## CHAPTER 1 : INTRODUCTION

### 1.1 Introduction

Bougainville Copper Limited (BCL) operates a large open-cut porphyry copper mine at Panguna, Bougainville Island, Papua New Guinea. The mine is situated at the headwaters of the Kawerong/Jaba river system at an altitude of 670 metres in the Crown Prince Range. It receives a mean annual rainfall of 4,400 millimetres and it is surrounded by rugged, steep sided, ridges and valleys. The natural vegetation ranges from high montane rainforest at the mine site to lowland swamp in the lower Jaba river system.

The principle environmental disturbance resulting from the mining operation is the disposal of waste rock and tailings. Approximately 100,000 tonnes of waste rock are disposed of per day by end-dumping into the sides of the upper Kawerong valley and approximately 130,000 tonnes of tailings are disposed of per day by piping into the upper Kawerong River at the toe of the waste dumps. Fifty to 60% of the tailings are deposited along the 35 kilometres of the Kawerong/Jaba River system, with the remainder being carried to Empress Augusta Bay on the west coast of Bougainville where a large marine delta is forming.

Under agreements held with the Papua New Guinea Government, BCL is required to investigate methods of revegetating the mine wastes (tailings and waste rock), to ensure that all waste dumps are left with a surface that will facilitate rapid revegetation, and where practicable, to encourage the establishment of vegetation. It is company policy to revegetate all finished waste dump surfaces. As well as being a legal requirement, revegetation of the mine wastes is important for ecological and aesthetic reasons. The ability to predict that a sustainable vegetative cover can be achieved on the mine wastes is also necessary so that future land use options can be formulated and planned for.

The nature of the mining operation by BCL is such that three They are waste main types of material require revegetation. rock, freely draining tailings and water-saturated tailings. Waste rock is merely fractured rock from the pit. Copper mineralisation in the waste rock is not significant enough to warrant extraction. Tailings are ground ore from which most of the copper (and to a lesser extent gold and silver) minerals have been removed. The majority of the tailings requiring revegetation are deposited either in the river system or in the delta that is forming at the mouth of the river in Empress Augusta Bay. These deposits are currently water saturated. Tailings that are deposited by floods on the banks of the river system or that have been dredged from the river system, are freely draining. Freely draining tailings and the waste rock become acid as a result of pyrite (sulphide mineral) oxidation.

The mine waste disposal system at Bougainville Copper is dynamic, with waste dumps being continually overdumped. The dynamic system, lack of available flat (storage) land and the very high rainfall experienced at the mine site, have meant that storage and re-use of topsoil for revegetation is not practical or ecomonic. It is therefore necessary to sow directly into the waste material.

Historically there has been little successful revegetation of Bougainville mine wastes. This has been for two main reasons. Firstly, the dynamic nature of the waste disposal system has meant that there have been few stable areas available for revegetation, and secondly, there has been a poor understanding of the limitations of the mine wastes as a media for plant growth.

Climatically Bougainville is suited to plant growth. The climate is typical of the humid tropics, with high and regular rainfall and high temperatures. There is little variation in climate with season. Extremes of temperature are rare.

Physically the mine wastes are coarse and they have a low cation exchange capacity. However, they contain sufficient material in the silt and fine sand size fractions to make them suitable as a rooting media for plants. Moisture stress is not common due to the high and frequent rainfall. Revegetation studies have therefore focused on plant nutrition.

From a plant nutritional point of view, the ability of the mine wastes to support plant growth depends upon their mineral content and their ability to release and retain essential nutrients in a plant available form. The acidification potential of the mine wastes raises the question of nutrient toxicities.

A waste's ability to support plant growth is site specific. This is due to the unique geological and climatic conditions experienced at each mine site, as well as the diverse ore treatment and wastes disposal systems. As such, site specific research is generally required.

## 1.2 Study Objectives

The specific aims of this study were -

- . to determine the ability of the porphyry copper mine wastes at Bougainville to supply nutrients for plant establishment and growth.
- to assess the ability of the mine wastes to retain plant nutrients that have been either released from mineral weathering, or added in fertilisers, when the wastes are subjected to a humid tropical climate.

. to determine the major nutrient limitations of the mine wastes to plant establishment and growth, and to prescribe means of overcoming the limitations.

# 1.3 Structure of the Thesis

The thesis is divided into seven chapters, each chapter outlining an integral part of the study.

Chapter 1 contains the introduction and study objectives. Chapter 2 provides background information on the mining operation at Bougainville Copper and Chapter 3 provides information on plant nutritional problems likely to be encountered in revegetating mineral (acid) soils in the humid tropics.

Chapters 4, 5 and 6 describe the research undertaken. Chapter 4 explains soil testing and a lysimeter leaching experiment used to outline likely plant nutritional problems. Chapters 5 and 6 describe pot and field trials used to investigate specific nutrient limitations and to suggest means of overcoming them.

Chapter 7 contains a general discussion and conclusions from the study programme and prescribes methods for establishing vegetation on the mine wastes.

## CHAPTER 2: THE BOUGAINVILLE COPPER ENVIRONMENT

## 2.1 Introduction

The ability of mine wastes to supply plant nutrients depends upon a number of factors including their geology, the climate, the milling and benefaction processes and the waste disposal technique. These factors are site specific.

## 2.2 Bougainville Island, Geography and Climate

Bougainville Island lies between latitude  $5^{\circ}$ S and  $7^{\circ}$ S in the Western Pacific Ocean and to the east of the New Guinea mainland at longitude  $155^{\circ}$ E. Bougainville and Buka Islands (Bougainville) form a single land mass separated from one another by a shallow channel one half to one kilometer wide (Figure 2.1). They form the northern end of the Solomon Islands archipelago.

Bougainville is 240 km long and 64 km wide at the widest part and it has a land area of approximately 9000 km<sup>2</sup>. It is an uplifted Cainozoic succession of volcanic rocks and limestone which is dominated by three clusters of volcanic cones peaking at 2600, 2300 and 1750m respectively. The latter is the still active volcano Mt. Bagana. Much of the land area consists of hills or mountains with steep to precipitous ridges and valley sides. The major plains have formed from volcanic material distributed by rivers or from an ancient plateau of uplifted coral limestone. The plains have high gradients, especially at the higher altitudes. Their seaward margins are subject to flooding and they frequently terminate in swamps.

The climate on Bougainville is wet tropical to tropical and varies little with season. Mean annual temperature at sea level (Loloho) is approximately 27.3°C with an average maximum of 30.8°C and an average minimum of 23.6°C. Variation in monthly means is only one to two degrees and the average diurnal range is approximately 10°C. Temperatures decrease with altitude with the average daily temperature at the Panguna mine site (altitude 640m) being 23.3°C. Cloudiness increases with altitude with the mean daily sunshine hours at the coast (Loloho) and Panguna being 4.9 and 3.6 hours respectively (BCL Hydrological Records, 1983).

Bougainville is affected by two principal wind systems. A variable set from the north-west, which occurs between December and April and a stronger, more continual set from the southeast which prevails from May to December.

Average rainfall at sea level is higher in the south than in the north and may be affected by regional topographical features. Rainfall tends to increase with elevation. The northFIGURE 2.1 : BOUGAINVILLE AND BUKA ISLANDS.



westerly winds distribute approximately the same rainfall over all of Bougainville. The south-easterly winds deposit more rainfall on the slopes of the southern mountains. Average rainfall at Loloho and Panguna is 2910 and 4386mm respectively (BCL Hydrological Records).

Relative humidity is constantly high at approximately 80% and evapotranspiration rarely exceeds precipitation. Mean annual evaporation at Loloho and Panguna is 1591 and 1105mm respectively (BCL Hydrological Records).

Landforms of Bougainville are diverse. They have been influenced by high rainfall and temperatures, with deeply incised streams and uniformly steep erosional hill slopes produced by intense weathering, landsliding and stream transport. Scott <u>et al</u>. (1967) delineate forty distinctive land systems on Bougainville, indicating the wide topographic and vegetative range.

Between 35 and 40% of the island is forested, with much of the usable timber unexplotied. Arable land is in short supply and the agricultural potential of much of the land has been reached. Subsistence agriculture is the mainstay of much of the indigenous population with some cash cropping and plantations on the coastal plains - mainly copra and cocoa.

Native vegetation generally varies with altitude (and therefore temperature). Three major environments have been distinguished. (Scott et al., 1967).

- Better drained lowlands from sea level to 600m, where conditions for tropical rainforest are approaching their optimum. <u>Vitex</u> - <u>Pometia</u> tall forest is regarded as the climax vegetation.
- Lower mountain environment from 600m to 1200m Garcinia
   Elaeocarpus mid-height forest is regarded as the climax vegetation.
- 3. Upper mountain environment above 1200m. It is shrouded in cloud for part of most days with <u>Gulubia</u> - <u>Pandanus</u> 'mossy forest' the climax vegetation.

The principal centres of population are at Kieta, Arawa and Panguna. Panguna is a company town situated at the mine site. Arawa was built in the early 1970's to accommodate employees of the mine, the local administration and business houses.

## 2.3 Bougainville Copper Limited

## 2.3.1 Company History

Conzinc Riotinto Australia (CRA) commenced exploration for Cu in the Panguna area in 1964. By 1969 the economic feasibility of the project had been established with proven reserves of 900 million tonnes of ore averaging 0.48% Cu and with small quantities of Au and Ag.

The mine was capitalised at just under \$A400 million and it went into operation in 1972. BCL is incorporated in PNG, has its headquarters at Panguna and is owned 53.6% by CRA, 20.2% by the PNG Government and 26.2% by public shareholders.

2.3.2 Mode of Operation

Bougainville Copper Limited operates an open-pit mine. Low grade ore requires the processing of large tonnages to achieve appropriate economies of scale.

Treatment of the ore begins with crushing to a size suitable for ball mill feed, where the ore is ground to fine sand consistency. From the ball mills the ground ore is passed to a flotation stage where it is agitated in water containing reagents. Low pressure air is added and the Cu, Au and Ag minerals are 'floated' and collected. The concentrate containing 30% Cu is thickened and piped across the Crown Prince Range to the BCL port at Loloho. At the port the concentrate is dried to 8% moisture content and stored prior to shipping.

From mine start up until the end of 1982, concentrate containing 1.9 million tonnes of Cu, 205 tonnes of Au and 475 tonnes of Ag has been produced. This represents a monetary value of \$A3.5 billion and 50% of PNG's exports. Also during this period contributions to the PNG Government from dividends, taxes and royalties have totalled \$A730 million which represents 20% of the internally generated Government revenue. The Bougainville workforce consists of approximately 4000 people of which 80% are PNG citizens.

2.3.3 Environmental Impacts

Thirteen thousand two hundred ha of land were acquired by BCL under mining leases and tenements for the mine site, tailings disposal, port-mine access road, the port and the townships of Arawa and Panguna. Land affected included portions of five principal land systems, the most significant being the Pirurari, Silibai and Moila (Scott <u>et al.</u>, 1967) through which run the Kawerong/Jaba river system. Significantly, each of the land systems is well represented elsewhere on the island and only a very small proportion of each land system is directly effected by the mining operation. Land alienated ranges from garden, cash crop and plantation land, through precipitous, densely forested mountain slopes to lowland riverine swamps.

Mine construction necessitated the relocation of 10 village communities and the payment of various forms of compensation to affected landowners. Construction of the port-mine access road, port and the town of Arawa resulted in considerable physical disturbance from civil engineering activities. For the mine, concentrator and the township of Panguna, 220 ha of tropical rainforest were cleared and up to 60 m of volcanic ash and overburden removed before commencement of construction and mining.

The principal environmental disturbance from the mining operation results from the disposal of waste rock and tailings. Current rates of disposal are approximately 100,000 tonnes of waste rock per day and 130,000 tonnes of tailings per day. Waste rock is disposed of by end dumping into the sides of the Kawerong valley. Tailings are piped into the upper Kawerong river below the toe of the waste dumps. Sixty percent of the tailings remain along the 35 km of the river system or are deposited on land and the remainder are deposited in Empress Augusta Bay on the west coast of Bougainville where a large marine delta is forming. For reference purposes the river is divided into 35 cross-sections (XS), each approximately one km apart (Figure 2.2).

At the end of currently planned mine life in 2003 there will be some 450 ha of waste rock and between 3,000 and 10,000 ha of tailings, depending upon future tailings disposal methods.

2.3.4 Policy/Requirements Regarding Revegetation

The Bougainville Copper Act (1969), as amended in 1973, the Agreement for Disposal of Waste Rock, Fine Overburden and Tailings (1971) and the Lease for Mining Purposes for the Disposal of Tailings, set out the legal requirements for revegetation. Essentially these agreements require the company to establish the agricultural suitability of tailings, to leave all dump surfaces in such a way as to facilitate early regeneration of vegetation and where practicable to revegetate finished surfaces and to control erosion.

It is company policy to revegetate all finished dumps and all other areas that are disturbed during the day to day mining operation.

#### 2.4 The Mine Wastes

2.4.1 Geology of the Mine Wastes

The Bougainville ore body is typical of porphyry Cu deposits. Pliocene Cu-bearing intrusions have invaded an older Oligocene to Miocene volcanic sequence. Radiometric age determination places the intrusions at 4 to 5 million years old and the mineralisation at 3.4 million years old (Page and McDougall, 1972). The intrusions range in composition from quartz diorite through to granodiorite. Copper has diffused outwards from these into andesite wall rock of the volcanic system, the degree of diffusion marking the boundary of the ore zone. There are seven ore types.



The principal economic mineral is chalcopyrite with bornite present in minor amounts. The sulphide ore is capped with an oxide zone up to 80m thick with malachite and cuprite the common oxides. In some areas chalcocite occurs between the oxide and sulphide zones. Gold and Ag occur in all rock types and some molybdenite is associated with Cu mineralisation. Pyrite forms an aureole around the main centre of mineralisation and some magnetite is present. Grades in excess of 0.3% Cu are associated with well developed vein-type mineralisations. Hypogene mineralisation forms a zonal pattern with strong relationships between silicate and sulphide assemblages that are independent of rock type (Ford, 1973).

2.4.2 Chemical Properties of the Mine Wastes

Mine wastes produced by BCL are of two types; waste rock and tailings. Small amounts of weathered overburden are enclosed in pockets of waste rock.

The seven major rock types present in the ore body can vary significantly in mineralisation and gangue mineral content. Of the four principal rock types that end up as waste rock, the feldspar content can vary from between 20 and 50% (Taimre, 1979), and the total P concentration can range from 0.04 to 0.10%, Ca from 1.3 to 3.9%, Mg from 0.63 to 3.20% and K from 1.5 to 2.3% (Ford, 1973). Sulphide content, and hence the potential for acidification, is also variable. It ranges from less than 0.1 to 0.5%. The result is a heterogeneous subtrate that can make sampling and interpretation of analyses difficult.

Tailings are generally more homeogeneous than waste rock because of mixing in the grinding and flotation circuit and in the river system. A composite analysis for total elements in tailings released in 1982 is presented in Table 2.1. It shows that there are significant quantities of the essential plant nutrients P, Ca, Mg and K in the wastes. However, these nutrients occur essentially as primary minerals, especially feldspars and micas which occur in abundance in the host rocks. The roots and associated mycorrhiza of some plants may be able to weather some of these nutrients from the wastes. There is unlikely to be any amorphous mineral in the freshly mined wastes.

From the total analyses there is nothing to suggest that revegetation cannot be carried out provided that sound agricultural practices are used. The sulphide content of the tailings raises the likelihood of acid generation which could result in nutrient imbalances or toxicities if not corrected. The lack of organic matter suggests that N addition will be essential.

TABLE 2.1:	TYPICAL ANALYSIS OF TAILINGS :	TOTAL CONCENTRATION
	OF ROUTINELY ANALYSED ELEMENTS.	*

ELEMENT	<b>%</b> (ppm)	ELEMENT	% (ppm)
$P_{2}O_{5}$	0.21	Cd	<0.5 ppm
K20	2.33	Ag	0.00004
CaO	3.62	Se	0.002
MgO	3.12	As	0.0004
$Na_2O$	4.12	Со	0.002
$A1_{2}0_{3}$	14.9	$Cr_2O_3$	0.020
Mn	0.050	TiÕ <sub>2</sub> õ	0.57
Cu	0.089	C1	0.061
Fe	6.4	SiO <sub>2</sub>	61.4
Zn	0.008	F	0.076
Мо	0.003	<b>v</b> <sub>2</sub> o <sub>5</sub>	0.026
Bi	0.002	SrO	0.42
Pb	0.001	BaO	0.030
Au	0.000020	Hg	0.02 ppm
Те	0.001	S	0.51
Sb	<0.001		

\* Average of quarterly composite analyses for year 1982; using instrumental and wet analyses techniques for complete element. A composite waste rock sample would contain higher concentrations of Cu, Fe, S, Au and Ag and lower concentrations of CaO. The concentrations of other elements would be similar. 2.4.3 Physical Properties of the Mine Wastes

Waste rock is coarse with large average particle size. Some finer material results from the blasting, trafficing and handling operations. Approximately 20% of the material is less than 2mm in diameter, of which the majority is greater than 50 micron. The remainder varies greatly in size and individual rocks may be up to 30 cm in diameter.

Particle size of tailings varies according to ore type and grinding technique. An approximate sizing is 30% sand, 45% fine sand and 25% silt and clay. The smaller size fractions are generally carried through the river system to the sea. As a result, in the upper river system, deposits are mostly sand and fine sand.

Bulk density of the mine wastes is variable and depends upon waste type and the degree of trafficing. Bulk densities of 1.15 to 1.25 gm/cm<sup>3</sup> were measured at Cross Section 29 (XS29) on tailings deposited by the river, while Hartley (1976), measured bulk densities between 1.44 and 1.52 gm/cm<sup>3</sup> for tailings dumped on land and worked with machinery. Bulk density of waste rock is difficult to measure. However, if there has been any degree of trafficing, ripping prior to revegetation would be mandatory.

Water holding capacity of tailings is low with generally less than 20% water filled pores at 0.2 bars suction (Marshman, 1980a). Although no measurements of the water holding capacity of waste rock have been carried out it would also be low. Moisture stress does not appear a problem due to the high and frequent rainfall experienced at the mine site.

Tailings deposits are highly susceptible to both gully and sheet erosion and for large deposits appropriately designed erosion control structures are essential. Waste rock is generally not susceptable to erosion if sound engineering practices are followed.

The physical properties of the mine wastes outlined are not major limitations to plant growth.

# 2.5 Early Revegetation Research - Items of Interest

Hartley (1976) reported growth responses to N, P and B fertiliser in early pot trials with fresh (alkaline) tailings and a range of plant species. Hartley (1976) also reported N, P and B responses for <u>Eucalpytus</u> <u>tereticornis</u> growing on alkaline tailings. He recommended monthly applications of fertiliser to be applied at the base of the trees.

Hartley (1976) carried out field trials with grasses and legumes on tailings. He encountered problems in plant establishment and maintaining nutrient levels in the tailings. He subsequently focused attention on the use of forest tree species. Following experiments with <u>E.</u> <u>tereticornis</u> he concluded that "trees can be used to pioneer growth on tailings provided there is a regulated supply of nutrients. Both placement and frequency of application are critical."

Later problems of tailings acidification became apparent. Hartley (1978) showed that after 16 months weathering, tailings at XS10 had acidified, with a decrease in exchangeable Ca and a shift to base unsaturation. Marshman (1980a) suggested that acid tailings deposits could prevent revegetation or kill existing stands (of vegetation). Marshman also showed that death and poor establishment of <u>Saccharum</u> (a native volunteer) at XS27 was associated with lowered sediment pH and that the decline of Saccharum at XS10 was associated with acification in the root In addition, both Hartley (1979) and Marshman (1980b) zone. showed that in lysimeter studies, tailings acidify through pyrite oxidation. Marshman (1980a) also found that lime could significantly increase growth and promote better root development of Albizzia sp. on tailings at XS10 (pH 5.4 to 8.9). Lysimeter studies and field monitoring have shown that the very acid phase of tailings weathering is short lived at one to three years. After this the pH rises slightly to between 5 and 5.5.

#### CHAPTER 3: LITERATURE REVIEW

## 3.1 Introduction

Revegetation is an ecologically desirable requirement of post-mining rehabilitation programmes and in many instances it is required by government regulation. Revegetation techniques employed are varied and site specific research is usually required to define and overcome the limitations to plant growth within each operation. For the Bougainville mine likely problem areas include the large volumes of wastes produced, acidification through residual pyrite oxidation, and deficiencies in organic matter, N, P and possibly K and micronutrients. Acidification may result in heavy metal toxicity and induced nutrient deficiencies.

The accepted way to overcome the nutrient limitations is to lime to an acceptable pH if acidity is a problem, and to correct nutrient deficiencies by the addition of fertilisers. These amelioration techniques are hindered in the humid tropics by the very high rainfall and the leaching of applied nutrients from the mineral substrate.

## 3.2 Mining Revegetation : An Overview

It is recognised in most western countries, and certainly in Australia, that resource exploitation must be environmentally acceptable and that land disturbed by mining must be rehabilitated.

Site stablisation and revegetation are the most important aspects of post mining rehabilitation programmes. In most cases the sole statutory requirement of a post mining rehabilitation programme is the establishment of a sustainable vegetative cover.

Vegetation is important in rehabilitation programmes for a number of reasons :

- . It aids site stabilisation through erosion control (USDA, 1974). Vegetation with its root system can physically hold soil together. The canopy can adsorb some of the destructive energy of raindrops, reduce the velocity and re-distribute the overland flow of water and it can reduce wind velocities and trap and hold wind and water borne soil particles.
- Vegetation can aid in noise suppression (Bradshaw and Chadwick, 1980).

- . A vegetated surface is generally perceived to be more aesthetically pleasing than a bare or concrete stablised surface and it is readily accepted by the community (Williamson and Johnson, 1981).
- Vegetation can remove some heavy metals from the environment through metal uptake and immobilisation in the rhizosphere (Hughes, 1981).
- Vegetation is generally the first step in the return of biological productivity to an area (Park, 1980).
- . Vegetated areas are generally more compatable with surrounding natural ecosystems (Bradshaw and Chadwick, 1980).

Difficulties encountered in revegetating mine wastes are numerous. The basic physical problems include temperature extremes, drought, poor drainage, wind scouring, over-compaction, slope instability and poor texture (Plass, 1978). Chemical difficulties include high alkalinity or acidity, acid generating potential, heavy metal toxicity, nutrient deficiencies and salinity. Fresh mine wastes are generally deficient in N, organic matter and P and, in many cases K (Plass, 1978).

The general approach to revegetating mine wastes is to define the limitations, apply amendments to modify the conditions that limit plant establishment and growth (Plass, 1978) and where possible use plant species adapted to that particular environment. (Hutchinson and Kuja, 1978; Bradshaw and Chadwick, 1980).

Physical amendments include covering wastes with topsoil or selected beneficial overburden (Hannan, 1979), regrading, contouring and ripping (Plass, 1978), irrigation and the use of various mulches (Bradshaw and Chadwick, 1980).

Chemical amendments include the correction of nutrient deficiencies through the use of fertilisers and the addition of acid or alkaline neutralisers (lime or acid and acid forming fertilisers; Bradshaw and Chadwick, 1980).

The selection of suitable plant species for a revegetation programme is important and will depend upon the final land-use objective and specific site features (Langkamp, 1978).

The general approach to revegetation is similar between mine sites. However, mining operations are diverse, with differences in product mined, geology, extraction and treatment processes, waste disposal and climate. As such, site specific research to define the limitations to revegetation and to develop amelioration techniques is necessary. 3.3 Porphyry Copper Mine Wastes : Their Nature and Likely Limitations

## 3.3.1 Introduction

The Bougainville mine is a porphyry Cu mine. Wyllie and Argall (1983) provide a definition of porphyry Cu -- "the word porphyry is a geological term ... the essential characteristics of the deposits that are universally, if not quite precisely designated as porphyry coppers are; their huge size, particularly with respect to horizontal dimensions; the relative uniformity with which the Cu minerals are disseminated throughout the mass; and the low average pound Cu content of mineable ore". Copper minerals in porphyry deposits are usually present as chalcopyrite, chalcosite and bornite. Chalcopyrite is generally associated with pyrite.

Processing of large quantities of material allows economies of scale to be realised so that low grades can be extracted economically. This is the general principle behind open-pit mining of porphyry Cu. The result has been the development of mining on a scale that a century ago would have been inconceivable (Bradshaw and Chadwick, 1980).

## 3.3.2 The Waste Products

Processing of large quantities of ore results in a co-committment production of large quantities of waste, the main types being overburden, waste rock and tailings.

Between 95 and 99% of the ore becomes waste as tailings after processing. Tailings generally consist of gangue minerals, rock fragments and ore minerals which have escaped the concentration process. They may also contain residual salts and reagents from processing.

In a comparison of tailings and soil parent materials, Rutherford and van Loon (1982) characterise tailings as being reasonably homogenous within a limited particle size range usually high in coarse silts and sand and low in clay-sized particles. The particle size distribution of fresh tailings will depend largely upon the milling process and the way in which they are disposed. Segregation before deposition can result in particle separation and deposits ranging in size fraction from sands to clays.

Fresh tailings lack any natural structure and are generally susceptable to dessication and to wind and water erosion. They are devoid of organic matter, microbiologically sterile, generally deficient in N, P, K and possibly other macro and micro nutrients and they are likely to develop an acid pH (Rutherford and van Loon, 1982). The separation process employed in modern sulphide (porphyry Cu) concentrators is essentially a physio-chemical change on the surface of the metal bearing mineral and is in contrast to metal processing plants (Creelman, 1975). With such metal extraction techniques, residual metal concentrations in tailings are generally quite low - often less than 0.1%. Subsequently residual metal toxicities are not a major problem unless wastes become very acid (Bradshaw and Chadwick, 1980).

Overburden usually consists of a heterogeneous mixture of topsoil, subsoil and partly weathered rock fragments. In some mines topsoil and subsoil are selectively handled for emplacement over completed waste dumps.

Waste rock is generally from the same parent material as the ore. Its metal content is sufficiently low so as not to warrant treatment. It is usually a heterogenous mixture of rock fragments with some sand, silt and clay fractions produced from blasting, handling and trafficking operations. The physical environment of waste rock dumps is generally harsher than that of tailings due to the larger average particle size. Metal toxicity problems may be greater for waste rock than for tailings as metal has not been removed by processing. Other characteristics are similar to those for tailings.

3.3.3 Pyrite Oxidation

Acid generated by pyrite (sulphide) oxidation is one of the most limiting factors to a successful revegetation programme on metalliferous mine wastes (Williamson and Johnson, 1981).

Oxidation of pyrite involves the release of H ions as sulphuric acid and ferric ions which are powerful chemical oxidants. Lowson (1983) suggested three possible pathways for pyrite oxidation; bacterial catalysis, sequential chemical reactions and electrochemical reactions.

I. Bacterial catalysis.

The role of micro-organisms can be that of production or regeneration of chemical reactants, or their catalytic influence can be exerted directly against the solid mineral substrate (Ralph, 1980). Reactions 1-3 depict oxidations which are catalysed by bacteria, while reactions 4-7 depict reactions reported to be directly affected by bacteria.

$4FeSO_4 + O_2 + 2H_2SO_4 > 2Fe_2(SO_4)_3 + 2H_2O$	1
$S_8 + 120_2 + 8H_20 > 8H_2SO_4$	2
$H_2 S + 20_2> H_2 SO_4$	3
$4FeS_2 + 150_2 + 2H_2O> 2Fe_2(SO_4)_3 + 2H_2SO_4$	4

 $4CuFeS_2 + 170_2 + 2H_2SO_4 ---> 4CuSO_4 + 2Fe_2(SO_4) + 2H_2O$  5

 $2Cu_2S + 0_2 + H_2SO_4 -----> 2CuS + 2CuSO_4 + 2H_2O$ 

 $CuS + 20_2 -----> CuSO_4$ 

Further, reaction 8 (7) can be regarded as typical of the direct attack mechanism of the bacterium <u>Thiobacillus</u> <u>ferro-oxidans</u> on divalent metal sulphides.

 $MS + 20_2 ----> MSO_4$ 

Bacterial oxidation is predominantly through the autotrophic <u>Thiobacillus</u> species (Ralph, 1980). They use pyrite as their energy source and excrete ferric iron, sulphate, or both.

At a low pH (3.5 to 2) ferric ions may undergo a complex series of precipitation reactions resulting in the formation of geothite and jarosite type minerals with further generation of H ions as depicted in reaction 9. A jarosite/ferric hydroxide couple has a very strong and persistent buffering effect on pH which can be important in the persistence of acidity generated by the oxidation of pyritic mine wastes (Ralph, 1980).

 $Fe^{3+}$  +  $3H_2O$  ----->  $Fe(OH)_3$  +  $3H^+$ 

II Sequential chemical reactions

There are three steps -

- . Oxidation of pyrite by molecular oxygen to sulphate and ferrous iron. There are no catalysts for this reaction and it increases non-linearly as the pH is increased from 1 to 10. Below pH 1 the rate is independent of pH.
- . Oxidation of ferrous iron by molecular oxygen to ferric iron. The reaction is first order with respect to oxygen partial pressure and below pH 2 is independent of pH. There are a number of catalysts to this reaction with the most active of the solution catalysts being cupric ions.
- . Oxidation of ferric iron by sulphate and ferrous iron; Some ferric iron precipitates as ferric hydroxide or jarosite as mentioned. It is a heterogenous surface reaction with poorly defined kinetics (Lowson, 1983).

III Electrochemical

The electrochemical pathway is the summation of two half cell reactions, one for the cathode;

 $0_{2} + 4H^{+} + 4e^{-} - - - - > 2H_{2}O$ 

and one for the anode;

8

6

7

 $FeS_2 + H_2O -----> Fe^{3+} + 2SO_4^{2-} + 16H^+ + 15e^-$ 

Pyrite does not undergo non-oxidative dissolution. The open circuit potential is a function of oxygen concentration and media anion. There is a Nernstian relationship for the open circuit potential of pyrite with pH and with the ferric/ferrous redox couple. The anodic reaction has an associated side reaction with S as a product but it is poorly understood (Lowson, 1983).

The nature and amount of acid generated from mine wastes is affected by a complex interaction of geochemical, thermal, climatic, hydraulic and mechanical properties (Miller, <u>et al</u>., 1983).

Obviously, the potential for acid generation is primarily dependent upon the geology and chemistry of the mine wastes, with gangue characteristics as important as sulphide minerals. For the sulphide minerals the presence of iron pyrite, nature and diversity of other sulphides and particle size and distribution of individual sulphides are important. For gangue components the important factors are their permeability to water and gases, capacity for acid neutralisation, stability to acid or heat degradation and the nature of degradation productions. Also important are their absorptive capacity for water, oxygen, H ions and metal ions, their ion exchange properties and their redox properties (Miller <u>et al</u>., 1983).

Climate influences sulphide oxidation via rainfall and runoff patterns, ambient temperature variations and humidity. Water plays a significant role in sulphide oxidation by providing H ions for chemical oxidation and removing oxidised cations, thus making sulphide surfaces more available for further oxidation (Miller et al., 1983). The composition of percolating water is also important. Factors to be considered are solutes present, pH, redox status, microbial status and toxic materials (Miller et al., 1983).

Mechanical properties including the geometry, size and stability of waste dumps and the particle size distribution of the waste material, can influence air and water movement in wastes and in turn the nature and rate of acid formation and weathering (Brierley, 1978).

Hydrogen ions generated by pyrite oxidation may be toxic to plants. However, it is generally their detrimental effects on the waste material which render it more inhospitable as a rooting medium (Bradshaw and Chadwick, 1980). The problems generally centre around metal toxicities and induced nutrient deficiencies. 3.3.4 Copper Release from Mine Wastes and Potential Copper Toxicity.

Copper is an essential plant nutrient. Copper deficiency is widespread, whereas Cu toxicity is less common. Copper toxicity occurs in limited areas of high natural availability, or after the indirect addition of Cu in sewage sludges, mine wastes or in pesticides (Robson and Reuter, 1981).

Acid produced from pyrite oxidation in mine wastes dissolves the exposed and more reactive gangue together with the naturally occurring oxide and silicate Cu. The range of significant solubility of acid soluble Cu in wastes is reached when the pH falls below 6 (Ralph, 1980).

The natural release of Cu from pyritic Cu wastes raises the possibility of Cu toxicity. However, Bradshaw and Chadwick (1980) consider that with most modern metal extraction processes, the concentration of residual metal in tailings and waste rock should be sufficiently low so as to render metal toxicity unlikely. However, as they suggest, toxicity will depend upon all the factors affecting metal availability to plants.

Plants draw most of their Cu requirements from the soil solution, thus factors affecting Cu concentrations in the soil solution will play a prominant role in its availability to plants (Jeffery, 1981).

Copper in the soil is strongly held on inorganic and organic exchange sites and in organic complexes. Subsequently a large proportion of soil Cu is unavailable to plants. Also, the proportion of total Cu taken up by plants has been found to be greater on mineral soils (Thornton, 1979).

Although the Cu immobilisation capacity of soils is generally high, cation exchange for Cu<sup>2+</sup> and Cu(OH)<sup>+</sup> can take place and is best effected by H ions (Thornton, 1979). The amount of copper in soil solution usually decreases with increasing pH because of stronger Cu adsorption. If the pH is raised with lime the availability of Cu to crops usually, but not always decreases (Thornton, 1979). The effect of pH on Cu availability appears to depend upon soil factors such as the complexes of Cu present, the activity of the Cu and the CEC of the soil (Jeffery, 1981). Robson and Reuter (1981) consider that Cu toxicity commonly occurs on Cu-enriched soils that are very acid (pH<5) with a low CEC.

Porphyritic mine wastes are likely to be low in CEC, organic matter and clay minerals and as such their ability to complex Cu will be low. If an acid substrate develops, Cu toxicity should be considered a possibility. The common symptoms of Cu toxicity of plants include reduced shoot vigour, poorly developed and discoloured root systems and leaf chlorosis. Often the chloritic symptoms in shoots superficially resemble those of Fe deficiency (Robson and Reuter, 1981).

3.3.5 Mine Wastes and Acid Mineral Substrates

Freshly deposited tailings contain little or no organic C and are usually microbiologically sterile (Rutherford and van Loon, 1982). They are inherently deficient in N and are often deficient in P and K. Plant growth can usually be initiated by supplying N and P fertiliser and by planting the desired species; assuming physical conditions to be adequate (Williamson and Johnson, 1981).

The situation changes if the wastes become acid. Poor plant performance in acid soils is attributed to a variety of factors, with the most common being Al and Mn toxicity and Ca deficiency. Similar problems are associated with acidity in mine wastes (Butterfield and Tueller, 1980). Other effects of acidity in mineral soils include a reduction in CEC, induced Mg, K, Mo and sulphate deficiencies and phosphate fixation (Bruce and Crack, 1978).

Problems of nutrient availability are compounded in mine wastes where there has been no opportunity for a labile pool of plant nutrients to develop. Thus it will be necessary to charge this pool as well as to supply nutrients to establishing plants (Bradshaw and Chadwick, 1980).

# 3.4 <u>Mineral Soils in the Tropics : Nutrient Limitations and</u> Their Relevance to Mine Wastes

3.4.1 Introduction

There is ample literature on the plant nutrition problems associated with acid mineral soils. However, there is much less available on the 'acid soil syndrome' as it relates to a geologically young soil (mine wastes), especially in a tropical environment.

Tropical soils are generally considered to be highly weathered and acid. Uehara and Gillman (1981) characterise tropical soils as an "insoluble residue of highly weathered material that has been stripped of its capacity to sustain and supply life-sustaining nutrients".

Most mine wastes are not highly weathered (with the possible exception of some of the overburden). However, many mineral tropical soils, have nutritional problems analagous to mine wastes. These include inherent deficiencies of N, P, Ca and possibly trace elements, basic cation depletion, low pH and possibly toxic concentrations of Al and Mn. 3.4.2 The Acid Soil Syndrome

Plant growth on acid mineral soils can be affected by a number of factors including Al and Mn toxicities and induced nutrient deficiencies. Mine wastes are mineral soils which can quickly become acid through pyrite oxidation.

The Nature of Soil Acidity

It is well known that soils become acid under humid tropical conditions. Factors governing soil acidity however, have been debated strongly and it appears, in circles, since the early 1900's (Jenny, 1961).

Irrespective of the reason(s) that soils become acid, it is now recognised that the chemical behaviour of acid soils is intimately linked to the solution chemistry of Al (Bohn <u>et al.</u>, 1979). The addition of acid to soils generally results in an increase in extractable Al and exchange acidity, with the amount of increase depending upon the degree of soil weathering (Heddleson et al., 1960).

During acid weathering H ions will replace basic cations on exchange sites. Hydrogen-saturated minerals are highly unstable (Bohn, <u>et al.</u>, 1979). Excess H ions will react with clay crystals (Al-minerals), becoming adsorbed internally and simultaneously releasing Al (Kamprath, 1978; McLean, 1983). Released Al is then able to occupy exchange sites (Coleman and Craig, 1961).

Since the solubilities of Al-containing soil minerals (gibbsite, hallosite, kaolinite) are pH dependent, the concentration of soil solution Al is also pH dependent, and is minimal at about pH 7 (Bohn <u>et al.</u>, 1979). The Al(OH)<sup>2+</sup> ion is of minor importance to soil acidity and exists only over a narrow pH range. Similarly,  $Al(OH)_5^{2-}$  occurs only at pH values above those of soils. Al<sup>3+</sup>is predominant below pH 4.7,  $Al(OH)_2^+$  between pH 4.7 and 6.5,  $Al(OH)_3^0$  between pH 6.5 and 8, and  $Al(OH)_4$  above pH 8. Solid phase  $Al(OH)_3$  precipitates throughout the pH range mentioned when its solubility product is exceeded (Bohn <u>et al.</u>, 1979).

The hydrolysis of Al ions releases H ions and is the reason Al saturated soils are acid (Kamprath, 1978). Typical reactions include (Lindsay, 1979);

A1 <sup>3+</sup> +	н <sub>2</sub> 0	A1(OH) <sup>2+</sup>	+	н+	K	=	10 <sup>-5.02</sup>
A1(OH) <sup>2+</sup>	+ H <sub>2</sub> 0 =	A1(OH) <sub>2</sub> +	+	н⁺	K	-	10 <sup>-4.28</sup>
A1(OH) <sub>2</sub> +	+ H <sub>2</sub> 0 ===	<b>а1(он)</b> 3 <sup>0</sup>	+	н <sup>+</sup>	K	Ŧ	10 <sup>-0.67</sup>

The H ions liberated lower soil solution pH unless a neutralising agent is present with which they can react. The stepwise production of H ions is similar to that which occurs in the dissociation of polyproponated acids (Bohn <u>et al.</u>, 1979).

The hydrolytic products of trivalent Al rapidly polymerise to form large, multicharged units. These polymers are strongly retained by soil colloid surfaces and normally behave as if they are virtually non-exchangeable (Bohn <u>et al.</u>, 1979).

Iron hydrolysis is similar to that of Al. However, H produced by  $Fe^{3+}$  hydrolysis is buffered by the reactions of Al. Thus most of the soil's large reserves of Al would have to react before hydrolysis of Fe could effectively control soil pH (Bohn et al., 1979).

Hydrogen ions per se are not considered detrimental to plant growth unless the pH falls below 4.0 to 4.5 (Jackson, 1967). The poor performance of plants in acid soils is generally a result of Al and Mn toxicity or other nutrient imbalances (Jackson, 1967; Black, 1968; Islam et al., 1980).

Aluminium and Acid Soil Infertility

Aluminium can be toxic to plants, or it can induce deficiency of other nutrients.

The retention of positively charged and virtually non-exchangeable hydroxy-Al polymers lowers the net negative charge of soil colloids. Thus the formation of hydroxy-Al polymers on the surface of inorganic soil colloids decreases their CEC. A zero net negative charge or even a small net positive charge may result for soils with a low pH and containing large quantities of adsorbed hydroxy-Al polymers (Bohn <u>et al</u>., 1979; Uehara and Gillman, 1981).

Hydroxy-Al polymers also increase the anion adsorption capacity of soils resulting in the fixation of anions - specifically phosphate, sulphate and molybdate.

Aluminium is the most strongly adsorbed cation in soils (Helyar and Anderson, 1974). As it enters the soil solution it gradually replaces basic cations held on exchange sites. The basic cations released into soil solution may then be taken up by plants or leached (McLean, 1983). As a result acid mineral soils in high rainfall regions generally have a low base saturation and deficiencies of Ca, Mg and K are common.

Aluminium toxicity of plants is a problem associated with many acid mineral soils (Bohn <u>et al.</u>, 1979). Aluminium toxicity is characterised by stunted brown root tips and inhibition of the newly emerging lateral roots (Hecht-Buchholz and Foy, 1981). The symptoms on plant tops are indistinguishable from those of P deficiency, with low growth rates and small, dark green to purplish leaves (Helyar, 1978). The symptoms suggest that toxic effects are mainly through interference in the P metabolism of the plant. Root damage can limit P uptake and transport and high levels of Al in roots may precipitate phosphates. Further, sufficient Al probably enters the cytoplasm to directly inhibit the role of P in cell metabolism (Helyar, 1978). MacLeod and Bradfield (1963) suggested that over a certain pH range, the primary cause of failure of susceptible plant species was the presence of Al in the ionic form. They found that failure in establishment occurred mainly in the phase of early seedling development when the source of nutrient supply was shifting from seed reserves to active uptake from the external medium.

The relationship between Al and plant yield is usually in the form of an exponential decline in production with increasing Al concentrations in soil solution. Aluminium toxicity is likely to affect legume nodulation, but the precise effects are unclear (Munns, 1978).

High concentrations of exchangeable Al have been shown to reduce Ca uptake (Kamprath, 1978). This could be significant where low levels of exchangeable Ca occur.

Kamprath (1970, 1978) suggested that soil solution Al concentrations were related to the percent Al saturation of the effective cation exchange capacity (ECEC) and that plants growing on soils with greater than 60% Al saturation were likely to be affected by Al toxicity. However, many factors such as soil type and fertiliser strategy can affect Al saturation and associated toxic affects. Liming to reduce Al saturation to less than 30% of the ECEC appears to be a realistic approach to overcoming toxicity (Kamprath, 1970).

Plants vary in their tolerance to Al toxicity. Tolerance is due to their ability firstly to exclude Al from the plant and secondly, to nullify the toxic effects of adsorbed Al. The use of tolerant species or cultivars in conjunction with a sound liming programme would be advisable on soils where Al toxicity is a problem.

Manganese Toxicity

Manganese is the other metal toxicity commonly associated with acid soils.

Manganese is an element essential for plant growth. It is a co-factor for the activity of many enzymes and a major result of Mn toxicity appears to be the loss of control of some Mn activated enzymes (Helyar, 1978).

Manganese toxicity symptoms are often quite characteristic but vary considerably between species. A common symptom is marginal leaf chlorosis with mild toxicity and marginal leaf necrosis with severe toxicity. The potential for high concentrations in soil solution lie in the soil becoming strongly acid and containing significant amounts of easily reducible Mn (Adams, 1978).

Manganese is taken up by plants primarily as the divalent Mn<sup>2+</sup> ion. However, it is difficult to find consistent relationships between various measures of soil Mn and toxic effects (Helyar, 1978). The concentration of available Mn can be highly variable in field situations. This is because concentration is a function of the biological and non-biological reduction and oxidation of Mn oxides and Mn respectively. Reduction is favoured by both waterlogged and very dry conditions and a pH less than 5.5. Oxidation is favoured by high soil pH and moist conditions amenable to aerobic microbial activity (Helyar, 1978; Siman <u>et al.</u>, 1974). As a result foliar Mn concentrations have been found more reliable as an integrated measure of soil Mn toxicity over the growing period (Helyar, 1978).

Liming to a pH in excess of 5.5 can generally correct or alleviate Mn toxicity (Truong <u>et al.</u>, 1971; Siman <u>et al.</u>, 1974). The use of tolerant species may also be an advantage (Helyar, 1978).

Soil Acidity and Micronutrient Availability

Micronutrients of major interest to plant nutrition are B, Mn, Fe, Co, Cu, Zn and Mo.

In general, Mn, Fe, Co, Cu and Zn increase in availability with increased soil acidity. Thus acid soils usually provide sufficient amounts of these micronutrients for plant growth (Bohn <u>et al</u>., 1979).

Molybdenum differs from the metal cations in that its availability decreases with increasing soil acidity (Tisdale and Nelson, 1975). Molybdenum fixation in acid soils is similar to that of phosphate and sulphate. Liming acid soils increases Mo availability by releasing Mo from soil minerals, primarily Fe and Al oxides (Adams, 1978). Legumes appear more responsive to Mo availability than non-legumes, mainly due to increases in the N fixation capacity of the <u>Rhizobium</u> organisms.

Boron deficiencies are most common on coarse, well drained mineral soils, particularly mine wastes. The relationship between pH, available Ca and the B status of soils is not well understood, although it has been shown repeatedly that B uptake is reduced by increasing soil pH (Tisdale and Nelson, 1975). It is suggested that the reduction in B availability with over-liming is the result of an unfavourable Ca:B ratio in the plant (Tisdale and Nelson, 1975). 3.4.3 Macronutrient Availability

Soil pH can affect the availability to plants of the macronutrients N,P,K, Ca and Mg. Other properties of tropical mineral soils can also affect the availability of these nutrients.

Nitrogen

Nitrogen is the soil element which most commonly limits plant growth (Bohn <u>et al.</u>, 1979). Most of the N present in soils is contained in complex organic compounds that are not readily available to plants. Thus available N will be a major limitation to growth of plants in mineral soils low in organic matter.

Nitrogen chemistry in soils includes the constant turnover of N during organic reactions, oxidation of organic N to  $N_2$  and  $N_2O$  (denitrification) or to  $NO_3$  (nitrification), and the reduction of  $N_2$  to organic N (N fixation). These steps usually require microbial catalysis (Bohn <u>et al.</u>, 1979). The forms and amounts of N made available to plants from organic reserves and fertiliser addition depends upon the balance that exists between these processes.

Nitrogen in some form is needed for the decomposition (mineralisation) of organic matter by soil micro-organisms. If the decomposing organic matter has a small amount of N in relation to C present, the micro-organisms will utilise any NH<sub>4</sub><sup>+</sup>or NO<sub>3</sub><sup>-</sup> present in the soil to further decomposition. As a general rule, where organic matter with a C to N ratio of greater than 30 is added to the soil there is immobilisation of soil N during the initial decomposition process (Tisdale and Nelson, 1975). This is of importance in revegetation programmes designed to rapidly build soil organic matter levels. If the future N supply is dependent upon the mineralisation of organic matter then the C to N ratio should be kept low so as to ensure net mineralisation.

Mineralisation is a microbial process, thus the rate of transformation will be greatly affected by soil environmental conditions. A supply of NH4<sup>+</sup> is essential and if conditions do not favour its release from organic matter or if ammonical fertilisers are not added the population of nitrifying bacteria will diminish. Even if all other environmental conditions are favourable, mine wastes that have not been vegetated or had fertiliser additions will have little or no activity of nitrifying bacteria.

Microbial populations build up rapidly in the presence of an adequate supply of substrate. There may be some lag time between the addition of an NH4\* source and NO3<sup>-</sup> build up, but the total amount of nitrification taking place would likely not be affected by the number of organisms initially present, provided that environmental conditions are favourable for sustained nitrification (Tisdale and Nelson, 1975). Nitrifying bacteria can be affected by pH. The optimum pH range is 5.5 to 10, although some nitrification has been reported at a pH as low as 3.8 (Tisdale and Nelson, 1975). Low pH is one factor that limits the population size of nitrifying bacteria growing in pyritic collery spoil (Williams, 1975).

Nitrification requires molecular oxygen, thus little nitrification can be expected under anaerobic conditions; conditions often found in tailings deposits. Nitrification is also affected by soil moisture and temperature. It is severely curtailed at low moisture tensions and low temperatures (Tisdale and Nelson, 1975).

Ammonium can be adsorbed and retained by soil colloidal matter. It may be retained for considerable periods if conditions are unfavourable for nitrification (Tisdale and Nelson, 1975). However, the retention of  $NH_4^+$  by the soil depends upon the soil having a sufficiently high CEC. Tailings and waste rock, with little clay mineralisation, large pore spaces and no organic matter, can be expected to have a low CEC (Rutherford and van Loon, 1982). Under such situations, appreciable leaching of  $NH_4^+$ could be expected.

Nitrate is very mobile and is readily lost from soils in percolating water. High rainfall will rapidly leach NO<sub>3</sub><sup>-</sup> from the upper portion of coarse-textured soil profiles. Bradshaw and Chadwick (1980) noted that where NO<sub>3</sub><sup>-</sup> was added to China clay wastes at the time of sowing, plant roots had difficulty in growing fast enough to keep up with its downward movement. Under such conditions an NH<sub>4</sub> form would be the preferred N fertiliser.

As well as leaching, N can be lost from soils by four other processes -

- . crop removal.
- . denitrification, which is the biochemical reduction of NO3 under anaerobic conditions. It occurs primarily where soils are water-logged and is affected by both pH and temperature, with bacterial activity limited below pH 5.5.
- . chemical reactions involving  $NO_2^-$  under aerobic conditions from well drained acid soil. How much N is actually lost under these conditions is uncertain (Tisdale and Nelson, 1975).
- . Volatile losses of  $\rm NH_3$  gas from the surface of alkaline soils. This process could be of significance where  $\rm NH_4$  fertilisers are added to freshly limed mine wastes.

For fresh mine wastes with no organic matter, N for plant growth must be supplied either by fertilisers or fixation. Organic manures are generally not practicable due to the large areas involved, whilst most inorganic fertilisers may be subject to rapid leaching. Nitrogen fixation is the conversion of the N<sub>2</sub> gas to forms utilisable in biological processes. In economic terms the most important source of biologically fixed N is that produced by the root nodule bacterium <u>Rhizobium</u> during its symbiotic relationship with legumes. The quantities of N fixed differ with the differences in host plants and the environmental conditions under which the two develop. Legumes are only valuable from the point of view of N fixation if they are nodulated with appropriate strains of <u>Rhizobium</u> (Frederick, 1978). <u>Rhizobium</u> are unlikely to be present in mine wastes, or they may be present in an inappropriate strain. In such cases seed should be inoculated with the correct stain (Bradshaw and Chadwick, 1980).

The legume-<u>Rhizobium</u> symbiosis has been well studied. However, a number of areas relating to nodulate formation and function in tropical acid soils still need to be clarified. Nodulation includes rhizobial colonisation of the soil and rhizosphere, development of roots and root hairs, infection, nodule development and maintenance of nitrogenase and energetic activity. Each of these steps is sensitive to soil acidity (Munns, 1978).

Little data are published on rhizobial tolerance of soil acidity factors other than pH itself (Munns, 1978). Calcium has a major function in rhizobial cell structure (Vincent, 1977). However, only very small amounts of Ca are needed. Munns (1978) suggested that Ca deficiency for rhizobial growth seems unlikely, although it may be limited in Ca-depleted rhizospheres. Low pH and low Ca may sufficiently affect rhizosphere colonisation to inhibit nodulation when the supply of inoculum is limited (Munns, 1978).

Infection of plant roots by <u>Rhizobium</u> is acid sensitive and in some circumstances may fail, even where rhizobia can grow (Munns, 1978). Low pH and low Ca specifically inhibit the initiation of infection during a phase lasting approximately one day and which coincides with the curling of root hairs (Munns, 1978). Calcium and pH interact in the way in which they affect infection and nodulation, with a low pH tolerated if Ca is high and vice versa (Munns, 1978). Calcium also moderates adverse effects of Mn although most observed effects of Mn on nodulation are not clearly distinct from the accompanying limitations to the growth of the host plant (Munns, 1978). The specific effect of Al on infection remains to be established (Munns, 1978).

Soil acidity can have an adverse effect on nodule function, but the degree of effect depends upon the host and rhizobia. The evidence is clear for pH and Ca but not so clear for Al and Mn (Munns, 1978).

Biological variation in rhizobia and host has led to difficulties in generalising the behaviour of the legume-rhizobia symbiosis in acid soils. In both soils and artificial media, large differences in tolerance to acidity and Ca deficiency have been shown (Munns, 1978). However, despite limited knowledge in many areas, some genetic tailoring of symbionts to specific soil media should be possible. This could be of practical importance in the choice of legumes for the revegetation of mine wastes.

#### Phosphorus

Phosphorus in soils can be classed either as organic or inorganic, depending on the nature of the compounds in which it occurs (Tisdale and Nelson, 1975). Between 40 and 50% of organic soil P can be identified as nucleic acids, inositol phosphate and phospholipids - the remainder is largely unidentified (Tisdale and Nelson, 1975). However, all of the organic P may not be associated with the humus fraction of the organic matter. In the early stages of a revegetation programme for mine wastes, organic P will not be an important source of P for plants.

Most of the native soil P originates from the primary mineral apatite (Tisdale and Nelson, 1975). In unweathered material such as mine wastes, the quantity of P in soil solution is governed by the weathering of apatite. Soil pH must fall below 7.5 before significant quantities of P are released from this source (Smeck, 1972). The soluble phosphate is then utilised by plants, leached, or complexed to form secondary minerals. Once the primary phosphate minerals have weathered from the system, phosphate in the soil solution is governed by the solubility of Ca, Al and Fe phosphates (Smeck, 1972).

Phosphorus is mainly absorbed by plants as primary and secondary orthophosphate ions  $H_2PO_4$  and  $HPO_4^{2-}$ . Some small quantities of soluble organic phosphorus may also be absorbed but they are generally considered to be of minor importance (Tisdale and Nelson, 1975).

The concentration of the various ion species in soil solution is pH dependent. For  $H_3PO_4$ , the pK<sub>1</sub> is approximately 2 and the pK<sub>2</sub> approximately 7. Thus, where the pH is less than 4.5  $H_2PO_4^$ predominates and as the pH rises, the proportion of  $HPO_4^2$ increases (Barrow, 1978).

Phosphorus is most soluble in soils at a pH between 6 and 7 (Hsu and Jackson, 1960; Smeck, 1972). Above this pH range phosphate is complexed with Ca, and below this range, phosphate complexes with Al and to a lesser extent Fe. This is supported by both chemical equilibria (Hsu and Jackson, 1960) and field observations (Tisdale and Nelson, 1975).

When P is added to the soil solution, especially as a soluble fertiliser, a two step reaction takes place (Barrow, 1978). The first is a rapid step in which some of the phosphate is adsorbed, while the second is a slower step in which some of the phosphate is converted to a more firmly held form. The bonds formed by the second sorption process can make it extremely difficult for plants to extract P.

The adsorption of phosphates has two opposing effects ; firstly, it restricts leaching and thus retains phosphate within the root zone. Secondly, fertilisers are less effective and heavy applications are needed to reach maximum yields (Barrow, 1978).

The exchange complex of acid mineral soils contains appreciable quantities of adsorbed Al and smaller but significant quantities of Fe and Mn. These ions, together with Al and Fe hydroxy complexes, combine with phosphates to form the insoluble compounds (Tisdale and Nelson, 1975). Thus P availability to plants tends to decrease as soils become more acid and the proportion of Al and Fe phosphates increase (Kamprath, 1978; Bohn et al., 1979).

Phosphorus sorption by mine wastes may be of concern, particularly if they become acid through pyrite oxidation. The oxidation processes release Fe and Fe-hydroxy compounds. In addition, acid attack of the gangue may release Al, Mn and Fe.

Phosphorus sorption in acid mineral soils is also thought to occur through direct combination with clay minerals by replacing a hydroxyl group from an Al atom or by forming a clay-Ca-phosphate linkage (Tisdale and Nelson, 1975). Kafafi <u>et</u> <u>al</u>. (1967) suggested that at low phosphate concentrations, binding of phosphate by kaolinite and Al oxides took place on the edge Al atoms that were linked into the crystals of the adsorbent. At high P concentrations they felt that P could be bound by penetrating into some amorphous region of the clay surface if the phosphate ion was accompanied by some relatively unhydrated cation such as K.

In alkaline soils the activity of Ca is generally high. This favours the precipitation of the relatively insoluble dicalcium phosphate and other basic Ca phosphates such as hydroxyapatite and carbonoapatite (Tisdale and Nelson, 1975).

Barrow (1972) showed that at given phosphate concentrations complexing increased as Ca concentration increased. In addition, the solubility of Ca orthophosphates decreases in the order mono-, di- and tricalcium phosphate (Tisdale and Nelson, 1975).

In soils containing free  $CaCO_3$ , phosphate can be adsorbed rapidly onto its surface as a monolayer. The amount adsorbed and the equilibrium concentration of phosphate varies with the surface area of  $CaCO_3$  (Mattingly, 1975). Phosphorus can also be fixed in alkaline soils through its retention by clays saturated with Ca by forming a clay-Ca-phosphate linkage (Tisdale and Nelson, 1975). Phosphorus complexation by Ca may be important in tailings fresh from processing, or in mine wastes that have been limed.

Phosphorus sorption is affected by temperature, soil clay types and the presence of other species that can compete for adsorption sites. Barrow (1973) showed that the fall in effectiveness of phosphate fertiliser (in terms of plant response), was very rapid in warm moist soils. He showed that each  $10^{\circ}$ C. increase in temperature caused a threefold increase in the rate of decrease of effectiveness of the fertiliser.

Clay types can affect P sorption through surface reactivity and specific surface area (Uehara and Gillman, 1981). Layered silicates such as smectites have low surface reactivities compared to the 1:1 clays such as kaolinite. Similarly, as clay content increases the specific surface area increases and P sorption will generally increase (Uehara and Gillman, 1981).

Some organic and inorganic ions other than phosphates can be adsorbed onto the surface of oxides and hydrous oxides, thus reducing soil P sorption capacity (Uehara and Gillman, 1981). Organic matter can decrease the P retention of soils (Lewis et al., 1981) although the precise mechanisms involved are uncertain (Tisdale and Nelson, 1975).

As plants deplete P from the soil solution the solution must be continuously recharged if growth is to be maintained. Recharge can occur when P is desorbed from the surface of soil particles. This will happen in sufficient quantity only if the soil has a large capacity to sorb, and therefore desorb P (Uehara and Gillman, 1981).

In soils that require a heavy initial application of P, the quantity removed by the crop and lost through leaching is generally very small compared to the amount added.

Substantial leaching of P can occur from sandy neutral soils with low amounts of Fe and Al. Gillman (1973) found that 50% of applied superphosphate was leached from the top 30 cm of a deep siliceous sand on the Cape York Peninsula over three wet seasons. Ozanne <u>et al</u>. (1960) and Alston and Chin (1974) found that significant leaching of superphosphate from siliceous sands was the function of 'active' Fe and Al concentrations, organic C content and P sorption.

The use of a less soluble material such as rock phosphate may be warranted under conditions where significant amounts of soluble fertiliser could be leached (Finke, 1982).

Leaching of applied soluble P may be significant from coarse textured mine wastes under conditions of high rainfall. Cation Exchange Capacity and Basic Cation Availability

Cation exchange capacity is a measure of a soil's capacity to retain (and supply to the soil solution) cationic nutrients such as K, Ca and Mg. It is often used as an index of soil fertility (Uehara and Gillman, 1981).

The fractions of the soil responsible for cation exchange are the organic and mineral fractions with effective particle diameters of less than 20 microns. This includes a portion of the silt and all of the clay and colloidal organic fractions (Tisdale and Nelson, 1975).

Cations are positively charged and are thus attracted to negatively charged surfaces. Negative charges in the organic fractions arise from disassociation of -COOH and -OH groups and perhaps from NH<sub>2</sub>groups. The charge on inorganic fractions arises from isomorphous substitution and ionisation of hydroxyl groups attached to Si atoms at the broken edges of tetrahedral planes (Tisdale and Nelson, 1975).

Two:one and 2:2 layer silicates possess permanent negative charge (Bell and Gillman, 1978). This charge results from isomorphous substitution of  $A1^{3+}$  for  $Si^{4+}$  in the Si tetrahedral layers or of  $Mg^{2+}$  for  $A1^{3+}$  in the alumina octahedral layers (Bell and Gillman, 1978). The existence of permanent negative charge in 1:1 layer silicates is more uncertain (Bell and Gillman, 1978). In addition to a small permanent negative charge, 1:1 layer silicates may develop a variable charge on the edges of crystals where broken bonds result in the exposure of surface oxygen atoms which can protonate. The variable charge is pH dependent (Bell and Gillman, 1978).

Cations are held on the exchange site with varying degrees of tenacity, depending upon their charges and their hydrated and unhydrated radii. Ions with higher valencies are generally held more tightly than monovalent cations and usually the greater the degree to which the ion is hydrated, the less tightly it will be held (Tisdale and Nelson, 1975).

The CEC of a soil is obviously affected by organic matter content and the nature and amount of clay minerals. An immature soil rich in feldspars has a low CEC - feldspars occurring as coarse particles. Coarse minerals in turn have low specific surfaces and thus a low CEC (Uehara and Gillman, 1981). It follows that mine wastes, low in both organic matter and clay minerals and with coarse primary minerals, will have a low CEC.

The effect of CEC can markedly affect soil fertility. One important consideration is the degree of base saturation, which is the proportion of the CEC taken up by the basic cations Ca, Mg, K and Na.

Base saturation for normal uncultivated soils is usually higher in arid than in humid regions and is related to both pH and soil fertility. For a soil of any given organic and mineral composition, pH, fertility and availability of basic cations for plants increases with an increase in the degree of base saturation (Tisdale and Nelson, 1975).

The relationship between base saturation and cation availability is modified by the nature of soil colloids. Soils with large amounts of organic or 1:1 colloids are able to supply basic cations to plants at a much lower degree of base saturation than soils high in 2:1 colloids (Tisdale and Nelson, 1975).

The basic cations K, Ca, Mg and to a lesser extent Na are essential for plant nutrition as well as affecting the soil chemistry (Tisdale and Nelson, 1975).

Potassium is adsorbed by plants in larger amounts than any other mineral element except N and it is present in soils in relatively large amounts. However, usually less than 1% of the total soil K is in exchangeable form and much smaller amounts are in soil solution (Doll and Lucas, 1983).

Much of the non-exchangeable soil K is in primary minerals such as K feldspars and muscovite and biotite mica, and the secondary minerals such as illite, vermiculite and chlorite (Doll and Lucas, 1983).

Unavailable K occurs in primary minerals and certain secondary minerals, which can trap K in their lattice structure (Doll and Lucas, 1983).

Slowly available K is much more available than K in primary minerals (Tisdale and Nelson, 1975). Readily available K occurs in soil solution and on the exchange complex. It is readily absorbed by plants. Most measurements of plant available K involve the replacement of exchangeable K with another cation, commonly  $NH_4^+$ . Such measurements provide reliable estimates of the relative amounts of K available for plant growth (Kamprath, 1978).

Fixation of K is thought to result from the re-entrapment of K ions between the layers of 2:1 minerals, especially illite. Fixed K reaches a maximum in soils high in 2:1 clays (Tisdale and Nelson, 1975). As with P, large additions of fertiliser K with time will result in less fixation of subsequent additions and an increase in the amount of exchangeable K.

The conversion of K to the slowly available or fixed forms reduces its availability to plants. This may be beneficial in sandy soils in high rainfall areas where appreciable losses from leaching may occur. The fixed K tends to become available with time and is not completely lost to plants. The amount of K in the soil solution is related to exchangeable K and soil texture and mineralogy. Sandy soils exhibit greater increases in soil solution K with increasing exchangeable K than do clay soils. This is due to the different bonding intensities for K of 2:1 minerals (Tisdale and Nelson, 1975). Conversely, fine textured soils generally possess a greater supplying power of K (Doll and Lucas, 1983).

Soil pH and base saturation may also affect K nutrition. The greater the degree of base saturation, the greater the adsorption by clay of K from soil solution. Subsequently liming may decrease the loss of exchangeable K. Whether soil pH <u>per</u> <u>se</u> actually affects the exchangeable K/fixed K equilibrium is uncertain. However, the exchangeable K lost by leaching is inversely related to the degree of base saturation (Tisdale and Nelson, 1975).

Tropical soils are usually low in exchangeable K due to high rainfall and intensive leaching (Graham and Fox 1971). Exchangeable K usually ranges from 0.1 to 4 me%. Buol et al. (1975) reported that K deficiency was likely if exchangeable K was less than 0.2 me% or if it is less than 2% of the sum of the exchangeable basic cations when these were less than 10 me%. Obviously these values can only be used as a guide. Low exchangeable K may be expected in the coarse, acid, mineral mine wastes.

Calcium is absorbed by plants as a cation with absorption taking place from the soil solution and by contact exchange (Tisdale and Nelson, 1975). The concentration of total Ca in soils is usually less than total K or Mg, although exchangeable Ca is usually much higher. Most of the non-exchangeable Ca in soils is present as primary minerals (Doll and Lucas, 1983).

Coarse-textured soils in humid regions and that are formed from parent materials low in Ca, are likely to be low in exchangeable Ca. These soils respond well to lime. However, it is difficult to tell whether the response is due to alleviation of Ca deficiency <u>per se</u>, the reduction of acidity and Al, or to improvement in the availability of other nutrients ( Isbell, 1978).

The concentration of Ca in soil solution depends upon the amount of exchangeable Ca. However, plant nutrition also depends upon the degree of Ca saturation of the exchange complex and the types of soil colloids. As the amount of Ca held in exchangeable form decreases in proportion to the total exchange capacity, the amount of Ca absorbed by plants decreases. Two:one clay minerals require a much higher degree of saturation for a given level of plant utilisation than 1:1 clays (Tisdale and Nelson, 1975). Few soils contain insufficient Ca per se for plant growth (Kamprath, 1978). However, many soils in the humid tropics contain insufficient Ca to maintain a suitable degree of base saturation. In such soils exchangeable Al dominates the exchange sites (Kamprath, 1970). Further, the amount of Ca required for optimum plant growth has been shown to increase with increasing H ion concentration in soil solution (Moser, 1942).

Plants show a reciprocal relationship in cation composition and for this reason cation relationships are often stressed. Calcium deficiencies have been produced in some crops where excessive levels of K, Mg, Na or NH4 salts have been used (Doll and Lucas, 1983).

The total Mg content of soils ranges from a fraction of one percent in coarse sandy soils in humid regions to several percent in fine-textured soils in arid regions and that have been formed from high Mg parent material (Tisdale and Nelson, 1975).

Magnesium is absorbed as  $Mg^{2+}$  from the soil solution and by contact exchange. The amount of Mg absorbed by plants can be affected by the total amount present, the degree of Mg saturation of the exchange complex, the nature of other cations present and the type of clay minerals (Tisdale and Nelson, 1975).

Acid soils of tropical and sub-tropical regions usually have low reserves of Mg unless montmorillonitic clays are present (Kamprath, 1978). These soils may contain only small amounts of exchangeable Mg, a condition that can be aggravated by the addition of large quantities of fertiliser salts not containing Mg (Tisdale and Nelson, 1975).

Soil pH, available K and lime may also affect Mg availability and uptake (Adams and Henderson, 1962). On coarse textured humid region soils, excessive use of lime may result in an unfavourable Ca:Mg balance and induced Mg deficiencies. Similarly Edmeades (1982) found that liming generally decreased exchangeable Mg. High levels of K fertiliser may also reduce Mg availability (Adams and Henderson, 1962).

Doll and Lucas (1983) considered that, in general, exchangeable Mg should exceed 10% saturation of the exchange capacity. Adams and Henderson (1962), reported Mg deficiencies for soils with less than 4% saturation of the CEC.

In summary, the CEC of mineral mine wastes can be expected to be low. This, in addition to a high tropical rainfall and an acid substrate, could result in low levels of exchangeable Ca, K and Mg.

#### 3.5 Amelioration

#### 3.5.1 Introduction

Uehara and Gillman (1981) aptly summarised the problems encountered with tropical soils; 'next to soil acidity, P deficiency is the most frequently encountered agronomic problem, but that does not mean that N, K, trace elements, or other nutrient deficiencies or excesses are not important. The cure for all is well known; the rule of thumb is to lime acid soils and apply fertilisers to nutrient deficient soils. But if the cure is known, there is less agreement on how best to diagnose the problem and administer the cure'. Simliar issues apply to mine wastes, although one important amelioration technique, the use of adapted plant species, should not be overlooked.

## 3.5.2 Control of Pyrite Oxidation

Kleinman <u>et al</u>. (1981) suggested that it was possible to forestall production of acid by alkalinity management during the early stages of pyrite oxidation. They suggested capping wastes with sufficient alkaline material. If oxidation is well underway this method is unlikely to be successful and the traditional method of control has been to limit available oxygen supply (Miller <u>et al</u>., 1983). This involved sealing the dumps through the use of compaction, clay seals, synthetic liners, sprayed membranes and rigid liners. Success is usually limited.

Kleinman (1982) suggested that a more direct method of controlling pyrite oxidation would be to use bactericides, although the practical utilisation of the method has only recently been demonstrated. To prevent recolonisation by bacteria a slow release form is required. This is a problem for high rainfall, tropical regions where the bactericides are more readily leached.

It has been suggested that oxidation could be promoted and the oxidation products removed by leaching. This process is likely to be slow and costly (Bloomfield, 1972).

The large areas of mine waste at Bougainville Copper and the lack of a benign material for covering them rules out such approaches as impractical and uneconomic. As such they have not been seriously considered.

## 3.5.3 Liming

Liming, as the term applies to agriculture, is the addition of any Ca or Ca and Mg containing compound to the soil that is capable of reducing acidity (Tisdale and Nelson, 1975). Adams (1978) considered that plant response to liming was because one or more of the following factors have been corrected; Al toxicity, Mn toxicity, H toxicity, Ca and/or Mg deficiency and Mo deficiency.

Despite the many effects that lime may have on soil and soil solution chemistry, the primary effect is neutralising acidity through provision of hydroxyl ions (Bohn <u>et al.</u>, 1979). The basic reaction is :

 $CaCO_3 + H_2O \longrightarrow Ca^{2+} + HCO_3^- + OH^-$ .

Soils behave like buffered weak acids and will resist sharp changes in pH. For example, if the exchange complex is saturated with Al, addition of small amounts of base will result in neutralisation of H ions and precipitation of Al ions from solution. The equilibrium of the system and hence the pH will be maintained by the movement of Al ions from exchange sites to the soil solution where they will hydrolise and produce more H ions. As more base is added to the system, more adsorbed Al ions will be neutralised and replaced on exchange sites with the cation of the added base. Thus there is a gradual increase in the pH of the system (Tisdale and Nelson, 1975).

The amount and nature of clays and organic matter will determine the buffering capacity of a soil. Sandy soils with small amounts of clay and organic matter are poorly buffered and require only a small amount of lime to effect a given pH change relative to strongly buffered soils (Tisdale and Nelson, 1975). Thus fresh mineral mine wastes would be expected to be poorly buffered.

Materials commonly used for liming soils are the oxides, hydroxides, carbonates and silicates of Ca or Ca and Mg. In addition to the cations, anions must be ones that will reduce the activity of H and Al in the soil solution. Perhaps the greatest single benefit of liming acid soils is the reduction in the activity or solubility of Al and Mn (Tisdale and Nelson, 1975).

Aluminium in soil solution will be too low to be toxic to even the most sensitive plants when soil pH is 5.5 or higher. Thus, in spite of the complex soil chemistry and plant biochemistry involved with Al toxicity, associated problems can be overcome by liming to convert most of the exchangeable Al into a solid phase Al oxide or hydroxide (Adams, 1978). Kamprath (1970) considered that there was no yield advantage for most tropical crops in liming to a pH above that which corresponds to a low Al saturation - in fact there may be disadvantages. As with Al, Mn toxicity is not generally a problem unless the soil pH is less than 5.5 (Adams, 1978) although Siman <u>et al</u>. (1974) considered that lime was only of limited benefit in alleviating Mn toxicity symptoms under extreme climatic conditions. Under most conditions liming to reduce exchangeable Al will reduce the likelihood of Mn toxicity. The exception is when the soil contains large amounts of easily reducible Mn.

Metal concentrations in soil solution are related to pH and generally increase with decreasing pH (Curtin and Smillie, 1983). As such, toxicity problems with acid metalliferous mine wastes can generally be overcome by liming to a pH in excess of 6 (Bradshaw and Chadwick, 1980).

Some of the lime response reported on acid soils in the humid tropics may be due to alleviating Ca deficiencies <u>per se</u> (Isbell, 1978). Adams (1978) suggested that Ca deficiencies should be suspected in highly leached, acid, sandy soils, where base retention is virtually nil at low pH. Under such conditions, liming may improve plant growth through improved Ca nutrition. Legume nodulation and <u>Rhizobium</u> growth are both sensitive to pH and Ca supply and add an extra dimension to the need for liming for legume growth (Adams 1978).

Liming increases the activities of the basic cations in soil solutions (Curtin and Smillie, 1983) and therefore, their availabilities are likely to increase.

Liming acid soils will generally increase the base saturation and the ECEC (Jokinen, 1981). In essence, the precipitation of Al and Fe hydroxides with increasing pH results in an increase in the net negative charge and therefore the capacity of the soil to retain cations. The issue is more complex for variable charge soils (Uehara and Gillman, 1981). An increase in base saturation and ECEC can result in an increase in basic cation availability, but not necessarily so. Liming can result in a decrease in exchangeable Mg through a number of processes, including adsorbtion on freshly precipitated Al-gels, the formation of Al-Mg compounds and the displacement of exchangeable Mg by Ca (Jokinen, 1981). Overliming of mineral soils can result in unfavourable Ca/Mg, and Ca/K ratios (Doll and Lucas, 1983). If exchangeable Mg is low prior to liming the use of a dolomite limestone should be considered (Kamprath, 1970).

The effect of pH on P availability has been discussed. In strongly acid soils, the most economic method used to increase P availability and utilisation is liming. Raising the pH to precipitate most of the Al and Fe from solution may decrease P sorption. However, excessive additions of lime will again result in decreased availability due to precipitation of Ca or Mg phosphates (Tisdale and Nelson, 1975). Although thermodynamics show that Al and Fe phosphate solubilities increase with increasing pH, there is little evidence to suggest that liming has any appreciable effect on availability of P already fixed in the soil (Adams 1978). Liming acid soils results in a marked increase in microbiological activity, a decrease in total organic P and a decrease in extractable organic P (Halstead <u>et al.</u>, 1963). Such a phenomena may explain the apparent increase in P availability in some experiments following liming (Adams, 1978). Apparent P responses following liming may also be due to improved root system development following a reduction in Al toxicity and improved Ca nutrition.

Liming acid soils low in available P can increase the availability of applied P in some instances (Robertson <u>et al.</u>, 1954). Other studies have shown that added P can be inactivated to a greater extent by freshly precipitated Fe and Al hydroxides formed by adding lime than by the soluble Al and Fe in the unlimed soil (Amarasiri and Olsen, 1973). When the effect of lime on other soil factors is removed, the pure effect of lime application on reducing P fixation is generally small (Uehara and Gillman, 1981). However, optimum availability of P applied after liming can be expected to coincide with the vanishing of available Al in most soils (Adams, 1978).

Liming an acid mineral soil can have a pronounced effect on the availability of both Mo and sulphate. Increased availability is thought to come primarily from release by Al and Fe oxides (Adams, 1978). Liming may also reduce the availability of the essential micronutrients B, Cu, Zn, Fe and Mn and in some soils induce deficiency symptoms (Bohn <u>et al</u>., 1979).

Soil microorganisms are important to soil fertility through the release of nutrients from organic matter by mineralisation, through nitrification and through the symbiotic relationship of <u>Rhizobium</u> and mycorrhizae with plants. These microorganisms respond favourably to the liming of acid soils due to the correction of pH and nutrient supply (Munns, 1978; Robson, 1978; Hartikainen, 1981).

There is agreement in the literature that a sound liming programme is beneficial to acid mineral soils. There is much less agreement on how to determine the rates to apply.

Plants, especially legumes, differ in their response to lime (Munns and Fox, 1977; Munns <u>et al.</u>, 1977). It is essential to consider the type of plants to be grown when choosing a lime rate. Indeed, the growth of certain legumes can be depressed by liming above pH 6 on some acid tropical soils (Munns and Fox, 1977). Traditionally agronomists have added lime to achieve optimum yield of a particular crop. Usually this has been done with a specific pH in mind. However, the pH at which a crop performs best varies with soil type. In addition, liming to neutrality on some highly weathered tropical soils may adversely affect them physically (McLean, 1983). As such, soil type needs to be considered. Liming to a specific pH after considering crop and soil types has been the preferred method because of convenience (Adams, 1978).

Other workers consider that liming to reduce exchangeable Al saturation rather than to raise the pH to a uniform level is a valid criterion on which to base lime rates for leached acid mineral soils that are adequately fertilised (Kamprath, 1970; 1978). Kamprath (1970) suggested liming such soils to reduce Al saturation of the ECEC to less than 30%.

Choosing lime application rates for pyritic mine wastes is further complicated by pyrite oxidation which can result in a continuous source of acid. Liming in excess of a crops optimum requirement or in excess of that needed to reduce exchangeable Al to an acceptable level may be required to provide residual acid buffering capacity in the soil.

3.5.4 Fertiliser Application

Porphyritic mine wastes are likely to be deficient in N, P and K, and acidity may induce deficiencies of Ca, Mg and Mo. Liming will provide Ca and result in better utilisation of applied fertilisers, but there will still be a need for fertiliser addition.

Most of the commonly used inorganic fertilisers are water soluble and leaching is one of the most frequently encountered soil fertility problems in tropical agriculture. Porphyritic mine wastes with their coarse, sandy texture and low CEC, are likely to have a leaching problem.

Susceptibility of fertilisers to leaching is also related to nutrient mobility. Where a leaching potential exists, the form of applied fertiliser together with the rate and frequency of application are important considerations.

Organic fertilisers are less susceptible to leaching than most inorganic forms and they have been used with some degree of success in the rehabilitation of mine wastes (Johnson <u>et al.</u>, 1977). Disadvantages associated with organic fertilisers are the limited availability and high cost of most types.

Leaching losses can be reduced by choosing less soluble types of inorganic fertilisers. An  $NH_4$  source of N fertiliser is generally less susceptible to leaching than a  $NO_3$  source,

although not all plants can utilise N as NH4 (Tisdale and Nelson, 1975). Some less soluble or slowly soluble forms of fertiliser are now being marketed. They include oxamide, isobutylidene urea, S-coated urea and K-Ca pyrophosphate (Finck, 1982). The main disadvantage of these materials is obtaining a reliable supply and the high cost in relation to the more soluble inorganic fertilisers. Various rock phosphates have proven useful as P fertilisers on acid soils susceptible to leaching (Kerridge, 1978) and they may prove beneficial for fertilising acid mine wastes.

Leaching losses can be reduced and fertiliser utilisation increased by reducing application rates and increasing the frequency of application. Alternatively fertilisers can be 'banded' and placed within the rooting zone of plants. The applicability of such methods to the revegetation of large areas of mine waste remains to be determined.

The other important consideration when selecting fertiliser types is their effect on the soil reaction.

Carriers (accompanying cation or anion in a fertiliser) of most P and K fertilisers have little effect on soil acidity. Some carriers of N however, can affect both soil pH and the loss of cations by leaching. Ammonium fertilisers with acidic anion carriers such as  $SO_4$  can contribute to the acidity of the soil, while  $Ca(NO_3)_2$  would leave a basic residue (Tisdale and Nelson, 1975).

The application of fertiliser salts to acid soils can increase the soil electrolyte concentration and cause a marked increase in soil solution Al. This can result in Al toxicities on soils with relatively low Al saturation (Kamprath, 1978).

Fertiliser carriers can also be important as sources of nutrients. It has been reported that responses to superphosphate in some instances have been due to the accompanying S or Ca (Finck, 1982). Thus the status of other nutrients in the soil should also be considered when selecting a specific fertiliser.

3.5.5 Use of Adapted Plants

Plants vary widely in their soil and nutrient requirements. Amelioration of mine wastes can be kept to a minimum by using plants adapted to conditions likely to be experienced.

Probably the most studied adaption of plants utilised in agriculture is the <u>Rhizobium</u> symbiosis with legumes. The need for after-care in terms of fertiliser N addition may be reduced, if not eliminated, by including a significant proportion of legumes in a species mix for the revegetation of mines wastes (Bradshaw and Chadwick, 1980). Legumes (and all plant species) vary widely in their tolerance to acid mineral soils (Munns and Fox, 1977; Andrew and Jones, 1978). In turn, grasses are generally considered to be more tolerant to soil acidity and heavy metal toxicity than legumes, shrubs or trees (Hutchinson and Kuja, 1978).

Many plant species have also been found to grow on soils contaminated with heavy metals. The use of these species in revegetationprogrammes has been advocated by a number of authors, for example, Bradshaw <u>et al.</u>, (1965). Plants have been found growing on soils with Cu concentrations sufficient to be toxic to most plants (Gregory and Bradshaw, 1965; Reilly, 1967). This is of specific interest to the revegetation of porphyritic copper mine wastes.

The identification and utilisation of plants adapted to growing under conditions likely to be encountered on mine wastes should form an integral part of an ameliatory programme.

Although the methods of ameliorating acidity and nutrient deficiencies are well recognised, a good understanding of a sites specific characteristics is required so that the measures and resources used can be optimised.

# CHAPTER 4: CHARACTERISATION OF BOUGAINVILLE MINE WASTES; SOIL TESTING, FERTILISER LEACHING AND NITRIFICATION

## 4.1 Introduction

Each ore body has inherent characteristics in terms of the type and chemical properties of the wastes produced. The studies carried out in this section had two main purposes; to define and characterise the properties of the BCL mine wastes, specifically as a source of nutrients for plant growth, and to provide information on fertiliser leaching rates from the wastes. Two methods were used, soil testing and a lysimeter leaching experiment.

## 4.2 Soil Testing

## 4.2.1 Introduction

The data on tailings composition (Table 2.1) provides some information on the likely products of the wastes after they have weathered. However, it provides little information on actual plant nutrient availability. Soil testing in the agricultural context has generally come to mean rapid chemical analyses designed to assess the plant available nutrient status of a soil.

## 4.2.2 Materials and Methods

Samples of mine wastes were collected either with a Lord soil sampler or a small hand shovel. Rigorous replication was used to overcome as much as possible the heterogenous nature of the mine wastes and where necessary care was taken to exclude surface organic matter and residual lime and fertiliser.

Samples were collected in new, clean, plastic bags and immediately sealed and taken to the Environmental Laboratory, BCL Analytical Services Department.

In the laboratory samples were sieved to less than 2mm and oversize discarded. They were air dried in a dust free environment at room temperature. The analytical methods used were :

Total N : Determined by the Kjeldahl digestion method.

Total P: The sample was digested with nitric, hydrochloric, perchloric and hydrofluoric acid and the P determined by the ammonium molybdate/vandate colo rimetric method using a Bausch and Lomb spectrophotometer, Model 88, Glack (1955). Available P: The Olsen, sodium bicarbonate extraction at pH 8.5. Phosphorus in the extract was determined colo rimetrically using a Varian UV/VIS model DMS80 spectrophotometer.

Exchangeable K, Ca, Mg, Na, Mn and CEC : The soluble and exchangeable salts were leached with neutral ammonium acetate. The ammonium ions retained were in turn leached with sodium chloride and determined by the Kjeldahl method as a measure of the CEC. Exchangeable cations were determined by atomic a-sorption spectrophotometry (AAS) using a Perkin Elmer 603 AAS.

Exchangeable Al : The Al was extracted with IN KCl and determined by AAS using a Perkin Elmer model 603 AAS.

Exchangeable H : Total exchangeable acidity determined by extraction with 1N KCl and titration of the extractant against a standard base. Exchangeable Al was determined by AAS and exchangeable H by difference.

Available Cu, Zn and Fe : The metals were extracted with citrate-EDTA at pH 8.5 and determined with a Perkin Elmer 603 AAS . Clack (1965).

Total S : Patented method of Leco Corporation using a Leco Induction furnace and automatic S titrator.

Sulphate S : Sulphate extracted by boiling with sodium carbonate and determined gravimetrically by weighing as barium sulphate.

Organic C : Determined by the Walkley Black wet oxidation method.

Available Mo : Extracted with Tamm's solution (acid ammonium oxalate) and determined by DC Plasma spectrophotometry (DCP) using a spectrospan lllB DCP with background compensator and autosampler. Plack (1965).

Available B : Extracted with hot water and determined by DCP as for Mo. lack (1965).

pH and Conductivity : Determined in a 1:5 soil to distilled water suspension. The measurements were carried out with electronic meters.

Samples of waste rock and tailings were collected and analysed. The waste rock was from a mixture of Panguna Andesite and Biotite Granodiorite that had been deposited 18 months to two years prior to sampling. Three types of tailings were collected from the river system. Two samples were taken from the banks of the Jaba river at XS29 and XS11 (Figure 2.2). They had been deposited naturally in a freely draining position on the banks of the river approximately two years and 18 months respectively prior to sampling. The third tailings sample (dredge) was collected from an area beside the Jaba River at XS25 where it had been deposited in a freely draining situation by a bucket wheel dredge three months prior to sampling.

4.2.3. Results and Discussion.

Soil analysis according to the specified procedure confirmed that waste rock and tailings are poor substrates for plant establishment and growth (Table 4.1). They can become acid and they are universally low in plant available N, P, K and B. Items of particular interest are summarised below.

Freshly removed waste rock can be of neutral to acid pH. However, upon dumping the material invariably becomes acid due to pyrite oxidation, with material in exposed waste dumps usually having a pH between 4.3 and 5.0. The pH of the waste rock analysed was 4.5.

The pH of tailings is more variable. Tailings are discharged from the concentrator at a pH between 9.5 and 11.0 and they contain free Ca that is added as  $Ca(OH)_2$  in the grinding circuit. The dredged sample is an example of fresh tailings. The pH is 9.4 and 89% of the ECEC (after Kamprath, 1978) is occupied by Ca.

If tailings are deposited so that they are freely draining, pyrite oxidation begins and the pH falls. The pH of the XSll tailings has fallen to 6.7 and that of the XS29 tailings to 4.8. The pH of the waste rock and XS29 tailings may be detrimental to plant establishment and growth (Bradshaw and Chadwick, 1980).

The organic matter and thus total N content of the wastes is very low. Although total P concentrations of the wastes are moderate, available P is very low for the tailings and low to moderate for the waste rock (Walsh and Beaton, 1983). The lowest available P is for the dredge tailings (0.4ppm) while the highest is for the waste rock (10.0 ppm). Available P increases with decreasing pH in the range of samples presented. Particle size (Table 4.2) may also affect available P with the dredge and XS11 tailings samples having very little material in the clay size fractions and little available P. Although the waste rock sample shows little material less than 53 micron, it does have a clay fraction; certainly more than the upper river tailings.

Exchangeable K is very low for each waste type and is likely to result in deficiencies (Buol et al., 1975).

Exchangeable Mg is very low for the acid XS29 tailings (0.09 me%) and low for the other waste types (Walsh and Beaton, 1983; Doll and Lucas, 1983). For each waste type exchangeable Mg is less than 10% of the ECEC. Exchangeable Mg is the highest in

# TABLE 4.1 : SOIL ANALYSES DEPICTING PLANT NUTRIENTAVAILABILITY FOR TYPICAL BOUGAINVILLE MINE WASTES

	Waste**	Tailings*	Tailings*	Tailings*
Ana lys is	Rock	<u>ex XS29</u>	ex Dredge	$\underline{ex}$ XS11
OC %	0.13	0.03	0.02	0.04
N tot ppm	<30	<30	<30	<30
P tot ppm	740	1192	678	992
P av ppm	10.0	3.7	0.40	1.1
K ex me %	0.08	0.06	0.07	0.06
Ca ex me %	0.6	0.4	1.6	1.6
Mg ex me %	0.23	0.09	0.17	0.16
Na ex me %	0.02	0.04	<0.03	<0.03
CEC me %	4.9	3.4	1.4	1.6
ECEC me %	6.3	2.8	1.8	1.8
H ex me %	2.02	0.53	<0.05	<0.05
Al ex ppm	300	149	<1	<1
Mn ex ppm	3.9	3.4	1.3	9.7
Cu av ppm	263	67	62	89
Fe av ppm	218	50	27	22
Zn av ppm not	determined	1.6	0.6	2.4
Mo av ppm	36	2.0	1.1	2.3
B av ppm	<0.02	<0.02	<0.02	<0.02
S tot %	0.80	0.12	0.18	0.26
SO <sub>4</sub> - S tot ppm	1740	83	49	41
pH 1:5	4.5	4.8	9.4	6.7

- \* Average of 10 bulked samples. Each sample consisted of 20 cores, 15cm deep, taken randomly over an area of like waste material.
- \*\* Average of 3 bulked samples. Each sample consisted of 20 randomly collected sub samples, 0-15 cm deep.

tot = total, av = available, ex = exchangeable

<u>% Passing</u> <u>Sieve</u> +	Waste** Rock	Tailings XS29	Tailings Dredge	Tailings XS11
600 micron	68	97	97	95
425 micron	44	97	95	87
300 micron	36	96	91	73
212 micron	29	96	78	53
150 micron	21	92	49	31
106 micron	14	73	19	16
52 micron	3	27	2	3

# TABLE 4.2 : PARTICLE SIZE ANALYSIS OF TYPICAL BOUGAINVILLE MINE WASTES\*

- \* Sizing was carried out on a representative sample obtained from the bulk samples used for the soil analyses of Table 4.1.
- \*\* Waste rock sizing for less than 2mm fraction.
- + <53 micron = fine sand, silt and clay. 53 212 micron = fine sand. 212 micron - 2,000 micron = coarse sand (N.S.W. Soil Conservation Service).

absolute terms for the waste rock. However, as a percent of the ECEC it is much lower than that for the dredge and XSII tailings.

Exchangeable Na is low to non-detectable for each waste type. Exchangeable Ca is low in absolute terms for all waste types although for the dredge and XS11 tailings the ECEC is 89% saturated with Ca. For the waste rock and XS29 tailings exchangeable Ca represents only 9.5 and 14.3% respectively of the ECEC. The ECEC (or CEC) for each waste type is low (Walsh and Beaton, 1983).

Available Mo is moderate to high for the tailings and very high for the waste rock (Johnson, 1973). Exchangeable Mn is moderate for all waste types (Truong <u>et al.</u>, 1971; Siman <u>et al.</u>, 1974) and EDTA extractable Fe appears adequate for all waste types (Viets and Lindsay, 1983). EDTA extractable Zn appears adequate although for the alkaline tailings from the dredge, large additions of P fertiliser may induce deficiencies (Trierweiler and Lindsay, 1969). EDTA extractable Cu is high for all wastes, with the possibility of toxicity for plants growing on the waste rock (Reuther and Labanauskas, 1973).

Sulphate levels are moderate for the tailings and high for the waste rock. This is to be expected following sulphide mineralisation. Total sulphur concentrations reflect the acid forming potential of the material.

Exchangeable Al was not detected in the alkaline to neutral tailings. Levels were high in the acid wastes, with 53 and 59% of the ECEC of the waste rock and XS29 tailings respectively saturated by exchangeable Al. This might cause toxicities (Kamprath, 1970, 1978; Helyar, 1978).

The particle size of the tailings decreases with distance down the river system. This is especially apparent for the tailings from XS11 and XS29. Although the dredge material was from XS25, the dredge favoured the larger size fractions. There is little material greater than 500 micron at either XS25 or XS29 compared with 27% greater than 300 micron at XS11. Conversely, only 27% of the material from XS29 was plus 106 micron while a further 27% of the same material was less than 53 micron.

Particle size of the wastes affects both physical and chemical properties. A decrease in size fraction results in an increase in the water holding capacity of the material and an increase in CEC.

The soil tests show that the mine wastes as represented in Table 4.1 can be divided into two distinct groups; acid and neutral to alkaline material.

Nutritionally, the acid wastes are deficient in organic matter, N and P. They have a low CEC, are base unsaturated and are likely to be deficient in K and Mg. Low Ca may affect the more sensitive plant species and rhizobial nodulation and function. Boron appears deficient, a factor that could be aggravated by liming. Aluminium and Cu toxicities may be a problem.

The alkaline and neutral tailings from the dredge and XSll are unlikely to cause metal toxicities in the plant establishment phase. However, they are deficient in organic matter, N and P. Despite the fact that they are base saturated, K deficiencies are likely. The CEC is very low and B deficiencies may occur.

The low CEC, coarse texture of the wastes and the high rainfall of Bougainville suggests high leaching of soluble fertiliser.

In summary, the soil tests indicate that liming of the acid wastes will be necessary and that applications of N, P, K, B and possibly Mg fertiliser may be required.

## 4.3 Fertiliser Leaching and Nitrification

## 4.3.1 Introduction

The high rainfall on Bougainville, together with the coarse texture and low CEC of the mine wastes suggests rapid and wasteful leaching of applied water soluble fertilisers. It is important to quantify this process in determining the optimum type, rate and frequency of fertiliser application. In addition, the form of N leached is of interest in assessing the effectiveness of nitrification.

### 4.3.2 Materials and Methods

Three, 200 litre drums (lysimeters) were cleaned and fitted with drainage and collection devices located in the bottom and 5 cm from the top. The lysimeters were filled with tailings collected from the braided Jaba River at XS12. They were water saturated and oxidation processes had not begun. The CEC of the tailings was 1.7 me% and the pH was 9.1.

The lysimeters were placed in the open under natural rainfall conditions. After two weeks equilibration, leachate from the lysimeters was collected after each significant rainfall event and analysed for total N, P, K and B.

Following the collection of background leachate information, a commercial NPK fertiliser (14:14:14) at 750 kg/ha and Solubor 20% B as  $Na_2 B_4 O_7$  .4H<sub>2</sub>O at 10 kg/ha B were added to the surface of each drum. The NPK fertiliser was an Australian Fertilisers product, with N present as NH<sub>4</sub>, P present as ammonium phosphate and K as KCl. Leachate was colleted after each significant rainfall event for 64 days and analysed for NH<sub>4</sub>, NO<sub>3</sub>, NO<sub>2</sub>, P, K and B. (Standard methods for Examination of Water and Waste Water, 15th Ed, 1980). At the end of 64 days, tailings samples were taken from each lysimeter in the 0 - 20 cm and 20 - 80 cm depths. They were analysed for total N and P, available P and B and exchangeable K. Methods of analysis were as cited in Chapter 4.

Rainfall was collected throughout the trial and analysed for total N.

4.3.3 Results

The results showed that soluble fertilisers can rapidly leach from tailings and that nitrification can occur.

Nitrogen, P or B could not be detected in leachates before the addition of fertiliser. K in the range 1 to 15 ppm was present in the background leachate. Copper mineralisation at Bougainville Copper is associated with K alteration and enrichment of the host rock (Ford, 1973). This is the likely source of K in the leachate. Total N could not be detected in rainwater (detection limit 0.1 ppm). Rainfall for the 64 days was ll66mm, slightly higher than average.

Following the addition of the fertilisers, 55.4% of the N, 65.2% of the K and 10% of the B was recovered in the leachate over the 64 day period. Phosphorus was not recovered (Table 4.3).

There was no significant difference between the amounts of NO<sub>2</sub> -N, NO<sub>3</sub> -N, K or B leached from each lysimeter. There was a significant difference between the amount of NH<sub>4</sub> -N leached (P < 0.05), with the amounts leached from the three lysimeters being 2.1, 26.8 and 0.8mg respectively. The reason for the discrepancy is uncertain. However, the total amount of NH<sub>4</sub> -N leached for each lysimeter was small in comparison to that added.

Although N was added as  $NH_4$ , little was recovered in that form (<1%). Thirty seven percent of the recovered N was  $NO_2$ , and the remaining 62% was  $NO_3$ . Initially, the N was  $NH_4$  -N. This was followed by  $NO_2$ -N and by day 18, when  $NO_3$  started to appear in the leachate, the bulk of the  $NO_2$  had been recovered (Figure 4.1). This is consistent with nitrification of the applied  $NH_4$ source, such that;

 $2 \text{ NH}_{4}^{+} + 3 \text{ O}_{2} - - - - - > 2 \text{ NO}_{2}^{-} + 2 \text{ H}_{2} \text{ O} + 4 \text{ H}^{+}$ 

 $2NO_{2}^{-} + O_{2}^{----->} 2NO_{3}^{-}$ 

The sediment was not analysed for N before the fertiliser was applied. After leaching,  $NO_2$  or  $NO_3$  could not be detected, while small amounts of NH<sub>4</sub> were present (Table 4.4). The origin of the NH<sub>4</sub> is uncertain.

# TABLE 4.3 : NUTRIENT APPLIED AND LEACHED FROM A COLUMN OF TAILINGS AFTER 64 DAYS BY NATURAL RAINFALL\*

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Nutrient	Added (mg)	Nutrient Recovered (mg)	% Leached
NH <sub>4</sub> -N	2440.0	8.2	0.3
NO <sub>?</sub> -N	0.0	499.7	20.5
NO 3 -N	0.0	845.4	34.6
Р	1049.0	0.0	0.0
K	2146.0	1339.7	65.2
В	320.0	31.9	10.0

\* Mean from three lysimeters.

# TABLE 4.4 : SOIL ANALYSES OF TAILINGS BEFORE AND AFTER FERTILISER ADDITION AND LEACHING\*

	p pm				T	me%	p pm	
TEST	N tot	: NH <sub>4</sub>	NO <sub>2</sub>	NO 3	B av	Кех	P tot P av	
Before Fertilizer Addition	<1	not m	easur	ed	<0.02	0.02	850 0.9	
After 64 Days 0-20 cm deep	10.4	0.67	<1	<1	<0.02	0.053	923 3.6	
20-80 cm deep	10.8	0.63	<1	<1	<0.02	0.063	930 3.1	

tot = total, av = available, ex = exchangeable

\* Mean of samples taken from each of three lysimeters.

# OF TAILINGS BY NATURAL RAINFALL IN 64 DAYS.\*



FIGURE 4.3: POTASSIUM FERTILISER LEACHED FROM AN 80 cm

COLUMN	OF	TAILINGS	ΒY	NATURAL	RAINFALL	OVER
64 DAYS	s.*					



The movement of K through the 80 cm of tailings was also rapid, with K detected in leachate in significant concentrations from day 7. The recovery by the end of the trial was 65% with the leaching of K continuing. There appeared to be a small amount of K retained by the tailings.

Boron did not appear in leachate in any quantity until day ll and by day 29, concentrations were below the detection limit (0.1 ppm). Available B could not be detected in the tailings either before or after leaching.

Phosphorus was not detected in leachate. The soil analyses show an increase of between 70 and 80 ppm of total P after fertiliser addition and leaching, an increase much too high for the amount of P added. There was also a small increase in Availabe P.

4.3.4 Discussion and Conclusions

Nitrogen was added as NH4 and the majority was recovered as NO2 and NO3, thus nitrification occurred. The pattern of release, NO2 before NO3 supports this. Whether nitrifying bacteria were present in the tailings in the river system or whether the tailings were inoculated during the trial is open to conjecture. Regardless, nitrifiers were able to rapidly multiply and function in the tailings. Similar leaching of NO2 and NO3 was found by Wright & Catchpole (1985).

Although 45% of the applied N was not recovered it is doubtful if a significant proportion of it would have remained available to plants. Other losses could have resulted from N loss and immobilisation by volatisation after reaction with the alkaline sediment, algal and microbial activity, and dilution by rainfall and failing to make detection limits. Some  $NH_4$  may have been retained on the exchange sites, although the low CEC (1.7 me%) suggests that it would be of minor importance to plant nutrition.

The rapidity with which the majority of the N passed through the tailings (80 cm in less than 35 days) points to the disadvantage of applying large amounts of N fertiliser at sowing because the majority was leached before the plants could utilise it.

Inaccuracies in the recovery of applied K may have been introduced due to concentrations of background K in the leachate. However, a large proportion of the applied K was leached from the system. Although some of the applied K may have ended up on exchange sites, again there is little justification for adding soluble K fertiliser to coarse, low CEC mine wastes, at the time of sowing.

Significant leaching of the Solubor did not occur. Solubor is extremely water soluble and at a high pH it is rapidly converted in the soil into B-forms that exist in the soil such as Ca-borate (Finck, 1982). P leaching from the alkaline tailings was not apparent. A significant proportion of the applied P may have been converted to insoluble Ca-phosphates. The addition of 47 kg/ha of soluble P only slightly increased available P and at 3 to 3.5 ppm, P deficiency would still be of concern. Thus much larger additions may be required before a sufficient labile pool is established.

In conclusion, the rapid leaching of soluble N and K fertiliser salts from coarse, low CEC mine wastes under the very high rainfall conditions at Bougainville has been confirmed. In addition, fresh tailings are such that effective nitrification of NH4 will result. To optimise fertiliser use, care will be required in selecting the type, rate and frequency of application of fertiliser.