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Reactive in-situ covers for the remediation of mine waste rock using BAUXSOL lime and biosolids

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Southern Cross University

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REACTIVE IN-SITU COVERS FOR THE REMEDIATION OF MINE WASTE ROCK USING BAUXSO L™ LIME AND BIOSOLIDS

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Bachelor of Applied Science (Hons.)

Submitted in fulfilment of the degree of Doctor of Philosophy, Department of Environmental Resource Management Southern Cross University 10th July 2009
THESIS DECLARATION

I certify that the work presented in this thesis is, to the best of my knowledge and belief, original, except as acknowledged in the text, and that the material has not been submitted, either in whole or in part, for a degree at this or any other university.

I acknowledge that I have read and understood the University’s rules, requirements, procedures and policy relating to my higher degree research award and to my thesis. I certify that I have complied with the rules, requirements, procedures and policy of the University.
ABSTRACT

Failure to design, construct and remediate waste rock and tailings storage facilities at mine sites leads to adverse environmental degradation and unforeseen financial costs. Typical closure options for these facilities include barrier or store and release covers. This thesis investigates the use of reactive in-situ covers as an alternative engineering design approach that involves mixing reagents (e.g. Bauxsol™) with waste rock to neutralise acidity and to immobilise major and minor metals. It was unknown whether this approach could be achieved at a field scale, whether the use of Bauxsol™ would achieve its primary objectives, whether there would be adverse effects on the soil chemistry or whether there would be adverse ecotoxicological problems.

Four 400 m² field trials were conducted at a mine site and included a Control; Bauxsol™ (25 kg / m²) plus biosolids (15 kg / m²); Lime (2.5 kg / m²) plus biosolids (15 kg / m²) and a fourth site that was encapsulated with 0.3 m of compacted clay and 0.1 m of topsoil. The results suggest that soil chemistry can be significantly improved by mixing Bauxsol™ with the top 0.5 m of the waste rock profile i.e., creating a reactive in situ cover. This was sufficient to create a root zone up to 1.6 m deep that had pH greater than 5 and lower concentrations of metals measured using a sequential extraction procedure. Treatment of the acid mine waste with Lime did not achieve marked improvement of soil conditions in soil layers below the amended zone. The capping treatment created a topsoil layer with higher pH, but the underlying mine soil remained unimproved. Leachate pH in the Control became increasingly acidic (pH 4.57 to pH 3.95). The addition of Lime and biosolids led to an initial increase in leachate pH, compared to the Control, however this decreased over the duration of the study (pH 5.37 to pH 4.89). In the Bauxsol™ and biosolids treatment leachate pH increased to 6.92 after the first rainfall event and continued to increase over the duration of the study to pH 7.4. After 24 months metal leachate concentrations (mg / L) in the lysimeters for Al, Cd, Cu, Mn and Zn were (Control: 32.6, 5.7, 12.7, 39.3, 121.8), (Bauxsol™: 0.07, 0.02, 0.07, 0.57, 0.23) and (Lime: 2.19, 1.19, 2.33, 3.6, 28.4). No leachate was available for collection from the Clay treatment indicating that this technique was functioning in terms of minimising the infiltration of water into the mine soil.

Ecotoxicological studies of major and minor metals in eucalypt leaves from the field trials and earthworm bioaccumulation studies were undertaken. The Bauxsol™, Ca(OH)₂ and Clay treatments in the field trials allowed good tree growth of four eucalypt species, compared to the Control. There was no statistical difference in tree growth between the Bauxsol™, Lime or Clay treatments over the two years of monitoring. However the growth of one tree species was poor in the Bauxsol™ treatment.

Laboratory bioaccumulation assessments found that there was good motility and no mortality of the earthworm species E. fetida after 28 days exposure to metal loaded Bauxsol™. The bioaccumulation of metals in E. fetida and bioaccumulation factors were below reported toxicity thresholds to cause mortality and below reported bioaccumulation factors for moderately contaminated soils, indicating that the metals bound to the Bauxsol™ reagents are mostly non-bioavailable E. fetida. Analyses of the 20 % treatment at 28 days using a sequential extraction procedure showed that > 95 % of the metals are bound within the Fe / Mn oxide fractions. However, changes occurred in metal fractionation after exposure to E. fetida for Cd, Cr and Fe, Mn. The data also showed that the exchangeable (1M MgCl₂) and the Toxicity Characteristic Leaching Procedure extractant are useful as indicators of metal bioavailability to E. fetida.
ACKNOWLEDGEMENTS

Foremost I would like to thank my wife for her patience, ongoing encouragement and support and my son Alec for his inspiration to complete this work. I would like to thank my supervisor David McConchie for his ongoing support and inspiration. Thanks also go to Malcolm Clark and Chuxia Lin. I would also like to thank the staff of the Environmental Analysis Laboratory at Southern Cross University for their analytical assistance and Virotec Global Solutions.

LIST OF PUBLICATIONS

I warrant that I have obtained, where necessary, permission from the copyright owners to use any third party copyright material reproduced in the thesis or to use any of my own published work in which the copyright is held by another party.

PRE-PhD THESIS

The following papers have been completed from previous work associated with my Southern Cross University Honours work. The published papers are related to the PhD thesis as the work included initial smaller scale pot trials to assess the potential for scaling up to larger field trials. The first two papers are provided in Appendix A.


PUBLICATIONS ASSOCIATED WITH THIS PhD THESIS

The following conference proceeding was completed from work that was principally conducted before the commencement of this PhD. However, this publication does include work that is directly associated with this PhD thesis. This publication is included as a chapter of the thesis. The author of this thesis contributed to less than % 25 of the content of the following publication.


The following publications have been completed from work directly associated with this PhD thesis and are included as chapters within this thesis. This statement is to verify that I, Greg Maddocks, am the principal author of the following published papers. I have undertaken the all laboratory and field work programs associated with these publications and have contributed to greater than 95 % of the writing and submission of these papers.


Appendix B provides the publication history for the papers that were accepted in 2008 by Environmental Geology. Appendix C provides the publication history and copyright statement for the paper that was published by Environmental Toxicology and Chemistry in 2005.

The following publication had been completed from work directly associated with this PhD thesis and is included as an abstract in the Proceedings of the Joint Conference of the 6th International Acid Sulfate Soils and the Acid Rock Drainage Symposium. I have contributed to greater than 90 % of the writing and submission of this publication.

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CHAPTER 1

THESIS OBJECTIVES

Chapter 1
This first chapter defines the objectives of the thesis as they are presented in each chapter of the thesis.

Chapter 2
The second chapter in this thesis defines the scope of the problems associated with metal contamination. This chapter then refines the scope and places it into the context of the problems encountered within the mining industry and more specifically how these problems are associated with the extraction and exposure of sulfide minerals to atmospheric conditions. Exposure of these minerals to atmospheric conditions coupled with an increase in the surface area of the waste rock as it blasted and extracted during mining can lead to an accelerated rate of chemical, physical and biological weathering that can then contribute to acid and metalliferous drainage (AMD). Acid and metalliferous drainage is also known as acid mine drainage (AMD) or acid rock drainage (ARD).

Chapter 3
The third chapter explores how an industrial waste product produced in the alumina industry (red mud) can be converted into a beneficial co-product that has applications in the field of environmental remediation. The applications described in this chapter include the provision of data that show how Bauxsol™ reagents can be used to neutralise acidity and to immobilise major and minor metals in soil and water.

Chapter 4
The fourth chapter builds upon the knowledge gained in Chapter 3 i.e., that Bauxsol™ reagents can be used to neutralise acidity and immobilise soluble metals in water, soils and mine waste rock. The field trials in this chapter were conducted at the Mt Carrington gold mine (Figure 1). The Mt Carrington gold mine is located in northern New South Wales, Australia, at an elevation of 480-570 m Australian
Height Datum (AHD near the town of Drake in the Drake mineral field which lies within the New England Fold Belt. The Mt Carrington mine site is currently under care and maintenance. The field trial involved the following aspects:

- The construction of four x 400m$^2$ on a haul road at the Mt Carrington mine site (Figure 2)
- The plots included:
  - Bauxsol and biosolids (Figure 3)
  - Lime and biosolids (Figure 3)
  - A compacted clay and topsoil cover (Figure 4)
  - An untreated “Control” plot (Figure 4)

The objectives of this chapter included the following.

- Ascertaining whether Bauxsol$^\text{TM}$ could be mixed with domestic sewage solids (biosolids) to create a plant growth medium that could be combined with potentially acid-generating metal-contaminated solid phase media, such as mine waste rock, to achieve in-situ acid neutralisation and major, minor and trace metal immobilisation.
- Assessing the effectiveness of the in-situ application at a scale that could be adapted to full-scale implementation at mining or industrial sites (Figure 2, Figure 3 and Figure 4).
- Comparing the results of treating sulfidic mine waste rock using a mixture of Bauxsol$^\text{TM}$ and biosolids mixed with other methods of mine waste remediation such as:
  - Neutralisation of sulfidic mine waste rock with a mixture of biosolids and lime, applied as Ca(OH)$_2$; and
  - Encapsulation of sulfidic mine waste rock with clay and topsoil.
- Quantifying the effect that the addition of the Bauxsol$^\text{TM}$ and biosolids would have on the soil conditions including defining changes to soil pH, cation exchange capacity and the operationally defined fractionation of major and minor metals.
Determining how the use of the above reagents would affect the fractionation or partitioning of major and minor metals in the treatments through the use of selective extractants and sequential extraction procedures.

Chapter 5

The fifth chapter builds upon the knowledge in Chapters 3 and 4 and assesses other aspects of the use of Bauxsol™ reagents when they are used, under the field conditions defined in Chapter 4, to neutralise soil acidity and to immobilise major and minor metals in the remediated soil profile. The environmental aspects investigated in this chapter were associated with water chemistry in the vadose zone and ecotoxicology. The objectives of the field trial in this chapter included the following.

- Installing three zero tension lysimeters in each of the test plots at the beginning of the study (Figure 5) and then collecting groundwater after rainfall events so that changes in water chemistry could be assessed and compared between the four field plots over time.

- Planting 100 seedlings in each of the treatment field plots. The seedlings were from four eucalypt species and were planted as tube stock at the beginning of the field trial.

- Assessing whether the reagents have adverse or beneficial ecotoxicological effects on the eucalypt tree species used in the field trials including;
  - Measuring the differences in tree growth of the four eucalypt tree species (Figure 6 and Figure 7);
  - Measuring the differences in tree mortality of the four eucalypt tree species;
  - Measuring and comparing the concentrations of major, and minor metals and major ions in the leaves of the four eucalypt tree species and determining what effect this may have on tree growth or mortality; and
Excavating test pits at 24 months (Figure 8) and comparing root development in the four plots (Figure 9).

Chapter 6

Although it is important to understand how and why the application of Bauxsol™ works when it is applied under field conditions it was also recognised very early in the study that is also important to understand how the use of the technology may affect biotic receptor such as earthworms.

This aspect of ecotoxicology was addressed in Chapters 4 and 5 by assessing major and minor metal and salt concentrations in the leaves of the eucalypt species that were used in the field trials. However this represents only one aspect of ecotoxicology and did not address the uptake of metals by soil biota that could transfer metals directly into the food chain of higher order species such as birds.

The sixth chapter addresses additional ecotoxicological questions related to the use of Bauxsol™ reagents. These questions included determining:

- What the possible chronic and acute toxic effects of a metal loaded Bauxsol™ reagent (MLBR), could be on the earthworm species *Eisenia fetida*: Each kilogram of MLBR contained approximately 6360 mg of metals that were sorbed from the AMD. This assessment was undertaken by conducting 30 day ingestion and bioaccumulation studies that measured acute and chronic ecotoxicological impacts; and

- Whether the bioavailability of the metals in the MLBR could be defined through the use of selective extractants and sequential extraction procedures.

Chapter 7

The conclusions of the thesis are summarised in Chapter 7

References

This chapter includes a list of references used throughout the thesis.

Appendices

The appendices in this thesis include;
• Appendix A, which contains two publications on the use of Bauxsol™ from preliminary work on the subject of this thesis;
• Appendix B, which contains the publication histories and published papers in Chapters 4 and 5; and
• Appendix C, the journal paper, copyright authorisation and reviewers comments from the publication in Chapter 6.
Figure 1 Site location
Figure 2 Field site prior to site development

Figure 3 Field site preparations in the Bauxsol™ plot

These figures show the Bauxsol™ and biosolids mixture as it was placed in the plot (top left and top right). These figures also show how the material was mixed into the waste rock using a 15 tonne excavator fitted with a single ripping tine (bottom left and bottom right).
Figure 4 Site development in the Clay plot (left) and the field site prior to planting of the seedlings

Figure 5 Lysimeter construction used in the field trials

These figures show how the lysimeters were constructed and installed.
Figure 6 Field trial tree growth at 12 months
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Figure 7 Field trial tree growth at 24 months

This figure shows the Control, Bauxsol™, Lime and Clay plots in each row (top to bottom). Each row of figures shows the plot as photographed from each corner of the plot at 24 months.
Figure 8 Field site test pit excavation method at 24 months
Each test pit was excavated to a depth of 2 m next to a tree so that observations could be made on root development. Soil samples were collected in each test pit. The test pits were backfilled after the samples were removed for analysis.
Figure 9 Root development in the Clay, Bauxsol™ and Lime Plots at 24 months

This figure shows the soil profiles in the three tests pits dug in each of the Clay, Bauxsol™ and Lime plots (top to bottom) at 24 months. The Control plots were not excavated because root growth in the Control plots was restricted entirely to the tube stock potting media i.e. there was no root development beyond the tube stock.
CHAPTER 2

INTRODUCTION

During the 1950’s and 1960’s soil science focused in part on enhancing the bioavailability of essential trace elements to plants to increase agricultural productivity. However, in recent decades the emphasis of geochemists and soil scientists has changed from enhancing the bioavailability of essential trace elements to enhancing the immobilisation of non-essential or potentially toxic trace elements (Sparks, 1995; Iskander and Kirham, 2001; Lombi et al., 2002a; Gao et al., 2003). This change in focus arose through the realisation that by increasing the bioavailability of essential trace elements the potential for the increased bioavailability of potentially toxic or non-essential trace elements could occur (Iskander and Kirham, 2001). Recent literature has espoused the need for quantitative information on the factors that control the bioavailability of elements in the pedosphere so that innovative and cost-effective methods of soil remediation can be developed (Sparks, 1995; Boisson et al., 1999; Vangronsveld et al., 2000; Hodson et al., 2001; Iskander and Kirham, 2001; Lombi et al., 2002b).

In environmental science, the term “metal” is used to describe a range of elements. The precise definition of heavy metals is vague throughout scientific literature. (Duffus, 2001) lists over 40 commonly used definitions for the term “metal” that are based on specific gravity, atomic weight or atomic number in addition to terminology referring to biological, chemical and toxicological sciences. Unless otherwise defined, in this thesis, the terminology “metal” will refer to major metals (e.g., Al and Fe), minor metals (e.g., Cd, Cr, Pb and Zn) and rare earth elements. In most terrestrial and aquatic environments, elements only occur at trace levels unless they are emanating from localised natural point sources such as hydrothermal springs or anthropogenic point sources such as mine sites (Vangronsveld et al., 1996). In this thesis, major ions such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, Cl$^-$ and SO$_4^{2-}$ are often referred to as salts.
BIOAVAILABILITY, SPECIATION AND FRACTIONATION

Bioavailability

Bioavailability is another overused and vaguely defined term within environmental literature and is often used to describe the extractable fraction of metals and major ions can be removed from soil or water using a selective leaching or sequential extraction method. Peijnenburg et al (1999) states that bioavailability should comprise two distinct and different phases: a physicochemically driven desorption process that involves the release of metals from a given matrix, “environmental availability”, and a physiologically driven uptake process, whereby biota assimilate elements “environmental bioavailability”. Environmental bioavailability requires the identification of a specific biotic species as an endpoint. The “toxicological bioavailability” associated with the redistribution of metals within an individual and to potential toxic effects, is the third aspect that can be distinguished as a better-defined sub-category of the (often) vague concept of bioavailability. Toxicological bioavailability is further complicated by the fact that once taken up, metals may be partitioned into biologically available, biologically unavailable, or storage fractions. When speaking of bioavailability and analytical soil extractants the terms speciation and fractionation are important.

Speciation

Speciation refers to specific metal species such as, organometallic compounds, metals bonded to different anions (e.g. chlorides, sulfates, sulfides, carbonates, oxides, etc.) or metals with different redox states that determine elemental toxicity such as Cr$^{3+}$ (limited toxicity) and Cr$^{6+}$ (highly toxic) (Templeton et al., 2000; Quevauviller, 2002).

Fractionation

Fractionation refers to and describes the physical or chemical properties or methods that are used to remove metals from a soil (Templeton et al., 2000). In this thesis the term operationally defined fraction (ODF) refers to the metals removed from a soil using a specific selective extractant. For instance the use of water or 0.01M CaCl$_2$ is often used to describe the “bioavailable” soil fraction. In effect these should be described as the water-soluble ODF or the 0.01M CaCl$_2$ ODF, and can only be referred to as a “bioavailable” fraction when a
specific biotic endpoint (e.g. the earthworm species *Eisenia fetida*) has total body tissue metal concentrations that correlate with either of the aforementioned extractants.

**SOURCES OF METAL CONTAMINATION**

Locally elevated metal concentrations can occur naturally through the weathering of rocks, the generation of volcanic gases and magmatic water from geothermally active areas and natural pedogenic processes. There are also increasing numbers of point and diffuse sources of anthropogenic trace metal contamination from smelters, refineries, sewage treatment plants, over-application of agricultural fertilisers, cars and other transportation utilising organic fuels, industrial plants, livestock husbandry and mining.

Mining is an industry where the release of trace metals into the environment occurs at an accelerated rate due to the exposure, physical weathering and chemical decomposition of sulfide and non-sulfide minerals, and the leaching of rocks by acid generated as a result of sulfide mineral oxidation. The focus of this work revolves around mine waste because mines are a “worse case” scenario of trace metal soil contamination. Mining can have serious adverse effects on the environment including the production of acid and metalliferous drainage (AMD) water, habitat destruction and landscape alteration (Mulligan *et al.*, 1999b). Acidic metal contaminated drainage is also known as acid mine drainage and acid rock drainage. AMD, as it is used in this thesis, refers to acidic to neutral saline drainage that may or may not have elevated concentrations of metals and salts. Environmental degradation associated with mining and industrial contamination is becoming an increasingly important environmental, health and socio-economic issue in Australia, the South Pacific region (Hill and Naidu, 1999), and the rest of the developed world due to the magnitude and widespread occurrence of the problem (Lombi *et al.*, 1998).

In this thesis “waste” is used a generic term to describe fresh to weathered mineralised and non-mineralised waste rock. Waste rock differs from soil in two ways. Firstly, it has a distinct lack of organic matter because it is essentially non-weathered rock and secondly, it shows no characteristic signs of soil horizon development unless the dumps or tailings dams are older than 100-200 years.
ACID AND METALIFFEROUS DRAINAGE

Acid and metalliferous drainage (AMD) is one of the highest priorities in the mining industry in terms of its prediction, prevention, control and treatment (Parker and Robertson, 1999; Chatwin and Verburg, 2008). In areas surrounding mine sites, contamination of the soil and water by metals and major ions can occur by the transportation of soluble and readily exchangeable species in surface water, and ground water, by physical redistribution of rock and mineral materials by gravity and water, or by airborne dispersion (Novotny, 1995).

The processes of AMD formation are well documented in the literature and will not be examined in detail in this thesis (Nordstrom and Alpers, 1999; Parker and Robertson, 1999; Nordstrom et al., 2000; Cherry et al., 2001; DeNicola and Stapleton, 2002). The process of AMD can be summarised as follows: when pyrite and other sulfide minerals are exposed to O₂ and H₂O, hydrogen ions are generated and the pH of mine waters can be reduced to as low as - 3.6 (Nordstrom et al., 2000); the associated drainage is frequently typically enriched in metals and other elements (Parker and Robertson, 1999) that become disassociated from primary and secondary minerals and organic components. The chemical generation of acidity from the most common sulfide mineral (pyrite) is described below.

In this step, sulfur is oxidised to release hydrogen ions and SO₄²⁻ (the dissociation products of sulfuric acid in solution) and soluble Fe²⁺, which is free to react further.

\[ \text{FeS}_2 + \frac{7}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \]

In the second step, the Fe²⁺ ions in the presence of oxygen and hydrogen ions react to form Fe³⁺ ions and water.

\[ \text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O} \]

In the presence of water Fe³⁺ can form oxyhydroxides and generate more acid

\[ \text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \]

Fe³⁺ ions can also act as an oxidant and increase the rate of pyrite oxidation and acid generation by up to a million times.

\[ \text{FeS}_2 + 7\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + \text{SO}_4^{2-} + 16\text{H}^+ \]

It was previously assumed that Fe³⁺ would only oxidise pyrite at pH < 4.5, however, studies by (Parker and Robertson, 1999) indicated that Fe³⁺ is still the better oxidant of pyrite even at near neutral pH and that the role of oxygen is to oxidise Fe²⁺ thereby perpetuating the
oxidation of pyrite. Ions such as Fe$^{3+}$, Fe$^{2+}$, Mn$^{2+}$, Al$^{3+}$, and H$^+$ are the major exchangeable components of acidity in AMD (Evangelou, 1995), however dissolved species that precipitate as hydroxides or oxides including Mg$^{2+}$, H$_2$CO$_3$, or H$_2$S, can also contribute to acidity (Shu et al., 2001). Under highly acidic conditions, many metals e.g. Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb and Zn can be released from waste rock in concentrations that can be toxic to terrestrial and aquatic plants and animals; the toxicity can also be enhanced by the stress caused to the organism by the low pH conditions. In aquatic ecosystems acidification is one of the worst causes of contamination due to its inherent toxicity and the resultant effects on metal concentrations, fractionation and speciation (Lopes et al., 1999). The direct effect of acidity on plants is the inactivation of most enzyme systems, the restriction of respiration and a reduced capacity to assimilate mineral salts and water (Shu et al., 2001).

REMEDIATION OF METAL CONTAMINATED SITES

Global remediation problems

The extent of problems associated with poor mining practices and the resultant soil contamination is substantial across the globe and in the European Union alone it is estimated that there are some 150,000 to 400,000 metal contaminated sites containing more than 1,000,000,000 m$^3$ of highly contaminated soil, and waste (Mule and Melis, 1999; Prokop et al., 2000). Although mining activities have generated AMD for over 2,000 years, much of this contaminated material is due to activities undertaken between 1800 - 1945 (Lepp, 1999) and the estimated cost to remediate these sites is in excess of 100 billion US dollars (Lombi et al., 1998; Prokop et al., 2000).

The costs associated with AMD liability in 1997 were estimated as A$ 0.9 billion in Australia, C$ 3-5 billion in Canada and US$ 2 to 35 billion in the United States (Chatwin and Verburg, 2008).

In Australia and New Zealand there are about 60,000 and 50,000 metal contaminated sites respectively (Hill and Naidu, 1999). In Australia the cost of AMD management at operating mines was estimated at approximately $60 million / annum (Lee, 1999), and the construction of cover systems for waste rock dumps in Australia ranges between $10,000 / ha for simple vegetative covers to about $100,000 / ha for multi layer barrier covers (Wilson et al., 2003).
In the U.S. it is estimated that 19,300 km of rivers and streams and more than 180,000 acres of lakes and reservoirs were adversely affected by AMD in 1989 and the cost of remediating these waterways was in the vicinity of 30 - 75 billion US dollars (Pierzynski et al., 2000).

In 1997 metal contamination contributed to 65 % of the superfund sites in the United States (Naidu et al., 1999). In 1998 the estimated number of seriously contaminated sites in the United States was 35,000 (Lombi et al., 1998) and by 1999 there were 1206 metal contaminated sites on the United States Superfund National Priority List (Pierzynski, 1999).

It is certain that the real costs associated with managing AMD and metal contamination are substantially higher than those reported above. For example;

- The costs to close an iron ore mine in Australia is reported to be A$ 190 million (Wilde, 2007);
- In New Zealand a coal mine is reported to be committed to spending NZ $1 million per annum for the next 100 years on treating AMD;
- In South Africa the cost to rehabilitate abandoned mines is S$US 14 billion (Weiersbye, 2007); and
- The Global cost to rehabilitate 300000 to 400000 metal contaminated sites was estimated at US$1 trillion in 1997 (Weiersbye, 2007).

Remediation definitions

In the past 20 years public opinion has forced major environmental restoration requirements on the mining industry in the form of environmental legislation (Bates, 1995; Ashby and Kolar, 1998; Beavis and Lindbeck, 1999). Prior to this mine site remediation was often not considered or was not successful. The move towards environmental responsibility has fostered four recognised states of remediation. Remediation refers to the overall improvement of an environment and includes restoration, reclamation and rehabilitation. Restoration implies returning an affected area or ecosystem back to its original condition (Silcock, 1992; Munshower, 1994; Jackson et al., 1995). Reclamation creates a condition that results in a stable, self-sustaining ecosystem that may or may not include some exotic species and includes a similar but not identical structure and function to the original land (Munshower, 1994; Jackson et al., 1995). Rehabilitation refers to making an area of land useful again after it has been used for some other purpose, as in creating a pasture or forest.
where there used to be a mine (Munshower, 1994; Jackson et al., 1995; Sengupta, 1995). The type of remediation practices adopted at a site depends very much on the needs of the proposed end land use along with contractual lease agreements. The final land use must be compatible with community needs, any legal requirements, climate, soils, the local topography, and the degree of management available after rehabilitation.

CURRENT PRACTICES: SOIL REMEDIATION

There are two distinct methods of treating soil contaminated with metals that include in-situ and ex-situ remediation. Some of the in-situ and ex-situ techniques utilised for soil remediation are shown in Table 1.

Table 1. Current remediation strategies used in the US to treat metal contaminated sites from Pierzynski, (1999).

<table>
<thead>
<tr>
<th>Ex-situ</th>
<th>In-situ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solidification / stabilisation</td>
<td>Addition of a cementing agent to produce a hardened, non-porous, non-leachable material</td>
</tr>
<tr>
<td>Vitrification</td>
<td>Heating to produce a glasslike, non-porous, non-leachable material</td>
</tr>
<tr>
<td>Washing</td>
<td>Chelate or acid extraction</td>
</tr>
<tr>
<td>Leaching</td>
<td>Pile or batch leaching with acids or chelates</td>
</tr>
<tr>
<td>Particle size segregation</td>
<td>Selective removal of fine particles that have the highest metal concentrations</td>
</tr>
<tr>
<td>Soil excavation</td>
<td>Soil removal and disposal</td>
</tr>
<tr>
<td>Soil aeration</td>
<td>Tillage or agitation of the soil induces aeration causing volatilisation of elements</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>Organic solvents separate organic and inorganic</td>
</tr>
<tr>
<td>Thermal desorption</td>
<td>Wastes are heated so that contaminants and water volatilise, temperatures may be high 320°C – 560°C (HTTD) or low 90 – 320°C (LTTD).</td>
</tr>
</tbody>
</table>

<p>| Solidification / stabilisation | As above |
| Vitrification | As above |
| Encapsulation | Cover site with impermeable layer |
| Attenuation | Dilution with uncontaminated material |
| Electrokinetics | Electric current induces movement of the ions to the electrodes |
| Phytostabilisation | Promote vegetative growth to immobilise metals |
| Phytoextraction | Removal of metals by plants |
| Thermally enhanced recovery | Heat increases the rate of volatilisation to facilitate extraction |
| Immobilisation | The addition of amendments to immobilise contaminants thereby reducing the bioavailability and mobility of metals |</p>
<table>
<thead>
<tr>
<th><strong>In-situ</strong> or <strong>Ex-situ</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bioreservation</strong></td>
</tr>
<tr>
<td><strong>Chemical treatment</strong></td>
</tr>
<tr>
<td><strong>Neutralisation</strong></td>
</tr>
<tr>
<td><strong>Soil vapour extraction</strong></td>
</tr>
</tbody>
</table>

The most common technique for the remediation of acidic or metal contaminated soil in Australia is *ex-situ* offsite management (Khan *et al.*, 2000) whereas encapsulation, topsoil addition and more recently liming are the common remediation strategies for waste at mine sites. *Ex-situ* operations are generally based on civil engineering techniques that are expensive, environmentally invasive, labour intensive (Vangronsveld *et al.*, 2000; Oste *et al.*, 2001) and pose ongoing problems with the removal, transportation and the subsequent redistribution of contaminants into the environment at landfill sites (Pierzynski, 1999). Khan *et al* (2000) state there are currently very few viable techniques for the *in-situ* removal of metals from soil or waste, however there is increasing work being conducted on the *in-situ* immobilisation (also known as inactivation or stabilisation) of metals in contaminated soil media (Vangronsveld *et al.*, 1995; Vangronsveld *et al.*, 2000; Friesl *et al.*, 2001; Lombi *et al.*, 2001).

The principle of *in-situ* immobilisation is to add soil amendments to the root zone of contaminated soils or, where possible, throughout the entire contaminated profile, to bind the metals in immobile ODF thereby limiting their environmental availability, while maintaining the availability of essential elements. The main objective of sound *in-situ* remediation techniques is to reduce the long-term environmental availability of contaminants in pedogenic and aquatic environments. Combined with sustainable revegetation practices *in-situ* techniques offer a viable alternative to the invasive and expensive practices that are currently being used (Vangronsveld *et al.*, 1999). However, one of the major problems with current remediation techniques is their failure to provide long-term neutralisation of soil acidity and prevent the release of metals into pedogenic and aquatic environments as bioavailable metals (Vangronsveld *et al.*, 1999).
CURRENT PRACTICES: MINE WASTE REMEDIATION

Current remediation practices used at mine sites typically involve re-shaping to reduce waste pile angles to 15-25 % (Ward, 1993; Bellairs, 1999), capping with clay or topsoil (Bell, 2001), and the addition of soil or waste amendments (attenuation) to stimulate plant growth and reduce the translocation of contaminants into the environment (Barnhisel et al., 1998; Brown et al., 2000). Other methods used in the mining industry include saturated covers, oxygen consuming covers, the generation of hardpans and the addition of bactericides (Parker and Robertson, 1999). In most cases the use of covers is largely ineffective, particularly in regions with extreme climatic variables (Parker and Robertson, 1999). A recent paper by Wilson et al (2003) states that the use of covers (encapsulation) is one of the few remaining options for the remediation of existing waste rock dumps but that the structural or chemical integrity of these systems may fail within 10 – 20 years. It is also acknowledged that remediating acidic waste with topsoil, clay capping or liming or a combination of these options works 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; Friesl et al., 2001).

A review by Fourie and Tibbett (2007) has shown that the complexity of covers for tailings and waste rock storage facilities is increasing within the mining industry and the analogues of multiple layers covers from the landfill sectors are becoming more widespread. However, the use of cover designs involving layers of compacted clay has had limited success because, climatic factors such as rainfall can rapidly render these covers ineffective through erosion (Parker and Robertson, 1999; Fourie and Tibbett, 2007).

Store and release covers are seen as a preferable option, in environments where evaporation exceeds rainfall, for storing seasonal rainfall in the cover so that it does not seep into and then through the underlying waste rock. The stored water is then slowly released through evapotranspiration. These cover designs are seen as offering substantial advantages over barrier systems but are relatively new in their design phase (Fourie and Tibbett, 2007). The basis of these designs is that the store and release cover should be able to retain the seasonal rainfall and be deep enough to contain the roots of the developing plants species. The downside of these designs may be that substantial volumes of material could be required and may not be available at the site. The designs are generally restricted to shallow layers requiring different machinery and skill sets to the mining phase. Additionally the depth of the
material may not be sufficient to contain the roots and prevent them from breaking through into the mine waste (which would lead to preferential pathways for rainfall and vadose water leaching).

In instances where waste rock dump remediation is to be undertaken on historic, abandoned or poorly managed sites encapsulation is commonly impossible because there is no suitable capping media available. In recent years, chemical stabilisation or immobilisation utilising 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) has been proposed as a means to remediate waste rock dumps where traditional encapsulation using clay or topsoil is unachievable or where the site managers are aware of the limitations of encapsulation.

Aims of mine site remediation

Many of the practices used in the past, and still used today, fail to solve problems associated with contaminant remediation in the long term (Schuiling, 1998) presenting problems for corporate managers and environmental regulators. The major obstacles to overcome from the managers point of view are problems associated with cost and functional ecosystem sustainability (Williams, 1995; Tordof et al., 2000) meaning that they need to be able to treat the site to a condition that will allow them walk away and avoid ongoing management and maintenance, whereas environmental regulators may be faced with future costs if the remediation measures fail over time. There is therefore, a clear need for the development of sound in-situ techniques for the remediation of metal contaminated soil and waste (Khan et al., 2000).

The aim of mine site remediation and the degree to which it is implemented varies within and between countries. In the past Australia has aimed to rehabilitate areas for uses such as grazing (Williams, 1995) but currently there is an increasing movement towards reclamation, that aims to create sustainable floral and faunal communities containing native components. This strategy has been adopted by Pacific Coal Pty. Ltd. (Bellairs, 1999), BHP (Mulligan et al., 1999b) Alcoa and many other companies.
Problems associated with waste rock and tailings remediation

Remediation at mine sites involves the treatment of waste rock dumps, exposed open pits, haul road verges, plant sites and tailings storage facilities. Depending on the mineralogy of the lithologies at the mine site, waste rock can be acidic or basic. Tailings are often basic when they reach a containment facility due to the processing of the ore to remove base metals. However, if the geology of the deposit contains sulfide minerals such as pyrite or chalcopyrite then these tailings will become acidic if they are oxidised at some point in the future. Other sulfide minerals in the waste rock or tailings such as galena or sphalerite can also release some acid but are of more concern in terms of their capacity to release metals into the environment as they are oxidised.

The view that waste rock and tailings constitute the largest volume of material that must be stabilised and remediated and are often the hardest to remediate because of their chemical and physical properties has not changed in the past decade (Kuhn, 1999; Fourie and Tibbett, 2007). The problems associated with remediating and revegetating acid waste rock are well documented and include metal toxicity, inherent acidity, high salt concentrations, poor nutrient content and poor physical structure (Kabata Pendias and Pendias, 1992; Alloway, 1995b; Dollhopf, 1998; Miekle et al., 1999; Brown et al., 2000). Clay-rich or hydrothermally altered waste rock can deteriorate rapidly due to accelerated weathering losing the intact properties of the original material and leading to lower strength, increased compressibility, a reduction in hydraulic conductivity and increases in consolidation and settlement (Kuhn, 1999). These geotechnical properties commonly compound the effects of poor soil chemistry and increase the difficulties faced when remediation of these sites is required.

While much attention is payed to the remediation of soil media for the establishment of vegetation there is often a failure to comprehend the importance of the geotechnical properties of the soil and rock material within waste rock dumps (Kuhn, 1999). Mining changes earth materials by breaking or loosening them and while engineers may require compacted stable material for structural purposes, revegetation work requires loose material and therefore a compromise and understanding is needed between the engineer and the revegetation scientist.
Processes of remediation

Initial mine site remediation is concerned with ensuring that the site is able to withstand the erosive forces of wind and water and is followed by the construction of encapsulating media or the reconstruction of a suitable soil profile to allow revegetation (Bell, 1999). This is achieved by the construction of a landform that satisfies future land use needs and invariably includes the incorporation of a suitable growth medium and vegetative cover (Bell, 1999) that assists in controlling the release of contaminants from the soil and water bodies to the hydrologic and pedologic environment. This vegetative cover should be self sustaining and require little further management (Phillips, 1994; Brown et al., 2000). There is also a need to treat AMD, waste rock dumps, open pits and tailings dams etc and to establish new and resilient ecosystems (Bell, 1999).

Landform design

Waste rock dumps are generally designed with minimising costs in mind and little or no thought is given to the requirements of future remediation (Kuhn, 1999). When remediation work is undertaken there is a need to consider the redesign of pit walls, waste piles, tailings impoundments and sludge ponds (Kuhn, 1999). Whereas pit walls often fail when driving forces from gravity, or water, or both exceed the resistance due to friction and cohesion along a failure surface such as a geologic discontinuity (Kuhn, 1999), one of the main problems associated with waste piles is the piling of waste material at the angle of repose (Kuhn, 1999). This angle will commence at \( \approx 40-45 \) degrees but as weathering proceeds or if the toe of the pile is removed the slope may eventually fail (Kuhn, 1999).

The objectives of landform design are to increase slope stability to reduce physical erosion, construct a functional drainage basin and provide suitable surfaces for plant establishment (Munshower, 1994; Bates, 1995; Lindbeck et al., 1998; McRae, 1999). Attaining erosive equilibrium of the landform means that the climatic forces must be balanced with the interacting factors of slope geomorphology, the physical properties of the soil material and the vegetation that is growing on the slope (Munshower, 1994).

Landform design deals with reshaping the landscape for vegetative re-establishment. Williams (1995) states that the best way of minimising the chances of a disaster in the initial stages of vegetative establishment is to create a very rough surface so that water ponds until it can be absorbed rather than running off the surface topography causing erosion. In areas with
large generally flat surfaces, contour cultivation with chisel ploughs is a common method of reducing erosion and preparing a surface for sowing but this procedure is limited to slopes below about 5°. Contour ripping, scalloping or moon-scaping of the slope face can be carried out along the contour lines in steeper areas to catch surface drainage and reduce gully erosion (Williams, 1995; Lindbeck et al., 1998). The size and depth of these structures varies with slope angle and the climate of the region (Silcock, 1992).

Reshaping of the landform includes removing and reshaping waste piles and waste dumps to angles of between 8% and 33% (Silcock, 1992). In Queensland angles of between 10% and 15% are recommended (Bell, 1987) but typical angles of reshaped waste dumps are around 20°(Williams, 1995). Lindbeck et al (1998) support the idea of waste piles with convex tops (to reduce infiltration) and berms that collect and funnel surface run-off into silt traps. This reduces AMD and collects sediment that may be laden with metals.

The final landform depends on available expenditure, is dependent on slope length, density of vegetative cover at ground level and the intended land use (Silcock, 1992) and must be hydrologically compatible with surrounding land (Ward, 1993; Ward, 1995; Hossner, 1999). Sinusoidal shapes that mirror natural landforms are preferred (Ward, 1993; Munshower, 1994; Ward, 1995) and ensures that slopes are lowest where the volume and velocity of overland flow is greatest (Silcock, 1992; Munshower, 1994). One of the main aims of good landform management is to reduce the rate of erosion of unconsolidated material (Munshower, 1994; Ward, 1995; Lindbeck et al., 1998), caused by the removal of vegetative cover. The rate of erosion at mine sites can reach or even exceed 5 - 25 mm / yr and is some 5 - 25 times greater than the acceptable erosion rates in Australian agricultural areas (Williams, 1995). Surface mining removes the vegetation and disturbs the natural soil profile, exposing the soil to the forces of erosion. Soil erosion occurs when the energy of moving water or air exceeds the forces binding the soil (Lindbeck et al., 1998). Wind erosion is initiated by coarse particles driven across the ground by wind. Wind erosion at mine sites is considered to be insignificant in terms of actual soil loss, but has implications in terms of dust control and impeding establishing plant life (Lindbeck et al., 1998). Water can cause raindrop splash, rill, sheet or gully erosion. Raindrops falling on exposed surface soil pulverise and compact the soil reducing infiltration and increasing the action of the water leading to rill, sheet or gully erosion. Rill, sheet and gully erosion is related to the flow velocity of the water and the cohesion and dispersivity of the soil particles. The cohesive ability of the soil is related to soil
physics and chemistry while the angle and length of the slope, the depth of the water and the texture of the soil surface affect the velocity of the water (Lindbeck et al., 1998). Although gully erosion is severe and obvious the effects of rill and sheet erosion, which are spread over a large area, can be just as severe (Lindbeck et al., 1998).

**Pedogenic reformation**

Pedogenic reformation of degraded sites involves a multidisciplinary understanding of plant biology and the physicochemical properties of the media in which the desired vegetation is to be grown. The major parameters that influence the ability of growth media to support life include moisture, nutrients, temperature, light, pH, electrical conductivity, sodium content, organic matter content, cation exchange capacity and the texture, structure, bulk density and porosity of the soil (Munshower, 1994).

Pedogenesis is a result of the interaction of climate, soil organisms, topography, parent material and time. Under natural pedogenic formation elements including Ag, As, Cd, Cu, Hg, Pb, Sb and Zn are often found in the surface layers while Al, Fe, Ga, Mg, Ni, Sc, Ti, V and Zr are accumulated in the lower profiles with translocated clays and hydrous oxides (Alloway, 1995b). This natural pattern is broken under cultivated conditions or during mining operations and allows unwanted or unneeded elements to enter the rhizosphere. Apart from the effects of AMD, low plant nutrient levels, poor physical soil structure and texture, and variable oxygen gradients compound the problems of utilising and repairing the soil profile for sustainable use.

During mining the topsoil and subsoil are removed and are generally stored for later use or are reapplied to areas undergoing remediation. The process of removal disturbs soil biota, and the chemical and physical properties of the soil. The productive capacity of the replaced soil profile will always be limited by the inherent chemical, physical and biological properties of the soil (Sengupta, 1995) and there are serious problems with soil collection preservation and application. (Sengupta, 1995) states that even if the exact thickness of topsoil and subsoil were replaced, two soil properties that likely would not be the same as those in the pre-mining profile are the size, shape, and volume of pore spaces and the number and kind of soil micro-organisms.

Waste dump construction generally occurs by end dumping at the angle of repose or by bottom up construction methods whereby the waste rock is placed in layers (benches) with
various degrees of compaction that are either intentional or a consequence of the trafficking during the dumping process. These construction methods often lead to well compacted layers on top of the waste dumps. During the remediation and revegetation process the compacted mine waste will need to be fractured to allow mulch and chemical stabilising media to be mixed into the profile. After this, the use of heavy machinery will contribute to a subsequent deterioration in physical soil properties including a loss of soil structure, an increase in bulk density and a reduction in porosity and permeability that will create an impediment to root growth. Dry soils are far more amenable to soil handling and resist compaction (McRae, 1999) and so spreading and working of the soil should be done when the soil is dry to reduce compaction.

Establishing an optimum soil profile requires the use of the right machinery at the right time. Deep ripping with winged tines can be used to open, break and shatter compacted soils in the initial stages but their operational depth is limited to about 450mm. Ashby (1997) states that deep ripping to a depth of 1.2m is useful and can increase tree growth by opening the soil and allowing root penetration. Bacon and Humphries (1988) in McRae (1999) suggests the “single row dump and turn” method for reducing compaction of soils whereas (McRae, 1999) supports the “loose tipping” method because it avoids compaction completely and utilises deep ripping methods combined with the application of topsoil with an excavator. Again the effectiveness and type of remediation operation that can be employed is linked to time and financial constraints.

Topsoil is always better for plant growth than shattered and less weathered rock from the lower horizons (Hossner, 1999). Silcock (1992) states that topsoil in mine site remediation contains the original organic and organo-mineral horizons and can include the underlying A and B horizons. Although mine soils initially have no pedogenic profile, Hossner (1999) claims that this problem can be corrected by using site specific chemical, biological and physical amendments that are combined with existing mine wastes or applicable layers from deeper in the soil profile. If the topsoil is sterile or unsuitable for sustainable development the use of mulches and other soil amendments can be used to improve soil pedogenesis. The success of topsoiling or mulching depends on the depth and type of amendment the existing phytotoxicity in the soil and available funds (Silcock, 1992). Mulching amendments can be natural organics like hay or may be artificially enhanced with engineered methods such as hydroseeding or Jutte matting.
Habitat development and ecosystem sustainability

Some restoration scientists consider that anthropogenically mediated ecological succession should follow an orderly and readily identifiable pattern (Bradshaw, 2000). However, most native Australian habitats are however in a non-stable state and are affected and regulated by disturbance regimes that make them vulnerable or adapted to ongoing change (Bellairs, 1999). A regulated pattern of ecosystem development is therefore unlikely to occur under natural succession where the outcomes of the remediation plan can only be defined in broad terms and where there is immigration of species not included in the expected vegetation regime. It is therefore more realistic to expect that successional development of derelict land will follow a natural pattern unless extensive and expensive interaction and management strategies are used. This means that the perception and expectation from the public that mine-site remediation should produce “instant” results, is neither rational nor ecologically invalid.

Natural mine site revegetation can be very successful. However, it can take 75-100 years to deliver fully functional ecosystems (Bradshaw, 2000): and this may only occur if the physical and chemical parameters of the soil are acceptable for plant growth (Williams, 1995; Prach and Pysjek, 2001) and if the surrounding region has seed bearing vegetation (Bradshaw, 2000). Acid mine waste presents an ongoing obstacle to plant growth and natural regeneration (Bengson and Thompson, 1998) and may do so for many years or decades until oxidation of the material ceases, acid generation is halted and the material is neutralised. Acid soil conditions inhibit fungal and bacterial ammonification processes (Silcock, 1992) and plant growth. Aluminium toxicity is also a major problem affecting plant growth in acid soils (Kochian and Garvin, 1999; Luster et al., 1999; Nietfeld, 1999) because aluminium interferes with cell division, increases cell wall rigidity, impedes DNA replication, reduces root respiration, interferes with enzymes and nutrient assimilation and fixes phosphorous in less bioavailable forms (Robert, 1995).

In order for rehabilitation to be successful ecosystem reconstruction should aim to initiate and maintain soil development as a primary goal rather than just establishing vegetation that may fail in successive years. The importance of a self-sustaining vegetative cover is highlighted by Partridge (1979 in Silcock, 1992) who states that without permanent vegetation, the cycling of nutrients and minerals through the system (essential for creating a stable ecosystem) cannot be achieved and the landscape will remain susceptible to damage.
Ground stability, initial nutrient content, the presence of nitrogen fixing species, microbial activity and the ability of the soil to capture and hold nutrients are all critical factors in developing and maintaining effective nutrient cycling (Bellairs, 1999). The key to long term habitat sustainability lies in not only in establishing pioneer species on amended soil but also in developing a self sustaining soil biological community (Frouz et al., 2001) that will achieve nutrient cycling and successional development of plants (Bell, 1999; Mulligan et al., 1999a; Wagner and Harrington, 2000).

When the required end land use of remediation at a mine site is a return to native forest, the starting point is an artificial system composed of native and or exotic pioneer species, or both (Wagner and Harrington, 2000). The exotic pioneer species can be used to provide shelter from direct sunlight, reduce surface soil temperature, accelerate soil stability, promote the development of soil micro-organism populations and enhance soil organic matter and nitrogen assimilation (Wagner and Harrington, 2000), until the native trees are established. However, fast growing and persistent exotic species may out-compete native plants: particularly the understorey species.

Native understorey tree, shrub and herb species are vital in Australian forests and are dynamic communities that support soil microbial and mesofaunal populations, provide a quick ground cover (until the secondary successional crop trees are well established), shelter the soil, improve soil structure, and provide food and shelter for fauna (Mulligan et al., 1999a; Mulligan et al., 1999b; Wagner and Harrington, 2000). Ground stability, initial nutrient capital, the presence of nitrogen fixing species, microbial activity and the ability of the soil to capture and hold nutrients are all critical factors in developing and maintaining successful nutrient cycling (Bellairs, 1999) in the understorey communities. The development of this community is, however, a slow process. Mulligan et al (1999a) found that little humus had developed in rehabilitated topsoil in tree trial areas even after 15 years indicating a deficiency in the cycling of nutrients.

The standard revegetation method at many Australian mines includes, propagating grass and pasture species in the initial season and planting shrubs and trees the following year (Macyk et al., 1998; Mulligan et al., 1999a; Hunt, 2000). The establishment of grass or pasture species helps protect the soil against the transport of sediment and nutrients off site (Silcock, 1992; Macyk et al., 1998; Mulligan et al., 1999a) and enhances soil moisture retention (Miller, 1998). However, where the post-mining land use requires a return to native
tree habitat these grass and pasture species can inhibit the growth of trees (Silcock, 1992; Kost et al., 1998; Miller, 1998; Bellairs, 1999), but the weeds species can be partly controlled by the use of suitable tree compatible ground cover, fire, herbicides (Ashby, 1997) or tree shelters (Miller, 1998).

In many large-scale remediation programs vegetation is established by broadcasting seed (Macyk et al., 1998; Bell, 2001) because this technique is cheaper and can give superior results over tube stock (Miller, 1998). This strategy is being used in many countries (Parrotta and Knowles, 2001) including Australia (Mulligan et al., 1999a). The species selected ultimately depends on the final land use intended soil conditions and climate. A quick cover crop of grass is usually established to minimise erosion but care must be taken in species selection so that later tree and shrub planting is not impaired by the grasses (Ward, 1995). In previous rehabilitation programs in the Bowen Basin, where grazing was favoured as the final land use, rapid growing exotic pasture grasses such as Cenchrus ciliaris (Buffel grass) and Chloris gayana (Rhodes Grass) have been used effectively as colonising vegetative species (Mulligan et al., 1999b). Silcock (1992) provides further information on suitable plant species for use in mine site rehabilitation. Stoloniferous grasses may have greater benefits to artificially planted grass / tree communities under anthropogenically mediated planting regimes than tall pasture species. Stoloniferous grasses are advantageous when a native forest habitat is required because they are low growing, almost incapable of setting viable seed and are well suited to vegetating dam walls and waste rock piles (Silcock, 1992).

Recently, a new development in Australia relating to remediation and pedogenic reformation of degraded farmland has been demonstrated by Peter Andrews1. The general approach is to allow, even facilitate, the establishment and growth of weeds on degraded farmland in the initial stages of remediation. These weeds are slashed and used as mulch over successive seasons to create an organic matter rich substrate. Successional development of native species is then facilitated and encouraged once sufficient organic matter has accumulated in the soil profile. This Natural Sequence Farming approach has considerable merit for mine sites where the availability of organic topsoils is often limited.

1 http://www.nsfarming.com/index.html
THE STUDY SITE

The field work in this thesis was undertaken at the Mt Carrington mine site which lies within the Drake mineral field and is near the village of Drake (Figure 1). Drake is 52 km east of Tenterfield and 76 km west of Casino on the Bruxner Highway in NSW, lies at 28° 50’ 00” latitude and 125° 20’ 30” longitude and has an elevation of between 480-570 m Australian Height Datum (AHD). The climate is cool to subtropical and the region has a distinct wet season between December and April. The mean annual rainfall and temperature values used for the site are based on the average records of the four closest Australian Bureau of Meteorology (ABM) weather stations at Tabulum (elevation 550 m AHD), Urbanville (elevation 370 m AHD), Girard (670.6 m AHD) and Tenterfield (860 m AHD). The rainfall records for 2001 were measured from a rain gauge at the project site.

REGIONAL GEOLOGY

The Drake mineral field lies within the New England Fold Belt, and is composed of Late Palaeozoic and remobilised older Palaeozoic complexes that have been intruded by Permian and Triassic orogenic granites (Markham and Basden, 1978). The Drake region lies in the Demon-Emu Creek Block and is characterised by north to northwest trending faults that separate the Drake volcanics from the older rocks to the west and younger rocks to the east. Upper Permian to Triassic rock intrudes the older sedimentary base rocks of the region (Offenburg and Cochrane 1974 in Knight, 1975). The rocks are primarily volcanic in the south and epiclastic in the north. The area is a complex combination of; andesite - dominated, calc - alkaline lavas, tuffs and epiclastic rocks together with sub volcanic, comagmatic stocks and dykes (Solomon and Groves, 1994) epiclastic breccias and laharc deposits (Herbert 1983 in McWatters, 1991). The oldest rocks in the Drake field are Carboniferous sandstones, siltstones, mudstones and silicified limestone (McWatters, 1991). Rhyolitic flows, agglomerate and breccia, known as the Mount Carrington Rhyolites overlie the Carboniferous sediments and these are in turn overlain by the Drake Volcanics. The Drake Volcanics are some 1000 m in thickness (Solomon and Groves, 1994) incorporate the Drake Andesites and include andesitic volcanics and sediments (Markham and Basden, 1978).

The ore genesis in the area has been described as epithermal to mesothermal by various authors although evidence by Perkins (1986 in McWatters, 1991) and...
geothermometry studies by Smith (1989 in McWatters, 1991), who give originating fluid temperatures of between 222-295°C, suggest that the area should be classified as leptothermal. Although the exact classification of the worked ore bodies at the Mount Carrington mine site differs between authors, several broad mineralisation types are represented and include fissure veins, vein stockworks, disseminated sulfide units and breccia infillings (Markham and Basden, 1978). Solomon and Groves (1994) classified the Mount Carrington pit as a fissure lode and the White Rock and Lady Hampden pits as a stockwork system and disseminated system respectively. Offenburg and Cochrane in Knight (1975) classify Lady Hampden, Adeline, Guy Bell, Mt Carrington and Kylo as fissure loads the Strauss Pit as a stockwork and Emu Creek and the eastern zone of the Strauss pit as disseminated. Houston (1993) describes the classification of the Drake mineral field in terms of stockworks and vein systems.

The area around the Drake mineral field is extremely rich in sulfide minerals but the precise source of the ore generating fluids within the different mineralised veins is unclear. Solomon and Groves (1994) state that the New England Fold Belt developed in a part terrestrial and part marine environment, and find that some of the gold-sulfide deposits are due to thermal cell development as sea water circulated through the rock mass. Herbert and Smith in McWatters (1991) concluded that the sulfur was derived from volcanogenic and biogenic sulfur in the country rocks and that the ore forming fluids were due to a combination of meteoric and magmatic water. In the available literature, there are at least two views on the mineralisation processes that have taken place. Smith (1989 in McWatters, 1991) states that the mineralisation of the Drake mineral field occurred in four stages and includes quartz-haematite veining and breccia cement, sphalerite +/- pyrite-galena, quartz-chalcopyrite-tennantite-pyrite +/- bornite-haematite-electrum-gold-aikinite and quartz-chalcopyrite-pyrite +/- carbonate.

Houston (1993) suggests two stages of mineralisation. The first includes an initial phase of gold and zinc rich fluids within the Kylo quartz andesite stock. The second stage of mineralisation occurred “slightly later” and shows dominant chalcopyrite overprinting of the earlier phase. This second phase is characterised by copper rich solutions. Within the Strauss pit two mineralisation systems are evident. Initial intensive intrusions of Zn rich fluids that are reasonably high in Cd were replaced or overprinted by secondary quartz flooding (or silicification) bringing jasper, pyrite, chalcopyrite, sphalerite and minor amounts of galena.
WASTE ROCK AND AMENDMENTS

In order to ameliorate mine site waste and contaminated soil with poor chemical and physical properties when suitable topsoil and construction materials is limited or absent one management option is to develop and incorporate an artificial soil media into the waste rock that will allow plant growth. The soil amendments used must be able to supply the waste with organic matter and nutrients, neutralise current and future acidity and be able to immobilise metals to reduce their translocation into the environment. There may also be a requirement to create soil structure and texture that is conducive either to the requirements of the vegetative habitat or geotechnical considerations such as reducing erodability or increasing or decreasing permeability. Mine wastes are highly heterogenous and generally require site-specific investigation to determine optimal amendments to facilitate their eventual remediation (Hawkins, 1998).

Waste rock

The waste rock from the mining operations at the study site is stored in four large waste rock dumps west of the tailings dam (Figure 1). This mine waste is a mixture of fresh lithic overburden from the oxidised geologic zones and sulfidic and gangue material from reduced geologic zones. This material is not in chemical equilibrium with the surface environment and is a primary source of contamination at the site through the oxidation of sulfide minerals and the subsequent generation of AMD. The mine waste in these dumps is typical of many waste rock dumps and is characterised by material ranging in size from large boulders of greater than 2 m to fine clay fractions less than 0.002 mm in diameter.

The sulfide minerals at the site include pyrite, chalcopyrite, sphalerite, galena, tetrahedrite, bornite and chalcocite and the gangue minerals include quartz, calcite, siderite, and rhodochrosite; pyrite is by far the most abundant sulfide mineral. Extensive alteration zones with varying amounts of sericite, quartz, calcite, dolomite, orthoclase, chlorite and clay minerals are common and are clearly visible within the Strauss and Mt Carrington open pits; the two major open pits on the site. The main mineral suite around the Mt Carrington area comprises quartz, illite, kaolinite and smectite, with smaller quantities of volcanic glass, chlorite, potash feldspars and plagioclase (Offenburg and Cochrane in Knight, 1975).
Biosolids

From 1998 the dumping of biosolids at sea has been banned in the European Union, necessitating the need for sustainable reuse of this resource (Gove et al., 1999). Biosolids are also being viewed as a resource rather than a waste product in Australia (Polglase and Myers, 1996; Simms, 1996) and have long been used as a soil amendment in the US (Brown et al., 2000) where by 1993, 72 mine sites had been reclaimed using biosolids (Sopper, 1993, in Rogers et al., 1998). Biosolids used as a soil amendment at mine sites are blended with lime, log yard waste, sawdust and more recently with coal combustion by-products (Semalulu et al., 1998; Gorman et al., 2000) to correct soil acidity, provide nutrients and organic matter (Roberts et al., 1988; Brown et al., 2000) and establish a functional microfaunal and microfloral community (Bendfeldt et al., 1998; VanderSpiegel and Evans, 1999; Whatmuff, 1999). Single applications of biosolids have been shown to sustain vigorous vegetative cover for several decades and for conventional soil restoration practices, biosolids appear to be the most effective and economic method that is currently available to restore soil nutrient requirements (Brown et al., 2000). It has been found that N added as an organic amendment rather than inorganic fertiliser provides a more stable source of soil N and also gives greater crop yield and quality (Schoenholtz et al., 1992, in Kramer et al., 1998).

Possible problems associated with using biosolids include their affinity for translocating excessive metal, pesticide, nutrient and poly chlorinated biphenyl concentrations into the environment (Phillips, 1994). These possible problems remain unresolved (Dowdy et al., 1999) and there is conflicting evidence regarding the chemical forms of metals in biosolids, their bioavailability and the long term effects on soil biota and plants (Rogers and McLaughlin, 1999). Rogers and McLaughlin (1999) also state that the metal species and bioavailability of metals in biosolids are highly variable from one source to the next. The soluble metal fraction in biosolids is usually only 0.5 – 7 % of the total amount of sludge borne metals but it can be a major contributor to the total metal load that is transported through the soil or taken up by plants following application (Vulkan et al., 1999): this is dependent on the environment that the biosolids are used. Metals in biosolids can be found as simple or complexed ions in the soil solution, readily exchangeable ions, organically bound ions, co-precipitated ions on metal oxides or other secondary minerals and as ions in the crystal lattice of primary minerals (Kaewrahun et al., 1999).
There appears to be general agreement that organic matter in biosolids will bind metals (Zasoski 1981, and others in Kramer et al., 1998) but it has also been found that as the organic matter content decreases over time (Rule and Martin, 1999) or as soil pH changes (Planquart et al., 1999; VanderSpiegel and Evans, 1999) the metals in biosolids will become more bioavailable. Whatmuff (1999) found that under conditions where the soil pH is < 5 Cd and Zn are bioavailable even when the total concentrations in the biosolids are very low. These findings are corroborated by Balik et al., (1999) who found a substantial increase in Cd and Zn concentrations in above ground biomass after biosolids application.

Despite the above findings there is detailed work that offers contrary evidence to that of the above authors. Brown et al., (1998) found that the possibility of increasing metal concentrations through biosolids application generally results in no observable increase in plant metal concentrations. This is corroborated by an eight-year study conducted by Bourgeois et al., (1999) who state that there is no indication of substantial effects on plants and soils due to biosolids application. Furthermore, when biosolids are used on mine sites, the heavy metals that could be available in the biosolids would represent a very small proportion of the total quantity of available metals.

The use of biosolids to supply nitrogen and phosphorous to nutrient deficient soils is well known but may have drawbacks because of the leaching of NH$_4^+$, NO$_3^-$ and PO$_4^{3-}$ from the soil. A study of native Australian forests irrigated with sewage effluent suggest that 75-100 kg total nitrogen /ha can be assimilated by trees before canopy closure is reached but the uptake rate drops off significantly at that point (Snow et al., 1999). This problem can be averted by controlled additions but in single applications for mine site remediation some leaching of nitrogen species (e.g. NO$_3^-$) may result. Where concerns over the leaching of excess NO$_3^-$ exist, biosolids have been combined with high organic carbon material such as sawdust or woodchips to reduce the potential for NO$_3^-$ leaching through the immobilisation of nitrogen (McLaughlin, 1996; Bhogal et al., 1997; Brown et al., 2000).

Early nitrification studies assumed that nitrification did not occur at soil pH < 5, but more recent studies confirm that nitrification, mostly by chemolitho - autotrophic bacteria, does occur in acid soil and will result in increased leaching of NO$_3^-$ from the soil. The loss of nitrogen from the soil can be decreased by changing the carbon (C): nitrogen (N) ratio. Pierzynski et al., (2000) suggest that nitrogen immobilisation and mineralisation are balanced when the soil has a C:N ratio of 25 : 1 and that a C:N ratio of less than 25:1 can lead to
excess soluble nitrogen being lost to the environment. Nitrogen mineralisation is mediated by heterotrophic organisms and immobilisation involves the assimilation of inorganic nitrogen by soil micro-organisms. Immobilisation is controlled to a large extent by the availability of carbon that is needed by the soil micro-organisms to produce amino acids and proteins. If there is an inadequate supply of carbon relative to inorganic nitrogen, microbial growth and consumption will be reduced leading to a reduction in the conversion of soluble nitrogen to biomass nitrogen and a loss of soluble nitrogen as NO$_3^-$ or NH$_4^+$. In Eucalypt forests the C:N ratio can be as high as 70:1 (Bellairs, 1999).

Phosphorous is often the nutrient that limits N fixation during the early stages of soil development and plant succession in the native Australian landscape (McLaughlin, 1996) and it can be made available through biosolids application. It can be seen from the above discussion that the effects of biosolids application are site, plant and media specific and that their use depends on several parameters and should be evaluated before field application commences.

Phosphorous concentrations in Australian soils are very low (Handreck, 1997; Atwell et al., 1999) and therefore phosphorous will most likely be deficient in mine spoil for introduced plant species, but may not be critical for native plant species such as eucalypts and acacias (Handreck, 1997). The plant availability of the phosphorous in the spoil will be affected by the acidity and the Al content of the spoil. From acid to alkaline conditions (pH 4-9) phosphorous exists mainly as di-hydrogen phosphate (H$_2$PO$_4^-$), hydrogen phosphate (HPO$_4^{2-}$) and PO$_4^{3-}$ (Pierzynski et al., 2000) and the phosphorous in the biosolids would most likely be released as PO$_4^{3-}$. Under acid conditions where there is a supply of Al, Fe or Mn, the formation of very insoluble metal phosphates could occur, however after the addition of Bauxsol™, increases in soil pH and the subsequent decreases in Al, Fe and Mn would allow the formation of plant available H$_2$PO$_4^-$ and HPO$_4^{2-}$ (Pierzynski et al., 2000). Under acidic conditions more positively charged binding sites are available on very fine mineral particles in the soil and these can also bind the negatively charged phosphate species.

If the neutralisation of acid and the removal of soluble Al, Fe and Mn occurs in the soil profile then soluble and plant available phosphorous could be leached through the upper profile, however, the leaching of phosphorous would not occur through the acid, metal rich unamended lower profile and the phosphorous would be bound as low solubility minerals in this zone.
Gregory A Maddocks

Bauxsol™

Red mud is the caustic residue produced during the production of alumina from bauxite by the Bayer process. In 1999 global red mud production was estimated to be in the order of 40 million tonnes per year. However, due to dramatic increases in alumina production, estimates of global red mud production are now closer to 100 million tonnes per year. Figures on the volumes of red mud in containment facilities worldwide are not available but can be assumed to be the order of 1000s of millions of tonnes range.

When red mud is discharged to containment facilities it contains insoluble solids and caustic liquor that could not be economically recovered. The supernatant liquor comprises the caustic-aluminate solution that is used to digest and remove the aluminium. It typically comprises NaOH, NaCO₃, NaHCO₃, and NaAlO₂ the insoluble bauxite minerals in the red mud are usually dominated by hematite (Fe₂O₃) and aluminous goethite ((Fe, Al)OOH) (Hind et al., 1999) along with the titanium dioxide, anatase (TiO₂) and rutile (TiO₂) (Hind et al., 1999). Some boehmite (AlOOH) may also be present if the process is not designed to extract this form of alumina (Hind et al., 1999). The remaining elements in bauxite are present in the muds only in minor or trace quantities (Mc Conchie et al., 2000). Clay minerals or quartz present in the bauxite also react with the digestion liquor to produce a mineral compound known as Bayer-sodalite, (3(Na₂O·Al₂O₃·2SiO₂·nH₂O)·Na₂X) where X may be CO₃, SO₄, 2OH, 2Cl or a mixture of any or all depending upon the impurity composition of the digesting liquor (Chvedov et al., 2001). Sodalite and cancrinite are desilication products and can contribute some additional alkalinity (Somes et al., 1998 in Hanahan, 2001). Lime is another primary component of the Bayer process and reacts to form CaCO₃, 3CaO·Al₂O₃·6H₂O and a form of calcium phosphate, i.e. carbonate or hydroxyapatite (Chvedov et al., 2001). At high bauxite digestion temperatures (230–260°C), the lime can also react with the titanium mineral anatase to form perovskite CaTiO₃ and or kassite (CaTi₂O₄(OH)₂) (Chvedov et al., 2001). These minerals are also potential sources of carbonate alkalinity in the red mud.

Given the large volumes of red mud being produced each year and the costs of building and maintaining containment facilities, re-use of this industrial by-product can be an economically and environmentally rational solution. If the red mud can be re-used then the costs associated with the construction and maintenance of containment facilities can be reduced. To decrease the environmental liabilities of red mud handling and storage the causticity of the red mud and supernatant liquor is reduced through various neutralisation
processes. The red mud produced by ALCOA in Western Australia is neutralised through the absorption of reducing the pH of the red mud from $\approx 11$ to $\approx 9$. The addition of CO$_2$ combined with Atomer gas sheering technology (developed by CVG – Bauxilum) is another method of reducing red mud pH (12.2 to 7.6) (Galarraga *et al.*, 2002). In the Northern Territory (Australia) the ALCAN refinery uses separates the SNL from the red mud by a red mud farming process and then treats the supernatant liquor with seawater to lower the basicity but elements that form oxyanions (e.g. As, Cr, Mo, Se & V) and some aluminium tend to remain in solution and the fluid has to be diluted before it can be discharged to the sea. At the Queensland Alumina refinery (QAL), seawater is used to neutralise the caustic (pH 11-13) red mud without separating the solids from the residual liquid and there is no loss of the elements that form oxyanions because they can be bound to the solid particles (McConchie *et al.*, 1996). At QAL some seawater is added before the red mud is pumped to the red mud dam (this is done to ensure the slurry can be pumped while conserving fresh water) and the rest of the required seawater is added at the red mud dam; excess seawater is discharged from the red mud dam to the sea. In some refineries acid has been used to neutralise the red mud and in others the red mud has been dumped directly into the sea. Stacking of red mud is also widely adopted as a method of separating supernatant liquor for solid residues and has been widely used by ALCAN since the 1970’s (Belanger, 2001).

Reuse of red mud is gaining increased acceptance throughout the world. Red mud is being sold by ALCOA in Western Australia as Alkaloam and is being used for the retention of phosphorous in sandy soils adjacent to coastal estuarine waters where the loss of phosphorus to the waterways contributes to eutrophication and algal blooms. Martinent-Catalot *et al.* (2002) report on another commercial product called Bauxaline that is produced from red mud and is used for dump remediation, as a colouring agent and for arsenic (As) fixation. Red mud has been used to bind heavy metals, neutralise soil acidity, and retain phosphorous in soil and in aqueous solutions (Apak *et al.*, 1997; Altundogan *et al.*, 2000; Gupta *et al.*, 2001; Hanahan, 2001; Kadirvelu *et al.*, 2001; Chunlei *et al.*, 2007; Garau *et al.*, 2007; Paradis *et al.*, 2007). Other authors have used red mud to adsorb carbon dioxide released from decomposing sewage sludge, thereby increasing the pH buffering capacity of compost (Qiao and Ho, 1997) while others have used it as a catalyst in hydrodechlorination reactions (Ivarez *et al.*, 1999; Ordonez *et al.*, 2001). Red mud is also being used as an additive
in cements, and is being used in building materials such as bricks, tiles and road construction material (Mymrin and Vazquez-Vaamonde, 2001).

Virotec International have patented the Basecon™ process that utilises seawater, or Ca and Mg rich brines, or Ca and Mg chlorides, or some combination of these alternatives to neutralise red mud by converting soluble alkalinity to solid alkalinity. The Basecon™ process produces a red mud derivative known as Bauxsol™ (Mc Conchie et al., 2003). Bauxsol™ is the base reagent in a variety of products being marketed by Virotec International for the treatment or beneficiation of AMD, acid sulfate soils, acid waste rock dumps, acidic aquaculture ponds, sewage water and solids, tannery wastes and the treatment of industrial process waters (McConchie and Clark, 1996; Lin et al., 2002a; Mc Conchie et al., 2002; Lin et al., 2004b; Maddocks et al., 2004; Maddocks et al., 2005). The quality and chemistry of the Bauxsol™ produced by this neutralisation process varies depending on the source of the bauxite and operational procedures at the refinery (Mc Conchie et al., 2003). In general the acid neutralising capacity of the Bauxsol™ ranges between 3.5 and 7.5 mol / kg. The Bauxsol™ produced by this process contains some soluble Ca^{2+}, Mg^{2+}, SO_{4}^{2-}, Cl^-, Na^+, and minor amounts of trace elements: all these metals fall below threshold values set by the NSW EPA for the US EPA’s TCLP test.

The Bauxsol™ reagents used in this thesis were obtained from the Queensland Alumina refinery (Gladstone, Queensland, Australia). Further detail is provided on the Basecon™ process and Bauxsol™ technology in Chapter 3.

Lime

In recent years some mining companies have responded to the challenges associated with reducing the risk of waste rock dumps discharging AMD by using in-situ remediation techniques in the construction of their waste rock dumps. At the Grasberg mine, operated by PT Freeport Indonesia in Indonesia, the addition of limestone has been trailed and found to be effective (Miller et al., 2003). Other studies designed to test the concept of in-situ remediation of mine waste (Taylor et al., 2005) and to assess the effectiveness of these approaches at field scale level (Rusdinar, 2005) have also been conducted.

Whereas limestone is a common soil additive used to immobilise heavy metals, at sites where the soil is likely to re-acidify, limestone may have limited use as a single addition treatment because it may not maintain the desired soil pH over time (Hamon et al., 2002) as
the particles become armoured by precipitates or leached out by groundwater. Other limitations on the use of lime are that although it will increase soil pH in the amended soil zone, it does not contribute to increased soil pH below the amended zone unless it is applied well in excess of the requirements indicated by acid-base accounting (Cregan et al., 1989, in Robson, 1989; Derome, 2000). The capacity of limestone to infiltrate into and neutralise acidity is also constrained by the application approach and the chemical and physical nature of the limestone (Rusdinar, 2005). Excessive applications of lime, as CaO or as Ca(OH)$_2$ are also undesirable because soil pH will become alkaline and may adversely affect plant establishment or growth and can also affect soil chemistry. The failure of lime to remediate sub-soil pH when the target soils contain sulfide minerals is mainly a result of armouring of lime particles particularly by precipitated Fe and Al oxyhydroxides (Rose and Elliot, 2000) and the fact that the neutralisation capacity of the lime is quickly consumed (Ren sheg Li et al., 1998); gypsum precipitation can also adversely affect soil texture and permeability. Lime applied as Ca(OH)$_2$ or CaCO$_3$ is also slightly soluble and consequently, it can be leached from the treated rock units over time. Any under-liming resulting from leaching the lime before all sulfides have oxidised can compound problems because the resulting bicarbonate ions can accelerate the decomposition of sulfides and the resulting generation of acid. The accumulation of heavy metal hydroxides and hydroxycarbonates following lime neutralisation can create phytotoxic conditions for plant growth (Vangronsveld et al., 1996) and if over-liming raises pH conditions much above 9, the higher pH can facilitate the mobilisation of Al as Al(OH)$_4^-$ and elements such as As, Cr, Mo, Se, V, etc that form oxyanions under oxidising conditions.

The addition of lime to acid waste is a common method used to increase soil pH and immobilise heavy metals like Cd, Zn, Cu and Ni through the formation of sparingly insoluble hydroxides (Khan et al., 2000). However, if the pH of the soil decreases later, the metal complexes may be destabilised and the metal ions will be released back into the environment (Gabler, 1996; Kramer et al., 1998; Schuiling, 1998; Gray et al., 2006).
CHAPTER 3

THE USE OF BAUXSOL™ TECHNOLOGY IN MINE SITE MANAGEMENT AND REMEDIATION

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CHAPTER 4

FIELD SCALE REMEDIATION OF MINE WASTES AT AN ABANDONED GOLD MINE, AUSTRALIA I-EFFECTS ON SOIL CHARACTERISTICS

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CHAPTER 5

FIELD SCALE REMEDIATION OF MINE WASTES AT AN ABANDONED GOLD MINE, AUSTRALIA II-EFFECTS ON PLANT GROWTH AND GROUNDWATER

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CHAPTER 6

BIOACCUMULATION OF METALS IN EISENIA FETIDA AFTER EXPOSURE TO A METAL LOADED BAUXSOL™ REAGENT.

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CHAPTER 8

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APPENDICES
APPENDIX A

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APPENDIX B

From: schwarzbauer@lek.rwth-aachen.de
To: gmaddocks@golder.com.au
Cc:
Subject: Environmental Geology - Decision on Manuscript ID EG-08-0280

Body: 05-Aug-2008

Dear Mr. Maddocks:

Manuscript ID EG-08-0280 entitled "Field Scale Remediation of Mine Wastes at an Abandoned Gold Mine, Australia I-Effects on Soil Characteristics" which you submitted to Environmental Geology, has been reviewed. The comments of the reviewer(s) are included at the bottom of this letter.

The reviewer(s) have recommended a further review step after some major revisions. Therefore, I invite you to respond to the reviewer(s)’ comments and revise your manuscript.

To revise your manuscript, log into https://mc.manuscriptcentral.com/eg and enter your Author Center, where you will find your manuscript title listed under "MANUSCRIPTS WITH DECISIONS." Under "Actions," click on "CREATE A REVISION." Your manuscript number has been appended to denote a revision.

You will be unable to make your revisions on the originally submitted version of the manuscript. Instead, revise your manuscript using a word processing program and save it on your computer. PLEASE ALSO HIGHLIGHT THE CHANGES TO YOUR MANUSCRIPT WITHIN THE DOCUMENT BY USING THE TRACK CHANGES TOOL IN MS WORD OR BY USING BOLD OR COLORED TEXT.

Once the revised manuscript is prepared, you can upload it and submit it through your Author Center.

When submitting your revised manuscript, you will be able to respond to the comments made by the reviewer(s) in the space provided. You can use this space to document any changes you make to the original manuscript. To expedite the processing of the revised manuscript, please be as specific as possible in your response to the reviewer(s).

IMPORTANT: Your original files are available to you when you upload your revised manuscript. Please delete any redundant files before completing the submission.

Because we are trying to facilitate timely publication of manuscripts submitted to Environmental Geology, your revised manuscript should be uploaded as soon as possible. If it is not possible for you to submit your revision in a reasonable amount of time, we may have to consider your paper as a new submission.

Once again, thank you for submitting your manuscript to Environmental Geology and I look forward to receiving your revision.

Sincerely,
Dr. Jan Schwarzbauer
Associate Editor, Environmental Geology
schwarzbauer@lek.rwth-aachen.de

Reviewer(s)’ Comments to Author:
Reviewer: 1
Comments to the Author
Product trade-names should not be used to identify the soil amendment throughout the paper. The trade-name may be used once in the paper (along with identified manufacturer) after the product has been briefly described, i.e. Treatment 2 was a solid amendment complex (henceforth referred to as "red mud") of Fe-Al oxyhydroxides and alumino-hydroxy-carbonates (TerraB, Virotec International Limited, Australia), applied along with Biosolids.

Reference to TerraB and Bauxosol should not occur after that and the products should then only be referred to as "red mud" (or whatever descriptors the authors wish to use to identify them). I would also strongly suggest that the same change be made to part II (companion manuscript) of this manuscript if trade-names have been used there as well. If the authors agree to make this suggested change, I will then review this manuscript in detail.

05-Aug-2008
It is a pleasure to accept your manuscript entitled "Maddocks 2008-Field Scale Remediation of Mine Wastes at an Abandoned Gold Mine Australia II-Effects on Plant Growth and Groundwater" in its current form for publication in Environmental Geology. The comments of the reviewer(s) who reviewed your manuscript are included at the foot of this letter.

Reviewer(s)' Comments to Author:
Submitted paper titled "Field Scale Remediation of Mine Wastes at an Abandoned Gold Mine, Australia II - Effects of plant Growth and Ground Water" by Maddocks et el., presents a continuation of already published investigations in this journal. In the manuscript the authors gave a lot of interesting experimental results with acceptable statistical interpretation. The paper is at the high professional level with some fundamental input.

Technically, the manuscript has been written at an acceptable level. English language is good, figures are of high quality as well as the tables. Because of that, with great pleasure, I would recommend the publishing of this paper in Environmental Geology journal without important changes.

Date Sent: 14-May-2008
APPENDIX C
March 19, 2004

Dr. Greg Maddocks
4 Sovereign Place
Goonellabah NSW
Australia

Dear Dr. Maddocks:

Re: 04-087 “Bioaccumulation of Metals in Eisenia fetida after Exposure to Metal Loaded Bauxsol Reagent”

Your paper has been reviewed for publication in Environmental Toxicology and Chemistry (ET&C) and has been judged:

Acceptable for publication with minor revisions
Acceptable for publication with major revisions X

One of the reviewers that evaluated your original manuscript still has concerns that you did not adequately address in your re-submission. Specifically, concern was raised regarding the experimental details. These comments are significant, thus a major revision is required. I would encourage you to pay particular attention to these comments.

Please consider carefully the comments of the reviewers and modify the manuscript as appropriate. Revisions should be completed within a three-month period. Submit the original and a copy of the revised manuscript with a letter stating (in detail) your disposition of each of the reviewers’ suggestions, item by item, indicating the page and line number of the revised text. **Highlight the sections that have been changed on the copy of the revised manuscript to aid the editor in checking revisions.** If you wish to reject all or specific suggestions, please state your reasons. Include an electronic version of the manuscript on a clearly labeled floppy disk (manuscript number, name of corresponding author). Place electronic versions of the figures in separate files on the same disk, if these are available.

If the revisions are acceptable, your paper will be scheduled for early publication in ET&C. If your revised manuscript is not received in my office within three months, it will be rejected for publication. However, the revised manuscript may be sent to the Editor-in-Chief as a new submission for peer review.

This manuscript should not be returned until necessary editorial changes, which will be sent from the office of the Editor-in-Chief, have been incorporated into your final, revised manuscript.

Sincerely,

Todd Anderson
Editor

xc: C.H. Ward
Title: Bioaccumulation of Metals in *Eisenia fetida* after exposure to a metal loaded Bauxsol reagent
by Greg Maddocks, Amanda Reichelt-Brushett, David McConchie, and Jaco Vangronsveld

**General**

<table>
<thead>
<tr>
<th>Question</th>
<th>Yes/No</th>
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<tr>
<td>Is the subject matter within the general scope of ET&amp;C?</td>
<td>Yes</td>
</tr>
<tr>
<td>Is new knowledge presented?</td>
<td>Yes</td>
</tr>
<tr>
<td>Do the title and abstract describe accurately the contents of the paper?</td>
<td>Yes</td>
</tr>
<tr>
<td>Should the title be shortened?</td>
<td>No</td>
</tr>
<tr>
<td>Are the hypothesis, methods, results, and discussion presented in a clear and logical way?</td>
<td>Yes</td>
</tr>
<tr>
<td>Is the manuscript too long?</td>
<td>No</td>
</tr>
<tr>
<td>Are experimental designs, statistical methods, and data-analysis techniques adequately described?</td>
<td>Yes</td>
</tr>
</tbody>
</table>

**Tables and Figures**

<table>
<thead>
<tr>
<th>Question</th>
<th>Yes/No</th>
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<tbody>
<tr>
<td>Are all the tables and figures relevant?</td>
<td>Yes</td>
</tr>
<tr>
<td>Are all columns in tables labeled properly?</td>
<td>Yes</td>
</tr>
<tr>
<td>Do inconsistencies between tables and figures exist?</td>
<td>No</td>
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</table>

**Language**

<table>
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<tbody>
<tr>
<td>Does the language or spelling need corrections?</td>
<td>No</td>
</tr>
<tr>
<td>Should the paper be returned to the author with instructions to seek assistance with the language?</td>
<td>No</td>
</tr>
<tr>
<td>Is the message of the author clearly and concisely conveyed by the language used?</td>
<td>Yes</td>
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**Determining Acceptability and Criteria for Rejection**

<table>
<thead>
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<th>Question</th>
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<td>Is the quality of the science adequate?</td>
<td>Yes</td>
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<tr>
<td>Is the scientific methodology flawed?</td>
<td>No</td>
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<tr>
<td>Are more experiments needed?</td>
<td>No</td>
</tr>
<tr>
<td>Does the experimental work address the aims stated in the introduction?</td>
<td>Yes</td>
</tr>
<tr>
<td>Do the results support the conclusion?</td>
<td>Yes</td>
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</table>

**Rank of Paper**

<table>
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<th>Rank</th>
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<tbody>
<tr>
<td>Please rank (1=highest; 5=lowest) the relative importance of the paper’s contribution to the field:</td>
<td></td>
</tr>
<tr>
<td>Relevance to the field</td>
<td>2</td>
</tr>
<tr>
<td>Scientific merit (quality of the science)</td>
<td>2</td>
</tr>
<tr>
<td>Relative degree of advancement of the field</td>
<td>3</td>
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</tbody>
</table>

**Ground-breaking research worthy of advance publicity**

<table>
<thead>
<tr>
<th>Answer</th>
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</thead>
</table>
Title: Bioaccumulation of Metals in *Eisenia fetida* after exposure to a metal loaded Bauxsol reagent

**General Comments**

I found this to be generally well-written paper and easy to understand. Lack of page numbers made reviewing the manuscript more difficult than it needed to be. The authors are reminded to include page numbers on future submissions. There are several places where there is a subject-verb tense disagreement; in particular – data are plural. The manuscript needs to be carefully reviewed to ensure tense agreement. My specific comments are listed below:

**Specific Comments**

<table>
<thead>
<tr>
<th>Comm. #</th>
<th>Page</th>
<th>Line</th>
<th>Correction/Suggestion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>4</td>
<td>“compared the metal concentrations in <em>Eisenia fetida</em> . . .”</td>
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<tr>
<td>2</td>
<td>4</td>
<td>18</td>
<td>While TCLP is defined in the previous sentence, I see no such definition of SEP. Please provide one.</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>20</td>
<td>“Australia, were . . .”</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>22</td>
<td>“reagent were added . . .” Watch proper tense usage throughout the manuscript.</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>20</td>
<td>“The outside of the containers was painted . . .”</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
<td>3</td>
<td>The worms were allowed to depurate gut contents for 48 hours. The most recent EPA guidance manual on sediment toxicity testing includes a discussion of depuration periods for the aquatic oligochaete, <em>Lumbriculus variegates</em>, indicating that depuration periods exceeding 6 hours may result in loss of material from tissues for chemicals with low octanol-water partition coefficients, such as metals. I think this same argument can be made for terrestrial oligochaetes. Please discuss how a 48-h depuration period could affect the concentration of metals in tissues.</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>2</td>
<td>“data were” “Data” are plural.</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>16</td>
<td>Simply throwing out “outlier” data to achieve better $r^2$ values is not necessarily a very good way to obtain data correlations. Were outlier statistical tests to determine if discarded values could truly be considered outliers? Additional explanation of this data elimination process is warranted.</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>18</td>
<td>Please explain why higher MLBR results in decreasing food mass.</td>
</tr>
</tbody>
</table>
“Bioaccumulation of metals in *Eisenia fetida* after exposure to a metal loaded Bauxsol reagent“

Please reference comments by page and line numbers; do not write comments on the manuscript unless critical to the review process (e.g., sketched changes to illustrations). Please consult general guidelines on the reverse side and rank the paper from 1 to 5 according to its relative importance as a contribution to scientific literature

This work examined the accumulation of metals by the worm after exposure to Bauxsol reagent that contained high metal load. The speciation of metals in the ‘soil’ was determined using traditional Tessier et al. sequential extraction method. Correlation was then conducted to examine the fraction that may control metal bioavailability. The approach is traditional and the finding that metals were not bioavailable (or very little bioavailable) is not surprising (given that these metals were essential in ‘granule’ forms). However, the methodology in conducting the experiment may have limitations (see below). The writings also have numerous problems. Given the confusion on data presentations, some of the findings are in fact not clearly discussed. The authors are encouraged to re-write this paper, with focus on important findings, and submitted it to other journals for possible publication.

Specific comments
1. Abstract: needs to be modified. Delete the unnecessary sentences (e.g., line 3-7). Combine the different paragraphs into one paragraph. Start the ‘however changes occurred….., line 16) with a new sentence.

2. Introduction. Line 6, ‘have a reaction pH of 9.0’ is not clear to me. Line 15, in turn should be ‘in turn’; line 18: SEP should be defined (even though it appears in Abstract).

3. Methodology (P4), last line, After mixing the Bauxsol reagent was allowed.. this is not clear.

4. P5. Line 10-22. The worm (12-15 individuals, each 5-7 cm) in 500 ml beakers. This ‘crowding’ effect can be a potential serious problem. The mixture of MLBR with cow manure: did these earthworms select the food, or they ingested the MLBR? These can considerably affect the experimental results. For example, the low BAF measured in this study may not be due to the low bioavailability of metals from MLBR, but was due to the very ingestion of these materials (e.g., reducing the dose to the animals). Without this information, it is in fact difficult to interpret the experimental results obtained from this study. A look at Table 6 in fact suggests that the earthworm weight had decreased as compared to the initial exposure. The authors mentioned that there was no mortality, but growth should be a critical parameter to assess the toxicity of these materials to the earthworm (or caused by starvation).

5. P6, line 12, at 0 and 28 days…. It seems that only 20% MLBR was measured for the speciation after exposure (see next page line 3).

6. P6, last paragraph and entire P7, these descriptions of methods need to be integrated and combined. The relationships between metal fraction and metal accumulation was mentioned in a few different places (P6, line 22, P7, line 19-22).

7. P7, line 18. Table 2 should be Table 3. However, this should be presented in the Results section.

8. Results, P8, last paragraph. The growth data may be presented here.
9. P9. Line 3. Estimation of bioavailability (EB): What is this and how is it quantified? I am very confused by Table 4. The data need to be clearly discussed.

10. P9, line 11. Correlations between…. This section can be combined with the previous section to talk about the correlation analysis.

11. P9, line 18. Again, I am also confused by Table 5. r2 is given for which metal? As it stands, there were 3 replicates for each treatment. How the correlation was conducted for different treatments? These data need to be clearly presented and discussed.

12. P9, line 24. Delete ‘These data in’ at the beginning of this sentence.

13. Discussion. P10, bottom, discuss their ingestion behavior. Approximately how much the earthworm ingest MLBR?


15. P11, line 23. The growth data should be mentioned. How about the growth dilution? For example, an increase or decrease in weight may result in dilution or increase in metal concentration.

16. P12, line 4, should not and did not occur.. should be revised.

17. P12, last paragraph and P13, first paragraph. I am not very convinced about the discussion. For example, Fe2+ can be rapidly re-oxidized into Fe3+. Cd does not have a strong affinity (line 19). Other metals have a much stronger affinity. Cr in soil is mostly associated with the residual (lattice fraction), instead of exchangeable fraction, etc. I suggest the authors remove these speculations.

P13, line 10, Relationships between selective metals.. This discussion can be important, but I find that 1) line 12-24 looks like a review 2) the correlation can be more mechanistic (P14). For example, which fraction is most important, whether it increases or decreases accumulation.

P14, Conclusion. Can be condensed. The last paragraph can be deleted.

P15. table 2 should be table 1.

All the table captions should be changed.
Table 3. Perhaps presenting the data in percentages (instead of concentration) such that it will be easier to make the comparison.

Table 4 and table 5. Very confusing. How these analyses were conducted?
Title of Article: Bioaccumulation of metals in Eisenia fetida after exposure to a metal loaded Bauxsol trade mark, serif reagent.

Author(s): Gregg Maddocks, Amanda Reichelt-Brushett, Jaco Vangronsveld, David Mc Conchie

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___ If one author on behalf of all authors: I certify that I am authorized to execute this document on behalf of all authors named above.

------------------------------------------------------------------------------------------------------------------------------------------------------------------
Signature       Printed name       Date

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Signature       Printed name       Date