

# A PRELIMINARY ASSESSMENT OF REMEDIATED SULFIDIC WASTE ROCK USING TERRA B™<sup>1</sup>

Greg Maddocks<sup>2</sup>

**Abstract** Terra B™ is chemically and physically modified red mud (waste residue from alumina refineries) and has been used in this study as an in-situ soil ameliorant to neutralize soil acidity, immobilize metals and allow simultaneous growth of trees in acid metal contaminated waste rock. Terra B™ + biosolids are compared with lime + biosolids and clay capping against a control in 4 x 400 m<sup>2</sup> plots. The Terra B™ + biosolids and lime + biosolids were mixed into the top 50 cm of the waste rock dump using an excavator. All amendments and waste rock was characterized chemically at the beginning of the study. 25 x *Eucalyptus microcorys* (Tallowwood), 25 x *E. resinifera* (Red Mahogany), 25 x *E. paniculate* (Narrow Leaved Grey Ironbark) and 25 x *E. grandis* (Flooded Gum) were planted in each plot as seedlings in December 2001.

After 15 months leachate was collected from lysimeters 50 cm below the amended soil profile. Leachate pH in the control has become increasingly acidic (pH ≈ 4.5 to pH 4). Whereas lime has failed to neutralize sub-soil acidity after 15 months (leachate pH ≈ 5), in the Terra B™ plot sub-soil acidity has been neutralized below the amended profile (leachate pH ≈ 7). After 15 months average heavy metal leachate concentrations (mg / L) in the lysimeters for Al, Cd, Cu, Mn and Zn were (control: 45.9, 5.7, 12.4, 49.3, 123.7), (Terra B™: < 0.1, 0.1, 0.3, 3.4, 13.1) and (lime: 6.5, 2.4, 4.4, 8.2, 56.2). In the clay-capping plot no leachate has been collected showing that the clay cap is fulfilling its purpose of restricting infiltration.

Statistically comparative tree growth has occurred in the Terra B™, lime and clay plots after 15 months. The average height (cm) of *E. microcorys*, *E. resinifera*, *E. paniculate* and *E. grandis* in the control, Terra B™, lime and clay plots was (control: 18, 20, 21, 20), (Terra B™: 80, 90, 80, 110) and (lime: 80, 80, 100, 120) and (clay: 90, 60, 90, 90).

Additional Keywords; red mud, lime, biosolids, revegetation, spoil, in-situ, immobilization, stabilization, eucalypt.

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## **Introduction**

In open cut operations, waste rock dumps constitute the largest volume of material that must be stabilized and remediated at mine sites (Bell, 1999; Lefebvre et al., 2001) and are often the hardest to remediate because of their chemical and physical properties (Kuhn, 1999; Tordof et al., 2000; Lefebvre et al., 2001). Acidic metal contaminated waste rock (spoil) has traditionally been dealt with utilizing encapsulation with saturated, dry or oxygen consuming covers, the generation of hardpans, the addition of bactericides or more recently chemical stabilization utilizing readily available chemicals or by-products from industrial, municipal and agricultural enterprises (Tordof et al., 2000) such as lime (Davis et al., 1999), gypsum, organic matter, biosolids, fly ash, and zeolites (Bengson and Thompson, 1998; Brown et al., 2000; Cox and Whelan, 2000; Gorman et al., 2000).

In the majority of cases the use of covers is generally ineffective, particularly in regions with extreme climatic variables (Parker and Robertson, 1999). It is also acknowledged that remediating acidic spoil with topsoil, clay capping and liming does work in the short to medium term but does not solve problems associated with long-term acid generation and ecosystem sustainability (Robson, 1989; Derome and Saarsalmi, 1999; Friesl et al., 1999; Pierzynski, 1999; Vangronsveld et al., 1999). The addition of lime to acid spoil is a common method used to increase soil pH and immobilize heavy metals like Cd, Zn, Cu and Ni through the formation of sparingly insoluble hydroxides (Khan et al., 2000), however when the pH of the soil decreases the metal complexes may be destabilized and the metal ions will be released into the environment (Gabler, 1996; Kramer et al., 1998; Schuiling, 1998).

At derelict and operational mines in-situ remediation is gaining increased acceptance as an economic and sound alternative to encapsulation, is a preferential management strategy (Vangronsveld et al., 1999) and is becoming increasingly accepted by regulatory authorities and mining operators (Bengson and Thompson, 1998; Bradshaw, 2000; Brown et al., 2000; Pierzynski et al., 2000). In addition to neutralizing soil acidity and immobilizing metals, suitable industrial, municipal or agricultural by-products can enhance the physical properties of the spoil (Tordof et al., 2000), reduce adverse environmental impacts associated with the treatment or containment of the by-products (Pierzynski, 1999) and reduce costs associated with topsoil harvesting (Bell, 1999; Mickle et al., 1999; Bradshaw, 2000). In general the inadequacy of this

technique is that only the area in contact with the ameliorants might be treated, therefore the effectiveness of these methods is limited by the application technique. Historic or abandoned waste rock dumps are often five to tens of metres in depth and it is only possible to incorporate the amendments to a depth of half to one and a half metres using large bulldozers fitted with rippers, unless large excavators are used. To capitalize on in-situ applications an amendment is needed that will not only neutralize acid and bind contaminants in the treated zone, but one that can treat contaminated material well below the application depth.

The aim of this study was to test the application of Terra B™ as an in-situ ameliorant for the simultaneous remediation and revegetation of acid spoil. Terra B™ is physically and chemically altered red mud; a ferruginous waste residue produced during the refinement of alumina from bauxite. When it is produced by the Bayer process, red mud is caustic with an  $\approx$  pH 13, however when red mud is converted to Terra B™ the pH is reduced to  $\approx$  9.0 (Mc Conchie et al, 2002). Terra B™ has an acid neutralizing capacity (ANC) of 2.75 - 3.75 mol / kg and is composed primarily of hematite, has abundant boehmite, cancrinite, gibbsite, quartz, sodalite and has lesser amounts of anhydrite / gypsum, aragonite, brucite, calcite, hydrocalumite, hydrotalcite, p-aluminohydrocalcite, whewellite and portlandite (Apak et al., 1997; Mc Conchie et al., 2002). The chemical and physical properties of Terra B™ have been tested extensively in the laboratory and are similar in many respects to that of red mud. Previous studies have demonstrated that red mud (Lombi et al., 2002; Doye and Duchesne, 2003) and Terra B™ (Lin et al., 2002b) can bind heavy metals and neutralize acidity in soil. Other studies have found that red mud will retain P (Summers, 1996) in soil and heavy metals in aqueous solutions (Apak et al., 1997; Altundogan et al., 2000; Gupta et al., 2001; Hanahan, 2001; Kadirvelu et al., 2001). The study was also designed to compare the use of Terra B™ technology for in-situ remediation with commonly used techniques for waste rock dump remediation that utilize encapsulation (clay capping + topsoil) or to lesser degree in-situ stabilization using lime + biosolids.

The objectives of the study included a detailed preliminary assessment of the soil chemistry at the site to calculate the required mass of amendments for complete soil remediation. Further objectives included the construction of four plots over 1600m<sup>2</sup> and the construction and installation of in-situ lysimeters to collect soil leachate for the analysis of heavy metal and salt concentrations after each rainfall event. Surface soil analysis was conducted at 0 months and will be undertaken again at 18 and 36 months. The growth of four native Australian tree species was

assessed in each plot and included measuring tree mortality and tree growth every three months. The study commenced in December 2001 and will go for three years.

## **Methodology**

### **Study area**

The study site lies within the Plumbago catchment near Drake in New South Wales, Australia and is dominated by dry sclerophyll forest. The climate is cool to subtropical and rainfall is relatively high, averaging over 1200 mm / yr. Due to an ongoing drought there was less than 500 mm of rainfall in the first 12 months of the study. The study site is a section of an acid spoil, haul road verge developed on top of the existing natural landform between 1988 and 1990. Revegetation was attempted in 1992 but failed and the site was 100% devoid of plant life at the beginning of the study (Fig. 1).



Figure 1. The study site before remediation and construction of the plots (right) and the typical batter of the study area.

The study site is  $\approx$  800 m in length, 15 - 30 m wide and between 2 and 4 m in depth. The spoil at the site has high concentrations of metals, is extremely acidic and has very low permeability. The spoil contains pyrite, chalcopyrite, sphalerite other sulfide minerals and associated gangue material such as siderite and jasper. The structure and composition of the material is highly heterogenous and anisotropic. Because drainage from the study site affects the water quality of the catchment, remediation of this site would improve water quality by

neutralizing soil acidity, reducing or halting the translocation of soluble and readily exchangeable metal species and decreasing further erosion and sediment transport at the site.

Four x 10 m wide x 40 m long plots were prepared on the haul road and included a control, a Terra B™ + biosolids plot, a lime + biosolids plot and a plot remediated using 30 cm of compacted clay capping and 10 cm of topsoil. Each of the plots was contained within a compacted earthen wall 3 m in width and 1 m in height to stop the transfer of ameliorants between treatments and to satisfy regulatory authorities. All plots were initially ripped to a depth of 50 cm using a 20 tonne excavator fitted with a single ripping tine. The control plot had lysimeters constructed at 100 cm, was backfilled and was planted with trees. Addition of the Terra B™ (Fig. 2) and lime to the waste rock was done to bring soil pH to  $\approx 7$  and required the addition of 25 kg of Terra B™ / m<sup>2</sup> and 2.5 kg of lime added as CaOH<sub>2</sub> / m<sup>2</sup>.



Figure 2. Application of the Terra B™ and biosolids to the plot.

The application rates for Terra B™ and lime were based on the acid neutralizing capacity (ANC) of the ameliorants, and by measuring total actual acidity (TAA) and total potential acidity (TPA) from four x 2 kg samples collected from each plot. Application rates were based on the lime and Terra B™ being able to neutralize all TAA + TPA. The application rates for the biosolids from the South Lismore Sludge Lagoon were based on the NSW EPA maximum

allowable one off application rate of 1200 kg Total Nitrogen (TN) / ha (Section 4.1.2; (EPA, 1999) and equated to an application of  $\approx 15 \text{ kg} / \text{m}^2$  (wet weight).

Three zero tension in-situ lysimeters with a 5 L capacity were installed in each plot, to collect soil leachate as it passed through the soil profile. Installation of the lysimeters occurred at a depth of 100 cm; that is 50 cm below the amended soil profile. The Terra B<sup>TM</sup> was mixed with the biosolids, applied to the surface of the plot then mixed into the profile to a depth of  $\approx 50 \text{ cm}$  with the excavator. In the lime plot, the lime was applied and mixed to a depth of  $\approx 50 \text{ cm}$  using the excavator. The biosolids were then applied and mixed into the profile using a backhoe after the incorporation of the lime (this was due to financial constraints and ideally application of soil ameliorants in the Terra B<sup>TM</sup> and lime plots would have been undertaken in the same manner). The preparation of the clay-capping plot included ripping to 50 cm to initiate similar conditions to the other plots. After installation of the lysimeters, oxide clay material was applied to the surface of the plot and compacted using “tracking” with the excavator to achieve a 30 cm deep compacted layer. 10 cm of topsoil was then added on top of the compacted clay. 25 x *Eucalyptus microcorys* (Tallowwood), 25 x *E. resinifera* (Red Mahogany), 25 x *E. paniculate* (Narrow Leaved Grey Ironbark) and 25 x *E. grandis* (Flooded Gum) were planted at random in five rows, in each plot, as seedlings in late December 2001. The seedlings were nursery stock and were between 30 - 40 cm in height when planted

#### Laboratory analysis

The soil collected for TAA and TPA analysis contained rock of less than 20 mm in diameter. The soil was roughly crushed and dried in an oven for 48 hours at 70°C. The dried soil was further crushed and sieved to retain the less than 2 mm soil fraction. This soil was then measured for water-soluble pH by adding 5 g of sieved soil with 25 mL of Milli-Q (double de-ionized) water in a 50 mL centrifuge tube. The soil was tumbled at 30 RPM for 5 minutes and pH and electrical conductivity (EC) were measured using a TPS W81 electronic meter. TAA was calculated on the soil samples using methods by (Lin et al., 2002a). TPA (as %S) was measured using the Chromium Reducible method (CRS) (Sullivan et al., 1999).

Water was collected from the lysimeters using a peristaltic pump when rainfall was adequate to allow infiltration of water through the soil profile. Water samples were measured for pH and EC immediately after collection using a calibrated TPS W81 electronic meter. Water samples collected for heavy metal analysis were filtered to 0.45 $\mu\text{m}$  and acidified with nitric acid

to below pH 2. Water samples collected for salt analysis were filtered to 0.45µm. All water samples were frozen until analysis at the laboratory.

TN and total carbon (TC) concentrations in the waste rock and biosolids were determined by Inductive Combustion and Infrared Gas Analysis (LECO™ CNS 2000). Phosphate (P), nitrate (NO<sub>3</sub><sup>-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>) were determined using a 1 : 10 - 1M KCl - 1 hour tumble, and analysis with a Lachat QuikChem 8000 Flow Injection Nutrient Analyser. Exchangeable cations, sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), chloride (Cl) and sulphate (SO<sub>4</sub><sup>+</sup>) were determined using 1: 5- 1M Ammonium acetate - 1 hour tumble and analysis with a Varian Automated Fast Sequential 2000 Atomic Absorption Spectrophotometer (AAS).

Concentrations of heavy metals in all solids were determined using a sequential extraction method (Tessier et al., 1979) adapted with the addition of 0.01 M CaCl<sub>2</sub> at the beginning of the process (ASEP). 0.01 M CaCl<sub>2</sub> has been found to correlate well with plant uptake (Becket, 1989 in McLaughlin et al., 2000) and has been to be especially effective in determining plant availability for Eucalypt species (Reichman, 2000) and was added at the beginning of the ASEP to measure plant available fractions. EC of all solid materials was determined using a 1 : 5 - Milli-Q - 1 hour tumble and measurement with a TPS W81 electronic meter.

Table 1. Methodology used to determine the operationally defined fractions of heavy metals in all solids in this study. Sample mass was 2 grams sieved to less than 1 mm.

Operationally defined fraction	Extractant	Volume	Time	Temp.°C
Plant available	0.01 M CaCl <sub>2</sub>	20 mL	1 hour	25
Exchangeable	1 M MgCl <sub>2</sub>	20 mL	1 hour	25
Carbonate	1 M NaOAc buffered to pH 5 with HOAc	20 mL	5 hour	25
Fe /Mn Oxides	0.04M HO.NH <sub>3</sub> Cl in 25% v/v HOAc	20 mL	5 hour	85
Organic / sulfide	0.1 mL of HNO <sub>3</sub> + 9.9 mL of 32% H <sub>2</sub> O <sub>2</sub> digested at 85°C for 3 hours followed by another 10mL of 32% H <sub>2</sub> O <sub>2</sub> for 2 hours	20 mL	5 hour	85
Residual	5ml of HNO <sub>3</sub> + 15 mL of 32% HCl	20 mL	1 hour	85

The pH of Terra B™ was determined by mixing 5 g of solids with 25 mL of water and tumbling at 30 RPM for 4 hours. A longer reaction time is required for Terra B™ because of the

low solubility of the alkaline minerals. The acid neutralizing capacity (ANC) of the Terra B™ was determined by mixing 1 g of Terra B™ (sieved to < 710 µm) with 50 mL of 0.05 M H<sub>2</sub>SO<sub>4</sub> and allowing it to react for 120 hours. After 120 hours the solution was titrated with 0.05 M NaOH<sub>2</sub> to pH 5.5 until a stable end point was reached. Leachable alkalinity expressed as mg L<sup>-1</sup> CaCO<sub>3</sub>, was determined by mixing 5 g of Terra B™ with 25 mL of Milli-Q water. The solution was then titrated with 0.01 M H<sub>2</sub>SO<sub>4</sub> to pH 4.3 to determine hydroxide, carbonate and total alkalinity. All biosolid, Terra B™ and waste rock data is listed in Tables 2, 3 and 4 respectively. The operationally defined fractions of heavy metals in the four plots were measured, from the samples collected for the determination of soil pH, TAA and TPA, before the addition of the soil ameliorants using the ASEP.

A Perkin Elmer Optima 4300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used to measure all heavy metal concentrations from aqueous and solid samples. All analysis was conducted at the Environmental Analysis Laboratory, Southern Cross University, Australia. The Environmental Analysis Laboratory is a commercial laboratory and follows strict QA and QC guidelines and is nationally accredited.

## **Results**

### **Solids analysis**

**Biosolids.** The biosolids were anaerobically digested and have been stored at South Lismore in a wet pond for approximately 10 years. The biosolids are suitable for agriculture, forestry, soil and site rehabilitation, landfill and surface land disposal (EPA, 1999). Summarized average concentrations are in Table 2. The biosolids used in this study are characterized by high concentrations of heavy metals however the bulk of the metals present are bound as relatively immobile and hence non-bioavailable fractions.

**Terra B™.** The Terra B™ used in this study (Table 3) has a reaction pH of 10.19 and an ANC of 3.35 mol / kg. This material has high EC due to the high concentrations of Na and Cl that are held within the interstitial pore spaces and are a result of the Bayer refinery process and seawater neutralization.

Waste rock analysis. The results in table 4 show that there is a high degree of variability in the 20 samples taken from the study site and is not uncommon in waste rock dumps that are known to exhibit a high degree of heterogeneity. Soil pH ranged from 2.97 to 6.14 and had an average concentration of 4.17. An average TAA concentration of  $\approx 86$  mmol / kg indicates a high proportion of actual acidity however the high standard deviation also shows a high degree of variability with a maximum concentration of 142 mmol / kg and a low of 41 mmol / kg. The high average CRS concentration of 0.85 % indicates a high proportion of non-oxidized sulfide minerals and demonstrates the potential for long-term acid generation and the release of heavy metals from the site. The low concentrations of TC and TN indicate that the germination and subsequent growth of vegetation in this soil media is limited and would be a major limiting factor in long-term sustainability. There was also a poor infiltration of rainfall at the site, prior to ripping, due to high surface strength. During prolonged dry periods patches of efflorescent salts formed on the surface of the study area (pers.comm. Scutts, 2003).

#### Leachate analysis

Since the start of this study in December 2001 there has been very little rain and Australia is in the grip of a drought that is recognized, at present, as the worst in 100 years and may be the worst in 500 years. The tree seedlings were planted in the four plots on the 24<sup>th</sup> December 2001 during a heat wave with 42°C + days that persisted for five weeks. During this time the seedlings were watered by hand every 3 days for 2 weeks; receiving about 5 L of water on each occasion. Since the study commenced there has only been adequate rainfall (50 – 100 mm) on three occasions to allow infiltration of water through the profile into the lysimeters. The total rainfall from the 24<sup>th</sup> December 2001 until the 1<sup>st</sup> January 2003 has been 499.1 mm; for the same period rainfall should be in the vicinity of 1200 mm. The drought conditions of 2002 appear to have broken with 321.9 mm of rainfall between the 1<sup>st</sup> January 2003 and the 1<sup>st</sup> of March 2003; which is approaching typical rainfall.

Leachate pH and EC. The data in figure 3 shows that leachate from the lysimeters dropped from  $\approx$  pH 4.5 to  $\approx$  4 in the control and dropped from  $\approx$  5.5 to  $\approx$  5 in the lime plot whereas the leachate in the Terra B™ plot has remained constant at  $\approx$  pH 7. EC in all three plots has shown a steady

Table 2. Operationally defined fractions of heavy metals, pH, EC, nutrient and salt concentrations in the biosolids from Lismore sewage treatment plant. All concentrations are in mg / kg unless stated otherwise.

Biosolids														
	Al		Cd		Cu		Fe		Mn		Pb		Zn	
	Av	St. Dev.	Av	St. Dev.	Av	St. Dev.	Av	St. Dev.	Av	St. Dev.	Av	St. Dev.	Av	St. Dev.
Plant Avl.	0.43	0.05	0.18	0.02	0.78	0.06	0.12	0.00	13.83	1.23	0.18	0.18	13.80	0.75
Exbl.	0.58	0.03	0.35	0.02	0.45	0.02	0.10	0.01	15.73	1.00	0.64	0.03	17.73	1.31
Carbonate	226.17	136.39	1.86	0.04	0.95	0.04	0.18	0.03	24.03	1.05	0.95	0.35	28.33	3.03
Fe / Mn	320.30	138.67	3.57	0.81	43.28	2.33	78.55	1.03	122.03	16.70	13.09	2.75	179.83	17.00
Organic	1638.33	161.66	2.95	0.10	2.95	0.35	3625.00	48.22	285.33	17.57	15.80	2.79	241.00	10.50
Aqua regia	12366.67	292.97	1.43	0.38	169.67	0.76	11483.33	1050.40	102.17	20.05	85.00	7.86	153.17	59.64
TOTAL	14646.60	445.29	10.34	1.67	218.08	4.99	15187.29	1094.49	563.13	70.79	115.66	15.49	633.87	89.35
					Av	St. Dev.							Av	St. Dev.
Soil pH (1:5 Milli-Q)					6.75	0.78			Total Phosphorus				26.60	1.35
Soil Conductivity (1:5 water mS / cm )					2.17	0.35			Phosphate				1.13	0.15
Total Nitrogen (%N)					1.60	0.05			Nitrate				5.28	0.03
Total Carbon (%C)					12.99	1.26			Ammonia				852.94	76.34

Table 3. pH, EC, exchangeable salts, ANC and alkalinity concentrations of the Terra B™. All concentrations are in mg / kg unless stated otherwise.

Terra-B™			
Soil pH (1:5 Milli-Q)	10.19	Alaklinity mg / L OH <sup>-</sup>	3.11
Soil Conductivity (1:5 water dS/m)	3.59	Alaklinity mg / L CO <sub>3</sub> <sup>-2</sup>	4339.84
Acid neutralising capacity mol / kg	3.35	Alaklinity mg / L HCO <sub>3</sub> <sup>-</sup>	3611.45
Alaklinity mg / L CaCO <sub>3</sub>	10289.21		
Na	3685.00	Mg	0.03
K	32.70	Cl	2745.53
Ca	0.77	S	685.00

Table 4. Operationally defined fractions of heavy metals, pH, EC, nutrient, TC, TS and TAA concentrations in the soil and waste rock from the haul road verge before remediation. All concentrations are in mg / kg unless stated otherwise.

Haul road verge waste rock								
	Al		Cd		Cu		Pb	
	Av	St. Dev.	Av	St. Dev.	Av	St. Dev.	Av	St. Dev.
Soluble	44.69	127.74	1.81	1.87	12.41	16.32	0.89	1.79
Exbl.	16.03	33.91	4.78	3.18	9.05	9.15	2.16	3.11
Carbonate	51.36	44.31	1.57	1.25	8.78	10.23	19.40	28.28
Oxide	28.14	17.46	1.42	1.41	18.82	12.88	28.32	20.99
Organic	242.38	203.19	2.11	2.59	94.09	72.27	263.13	194.90
Residual	5768.33	1277.70	3.25	0.92	197.92	105.38	284.92	101.07
TOTAL	6159.87	1168.88	15.30	4.25	343.55	167.39	598.99	281.17
	Fe		Mn		Zn			
	Av	St. Dev.	Av	St. Dev.	Av	St. Dev.		
Soluble	64.74	215.92	23.36	26.04	30.36	32.44		
Exbl.	7.69	17.39	30.60	18.03	58.48	41.90		
Carbonate	5.92	8.21	19.57	21.06	36.66	44.43		
Oxide	8.90	9.03	18.73	7.59	40.71	42.30		
Organic	3527.50	1610.22	348.15	364.25	193.43	161.43		
Residual	20387.50	2104.99	202.67	70.96	444.17	138.98		
TOTAL	24015.19	2284.44	647.75	400.32	809.87	234.37		
				Av	St. Dev.			
Soil pH (1:5 Milli-Q)				4.17	0.98			
Soil Conductivity (1:5 water mS / cm)				0.52	0.57			
Phosphate				0.24	0.02			
Total Nitrogen (%N)				< 0.01	< 0.01			
Total Carbon (%C)				0.14	<0.01			
Sulphur CRS (%)				0.85	0.69			
Total Actual Acidity (mmol / kg)				86.33	25.03			

decline over the duration of the study from  $\approx 3$  mS / cm to  $\approx 1.8$  mS / cm in the control plot,  $\approx 8.7$  mS / cm to  $\approx 3$  mS / cm in the Terra B™ plot and  $3.7$  mS cm<sup>-1</sup> to  $\approx 2$  mS / cm in the lime plot (Fig. 3).

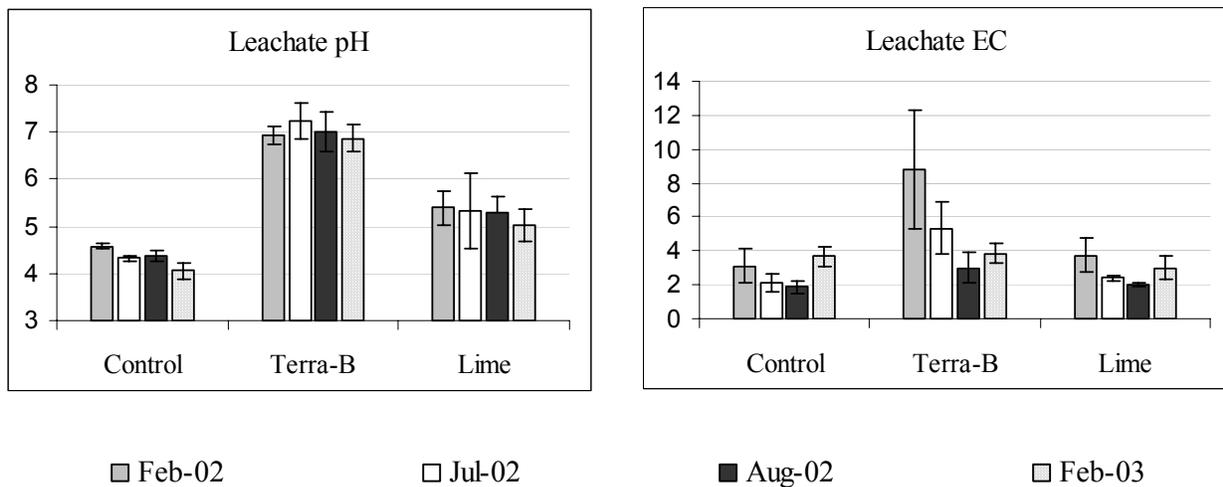


Figure 3. Leachate pH and EC concentrations from the control, Terra B™ and lime plots. Leachate concentrations are on the “y” axis in pH units for pH and mS / cm for EC. The Control, Terra B™ and Lime plots are labeled on the “x” axis. The four sampling periods are indicated by the legend at the base of the figure.

Leachate salts. Lime contributes to the greatest concentrations of Ca whereas Terra B™ contributes to high concentrations of Na and Cl in the leachate (Fig. 4). The leachate Mg data shows that Mg is being retained in the soil profile by the Terra B™ and lime treatments whereas Mg is leaching in increasing concentrations from the control. There is no discernable difference in K leachate concentrations. Sulfate concentrations in the control continue to increase over time whereas there is a steady decline in sulfate concentrations in the Terra B™ and lime treatments. Terra B™ contributes to high Cl concentrations, but the Cl is being leached from the soil profile over time and is reaching concentrations similar to that in the lime and control plots (Fig. 4).

Leachate metals. Heavy metal concentrations in the leachate from the plots show a very clear pattern. In the control plot concentrations of all metals, except Fe, are increasing over time (Fig. 5). The addition of Terra B™ has had a significant effect on all metals and at 15 months the average concentrations (mg / L) are Al (< 0.05), Cd (0.08), Cu (0.34), Fe (< 0.05), Mn (3.39), Pb (< 0.05) and Zn (13.09). Whereas the addition of lime had an initial effect on decreasing metal concentrations metal concentrations in the lime plot continue to increase over time (Fig. 5).

Statistical analysis by SPSS: Tree mortality. Statistical analysis using Chi-square tests shows that for Tallowood 49% of all trees in the four treatments were dead at 15 months (Fig. 6). Using Fishers exact test the rate of mortality was found to differ significantly between treatments ( $p = 0.00$ ). Whereas 32 – 40% of the trees in the control (40%), lime (32%) and clay capping plots (32%) died, 92% of this species died in the Terra B™ treatment after 15 months. For Red

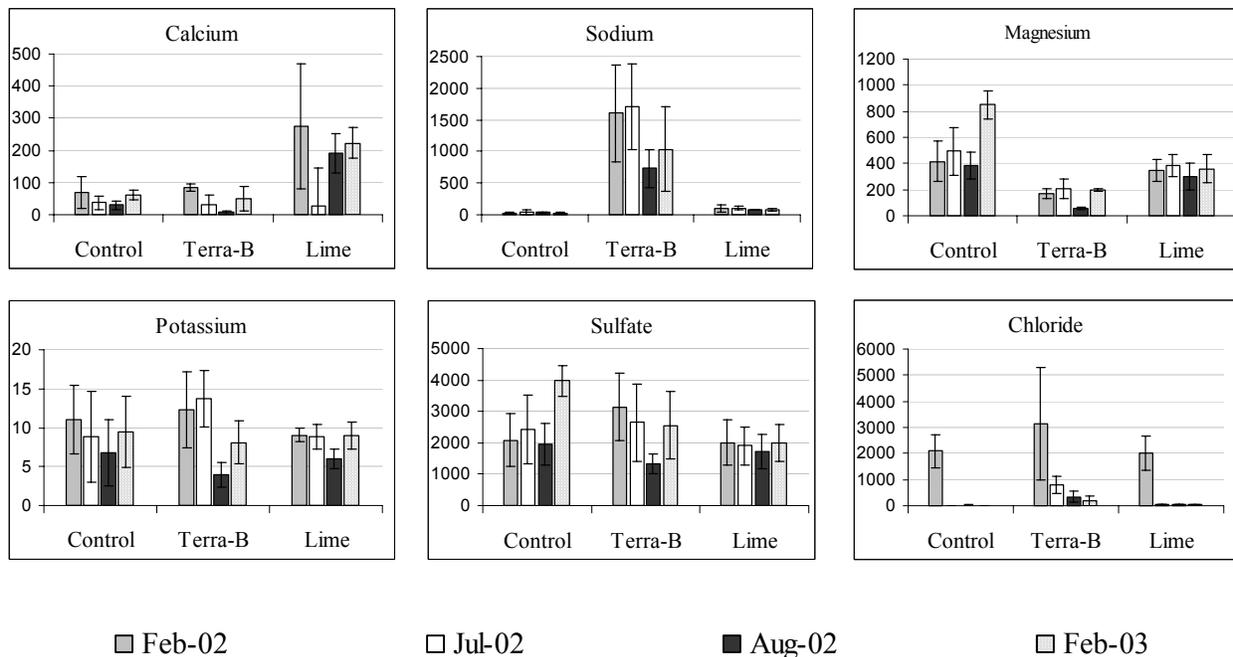


Figure 4. Leachate salt concentrations in the control, Terra B™ and lime plots. Leachate concentrations are on the “y” axis in mg / L. The Control, Terra B™ and Lime plots are labeled on the “x” axis. The four sampling periods are indicated by the legend at the base of the figure.

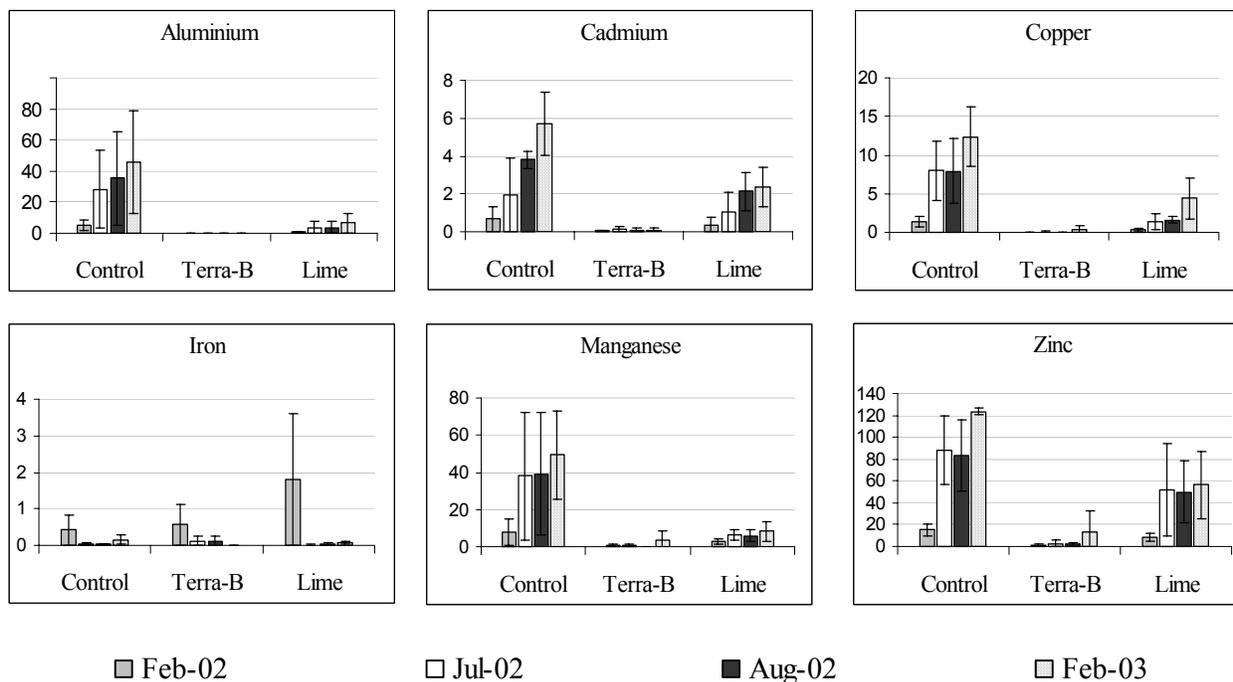


Figure 5. Al, Cd, Cu, Fe, Mn, and Zn concentrations in the leachate from the control, Terra B™ and lime plots. Leachate concentrations are on the “y” axis in mg / L. The Control, Terra B™ and Lime plots are labeled on the “x” axis. The four sampling periods are indicated by the legend at the base of the figure.

Mahogany 46% of all trees in the four treatments were dead at 15 months. Using Fishers exact test the rate of mortality was found not to differ significantly between treatments ( $p = 0.62$ ) indicating that mortality between treatments for this species was insignificant. For Grey Ironbark 23% of all trees in the four treatments were dead at 15 months. Using Fishers exact test the rate of mortality was found to differ between treatments ( $p = 0.051$ ). Whereas 12 – 20% of the trees in the control (20%), Terra B™ (12%) and lime plots (20%) died, 44% of this species had died in the clay capping treatment after 15 months. For Flooded Gum 38% of all trees in the four treatments were dead at 15 months. Using Fishers exact test the rate of mortality was found to differ significantly between treatments ( $p = 0.008$ ). Whereas 40 – 56% of the trees in the control (40%), lime (44%) and clay capping plots (56%) died, only 12% of this species died in the Terra B™ treatment after 15 months.

Statistical analysis by SPSS: Tree Growth (height cm). A two-way, between-groups ANOVA found the treatment by species interaction to be non-significant ( $F = 1.17$ ,  $df = 9$ ,  $p = 0.318$ ). This indicates that the effect of treatment does not differ between species. The model was re-fitted without the interaction effect. The results show a significant effect on tree growth, due to the treatment type ( $F = 43.69$ ,  $df = 3$ ,  $p = 0.00$ ), and for individual species within treatments ( $F = 3.43$ ,  $df = 3$ ,  $p = 0.018$ ). Tukey's post hoc tests identified that the following pairs of treatments differed significantly. The tree growth in the control ( $M = 195.08$ ,  $SD = 115.72$ ) differed significantly to the Terra B™ ( $M = 926.93$ ,  $SD = 600.63$ ), lime ( $M = 973.77$ ,  $SD = 457.95$ ) and clay treatments ( $M = 800.89$ ,  $SD = 311.08$ ). There was no significant difference in tree growth for the other treatments (Fig. 7).

## **Discussion**

The major problem with mine site waste dumps is the pollution of surface and groundwater by soluble solids leached from the waste (Rybicka, 1996). As metals become dissociated from the parent material or soil media they can form soluble, efflorescent salts, may be translocated as adsorbed soil constituents or transported in solution (Parker and Robertson, 1999). Soluble salts such as chalcantite, jarosite, and halotrichite form by the evaporation of acid waters during dry periods. Acidity and metals, formerly contained in AMD are stored in the salts, which may dissolve when exposed to rain and flowing surface waters (Lee, 1999; Parker and Robertson,

1999). Due to these processes and the subsequent translocation of contaminants the study site is an environmental liability. To complete remediation of the site, it is necessary to neutralize soil

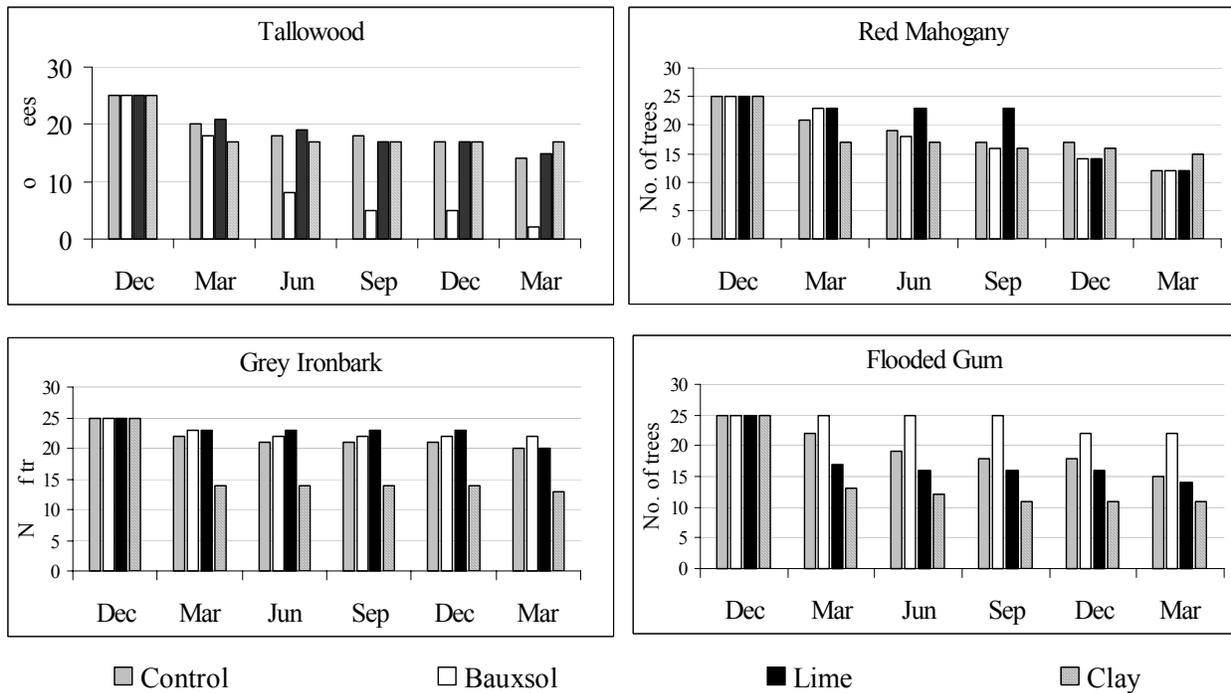


Figure 6. Tree mortality for Tallowood, Red Mahogany, Narrow Leaved Grey Ironbark and Flooded Gum from December 2001 to March 2003.

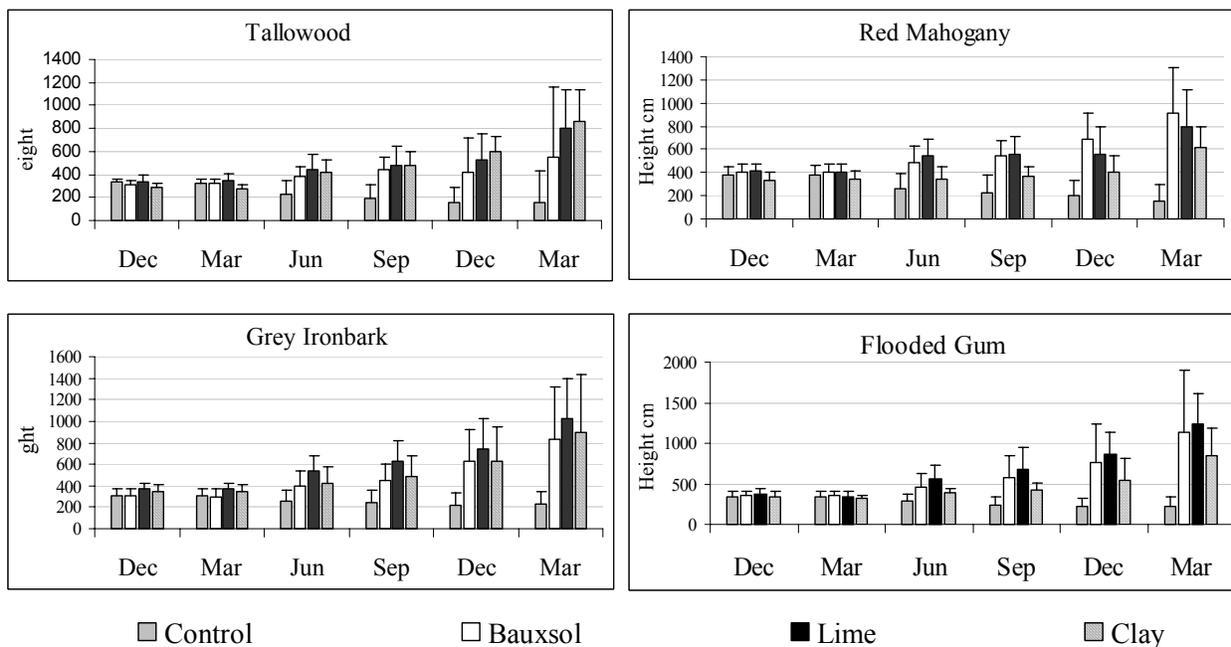


Figure 7. Tree growth for the Eucalypt species over 15 months. This figure shows average tree height for each species in each plot every three months. The upper standard error shows the maximum height of the trees in that species.

acidity and to immobilize metals. To undertake revegetation of the remediated spoil it is necessary to create a sustainable soil profile that is suitable for the establishment of, and long term sustainability of plant growth. While this three year study has only been underway for 15 months some patterns have emerged.

### The control plot

Leachate pH (Fig. 3) has decreased over the four sampling events and is due to the ripping of the haul road, which exposed secondary precipitates held within the voids of the spoil and also fractured consolidated waste rock and unconsolidated spoil, thereby increasing the surface area of sulfide material to oxidation. The increase in acidity being released from the waste rock is likely to continue until oxygen diffusion and advection is reduced within the soil profile due to blocking of preferential pathways by fines and clay minerals. In the control plot there was an initial decrease in EC due to the release of chloride (Fig. 4). Over the subsequent leaching events the main components contributing to increases in leachate EC are sulfate, due to the dissolution of secondary precipitate salts, the oxidation of primary sulfide minerals and the increase in magnesium being released from the spoil. Increases in Mg in the leachate may be due to cation exchange between Mg and the increased mass of mobilized metals.

The results from the leachate data show that the concentration of soluble metals is increasing in the control (Fig. 5). This is due again to the dissolution of secondary precipitate salts that were held within voids of the profile after ripping, and the oxidation of exposed sulfide minerals (Parker and Robertson, 1999). The release of soluble metals to the environment will continue but should reach a steady state condition over time as equilibrium processes come into effect, either through reformation of secondary precipitates in the profile or through filling of voids by clay minerals.

In the control plot tree growth has essentially failed (Fig. 6, 7 and 8). Whereas the mortality of the trees has been quite low, tree growth has suffered and may be due primarily to the effects of Al, Cu and Mn toxicity. Aluminum toxicity is however likely to be the most inhibitory element for plant growth in the initial stages of development as it that interferes with cell division in root tips and lateral roots, the uptake of water and nutrients (Rout et al., 2001), increases cell wall rigidity, reduces DNA replication, reduces root respiration, interferes with enzymes and nutrient assimilation and fixes P in less bioavailable forms (Robert, 1995; Pan et al., 2001; Rout et al., 2001). There is a paucity of information on Al toxicity in Eucalypts

however the literature indicates that root tip death and inhibited root development is a common effect of  $Al^{3+}$  (Ma et al., 2001; Pan et al., 2001). Plant growth is not likely to improve due to the high TAA and TPA causing ongoing acid generation and metal toxicity. This is evident in previous failed revegetation attempts at the site.



Figure 8. The control plot after 12 months.

### The Terra B™ plot

Statistical analysis shows differences in tree growth due to the treatments. The addition of Terra B™ has allowed good tree growth in this study compared to the control but there is no statistical difference for the lime and clay plots. Terra B™ has bound mobile metal species as immobile forms and neutralized surface and sub-soil-acidity. The data in figure 3 shows that the addition of Terra B™ to the spoil has increased leachate pH to  $\approx 7$  indicating that Terra B™ has the capacity to not only neutralize surface soil acidity but neutralizes sub-soil acidity and has the capacity to do so for much longer than lime. This is based on the fact that the lysimeters collecting leachate are 50 cm below the amended soil profile; soluble acid has been neutralized in this 50 cm profile by the actions of Terra B™. This offers distinct advantages over lime, that generally fails to neutralize sub-soil acidity (Liu and Hue, 2001; Tesfaye et al., 2001) and is evident in the leachate data (Fig. 3).

The initial high leachate EC in the Terra B™ plot, is due to the soluble sodium and chloride present in the interstitial pore spaces of the Terra B™, and is a result of the Bayer process and the

neutralization of the caustic red mud by seawater. EC in the Terra B™ plot does decrease with rainfall and subsequent leaching, resulting in EC approaching background concentrations in the control after 15 months. The high EC did not have a visible effect on plant growth and is corroborated by studies using gypsum neutralized red mud in Western Australia (Summers, 2001). The low magnesium concentrations compared to the lime and control plots shows that there may be some retention of magnesium by Terra B™ or that there has been an exchange of magnesium for sodium in the soil profile or with Terra B™ due to cation exchange.

The data demonstrates that the addition of Terra B™ has bound nearly all mobile metals as immobile forms. This has occurred not only in the amended soil zone but at depth well below the amended soil zone (Fig. 5). The immobilization of metals has been so effective that the leachate water is approaching concentrations that would allow its reuse for domestic livestock consumption (ANZECC, 1999). Extensive sequential extraction procedures from other studies have demonstrated that the retention of metals by Terra B™ is very strong, with between 95 – 99.5% of all metals being retained in the carbonate / oxide / organic and residual fractions, and subsection to the US TCLP generally only removing 0.1 - 1 % of all metals bound to Terra B™ (Maddocks and Reichelt-Bruschett, 2003).

Visual observation and statistical analysis of the Terra B™ plot shows it has equal biomass production to the lime plot after 15 months and is not statistically different to the clay plot. The growth and mortality of the four eucalypt species is markedly different to the control and less obvious patterns of growth and mortality can be found in the data.

Tree mortality for the four eucalypt species varies at  $\approx$  92 %, 52 %, 12 % and 12 % for Tallowwood, Red Mahogany, Grey Ironbark and Flooded Gum respectively. Tree mortality does not however correspond with tree growth and biomass production. This is demonstrated by the high mortality – but low variation in Tallowwood growth. Tallowwood suffered high mortality in the Terra B™ plot indicating that this species is particularly sensitive to mildly alkaline soil chemistry and would not be suitable for revegetation using Terra B™ unless a lower target pH was used ( $\text{pH} < 7.5$ ). The average growth of the remaining two trees (while not statistically valid) is similar to that in the lime and clay plots and indicates that the growth of the surviving trees may be due to preferred soil chemistry.



Figure 9. Terra B™ plot at 12 months.

The mortality of Red Mahogany in the Terra B™ plot was 52% but was not statistically different to mortality in the other plots. The average height of this species ( $\approx 90$  cm) was greatest in the Terra B™ plot, was not significantly different to the lime plot (80 cm), but was significantly different to the clay plot (60 cm). This data suggests that because mortality was not statistically different between treatments soil chemistry did not play a significant role in tree death and that mortality for all plots may have been in response to initial planting and the dry conditions over the first 12 months. There was no statistical difference in mortality for Narrow Leaved Grey Ironbark between all treatments and no statistical difference in average tree height of the Terra B™ plot (80 cm), with the clay plot (90 cm), however the average tree growth was below that of the lime plot (100cm). This suggests that soil chemistry has little significant effect on tree growth in the Terra B™, lime and clay plots and that this species is tolerant of mildly alkaline soil chemistry and would be suitable as a species for revegetation using Terra B™.

The highly variable growth of the eucalypts in the Terra B™ plot is attributed mainly to the poor mixing of the Terra B™ + biosolids into the waste rock. Mixing of Terra B™ into the spoil was hindered by the heterogeneous physical nature of the spoil and the machinery that was available to incorporate the Terra B™ to the correct depth (refer to methods). As a result of the poor mixing some trees are growing in  $\approx 50\%$  -  $80\%$  Terra B™; they are growing in mildly alkaline conditions that are not conducive to plant growth due to nutrient deficiency. It is expected that the trees showing poor growth at present will improve in time as their roots

penetrate further into the profile. There is not expected to be further mortality as mortality rates have stabilized over the past 6 months and recent rain should assist in good growth of all surviving trees over the next 4 - 8 weeks.

Theories on Acid neutralization by Terra B™. Acid neutralization is thought to be due to a mixture of carbonate, hydroxide and hydroxycarbonate minerals present in Terra B™ (Mc Conchie et al., 2002) that contribute to a slow release of carbonate and bi-carbonate alkalinity. Hydroxide alkalinity is due to the use of sodium hydroxide in the manufacturing of alumina from bauxite (Hind et al., 1999) and is converted along with soluble carbonate alkalinity to low solubility mineral precipitates during the neutralization of red mud with the Basecon™ process (Hanahan, 2001; Mc Conchie et al., 2002). The low solubility minerals include carbonates (calcite and aragonite), low solubility metal hydroxides (brucite and hydrotalcite) and non-soluble variably charged trivalent metal hydroxides (hematite, boehmite and gibbsite). Each of these alkaline phases may act in different ways to achieve acid neutralization. The author is investigating these processes in another study.

Theories on metal immobilization by Terra B™. In soil there are at least five potential mechanisms that contribute to the immobilization of metalloids by Terra B™. The leaching of alkalinity through the soil profile from hydroxide, carbonate and hydroxycarbonate minerals could cause the precipitation of metal ions, as metal hydroxides within or to soil particles or by direct precipitation to Terra B™. The dissolution of low solubility carbonate minerals in Terra B™ that are located in a dominant acid environment + metal ions + translocation and subsequent contact with Terra B™ in an alkaline environment causes precipitation as carbonate metal fractions. Due to the high surface area and negative charge of the trivalent metal hydroxides present in Terra B™ there is the potential for external adsorption to mineral surfaces, via chemisorption processes, via crystal growth or by isomorphous substitution. In red mud there is the potential for specific chemisorption and diffusion of metals into the crystal lattice of Fe and Al oxides (Lombi et al., 2002).

## The lime plot

As with Terra B<sup>TM</sup> the addition of lime + biosolids has allowed better tree growth compared to the control, and there is no statistical difference in plant growth with the clay treatment. Lime has not been as effective as Terra B<sup>TM</sup> in reducing the concentration of mobile metal species and has neutralized surface not sub-soil acidity. The data shows that the addition of lime to the spoil initially increased leachate pH to  $\approx 5.5$  but that over the past 15 months leachate pH has dropped to pH 5 (Fig. 3), corresponding with data indicating that lime fails to neutralize sub-soil acidity (Liu and Hue, 2001; Tesfaye et al., 2001). EC in the lime plot was not as high as that in the Terra B<sup>TM</sup> plot and has approached the EC concentrations in the control after 15 months. The major contributor to EC in this plot is Ca that is dissociating from the lime (Fig. 4).

The data demonstrates clearly that the addition of lime initially reduced mobile metal concentrations (Fig. 5) but has not had the same effect as the Terra B<sup>TM</sup> and is due primarily to its failure to treat sub-soil acidity. The addition of lime to acid soil is a common method used to increase spoil pH and immobilize heavy metals like Cd, Zn, Cu and Ni through the formation of sparingly insoluble hydroxides (Khan et al., 2000). Work by the author on associated studies shows that the immobilization of metals by lime is the same as Terra B<sup>TM</sup>, but that the chemical stability of the metals is less for lime than that for Terra B<sup>TM</sup>. This is corroborated by studies using red mud that show stronger immobilization using red mud than for lime, especially when pH of the soil is reduced (Gabler, 1996; Kramer et al., 1998; Lombi et al., 2002). The ongoing generation of acid in the 50 – 100 cm profile is likely to be the source of the difference in metal concentrations between the lime and Terra B<sup>TM</sup> plots but the increasing metal concentrations could also be a response to destabilization of the hydroxide / metal species as pH declines.

After 15 months, visual observation and statistical analysis on biomass production for the lime and Terra B<sup>TM</sup> plots is similar but there are differences in mortality and growth (Fig. 6, 7 & 10) with mortality for the four eucalypt species varying at  $\approx 32\%$ ,  $52\%$ ,  $16\%$  and  $44\%$  for Tallowwood, Red Mahogany, Grey Ironbark and Flooded Gum respectively.

Unlike the Terra B<sup>TM</sup> plot there is a better correlation between tree mortality and tree growth in that the standard deviations are lower. Whereas the highly variable growth of the eucalypts in the Terra B<sup>TM</sup> plot is attributed mainly to the poor mixing of the Terra B<sup>TM</sup> + biosolids into the



Figure 10. The lime plot at 12 months.

waste rock, the mortality / growth relationship is attributed to the better application of the lime and biosolids into the plot and the solubility of the lime that has minimized root contact with mildly alkaline conditions. The difference in mixing is due to differences in application methodology. In the Terra B™ plot, the Terra B™ and biosolids were mixed together before application to the soil profile resulting in wet clods having to be incorporated into the profile; thereby causing areas of concentrated Terra B™. In the lime plot the lime was mixed into the soil profile first and was followed by the incorporation of the biosolids. Unlike the Terra B™ plot, tree growth in the lime plot is expected to fail over time as the acid neutralizing capacity of the lime fails causing Al root toxicity issues. That pH is decreasing is apparent in the leachate data (Fig. 3) and is supported by common agricultural application whereby ongoing application of lime is required over subsequent years to maintain soil pH.

#### The clay capping plot

There has been no leachate data collected from the clay capping plot since the commencement of the study nor is there expected to be until heavy (flood event) rainfall occurs. This demonstrates that the clay capping has been effective in halting the infiltration of water into the waste rock thereby halting the translocation of contaminants into the environment. This is not expected to have a permanent effect. The release of oxidizing metals from the waste rock below the clay capping is inevitable when a large and prolonged rainfall event occurs or when tree

growth breaks the clay capping seal. The breaking of topsoil - clay capping has been observed at the site in areas where clay capping + topsoil encapsulation has been practiced. This occurs because lateral root growth is encouraged, in the clay / topsoil zone, rather than vertical tap root development (because the roots are unable to penetrate the acid waste rock). Tree growth can be adequate for 5 -10 years, however as the trees reach a critical biomass, the weight of the trees reaches a point where lateral root development is unable to support tree biomass, resulting in the trees falling over and usually fracturing and exposing the waste rock below the clay and topsoil. This then leads to preferential infiltration pathways and the upward migration of metals, salts and acidity and the demise of the encapsulated dump. There is quite a wealth of information on the long term instability of encapsulation techniques in Parker and Robertson (1999).

Tree biomass production in the clay capping plot has been statistically better than the control plot and only slightly poorer than the Terra B™ and lime plots. Tree mortality for the four eucalypt species is not statistically different compared with the lime and Terra B™ plots at ≈ 32 %, 36 %, 44 % and 56 % for Tallowwood, Red Mahogany, Grey Ironbark and Flooded Gum respectively. However mortality for Tallowwood and Flooded Gum was the highest in all treatments and it is proposed that the dry conditions and the non-wetting nature of the topsoil contributed to this mortality rate. Further support for poor soil moisture retention being the major contributing factor is that these capping materials support plant growth in the area. One point that should be noted is that overall per cent ground cover is greatest in the clay treatment due to the use of topsoil. After being stockpiled for 12 years the topsoil still has viable native seed in it that has led to the germination of numerous, native eucalypt, acacia and grass species. Whereas this does not form part of this study it is an important point in terms of successful remediation / revegetation.



Figure 11. Clay plot at 12 months.

### **Conclusion**

The addition of lime + biosolids and Terra B™ + biosolids and to a lesser extent the use of clay capping + topsoil has contributed to good plant growth over the first 15 months of this study. The mortality rates in the control have not been significantly different to the other treatments but tree growth has decreased since the beginning of the study. Terra B™ has led to the highest mortality of Tallowwood, average mortality of Red Mahogany but the lowest rates of mortality for Narrow Leaved Grey Ironbark and Flooded Gum. Mortality in the lime and clay treatments was not significantly different to the control treatment. There was no statistical difference in tree growth for the surviving trees in the Terra B™, lime and clay treatments.

Metal concentrations in the leachate from the control continue to increase and are environmentally significant and contribute to AMD from the site. Metal immobilization by Terra B™ has been very high in the amended and non-amended profile whereas lime metal leachate concentrations continue to increase over time. Terra B™ has neutralized surface and sub-soil acidity whereas lime has failed to treat sub-soil acidity. There is evidence to suggest that lime has begun to fail in terms of both metal immobilization and acid neutralization and that plant growth will decline as the lime continues to fail. While no leachate has entered the lysimeters in the clay

treatment, indicating that the capping technique is functioning, long term stability of the capping media is not assured and may fail over time as falling trees fracture the capping.

There is evidence from this study showing that Terra B™ is an optimum in-situ soil remediation ameliorant because it has an outstanding ability to bind heavy metals both in and below the amended soil zones, it can treat surface and subsoil acidity, is beneficial in retaining nutrients for plant growth and allows similar plant growth to lime and clay capping / topsoil revegetation methods for species tolerant of mildly alkaline conditions. The long term stability and capacity of Terra B™ to continue neutralizing soil acidity and immobilizing metals is being assessed by associated laboratory studies.

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