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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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A b s t r a c t

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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