER} of $30 \text{ kg CaCO}_3 \text{ t}^{-1}$. The maximum reduction in Al_{exc} was in the C_{ER} range of 10 to $20 \text{ kg CaCO}_3 \text{ t}^{-1}$. At this rate, DOL and FBA were the most effective whereas the reduction of Al_{exc} in LST and RPR treated pitwall rock were significantly less ($p=0.05$). Overall, the decrease in Al_{exc} showed an exponential (function) trend with increasing rates.

Since the concentration of Al in soil solution is highly pH dependent, the observed reduction of Al_{exc} at a buffer lime requirement ($\text{LR}_{\text{Buffer}}$) rate of $30 \text{ kg CaCO}_3 \text{ t}^{-1}$ is sufficient to ameliorate Al toxicity in the weathered pitwall rock material. Highly acidic conditions in pitwall rock resulting from oxidation of FeS_2 increases both soluble and Al_{exc} concentration whereas introduction of neutralising materials to increase pitwall rock pH has the opposite effect. The results of this incubation study showed that, irrespective of type of neutralising materials used, Al_{exc} in the pitwall rock can be effectively reduced to levels $\leq 2 \text{ cmol}_c \text{ kg}^{-1}$ at C_{ER} of $30 \text{ kg CaCO}_3 \text{ t}^{-1}$.

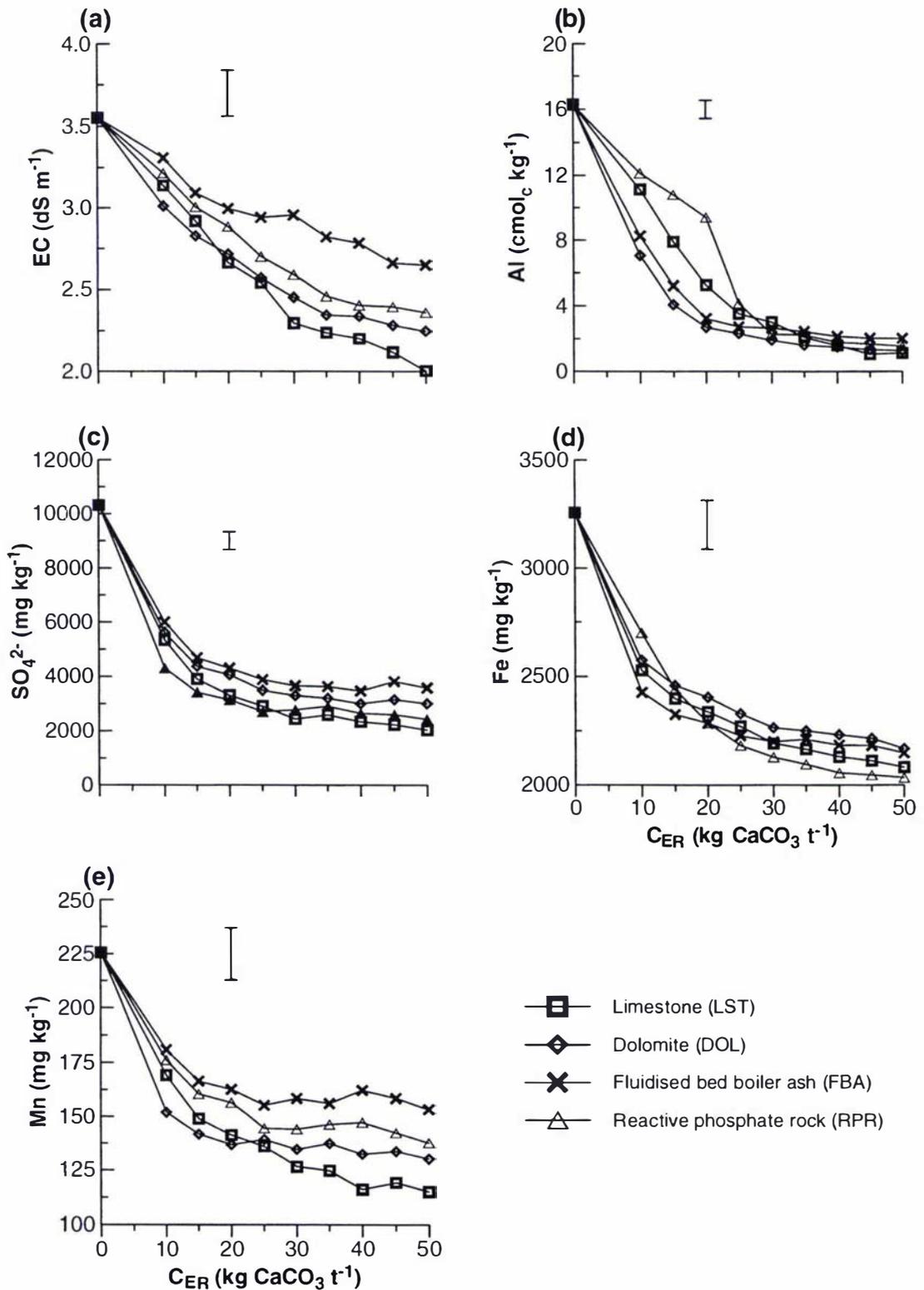


Figure 4.4 Effect on selected chemical properties of the pitwall rock after 90 days incubation with varying C_{ER} of neutralising materials. Vertical bars represent interaction LSD(5%).

The importance of Al in soil acidity and its physiochemical effects on plant growth is well recognised (Foy, 1971; Wright, 1989). Liming acid soils has been shown to significantly reduce Al_{exc} (Reeve and Sumner, 1972; MacLean et al., 1992). Neutralisation of acid pitwall rock to a pH value of 6.0 can require very large amounts of neutralising materials because of high buffer capacity exerted by Fe and Al hydroxide precipitates. Although Al_{exc} is a measure of reserve acidity and has been found to be related to plant root growth and yield, it does not always relate well in soil materials containing high concentrations of metal ions that readily form oxyhydroxide gels under alkaline environments. High concentration of Al_{exc} ($> 1 \text{ cmol}_c \text{ kg}^{-1}$) are known to be detrimental to plant root growth and interferes with P and Ca uptake by plants (Fox et al., 1964; Alva et al. 1986; Sloan et al. 1995). Although RPR was less effective in raising the pitwall rock pH, it significantly reduced Al_{exc} (Figure 4.1c). This reduction is likely to be due to formation of Al- PO_4 polymers and thereby reducing the solubility and exchangeability of Al in the pitwall rock.

4.3.2.4 Sulphate (SO_4^{2-})

Levels of SO_4^{2-} in the 90 days-incubated pitwall rock was significantly reduced to half the amount (10000 mg kg^{-1} to 5000 mg kg^{-1}) in the control by all the treatments at the low C_{ER} of $10 \text{ kg CaCO}_3 \text{ t}^{-1}$ (Figure 4.4c). At $C_{ER} > 10 \text{ kg CaCO}_3 \text{ t}^{-1}$ there was no significant decrease in the SO_4^{2-} levels. FBA incubated pitwall rock generally had higher levels of SO_4^{2-} due to the contribution from gypsum. The initial decrease in SO_4^{2-} levels is due to formation of salt precipitates with Fe, Al and possibly with Mg and K. The constant level of SO_4^{2-} at $C_{ER} > 20 \text{ kg CaCO}_3 \text{ t}^{-1}$ indicates that no further generation of acid from oxidation of pyrite is taking place.

4.3.2.5 Fe and Mn

Soluble Fe was significantly reduced from the control value of 3300 mg kg^{-1} to less than 2500 mg kg^{-1} at C_{ER} of $10 \text{ kg CaCO}_3 \text{ t}^{-1}$ but it remained constant at around 2200 mg kg^{-1} with higher rates of application (Figure 4.4d). There was no significant difference in the Fe levels ($p=0.05$) between the various treatments. In the case of RPR the initial reduction in Fe level is mostly due to formation of Fe- PO_4 compound because at $pH < 4$, very little $Fe(OH)_3$ is likely to be formed.

The soluble Mn level was reduced from 228 mg kg⁻¹ in the control to about 175 mg kg⁻¹ by all the treatments at low rate application of 10 kg CaCO₃ t⁻¹. At the C_{ER} of 30 kg CaCO₃ t⁻¹, the Mn level was reduced to less than 150 mg kg⁻¹ by LST, DOL and RPR but it remained above 150 mg kg⁻¹ in the FBA treated pitwall rock. At C_{ER} > 30 kg CaCO₃ t⁻¹, the Mn levels in FBA incubated pitwall rock were significantly less than for LST, DOL and RPR.

4.3.2.6 Overall effectiveness of neutralising materials

Analysis of variance of the overall mean difference in the neutralising values between the neutralising materials indicated that LST, DOL and FBA were similar in their effectiveness in ameliorating low pH conditions in the pitwall rock. They significantly increased the pitwall rock pH to above 5.0 from the control (nil treatment) value of ≤ 2.5 (Figure 4.5a). Although EC levels in FBA incubated pitwall rock were slightly higher, the overall mean differences between the neutralising materials effects on EC, SO₄²⁻, Fe, Mn and Al were insignificant at p=0.05. There was a significant reduction in the levels of these measured parameters in the neutralising material incubated pitwall rock from that of control levels of nil treated pitwall rock (Figure 4.5b, c, d, e and f). Addition of RPR caused a significant reduction in the acidity of the pitwall rock, but it was not effective in raising the pH to optimum level for plant growth (pH 6.0) even at the highest levels of C_{ER}.

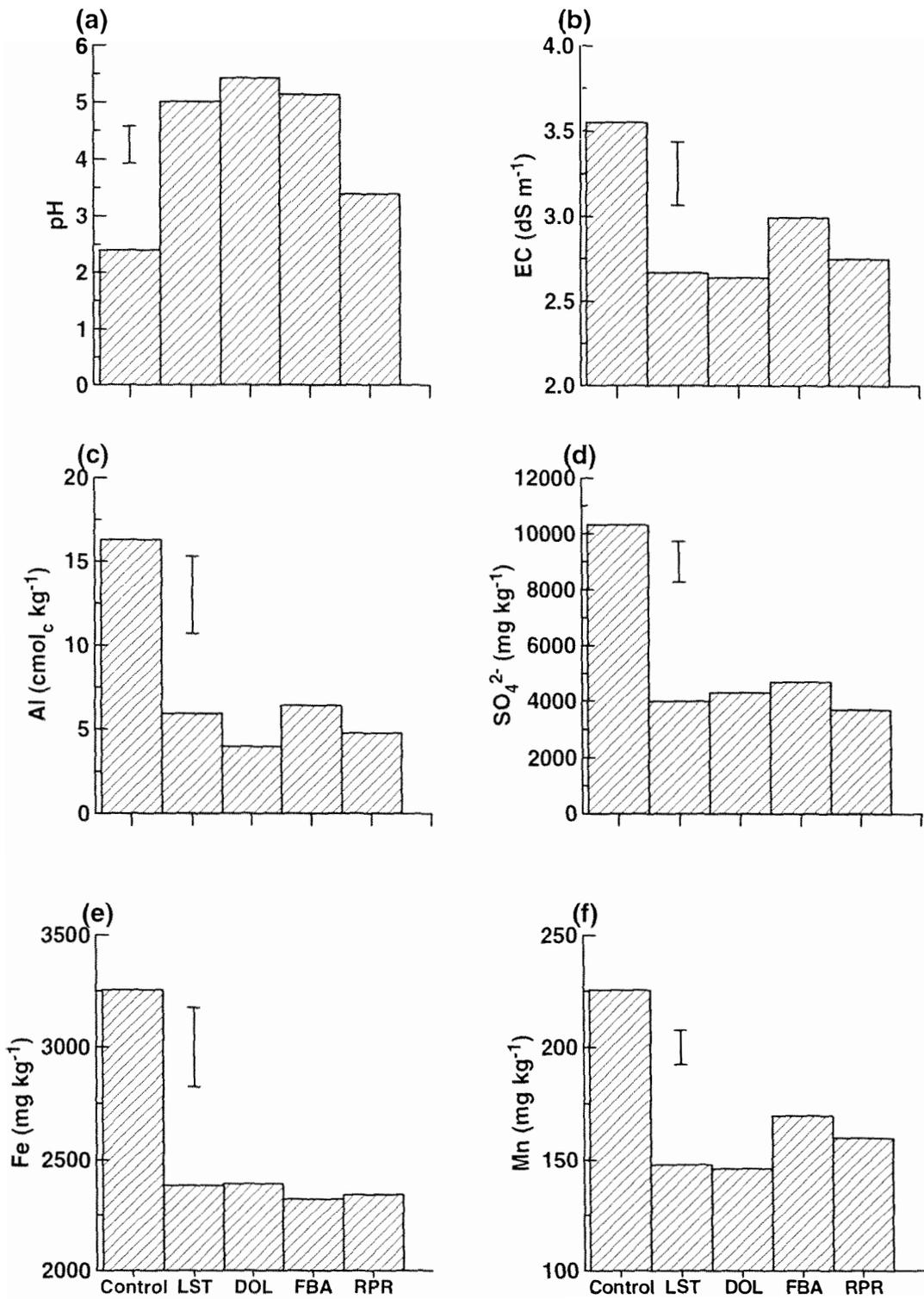


Figure 4.5 Overall effect of neutralising materials on selected chemical properties of the pitwall rock after 90 days incubation. LST, limestone; DOL, dolomite; FBA, fluidised bed boiler ash; RPR, reactive phosphate rock. Vertical bars represent LSD(5%).

4.3.3 Neutralising effect of limestone particles on pitwall rock

4.3.3.1 Lime requirement based on limestone particle size

Lime requirements of the pitwall rock obtained from rate versus pH curves (Figure 4.6a) based on the varying sizes of limestone particles are given in Table 4.5. The Te Kuiti limestone which is currently used at Waihi mine to control AMD in waste rock has a CaCO_3 value of 95% and fineness (≤ 2 mm) of about 55%. The 90 days incubation study showed that the effectiveness of the graded limestone in raising the pitwall rock pH was directly related to the particle size. There was no significant effect on pH of the pitwall rock by limestone > 2 mm. Only very fine-grained limestone (LST_{VF} , < 0.5 mm) was effective in raising the pH to > 5 at a C_{ER} of $30 \text{ kg CaCO}_3 \text{ t}^{-1}$. Based on the LR_{NAPP} of $82 \text{ kg CaCO}_3 \text{ t}^{-1}$ ($86 \text{ kg LST}_{\text{AR}} \text{ t}^{-1}$, 95% CaCO_3), under the current practice of liming at Waihi, it would require LR_{Total} of $194 \text{ kg LST}_{\text{AR}} \text{ t}^{-1}$ ($272 \text{ t LST}_{\text{AR}} \text{ ha}^{-1} 10 \text{ cm}$) of Te Kuiti limestone to effectively control AMD from pyritic waste rock materials.

Table 4.5 Graded limestone requirement of the pitwall rock to raise pH to > 6 .

Limestone	$\text{LR}_{\text{Buffer}} (C_{\text{ER}})$ $\text{kg CaCO}_3 \text{ t}^{-1}$	CaCO_3 equivalent (%)	Actual rate kg t^{-1}	LR_{Total} kg t^{-1}
LST_{VF}	32 [#]	95	34	120
LST_{F}	62 [*]	95	65	151
LST_{C}	414 [*]	95	436	522
LST_{AR}	103 [*]	95	108	194

Same as LST * Extrapolated rates from linear equations: LST_{F} , $\text{pH} = 0.07 * C_{\text{ER}} + 1.93$, $R^2 = 0.96$; LST_{C} , $\text{pH} = 0.01 * C_{\text{ER}} + 2.31$, $R^2 = 0.86$; LST_{AR} , $\text{pH} = 0.04 * C_{\text{ER}} + 2.03$, $R = 0.93$

4.3.3.2 Limestone particle size effect on chemical properties

The effective final in pH at the highest C_{ER} ($50 \text{ kg CaCO}_3 \text{ t}^{-1}$) for LST_{VF} , LST_{F} and LST_{C} were 7.3, 5.0 and 4.0 (Figure 4.6a). The LST_{AR} , although it had 55% fines, did not raise the pH above 2.5 at the highest C_{ER} . Coarse grained limestone (LST_{C}) was ineffective in raising the pitwall rock pH to desired level of 6.0, even at the highest C_{ER} ($\text{kg CaCO}_3 \text{ t}^{-1}$) due to an armouring effect of metal hydroxide and sulphate salt coating on the limestone grains. Very fine grained limestone (LST_{VF}) provided efficient neutralisation and raised the pH to the desired level of 6.0 at C_{ER} of $34 \text{ kg CaCO}_3 \text{ t}^{-1}$ ($48 \text{ t L}_{\text{VF}} \text{ ha}^{-1} 10 \text{ cm}$). The rate of increase in pH with lime addition for LST_{F} , LST_{C} and

LST_{AR} followed a linear function and the predicted C_{ER} shown in Table 4.5 indicated that it would require $610 \text{ t } LST_C \text{ ha}^{-1}$ (LR_{Total} of $731 \text{ t } LST_C \text{ ha}^{-1}$) of pitwall surface to effectively raise the pitwall rock pH to 6.0 and above. The pit slope angle and local environmental conditions will restrict application of such a large amount of LST_C on the pitwall surface.

Although larger particle limestone was not effective in raising the pH of the pitwall rock, the trend in reduction in the levels of EC, SO_4^{2-} , Fe, Mn and Al in the pitwall rock (Figure 4.6b, c, d, e and f) were significant at $p=0.05$ and were very similar to the reduction by the neutralising materials. The reduction in EC, Mn and Al by LST_C was significantly less than that for LST_{VF} , LST_F and LST_{AR} .

The LST_{VF} , LST_F and LST_{AR} all reduced acidity to levels $< 100 \text{ g CaCO}_3$ at C_{ER} of $30 \text{ kg CaCO}_3 \text{ t}^{-1}$ (Figure 4.7a). The reduction in acidity by LST_C was significantly lower than that of LST_{VF} , LST_F and LST_{AR} . Generally, the trend in the reduction of acidity by LST_C followed a linear function ($\text{Acidity} = -8.4 * C_{ER} + 495, R^2 = 0.99$) and only at the highest C_{ER} ($50 \text{ kg CaCO}_3 \text{ t}^{-1}$), was the reduction $< 100 \text{ g CaCO}_3$. The overall comparison of acid reduction by varying particle size limestone showed (Figure 4.7b) that LST_{VF} , LST_F and LST_{AR} all reduced acidity by about 80% of the control value at the C_{ER} of $30 \text{ kg CaCO}_3 \text{ t}^{-1}$ whereas LST_C only reduced acidity by about 50%.

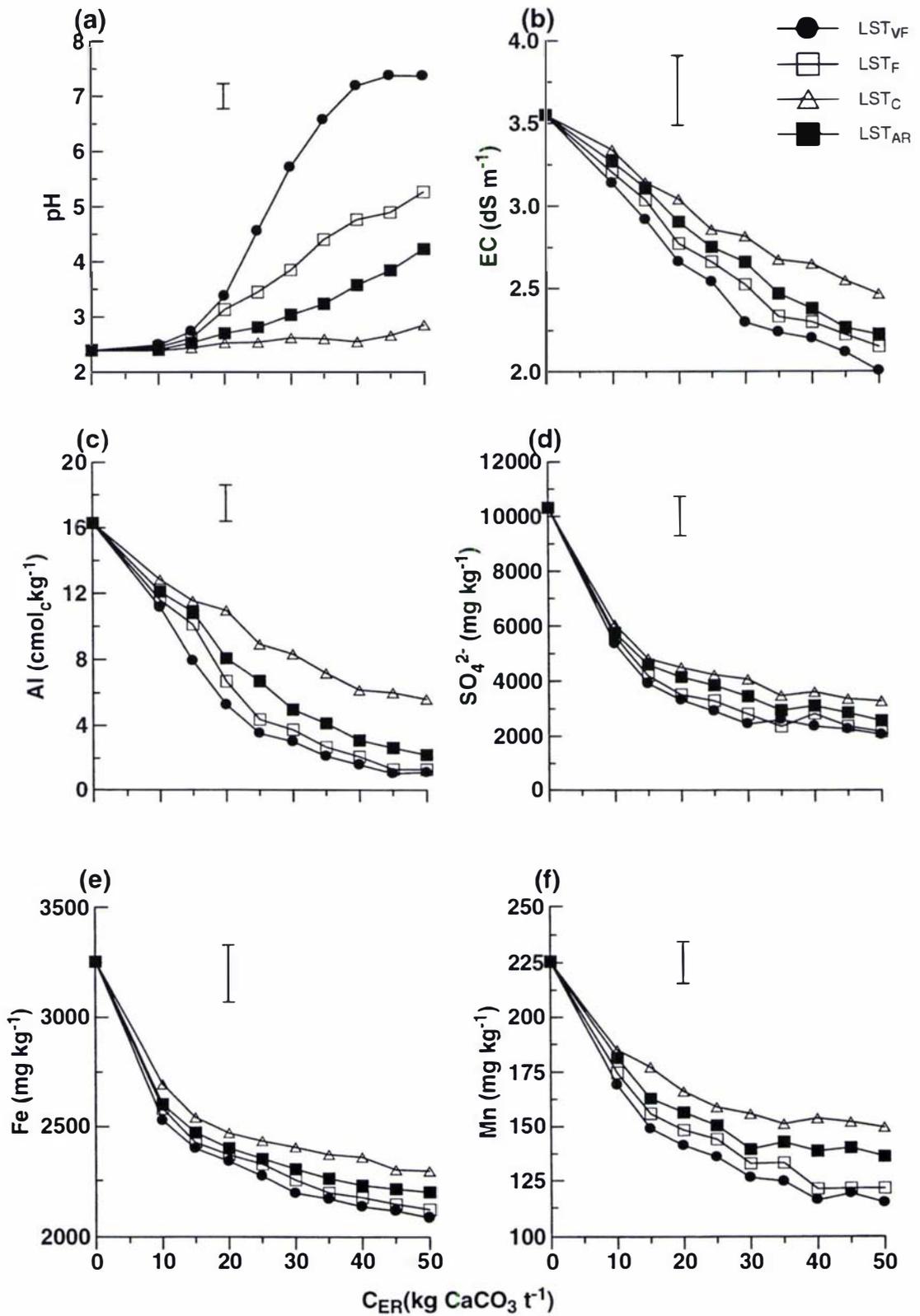


Figure 4.6 Effect on selected chemical properties of the pitwall rock after 90 days incubation with varying C_{ER} of different particle size limestone. LST_{VF}, very fine limestone; LST_F, fine limestone; LST_C, coarse limestone; LST_{AR}, as received limestone. Vertical bars represent LSD(5%).

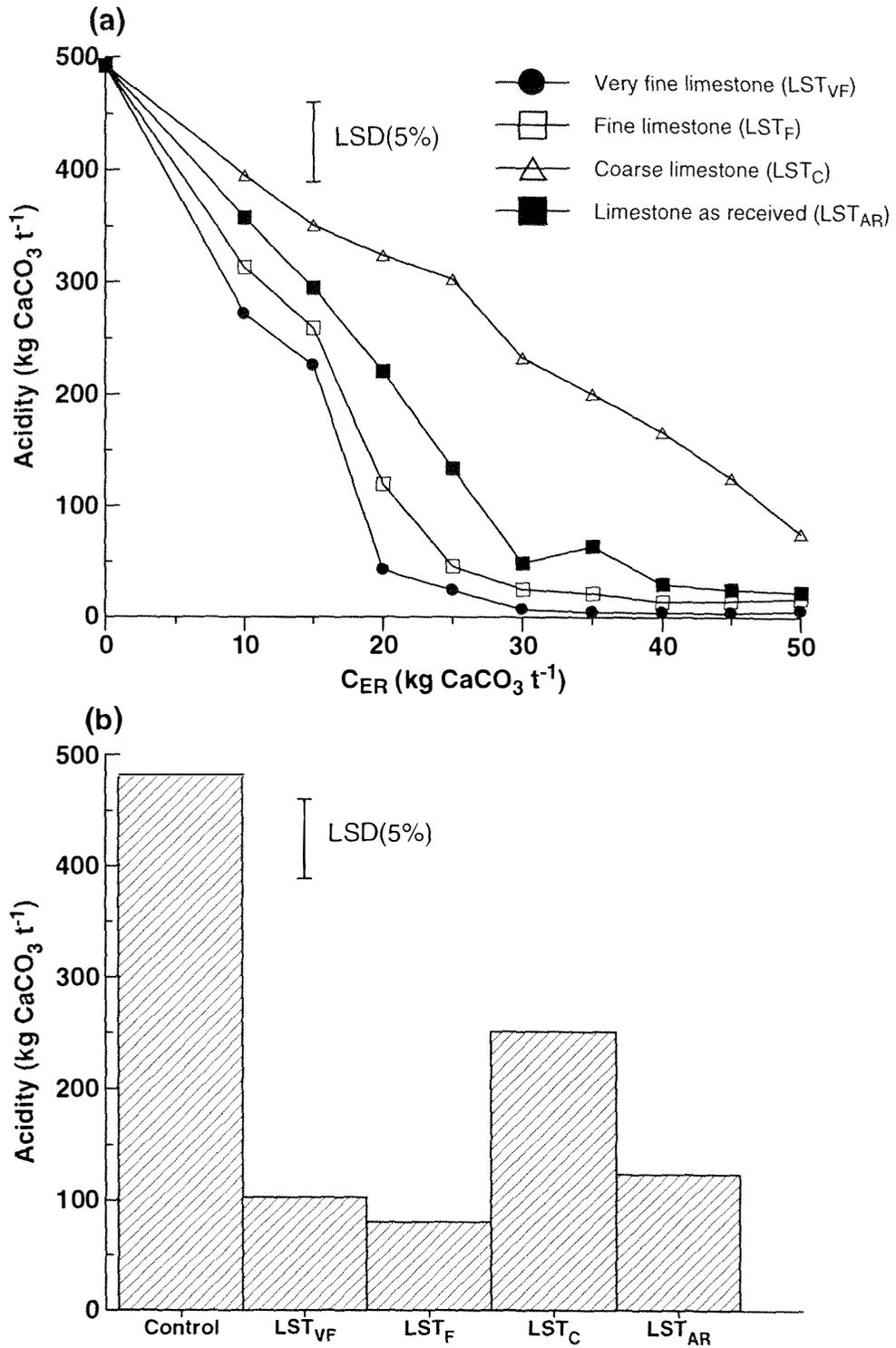


Figure 4.7 Reduction in acidity in 90 days incubated pitwall rock. (a) With varying C_{ER} of graded limestone and (b) overall comparison between the graded limestone.

4.3.3.3 Characterisation of the hydroxide coating

The behaviour of pH response curves (Figure 4.6a) with incremental application rates of graded limestone in 90 days incubated pitwall rock showed that in sulphidic rock materials, limestone particle size had a marked effect on reactivity and neutralisation of acidity. A SEM scan of the 90 days incubated limestone grain (8 mm longest diameter) is shown in Plate 4.1. After 90 days, the edge (Middle, in the EDS path) of the limestone grain was coated with about a 1.0 mm thickness of reddish-brown metal hydroxides.

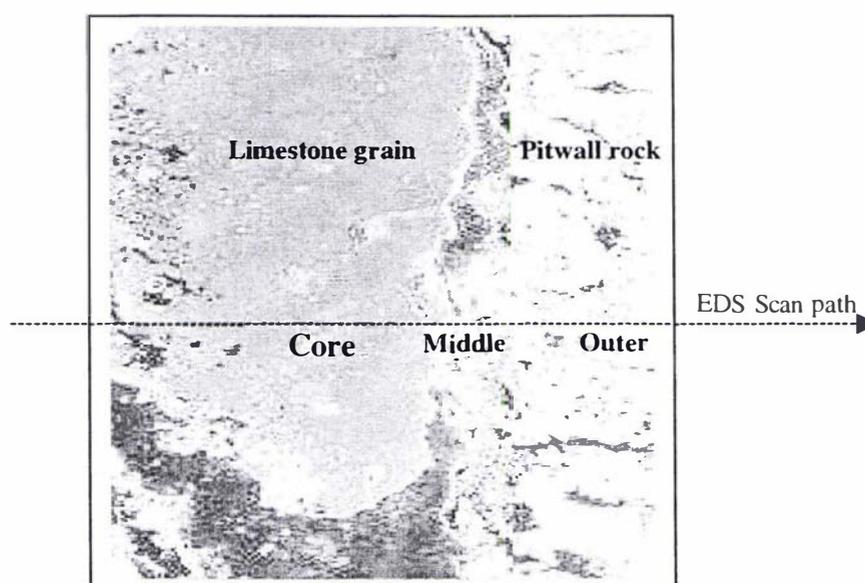


Plate 4.1. SEM scan of sectioned 90 days incubated limestone grain. Refer Figure 4.8 for EDS spectra.

Quantitative determination of elemental concentrations in the hydroxide-coated limestone grain by EDS (Figure 4.8) showed that the unreacted limestone core consisted of mainly Ca (95%) with minor Si (2.7%) and S (2.3%). The coating on the grain (Middle) contained Si (63%), S (13%), Al (10%), Fe (8%), K (4%) and Mg (1.5%). At the contact zone of the limestone grain with the pitwall rock acid front (Outer section), the major elements present were Si (73%), Ca (17%), Mg (3%), K (2.3%), Na (1.8%) Al (1.4%) and S (1.2%).

It is evident from the SEM/EDS analysis that when the limestone grain came in contact with highly acidic pitwall rock, containing elevated levels of Fe, Al and S, the sudden increase in pH at the alkaline front precipitated most of the Fe^{3+} and Al^{3+} in an amorphous silica matrix. This may suggest that the silica dominated oxyhydroxide coatings may result in more acid resistant armouring effect to the dissolution of limestone grains. The coating also contained a significant amount of S, indicating that these elements may have also precipitated as sulphate salts together with Mg, K and Cl released from the decomposition of clay minerals (mainly chlorite, $\text{Mg}_3\text{Al}_2(\text{Si}_6\text{Al}_2)\text{O}_{22}(\text{OH})_{16}$) and feldspars (albite, $\text{NaAlSi}_3\text{O}_8$; orthoclase, KAlSi_3O_8) during weathering of the pitwall rock under acid conditions.

Most of the Fe and Al in the pitwall rock front is probably precipitated as hydroxide and sulphate compounds, as indicated by the absence of Fe and depletion of Al in the outer zone and their subsequent precipitation in the middle zone (coating). A significant amount of Ca (17%) has moved into the pitwall rock front as result of dissociation from $\text{Ca}(\text{OH})_2$ although a large part of the Ca from the dissolution of CaCO_3 and calcic feldspars would also be precipitated as gypsum on the pitwall rock front.

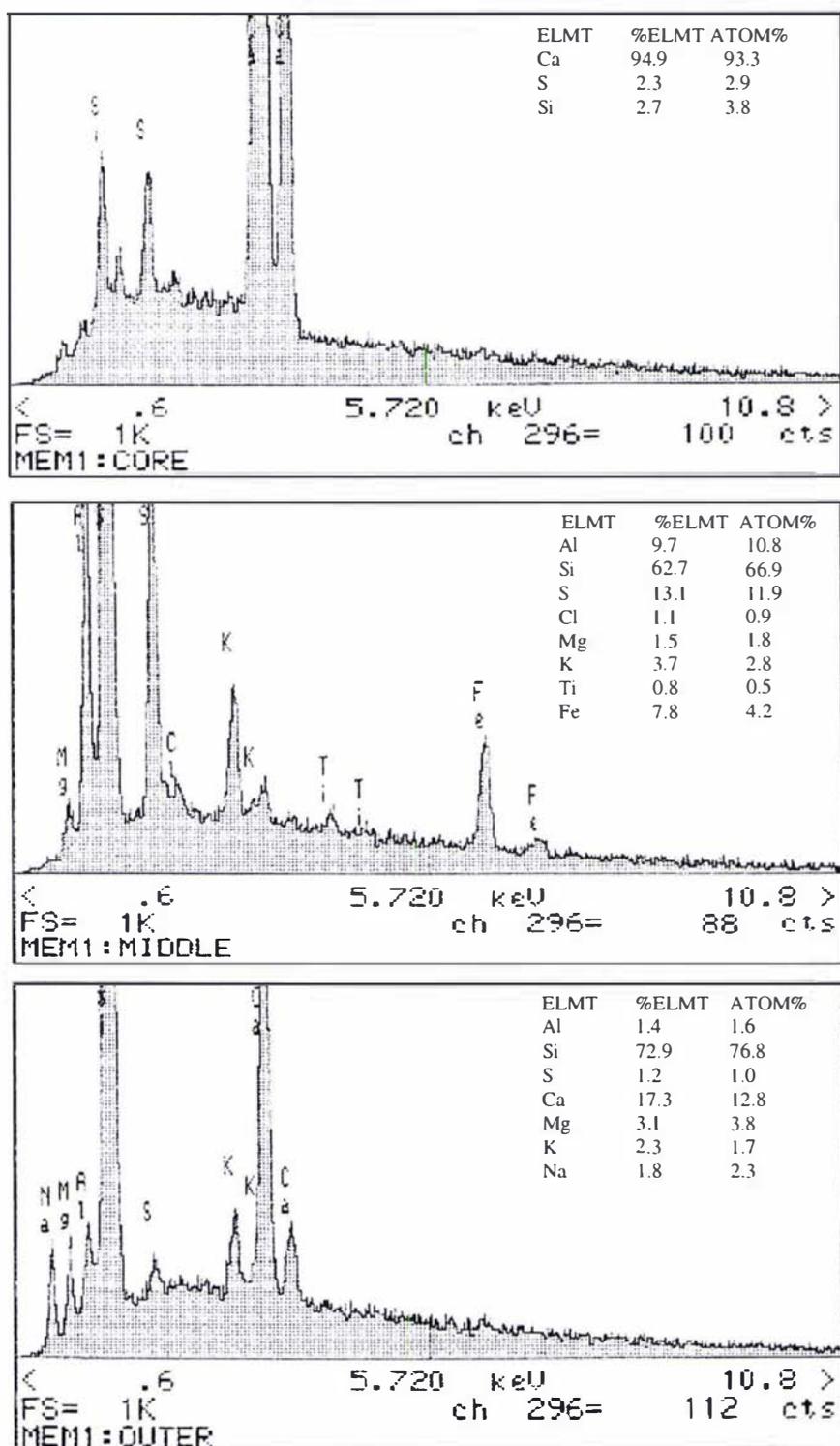


Figure 4.8 EDS spectra with accompanying tables of elemental concentrations of hydroxide coated limestone grain incubated for 90 days. Core (limestone), Middle (hydroxide coating) and Outer (pitwall rock front).

4.3.3.4 Quantification of elements in the hydroxide coating

In order to quantify the amount of Fe, Al and SO_4^{2-} in the hydroxide coatings, and whether duration of incubation had any effect on the amount of metals and SO_4^{2-} precipitated in the coatings, limestone grains that had been incubated for 45 and 90 days were dissolved in 1 M HCl. The amount of Fe, Al and S dissolved from coatings on the 2 and 4 mm grains was proportionate to the diameter of the grains but there was no difference in the amount between the 4 and 8 mm particles (Table 4.6). Since the reactivity and relative coating by the Fe hydroxide are directly proportional to the surface area of the limestone grain, smaller grains which have larger surface areas are expected to adsorb higher concentrations of metal precipitates. On a specific surface area basis, SO_4^{2-} in the 45 days incubated grains followed the expected trend with adsorption of 5.2, 2.7 and 0.7 $\mu\text{g mm}^2$ for 2, 4 and 8 mm grains respectively. A similar trend was observed for Al. Whereas Fe adsorption in the 8 mm grain was twice ($2.6 \mu\text{g mm}^2$) the amount adsorbed on 2 and 4 mm grains.

Table 4.6 Metal and sulphate analysis of the coated limestone grain

Grainsize, mm	45 days			90 days		
	Fe, μg	Al, μg	SO_4^{2-} , μg	Fe, μg	Al, μg	S, μg
2	16 ± 2	6 ± 1	67 ± 2	15 ± 2	4 ± 0.5	44 ± 5
4	52 ± 8	11 ± 1	137 ± 5	53 ± 5	13 ± 1	98 ± 7
8	76 ± 6	12 ± 2	132 ± 11	68 ± 3	9 ± 1	112 ± 8

The results showed that there was in fact a reduction in the amount of coating of the relative quantity of Fe, Al and SO_4^{2-} in the 90 days incubated grains compared with the 45 days incubated grains. This may indicate that the amount of precipitate is directly dependent upon the reactivity of the limestone and the degree of acidity of the pitwall rock. Once a certain thickness of coating is developed, no more Fe, Al or SO_4^{2-} will precipitate. When a new front of acid lowers the pH of the contact zone, some of the coating may start to dissolve and may finally expose the limestone once again to provide further neutralisation. While fine grained limestone provide immediate neutralisation of the active acidity, the possibility of providing long-term slow release

neutralisation of sulphide acidity by coarse grained limestone in pitwall rock seem feasible.

4.3.4 Effect of incubation time on pitwall rock chemical properties

Comparison of the 45 days and 90 days incubated pitwall rock showed that there were no significant differences in the changes in the chemical properties due to the addition of neutralising materials (Figure 4.9a,b, c, d, e, f). The mean pH of the 90 days incubated pitwall rock were generally slightly higher whereas the levels of EC and Mn were lower than that of 45 days incubated pitwall rock. However, the differences were not statistically significant at $p=0.05$. Interesting to note though was that levels of EC, Fe and Mn in the control (nil treated pitwall rock) were lower in 90 days incubated pitwall rock whereas there was an increase in the exchangeable Al. This may indicate possible reduction of Fe and Mn, making them less soluble, and release of Al from the silicate matrix.

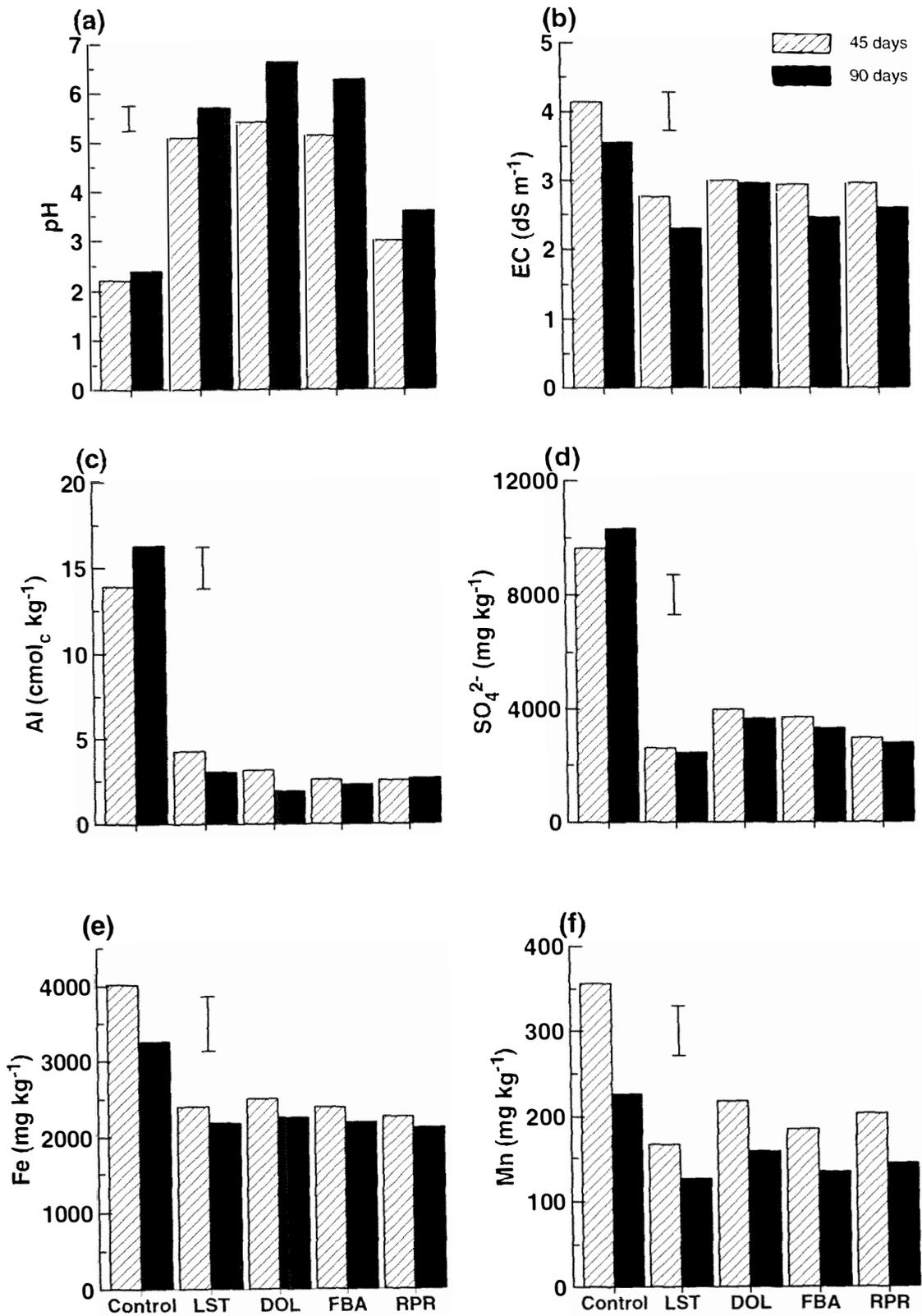


Figure 4.9 Effect of incubation time on selected chemical properties of the pitwall rock treated with neutralising materials at $C_{ER} = 30 \text{ kg CaCO}_3 \text{ t}^{-1}$. Vertical bars represent LSD(5%).

4.3.5 Effect of incubation on physical properties of the pitwall rock

Application of higher rates of neutralising materials were not only effective in raising the pitwall rock pH and reducing levels of EC, SO_4^{2-} , Fe, Mn and Al but also changed pitwall rock consistence from clayey (control) to structurally better friable forms. The LST_C and LST_{AR} incubated pitwall rock were the least structurally developed. There was a marked colour change from earthy bluish grey (5Y6/1, control) to reddish brown with increasing rates of application of LST and DOL, as indicated by changes in Munsells colours (Table 4.7 and Plate 4.2). At the highest C_{ER} ($50 \text{ kg CaCO}_3 \text{ t}^{-1}$) the colour change was most pronounced in the pure CaCO_3 (10YR7/6), DOL (10YR6/8) and LST (10YR7/8) incubated pitwall rock. These changes in colour are indicative of increasing precipitation of ferric-hydroxide with increase in pitwall rock alkalinity. However, very little colour change was observed in the pitwall rock incubated with LST_C and RPR. Hydroxide coating on limestone particles were observed all through low C_{ER} ($10 \text{ kg CaCO}_3 \text{ t}^{-1}$) to high C_{ER} ($50 \text{ kg CaCO}_3 \text{ t}^{-1}$) in both LST_C and LST_{AR} . The FBA treated pitwall rock had the best structure development but at high rates of application ($50 \text{ kg CaCO}_3 \text{ t}^{-1}$), cementitious matrix formation was observed.

Table 4.7 Munsells colours after 90 days incubation

Neutralising materials	Nil	Low rate	Medium rate	High rate
Control	15Y6/1			
Pure CaCO_3		10YR7/6	10YR6/8	7.5YR5/8
LST_F (0.5 - 2 mm)		10YR6/1	10YR8/8	10YR7/8
LST_C (2 - 4 mm)		2.5Y6/0	2.5Y6/0	2.5Y6/0
LST_{AR} (55% < 2 mm)		2.5Y7/0	2.5Y8/4	2.5Y7/4
DOL (< 0.5 mm)		10YR8/6	10YR7/8	10YR6/8
RPR (< 2 mm)		2.5Y6/0	2.5Y6/0	2.5Y6/0
FBA (< 2 mm)		10YR6/1	10YR7/4	10YR7/6

Low rate = C_{ER} 10, Medium rate = C_{ER} 25, High rate = C_{ER} 50

4.4 Conclusions

In a highly acidic pyritic pitwall rock containing high levels of Fe, Al, SO_4^{2-} and soluble salts, lime requirement assessed from standard buffer methods grossly underestimates the actual lime requirement of the pitwall rock. Both the buffer exerted by Fe-Al-hydroxides and potential acidity of the pitwall rock contribute significantly to the neutralisation requirement of the pitwall rock. The type of neutralising material required is directly dependent upon their relative reactivity of the carbonate fraction.

The lime requirement predicted from the NaOH-pH and CaCO_3 -pH buffer curves indicated that a buffer lime requirements ($\text{LR}_{\text{Buffer}}$) of $29 \text{ kg CaCO}_3 \text{ t}^{-1}$ was required to raise the pH of the pitwall to 6.0. The lime requirement to neutralise active acidity of the pitwall rock, determined by the incubation method, is substantially less than that estimated from ABA. The total lime requirement (LR_{Total}) of the pitwall rock ($111 \text{ kg CaCO}_3 \text{ t}^{-1}$) for complete neutralisation of acidity in the pitwall rock material, is nearly four times the $\text{LR}_{\text{Buffer}}$.

LST, DOL and FBA were equally effective in overcoming the large buffer exerted by Fe and Al hydroxides to raise pH to 6.0 at the same C_{ER} of $30 \text{ kg CaCO}_3 \text{ t}^{-1}$. At lower C_{ER} , DOL was significantly more effective than LST and FBA in overcoming the Fe-Al buffer. RPR did not raise the pH above 4.2 even at the highest C_{ER} of $50 \text{ kg CaCO}_3 \text{ t}^{-1}$, despite it having a higher theoretical neutralisation potential than FBA. Under the present conditions of the pit slope, the weathered pitwall rock would require a LR_{Total} of 170, 131, 392 and $576 \text{ t ha}^{-1} \cdot 10 \text{ cm}$ of LST, DOL, FBA and RPR respectively

Overall, there was a significant reduction in acidity in the pitwall rock material amended with neutralising materials compared with that of the control with nil treatment. Acidity in the pitwall rock was reduced to $\leq 50 \text{ kg CaCO}_3 \text{ t}^{-1}$ at $C_{\text{ER}} \geq 30 \text{ kg CaCO}_3 \text{ t}^{-1}$ for LST, DOL and FBA treatments whereas acidity in the RPR treated pitwall rock remained above $75 \text{ kg CaCO}_3 \text{ t}^{-1}$ at the same C_{ER} . At a $C_{\text{ER}} = 30 \text{ kg CaCO}_3 \text{ t}^{-1}$, the overall reduction in acidity in the 90 days incubated pitwall rock was 85%. At $C_{\text{ER}} > 30 \text{ kg CaCO}_3 \text{ t}^{-1}$, all the neutralising materials were equally effective in reducing the acidity of the 90 days incubated pitwall rock.

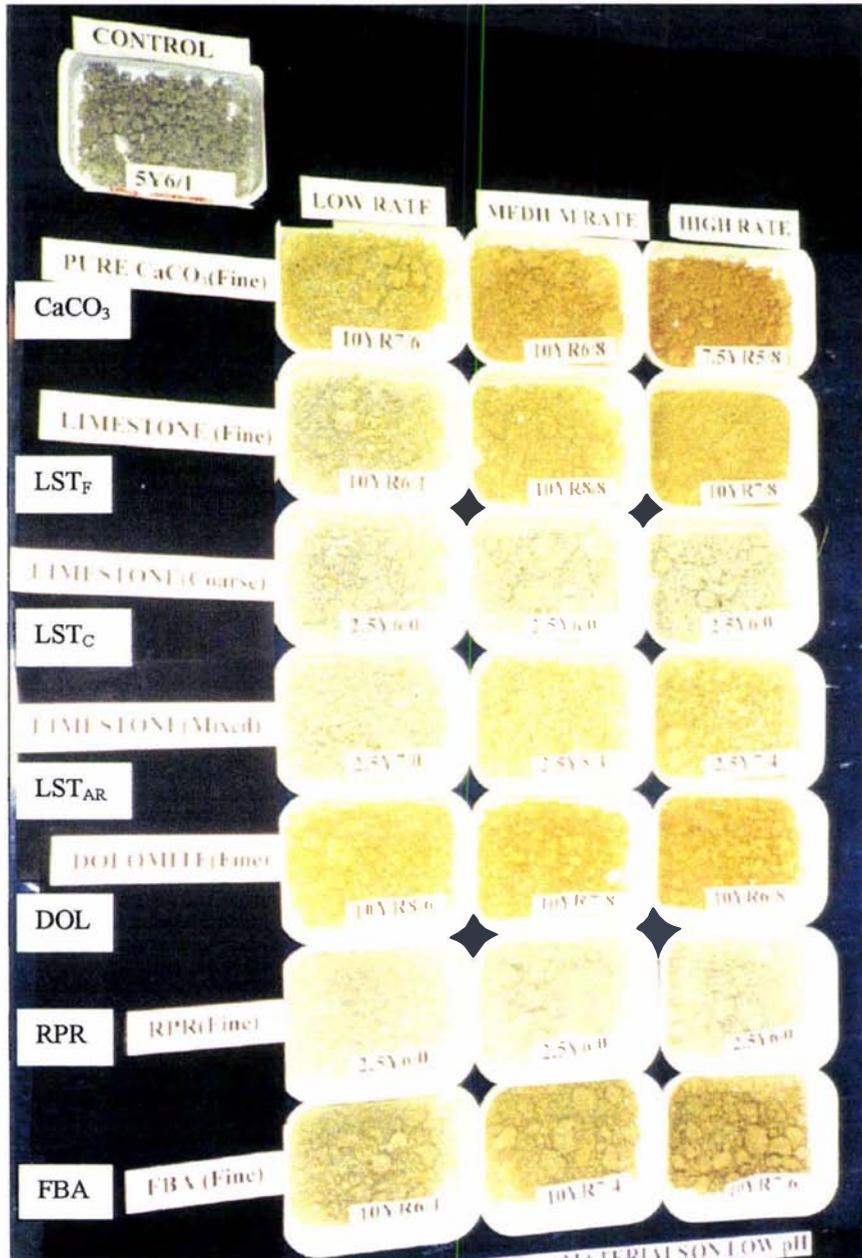


Plate 4.2 Physical effect on pitwall rock incubated with nil (Control), low (10 t CaCO₃ Mt⁻¹), medium (25 t CaCO₃ Mt⁻¹) and high (50 t CaCO₃ Mt⁻¹) rates of neutralising materials. Labels on pitwall rock indicate Munsells colour notations.

The incubation experiment showed that although RPR had a higher theoretical NP value than FBA, it was ineffective in neutralising pitwall rock acidity. Amendment with RPR however, may have the beneficial effect of providing a slow release, long-term acid neutralisation effect as well as reducing the oxidant (Fe^{3+}) level and raising the P content of the pitwall rock.

The overall mean differences between the neutralising materials' effects on EC, SO_4^{2-} , Fe, Mn and Al were insignificant at $p=0.05$. However, incubation with neutralising materials caused a significant reduction in the levels of these measured parameters from that of control levels of nil treated pitwall rock.

Incubation with neutralising materials caused a sharp decrease in exchangeable Al in the pitwall rock and all the treatments were equally effective in reducing exchangeable Al. Since the concentration of Al in soil solution is highly pH dependent, the observed reduction of exchangeable Al at buffer lime requirement ($\text{LR}_{\text{Buffer}}$) rate of $29 \text{ kg CaCO}_3 \text{ t}^{-1}$ is sufficient to ameliorate Al toxicity in the weathered pitwall rock material.

Limestone particle size had a marked effect on reactivity and neutralisation of acidity. Coarse grained limestone (LST_C) was ineffective in raising the pitwall rock pH to desired level of 6.0, even at the highest C_{ER} ($\text{kg CaCO}_3 \text{ t}^{-1}$) due to an armouring effect of metal hydroxide and sulphate salt coating on the limestone grains.

Although the neutralisation effect of coarse grained limestone ($> 2 \text{ mm}$) was affected by hydroxide coatings, the initial neutralisation provided by the larger particle limestone was sufficient to significantly lower levels of EC, SO_4^{2-} , acidity, Fe, Mn and Al in the acidic pitwall rock. While fine grained limestone provide immediate neutralisation of the active acidity, the possibility of providing long-term slow release neutralisation of sulphide acidity by coarse grained limestone in pitwall rock seems feasible.

When the pH of pitwall rock is increased, as would happen with contact with the incremental addition of neutralising materials, metal ions such as Fe and Al readily form hydroxide precipitates and possible sulphate salts, which is shown to have an armouring

effect on larger particle size limestone. SEM/EDS examination showed that the coating on limestone particles consisted mainly of Fe and Al hydroxides and sulphate salts in a matrix of amorphous silica. Significant amounts of Ca had moved into the pitwall rock and may have complexed with SO_4^{2-} to form $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as reflected in the relatively high levels of EC.

Amendments with neutralising materials were not only effective in raising the pitwall rock pH and reducing levels of EC, SO_4^{2-} , Fe, Mn and Al but also changed pitwall rock consistency from clayey (control) to structurally better friable forms. The LST_C and LST_{AR} incubated pitwall rock were the least structurally developed. Hydroxide coating on limestone particles were observed all through low C_{ER} ($10 \text{ kg CaCO}_3 \text{ t}^{-1}$) to high C_{ER} ($50 \text{ kg CaCO}_3 \text{ t}^{-1}$) in both LST_C and LST_{AR} . Best structure development was observed in FBA incubated pitwall rock.

Chapter 5

Effectiveness of Surface Broadcasted Neutralising Materials in Ameliorating Low pH conditions in Pyritic Mine Pitwall Rock

5.1 Introduction

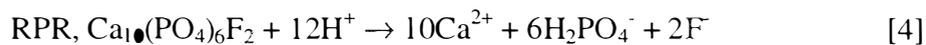
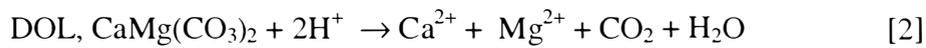
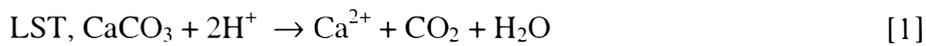
Acid mine drainage (AMD) from oxidation of pyritic waste rock generally produces low pH drainage capable of mobilising heavy metals. The resulting low pH conditions not only facilitate mobilisation of toxic metals but also accelerate geochemical weathering, growth of acidophilic bacteria and the rate of sulphide oxidation. The release of metals potentially toxic to plants such as Fe, Mn, Al and SO_4^{2-} and dissolved salts from pyritic waste rock depends on several chemical and physical processes. Geochemical processes under given environmental conditions largely control the evolution of low pH from oxidation of pyrite in the presence of oxygen and moisture. The quality of drainage emerging from pitwalls as surface runoff depends in large part on the reactions with minerals capable of neutralising the AMD as it migrates downslope. The reactions and relative effectiveness of most processes, which neutralise AMD under leaching conditions, have not been fully assessed.

Alkaline addition to pyritic waste rock has had mixed success in preventing AMD. For example, of eight alkaline addition sites studied by Brady et al (1990), six sites still produced acid after reclamation, though generally at reduced concentrations. In a field experiment to investigate the process of AMD generation in pyritic shale treated with alkaline material, Evans and Rose (1995) found that although lime treated cells showed significantly reduced acidity, SO_4^{2-} , Al, Fe and Mn, the effluent pH remained below 3, irrespective of treatments. At the same time higher rates of lime did not further decrease acidity as expected, leading to the conclusion that there was no clear cut relationship between the lime requirement and the AMD released.

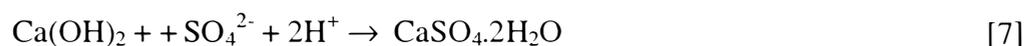
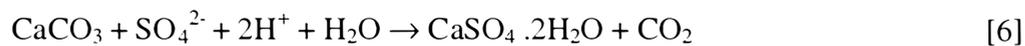
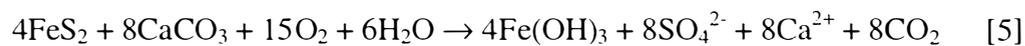
The rate of acid neutralisation is difficult to measure because of several factors affecting the neutralisation processes. Ferguson and Morin (1991) and Morin and Hutt (1994) suggested that the dissolution of carbonate minerals and acid neutralisation can simply be represented by the ratio of the molar concentrations of dominant cation (Ca and Mg) and SO_4^{2-} (Ca/SO_4 or $\text{Ca}+\text{Mg}/\text{SO}_4$). Ferguson and Morin (1991) defined a number of curves

for sulphate production from 281 kinetic tests and found that most test cases produced logarithmic growth curves for cumulative sulphate, indicating gradual decrease through time in the rate of acid generation.

The effectiveness of various materials in neutralising acid will largely depend on the mineralogical characteristics of the mine waste rock and the environmental conditions of the mine location. Each treatment measure for acid neutralisation is therefore site specific. The acid consuming reactions involved during neutralisation processes using neutralising materials selected can be summarised in the following equations.



In the presence of pyrite, the carbonate fraction of the neutralising materials will react according to equation 5 and the SO_4^{2-} released from oxidation of pyrite will further react with CaCO_3 to form gypsum (Eqns.6 and 7).



Beside carbonates, the decomposition of clay minerals and alkali feldspars (even under moderately acidic conditions) can also contribute towards acid neutralisation processes. Under acidic environments aluminosilicates such as mica and clay minerals are capable of removing H^+ ions by ion exchange reactions (see section 2.4.4, Chapter 2).

The effectiveness of alkaline materials in neutralising acid conditions in oxidising pyritic waste rock is also dependent on the depth of weathered cover material available for neutralisation. In the presence of elevated levels of SO_4^{2-} , heavy precipitation of CaSO_4 and metal hydroxides at the surface may deter the downward movement of the alkaline front. The effectiveness of limestone in ameliorating subsoil acidity is generally

considered poor due to the slow rate of downward movement of the alkaline front (Costigan et al., 1981; Dollhopf, 1992). Therefore, an alternate choice of amendments and the method of application are vital in creating a suitable depth of growing media. The methods of application of neutralising materials (surface broadcast versus incorporation) are going to be the determinant factor in their effectiveness in alleviating subsurface acidity in the pitwall rock.

Chemical characterisation of pitwall bulk samples and the AMD from runoff showed that high levels of dissolved Fe, Al, Mn, SO_4^{2-} and soluble salts are the major components of the AMD besides its characteristic low pH (Chapter 3). Neutralisation of acid in the pitwall rock material by pH modification will undoubtedly result in the precipitation of the metals as sulphate and hydroxide complexes, which will affect the nature, and chemistry of the leachate. Since addition of neutralising materials to ameliorate AMD conditions in mine waste materials is currently a standard practice, it is important to evaluate the characteristic effectiveness of some selected neutralising materials.

The objective of this study was to determine the effect that surface broadcasted neutralising materials has on leachate quality and subsurface amelioration of low pH condition in weathered pyritic pitwall rock. Column leaching cycles under glasshouse conditions were intended to provide conditions that closely approximate field conditions.

The main quantitative aspect of this study involved an assessment of the effectiveness of selected neutralising materials in ameliorating low pH conditions in weathered pitwall rock under accelerated leaching conditions.

The specific objectives of this experiment were:

1. Characterisation of leachate from pitwall rock columns broadcasted with selected neutralising materials
2. Assessing the extent of subsurface amelioration of low pH condition by surface broadcasted neutralising materials

5.2 Materials and Methods

5.2.1 Pitwall rock bulk sample

The pitwall rock bulk sample used in the column study was from the north face of the pit at Martha mine, Waihi. The sampling location and chemical characteristics of the bulk sample are described in section 4.2.1 and Table 4.1 respectively (Chapter 4). The bulk sample was air-dried and crushed to nominal 4 mm fractions prior to packing into the columns. The samples contained approximately 35% fines (< 0.5 mm) and had a composite pyrite content of 4.5%.

5.2.2 Neutralising materials

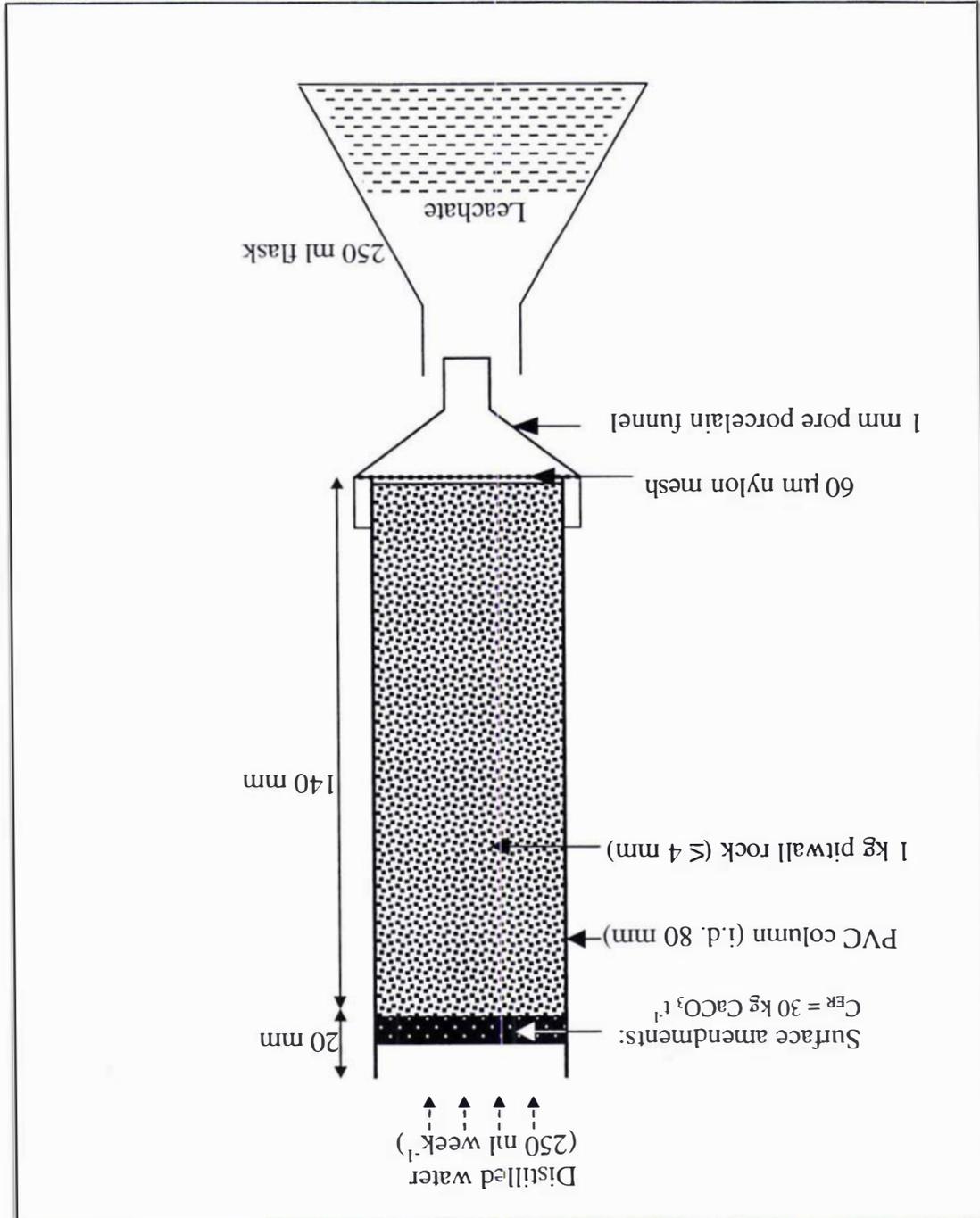
The neutralising materials used were fine limestone (LST), dolomite (DOL), reactive phosphate rock (RPR) and fluidised bed boiler ash (FBA). These materials were described in Chapter 4 under section 4.2.2 and Table 4.2.

5.2.3 Column set up

Controlled leaching columns as shown in Figure 5.1 were used to evaluate the effectiveness of surface broadcasted neutralising materials in ameliorating acidity on weathered partially oxidised pitwall rock. The columns were 16 cm long with an internal diameter of 8 cm. One kilogram of pitwall rock bulk sample was packed to a column depth of 14 cm (approximate average depth of weathered pitwall rock on the pitwall). Neutralising materials (LST, DOL, RPR and FBA) at a carbonate content equivalent rate (C_{ER}) of 0 (control) and 30 kg $CaCO_3 t^{-1}$ were uniformly spread on the surface of the pitwall rock column. The column set up was then left to equilibrate undisturbed for one week at a moisture content of 80% field capacity. At the end of the week, the columns were weighed and leached as per the protocol outlined in section 5.2.4 below.

This experiment was designed to investigate the effects of four different neutralising materials at two rates of applications ($C_{ER} = 0$ and 30 kg $CaCO_3 t^{-1}$) on the AMD compositions of repacked and leached pyritic pitwall rock columns. The experimental design was a randomised block design (consisting of 4 treatments x 2 rates x 4 replicates) and was carried out under glasshouse conditions. SAS for Windows software was used to perform relevant statistical analyses to test significant differences in the interaction between time x treatment, treatment x depth and time x treatment x depth effects from neutralising materials.

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



5.2.4 Column leaching protocol

Preliminary tests using pitwall rock ≤ 2 mm fractions showed that water flow through the column was impeded due to clogging of the pore space with Fe-Al hydroxide coatings formed during reaction with the neutralising materials. Columns packed with pitwall rock of nominal grain size of 4 mm were found satisfactory in eluting ≥ 70 % of the saturated pore volume. In the case of FBA application, surface encrustation from reaction with $\text{Ca}(\text{OH})_2$ to form cementitious gel (ettringite) was observed during non-leached periods. The cement had to be broken regularly during leaching to facilitate water infiltration.

After one week of equilibration, the columns were wetted to saturation by gradually adding 350 ml of distilled water over 7 days (50 ml per day). The effluent was allowed to drain into collection flasks and the leachate collected was labelled as week-2 leachate. When leaching stopped, the wet weight of the column was recorded and compared with the dry weight for estimation of the saturated pore volume. The wetted columns were then allowed to react for one week, ensuring that the saturation water content was kept constant by daily weighing the columns. The subsequent leaching during alternate weeks (week 2, 4, 6, 8, 10 and 12) were done with 250 ml of distilled water (36 ml per day). The leaching volume of 250 ml over a one week period was approximately equivalent to mean weekly rainfall amounts at Waihi (~50 mm, ~250 ml).

The overall cycle of alternate dry reaction period and wet leaching period were repeated every 7 days for 12 weeks. The leached and non-leached weeks were thus simulative of wet and dry period field conditions at the Martha Mine site. The leaching was discontinued after 12 weeks when the measured parameters in the leachate were deemed to have stabilised.

5.2.5 Leachate analysis

For each leaching cycle, leachate pH and EC were measured immediately after collection. For total dissolved elemental analysis, about 50 ml of the leachate samples were acidified with 2 ml of 10 M HCl and filtered through Whatman #42 in order to bring into solution any metals adsorbed in the suspended materials. Total dissolved Fe, Mn and Al in the leachate were measured by atomic absorption spectroscopy (AAS) using water analysis methods outlined by Rayment and Higginson (1994). Leachate sulphate (SO_4^{2-}) was

measured by turbidimetric method in an Auto Analyser (Blakemore et al. 1987). Major cation concentrations in the leachate were analysed by atomic absorption/emission spectrophotometry.

5.2.6 Column section analysis

At the end of the 12 weeks leaching period, the pitwall rock columns were sliced into 20 mm sections (0-20, 20-40, 40-60, 60-80, 80-100, 100-120, 120-140 mm). The sliced sections were crushed and air-dried prior grinding to ≤ 2 mm fractions for chemical analysis.

Column section pH, EC, SO_4^{2-} , acidity, soluble Fe, Mn, and exchangeable Al (Al_{exc}) were determined according to methods outlined in section 3.2.1.3 (Chapter 3).

Compositional volume percentage (semi-quantitative) of minerals present in the sectioned samples were analysed by X-ray diffraction (XRD).

5.3 Results and Discussion

The average volume of the leachate collected was 140 ml week^{-1} and the rate of elution during leaching was about 2 ml per hour. The glasshouse temperature during the leaching period was $22 \pm 5^\circ \text{C}$ and at this temperature the rate of evaporation of column surface water was approximately $0.5 \text{ ml m}^{-2} \text{ day}^{-1}$ (0.1 ml day^{-1} from a column surface area of 0.13 m^2). Since the downward leaching of solute in the column depended upon the pore volume, solubility of the reaction products, hydraulic conductivity of the material and surface evaporation, the volumes of leachate collected were highly variable.

In general, there was a rapid release of dissolved metals (Fe, Mn and Al), SO_4^{2-} and EC over the first 8 weeks of leaching period followed by steady decrease until a constant level was released. The initial high concentrations in the leachate are considered to be flushing of the accumulated oxidation products but the rapid decline from week-6 onwards was considered to be due to the effect of neutralising materials. In describing the leachate and column characteristics of the pitwall rock, the following assumptions were made:

- Sample characteristics were uniform in the column.

- Downward migration of leachant was uniform and unimpeded by oxyhydroxide formations.
- All the reaction products were flushed by 250 ml deionised water used.

5.3.1 Characterisation of the leachate quality

5.3.1.1 Leachate pH

Surface amendment of pitwall rock columns with neutralising materials had no statistical significant effect on the leachate pH throughout the 12 weeks period of leaching. The leachate pH remained below 2.5 throughout the 12 weeks period of leaching, irrespective of surface amendments (Figure 5.2a). A stable pH plateau between 2.0-2.5 existed after week 6, indicating no net neutralisation of the acid in the leachate by surface amendment of neutralising materials. The equivalent rate of neutralising materials ($C_{ER} = 30 \text{ kg CaCO}_3 \text{ t}^{-1}$) although being sufficient to raise the pitwall rock pH to 6 during incubation to 90 days, had no significant effect on the leachate pH. The consistent low leachate pH from the neutralising material broadcasted pitwall rock may suggest that bacterially catalysed oxidation of pyrite produced acid more rapidly than the ability of the neutralising materials to neutralise microenvironments of acid formation. Since the downward movement of the alkaline front was limited to the upper 60 mm of the 140 mm pitwall rock column (see section 5.3.2.1), it is possible that the acid produced in the lower half of the column will not be affected by the surface broadcasted neutralising materials.

Low pH ($\text{pH} < 2.5$) leachate from columns broadcasted with neutralising materials was unusual but consistent with observations made by other workers in results of alkaline additions to pyritic materials. (Evans and Rose, 1995; Parisi et al, 1994; Brady et al, 1990). Bloomfield (1972) also noted that, although liming had considerably raised the subsurface pH of the leached pyritic soil cores, it had no significant effect on the pH of the effluent. Hoving and Hood (1984) and Doepker (1988) also observed a similar effect in their studies on the treatment of pyritic material with lime and phosphate respectively.

The pH of the leachate is primarily controlled by the oxidation of pyrite and subsequent dissolution of buffering minerals in the pitwall rock material and the neutralising effect of the amendments. After complete dissolution of a buffering mineral, the pH decreases until equilibrium is attained with respect to the next buffering mineral. These pH-buffering

reactions are indicated by near-constant pH-plateaus after week-5 of leaching. Such low pH leachate, despite surface amendment with neutralising materials, showed that AMD from pitwall surface runoff can be considerably more acid than the bulk of the surface material partially neutralised by surface application of neutralising materials.

Correlation coefficients (Table 5.1) showed that the pH of the leachate, although remaining unchanged over the leaching period, had a highly significant ($p=0.001$) negative linear relationship with EC, SO_4^{2-} , acidity, Fe, Mn and Al. However, there was no significant correlation with the base cations (Ca, Mg, K and Na). This may suggest mass precipitation of sulphate salts in the presence of elevated levels of SO_4^{2-} in the upper section of the column affected by the neutralising materials. At the same time, the displacement of H^+ and Al^{3+} from exchange sites by the base cations will lower the pH of the leachant as it moves down the column. This is possibly one of the reasons for continued low pH leachate from surface broadcasted columns.

5.3.1.2 Leachate EC

Leachate EC in the untreated column remained high ($\text{EC} > 6 \text{ dSm}^{-1}$) through to 12 weeks of leaching although it was significantly lower than the initial EC level of about 11 dSm^{-1} (Figure 5.2b). The EC from the untreated column was higher than from surface broadcasted columns throughout the leaching period. This indicated that most of the SO_4^{2-} accumulated as surface precipitations of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and alunite [$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$], which are solubilised during leaching and thus produce a highly salt laden leachate. Jarosite [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$] accumulated under low pH conditions during non-leached periods (when oxidative reaction takes place) will also be solubilised by the leachate water and contribute towards the increase in EC levels in the leachate and corresponding decrease in pH.

The apparent reduction in EC level in the leachate was due to precipitation of gypsum and metal hydroxide at higher pH effected by the neutralising materials. The leachate volume of 250 ml was thus sufficient only to partially solubilise a fraction of the salt in the leachate. The initial (week 2 and 4) EC levels in the surface broadcasted column were also high, in the range 7 to 10 dS m^{-1} , but there was rapid decrease after week-6 until it stabilised in the range $2\text{-}4 \text{ dS m}^{-1}$ from week-8 onward. Irrespective of neutralising

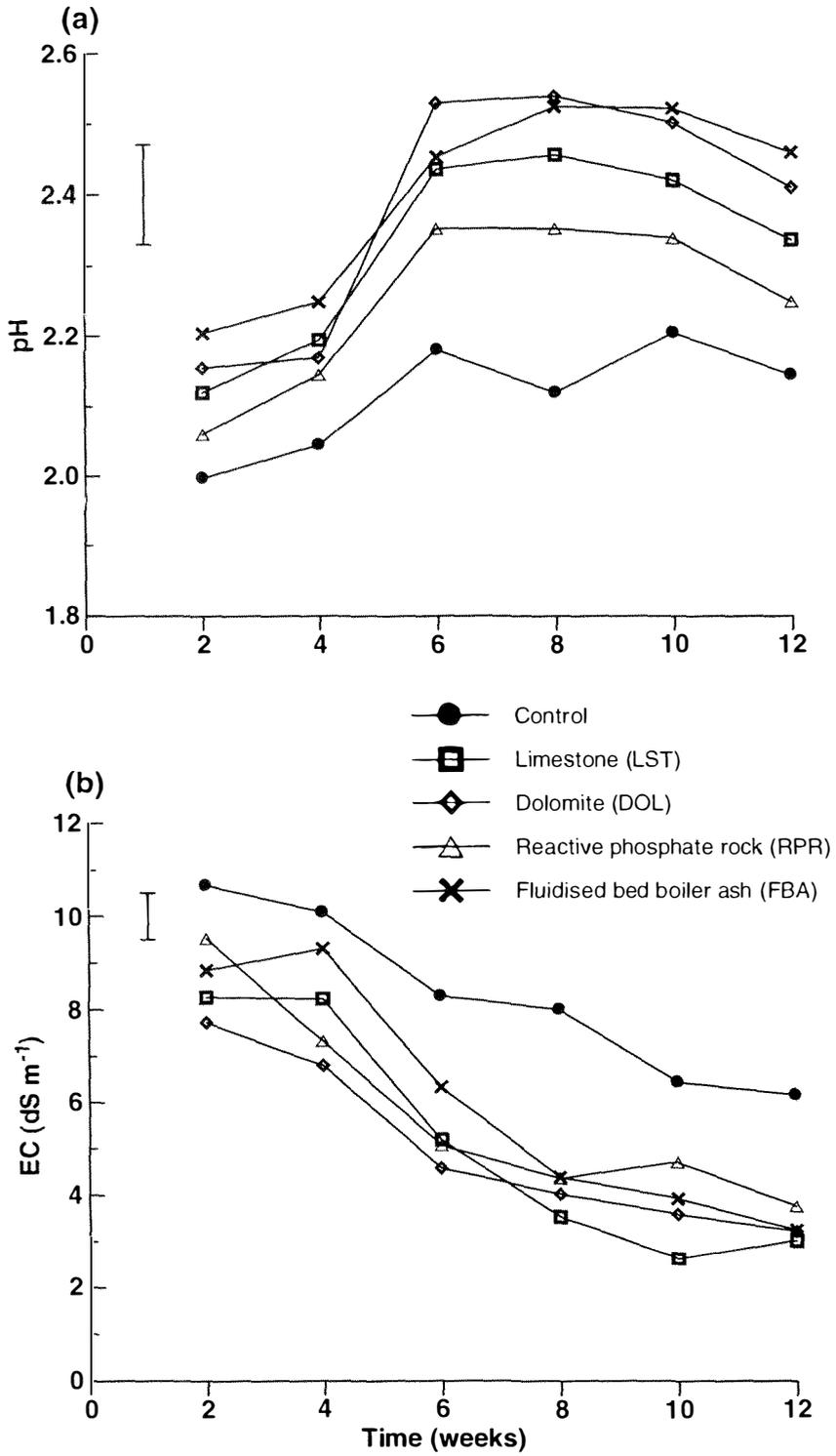


Figure 5.2 (a) pH and (b) EC of the leachate from columns broadcasted with neutralising materials. Vertical bars represent LSD(5%).

material type, the EC level did not fall below 2 dSm⁻¹ during the leaching period. There was no significant difference in the EC of the leachate treated with the four types of neutralising materials. Initially, the FBA broadcasted column produced slightly higher EC than the other three neutralising materials. This was to be expected as FBA already had CaSO₄·2H₂O, which would contribute total salt level in the leachate. The soluble salt concentrations in the leachate, as indicated by the EC, depend on the composition and solubility of the amendments applied at the surface and the extent of their reactivity within the column. The exchangeable ions displaced from the soil exchange sites and their cumulative concentrations in the leachate also strongly contribute towards the total electrolyte concentrations. Strong positive correlation of the EC with SO₄²⁻, acidity, Fe, Mn, Al, Mg and K and (Table 5.1) showed that these are the major components significantly (p=0.001) affecting the salt concentration in the leachate.

Table 5.1 Correlation coefficients (r) of the measured parameters in the leachate.

	pH	EC	SO ₄ ²⁻	acidity	Fe	Mn	Al	Ca	Mg	K
EC	-0.83									
SO ₄ ²⁻	-0.76	0.93								
acidity	-0.89	0.92	0.90							
Fe	-0.86	0.93	0.90	0.97						
Mn	-0.81	0.92	0.89	0.95	0.95					
Al	-0.88	0.93	0.92	0.96	0.97	0.96				
Ca	0.21	0.16	0.21	0.05	0.04	0.21	0.08			
Mg	-0.27	0.57	0.50	0.53	0.52	0.67	0.53	0.73		
K	-0.11	0.47	0.48	0.37	0.38	0.50	0.38	0.85	0.85	
Na	0.13	0.26	0.26	0.07	0.07	0.20	0.10	0.88	0.68	0.87

Coefficients $r \geq 0.46$ and $r \geq 0.36$ are significant at $p=0.001$ and $p=0.005$ level of significance respectively (n=30).

5.3.1.3 Leachate SO₄²⁻

Sulphate flux in the leachate is an indication of rates of pyrite oxidation, assuming optimum conditions for both chemical and bacterial reactions. Generally, it is reasonable to assume that sulphate concentration in the leachate is proportional to the sulphate flux and hence the extent of acid generation from pyrite oxidation (Morin and Hutt, 1994; Miller et al., 1994). From the correlation matrix (Table 5.1) it is evident that sulphate flux in the leachate is directly proportional to release of acidity, Fe, Mn, Al, Mg and K. Significant positive correlation with pH and EC also indicated the generation of acid and corresponding precipitation of salts were probably occurring simultaneously.

Leachate SO_4^{2-} from the untreated column remained higher than from the treated columns throughout the 12 weeks of leaching period. The SO_4^{2-} flux from the untreated and broadcasted columns rapidly decreased over the 12 week period (Figure 5.3a). The untreated column initially released 5588 SO_4^{2-} mg L^{-1} in the leachate which gradually stabilised at around 3500 $\text{mg SO}_4^{2-} \text{L}^{-1}$ after week 8 onwards. Leachate from the amended columns generally produced lower concentrations of SO_4^{2-} . Compared to the untreated column, LST and DOL induced the most significant reduction in SO_4^{2-} level.

The cumulative rate of release of SO_4^{2-} in the leachate is compared in Table 5.2. LST and DOL caused the largest reductions in SO_4^{2-} and they were significantly more effective than FBA and RPR by about 21%. The overall effectiveness of reductions in the concentration of SO_4^{2-} in the leachate compared with that of control with nil treatment were in the order: DOL>LST>>RPR>FBA.

5.3.1.4 Leachate acidity

Acidity release from the untreated column was 3121 $\text{mg CaCO}_3 \text{L}^{-1}$ in week-2 to about 1477 $\text{mg CaCO}_3 \text{L}^{-1}$ from week 8 onward, after which the level remained constant. Generally, LST, DOL and FBA broadcasted columns showed significant reduction in acidity compared with the untreated column (Figure 5.3b). The RPR broadcasted column produced significantly higher leachate acidity than LST, DOL and FBA but from week 10 onwards, there was no difference between the amendments. With time, the surface broadcasted columns generally produced lower acidity compared with the untreated column with nil amendment. At the end of 12 weeks, the comparative average acidity levels and relative reduction by the neutralising materials were as shown in Table 5.2.

The relative effectiveness of neutralising materials in reducing leachate acidity were in the order: FBA>LST>DOL>>RPR. The results of the leaching experiment showed that although leachate pH remained low, surface applied neutralising materials had significantly lowered SO_4^{2-} and acidity in the leachate towards the end of the leaching cycle as a result of oxyhydroxide formation and precipitation of sulphate minerals.

Table 5.2 Average release rates of the concentrations of measured parameters in the leachate from broadcasted pitwall rock column.

	Overall means comparison					LSD $\alpha=0.05$	% reduction (-) / increase (+)			
	Control	LST	DOL	RPR	FBA		LST	DOL	RPR	FBA
SO ₄ ²⁻	4213	2327	1977	3000	3113	224	-45	-53	-29	-26
Acidity	2196	1066	1132	1485	992	24	-51	-48	-32	-55
Fe	3253	1575	1492	1773	1153	153	-52	-54	-45	-65
Mn	134	79	82	91	63	7	-41	-38	-32	-53
Al	377	211	179	245	160	21	-44	-52	-35	-58
Ca	234	368	351	303	412	13	+57	+50	+29	+76
Mg	82	106	138	90	111	7	+29	+68	+10	+35
K	18	22	24	17	28	2	+24	+34	-4	+54
Na	24	36	38	29	51	2	+46	+54	+20	+110

Except for acidity (mg CaCO₃ L⁻¹ week⁻¹), the units are in mg L⁻¹ week⁻¹

As a measure of acid neutralisation by neutralising material addition in the pitwall rock column, cumulative acidity was calculated for 12 weeks duration of leaching. Cumulative acidity, given in equivalent mg CaCO₃ L⁻¹ represents the total acidity discharged since the beginning of the experiment. The mean cumulative rate of acidity released from the untreated control column was 2196 mg CaCO₃ L⁻¹ week⁻¹. In the untreated column, the cumulative increase in acidity followed a linear trend with time ($y = 394 * X + 410.31$, $R^2 = 0.99$) indicating continued generation of acid in the column. The initial high levels of acid release from all the columns represented the initial flushing of stored SO₄²⁻ and dissolution of jarosite type minerals.

The corresponding cumulative release of acidity from the amended columns followed trends:- RPR: $y = 713 * \text{Log}(x) + 557$, $R^2 = 0.99$; LST and DOL: $y = 494 * \text{Log}(x) + 537$, $R^2 = 0.98$; FBA: $y = 410 * \text{Log}(x) + 464$, $R^2 = 0.99$]. A strong positive correlation (Table 5.1) of the acidity with the major components of the leachate indicated that the solubility of Fe, Mn, Al, salt and cations in the leachate will be directly controlled by the high acidity and low pH of the emerging leachate.

5.3.1.5 Leachate Fe and Mn

A significant reduction in the concentrations of soluble Fe and Mn were observed in leachate irrespective of treatments. The concentrations in the leachate from amended columns were significantly lower than that of control column throughout the leaching period (Figure 5.3c & d). The mean release rate of Fe and Mn concentrations from the

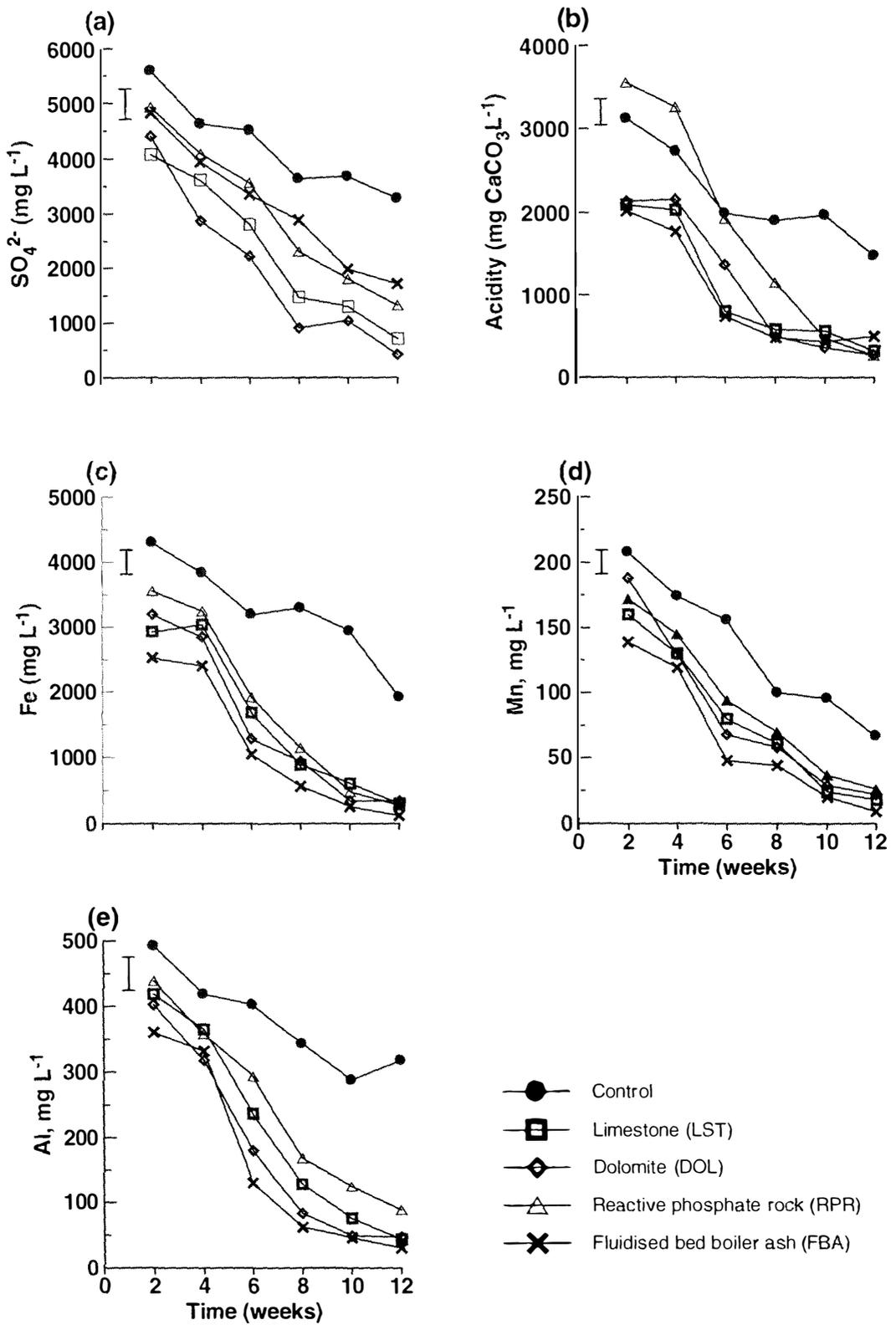


Figure 5.3 Concentrations of (a) SO_4^{2-} , (b) acidity, (c) Fe, (d) Mn and (e) Al in the leachate from columns broadcasted with neutralising materials. Vertical bars represent LSD(5%).

control columns were 3253 mg Fe L⁻¹ week⁻¹ and 134 mg Mn L⁻¹ week⁻¹ respectively (Table 5.2). All the treatments caused rapid reduction in the concentration of Fe and Mn after the second cycle of leaching. The relative reduction of both Fe and Mn contents was generally higher in the leachate from the FBA broadcasted columns.

Both Fe and Mn showed strong positive correlation with EC, acidity, SO₄²⁻, Al, Mg and K but showed insignificant (at p=0.005) relationship with Ca and Na in the leachate. Highly significant (p=0.001) negative correlation of Fe and Mn with leachate pH and corresponding positive significance with acidity (Table 5.1) confirm their solubilised state in very low pH conditions.

In general, the reduction in the concentrations of Fe and Mn in the leachate from the control columns followed the trends:- Fe = 3079 * X + 1813, R² = 0.99 and Mn = 336 * Ln(X) + 182, R² = 0.99. In the presence of elevated levels of sulphate, raising the pH with neutralising materials has resulted in the precipitation of these metals as sulphate (FeSO₄, MnSO₄) and hydroxides (Fe(OH)₃, Mn(OH)₃) along with gypsum (CaSO₄.2H₂O). The FeSO₄ can further react with the CaCO₃ to form more Fe(OH)₃ and CaSO₄.2H₂O resulting in immobilisation of Fe and Mn in the column.

5.3.1.6 Leachate Al

Surface application of lime in acid agricultural soils is commonly intended to raise the pH and neutralise or precipitate plant-toxic levels of Al. In the absence of mobile anions such as SO₄²⁻ the downward movement of lime has been found to be extremely slow especially in variable charge soils. Under severely acid conditions (pH<3), the low pH condition is largely buffered by acid hydrolysis of aluminosilicates and is characterised by high Al contents in both leachate and column sections of untreated columns (Figure 5.3e and 5.5e). As the pH of the column surface is raised by the alkaline amendments, Al is likely to precipitate as hydroxide [Al(OH)₃] or basic sulphate (van Breemen, 1973) releasing more soluble acid that can be leached from the system.

The solubilised Al content in the leachate from surface broadcasted columns compared with the untreated column showed a rapid decrease with time (Figure 5.3e). The average release of Al in the leachate from the untreated control column was 377 mg L⁻¹ week⁻¹

whereas the concentration in the leachate from broadcasted columns was significantly lower (Table 5.2). The Al in the leachate was shown to be strongly correlated with pH, EC, SO_4^{2-} , acidity, Fe, Mn, Mg and K (Table 5.1) indicating that in low pH conditions all of these dissolved constituents are likely to influence the release of Al in the leachate. The relative reduction in Al (Table 5.2) in the leachate from amended columns were in the order FBA (58%) > DOL (53%) > LST (44%) >> RPR (35%).

5.3.1.7 Leachate Ca - Mg - K - Na

Amendment with neutralising materials caused significant increase in the leachate Ca concentration compared to that from control column. The FBA treated column produced leachate with highest Ca concentration whereas Ca level in the leachate from RPR was not significantly different from that of control column (Figure 5.4). This may suggest that in the presence of high amounts of SO_4^{2-} , Fe, Mn, Al and dissolved salts, the contribution of Ca from the carbonate fraction of the neutralising material may be minimal. Under alkaline conditions created at the surface by the neutralising materials, most of the Ca is likely to be paired with SO_4^{2-} and precipitated as gypsum, as reflected in the significant ($p=0.001$) linear correlation coefficients (Table 5.1). It is possible that some Ca in the leachate may have dissolved from decomposition of clay and Ca-feldspar minerals in very acid pore solutions. The relative increases of 57%, 50%, 29% and 76% in Ca concentrations of the leachate from LST, DOL, RPR, and FBA amended columns respectively were statistically significant.

There was also significant reduction in the Mg concentrations except for the DOL amended column, which showed an 68% relative increase in the Mg concentration of the leachate compared with that of control column (Table 5.2). Both FBA and DOL broadcasted columns produced leachate with increased concentrations of K in the leachate. There was a large increase (110%) in Na concentration in the leachate from the FBA amended columns. The FBA used in this experiment had a Na content of 7000 mg Na kg^{-1} (0.7%, Wang et al, 1994) and because Na is highly mobile, the high concentration reflected in leachate is to be expected. Both Mg and K showed strong positive correlation with EC, SO_4^{2-} , acidity, Fe, Mn and Al (Table 5.1) indicating that their mobility in the acid environment is strongly affected by acidity generated from pyrite oxidation.

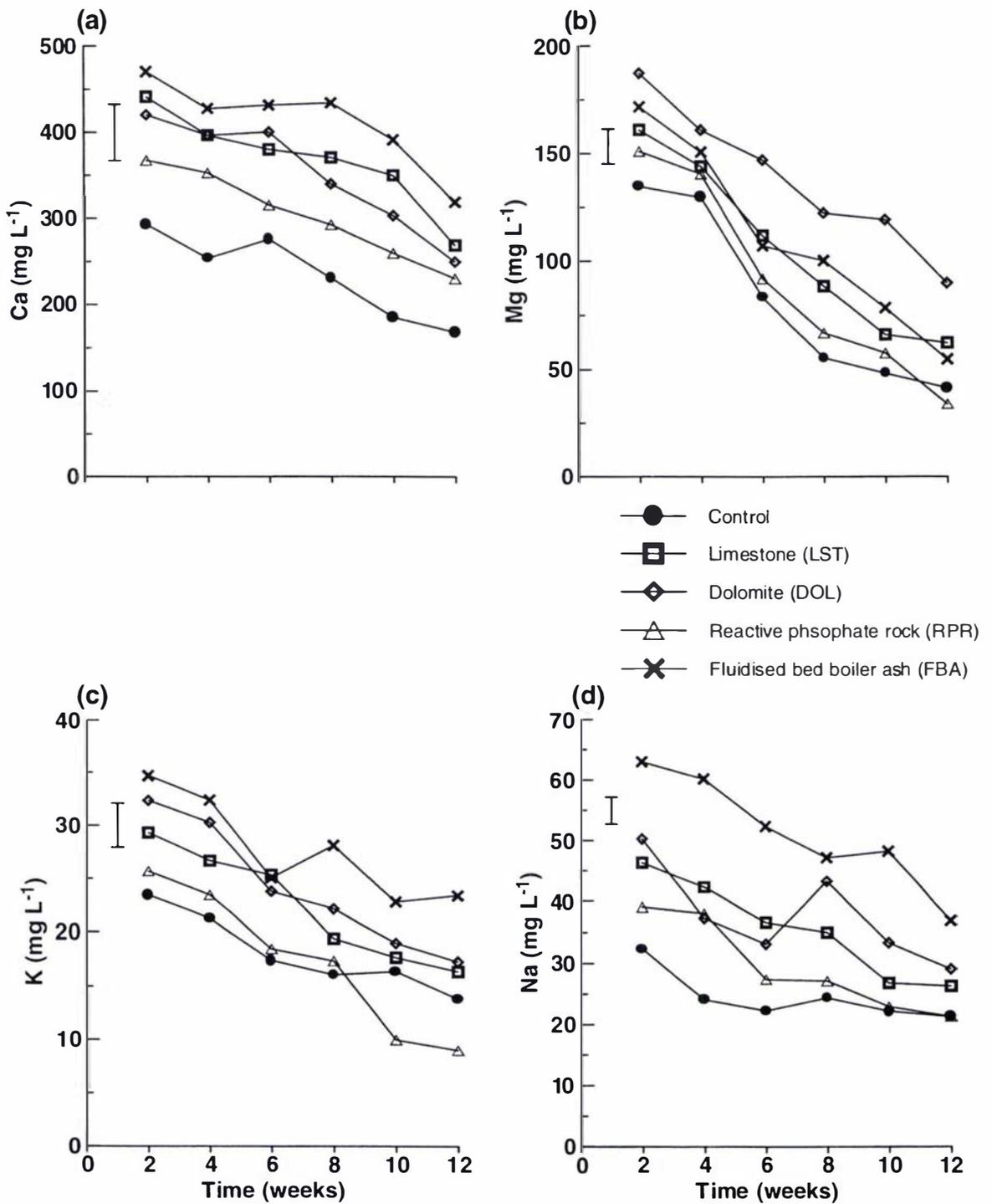


Figure 5.4 Concentrations of (a) Ca (b) Mg (c) K and (d) Na in the leachate from columns broadcasted with neutralising materials. Vertical bars represent LSD(5%).

5.3.2 Column section chemistry

5.3.2.1 Column section pH

Surface application of neutralising materials significantly increased the pH in top 50 mm of the column (Figure 5.5a). The degree of effectiveness of raising the pH was in the order FBA > LST, DOL > RPR. A large fraction of the surface applied FBA remained undissolved at the surface, resulting in very high pH (>8.0) in the 0-30 mm of the column. FBA amendment also caused formation of a cementitious crust on the surface of the column during the non-leached period, which impeded the infiltration of the leachate water. The FBA used in this study contained a large fraction of burnt lime (CaO) and reactive CaSO₄ as well as significant amounts of amorphous aluminosilicates (Wang et al., 1994). When FBA is mixed with water it quickly forms hydrated calcium sulphate (CaSO₄·2H₂O) or calcium aluminium sulphates (ettringite, Ca₃Al₂O₅·3CaSO₄·32H₂O), resulting in the formation of a cementitious constituent of portland cement called the C-S-H gel (Morin et al, 1995).

Both LST and DOL raised the pH to about 7 in the upper 0-30 mm section of the column. RPR raised the pH to about 5 only in the top 20 mm of the column, and at column depth > 20 mm, it remained below 4. FBA, LST and DOL were all able to raise the pH to >4 up to a column depth of 60 mm. Although the neutralising materials had significantly raised the surface pH, there was little effect at depths greater than 60 mm. The results suggested that in acidic materials with high levels of SO₄²⁻ and metal concentrations, the downward mobility of the alkaline front created by the neutralising materials is severely restricted by mass precipitation of salts and hydroxide compounds. These compounds can keep the material buffered against further rise in pH, at lower section of the pitwall rock column.

The pH of the untreated column remained unchanged (<2.5) throughout the 140 mm column depth. As with the leachate analysis, the pH of the column section was negatively correlated with EC, SO₄²⁻, Fe, Mn and Al. However, significant amounts of Ca, Mg, K and Na accumulated in the columns affected by the neutralisation processes as ion pairs with SO₄²⁻. This is reflected in the strongly positive correlation (p=0.001) of pH with these cations (Table 5.3).

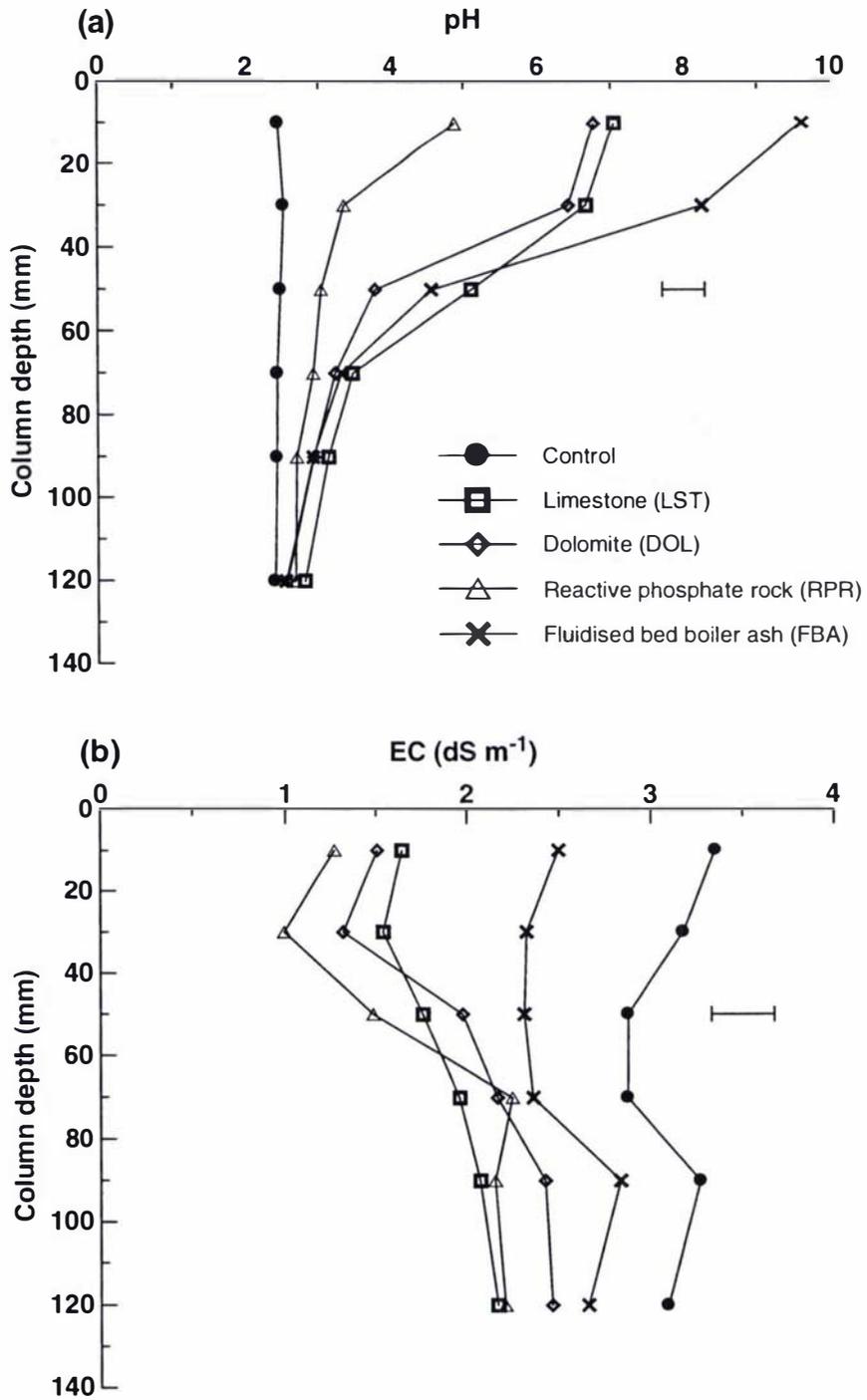


Figure 5.5 (a) pH and (b) EC of the sectioned samples from leached columns. Horizontal bars represent LSD(5%).

The initial dissolution of carbonate and hydroxide fractions of the neutralising materials is relatively fast, resulting in the precipitation of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$, thereby increasing the buffering capacity of the pitwall rock. However, the downward movement of the alkaline front was not sufficient to significantly raise the pH at column depth > 60 mm due to possible armouring effect of the carbonate grains with $\text{Fe}(\text{OH})_3$ and dissolution of jarosite [$(\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6)$]. Thus in upper sections of the column the pH of the leachate will be controlled by the large buffer exerted by $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ whereas at depth the rate of acid generation and dissolution of jarosite may keep the leachate at a low pH level at all times. The acid neutralisation processes are, therefore primarily controlled by the dissolution reactions of the carbonate, hydroxide and aluminosilicate minerals, as suggested by Blowes et al.(1994).

5.3.2.2 Column section EC

The EC in the control column remained high and constant ($3.1 \pm 0.2 \text{ dSm}^{-1}$) throughout the column depth. Application of amendments resulted in significant reductions in the EC levels in the upper 0-80 mm depth of the columns (Figure 5.5b). The FBA had significantly higher EC than LST, DOL or RPR in the 0-40 mm section but at depths >40 mm, there were no differences in the EC levels between the amended columns. The higher EC level in the upper section of the FBA amended column is attributed to the gypsum contained in the FBA. At depths of 0-80 mm the EC in the LST, DOL and RPR was $< 2 \text{ dSm}^{-1}$ but increased at greater depths as a result of accumulated salt. The low level of EC in the column was expected since it was sectioned after leaching of the soluble components. Therefore, any salt left in the column is either from incomplete flushing or from SO_4^{2-} generated thereafter.

Significant positive correlation of EC with SO_4^{2-} , acidity, Fe, Mn and exchangeable Al (Al_{exc}) suggested that metal sulphate salt formation under a highly acid leaching environment is a common occurrence. The laboratory (section 3.3.2.4, Chapter 3) and field evidence of copious amounts of salt encrustation on the surface support this above postulation. The relative reductions in the amount of EC were in the order: RPR>LST>DOL>FBA (Table 5.4).

Table 5.3 Correlation coefficients (r) of measured parameters in the column section.

	pH	EC	SO ₄ ²⁻	acidity	Fe	Mn	Al _{exc}	Ca	Mg	K
EC	-0.43									
SO ₄ ²⁻	-0.66	0.78								
acidity	-0.88	0.58	0.70							
Fe	-0.88	0.68	0.86	0.83						
Mn	-0.86	0.64	0.73	0.78	0.85					
Al _{exc}	-0.78	0.84	0.89	0.82	0.89	0.89				
Ca	0.89	-0.31	-0.52	-0.71	-0.77	-0.74	-0.67			
Mg	0.53	-0.32	-0.42	-0.51	-0.49	-0.29	-0.46	0.60		
K	0.62	0.15	-0.25	-0.31	-0.49	-0.43	-0.29	0.68	0.30	
Na	0.58	-0.04	-0.18	-0.33	-0.45	-0.54	-0.39	0.72	0.30	0.75

Coefficients $r \geq 0.46$ and $r \geq 0.36$ are significant at $p=0.001$ and $p=0.005$ level of significance respectively ($n=30$).

Table 5.4 Overall comparison of the mean concentrations of chemical properties of the leached pitwall rock columns broadcasted with neutralising materials.

	Overall means comparison					LSD	% reduction (-) / increase (+)				
	Control	LST	DOL	RPR	FBA	$\alpha=0.05$	LST	DOL	RPR	FBA	
pH	2.5	4.6	4.3	3.3	5.2	0.12	+86	+75	+34	+113	
EC	3.1	1.8	2.0	1.7	2.5	0.14	-41	-37	-45	-21	
SO ₄ ²⁻	3263	2197	2072	1953	2555	141	-33	-37	-40	-22	
Acidity	2761	1014	1058	2139	1194	16	-63	-62	-23	-57	
Fe	2538	1585	1638	1745	1588	108	-38	-35	-31	-37	
Mn	260	145	195	155	135	11	-44	-25	-40	-48	
Al _{exc}	806	339	358	300	377	29	-58	-56	-63	-53	
Ca	1513	10255	9111	5127	13645	601	+578	502	+239	+802	
Mg	382	421	1241	500	631	41	+10	225	+31	+65	
K	236	198	198	207	298	15	-16	-16	-12	+26	
Na	57	81	108	156	249	7	+41	+88	+172	+335	

Except for pH, EC(dS m⁻¹) and acidity (mg CaCO₃ kg⁻¹), the units are in mg kg⁻¹.

5.3.2.3 Column section SO₄²⁻

Average soluble SO₄²⁻ concentrations in the untreated column ranged from 3150 mg kg⁻¹ at the surface to 3720 mg kg⁻¹ in the bottom section of the column, indicating that not all the sulphate was leached. The mean SO₄²⁻ concentration in the 140 mm column was 3263 ± 376 mg kg⁻¹ compared to the original concentration of 7440 mg kg⁻¹ in the bulk sample (Table 4.1, Chapter 4). This indicated that intermittent leaching of the column without amendment alone was responsible for reducing the SO₄²⁻ level in the column by about 75%.

Soluble SO_4^{2-} concentrations in the pitwall rock column sections after 12 weeks of leaching cycle showed that the LST, DOL and RPR broadcasted columns had significantly reduced concentrations up to 0-60 mm depth (Figure 5.6a). The FBA amended column had an elevated level of SO_4^{2-} in the top 0-40 mm section as a result of solubilised CaSO_4 from FBA as well as the mass precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. However, in lower sections of the column (>60 mm depth), the SO_4^{2-} levels of the broadcasted columns were not significantly different from that of the untreated column.

Although surface broadcasted columns had significantly lower sulphate levels at 0-40 mm depths, it is probable that a large fraction of the sulphate diffused to low pH section of the column and remained trapped as insoluble salts in the pore spaces. A significant amount of soluble SO_4^{2-} in the column section samples indicated that either not all SO_4^{2-} was flushed or pyrite oxidation is still active despite amendment at the surface by highly alkaline neutralising materials. The reduced level of SO_4^{2-} in the 0-40 mm section of the column broadcasted with LST, DOL and RPR indicated that these materials facilitated precipitation of sparingly soluble sulphate salts. This possibility is reflected in the significant correlation of SO_4^{2-} with Ca, Mg (Table 5.3).

Column leaching affected by gypsum precipitation and hydroxide coatings can be due to insufficient rinse water and incomplete rinsing of the reaction products due to channelling. At high sulphate production, gypsum and metal sulphate precipitate at the surface when rinse water is added (increase in pH) resulting in apparent low sulphate levels in the leachate. When sulphate production is decreased due to reduction in pyrite oxidation (exhaustion of exposed pyrite grains or non-reactive coating by hydroxides), the rinse water can flush the accumulated gypsum and thus providing an apparent increase in sulphate levels in the leachate.

5.3.2.4 Column section acidity

Acidity in the untreated column remained high at around $2000 \text{ mg CaCO}_3 \text{ kg}^{-1}$ throughout the column depth (Figure 5.6b). There was an apparent elevated level of acidity at median column depths of 50-70 mm depth of the control column indicating possible acid generation by bacterial activity. There was significant reduction in acidity in the upper 60 mm section of the columns broadcasted with LST, DOL and FBA. Acidity reduction by

RPR was approximately 60% less effective than either LST, DOL or FBA. Compared to the untreated column, there was significant reduction in acidity up to a depth of 80 mm in the surface broadcasted columns.

Column section acidity showed strong negative correlation with Ca, Mg and K, indicating dissolution of these ions from silicate matrix and rapid removal from the system (Table 5.2). As expected, acidity showed a strong negative correlation with pH and a strong positive correlation with EC, SO_4^{2-} , Fe, Mn and Al. Although there was a gradual reduction of the leachate acidity in the untreated column with each successive leaching (Figure 5.4b), acidity levels in the leached columns remained high through the column. On the other hand, the surface broadcasted columns showed a significant decrease in acidity in both leachate and in column sections (Figures 5.3b and 5.6b). This characteristic corresponds to the raised pH level in the upper 60 mm of the column depth by the surface broadcasted neutralising materials. The result showed that under the leaching conditions of this experiment, there was significant amelioration of subsurface acidity by neutralising materials despite generation of very low pH leachate.

Free acid may be readily leached from the column, however, in the presence of heavily adsorbed Fe and Al, acidity represented by these species may remain in the column as indicated by high acidity content throughout the column. The amount of acid generated depends on the amount of oxidisable pyrite present and solubilisation of the reaction products. In order to assess the extent of acid neutralisation by surface applied alkaline amendments under oxidative leaching conditions, total acidity and the rate of acid production and leaching need to be monitored over a length of time. Most of the acidity generated from oxidation of the pyrite in the column should ideally be consumed in the subsequent oxidation of Fe^{2+} to Fe^{3+} , but the resulting net precipitation of Fe-hydroxide would generate further acidity. Under very low pH conditions, jarosite may precipitate in pores and micro-channels as yellowish-brown deposits of Na, K and H_2O polymorphs. In severely acid and oxidising conditions of $\text{pH} < 4$, jarosite is considered to be the dominant precipitate over goethite resulting in temporary storage of acidity (van Breemen, 1973).

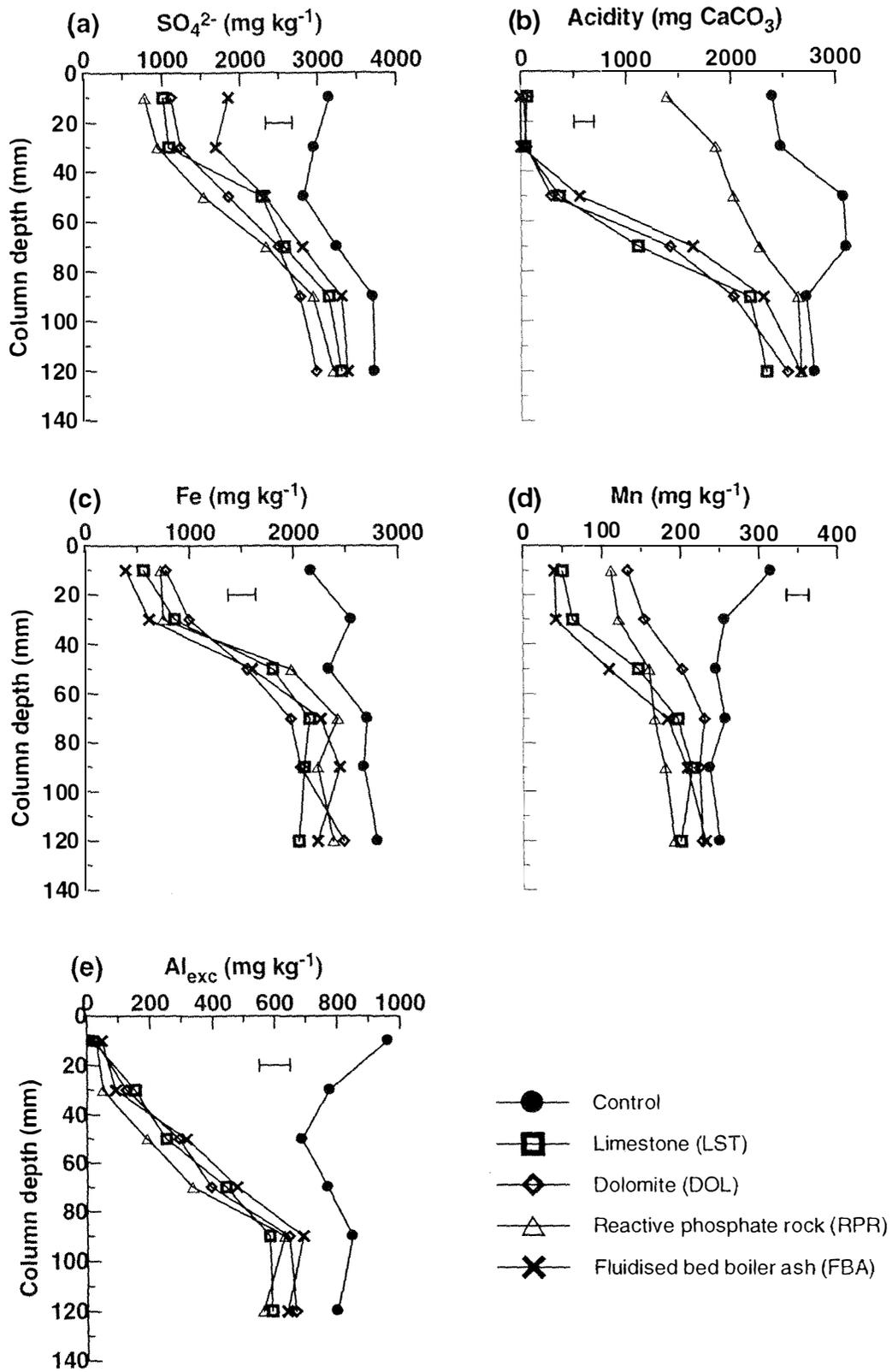


Figure 5.6 Distribution of (a) SO_4^{2-} , (b) acidity, (c) Fe, (d) Mn and (e) Al_{exc} in the sectioned samples from leached columns. Horizontal bars represent LSD(5%),

However, a likely scenario would be that as exposed pyrite grains are exhausted or coated by Fe-hydroxide and Fe-phosphate coatings, the pH of the pitwall rock column would increase and at $\text{pH} > 4$, jarosite is metastable and will hydrolyse to goethite (FeO.OH) and Fe(OH)_3 , resulting in further release of acidity in the leachate.

5.3.2.5 Neutralisation of acidity in the pitwall rock column

The continued release of acidity in the leachate from surface broadcasted columns indicated that dissolution of the neutralising materials was not fast enough to counterbalance the rate of acid generation in the pitwall rock column. Since partially oxidised pitwall rock was used, there was already a large amount of pyrite oxidation products formed in the column. In the presence of elevated levels of Fe, Mn, Al and SO_4^{2-} , the alkalinity generated by the surface placement of the neutralising materials was therefore rapidly consumed in the precipitation of metal hydroxide complexes and salt precipitates in the upper section of the column.

Initially, the rate of amendment application used was only sufficient to neutralise the active acidity present in the pitwall rock up to a column depth of 60 mm from the surface. A large part of the hydroxyl ions generated by the broadcasted neutralising materials were consumed by the formation of Fe and Al hydroxide precipitates which kept the system buffered against increases in pH. Since grain size and reactivity affect the dissolution of alkaline fraction in a very acidic environment, the reaction with finer carbonate fractions will be relatively fast and effect the immediate precipitation of metal hydroxides.

In contrast, larger grains of the neutralising materials may be armoured by oxyhydroxide coatings by initial reactions in the neutralisation process. This is evident in SEM/EDS scans of the limestone grains in contact with acidic solutions containing high concentrations of Fe and Al (Chapter 4). Therefore, neutralisation of acidity by addition of neutralising materials has some drawbacks because solutes are precipitated as insoluble precipitates such as flocs of Fe and Al oxides and hydroxides which can severely affect the micro-environment by clogging the free pore spaces.

The neutralisation of acid by the carbonate fraction of the neutralising materials (Eqn.5, 6 & 7)) and /or decomposition of silicate minerals is a function of the total acidity produced

in the system and formation of secondary minerals such as gypsum (Eqns. 6 & 7), Fe-Al sulphates and jarosite. According to an ideal oxidation of pyrite, 2 moles of acidity are produced for every one of SO_4^{2-} and the neutralisation of acid follows at the rate of 2 moles of H^+ consumed for each mole of CaCO_3 equivalent (Eqns. 1 & 8, Chapter 2). Therefore, any deviation from the ratio of acidity to SO_4^{2-} ($100 \text{ mg CaCO}_3 \text{ L}^{-1} / 96 \text{ mg SO}_4^{2-} \text{ L}^{-1} = 1.04$) is an indication of the acid generation/neutralisation.

Regression plots showed close linear relationships between acidity and sulphate by all the treatments (Figure 5.7). The slope of the regression equation for the untreated column leachate was 0.66 whereas the combined average slope of the LST, DOL, RPR and FBA amended column leachate was about 0.49. These slopes were unusually low in comparison to the slope of 1.04 for acid generation. Therefore, if the acid released in the leachate was proportional to the acid generation (SO_4^{2-} flux) in the column, these slopes indicated acid neutralisations of 37% ($0.66 / 1.04 * 100 - 1$) and 53% in the untreated and amended columns respectively.

However, acidity measurements of the column section showed that only LST, DOL and FBA had significantly reduced the column acidity (Figure 5.6b) and that the untreated column, still had a similar level of acidity as in the leachate. This observation suggested that SO_4^{2-} , and acidity levels in the leachate from pyritic waste rock may not reflect the acid generation and neutralisation processes in the columns as suggested by Evans and Rose (1995) in their study on the effect of alkaline additions to coal mine spoil.

The ideal molar ratio of 1.04 for acidity to sulphate is never achieved under field conditions and, therefore, the measurement of acidity does not indicate the rate of release of acidity in the leachate because some of the acidity is neutralised by the dissolution of alkali minerals. Neither can sulphate release be indicative of acid production because some of the sulphate will be involved in the formation of gypsum and metal sulphate precipitates. Gypsum precipitation and solubility under low pH has been shown to affect the sulphide oxidation and acid generation resulting in apparent lower rates of sulphide oxidation (Ferguson and Morin, 1991; Morin et al, 1995). The measurement of SO_4^{2-} in the leachate therefore, is not indicative of acid generation and hence pyrite oxidation in the pitwall rock sample. The weekly rinse water equivalent to the weekly average rainfall

amount at Waihi (50 mm) or the equivalent pore volume often used to flush the reactants are in reality insufficient for the removal of all of the leaching cycle's reaction products.

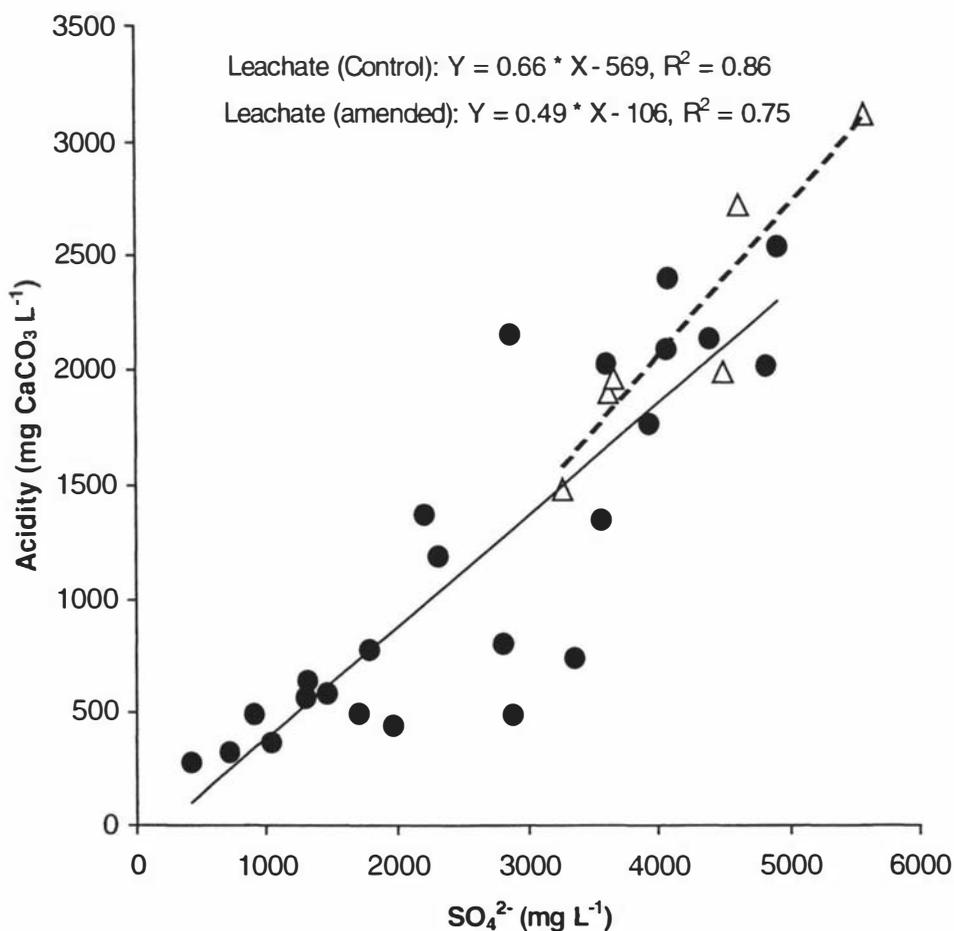


Figure 5.7 A regression plot of overall mean acidity and SO_4^{2-} values in leachate from control and amended columns. Data points are means of four replicates.

The comparison of sulphate releases between the untreated column and the surface broadcasted columns showed that although sulphate release rates were limited by gypsum precipitation and metal sulphate complexing, there was a general trend of decreasing SO_4^{2-} release with time. Although there was a strong linear relationship between sulphate and acidity levels in the leachate, the relative slope of the curve did not relate to the molar ratio slope for ideal oxidation of pyrite.

5.3.2.6 Column section Fe and Mn

Most of the soluble Fe mobilised by oxidation of pyrite remained in the untreated column and for surface broadcasted columns, increased pH caused rapid precipitation of Fe as goethite or amorphous Fe-CaCO₃ compounds. The precipitation of Fe and Mn as hydroxides and sulphate metal salts is reflected in the correlation matrix which shows significant ($p=0.001$) positive relationship with EC, SO₄²⁻ and acidity and corresponding negative correlation with base cations (Table 5.3). Strong correlation ($p=0.001$) was also found between Fe and Mn in both leachate and column sections, indicating that these metals may be co-precipitating under alkaline conditions created by surface broadcasted neutralising materials.

There were no significant differences between the effect of different types of neutralising materials on the Fe content of the column sections. Soluble Fe in the treated columns was reduced to <100 mg kg⁻¹ at 0-40 mm depth and remained significantly less than the soluble Fe content of the untreated column (Figure 5.6c). On the other hand, FBA and LST amended columns showed significant reduction in Mn in the upper 60 mm column depth (Figure 5.6d). The reductions in soluble Fe and Mn were less than 50 mg kg⁻¹ (Table 5.4), indicating that these metals remained in the pitwall rock as insoluble metal hydroxide complexes.

5.3.2.7 Column section exchangeable Al (Al_{exc})

Surface amendments with neutralising materials resulted in significant reduction of Al_{exc} at 0-80 mm column depths (Figure 5.6e). At 0-60 mm depths, Al_{exc} was less than 180 mg kg⁻¹ in the broadcasted columns. The increase in pH at the upper section of the column was primarily responsible for precipitating Al_{exc} as insoluble complexes. Although RPR did not raise pH to > 3.5 in the 0-60 mm depth, it was effective in reducing Al_{exc} possibly as Al-PO₄ complexes. Strong correlation of Al_{exc} with pH, EC, SO₄²⁻, acidity, Fe and Mn suggested that as pH increased, most of the Al in the upper section of the column precipitated either soluble salt (alunite) or hydroxide precipitates (gibbsite). Strong negative correlation with cations also indicated that Al³⁺ is preferentially displaced from the exchange sites along with H⁺. The relative reduction in the overall means of Al_{exc} in the amended columns were in the order: RPR>LST>DOL>FBA (Table 5.4)

5.3.2.8 Column section Ca - Mg - K - Na

The distribution of the base cations in the sectioned columns is shown in Figure 5.8. As expected, FBA caused the greatest increases in Ca, K and Na concentrations of the column section. Downward migration of Mg, K and Na was evident in FBA and DOL broadcasted columns but Ca was raised only at the 0-40 mm section of the column. High Mg concentrations were observed only in the DOL broadcasted column and at the surface section (0-20 mm) of the FBA broadcasted column. The cation concentrations in the untreated column remained low and at depth greater than 20 mm, both LST and RPR broadcasted columns contained similar levels of cation concentrations to the untreated column. The distribution of cations in the column is largely controlled by the degree of alkalinity created by the neutralising materials. Thus FBA, which created a highly alkaline condition at 0-40 mm depths, would in fact contribute high amounts of Ca as reflected in Figure 5.8a and in the strong positive correlation of the cations with the pH and corresponding negative trend with the acidity (Table 5.3). Significant negative correlation of the cations with Fe, Mn and Al_{exc} suggested preferential displacement and precipitation of the metal ions.

Although surface broadcasted columns produced low pH leachate and significant amounts of acidity were resident in the columns, there were significant increases in the base saturation (BS%) of the pitwall rock as a result of Ca and Mg input from the dissolution of neutralising materials. Generally there was a 2-fold increase in BS% at the surface in all the amended columns (Table 5.5). This may have important implications for the availability of nutrient cations (Ca, Mg, K and Na) for plant growth. There were no significant differences ($P > 0.05$) in the BS% distributions between the amendments, especially at 0-40 mm depth. As expected, there were gradual decreases in the BS% down the column profile. It is interesting to note that RPR was equally effective in providing base cations as the other three amendments. The BS% of the untreated column remained low (< 65%) and relatively uniform throughout the column depth.

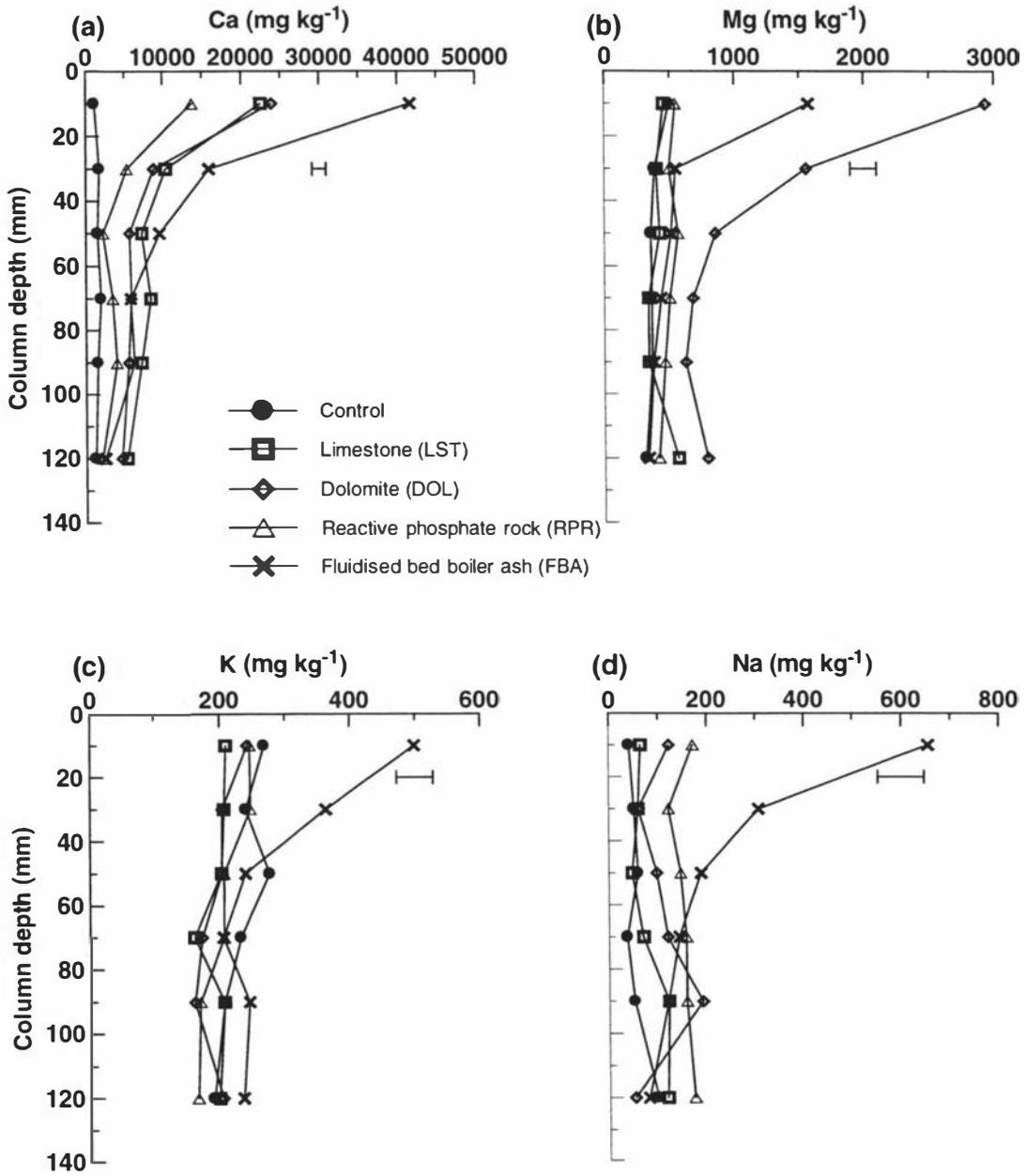


Figure 5.8 Distribution of (a) Ca, (b) Mg, (c) K and (d) Na in sectioned samples from leached columns broadcasted with neutralising materials. Horizontal bars represent LSD(5%).

Table 5.5 Depth-wise base saturation (BS%) in the broadcasted columns.

	Control	LST	DOL	RPR	FBA
Depth, mm	-----BS%-----				
0-20	50	100	100	100	100
20-40	61	97	98	98	99
40-60	62	94	92	89	94
60-80	62	90	89	86	87
80-100	56	86	83	78	83
100-140	53	83	81	71	70

$$\%BS = [\sum \text{base (cmol}_c \text{ kg}^{-1}) / \text{ECEC (cmol}_c \text{ kg}^{-1})] * 100 \text{ where ECEC} = [\sum \text{base} + \text{Al}_{\text{exc}} \text{ (cmol}_c \text{ kg}^{-1})]$$

5.3.3 Mineralogical composition of leached columns

An X-ray diffraction (XRD) analysis of the sectioned samples indicated anomalously high amounts of pyrite and gypsum at a column depth of 50 mm (Figure 5.9). Both untreated and FBA broadcasted columns showed unusually high amounts of pyrite at a column depth of 60 mm. This may have been due to selective accumulation of hydroxide coated pyrite being analysed by the XRD, since there was no anomalous high acidity or SO_4^{2-} generation at this depth. Another possible explanation for the anomaly could be that during column packing, this section of the column depth might have contained a greater amounts of unliberated pyrite. The weight percent pyrite analysed by XRD ranged from 0 to 9% in the untreated and FBA treated columns whereas it remained at 2 to 4 % in the LST, DOL and RPR broadcasted columns. The high pyrite content throughout the column indicated that only a fraction of the pyrite in the column oxidised, either due to the armouring effect of oxyhydroxide precipitates and Fe-PO_4 coatings, or because of incomplete oxidation due to “entombment” in the pitwall rock material.

High gypsum contents at 50 mm depth for LST and DOL amendments (Figure 5.9b) could be either due to residual precipitation of the mineral in macropores resulting from aggregation of large particles sample during column packing or selective coating of the precipitated gypsum crystals by the carbonate from LST and DOL, as suggested by Keren and Kauschansky (1981). In the presence of elevated levels of Ca and SO_4^{2-} ions in the pore solution, dissolution of gypsum is also found to decrease due to the common-ion effect between Ca and SO_4^{2-} (Kemper et al, 1975).

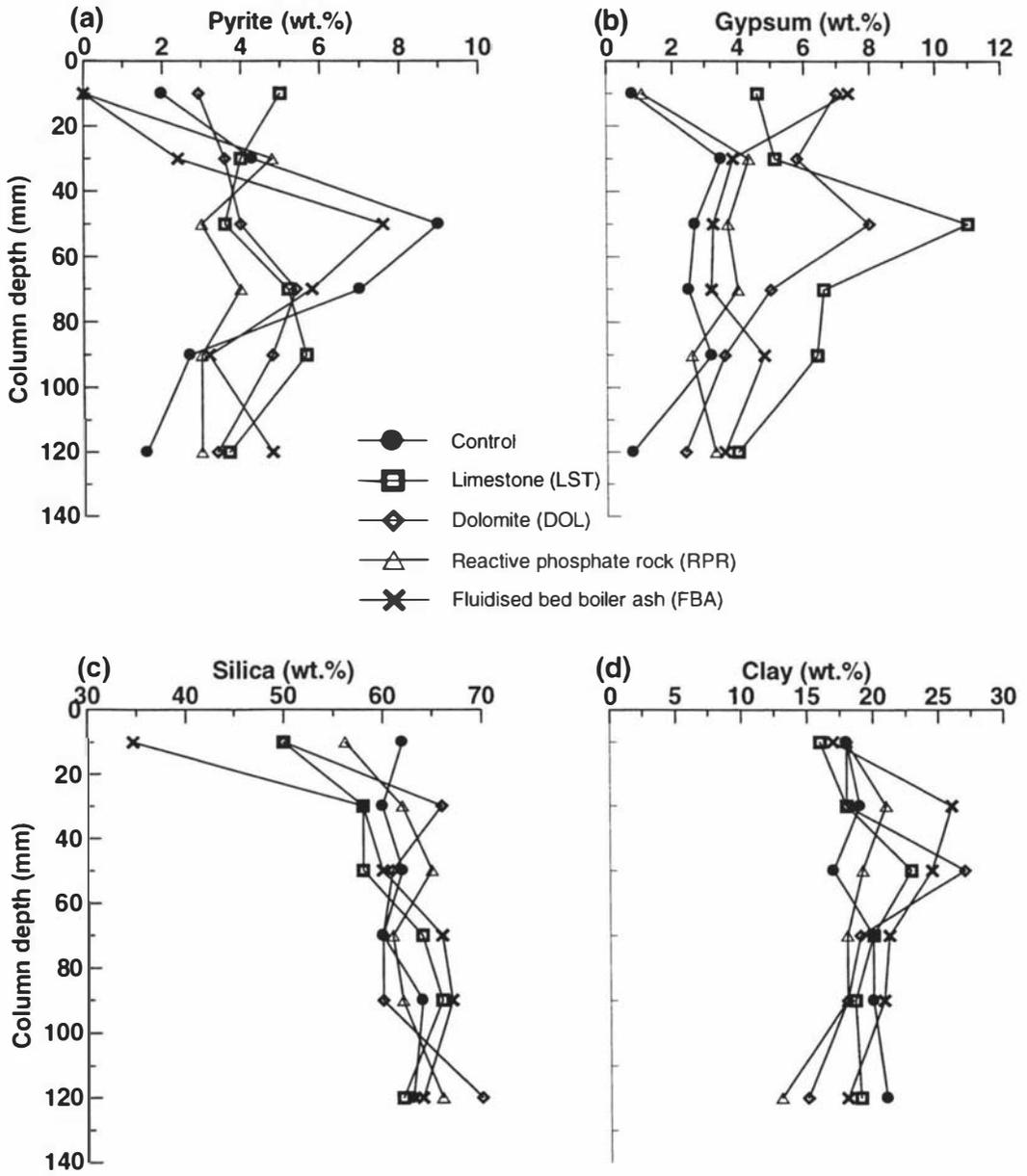


Figure 5.9 Distribution of (a) pyrite, (b) gypsum, (c) silica and (d) clay minerals in the leached columns broadcasted with neutralising materials.

The significant reduction of silica in the surface section of the FBA broadcasted column (Figure 5.9c) confirms the suggestion of cement formation at the surface of the column. A large fraction of silica at the surface may have been incorporated in the formation of calc-silicate hardpan at the surface. There were no significant changes in the clay content of the column section as a result of surface broadcasted neutralising materials (Figure 5.9d).

5.4 Conclusions

Surface amendment of pitwall rock with neutralising materials (LST, DOL, RPR and FBA) had no significant effect on the leachate pH, which remained low ($\text{pH} < 2.5$) throughout the 12 week period of leaching. This indicated that acid generation from oxidation of pyrite at lower sections of the columns continued irrespective of the presence of neutralising materials at the surface.

Observation of sectioned columns showed that there was marked evidence of flow impediment due to blockage of pores by precipitate formation during the non-leaching period. This raises the question that although alkaline amendments may initially create higher pH environments at the surface and an increase in CEC, rapid reaction of the neutralising materials with highly acid pore solutions causes mass precipitation of oxyhydroxides and sulphate salts which may create a reducing environment. In the case of FBA, surface amendment resulted in highly alkaline pitwall rock material at 0-40 mm depths as well as forming cementitious crust that impeded surface infiltration.

Products of pyrite oxidation (SO_4^{2-} , Fe^{2+} , H^+) stored in the oxidising pitwall rock were initially leached from the untreated column, whereas in the amended columns these products quickly reacted with the carbonate phases of the neutralising materials and resulted in mass precipitation of Fe and Al oxyhydroxides and gypsum.

The rate of sulphide oxidation, as indicated by SO_4^{2-} production in the control column ranged from $5588 \text{ mg SO}_4^{2-} \text{ kg}^{-1} \text{ week}^{-1}$ in the initial week of leaching to $3270 \text{ mg SO}_4^{2-} \text{ kg}^{-1} \text{ week}^{-1}$ in the final week of leaching indicating an overall reduction in SO_4^{2-} production of 41%. The corresponding reduction in SO_4^{2-} production by the surface broadcasted neutralising material over 12 week period were in the order DOL (90%) > LST (83%) > RPR (73%) > FBA (65%).

Although SO_4^{2-} and acidity were linearly correlated, the slope of acidity versus SO_4^{2-} indicated only about 51% and 20% neutralisation of the leachate and column section acidity respectively. There were however, significant reductions in acidity of the leachate and column section, indicating that despite low pH leachate, subsurface amelioration of exchangeable acidity was achieved by amendments with neutralising materials.

High alkalinity created by surface broadcasted neutralising materials resulted in significant increase in the base saturation properties of the pitwall rock as well as oxyhydroxide precipitates which, may have kept the material buffered against further rise in pH.

The amount of liberated pyrite in any given sample of the pitwall rock is responsible for the level of acid generation and efficiency of neutralisation. Surface broadcasting of neutralising materials, although it did not improve leachate quality, significant pH modification and acidity reduction were obtained in the subsurface. This indicated that plant materials with minimum rooting depth could be grown on surrogate soils placed over the surface modified pitwall rock materials.

Chapter 6

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

6.1 Introduction

Surface broadcasting of neutralising materials on pyritic pitwall rock columns resulted in significant reductions in the levels of EC, SO_4^{2-} and soluble metals (Fe, Mn, Al), in the leachate and column sections (Chapter 5). However, the leachate pH remained low despite a significant rise in pH in the column section of the pitwall. Soil solution chemistry of the column sections showed that the downward movement of the alkaline front effected by the broadcasted neutralising materials was limited to the upper 40 mm section of the pitwall rock column. The reaction of neutralising materials with acid solution has resulted in mass precipitation of Fe and Al hydroxides on the surface as well as elevated levels of sulphate salts. Formation of metastable precipitates such as Fe-Al hydroxides and dissolution of jarosite may also have been responsible for keeping the lower section of the pitwall rock column buffered at low pH at all times.

Other than improving the leachate quality, one of the major objectives of applying various amendments was to ameliorate subsurface low pH conditions in pitwall rock so that a suitable plant growth medium could be created. The choice of amendment methods will become important, especially on pitwalls where the slope factor may facilitate accelerated weathering and thus limit the effectiveness of amendments to ameliorate low pH conditions. Thus, the choice of neutralising material and the method of amendment are important in providing an effective and economically viable option for treating pit slope areas affected by low pH conditions created by acid generation from pyrite oxidation.

Pit slopes and mine waste dump sites are commonly engineered to the most stable slope angle and it is likely that any amendments applied by surface broadcast will result in high losses due to erosion. This will result in incomplete neutralisation of acid due to insufficient residence time of the neutralising materials on the pit slope. In steep pitwall, the methods of application of neutralising materials (broadcasted versus incorporated) are going to be the determinant factor in their effectiveness in alleviating subsurface acidity in the pitwall rock. Provided the pitwall contains sufficient cover materials,

incorporation of neutralising materials by mixing may help prevent losses from runoff erosion and thus provide longer residence time and more effective neutralisation of acid.

The objective of this study was to examine the effect that depth incorporated neutralising materials have on leachate and subsurface chemistry of pyritic pitwall rock columns. The results are compared with the surface broadcasted amendments (Chapter 5) in order to assess their relative effectiveness.

6.2 Materials and Methods

6.2.1 Materials

The pitwall rock bulk samples and the neutralising materials used in this study were the same as that for the surface broadcast experiment and are described in Tables 4.1 and 4.2 respectively (Chapter 4). The pitwall rock was crushed to a ≤ 4 mm nominal size fraction and one kilogram of it was packed into each column (Figure 5.1, Chapter 5).

6.2.2 Methods

Except for incorporation of neutralising materials ((limestone, LST; dolomite, DOL; reactive phosphate rock, RPR; fluidised bed boiler ash, FBA) in the top 50 mm of the pitwall rock column, the experimental design, column specifications, leaching protocol, analytical and statistical methods were the same as that for the surface broadcasted amendments. Once the column was packed, the top 50 mm of the pitwall rock was taken out and mixed thoroughly with neutralising materials (≤ 2 mm) at a carbonate content equivalent rate (C_{ER}) of $30 \text{ g CaCO}_3 \text{ kg}^{-1}$. The mixture was replaced in the column and left standing for one week prior to the commencement of leaching.

6.3 Results and Discussion

The average volume of the leachate collected from the control column was 140 ml week^{-1} whereas the columns incorporated with neutralising materials produced significantly lower volumes of leachate. The corresponding mean leachate volumes were 119, 115, 123 and 115 ml week^{-1} for LST, DOL, RPR and FBA respectively. The treated column leachate colour appeared dark reddish-brown because of high concentrations of particulate Fe-oxyhydroxides. Due to formation of excessive Fe and Al hydroxides, the downward movement of leachant was slow and in some columns, there was a significant decrease in the flow rate of the leachate.

The trends in the distribution of measured chemical parameters in the leachate and column sections were very similar to that of broadcasted method of amendments. Instead of describing the results in detail, this chapter briefly highlights the significant outcome of the experiment and then focuses on the overall comparison of the results with that of the broadcasted method of amendments discussed in Chapter 5. In doing so, a qualitative assessment of the ameliorating effectiveness of neutralising materials under broadcasted and incorporated conditions can be made in terms of their suitability for alleviating low pH conditions in the pit wall rock. Table 6.1 and 6.2 summarises the overall effect of incorporated neutralising materials on some selected chemical properties of the pitwall rock.

6.3.1 Effect on chemical properties of the pitwall rock by incorporated neutralising materials.

6.3.1.1 pH and EC

Incorporation of neutralising materials in 0-50 mm depth of the pitwall rock column resulted in no significant effect on the leachate pH throughout the 12 weeks period of leaching. All the columns produced very low pH leachate irrespective of amendments (Figure 6.1a). Although the 12 weeks mean pH remained in the range 1.9 to 2.4, the gradual increase in pH from week 2 to week 8 was statistically significant. Low pH leachate from columns incorporated with neutralising materials was consistent with the observations made by several other workers (Bloomfield, 1972; Hoving and Hood, 1984; Doepker, 1988; Brady et al., 1990; Parisi et al., 1994; Evans and Rose, 1995).

Despite low pH leachate, there was a significant rise of the column section pH by depth incorporated amendments (Figure 6.2a). As expected, FBA incorporation resulted in highly alkaline conditions within the depth of incorporation (50 mm) but indicated no subsurface effect on the pH. Both LST and DOL raised pH above 7 at the near surface sections but pH gradually decreased towards the unamended interface. On the whole, RPR was more consistent in keeping the pH uniform at around 4 within the depth of incorporation. All the amendments were ineffective in raising the pitwall rock pH below 70 mm column depth. The overall relative effectiveness of the neutralising material on pH modification in the pitwall rock columns were in the order: FBA>>LST=DOL>RPR.

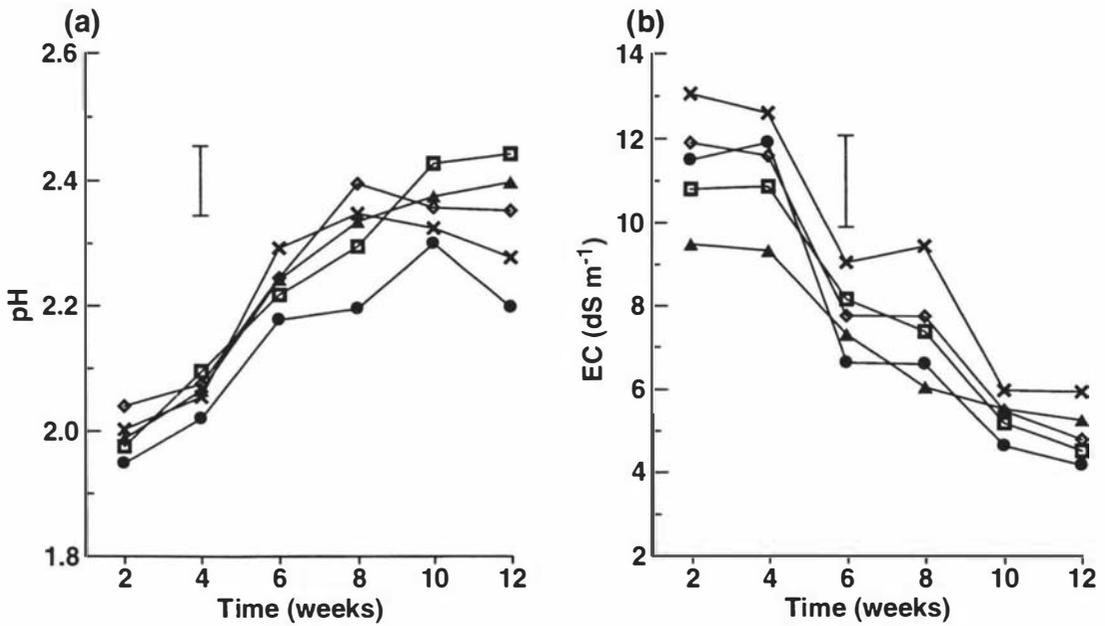


Figure 6.1(a) pH and (b) EC of the leachate from columns incorporated with neutralising materials. Vertical bars represent interaction LSD(5%).

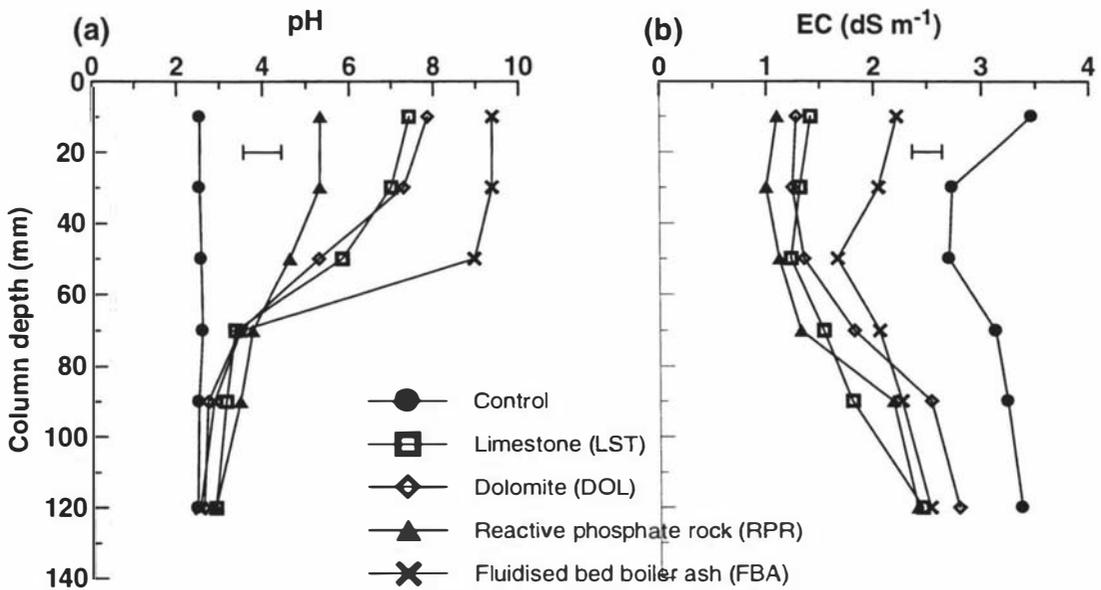


Figure 6.2 (a) pH and (b) EC of the sectioned samples from leached columns. Horizontal bars represent interaction LSD(5%).

All the columns, irrespective of treatments, produced leachate with very high EC (9-13 dS m⁻¹) during first two weeks of leaching after which it decreased significantly (p<0.05) to levels 4-6 dS m⁻¹ (Figure 6.1b). The decrease in EC for all the treatments over 12 weeks period was significant (P<0.05). The EC levels did not fall below 4 dS m⁻¹ within the 12 week leaching period. In the presence of high levels of SO₄²⁻, the decrease in EC level in the leachate was probably due to precipitation of gypsum and metal hydroxide at higher the pH effected by the neutralising materials.

The neutralising materials incorporated columns consistently had EC significantly lower than the control column (Figure 6.2b). The FBA incorporated column had significantly higher EC at 0-40 mm depth than LST, DOL or RPR incorporated column as a result of contribution of SO₄²⁻ from dissolution of gypsum.

Successive leaching of the columns significantly reduced levels of EC in the neutralising material incorporated column and this is considered to be due to preferential leaching of the soluble electrolyte components. High concentration of SO₄²⁻ in the pitwall rock should ideally facilitate downward movement of base cations (Ca and Mg) through the ion pairing effect. However, in the presence of excessive base cations, a significant amount of Al³⁺ and H⁺ will also be displaced from the exchange sites, resulting in a build up of reserve acidity.

Comparisons of the overall means showed significant leaching of soluble salts from the columns during the 12 weeks leaching cycle (Table 6.1). The higher EC level in the FBA treated column is likely to be due to residual gypsum from incomplete dissolution of FBA. All the treatments were equally effective in reducing the pitwall rock EC. The overall reduction in column section EC was in the order RPR (51%) > LST (48%) > DOL (41%) > FBA (31%) and the means differences in the relative effectiveness of the neutralising materials were significant at P>0.05 (Table 6.2).

6.3.1.2 SO₄²⁻ and acidity

Leachate SO₄²⁻ concentrations significantly decreased with each successive leaching cycle for all the treatments. Generally, all the treatments produced leachate with significantly (P>0.05) lower SO₄²⁻ concentration than the control column with nil incorporation of neutralising materials. The LST and DOL incorporated columns

showed release of similar amounts of SO_4^{2-} whereas SO_4^{2-} releases from RPR and FBA incorporated columns were significantly higher. By the end of 12 weeks of leaching period, the SO_4^{2-} flux in the leachate from incorporated columns decreased from 4500 mg L^{-1} to <2000 mg L^{-1} while the corresponding decrease in the control column was from 5500 to 3200 mg L^{-1} . Comparison of the overall means of the SO_4^{2-} release over 12 weeks leaching period (Table 6.1) relative to the control value (4155 $\text{mg SO}_4^{2-} \text{ kg}^{-1} \text{ week}^{-1}$) showed that although there was significant lowering of the SO_4^{2-} concentration in the leachate, the apparent reduction was <50% for all the treatments. The order of reduction in leachate SO_4^{2-} were LST (42%) > DOL (39%) > RPR (29%) > FBA (20%).

Table 6.1 Average release rates of the concentrations of measured parameters in the leachate from incorporated pitwall rock column.

	Overall means comparison					LSD $\alpha=0.05$	% reduction (-) / increase (+)			
	Control	LST	DOL	RPR	FBA		LST	DOL	RPR	FBA
SO_4^{2-}	4155	2413	2531	2958	3305	192	-42	-39	-29	-20
Acidity	1437	701	675	842	679	119	-51	-53	-41	-53
Fe	2862	1908	1726	1500	2027	172	-33	-40	-48	-29
Mn	122	91	97	101	78	8	-26	-20	-17	-36
Al	389	163	153	183	131	12	-58	-61	-53	-66
Ca	247	376	355	294	457	16	+52	+44	+19	+85
Mg	122	158	231	134	169	7	+29	+90	+10	+39
K	20	23	24	22	33	2	+11	+19	+5	+59
Na	23	28	35	34	58	3	+25	+56	+51	+160

Except for acidity ($\text{mg CaCO}_3 \text{ L}^{-1} \text{ week}^{-1}$), the units are in $\text{mg L}^{-1} \text{ week}^{-1}$

Table 6.2 Overall comparison of the mean concentrations of chemical properties of the leached pitwall rock columns incorporated with neutralising materials.

	Overall means comparison					LSD $\alpha=0.05$	% reduction (-) / increase (+)			
	Control	LST	DOL	RPR	FBA		LST	DOL	RPR	FBA
pH	2.5	4.9	4.9	4.2	6.1	0.1	+95	+92	+67	+141
EC	3.1	1.6	1.8	1.5	2.1	0.1	-48	-41	-51	-31
SO_4^{2-}	3353	1853	1952	1618	2265	105	-45	-42	-52	-32
Acidity	2519	655	692	1256	631	94	-74	-73	-50	-75
Fe	2097	977	1072	912	995	67	-53	-49	-57	-53
Mn	149	41	52	36	41	5	-73	-65	-76	-73
Al	245	17	45	27	59	4	-93	-82	-89	-76
Al_{exc}	812	214	203	209	211	32	-74	-75	-74	-74
Ca	1682	11605	10624	6880	16357	559	+590	+532	+309	+873
Mg	299	424	1460	455	523	52	+42	+388	+52	+75
K	207	105	82	90	190	10	-50	-61	-57	-8
Na	54	86	114	139	310	13	+60	+112	+159	+478

Except for pH, EC (dS m^{-1}), Al_{exc} ($\text{cmol}_c \text{ kg}^{-1}$) and acidity ($\text{mg CaCO}_3 \text{ kg}^{-1}$), the units are in mg kg^{-1} .

Incorporation of neutralising materials to 0-50 mm depth had significantly reduced the distribution of SO_4^{2-} concentration in the upper 80 mm section of the pitwall rock column. There was no change in the SO_4^{2-} distribution of the control column indicating continual oxidation of pyrite. The SO_4^{2-} level in the control column remained at around 3353 mg kg^{-1} throughout the column section (Table 6.2) compared to the original concentration of 7440 mg kg^{-1} in the bulk sample (Table 4.1, Chapter 4). Although a significant amount of SO_4^{2-} was leached ($4155 \text{ mg SO}_4^{2-} \text{ kg}^{-1}$) from the control column, it appeared that about 45% of the SO_4^{2-} ($3353/7440 \times 100$) remained in the column as insoluble precipitates and complex sulphate salts. The FBA incorporated column generally showed higher SO_4^{2-} content whereas RPR incorporation resulted in the most significant lowering of SO_4^{2-} in the pitwall rock column. Both LST and DOL showed similar distribution of SO_4^{2-} throughout the column depth. There was significant overall reduction in SO_4^{2-} concentrations in the pitwall rock columns amended with incorporated neutralisation materials (Table 6.2). The RPR incorporated column showed the highest reduction in SO_4^{2-} , possibly due to inhibition of pyrite oxidation by Fe- PO_4 coatings. Several workers (Evangelou, 1994; Fytas et al., 1994; Georgopoulou et al., 1995) have demonstrated micro-encapsulation of pyrite grains by Fe- PO_4 coating in laboratory scale experiments. The relative reduction in SO_4^{2-} distribution in the neutralising material incorporated columns were RPR (52%) > LST (45%) > DOL (42%) > FBA (32%).

There was a rapid decrease in acidity levels in the leachate from all the amended columns. The overall mean acidity release rate in the leachate from control column over 12 weeks period was $1437 \text{ mg CaCO}_3 \text{ L}^{-1} \text{ week}^{-1}$ (Table 6.1). The reduction in acidity in the neutralising materials incorporated columns compared to the acidity level from the control column were 53%, 53%, 51% and 41% DOL, FBA, LST and RPR respectively.

Significant reduction in acidity was observed in the neutralising materials incorporated columns. The LST, DOL and FBA incorporated columns showed similar reduction in acidity whereas the acidity in the RPR incorporated column was generally higher. The untreated control column contained consistently higher acidity of $2519 \text{ mg CaCO}_3 \text{ kg}^{-1}$ throughout the column depth. Although the leachate pH remained low (pH ~2.5) in the neutralising material incorporated columns, amelioration of subsurface acidity in the pitwall rock column was significant ($P > 0.05$) throughout the column depth (140 mm).

The relative reduction in acidity in the column section by incorporated neutralising materials were in the order: FBA (75%) > LST (74%) > DOL (73%) >> RPR (50%). The continued release of acid in the leachate from incorporated columns indicated that the liming rate required to raise the pH of the pitwall rock to 6 (30 kg CaCO₃ t⁻¹) is sufficient to provide only a short-term elevation of pH in the pitwall rock. Armouring effects on the neutralising materials from hydroxide coatings may result in re-acidification of the entire column section.

The rapid precipitation of gypsum from dissolution of neutralising materials is likely to result in the reduction of the neutralisation capacity through an armouring effect and possible cement formation. Thus in the presence of gypsum or elevated levels of sulphate salts, the SO₄²⁻ concentration in the leachate will not reflect the acid generation due to pyrite oxidation.

Regression fits between SO₄²⁻ and acidity concentrations of the leachate and column section gave slopes of 0.36 and 0.76 respectively. Compared to the ideal slope of 1.04 for complete neutralisation of acid (see section 5.3.2.5, Chapter 5), these slopes indicated corresponding neutralisation of 65% and 27% of total acidity in leachate and column section respectively. These values were comparatively less than the reductions indicated by the overall effect of incorporation of neutralising materials on leachate and column section acidity (Tables 6.1 & 6.2). The observations above indicated that although there was a significant linear relationship between the SO₄²⁻ and acidity in the leachate and column section, the relationship may not reflect the acid neutralisation processes under leaching conditions (or field conditions). Since a large fraction of the SO₄²⁻ produced from oxidation of pyrite will be precipitated as sulphate salts of Fe, Al, Ca and Mg, the SO₄²⁻ fluxes in the leachate may vary considerably depending on leaching conditions and the volume of leachant used. This observation suggested that SO₄²⁻ and acidity fluxes in the leachate from pyritic waste rock may not reflect the actual acid generation and neutralisation processes in the column.

The results indicated that although leachate pH from neutralising materials amended columns remained low during the leaching period, significant reductions in the acidity levels were observed. This suggested that in subsurface, most of the acid is “locked” in

Al and Fe hydroxide and sulphate complexes as a result of downward intrusion of alkaline front. Formation of jarosite in lower sections of columns would also consume acidity and as long as the system is kept buffered by Al and Fe hydroxide gel formation, acidity will remain at reduced level despite low pH.

6.3.1.3 Fe, Mn and Al

Leachate Fe and Mn concentrations decreased rapidly with each successive leaching cycle for all the treatments. Most of the decrease in Fe and Mn in the leachate occurred during 2 to 6 weeks of leaching, after which, they remained constant during further leaching cycles. The Fe and Mn concentrations decreased from initial values of about 5000 mg L⁻¹ and 150 mg L⁻¹ in the week 1 leachate to < 1000 mg L⁻¹ and 80 mg L⁻¹ respectively in the week 6 leachate. Soluble Fe and Mn concentrations in the leachate from the control columns were significantly higher ($P>0.05$) than the leachate from amendments incorporated columns. Leachate from FBA incorporated column contained consistently higher Fe whereas the RPR incorporated column produced leachate with the lowest Fe concentration. Overall mean distributions of Fe and Mn in the leachate from untreated columns were 2862 mg L⁻¹ week⁻¹ and 122 mg L⁻¹ week⁻¹ respectively (Table 6.1). The relative reduction of Fe in the leachate were RPR (48%)> DOL (40%)> LST (33%)> FBA (29%) and the corresponding reduction in Mn were FBA (36%)> LST (26%)> DOL (20%)> RPR (17%). The alkalinity generated by incorporated neutralising materials had a contrasting effect on the distribution of Fe and Mn in the leachate. While RPR may have fixed Fe in the column by formation of an insoluble Fe-PO₄ compound, the higher release of Mn in the leachate from RPR incorporated column indicated that it had little effect on the mobilisation of Mn. It appears that the high alkalinity created by the FBA was more effective in solubilising Mn in the leachate. The precipitation of sulphate salts of Fe and Mn (FeSO₄, MnSO₄) and oxyhydroxides (Fe(OH)₃, Mn(OH)₃) may also have affected the downward movement of the metals in the alkaline pore solutions formed by the neutralising materials.

Both soluble Fe and Mn distribution in the untreated control column remained significantly ($P>0.05$) high at 2097 mg kg⁻¹ and 149 mg kg⁻¹ respectively throughout the column depth. All the neutralising materials showed similar effects in reducing the Fe and Mn concentrations in the column sections. There were no significant differences

among the different types of neutralising materials on the Fe and Mn content of the column section. In the neutralising material incorporated columns, soluble Fe was reduced to $<1000 \text{ mg kg}^{-1}$ at 0-60 mm depth and remained significantly less than the Fe content of the untreated column in the 140 mm column depth. Soluble Mn was lowered to $< 75 \text{ mg kg}^{-1}$ throughout the column depth by the amendment effects. The overall reduction in Fe and Mn contents of the amended columns was approximately 50% and 72% respectively (Table 6.2).

The distribution of Al in the leachate was strongly affected by the incorporated neutralising materials. There was a significant ($P<0.01$) decrease in the Al in the leachate during 2 to 6 weeks of the leaching cycle after which it remained consistently low at $\text{Al} < 100 \text{ mg L}^{-1}$. The average release of Al in the leachate was $389 \text{ mg L}^{-1} \text{ week}^{-1}$ in the untreated column whereas the concentrations in the leachate from neutralising material incorporated columns was significantly lower (Table 6.1). The overall reduction in leachate Al in the surface incorporated neutralising materials were in the order: FBA (66%) > DOL (61%) > LST (58%) >> RPR (53%).

Exchangeable Al (Al_{exc}) concentration in the control column sections showed no change throughout the 140 mm column depth of pitwall rock. The mean depth profile distribution of Al_{exc} was 812 mg kg^{-1} . The pitwall rock material initially had Al_{exc} content of 1341 mg kg^{-1} ($14.9 \text{ cmol}_c \text{ kg}^{-1}$, Table 4.1). Assuming the leached pitwall rock column had similar chemical properties and pyrite content to the bulk sample, a 12 week leaching cycle resulted in about 39% displacement of Al_{exc} from the exchange sites. This indicated that a large fraction (61%) of the Al_{exc} remained mobilised in the column section, possibly as sulphate and hydroxide precipitates in the upper section of the column where the pH was significantly raised. Most of the reduction in Al_{exc} was observed in the upper 80 mm section of the column. The overall reduction of Al_{exc} in the column section was about 74% for all the neutralising materials.

6.3.1.4 Base cations (Ca, Mg, K and Na)

The distribution of base cation concentrations in the leachate decreased gradually over the 12 week cycle of leaching. The FBA incorporated columns consistently produced leachate with significantly ($P>0.05$) higher concentrations of Ca, K and Na while DOL

incorporated released the highest amount of Mg. The higher levels of Ca and Mg in the leachate from FBA and DOL amended columns can be due to downward movement of Ca and Mg, paired with SO_4^{2-} . This is reflected in the relatively high concentration of Ca (derived from decomposition of alkali feldspars) leached from the control column as well. Higher cumulative K and Na released in the leachate from FBA incorporated column may have resulted from the significant amount of these cations contained in the FBA used as well as preferential displacement of these ions by Ca. The LST, DOL and RPR released similar amounts of Ca, K and Na in the leachate.

Amendment incorporation significantly raised the concentration of Ca in the upper 80 mm section of the column depth (Figure 6.3a). This may suggest that although there was a significant amount of Ca leached from columns irrespective of amendments, a large fraction of it has remained unreactive possibly due to the armouring effect from oxyhydroxide precipitates and gypsum coating on the carbonate fractions. The FBA treated column had the greatest amount of Ca immobilised possibly in the formation of cementitious material. The distribution of Ca in the LST and DOL amended columns were similar at all depths. As expected there was a significant ($P>0.01$) increase in Mg content of the DOL incorporated column in the upper 0-80 mm depth (Figure 6.3b). Except for the FBA incorporated column, the distribution of K was significantly lower than that of the control value, throughout the column depth (Figure 6.3c). The K content of the FBA treated column was higher than the control value at the 50 mm depth of incorporation possibly due to dissolution of potassic minerals in highly alkaline solution. The high anomalous amount of Na in the upper 60 mm section of the FBA incorporated column may have been due to dispersive effect on Na by alkaline conditions (Figure 6.3d). A significant amount of Na could be contributed from initial high concentration of this ion in the FBA (Wang et al., 1994). There were significant increases in the overall distribution of Ca, Mg and Na in the amendments incorporated columns. A general depletion in K was observed in columns incorporated with LST, DOL and RPR (Figure 6.3c). Except for K, the base cation concentrations in the untreated column remained low at all depths. The high K content in the control column may have been due to decomposition of potassic feldspars by acidic solution in the pitwall rock and subsequent formation of jarosite $\text{K}[\text{Fe}(\text{SO}_4)_2 \cdot 2\text{Fe}(\text{OH})_3]$ under low pH (~2.5) conditions.

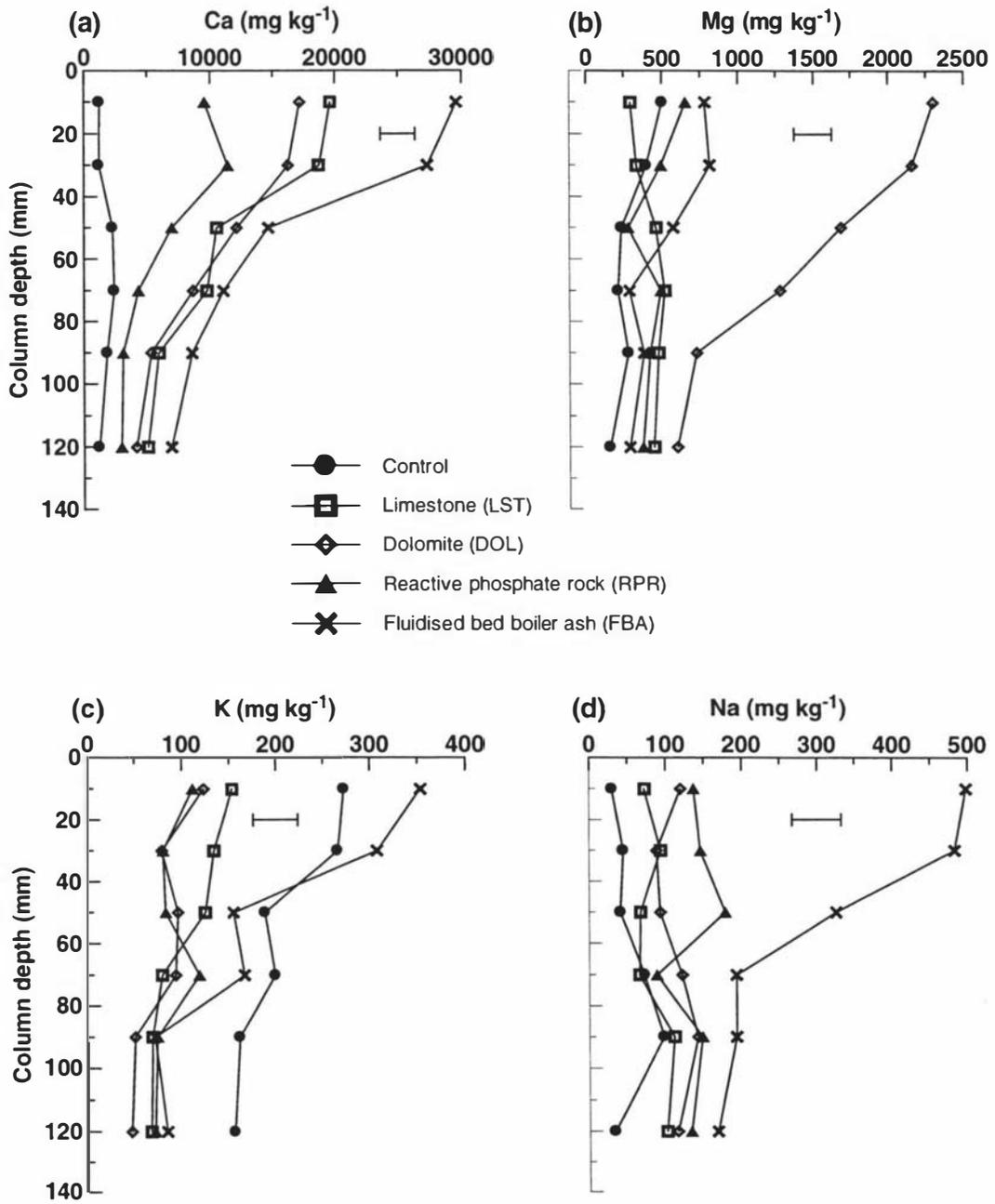


Figure 6.3 Distribution of (a) Ca, (b) Mg, (c) K and (d) Na in the sectioned samples from leached columns incorporated with neutralising materials. Horizontal bars represent interaction LSD(%).

6.3.2 Comparison between broadcasted and incorporated methods of application of neutralising materials

6.3.2.1 Leachate chemistry

Treatment-wise comparison of the leachate chemical properties of the broadcasted and incorporated columns showed that although there were close similarities in the general trends in the characteristics of the chemical properties of the leachate and columns, significant differences were observed in the overall distribution of the chemical properties. Despite leachate pH remaining low for both methods of amendment, incorporated columns generally produced leachate with lower pH (Figure 6.4a) and significantly higher EC (Figure 6.4b) particularly for LST, DOL and FBA amended columns.

There were no differences in the overall treatment-wise SO_4^{2-} release rates in the leachate from broadcasted and incorporated columns but acidity of the leachate from incorporated columns was consistently lower (Figure 6.4c and 6.4d). Except for significant increase in Fe in the leachate from the FBA incorporated column, both Fe and Mn also remained similar in both the methods of amendments (Figure 6.4e and 6.4f). There was also no difference in the leachate Al from both methods of amendments.

The distribution of base cations (Ca, K and Na) in the leachate was similar in both the methods of amendments. The Mg distribution, however, was significantly higher ($P > 0.01$) in the leachate from incorporated columns. The Mg level in the leachate from incorporated columns was generally two-fold higher than in the leachate from broadcasted columns as a result of high solubility of MgSO_4 .

Week-wise comparison of the chemical parameters in the leachate showed that incorporated columns produced significantly ($P > 0.05$) lower pH than the broadcasted columns in the first 10 week period of leaching cycle (Figure 6.5a). Low pH inducement with high rates of limestone application in acidic mine waste was also observed by Costigan et al. (1982). The trend was reversed for EC, which remained consistently higher in the leachate from incorporated columns (Figure 6.5b). This suggested that

hydrolysis and precipitation of metal salts maybe inducing low pH conditions at subsurface depths.

There was no difference in the week-wise leachate SO_4^{2-} release from both methods of amendment applications throughout the 12 week leaching cycle (Figure 6.5c). Amendment incorporated columns however, produced leachate containing significantly lower acidity than the leachate from broadcasted columns (Figure 6.5d). The greater depth of neutralisation effect by the incorporated amendments may have caused dissolution of metastable salts such as jarosite, thereby releasing stored acid in the leachate.

Soluble Fe was initially higher in the leachate from incorporated columns but this maybe just a flushing effect because there was no difference observed in the leachate Fe concentration in the weeks there after (Figure 6.5e). High alkalinity created by the incorporated amendments in the column section may have initially precipitated Mn as $\text{Mn}(\text{OH})_2$ as reflected in the lower Mn content in the leachate from incorporated columns (Figure 6.5f).

The week-wise distribution of leachate Al and the base cations were similar for both the methods of application of amendments. Generally, the incorporated columns produced leachate with lower concentrations of Al and higher concentrations of base cations but the overall differences between the methods of amendments were not significant at $P > 0.05$ except for Mg, which showed consistently higher amounts in the leachate from incorporated columns irrespective of treatment types.

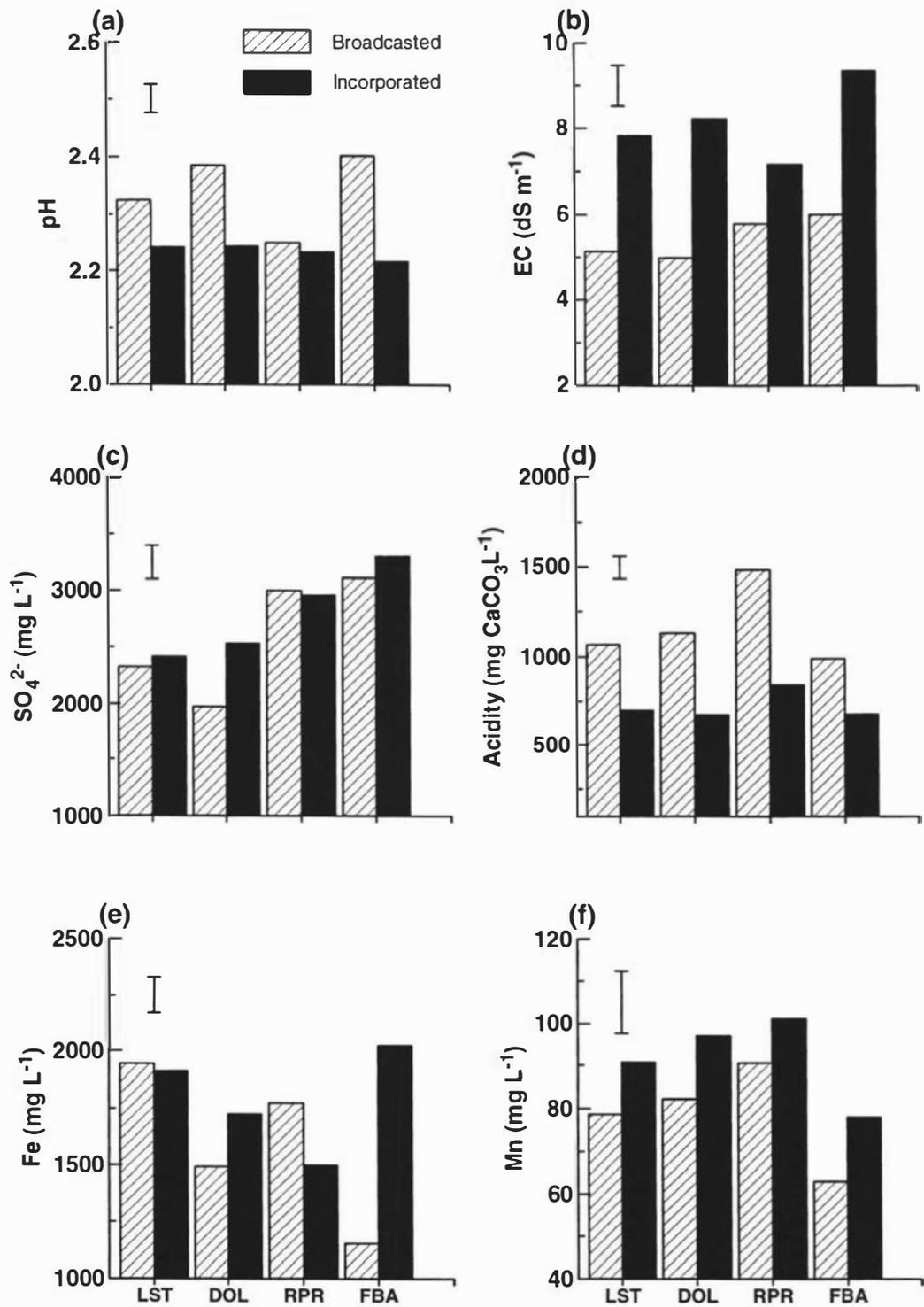


Figure 6.4 Treatment-wise comparison of leachate chemical properties of the broadcasted and incorporated columns. Vertical bars represent method x treatment interaction LSD(5%).

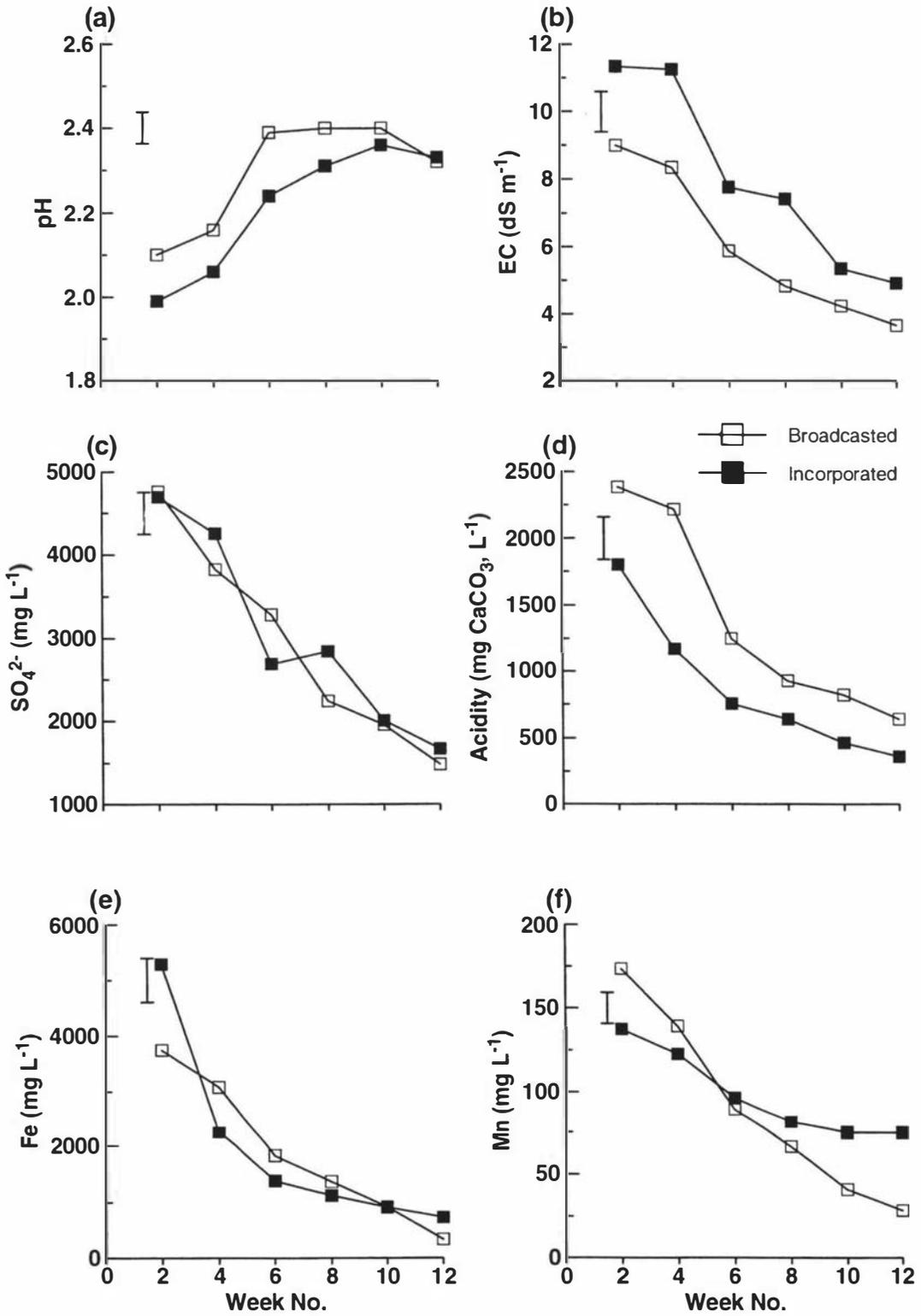


Figure 6.5 Week-wise variations in leachate chemical properties of broadcasted and incorporated pitwall rock columns. Verical bars represent interaction LSD(5%).

6.3.2.2 Column section chemistry

Treatment-wise comparisons of the column section chemical properties of broadcasted and incorporated amendments showed that there was some significant improvement in amelioration of subsurface low pH conditions by the incorporated neutralising materials. Except for LST, the pH in the depth-incorporated column was significantly higher in the column broadcasted with DOL, RPR and FBA (Figure 6.6a). There was no difference in the distribution of EC except for FBA incorporated columns, which had significantly, lower EC than broadcasted columns. Generally, the incorporated columns had lower EC for all the amendments (Figure 6.6b).

Amendment incorporation also resulted in generally lower levels of SO_4^{2-} than the broadcasted columns but the difference was not significant at $P > 0.05$ (Figure 6.6c). Acidity, however, was significantly lower for all the treatments in the incorporated columns (Figure 6.6d). This was to be expected since incorporation of neutralising materials affected a greater column depth (0-80 mm) of acid neutralisation compared to broadcasted columns in which the maximum depth of effective neutralisation was only in the top 50 mm section of the pitwall rock column. Incorporation of fine-grained neutralising materials may also provide greater reactivity with the acid solution and hence resulting in more effective neutralisation. However, this might not be the case if the grain sizes of the neutralising materials were larger, in which case, armouring effect from hydroxide coatings may result in incomplete dissolution of the amendment materials

The reductions of soluble Fe and Mn in the incorporated columns were significantly ($P < 0.01$) higher for all the treatments (Figure 6.6e & f). The lower concentrations of soluble Fe and Mn in the incorporated columns may have been due to precipitation of insoluble Fe and Mn hydroxides at elevated pH conditions. There was a similar decrease in the exchangeable Al (Al_{exc}) of the incorporated columns compared to that of broadcasted columns (Figure 6.7a). Greater displacement of the Al_{exc} from the exchange site by dissolved Ca would have resulted more effective reduction in exchange acidity of the amendment incorporated materials.

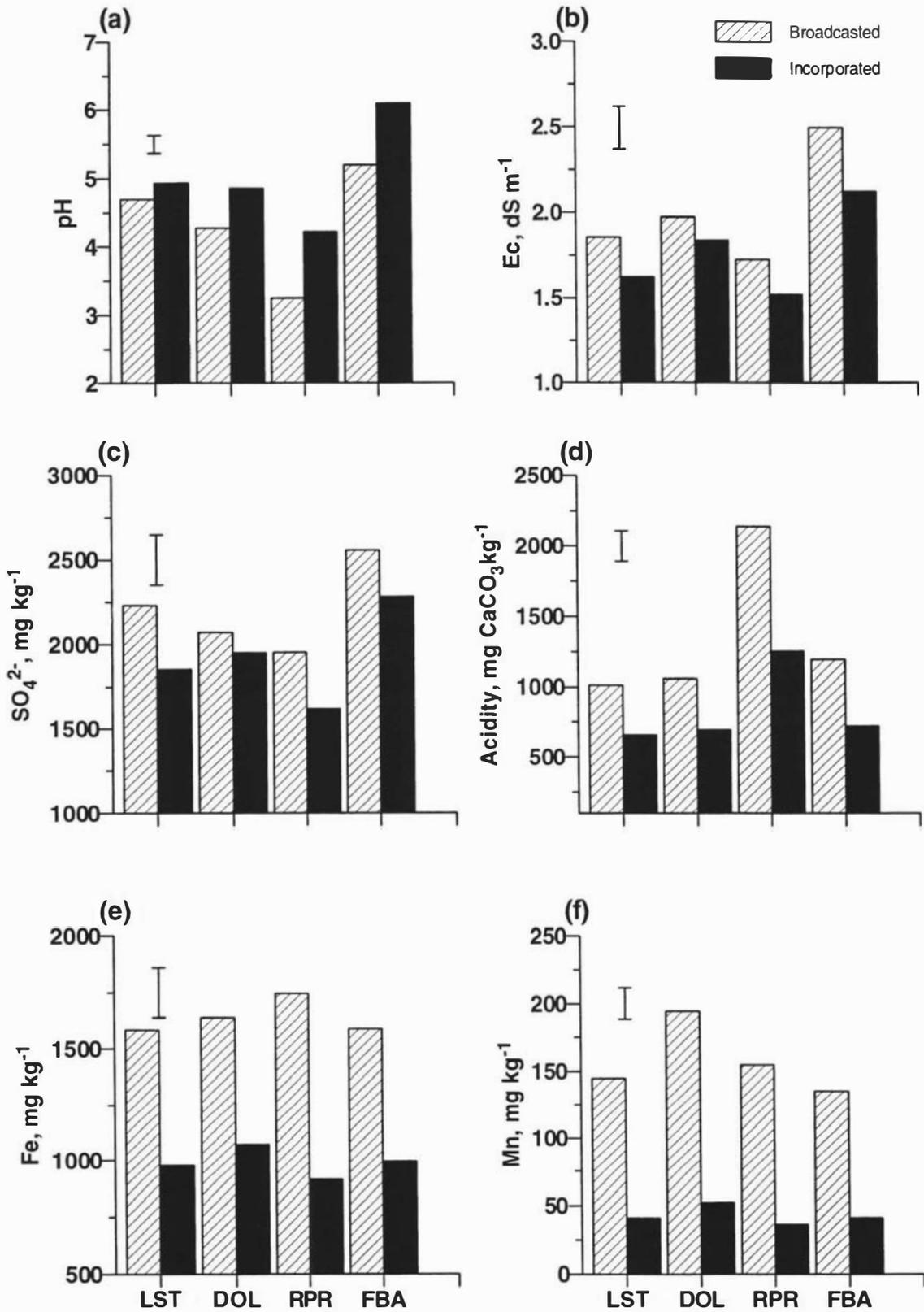


Figure 6.6 Treatment-wise comparisons of mean chemical properties of the broadcasted and incorporated columns for all deaths. Vertical bars represent interaction LSD(5%).

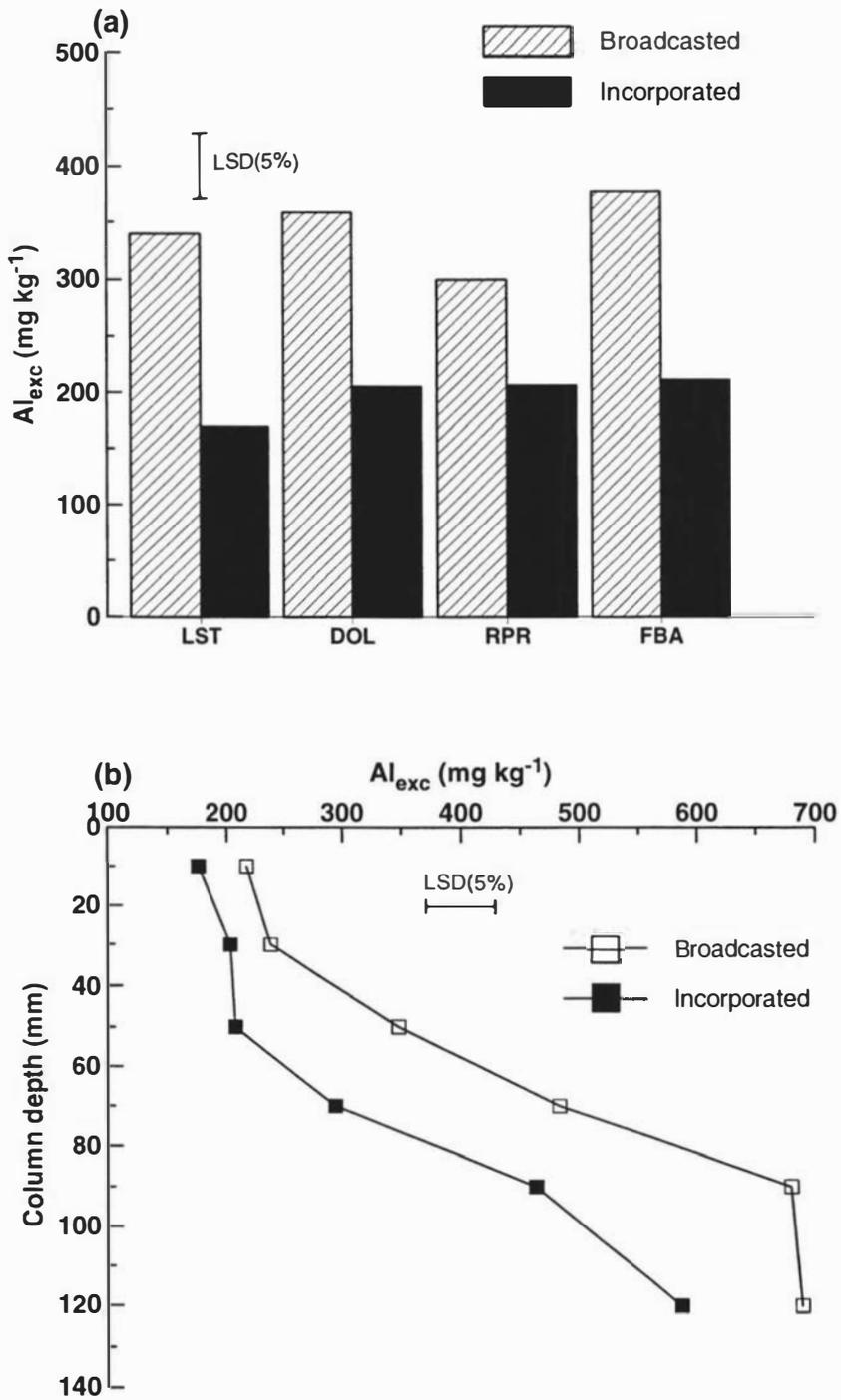


Figure 6.7 Comparisons of (a) treatment-wise and (b) depth-wise distributions exchangeable Al (Al_{exc}) in the broadcasted and incorporated columns.

There was no significant difference in the distribution of Ca in the columns amended with either broadcasted or incorporated materials. The Mg distribution however, was significantly higher in the incorporated columns for all the treatments. The Mg distribution was generally twice higher in the incorporated columns irrespective of treatment types. Except for FBA amended columns, which generally showed high K and Na contents in the incorporated columns, the distributions of these cations were similar for both the methods of amendment.

Depth-wise comparisons of the means of the measured parameters showed that the variations in pH with depth was similarly effected by either method of amendment except at the 40-60 mm depth in the column where the pH was significantly higher for the incorporated column (Figure 6.8a). The distribution of EC showed no significant difference between the two methods of amendment (Figure 6.8b). The SO_4^{2-} concentration and acidity were generally lower for the incorporated columns with significance differences at 60-80 mm and 60-140 mm depths for SO_4^{2-} and acidity respectively (Figure 6.8c & d). Soluble Fe was significantly lower in the incorporated column at 40-140 mm depth (Figure 6.8e) whereas Mn showed consistently higher reduction in the incorporated columns throughout the column depth (Figure 6.8f).

Incorporation of neutralising materials resulted in significantly lower distribution of Al_{exc} at column depths greater than 40 mm (Figure 6.7b). As discussed earlier, the higher reduction in Al_{exc} by the incorporated amendments was mainly due to base saturation, particularly Ca, which has a greater affinity for displacement of Al_{exc} from the exchange sites.

Except for K, which showed significantly ($P>0.05$) higher amounts throughout the column depth for incorporated amendments, there were no differences in the distribution of Ca, Mg and Na in the columns from both methods of amendment application. The higher K content in the amendment-incorporated column may have been mainly due to the contribution from dissolution of FBA, which initially had a high K content.

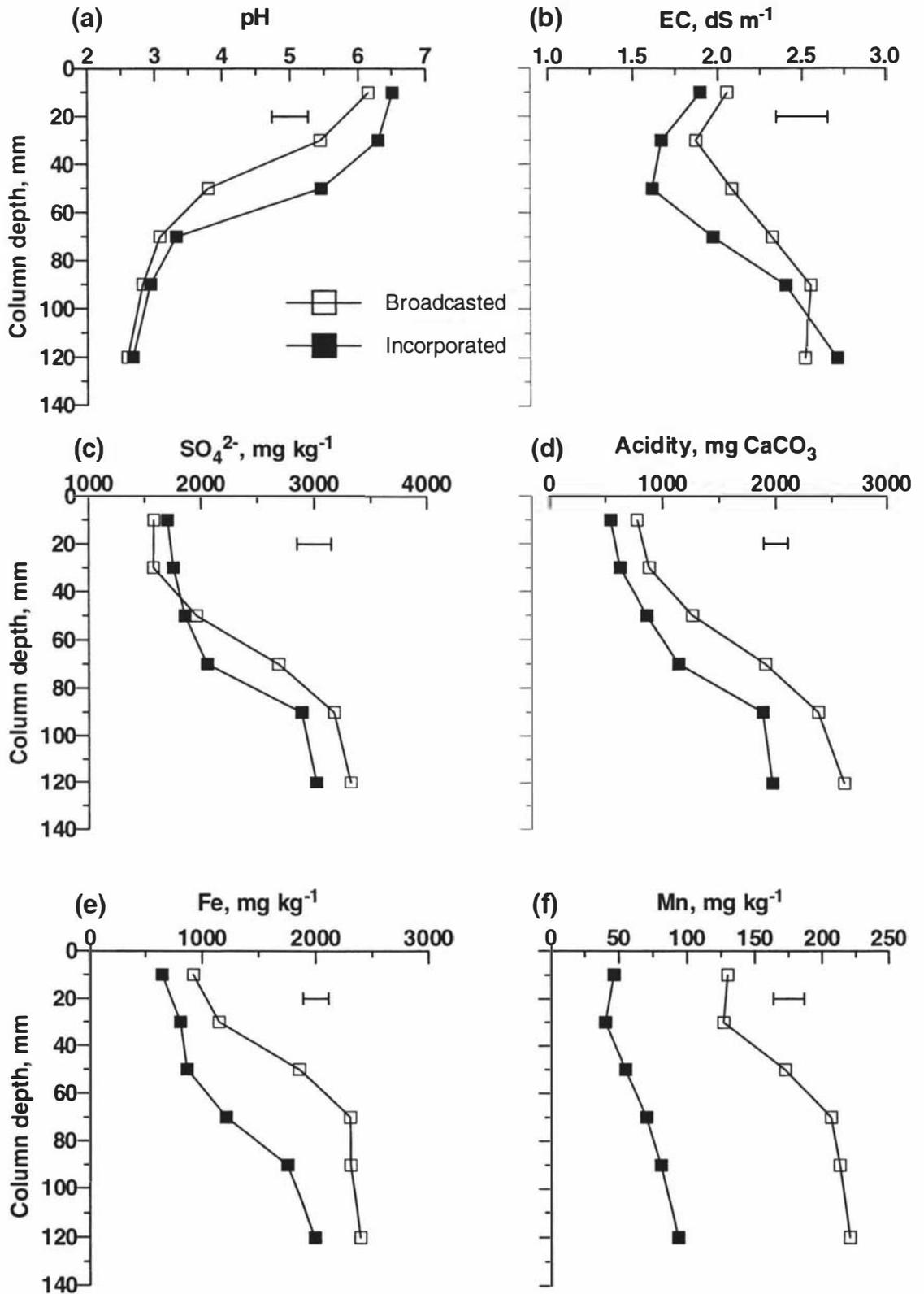


Figure 6.8 Overall depth-wise distribution of chemical parameters in broadcasted and incorporated columns. Horizontal bars represent interaction LSD(5%).

6.3.2.3 Overall effectiveness of amendment methods

The individual treatment-wise and depth-wise statistical treatment of the data showed varying differences in the chemical parameters measured in the leachate and column sections amended with broadcasted and incorporated neutralising materials. When the same data were statistically tested to show the overall differences (method x treatment x time) between the method of application of amendments, the incorporated columns consistently showed significantly lower pH, acidity and Al and higher EC, SO_4^{2-} , Fe, Mn, Ca and Mg in the leachate (Table 6.3). The corresponding overall differences in means for the columns showed significantly ($P>0.05$) higher pH and Ca and lower distribution of EC, SO_4^{2-} , acidity, Fe, Mn, Al, Mg, K and Na in the incorporated columns.

The incorporated method of amendment, although indicating a more effective amelioration of the low pH pitwall rock, requires that at a reasonable depth of weathered material remain stable on the pit slope ($\sim 43^\circ$) in order for application to be effective. Because the pitwall contained only a thin layer of weathered cover materials which is prone to rill and sheet erosion, incorporation of neutralisation materials may not have the desired effect of pH modification. On the other hand, surface broadcasted neutralising materials was just as effective in significantly improving the leachate quality (except for pH) and subsurface amelioration up to 0-40 mm depth of pitwall rock. However, in steep slope areas, the residence time of the broadcasted neutralising materials may be short due to loss from erosion and re-acidification of the pitwall rock.

Revegetation of the steep pitwall no doubt requires engineered slope modification for stabilised placement of amendments and plant growth media on which vegetation can be established long enough for natural succession. Provided this criterion is met, the results of this study indicated that amelioration of low pH conditions in the pyritic pitwall can be achieved by either methods of application of suitable neutralising materials.

Table 6.3 Overall comparison of means between the broadcasted (BC) and incorporated (IC) methods of amendment.

	Leachate			Column section		
	BC	IC	LSD(5%)	BC	IC	LSD(5%)
pH	2.30	2.22	0.02	3.98	4.53	0.05
EC	6.00	8.03	0.22	2.23	2.04	0.06
SO ₄ ²⁻	2926	3072	93	2382	2211	55
acidity	1374	867	58	1634	1168	40
Fe	1880	2004	73	1819	1210	41
Mn	90	98	3	178	64	4
Al	234	204	8	436*	322*	13
Ca	334	346	7	7930	9430	258
Mg	105	163	3	635	632	20
K	23	24	1	228	135	6
Na	36	37	1	130	141	5

Except for pH, EC (dS m⁻¹) and acidity (equivalent mg CaCO₃), the units are in mg L⁻¹ for leachate and mg kg⁻¹ for the column section. * = exchangeable Al (Al_{exc})

6.4 Conclusions

Results of this study showed that depth incorporation of neutralising materials had no significant effect on the leachate pH, which remained low (pH<2.4) throughout the 12 weeks period of leaching. The oxyhydroxide precipitates of Fe and Al formed due to a sudden rise in pH within the column may have rendered a large fraction of the incorporated neutralising material ineffective due to possible armouring effect. These precipitates may also have buffered the leachate pH against further increase. This may have been the cause for only 50% reduction in the release of acidity over the 12 weeks period despite >70% reduction in the column section acidity.

The rapid precipitation of gypsum and metal sulphate salts during neutralisation made it difficult to estimate the acidity from SO₄²⁻ production. The predicted value of neutralisation of acidity, as estimated from the rate of SO₄²⁻ production, were 66% and 27% for the leachate and column section respectively. The actual reduction in acidity in the leachate (~50%) and in the column section (~70%) by all the treatments with varying neutralising potentials indicated that neutralisation of acid in the column may occur only during the initial contact but will stop immediately after sulphate salts begin to form.

The effect of incorporation of the neutralising material was to significantly increase base cation concentrations in the leachate as well as in the column section. The FBA treatment caused the largest increase of Ca in both leachate and column section while DOL incorporation resulted in 90% and 388% increases in the Mg concentration of the leachate and column section respectively. An anomalous high K and Na contents were observed in leachate (160%) as well as in column section (478%) in FBA amended pitwall rock and this was thought to be dissolving directly from the FBA.

Among the treatments, LST and DOL gave the most consistent ameliorative effects on low pH. The FBA amendment created a very highly alkaline material ($\text{pH} > 8$) in the 50 mm depth of incorporation. The RPR incorporated column generally produced larger volumes of leachate and that a significant amount of RPR remained unreacted in the upper section of the column.

Physical effects on the pitwall rock were evident in the LST and FBA incorporated columns. The depth of incorporation (50 mm) contained mottled grains of Fe-hydroxide-coated limestone and orange brown precipitates in the LST and DOL incorporated columns. Hard concretions of cement were common in FBA incorporated columns. Both these decreased the rate of downward infiltration of leachate during leaching cycles. In a pitwall rock column of 140 mm depth, only the top 60 mm of the column was significantly ameliorated by depth incorporation of neutralising materials.

Very high pH, Ca and Mg concentrations in the top 50 mm section of the column indicated that there was very little downward movement of the alkaline front. It is possible that the high Fe and SO_4^{2-} content of the pitwall rock will have caused rapid precipitation of gypsum, Fe and Al hydroxides (and sulphates) in contact with the highly alkaline neutralising material. These precipitates not only buffer against an increase in pH but also severely reduce the neutralising capacity of the amendment materials by the armouring effect of the hydroxide coatings. Although RPR was the least effective material in improving the pitwall rock pH, it had significant effect on the overall reduction of SO_4^{2-} , acidity, Fe, Mn and Al, possibly due to ready formation of insoluble phosphate complexes which may have coated pyrite grains and thus partially inhibited the production of SO_4^{2-} from biochemical oxidation of pyrite.

Amelioration of low pH conditions in pitwall rock materials with large amounts of neutralising materials may result in the discharge of leachate saturated with sulphate salts. This may eventually lead to leachate waters containing high levels of dissolved metal sulphate salts. Since the pitwall rock contains very high levels of SO_4^{2-} , precipitation of metal sulphate salts is most likely when large amounts of highly alkaline neutralising materials are used to ameliorate the acidity problem. Thus precipitation of sulphate salts like epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) is likely to strongly influence the leachate chemistry.

It is most likely that the discharge of low pH leachate despite amendments is largely due to release of acid from dissolution of Al and Fe hydroxides as well as jarosite precipitated at lower depths. Since metastable precipitates such as Al and Fe-oxides/hydroxides and jarosite strongly buffer the system to a low pH at lower depth, amendment with neutralising materials may have the desired effect of reducing acidity provided moisture at depth is kept at a minimum. With appropriate rates of application of neutralising material amendments, the pitwall rock material can be ameliorated for plant growth as long as water infiltration is controlled to prevent leaching and re-acidification.

Incorporated amendments were found to be more effective than broadcasted method in the overall amelioration of low pH conditions in the pitwall rock, provided that the neutralising materials are fine-grained (≤ 2 mm). Large particle size neutralising materials may be rendered less effective by the armouring effect of oxyhydroxide coatings.

Chapter 7

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

7.1 Introduction

Soil covers are often used as barriers to prevent influx of oxygen and water to limit acid generating processes in the waste rock (Nicholson et al., 1989). The cover materials also provide organic ligands that readily complex with mobilised metals such as Fe, Mn and Al (Miller and Ohlrogge, 1958; Hargrove and Thomas, 1981; Davis, 1984). Organic cover materials, such as topsoil and compost, have been shown to provide an effective means of reclaiming acidic soil material and have been shown to provide a protective layer which inhibits sulphide mineral oxidation (Pierce et al., 1994; Stogran and Wiseman, 1995). Several workers have demonstrated the role of soil organic matter in ameliorating Al toxicity in acidic soils and mine waste materials (Hargrove and Thomas, 1981; Young and Bache, 1985; Hue et al., 1986; Shuk-Ching and McColl, 1990; Gurung et al., 1996; Smith et al., 1997).

The use of topsoil as cover material serves not only to reduce acid generation processes but also to assist in achieving the aesthetic and ecological benefits of revegetation by acting as a substrate for plant growth (Gregg et al., 1998). The effectiveness of soil cover is however, strongly dependent on the local climatic conditions, organic matter content, nutrient levels (N, P, K) and the depth of soil cover placement although Gregg et al. (1998) indicated that in oxidised mine waste materials topsoil depth was not a major factor for vegetative establishment. On steep pitwalls however, the slope factor is going to be the major limitation to effective placement of soil cover. Except for limited research by Hoving and Hood (1984) and Tisch and Winterhalder (1995), very little research has been conducted on the effect of topsoil cover material on the leachate and subsurface chemistry of pyritic mine waste materials.

In recent times, commercial grade bactericide has been used increasingly in the reclamation of mined lands with varying degree of success (Parisi et al., 1994; Splittorf and Rastogi, 1995). Since mine waste rock materials are deemed site specific in their geochemical properties, the effectiveness of the bactericide in controlling AMD may not

be universally applicable. Attempts have also been made to formulate slow-release forms of surfactants (Erickson et al., 1985) and some of the products such as ProMac slow release pellets are now commercially available (Shellhorn et al., 1985). To date, no bactericide products have been used to control or inhibit AMD conditions in sulphidic mine wastes in New Zealand mines.

The objectives of this study were to investigate the influence of topsoil cover and a commercial bactericide (ProMac) on leachate and subsurface column chemistry of partially oxidised pyritic pitwall rock columns under accelerated leaching cycles in glasshouse conditions.

7.2 Materials and Methods

7.2.1 Materials

The columns used for the leaching study were the same as shown in Figure 5.1 (Chapter 5). The physical and chemical properties of the pitwall rock bulk samples and neutralising materials used in this study are described in Chapter 4 (Table 4.1). The topsoil (TS) was from the Waihi mine site area (Baxter Road location) and its selected chemical properties are given in Table 7.1.

The ProMac (PM) product used in this study was in powder form (ProMac 2000SB). It had a solution pH of 6.8 (1:2.5 ProMac to water ratio) and electrical conductivity (EC) of 22 dS m⁻¹. The recommended dosage for column a test according to MVTechnologies guidelines was 0.5 kg Mg⁻¹ material (0.5 g kg⁻¹) dissolved in water to make 5% solution (MVTI, 1995).

Table 7.1 Selected properties of Waihi topsoil

Organic matter (%)	pH	EC (dS m ⁻¹)	SO ₄ ²⁻ -----	Al _{Cu} mg kg ⁻¹	Al _{exc} -----	Al _{Ca} -----	CEC cmol _c kg ⁻¹
31%	5.2	1.3	257	756	170	7	34

Al_{Cu} = 0.5 M CuCl₂-extractable organic (Al_{org}) + exchangeable (Al_{exc}) + soluble (Al_{Ca}) aluminium.

7.2.2 Methods

About 50 mm of topsoil was placed on the pitwall rock column. Only 700 g of pitwall rock (about 90 cm column depth) was used in order to create space for topsoil placement. Where neutralising material was applied (at C_{ER} of 30 kg $\text{CaCO}_3 \text{ t}^{-1}$, required to raise pitwall rock pH to 6), it was incorporated in the top 50 mm of the pitwall rock column prior to placement of topsoil. In this study, ProMac powder at the rate of 0.5 g kg^{-1} pitwall rock (Vijay Rastogi, pers comm., 1998) was directly incorporated in the top 50 mm section of the pitwall rock column since surface application created excessive foam which slowed the downward movement of the leachate considerably.

The leaching protocol, analytical methods and statistical data analyses were carried out according to methods described in Chapter 3 (section 3.2.1.3) and Chapter 5 (section 5.2.4). The experiment was initially set up as a factorial design comparing various combinations of five amendments (Table 7.2). The results discussed in this chapter relate mostly to selected four treatments that include control (nil treatment), topsoil (TS), ProMac (PM) and TS+PM.

The remediation of low pH conditions in pitwall rock by pH modification using acid neutralising materials or topsoil placement to inhibit oxidation and provide an organic ameliorant to immobilise toxic metal concentrations (especially Al), or bacterial inhibition of pyrite oxidation, may all become complimentary in their relative effectiveness. Often a combination of treatments may be necessary to achieve the desired results. Thus various combinations of treatments using the amendments TS and PM with three other amendments [neutralising materials: limestone (LST), fluidised bed boiler ash (FBA) and reactive phosphate rock (RPR)] were used (Table 7.2) and discussed briefly in section 7.3.1.8.

Thiobacillus ferrooxidans is considered to be most active at optimum pH and temperature ranges of 1.5-3.5 and 30-35⁰C respectively (Walsh and Mitchell, 1972; Roman and Benner, 1973; Ahonen and Touvinen, 1991; Brown et al., 1993). Therefore, the columns amended with ProMac were heated with overhead high wattage lamps to provide an approximate constant surface temperature of about 35⁰C. The lamps were frequently shifted around to provide even distribution of temperature on column surface.

Table 7.2 Amendments and treatment design.

Pitwall rock (g)	Treatments	Treatment rate
1000	Control	Nil
700	Topsoil (TS)	50 mm placed on top
1000	ProMac (PM)	0.5 g PM
700	TS+PM	50 mm TS + 0.35 g PM
700	TS+LST	50 mm TS + 22 g LST
1000	PM+LST	0.5 g PM + 22 g LST
700	TS+FBA	50 mm TS + 49 g FBA
1000	PM+FBA	0.5 g PM + 70 g FBA
700	TS+RPR	50 mm TS + 39 g RPR
1000	PM+RPR	0.5 g PM + 56 g RPR
700	TS+PM+LST	50 mm TS + 0.35 g PM + 22 g LST
700	TS+PM+FBA	50 mm TS + 0.35 g PM + 49 g FBA
700	TS+PM+RPR	50 mm TS + 0.35 g PM + 39 g RPR

PM and neutralising materials (LST, FBA and RPR) were incorporated in the top 50 mm depth of pitwall rock column.

The pH, electrical conductivity (EC), SO_4^{2-} , acidity, Fe, Mn and Al were measured in the leachate from each leaching cycle. At the end of the 12 weeks leaching period, the TS amended columns were sliced into sections (0-20, 20-40, 40-50, 50-70, 70-90, 90-110, 110-140 mm), crushed and air-dried prior to grinding to ≤ 2 mm for chemical analysis. The PM and neutralising material incorporated columns were sliced into 20 mm sections.

Soluble labile Al (Al_{Ca}) and organic+polymeric+exchangeable Al (Al_{Cu}) in the sectioned pitwall rock samples were extracted with 0.02 M CaCl_2 (Hoyt and Nyborg, 1972), and 0.5 M CuCl_2 (Juo and Kamprath, 1979) respectively and their concentrations were measured by atomic absorption spectrometry (AAS).

7.3 Results and Discussion

Columns with topsoil (TS) placements consistently produced leachate volumes of about 80% of the input volume applied (250 ml). On the other hand, leachate volumes from ProMac (PM) treated columns were considerably lower (46% of input volume) as a

result of impediment of infiltration from blockage of pore spaces with clay particles dispersed during foaming and as well as loss from evaporation under heated lamps. The average volume of leachate collected from the control column was 191 ml week⁻¹. In most cases, the leachate colour from all the treatments was dark orange brown which changed to a clear solution when acidified with 10 N HNO₃, indicating the coloration was mainly due to dissolution of particulate Fe³⁺ in the solution.

In the discussion of results for the distribution of measured parameters in the TS amended pitwall rock column sections, the equivalent column depth 50-130 mm is compared with the 0-80 mm section of the control and PM treated columns.

7.3.1 Characterisation of the leachate

7.3.1.1 Leachate pH

Topsoil (TS) and ProMac (PM) treated columns produced leachate with very low pH (< 2.6) throughout the 12 week leaching cycle (Figure 7.1a). The overall mean pH of the leachate from control and TS amended columns remained below 2.2 whereas leachate pH from PM treated columns was higher by about 0.2 pH units. The production of very low pH leachate from the TS and PM amended columns is comparable to results obtained from the neutralising material amended columns (Chapter 5 and 6). In a column test (9 weeks duration) on partially oxidised silver mine waste (pH 4.8), Parisi et al. (1994) indicated an effluent pH improvement of about 16% (pH 3.3 to 4.3) in PM treated columns (7 g PM kg⁻¹) compared to control columns. However, no significant improvement in leachate pH from PM treated columns was observed in this study. This may indicate that in partially oxidised pyritic pitwall rock materials, ProMac may not have inhibited bacterial oxidation as suggested by Watzlaf (1988a). ProMac solution had near neutral pH (6.8) and therefore, the slight increase in pH of the leachate from ProMac treated columns may well be due to pH dilution effect.

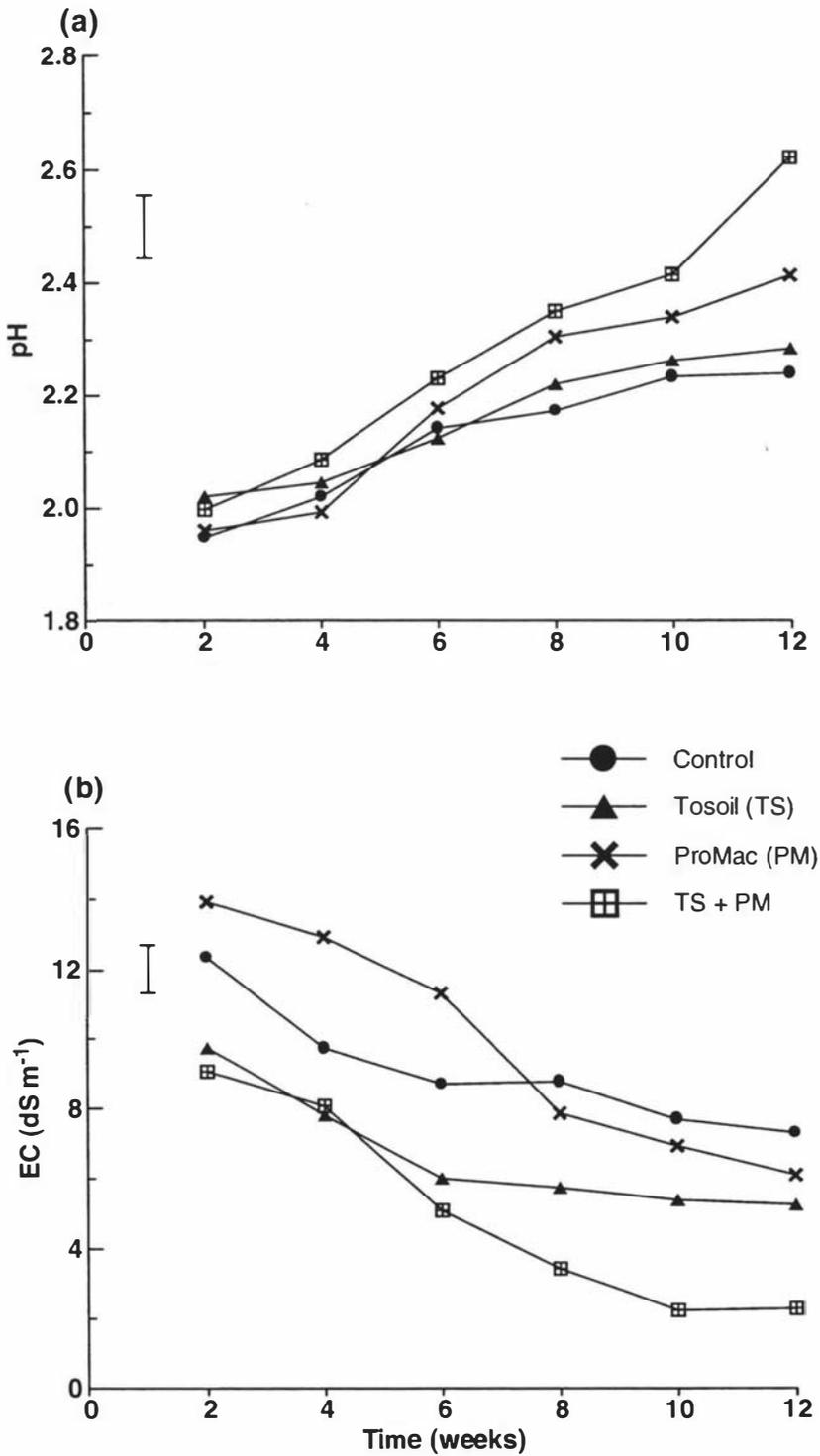


Figure 7.1 (a) pH and (b) EC of the leachate from columns amended with TS and PM. Vertical bars represent LSD(5%).

7.3.1.2 Leachate EC

The distribution of EC in the leachate over 12 weeks period showed a gradual decrease for all the treatments (Figure 7.1b). During week 2 to week 6, the PM treated column produced leachate with the highest EC, after which it remained similar in value to that of the leachate from the control column. At the end of the 12 week leaching period, the EC in leachate from the control, TS and PM treated columns remained above 5 dS m⁻¹. The TS treated column consistently produced leachate with significantly lower EC than either control or PM treated columns during week 2 to week 8. During week 2 to week 6, both TS and TS+PM treated leachate EC were similar but thereafter, the TS+PM treated column produced leachate with EC significantly lower (EC < 3.5 dS m⁻¹) than all the other treatments as a result of continued flushing of the columns during leaching cycles.

7.3.1.3 Leachate SO₄²⁻

The SO₄²⁻ concentration in the leachate from the control columns varied from 4650 mg L⁻¹ in week 2 to 2350 mg L⁻¹ in the final week of leaching (Figure 7.2a). The TS and ProMac amendments significantly lowered the SO₄²⁻ levels in the leachate. The TS and TS+PM amended columns produced the lowest levels of SO₄²⁻ while PM treated column released twice as much SO₄²⁻ in the leachate as that from either TS or TS+PM treated columns. The overall mean release of SO₄²⁻ in the control column leachate (Table 7.3) was 3480 mg SO₄²⁻ kg⁻¹week⁻¹ and the corresponding reduction of SO₄²⁻ relative to the control value were 74%, 47% and 74% for TS, PM and TS+PM respectively.

While reductions in leachate SO₄²⁻ levels from PM treated columns reflected an apparent inhibition of acid generation by *Thiobacillus ferrooxidans* activity, the significantly lower release of SO₄²⁻ from TS amended columns could be either due to restricted oxygen diffusion or immobilisation of SO₄²⁻ in the column as metal salt complexes. Preliminary results of a 9 week column leaching experiment on ProMac amended (7 g kg⁻¹) silver mine waste rock containing total S of about 0.5% was shown to improve SO₄²⁻ reduction by about 72% (Parisi et al., 1994). *In situ* reclamation trials carried out by MVTI (1989) using ProMac spray have been shown to reduce SO₄²⁻ concentration in lysimeter samples by as much as 82%.

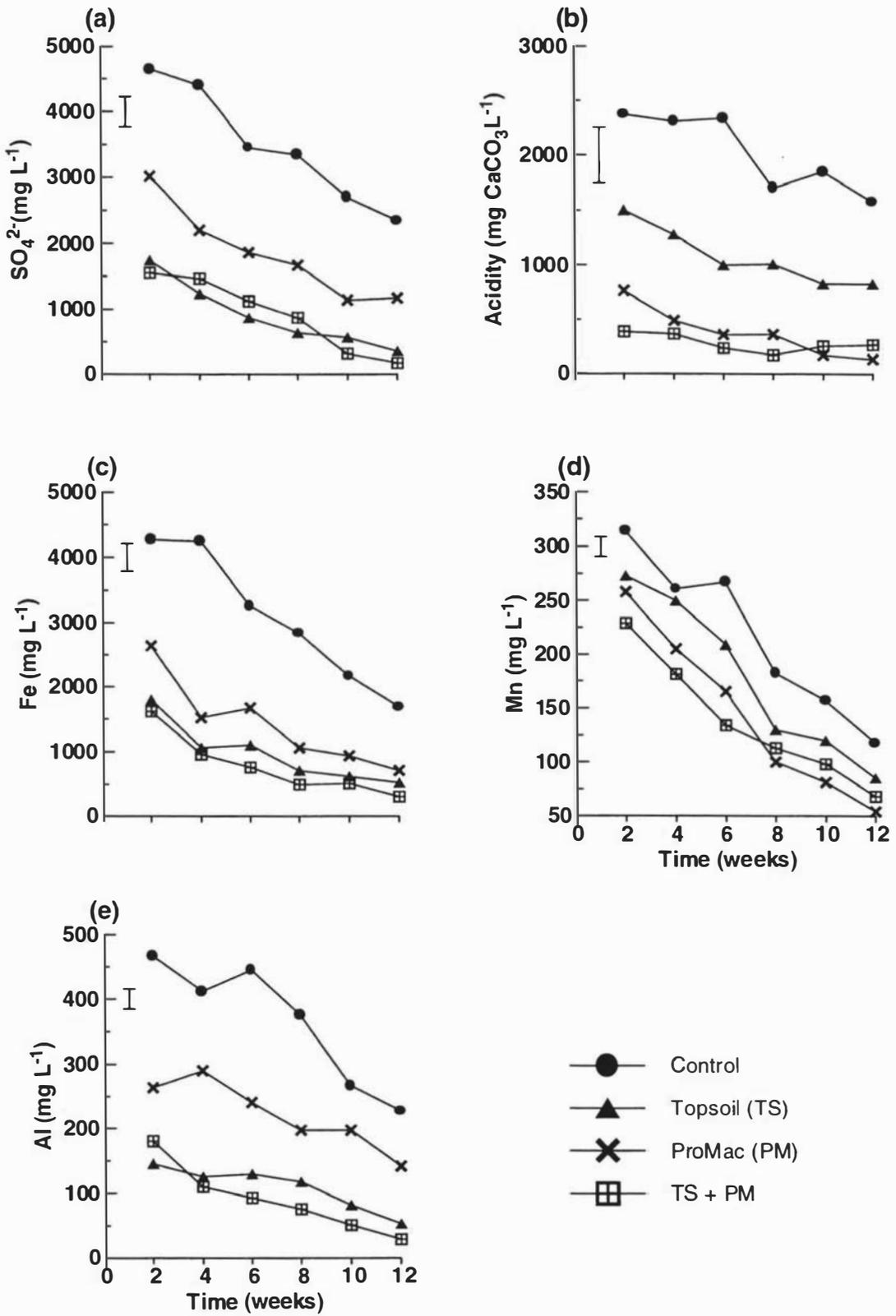


Figure 7.2 Concentrations of (a) SO₄²⁻, (b) acidity, (c) Fe, (d) Mn and (e) Al in the leachate from columns amended with TS, PM and TS+PM. Vertical bars represent LSD(5%).

Result of this study however indicated SO_4^{2-} reduction of only about 47% in leachate from the PM treated columns. The site-specific nature of the mine waste rock type and pyrite content may have affected the performance of ProMac in alleviating SO_4^{2-} levels in the leachate. ProMac is a sulphonic salt (EC, 22 dS m^{-1}) and therefore it would be contributing some SO_4^{2-} to the system rather than reducing SO_4^{2-} in the leachate.

Table 7.3 Average release rates of the concentrations of measured parameters in the leachate from columns treated with various combinations of amendments.

	SO_4^{2-}	acidity	Fe	Mn	Al
Control	3480	2025	3078	217	366
TS	902	1075	968	178	109
PM	1842	382	1423	144	222
TS+PM	915	282	773	137	90
<i>LSD(5%)</i>	247	209	234	67	27
Relative reductions (-) in the measured parameters					
TS	-74	-47	-69	-18	-70
PM	-47	-81	-54	-34	-39
TS+PM	-74	-86	-75	-37	-75

Except for acidity ($\text{mg CaCO}_3 \text{L}^{-1}$), the units are in mg L^{-1} .

7.3.1.4 Leachate acidity

Acidity in the leachate from amended columns decreased significantly in the initial week of leaching cycle (Figure 7.2b). Leachate acidity from the control column decreased from 2372 $\text{mg CaCO}_3 \text{kg}^{-1}$ in week 2 to 1690 $\text{mg CaCO}_3 \text{kg}^{-1}$ in week 12 whereas the corresponding range in the TS and PM amended column leachate were 1501-830 $\text{mg CaCO}_3 \text{kg}^{-1}$ and 765-135 $\text{mg CaCO}_3 \text{kg}^{-1}$ respectively. The lowest release of acidity was obtained in the TS+PM amended column leachate (389-270 $\text{mg CaCO}_3 \text{kg}^{-1}$).

Comparisons of the overall differences in means (Table 7.3) indicated that the PM amendment caused an 81% reduction in the level of leachate acidity relative to the control mean of 2025 $\text{mg CaCO}_3 \text{kg}^{-1}$. This reduction in acidity due to PM amendment is comparable to 93% reported by Parisi et al. (1994) and mine water quality improvement of 87-98% under ProMac treatment systems (MVTI, 1994). The corresponding reduction in the leachate acidity by TS amendment was 47% whereas the combination treatment of TS+PM resulted in 86% reduction.

The ratio of acidity to SO_4^{2-} is an indication of the amount of acid generated or neutralised/inhibited. According to the ideal oxidation of pyrite (section 5.3.2.5, Chapter 5) the acidity to SO_4^{2-} ratio is 1.04. The level of SO_4^{2-} and acidity in the leachate showed a highly significant ($p=0.001$) linear relationship ($R^2 > 0.95$) for all the treatments. The slope of the regression fit for the distribution of acidity and SO_4^{2-} in the leachate from the control column was 0.58, indicating that despite nil treatment, about 42% of the acid was being neutralised by possible dissolution of silicate minerals and precipitation of jarosite type minerals. The corresponding slopes of the regression fits for TS and PM amended columns were 1.19 and 0.21 respectively. This ratios indicated neutralisation of 79% and 19% acidity in the leachate from PM and TS treated column respectively. Overall mean reduction of acidity compared to nil treatment were 81% and 47% in the leachate from PM and TS amended columns respectively (Table 7.3).

7.3.1.5 Leachate Fe and Mn

Both Fe and Mn concentrations in the leachate decreased significantly over the 12 weeks leaching period (Figure 7.2c & d). Incorporation of PM powder and TS placement resulted in significant reduction in the level of Fe in the leachate. The Fe concentration in the control column leachate decreased from 4270 to 1690 mg L^{-1} (60%) over 12 weeks period. The TS and PM amended columns produced leachates that were significantly lower in Fe and Mn concentrations than the values for the control column. The cumulative concentration of Fe followed a logarithmic trend with $R^2 > 98$ for all the treatments. The TS+PM amended columns produced the lowest level of Fe in the leachate while the PM treated column produced leachate with a significantly higher Fe content. The overall mean release of Fe by the control column was 3078 $\text{mg L}^{-1}\text{week}^{-1}$ (Table 7.3). The reduction in Fe concentration by the TS, PM and TS+PM amendments were 60%, 54% and 75% respectively. This reduction by PM in the present study was much lower than the reduction of 95% (Parisi et al., 1994) and 88% (MVTI, 1995) in ProMac affected leachate from silver mine waste rocks.

The soluble Mn levels decreased rapidly with each successive leaching for all the treatments (Figure 7.2b). There was a gradual decrease in the concentration of Mn in the leachate from all the treatments. Generally, the Mn in the control column remained high throughout the 12 week leaching cycle. The PM treated column produced significantly

lower Mn levels in the leachate than the TS amended columns. The overall mean distribution of Mn in the leachate (Table 7.3) indicated a relative reduction of 18%, 34% and 37% respectively for TS, PM and TS+PM amendments. The reduction in Mn in leachate from PM treated columns could be due to a slight increase in soluble Mn in the column sections.

7.3.1.6 Leachate Al

The leachate Al gradually decreased with each successive leaching cycle (Figure 7.2e). The TS amended columns produced a significantly lower level of Al in the leachate compared to that of PM and nil treatment control columns. It is possible that a high fraction of the Al may have been retained in the column complexed with water-soluble organic ligands leaching from the topsoil. The order of overall reduction in the leachate Al were TS+PM (75%) > TS (70%) > PM (39%). Soluble Al reduction in leachate from PM amended waste rock columns reported by Parisi et al (1994) and MVTI (1994) was about 95%. The lower reduction in leachate Al in this study may have been due to site specific characteristic of the waste rock and the leaching conditions.

7.3.2 Column section chemistry

7.3.2.1 Column section pH

The column section pH remained constantly low (2.5) throughout the column depth (80 mm) for both the control and TS amended columns (Figure 7.3a). The pH in the PM treated columns was significantly raised to pH > 4.0 at 0 to 40 mm depth and remained above 3.5 at lower depths. The distribution of pH in the TS+PM treated pitwall rock column was similar to that of PM alone treatment. The rise in pH effected by the bactericide ProMac was significantly higher ($P > 0.05$) than either control or TS treated columns. Since at pH > 3.5, *Thiobacillus ferrooxidans* is considered inactive (Walsh and Mitchell, 1972; Kleinmann and Crerar, 1979; Brown et al., 1993), the continual discharge of low pH leachate from the PM treated column indicated that abiotic oxidation of pyrite alone maybe creating low pH leachate.

7.3.2.2 Column section EC

Column section EC levels were significantly lower in PM ($EC < 1 \text{ dS m}^{-1}$) and TS ($EC < 2 \text{ dS m}^{-1}$) treated columns throughout the depth profile compared to the control columns (Figure 7.3b). The distribution of the EC in the column depth profile of the TS

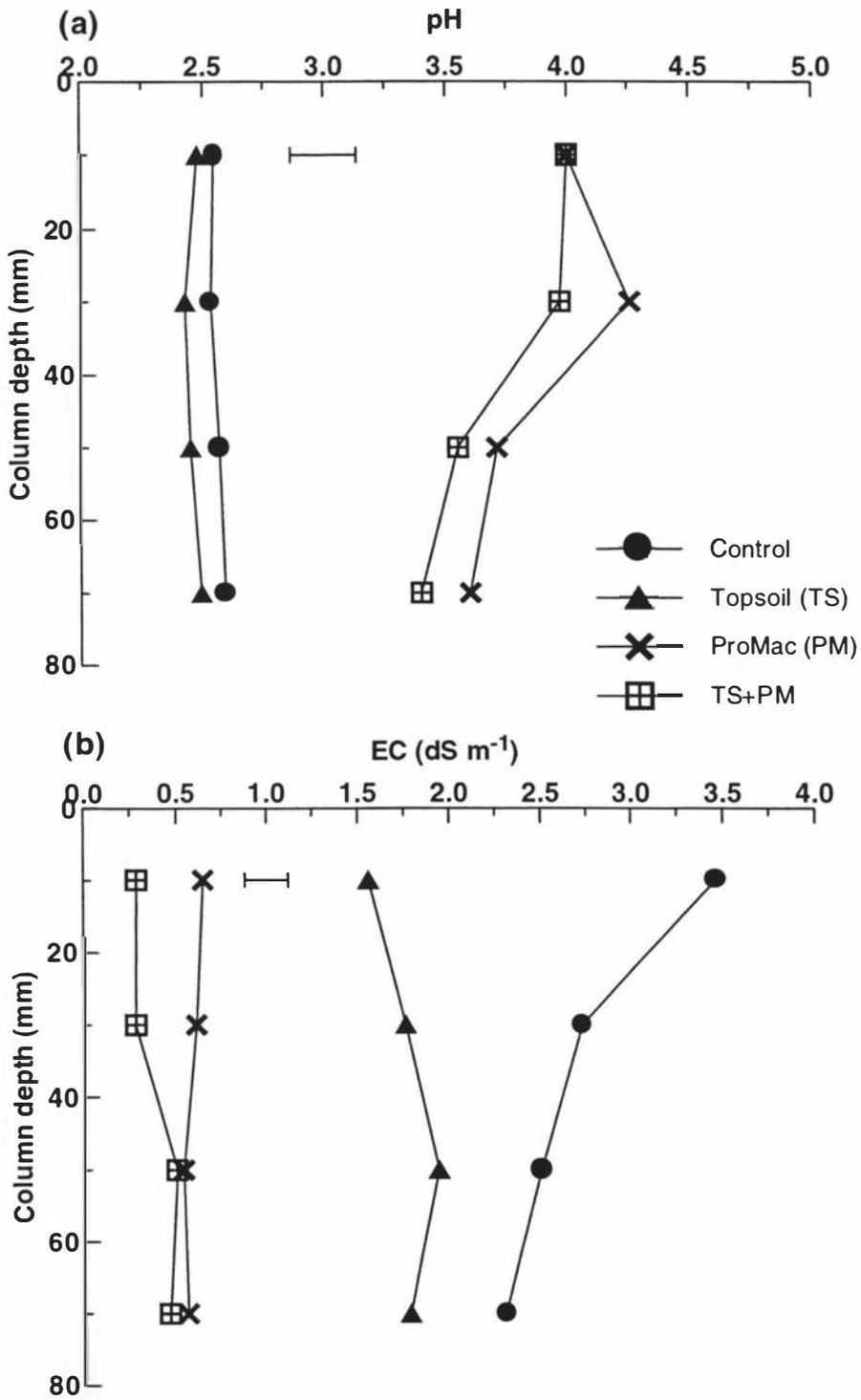


Figure 7.3 (a) pH and (b) EC of the sectioned samples from leached columns. Horizontal bars represent LSD(5%).

and PM treated columns were similar to that of the neutralising material incorporated columns (Chapter 6). The control column EC was slightly higher at the surface, possibly due to metal salt precipitation under drying conditions. The lower EC down the profile may reflect the removal of solute during successive leaching of the columns. The overall mean EC was 2.8 dS m^{-1} for the control column which was significantly reduced to 1.8, 0.6 and 0.4 dS m^{-1} respectively by TS, PM and TS+PM treatments. The relative reduction of the EC by the amendments were 86%, 79% and 36% for the TS+PM, PM and TS treatments respectively.

7.3.2.3 Column section SO_4^{2-}

The TS, PM and TS+PM treatments caused a significant reductions ($P > 0.05$) in the distribution of SO_4^{2-} in the leached pitwall rock column compared to the control columns with nil treatment (Figure 7.4a). The PM and TS+PM amended columns showed the largest reduction in the SO_4^{2-} levels throughout the column depth of 80 mm. Although the PM treatment resulted in only a 47% reduction in leachate SO_4^{2-} , the column section SO_4^{2-} level was reduced by 88% (Table 7.4). Combination of TS+PM caused an overall reduction of SO_4^{2-} by 97%. The elevation of pH to > 3.5 and the subsequent significant reduction in the SO_4^{2-} indicated that the PM treatment may have inhibited bacterial activity and this reduced the acid generation process in the column section.

Although the TS amendment significantly reduced ($P > 0.05$) the SO_4^{2-} in the 80 mm section of the column by 35% (Table 7.4), the mean SO_4^{2-} distribution remained $> 2000 \text{ mg kg}^{-1}$. The reduction in SO_4^{2-} by TS amendment may be due to reduced pyrite oxidation under restricted diffusion of oxygen because of the 50 mm thick topsoil placement.

7.3.2.4 Column section acidity

The mean distribution of acidity in the column sections closely followed the trend shown by SO_4^{2-} distribution. All the treatments caused significant reductions in column section acidity throughout the 80 mm column depth (Figure 7.4b). This was to be expected as the level of acidity retained in the column section would in fact be directly proportional to the production of SO_4^{2-} . Overall mean acidity level in the control column was $2432 \text{ mg CaCO}_3 \text{ kg}^{-1}$, and was reduced by 59% in the PM incorporated column whereas the TS amendment resulted in 35% reduction in acidity (Table 7.4). The TS+PM treatment caused 71% reduction in the column section acidity.

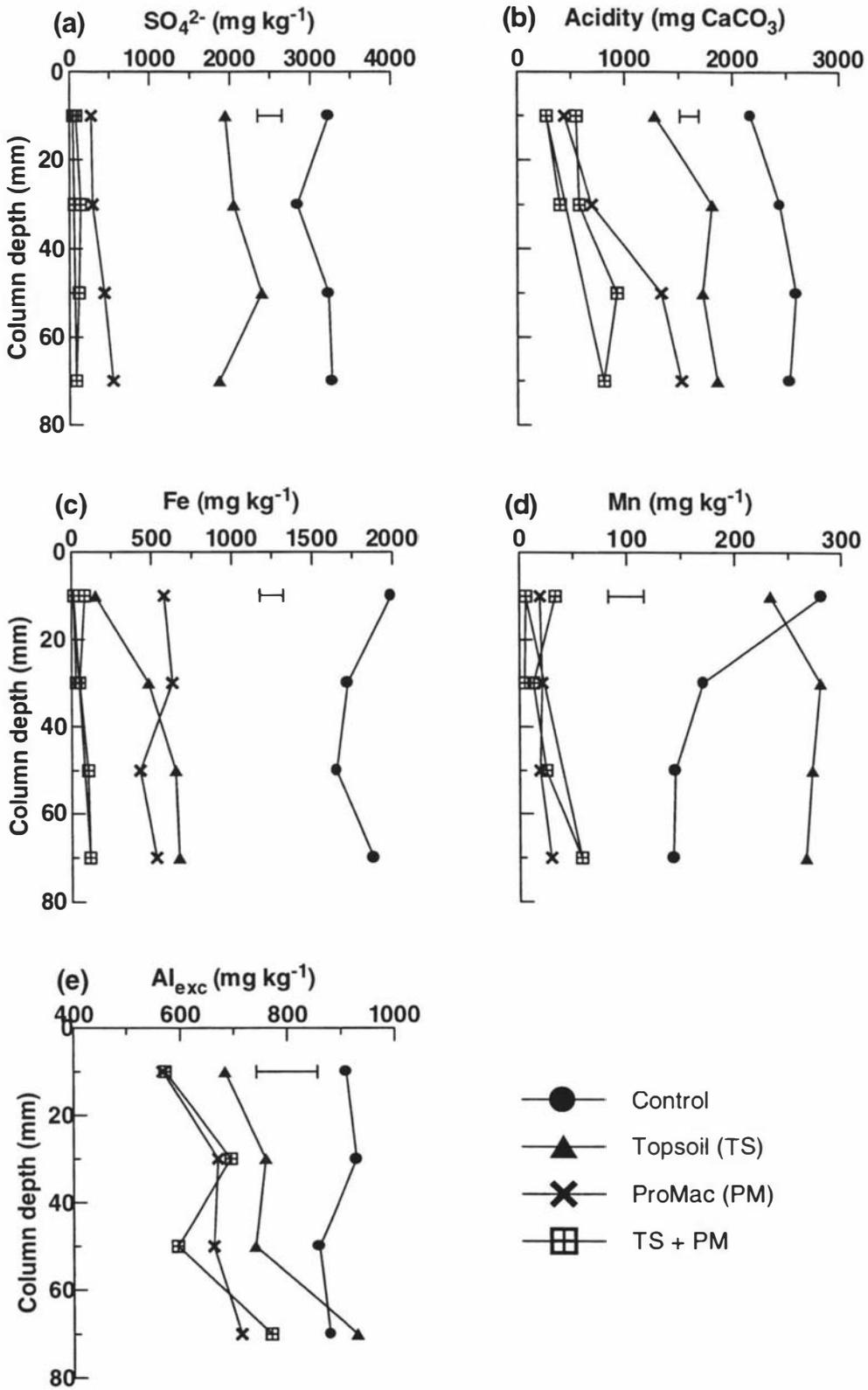


Figure 7.4 Distribution of (a) SO_4^{2-} , (b) acidity, (c) Fe, (d) Mn and (e) Al_{exc} in the sectioned samples from leached columns. Horizontal bars represent LSD(5%),

Table 7.4 Comparison of the mean distribution of selected chemical parameters in leached column treated with various amendments.

	SO ₄ ²⁻	acidity	Fe	Mn	Al	Al _{exc}
Control	3143	2432	1810	185	353	894
TS	2067	1583	488	263	192	779
PM	389	1001	543	22	7	654
TS+PM	106	718	89	32	68	718
LSD(5%)	220	188	156	26	28	108
Relative reductions (-) in the measured parameters						
TS	-34	-35	-73	42	-46	-13
PM	-88	-59	-70	-88	-98	-27
TS+PM	-97	-71	-95	-82	-81	-20

Except for acidity (mg CaCO₃ kg⁻¹), the units are in mg kg⁻¹.

The available literature (Parisi et al., 1994; MVTI, 1994) on column leaching studies using bactericide and soil cover materials characterises only the improvements on leachate water quality and to date no data are available to compare the subsurface amelioration of subsurface low pH conditions. Field and laboratory studies conducted by Cravotta (1996) on the biogeochemical interactions and transport processes affecting the oxidation of pyrite and the formation of AMD in surface coal mines showed that despite low concentrations of dissolved O₂ (<1 mg L⁻¹) in ground water beneath sludge-treated spoil, concentrations of SO₄²⁻ and acidity increased down gradient. The present study showed that both subsurface SO₄²⁻ and acidity are significantly reduced by TS, PM and TS+PM amendments. The depth of amelioration of low pH conditions in the column section (~80 mm) was comparable to that of neutralising material amended columns (Chapter 5 & 6). The acidity versus SO₄²⁻ distribution in the column section was linearly regressed ($y = 0.52 * x + 733$, $R^2 = 0.88$) with a slope of 0.52, indicating overall reduction of acidity of about 50%. The corresponding acidity to SO₄²⁻ ratio for the TS, PM and TS+PM treated columns were 0.65, 0.41 and 0.29 respectively. These reduction in slopes (compared to 1.04 for ideal oxidation of pyrite) indicated relative acid neutralisation of 38%, 61% and 72% by TS, PM and TS+PM amendments respectively.

7.3.2.5 Column section Fe and Mn

Soluble Fe in the columns treated with various amendments was significantly reduced ($P > 0.05$) when compared to that of the control column (Figure 7.4c). The columns with the nil treatment showed a uniform distribution of Fe throughout the 80 mm depth

section. The TS amended columns reduced Fe to $< 200 \text{ mg kg}^{-1}$ in the top 0-20 mm section but the Fe distribution appeared to increase down depth. This reduction in Fe is reflective of the possible inhibitory effect by TS and PM amendments on the oxidation of pyrite, as indicated in the suppression of SO_4^{2-} and acidity production in the amended columns. The overall comparison of means showed Fe reduction in the column to be 73%, 70% and 95% by TS, PM and TS+PM respectively (Table 7.4).

The distribution of Mn in the column section was significantly reduced by the incorporation of PM in the top 50 mm section of the pitwall rock column. At depth 30-80 mm, there was an apparent increase in the distribution of Mn in the TS amended column sections, and this increase was significantly greater ($P>0.05$) than in the column with nil treatment (Figure 7.4d). This apparent increase of Mn in the TS amended column section may be due to mobilisation of Mn by dissolved organic matter in the leachate. The overall reductions in column section Mn were 42%, 88% and 82% respectively for TS, PM and TS+PM treatments.

Ferric-sulphate and Fe-Mn oxide minerals, which may have formed under oxidising conditions before the application of topsoil, were likely to dissolve close to the surface locations producing SO_4^{2-} and Fe^{3+} ions and precipitates salts. The increased EC, SO_4^{2-} , Fe, Mn and Al in the topsoil at the interface indicated that there was upward migration of salts and metals, which may affect the plant root system.

7.32.6 Column section Al

Soluble Al (Al_w) in the column section was most affected by PM treatment possibly due to an increase in the column section pH and hence reduction in the solubility of monomeric Al (Table 7.4). At $\text{pH}>3.5$, Al_w may go into polymeric forms as well as precipitating as hydroxy gels and sulphate salts such as alunite in the presence of elevated levels of SO_4^{2-} . In acidic conditions of $\text{pH}<2.5$, as is present in the control column, Al_w was highly mobile and remained high at 300 mg kg^{-1} . As reflected in the reduced release of Al_w in the leachate, a large fraction ($\sim 192 \text{ mg kg}^{-1}$) of Al_w was retained and distributed evenly in the 80 mm depth section of pitwall rock (Figure 7.8a). The overall reduction in the Al_w was in the order PM (98%) > TS+PM (81%) > TS (46%).

The levels of exchangeable Al (Al_{exc}) in the amended columns were $>500 \text{ mg kg}^{-1}$ ($>6 \text{ cmol}_c \text{ kg}^{-1}$) throughout the 80 mm column depth and was similar for all the treatments (Figure 7.4e). The mean Al_{exc} in the control columns remained constant at 894 mg kg^{-1} ($9.9 \text{ cmol}_c \text{ kg}^{-1}$). At depth 0 to 50 mm, the amended column had significantly lower Al_{exc} than the nil treated control columns. PM amendment appeared to have significantly lowered Al_{exc} at all depths possibly either due to the pH effect caused by ProMac solution (pH 6.8) or the dispersive effect on clay by PM may have released Al_{exc} in the effluent solution. The relative reduction in the distribution of Al_{exc} were 13%, 27% and 20% respectively for TS, PM and TS+PM.

7.3.2.7 Effect of topsoil placement on total Al pool

Topsoil (TS) covers not only provide an oxygen diffusion barrier (and plant growth media where vegetative reclamation is a necessity) but also act as a source of soluble organic ligands that can bind readily with the labile Al in the pore water solution. An earlier investigation by Gurung et al. (1996) has shown that organic matter leachate from topsoil cover on oxidised mine waste rock was responsible for providing organic ligands which complexed with labile exchangeable Al (Al_{exc}) and thereby reduced the phytotoxic levels of Al.

The reactive Al pool in very acid soils would ideally include soluble monomeric and total exchangeable Al, Al in octahedral clays and Al-hydroxide-organic matter complexes (Juo and Kamprath, 1979). Aluminium extracted with 0.5 M CuCl_2 solution (Al_{Cu}) is mainly attributed to total Al pool containing organic-Al + hydroxy-Al complexes + exchangeable-Al + labile-Al.

In the absence of organic ligand sources, the largest fraction of the total Al pool extracted by 0.5 M CuCl_2 solution should ideally be hydroxy-bound Al + exchangeable Al + soluble Al. Significantly, higher levels of Al_{exc} followed by Al_{Cu} dominate the Al distribution in the pitwall rock (Figure 7.5). The distribution of Al in the TS amended pitwall section of columns was not significantly different from that of the control column (nil amendment) which had mean column section Al concentrations of $601 \pm 103 \text{ mg kg}^{-1}$ (Al_{Cu}), $912 \pm 59 \text{ mg kg}^{-1}$ (Al_{ex}) and $291 \pm 151 \text{ mg kg}^{-1}$ (Al_{Ca}) respectively.

This suggested that the 0.5 M CuCl₂ solution only extracted hydroxy-bound Al and very little exchangeable Al.

Results of this experiment showed that there was no evidence of Al-organic matter complexation in TS amended columns, which were leached for 12 weeks although there was an apparent increase in the Al_{Cu} just above the topsoil-pitwall rock interface (Figure 7.5). The TS sections (0-50 mm) contained mostly Al_{Cu} and very little Al_{exc}, indicating that the organic ligands in the topsoil were probably already bound with labile Al and that the residual organic ligands moving down the column during leaching cycles was not sufficient to cause significant changes in the Al pool of the pitwall rock below the depth of placement. It is also probable that in the pyritic rock, most of the labile Al would be already hydroxy-bound or in the presence of elevated SO₄²⁻ level, sulphate-bound.

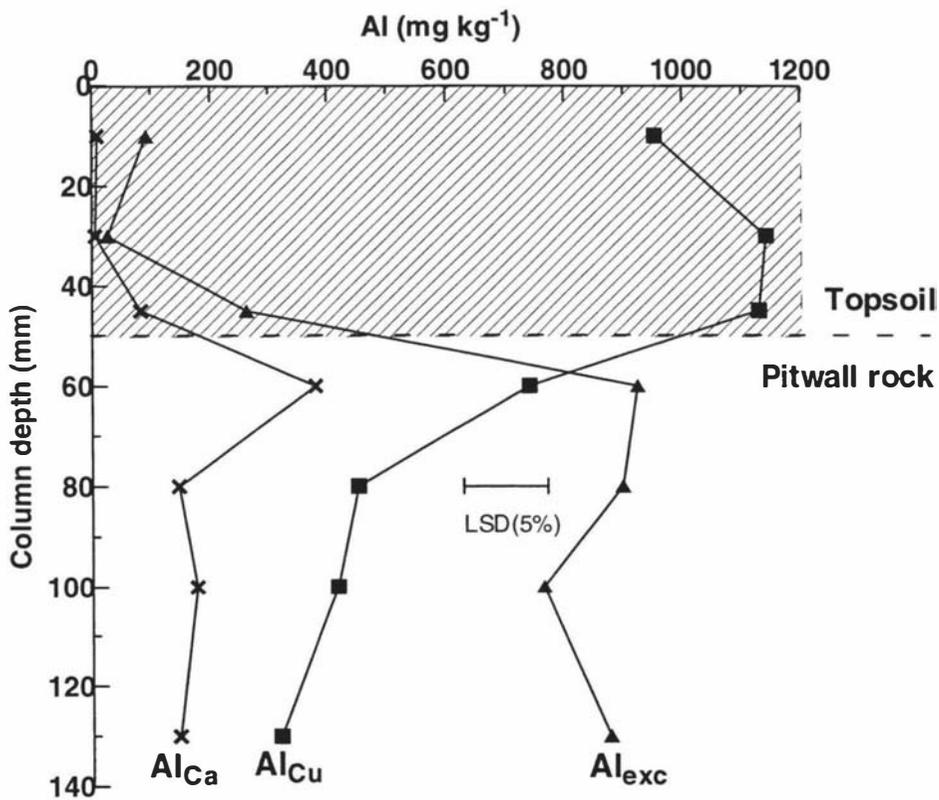


Figure 7.5 Distribution of different forms of Al in topsoil amended columns.

7.3.3 Effect of combination amendments

Research has shown that no single treatment system alone is effective in the control and treatment of AMD. Since the geochemical environment in which pyrite oxidation and hence acid generation occur is so complex, a combination of treatments may be more advantageous than a single ameliorant in mitigating low pH conditions in acidic mine waste rocks.

While neutralising materials may provide short-term amelioration of low pH conditions, their effectiveness was commonly affected by rapid exhaustion of neutralisation capacity by the armouring effect of oxyhydroxide precipitates (Chapter 4). Fluidised bed boiler ash (FBA) caused excessive alkalinity and cement formation while reactive phosphate rock (RPR) was ineffective in raising pH to 6 achieved at carbonate equivalent rates of application. Mine site rehabilitation by revegetation methods requires control of acid generation and subsurface amelioration of the growing media long enough for vegetation to establish permanently. Topsoils, bactericides and neutralising materials are therefore some of the important materials in the amelioration of low pH conditions in pyritic pitwall rock and in the creation of a suitable plant growth medium. The overall effects of various combination treatments on leachate quality and column chemistry are briefly discussed below and summarised in Table 7.5 and 7.6 respectively.

7.3.3.1 Effects of combination treatments on pH and EC

Combined treatments did not raise the leachate pH > 2.3 although the increase in pH effected by combination of TS with either PM, LST and FBA where significantly higher (Figure 7.6a). Except for the RPR amended column, there were significant increases in pH of the pitfall rock columns amended with combination treatments of TS, PM, LST and FBA (Figure 7.6b). The PM amended columns produced high leachate EC level similar to that of the control column and the improvement on leachate EC by combination treatments were not significantly different to that of TS or PM amendment alone (Figure 7.7a). Amendment combinations of either TS or PM with LST and FBA caused significant increases in the EC content of the pitwall rock column (Figure 7.7b). This increase in EC of the pitwall rock could be due to contribution of SO_4^{2-} from FBA and sulphonic salt from PM.

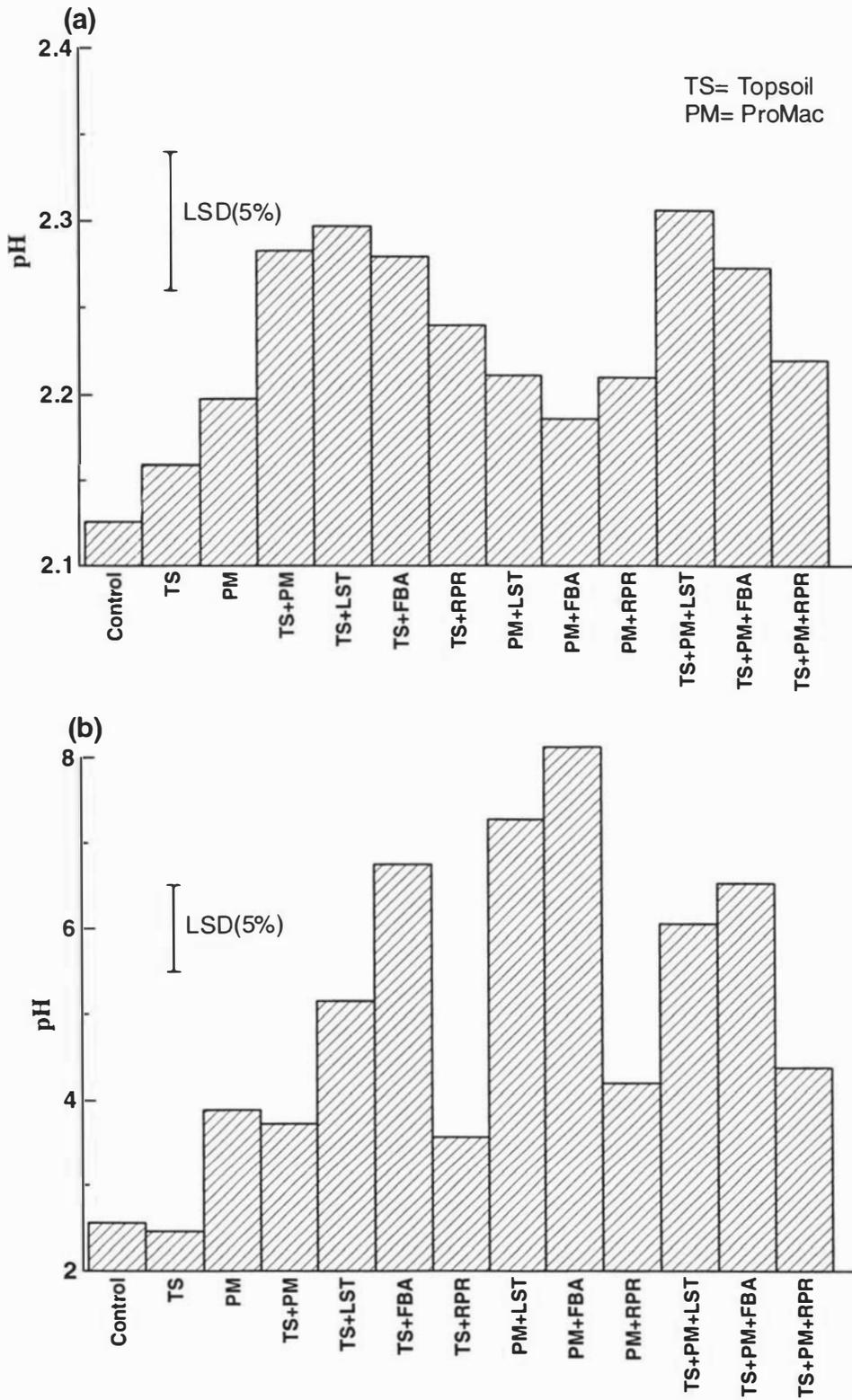


Figure 7.6 Overall effect on (a) leachate pH and (b) column pH by various combinations of treatments.

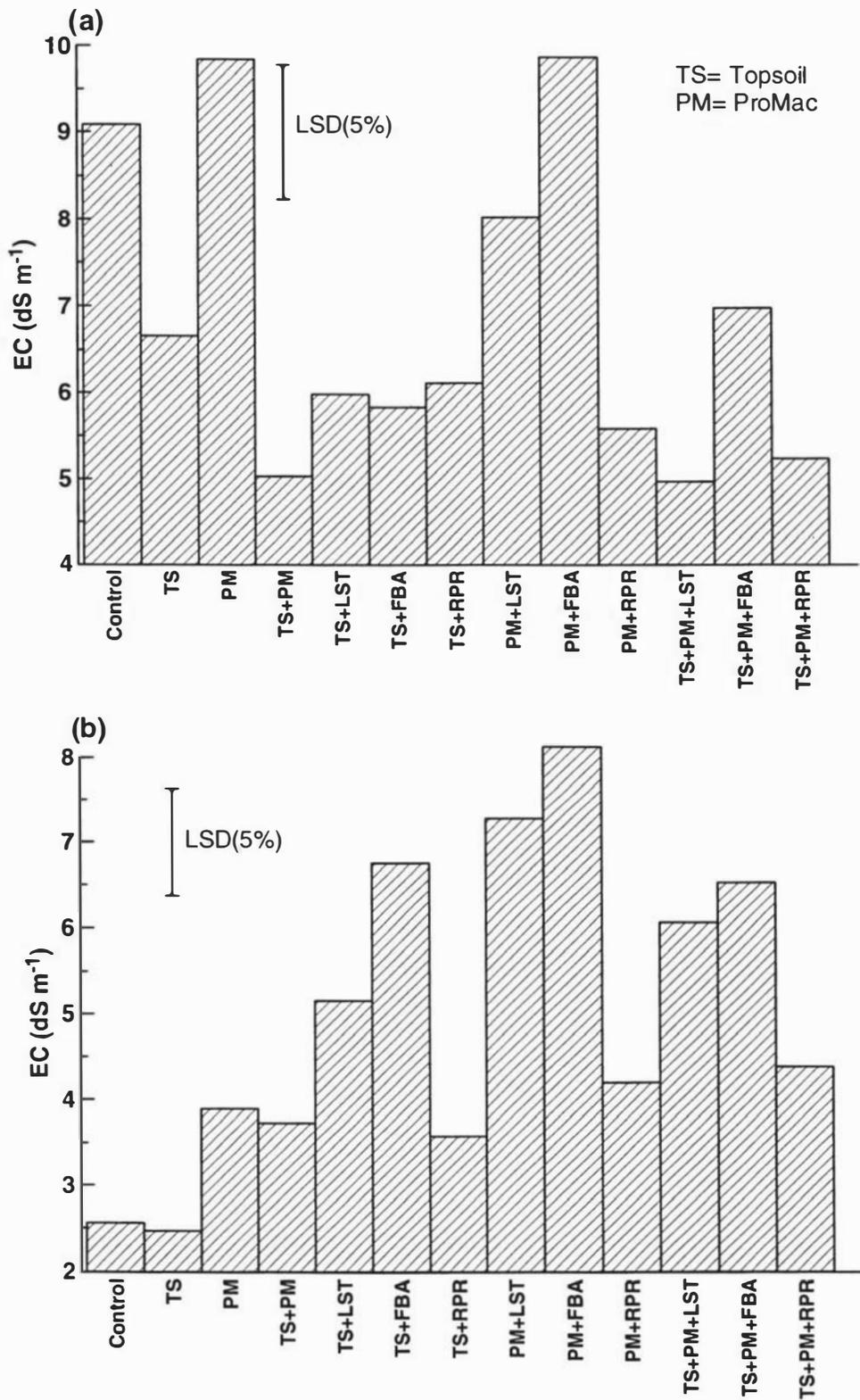


Figure 7.7 Overall effect on (a) leachate EC and (b) column EC by various combinations of treatments.

7.3.3.2 Effects of combination treatments on SO_4^{2-} , acidity, Fe, Mn and Al

Combination of TS and PM treatments with neutralising materials-amended pitwall rock columns resulted in higher improvement in leachate quality than the TS or PM alone treatment (Table 7.5). The overall reductions in the release levels of SO_4^{2-} , acidity, Fe, Mn and Al in the leachate were generally higher for pitwall rock columns amended with combinations of TS and PM with either LST or FBA. The PM+LST amendment caused significantly higher release of SO_4^{2-} than other combinations. All the combination treatments had similar effect on the release of acidity, Fe and Al in the leachate and were significantly lower than the levels in the leachate from control column with nil treatment.

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

	SO_4^{2-}	acidity	Fe	Mn	Al
Control	3480	2025	3078	217	366
TS+LST	731	200	677	105	59
PM+LST	1458	220	1010	116	65
TS+FBA	409	763	906	66	26
PM+FBA	692	343	1090	135	43
TS+RPR	500	171	895	163	33
PM+RPR	713	289	967	151	29
TS+PM+LST	459	271	549	85	41
TS+PM+FBA	476	243	1053	78	28
TS+PM+RPR	397	164	890	146	25
<i>LSD(5%)</i>	247	209	234	67	27
Relative % reductions (-) in the measured parameters					
TS+LST	-79	-90	-78	-51	-84
PM+LST	-58	-89	-67	-46	-82
TS+FBA	-88	-63	-71	-70	-93
PM+FBA	-80	-83	-65	-38	-88
PM+RPR	-80	-86	-69	-30	-92
TS+RPR	-86	-92	-71	-25	-91
TS+PM+LST	-87	-87	-82	-61	-89
TS+PM+FBA	-86	-88	-66	-64	-92
TS+PM+RPR	-89	-92	-71	-32	-93

Except for acidity ($mg CaCO_3 L^{-1}$), the units are in $mg L^{-1}$.

7.3.3.3 Effects of combination treatments on column section chemistry

The effect of using neutralising materials (LST, FBA and FBA) in combination with either TS or PM caused a general decrease in the efficiency in reduction of SO_4^{2-} compared to reductions with TS or PM alone (Table 7.6 and compare with Table 7.4). There was however, a general increase in the reduction efficiency (compared to individual treatments with TS, PM, LST, FBA or RPR) of acidity, Fe, Mn and Al in the columns amended with combination treatments. The result demonstrated the fact that under real field situations, amendment of pyritic materials may require combinations of treatment measures for effective amelioration of low pH conditions created by pyrite oxidation.

Table 7.6 Comparison of the mean distribution of selected chemical parameters in leached column treated with various amendments.

	SO_4^{2-}	acidity	Fe	Mn	Al	Al_{exc}
Control	3143	2432	1810	185	353	894
TS+LST	2306	292	420	118	84	98
PM+LST	877	57	370	5	18	99
TS+FBA	1469	373	211	80	75	298
PM+FBA	1327	251	335	12	32	77
TS+RPR	1352	723	234	126	86	351
PM+RPR	1033	366	212	34	44	110
TS+PM+LST	65	364	22	6	3	102
TS+PM+FBA	715	536	11	6	4	205
TS+PM+RPR	204	735	18	23	9	126
<i>LSD(5%)</i>	221	188	156	76	18	108
Relative % reductions (-) in the measured parameters						
TS+LST	-27	-88	-77	-36	-76	-89
PM+LST	-72	-98	-80	-97	-95	-89
TS+FBA	-53	-85	-88	-57	-79	-67
PM+FBA	-58	-90	-81	-93	-91	-91
TS+RPR	-57	-70	-87	-32	-76	-61
PM+RPR	-67	-85	-88	-82	-88	-88
TS+PM+LST	-98	-85	-99	-97	-99	-89
TS+PM+FBA	-77	-78	-99	-97	-99	-77
TS+PM+RPR	-94	-70	-99	-87	-97	-86

Except for acidity ($\text{mg CaCO}_3 \text{ kg}^{-1}$), the units are in mg kg^{-1} .

7.4 Conclusions

Topsoil and bactericide ProMac were found effective in the amelioration of low pH conditions in pyritic pitwall rock from Martha mine. Placement of 50 mm thick topsoil layer on a 80 mm depth pitwall rock column effectively reduced leachate SO_4^{2-} (74%), acidity (47%), Fe (69%) and Al (70%).

Significant reduction in SO_4^{2-} (47%) and acidity (81%) in leachate from ProMac treated columns indicated evidence of possible inhibition of acid generation from biochemical oxidation by *Thiobacillus ferrooxidans* had occurred. Use of topsoil in combination with ProMac further improved the leachate quality.

Irrespective of amendments, the leachate pH remained very low (<2.5) throughout the 12 weeks period of the leaching cycle. Such a low pH leachate is responsible for mobilising soluble Fe, Mn, and different forms of Al in the pore solution. Incorporation of neutralising materials (LST, FBA and RPR) in combination with topsoil or ProMac resulted in an overall efficiency but did not result in significant rise in the leachate pH

Topsoil cover had no significant effect on the pH of the pitwall rock material but the bactericide ProMac significantly raised the pH > 3.5, resulting in the possible inhibition of bacterial oxidation of pyrite. Incorporation of neutralising materials in combination with topsoil and ProMac significantly raised the column section pH.

Limestone incorporation in the pitwall rock material with either topsoil or ProMac created the most favourable increase in pH (5.2-7.3) while combination with RPR did not raise the pH above 4.5. The ProMac + FBA combination raised the pH above 8, thereby creating a highly alkaline pitwall rock material, whereas ProMac + topsoil resulted in more favourable pH of about 6.8.

Conclusions from Chapters 4, 5 and 6 showed that with appropriate rates of application of neutralising materials, the pitwall rock can be modified to create a pH environment suitable for plant growth. Results of this chapter indicated that topsoil and ProMac could also be used as suitable amendments. For plant growth to establish, suitable growing media must be placed on top of the modified pitwall rock material. Partially

oxidised pyritic pitwall on steep slopes is difficult to revegetate mainly because amendments have low residence time and lack of sufficient cover material depth for plant establishment. Provided the pitwall slope gradient is engineered for stable placement of minimum depth of topsoil, revegetation of the pitwall may be achieved with suitable amendments. The results of this study must be however, be tested with plant growth trials in glasshouse and under *in situ* field conditions. Developments of site-specific combinations of treatment measures are required for successful revegetation of the pyritic pitwall materials on engineered pit slopes. In the case of pitwalls, engineered slope configuration modification is a requirement for stabilised placement of materials. A section of the micro-bench depicting a likely scenario for amendment of the pitwall rock cover material is shown in Figure 7.8. Suitable amendment materials can however, be placed on current pit bench for establishment of wide canopy native plants that can serve the purpose of aesthetic requirement of revegetating the pitwall in general.

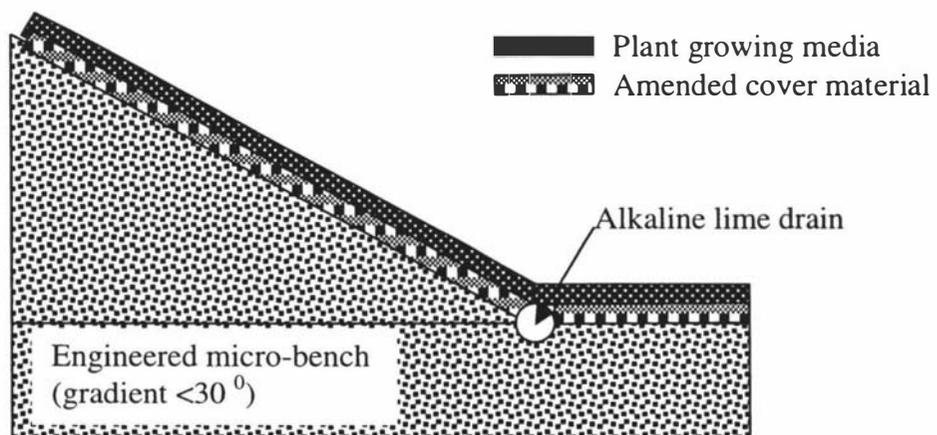


Figure 7.8 A conceptual scenario of micro-bench amendment on pyritic pitwalls at Martha mine.

Chapter 8

Summary and Conclusions

8.1 Background

Mining is a disruptive activity, especially so when it involves open-pit mining methods. Pyritic pitwalls are dynamic environments where steep slope gradients facilitate rapid weathering and erosion, resulting in continued exposure and oxidation of pyrite and migration of acid mine drainage (AMD). Approximately 25% of the current pitwall area at Martha mine (Waihi) contains pyritic host rock undergoing varying degrees of oxidation and weathering processes. Acid generation from oxidation of pyrite exposed on parts of the pitwall has created a highly acidic pitwall rock material with serious limitations to plant growth. Under the current mining licence, revegetation of the upper pitwalls is a requirement primarily for aesthetic reason as well as to prevent erosion. The primary objective of this thesis was to characterise the factors limiting plant growth on pyritic pitwalls and to investigate the ameliorating effectiveness of some selected amendments.

8.2 Literature Review

Acid mine drainage (AMD) from abandoned and active mine sites is a major environmental problem facing the mining industry. AMD occurs when sulphide minerals such as pyrite are exposed and undergoes biochemical oxidation, resulting in the generation of acidic effluent typically characterised by low pH and high levels of dissolved heavy metal. Pyrite oxidation and its oxidation by-products are as much environmental problem as AMD itself.

The ability to predict acid generation from mine waste materials is an important step in preventing AMD. Predictive tests specifically designed for coal mine waste have been used for decades and significant advances in predictive techniques applied to hard rock metal mine waste have been made in the last 5 to 10 years. Geochemical static and kinetic tests form the most commonly used techniques currently used for prediction of acid generation from mine waste rock materials. The objective of the geochemical tests is to provide data on the acid generating potential of sulphidic mine waste materials so

that control and treatment of AMD could be incorporated in environmentally safe management and reclamation of mine sites. Current predictive techniques are however, still in developing stages and subject to queries about their accuracy in predicting real situation AMD conditions. Because of variability in the ore types, these tests are currently accepted only on site specific basis. Even then, with increasing worldwide focus on environmental issues, the geochemical static and kinetic tests have become a mandatory requirement of regulatory guidelines in mining industry.

Lime requirements for acidic mine waste materials are commonly determined from standard acid base accounting (ABA) procedures rather than from conventional pH buffer methods used for agricultural soils. The liming rate assessed from ABA analysis, however, is found to vary considerably and does not always bring the expected results in long-term neutralisation of acidity and prevention of mobilisation of heavy metals. Site specific variations in the mine waste materials and continued generation of acid from sulphide mineral oxidation have made it difficult to standardise lime requirement to sustain long-term neutralisation. Large amounts of liming materials are therefore, commonly used to treat AMD and in the reclamation of mine waste.

The acid produced from pyrite oxidation is neutralised, *in-situ*, by dissolution of basic minerals if in contact with the migrating AMD. This neutralisation process is the basis for developing many of the current treatment strategies to mitigate AMD problems in mine wastes and reclamation sites. Alkaline addition to acid producing sites during surface mining and reclamation has shown variable success in ameliorating low pH conditions. Several studies have been conducted on the efficacy of alkaline amendments to ameliorate acidity problems in reclaimed coal mine sites. The effectiveness of alkaline materials in ameliorating low pH conditions is however, a topical issue amongst researchers investigating cost-effective means of treating AMD problems.

Various physical, chemical and biological control measures have been used to prevent, minimise and treat AMD. Methods attempted for the prevention and control of AMD generation include treatment of sulphide surfaces via the formation of inert surface "coatings", soil cover, subaqueous burial, bactericide treatment and segregation of sulphidic waste fraction. Neutralisation with liming agents and precipitation of metals as

hydroxides is currently an effective method for treating AMD generated from coal refuse, waste rock heaps and tailings ponds.

Reclamation and revegetation of sulphidic mine waste rock materials contaminated by AMD conditions have become a challenging practical problem for mining industries worldwide. Several studies on the prevention and treatment of AMD have been mainly directed towards improving the effluent drainage quality of the mine wastes. Long-term preventative measures and effective treatment prescriptions adapted to site-specific criteria have been recognised as viable options for mitigating low pH environment created by AMD. Many of the currently practised remediation measures are therefore, learning curves for the mine operators and “reclaimers” alike.

Open pit mining can expose very large areas of sulphide-bearing rock to air and water. Although mine pitwalls are recognised as one of the major sources of AMD, no detailed studies on the characterisation and reclamation of pitwall rock *in situ* materials were cited.

8.3 Characterisation of the Pyritic Pitwall Rock

Pyritic pitwall rock at the Martha mine is a significant source of AMD and metal contaminants. Acid generation from oxidation of pyrite has created hot spots of low pH / high acidity microenvironments with elevated levels of Fe, SO_4^{2-} , Mn, Al and soluble salts. Low pH conditions in parts of the pitwall rock exposed on the north face pitwall of Martha mine has been recognised as a major limitation to revegetation. Steep slope, thin cover material distribution and a high erosion index are some of physical characteristics restricting plant establishment. Progressive weathering of the pyritic pitwall rock has accelerated the acid generation process by rapidly liberating pyrite grains from the host rock.

Petrography and mineralogy of the pitwall rock indicated that the weathered cover materials contained localised concentrates of pyrite as a result of a “panning” effect from weathering. Completely weathered samples contained <5% pyrite compared with >10% pyrite in fresh to moderately weathered rocks. With progressive weathering, the reduction in rock grain-size resulted in only moderate liberation of the pyrite grains.

Completely weathered samples contained about 2.5% gypsum, indicating that salt precipitation is a common phenomenon during weathering of pyritic pitwall rock under dry environmental conditions.

Weathering and biological oxidation has resulted in the deformation of pyrite crystals as reflected in the range of grain shapes and etches pits. SEM/EDS examinations showed that the sulphide mineral in the fresh rock is dominantly pyrite with minor calcite vein mineral. Liberated pyrite grains showed moderate degree of roundness due to weathering. Possible evidence of bacterial activity was indicated by characteristic etch pit on some pyrite grains. XRD analysis of the rock samples indicated that the fresh rocks contained up to 12% by weight CaCO_3 . Pyrite content was greater in the rocks containing both vein as well as disseminated pyrite mineralisation.

Acid base accounting (ABA) analysis indicated that, irrespective of the degree of weathering, the pitwall rock showed a positive net acid producing potential (NAPP) and that the NAPP values were proportional to the amount of pyrite contained in the representative samples. Although pyrite grains and veins that are directly exposed undergo rapid oxidation to produce a very low pH in weathered pitwall rock, a significant amount of disseminated pyrite grains will not be immediately oxidised in the host rock and will form an unoxidised pyrite concentrate as weathering progresses. Even with an advanced degree of weathering and oxidation, fine-grained pyrite crystals may remain 'entombed' in coarse-grained fractions of the pitwall rock and may thus eventually produce acid. A completely weathered pyritic rock will therefore, still have the potential to generate acidity.

Kinetic NAG test indicated that the pitwall rock materials are potentially acid generating types, as indicated by their $\text{NAGpH} < 3$. Samples containing pyrite lenses as well as disseminated crystals that are undergoing a moderate degree of weathering had potential to produce higher acidity than samples with disseminated pyrite crystals alone. Based on kinetic test results, the fresh pyritic pitwall rock had a "lag-period" of approximately 22 weeks before the onset of acid generation from pyrite oxidation. However, this lag period is likely to vary under site-specific conditions.

Chemical characteristics of the pitwall rock showed that, with progressive weathering and oxidation, there were gross chemical changes in the composition of the rocks. While the freshly weathered pitwall rock had a near neutral pH of 7, the completely weathered rock sample had a mean pH of 2.3 and $EC > 2 \text{ dS m}^{-1}$ as a result of accumulated salts. There was a general increase in SO_4^{2-} , soluble Fe, Mn and Al from fresh to weathered pitwall rock. Soluble Fe and SO_4^{2-} in the samples ranged from as low as 477 mg kg^{-1} and 460 mg kg^{-1} to 4055 mg kg^{-1} and 7440 mg kg^{-1} from fresh to weathered pitwall rock, respectively. Both exchangeable Al and soluble Al increased from fresh to weathered rock samples due to increasing solubility with higher acidity.

A 60 cm depth profile of the weathered pitwall rock material indicated no variation with depth in pH, EC, SO_4^{2-} , Al and Mn. In terms of plant growth potential of the weathered pitwall rocks, it is evident that high acidity, soluble salts and Al remained at toxic levels even up to 60 cm depth and may persist to greater depths. Coarse texture and high porosity of the weathered rock material facilitate diffusion of moisture and oxygen through to greater depth to facilitate biochemical and abiotic pyrite oxidation and hence acid generation. This characteristic of the weathered pitwall rock has important implications to remediation measures for revegetation. Any amendments for amelioration of low pH conditions in the pitwall rock must take into consideration the additional acid generated at depth, especially in the selection of suitable plant species to be grown under such acidic conditions.

Geochemical analysis of the pitwall rock showed that weathered materials generally had higher SiO_2 contents whereas Fe_2O_3 was highest (6%) in the fresh rock. An anomalously high K_2O content in moderately weathered pitwall rock is considered to be residual incorporation of K in the formation of clay minerals and possible re-precipitation of alunite and jarosite under low pH and dry conditions. The trace element compositions of the pitwall rock indicated a nearly two-fold increase in Ba in weathered samples indicating possible immobilisation by SO_4^{2-} to form BaSO_4 . Arsenic increased with progressive weathering from 2 mg kg^{-1} in fresh rock to 10 mg kg^{-1} in completely weathered rock indicating that it has probably accumulated in the weathered rocks as insoluble metal complexes under low pH high Eh condition.

Spatial characterisation indicated that the pitwall is a dynamic environment undergoing progressive weathering and oxidation of pyrite. There was a strong spatial relationship in the distribution of pyrite oxidation products in the weathered pitwall rock over an area of 1200 m². Cover material and moisture content were both associated with the spatial distribution of pyrite oxidation products in the pitwall. The distribution of the weathered pitwall rock material primarily controlled the spatial variations in pH, EC, SO₄²⁻, acidity, Fe, Mn, Al, Ca, Mg, K and Na in pitwall area in this study. Variations in the distributions of metals, salts and cations indicated that the pitwall contained highly variable micro-environments, largely controlled by the distribution of pyrite and degree of liberation of pyrite grains during weathering of the pitwall rock.

Physical constraints such as steep slopes, insufficient weathered covered material, high macroporosity, low moisture content and lack of textural development are going to be major physical limitations to plant growth potential of the pitwall rock. Both H⁺ and Al³⁺ species as well as a significant amount of reserve acidity must be chemically modified with suitable amendments prior to emplacement of growing media on the pitwall surface.

8.4 Lime Requirements of the Pitwall Rock

In a highly acidic pyritic pitwall rock materials containing high levels of Fe, Al, SO₄ and soluble salts, the lime requirement assessed from standard buffer methods grossly underestimates the actual lime requirement of the pitwall rock. Both the buffer exerted by Fe-Al-hydroxides and potential acidity of the pitwall rock contribute significantly to the neutralisation requirement of the pitwall rock. The total lime requirement of the pitwall rock must take into account both active acidity and the potential acidity from complete oxidation of pyrite present in the pitwall rock.

Neutralisation of acid pitwall rock to the often recommended pH value of 6.0 will require very large amounts of alkaline materials because of the high buffer capacity exerted by Fe and Al hydroxide precipitates. Neutralising material particle size had a marked effect on reactivity and neutralisation of acidity. Coarse grained neutralising material was ineffective in significantly raising the pitwall rock pH due to an armouring effect of metal hydroxide and sulphate salt coatings. Whereas, fine grained neutralising

materials provided an immediate neutralisation of the active. There is a possibility though that once reacidification occurs, the hydroxide coating may redissolve to neutralisation source once again. The possibility of providing long-term slow release neutralisation of acidity by coarse grained neutralising materials in pitwall rock seem feasible. An incubation assessment of the neutralising effects of selected alkaline materials indicated that LST, DOL and FBA were equally effective in overcoming the large buffer exerted by Fe and Al hydroxides to raise pH to 6.0. RPR did not raise the pH above 4.2 even at the highest C_{ER} of 50 kg $\text{CaCO}_3 \text{ t}^{-1}$.

8.5 Ameliorating Effectiveness of Selected Amendments

Both broadcasted and incorporated methods of application of neutralising material amendments had no significant effect on the leachate pH, which remained below 2.5 throughout the 12 weeks period of leaching. The consistently low leachate pH from the neutralising material amended pitwall rock suggested that the alkalinity released from dissolution of neutralising materials was ineffective in ameliorating subsurface pH. At subsurface depths, both bacterially catalysed generation of acid and the acid stored as hydronium sulphate salts such as jarosite are likely to influence the effluent characteristics irrespective of amendment at the surface.

Despite low pH effluent, there was significant reduction in acidity in the upper 60 mm section of the columns amended with LST, DOL and FBA. This indicated that under the leaching conditions of this experiment, there was significant amelioration of subsurface acidity by neutralising materials despite generation of very low pH leachate. Continued release of acidity in the leachate from neutralising material amended columns indicated that the dissolution and downward migration of alkaline front was restricted by the large buffer exerted by the hydrolysis of Fe, Mn and Al.

There was however, a significant increase in the base saturation of the pitwall rock amended with neutralising materials. Downward migration of Mg and K and Na was evident in FBA and DOL broadcasted columns but Ca remained immobilised in the 0-40 mm section of the column. High Mg concentrations were observed only in the DOL amended columns.

Incorporation of neutralising materials to 0-50 mm depth had significantly reduced the distribution of EC, SO_4^{2-} , acidity, Fe, Mn and Al concentrations in the upper 80 mm section of the pitwall rock column. There were no differences in SO_4^{2-} release rates for the broadcasted and incorporated columns but acidity of the leachate from incorporated columns was consistently lower. The Mg level in the leachate from incorporated columns was generally two-fold higher than in the leachate from broadcasted columns.

Of the four types of neutralising materials used, LST provided the best circumneutral pH range suitable for plant growth. RPR was ineffective in raising the pH of the pitwall rock material above 4.5 while FBA created highly alkaline conditions as well as forming cementitious material, both of which make it an unsuitable candidate for ameliorating low pH pyritic rock. On the other hand, the cement forming properties of the FBA can be utilised to stabilise the cover materials on the pitwalls as well as to provide infiltration barriers against runoff water.

Placement of topsoil cover significantly lowered metal levels in the leachate and immobilised most of the soluble aluminium in the partially pitwall rock. The bactericide ProMac applied at a rate of 0.5 kg t^{-1} resulted in the leachate pH increase of 1 unit from control value of 2.5. A significant reduction in SO_4 , Fe, Mn and Al was associated with this change. ProMac seemed to buffer pH at slightly above 3.5 but whether this increase is as a result of inhibition of bacterial oxidation of pyrite, remains questionable.

It is evident from this study that slope factor and high acidity condition are the two main constraints limiting plant growth potential of the pitwall rock. However, pH modification with suitable amendments seems a viable option for creating growth a medium conducive to plant growth provided the slope is engineered to gradients suitable for stabilised placement of amendment materials. The effectiveness of amendment materials in ameliorating low pH conditions on the pitwall will largely depend on the prescriptive combination rather than their acid-neutralising capacity. The success of effective neutralisation of acid will ofcourse, ultimately depend on the assessment of the amendment materials under field conditions, although in active mine pitwalls this may be limited by ever extending mine wall. In such a case, one of the best

options may be to leave the pitwall materials to fully oxidise naturally prior to implementation of reclamation measures.

8.6 Future Directions

This thesis discussed the physical and chemical characteristics of the pitwall rock and its intrinsic hostile nature to plant growth. Whilst laboratory and glasshouse experiments explored the possibility of ameliorating the low pH conditions in the pitwall, field testing of the findings is imperative in validating the results under *in situ* conditions.

Whilst revegetation of the pyritic pitwall area is limited by the steep slope and rapid acid generation, several options are open for future research directions. These include:

- Bioengineering of part or all of the pitwall for slope stabilisation and erosion control.
- Field plant growth trial with a combination of amendments on the lower section of the pitwall containing maximum thickness of weathered materials.
- Use of FBA slurry to stabilise the cover materials.
- Grouting the pitwall with alkaline rods to provide continual source of *in-situ* neutralisation.
- Revegetation of pit bench with large canopy native species to provide screening effect to the exposed pitwall.
- Placement of moveable “biomats” on which vegetation could be established.
- Use of acid tolerant creeper plants and grass species.
- Retardation of acid generation by injecting slow release bactericide pellets
- Engineered micro-benches or micro-trenches to hold plant growing media
- It is evident from the characterisation part of this research that acid generation on the pitwall materials is rapid under accelerated weathering conditions. A likely option is therefore to promote oxidation of the pitwall until reasonable depth of surface materials is completely oxidised. The kinetics of pitwall weathering and temporal variations in oxidation processes offers an important area of research.

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