Leach Testing of Bayer Residue Products in Various Environments

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material that has been accepted for the award of any other degree or diploma in any university.

Signature: [Signature]

Date: 2nd May 2013
DEDICATION

This thesis is dedicated to Richard and Aron Attiwell, my husband and son, who constantly reminded me to balance family, work and study and who supported me through writing this thesis.

This thesis is also dedicated to my late supervisor, Chanelle Carter, who was tragically killed in a cycling accident in April 2010 during the writing of this thesis. This dedication is in recognition of the technical support and encouragement she provided during my research and for continuing to remind me not to be discouraged, but to give everything a go to the best of my ability.
ABSTRACT

Two bauxite residue products, Alkaloam® and Red Lime™, generated from Alcoa of Australia’s Western Australia alumina refineries, have the potential to be re-used in a range of applications, in particular in agricultural land management as soil amendments for phosphorus retention and as an agricultural liming agent.

Currently there are no regulatory frameworks or guidelines in Western Australia to promote and facilitate the re-use of industrial by-products. This is partly due to the lack of assessment protocols required to ensure that all regulatory standards have been met, with assurance that a by-product is safe and acceptable by the community as a suitable raw material for re-use. In addition, the Australian Standard Leaching Procedure (ASLP), the standard leach test adopted in Australia for environmental assessments, is significantly limited and not suitable for assessing leaching in industrial by-products, such as Alkaloam® and Red Lime™.

The aim of this thesis was therefore to determine whether a more suitable leach test could be used as an alternative to ASLP for assessing industrial by-products and apply this leach test to Alkaloam® and Red Lime™ for investigating their leach behaviour when used as a soil amendment or liming agent.

This thesis reported on relevant literature on the re-use of bauxite residue products, international leach test procedures and current assessment of industrial by-products for re-use.

The European standard pH dependent leach test was compared to ASLP for assessing the leaching behaviour of Alkaloam® and Red Lime™ and for determining its suitability for assessing industrial by-products for re-use in different pH scenarios. This leach test was more superior to ASLP in that it provided more accurate and fundamental leaching information on Alkaloam® and Red Lime™ and was considered more suitable for assessing by-products for re-use, in particular materials that were highly alkaline and exhibited high buffering capacity.

Method optimisation was conducted on the pH dependent leach test to improve leaching assessments on clay type soils and to allow nitrate leaching to be assessed in WA soils ameliorated with Alkaloam® and Red Lime.
The main focus of this thesis was on characterising and assessing the pH dependent leaching behaviour of Alkaloam® and Red Lime™ and determining changes in leaching at different pH for a range of WA soils, when ameliorated with Alkaloam® and Red Lime™ at an application rate of 6.25g/kg (Alkaloam®) and 1.6g/kg (Red Lime™). A Bassendean soil and agricultural soils in the Peel Harvey catchment and Merredin and Newdegate region were assessed in this study. LeachXST™ geochemical modelling was applied to the pH dependent leach data to identify the processes controlling leaching of species in these scenarios as well as the speciation likely to be present in the liquid and solid phase during leaching.

It is anticipated that this information will be a key input into the environmental assessment of Alkaloam® and Red Lime™ as an agricultural soil ameliorant and liming agent as these products progress towards becoming commercialised as raw material commodities.
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5) Pinjarra Community Consultation Network Group, April 2011 – ‘Re-use of Red Sand™.’
6) Waroona/Yarloop Community Consultation Network Group, June 2011 – ‘Alcoa Residue Re-use.’

7) Peel Development Commission, June 2011 – ‘Re-use of Residue Sand and Residue Mud (Alkaloam®).’

8) Royal Melbourne Institute of Technology (RMIT), August 2011 – ‘Re-use of Alcoa bauxite residue in Western Australia.’

9) Pinjarra Progress Association AGM, September 2012 – Re-use of Red Sand™
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Chapter 1

INTRODUCTION

1.1 Background
As society enters into an era of environmental sustainability, there has been a heightened awareness that supplies of natural raw materials (e.g. sand, limestone, etc.) and land resources are progressively depleting. At the same time, the demand for these materials is increasing through progressive development and increased population.

In the mining industry large areas of land are required to store residue, the insoluble by-product remaining from the refining and extraction of natural ores. As mining companies continue to expand and refinery production rates increase, the volumes of residue to be stored also increase. Conversely, community expectations are that mining companies should not increase their land usage requirements in future operations, so that valuable land resources can be retained.

The goal to decrease or maintain current land usage requirements, whilst increasing production and maximising social benefit, has led industries, such as the alumina industry, to explore opportunities for re-using residue. Acceptance by community, government and industry alike towards the use of industrial by-products (residue) as alternatives to natural raw materials would not only increase availability of resources for future developments, but ensure that industrial processes become more environmentally, economically and socially sustainable.

An industrial by-product in the alumina industry, bauxite residue, is the insoluble material remaining when bauxite is refined to produce alumina. Bauxite residue has been categorised into three potential products that could be considered for re-use. The three products are: the fine fraction of bauxite residue, termed ‘red mud’; the solid alkaline component of red mud, known as ‘Red Lime™’; and the coarse fraction of bauxite residue, known as ‘Red Sand™’. Research described in this thesis relates to the two former products, red mud and Red Lime™.

Red mud has been extensively researched over the past two decades for its use as an agricultural soil amendment under the tradename “Alkaloam®”. Broad scale agricultural field trials conducted in the Peel Harvey catchment by the Department of Agriculture and
Food, Western Australia (DAFWA, formerly Department of Agriculture), have shown that Alcoa’s Alkaloam® can successfully improve the nutrient retention properties of Western Australia’s (WA’s) infertile and poor water retaining sandy soils, and consequently reduce eutrophication in the Peel-Harvey water systems (Rivers, 1999; EPA WA 2000).

In addition, Red Lime™ has been trialled as an alternative to conventional agricultural lime in DAFWA field and pot soil amendment trials, using soils across the Peel Harvey Catchment and Wheatbelt area (Clarendon et al., 2010). The emphasis on these trials was to illustrate the yield increase and nutrient retention benefits from ameliorating soils with Alkaloam®, and the benefits from increasing the buffering capacity of the soils using Red Lime™ amelioration.

Very limited information was provided on the leaching properties of these ameliorants in the different types of soils and whether there are likely to be any potential impacts on the environment when these materials are utilised in these applications.

Environmental monitoring of the broad scale Alkaloam® field trials in the Peel-Harvey Catchment required leach testing to be conducted on soils using lysimeters and the Toxicity Characteristic Leaching Protocol (TCLP), as recommended by the EPA (EPA WA, 2000). These tests were to assess both the short and long-term impacts of soil amendment with Alkaloam® at (cumulative) amounts greater than 20 tonne per hectare (t/ha) application rate. Understanding the leaching behaviour of industrial by-products, such as Alkaloam® and Red Lime™, in specific re-use scenarios is a critical factor for assessing their feasibility in different re-use applications.

Characterising the leaching behaviour of a material can provide insight into whether species are likely to be released into a receiving environment – whether it is from direct leaching into groundwater, mobility via run off, or whether species are likely to remain bound in the soil, becoming potentially bio-available for flora or fauna. In turn, this information will determine whether a material is likely to cause any detrimental impact to the environment.

The reliability of the TCLP data obtained during the trials for assessing Alkaloam® leaching was questioned by Gerritse (2000). This is because the TCLP test is designed to assess leaching of materials co-disposed into landfill systems at acidic pH, and therefore may not be appropriate for assessing leaching from highly alkaline materials, such as Alkaloam®. No final pH values were reported using the TCLP method, and since control of pH is required to generate accurate data, the method is not considered suitable.
The information provided from the TCLP also lacked information regarding the mechanisms controlling leaching, the chemical speciation present, or if leaching behaviour can change if the environment pH changes over time. This information would be valuable in providing a more thorough environmental risk assessment for using industrial by-products for re-use. The European standard pH dependent leach test, with the use of leachXST™ geochemical modelling, has been shown to provide such information and is considered more representative than TCLP for the environmental assessment of industrial by-products for re-use. Application of this test will be demonstrated in this thesis.

Currently there are no regulatory frameworks or guidelines in Western Australia (WA) to promote and facilitate the re-use of industrial by-products or encourage international marketing of these products, in particular for use in land applications such as soil amelioration or in construction. Whilst resource synergies have been identified in WA, with the potential for exchanging industrial by-products amongst companies for mutual benefit, industry has been reluctant to invest in these synergies. This is partly due to the lack of assessment protocols required to ensure that all regulatory standards have been met, with assurance that their product is safe and acceptable by the community as a suitable raw material for re-use (Harris, 2007). Until such time that government provide a suitable framework for assessing by-products for re-use, or economics drive private companies to engage with industry to promote and market new environmentally sustainable products to the community, it is unlikely that significant progress will be made towards by-product re-use in WA. Raw materials will continue to deplete at an increased rate and the cost of these commodities will progressively increase.

Given the significant limitations of the TCLP and the absence of suitable legislative guidelines, an investigation was launched through the Centre for Sustainable Resource Processing (CSRP), Curtin University and Alcoa to:

(i) determine the suitability of existing leach testing methods in Australia for assessing industrial by-products for re-use applications, and how they compare to the European standard pH dependent leach test;

(ii) determine the optimum conditions for conducting pH dependent leach testing on clay type soils; and

(iii) assess the likely acceptability of Alkaloam® and Red Lime™ as raw material products.
To this end, the focus of this thesis is on characterising and assessing the leaching behaviour of two industrial by-products produced from Alcoa of Australia’s WA alumina refineries, namely Alkaloam® and Red Lime™, amended in various WA soil environments. LeachXS™ geochemical modelling was used to identify the processes that control short-term leaching of major and trace elements in these scenarios and the speciation present during leaching. It is anticipated that this information will be a key input into the environmental assessment of Alkaloam® and Red Lime™ as an agricultural soil ameliorant and liming agent respectively when these products progress towards becoming commercialised as raw material commodities.

1.2 Plan of Thesis
The thesis is divided into 12 chapters as follows;
Chapter 1 – provides the introductory overview of this research, and the aim of the work.

Chapter 2 – reviews relevant literature on the re-use of bauxite residue products, leach test procedures and assessment of industrial by-products for re-use.

Chapter 3 – provides details of the samples and methodologies used in this thesis.

Chapter 4 – reports on method development conducted on the ECN pH dependent leach test, in particular the use of centrifugation for improved solid/liquid separation and the use of hydrochloric acid as an alternative extractant to nitric acid for investigating nitrate leaching.

Chapter 5 – discusses a comparison between the Australian Standard Leaching Procedure (ASLP) and the European standard pH dependent leach test; and the feasibility of using ASLP and/or the pH dependent leach test for assessing by-products for re-use applications in different scenarios is assessed.

Chapter 6 – reports on the characterisation of Alkaloam®, Red Lime™ and the agricultural soils and amended soils used in the Department of Agriculture and Food, WA (DAFWA) broad scale soil amendment and lime field trials. This chapter also discusses the composition of construction materials and natural beach sand to contextualise the data for Alkaloam® and Red Lime™.

Chapter 7 – reports on the leaching profiles of Alkaloam®, Red Lime™, four WA agricultural soils and a Swan Coastal Plain soil. Geochemical modelling is used to identify
the partitioning of species across a pH range of 1 to 12, and the mechanisms controlling leaching in these matrices.

Chapter 8 - investigates the leaching behaviour of Alkaloam® as a soil ameliorant in four WA agricultural soils and the Swan Coastal Plain soil across a pH range of 1 to 12. Geochemical modelling is conducted on the leach data to predict the mechanisms controlling leaching for particular species in the individual ameliorant and soils, and when combined as a treated soil. Comparisons of the leaching behaviour in the amended soils are compared against leaching behaviour of the individual components to determine changes in leaching attributed to a 6.25g/kg (10t/ha equivalent) amelioration rate. The assessment is also used to identify any necessary process development or product refinement required of Alkaloam® for developing a sustainable market for re-use.

Chapter 9 - investigates the leaching behaviour of Red Lime™ as a liming agent or soil ameliorant in four WA agricultural soils and a Swan Coastal Plain soil across a pH range of 1 to 12. Geochemical modelling is conducted on the leach data to predict the mechanisms controlling leaching for particular species in the individual ameliorant and soils, and when combined as a treated soil. Comparisons of the leaching behaviour in the amended soils are compared against leaching behaviour of the individual components to determine changes in leaching attributed to a 1.6g/kg (2.56t/ha equivalent) amelioration rate. This chapter also reports on the assessment of Red Lime™ against Western Australian Department of Environmental Conservation (DEC) environmental guidelines to determine the likely acceptability of it being used as a soil ameliorant or alternative liming material. The assessment is used to identify any necessary process development or product refinement required on Red Lime™ for developing a sustainable market for re-use.

Chapter 10 and 11 – summarises the overall conclusions and recommendations arising from the research work.

Chapter 12 – list of references.

Appendices are provided on the disk that accompanies this thesis.
Chapter 2

LITERATURE REVIEW

2.1 Background

Bauxite residue is a by-product generated when bauxite is refined to produce alumina, using the Bayer Process as illustrated in Figure 2-1.

The Bayer Process involves the digestion of ground bauxite ore in hot caustic (sodium hydroxide) to dissolve available gibbsite, which is then calcined into alumina. The insoluble material remaining after digestion is known as bauxite residue, which is predominantly composed of iron and silica oxide minerals. Bauxite residue is separated from the dissolved gibbsite by filtration to remove fines and by settling in thickeners. The residue is washed to recover the caustic before being removed from the Bayer circuit and piped to a residue storage area. Temperatures in the Bayer circuit are then decreased to precipitate aluminium hydroxide. Aluminium hydroxide is calcined at temperatures above 1000°C to remove the water of hydrolysis and produce α-alumina.
Worldwide the alumina refining industry generates 80 million dry metric tonnes of bauxite residue per annum, with at least 30 million tonnes produced in Australia (Angevin-Castro, 2006). At current production rates, Alcoa of Australia (Alcoa) in WA generates 18 million tonnes of bauxite residue per annum, which is stored in large geomembrane and clay lined areas, specifically designed for long term storage. Storing residue increases the cost of alumina production, through construction of new residue storage areas, management of existing storage areas and rehabilitation of closed areas.

Alcoa’s three WA refineries currently operate across 1380 hectares of land. On the basis that production will only continue to increase, residue storage is unsustainable due to the large area of land required. Alcoa Inc has therefore set global 2020 and 2030 internal targets\(^1\) around specific residue management strategies that will reduce residue going to storage. One of these strategies is to find high tonnage solutions for re-using bauxite residue in different applications.

2.2 Re-use of bauxite residue products

Unprocessed bauxite residue is typically alkaline in nature with high pH (~13) due to residual caustic being entrained in the material from the refining process. The entrained caustic constitutes the material hazardous, as defined by Worksafe Australia Standards (2004)\(^2\). Re-use of bauxite residue would therefore require some form of neutralisation to remove the entrained caustic and produce a non-hazardous material in order to be accepted as a raw material.

Several groups have attempted to neutralise the high pH in residue. McConchie \textit{et al.} (2005) and Fergusson (2007) successfully neutralised red mud using Basecon™ Technology, developed by Virotec International plc. to produce an inert and safe raw material called Bauxsol™ Raw Material (BRM). BRM is currently applied in a selection of environmental reagents for a wide range of applications, such as treatment of acid rock drainage waters to remove inorganic contaminants, or treatment of sulphidic waste rock to reduce leaching from mine sites.

Other neutralisation methods that have been investigated for red mud include acid neutralisation (Fois \textit{et al.}, 2007), sea water/bitterns neutralisation (Hanahan \textit{et al.}, 2004;\footnote{1 \ Alcoa Inc has set internal environmental targets to reduce residue going to storage through re-use by 30% by 2030 (with an intermediate goal of 15% by 2020).}

\footnote{2 \ A material is hazardous if it contains more than 0.5\% w/w NaOH or more than 20\% w/w Na\textsubscript{2}CO\textsubscript{3}.}
Menzies et al., 2004), microbial neutralisation (Hamdy et al., 2001; Krishna et al., 2005), carbonation neutralisation (Cooling et al., 2005; Khaitan et al., 2009), and partial neutralisation using gypsum.

The method of neutralising bauxite residue at Alcoa of Australia (Alcoa) is by atmospheric carbonation through frequent rotary hoeing of the red mud on residue drying beds. The atmospheric carbonation process converts the residual entrained sodium hydroxide in the red mud to sodium carbonate, effectively decreasing its alkalinity (from pH 13 to pH<10.5) and converting the mud to a benign product, suitable for re-use. Alcoa trades its carbonated red mud product under the name Alkaloam® when referred to as a soil ameliorant. The terms Alkaloam® and ‘red mud’ have been used interchangeably throughout literature reported on soil amelioration, but for the purposes of this thesis are considered to be the same, and will be referred to herein as Alkaloam®.

Forced carbonation has also been used at Alcoa to neutralise residue. Forced carbonation uses carbon dioxide gas under controlled conditions to neutralise the material (Cooling et al., 2002; Cooling et al., 2005). This process is applied to the fine fraction of residue at Alcoa’s Kwinana refinery prior to it being stored on the drying beds. The forced carbonation process has also been applied to the coarse fraction of Alcoa’s residue, Red Sand™, in a washing, carbonation pilot plant at Alcoa’s Wagerup and Kwinana residue sites (Jones, 2009). This processed sand has been demonstrated as a suitable aggregate material for use in road construction (Jamieson, 2009), a top dressing soil amendment media for recreational sports oval (MBS Environmental, 2009; Attiwell, 2010) and as fill in industrial land developments (Alcoa of Australia, 2012). Uses for bauxite residue in the alumina industry have been investigated for a range of applications. Some of the research is listed in Table 2-1.

---

3 Washed and force carbonated.
Table 2-1: Re-use of bauxite residue

<table>
<thead>
<tr>
<th>Feedstock for Cement production</th>
<th>(Singh et al., 1996)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production of Portland cement clinker.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Civil works</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Use in building materials, and pigments.</td>
<td>(Thakur and Sant, 1983)</td>
</tr>
<tr>
<td>Use as sub-grade and sub-base materials in road construction to replace limestone and sand.</td>
<td>(Jamieson, 2009), (WML, 2010) and (DAFWA, 2009)</td>
</tr>
<tr>
<td>Production of bricks.</td>
<td>(Yang et al., 2008)</td>
</tr>
<tr>
<td>Road embankment construction.</td>
<td>(Kehagia, 2010)</td>
</tr>
<tr>
<td>Use as industrial fill.</td>
<td>(Golder Associates, 2011)</td>
</tr>
<tr>
<td></td>
<td>(MBS Environmental, 2011)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soil amelioration</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Use as a soil amendment in agricultural farming.</td>
<td>(Summers et al., 1993a), (Summers et al., 1996), (Summers, 2001) and (Clarendon et al., 2010)</td>
</tr>
<tr>
<td>Use as soil ameliorant on golf courses.</td>
<td>(Allen et al., 2009)</td>
</tr>
<tr>
<td>Use for top dressing recreational sports pitches</td>
<td>(MBS Environmental, 2009) and (Attiwell, 2010)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Removal of contaminants from water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment of acid rock drainage waters</td>
<td>(Lapointe et al., 2005)</td>
</tr>
<tr>
<td>Treatment of contaminated water and use in domestic sewage treatment (septics) for retention of pollutants.</td>
<td>(Genc-Führman et al., 2007) and (Wallis Group Ltd, 2007)</td>
</tr>
</tbody>
</table>

Alcoa’s bauxite residue has been separated into three potential commodity products, namely Alkaloam®, Red Sand™ and Red Lime™. The fine particle size fraction of the bauxite residue (<75µm) is called Alkaloam®, and the larger particle size fraction is known as ‘Red Sand™’. The solid alkaline component of bauxite residue is Red Lime™, which constitutes up to 5% of the total mass of Alkaloam®.

The potential suitability of these residue products for a range of re-use applications is derived from their unique physical and chemical properties (Jamieson et al., 2005; Bott et al., 2005). For example, Alkaloam® has been recognised as a potential value adding product because of its high phosphorus retention capacity, attributed to the high aluminium
and iron content in the material (Barrow, 1982). Alkaloam® has been successfully used as a soil amendment for improving phosphorus retention and increasing crop yields on WA sandy soils (Summers et al., 1996; Summers, 2001), for reducing mobility of metals in polluted soils (Lombi et al., 2003) and for blending with compost to retain heavy metals in composting materials (Holfstede et al., 1991).

Red Lime™ is recognised as a value adding product due to its alkalinity and high buffering capacity (acid neutralising value) properties. Red Lime™ also exhibits phosphorus retention benefits similar to Alkaloam® (Carter et al., 2009). These qualities render the material attractive as an alternative to conventional liming agents for raising pH in acidic agricultural soils, as well as providing the added benefit of improving phosphorus retention properties in the soil (Jamieson et al., 2005).

2.3 Use of Alkaloam® and Red Lime™ as soil amendments
Alkaloam® and Red Lime™ have been a focal point for several WA government departments4 for their potential use as soil amendments on agricultural land, in particular for use in the WA Wheatbelt areas and the Peel-Harvey catchment and Swan Coastal Plain in Western Australia’s south west, due to the elevated use of phosphorus fertiliser (Summers et al., 2002). Over the last decade high usage of phosphorus fertilisers in the poor nutrient retaining and infertile WA sandy soils has been one of the major causes of phosphorus related algal blooms and eutrophication affecting the Ramsar5 listed Peel Inlet and Harvey Estuarine System (Summers, 2001). Use of Alkaloam® and Red Lime™ for soil amelioration has been identified as one potential solution for reducing phosphorus discharges to the waterways and in turn assist in reducing eutrophication.

Extensive research conducted on the use of Alkaloam® as a soil amendment over the last twenty years has demonstrated the material’s benefits in decreasing water repellence in soils (Ward, 1986), increasing the phosphorus retention properties of sandy soils in the Swan Coastal Plain in WA (Vlahos et al., 1989; Summers et al., 1993a) and increasing crop yields (Summers, 2001; Summers et al., 2001). DAFWA field trials, using Alkaloam® soil amendment, were conducted on a broad agricultural scale in the Peel-Harvey catchment and

4 Department of Agriculture and Food, Western Australia (DAFWA), WA Environmental Protection Agency (EPA), Department of Environment and Water Resources (DEWR) and Peel Harvey Catchment Council (PHCC).

5 Wetlands which are recognised as internationally important are registered on a list of the Convention on Wetlands (Ramsar, Iran 1971), commonly referred to as the Ramsar Convention.
in localised areas of the Wheatbelt in WA (Figure 2-2). These trials were to demonstrate improvements to the water quality of the hydrological catchments by reducing phosphorus export to waterways and increased crop growth with less fertiliser application, through increased retention of nutrients such as phosphorus (EPA WA, 1993; Summers et al., 2001).

Environmental monitoring recommended by the EPA was conducted during the field trials (EPA WA, 1993), by way of monitoring phosphorus mobility from soil, pasture growth, health of cattle grazing on Alkaloam® amended paddocks, and physical and chemical changes to water quality in the drainage water, groundwater and surface water run-off from paddocks and sub-catchments (Rivers, 1999). Following EPA approval to extend the trials, a more extensive monitoring program was conducted, through the implementation of an Environmental Management System, also recommended by the EPA (EPA WA, 2000). Lime field trials were also conducted to investigate the use of Alkaloam® and Red Lime™ as alternative lime agents (DoA, 2002; Clarendon et al., 2010).

In order to seek government and community acceptance of the use of Alkaloam® as a soil amendment in the Peel-Harvey catchment, an environmental risk and sustainability review was completed (URS Australia, 2009) under the auspice of the CSRP. The review encompassed an extensive engagement with stakeholders and community to determine the current acceptance of Alkaloam® for soil amelioration, a technical review of all Alkaloam®
field studies and laboratory work conducted to determine the safety and effectiveness of Alkaloam®, and an assessment of the economic benefits to the community.

This review concluded that Alkaloam® is safe for use at the optimum application rate of 20t/ha, however assessment against regulatory criteria indicates that an 80t/ha application would be acceptable. Some additional vet studies to determine the long term health effects on cattle grazing on Alkaloam® amended paddocks was recommended to provide more support for the existing data. A net economic benefit to community is projected to be approx. $70 million over 25 years. This is based on the benefits of increased crop production to farmers, a reduction in phosphorus fertiliser use and reduced agency monitoring as a result of reduced phosphorus loads to the Peel inlet and Harvey estuarine system. Feedback from stakeholders and community in the Peel-Harvey catchment suggests that acceptance of Alkaloam® for soil amelioration has increased compared to the previous decade, with farmers expressing a keen interest to implement Alkaloam® into their farming management practices. However further consultation is required with some community stakeholders to alleviate reservations regarding heavy metal leaching.

A Water Quality Improvement Plan (WQIP) has been produced by the Environmental Protection Agency, WA (EPA WA, 2008), with support from State and Federal departments, and Peel Catchment groups. The WQIP outlines recommended best management practices, such as the use of bauxite residue soil amendments for reducing phosphorus loadings to the Peel-Harvey estuarine system and its connecting sub-catchments. The WQIP has since been extended to other catchments in the southwest of WA, namely the Swan-Canning, Leschenault, Vasse-Wannerup and Scott catchments to adopt similar practises.

Since the WQIP was established, alternative recommended practices to soil amelioration have been implemented, such as the removal of highly soluble phosphorus fertiliser products from the commercial market and replacement with low soluble alternatives. Implementations of these practices however have not shown any marked reductions in phosphorus loadings to the Peel-Harvey water systems. In contrast, soil amendment field trials have demonstrated that a potential reduction in phosphorus runoff by 30% can be achieved using Alkaloam® on a broad catchment scale. In the Peel-Harvey catchment this would equate to reducing the current phosphorus loadings of 140tP/ha to 98tP/ha, a

---

6 Murray, Harvey and Serpentine rivers.
7 Reductions based on 50,000ha of deep grey sandy soils and 70,000ha of sand over clay that could be treated in a catchment with a total area of 190,000ha (DEC, 1984).
substantial step forward to achieving the reduced EPA target of 75tP/ha (Summers et al., 2002).

The use of soil amendments, in particular bauxite residue, has now been identified as the predominant strategy for achieving reduced phosphorus loadings in the southwest WA catchments. In light of this, there has been renewed interest for the use of soil amendments. Catchment councils and environmental government agencies have recently engaged with Alcoa and other industries to offer support to expedite the commercial release of industrial by-products for use as soil amendments, and to facilitate the setting up of a government regulatory framework for assessing materials potentially suitable as soil amendments.

2.4 Assessment of industrial by-products for re-use applications, including Alkaloam® and Red Lime™

2.4.1 National

Whilst benefits from re-using industrial by-products have been recognised in Australia, very little has progressed in WA to promote their widespread use. Almost 50 regional resource synergies were identified in the Kwinana Industrial Area (KIA) in WA, with the potential for exchanging by-products amongst companies for mutual benefit. Companies located in this area have been reluctant to invest in these regional synergies due to the lack of regulations and guidelines to assess industrial by-products for acceptable re-use and the potential for related community issues and concerns. As a result, the approvals process has been slow and open ended. The need for a formalised framework with developed standards and guidelines for by-product re-use is therefore essential to the support of resource synergies in WA, and for assisting companies in showing that they have met the required regulatory standards, which are deemed scientifically safe (Harris, 2007).

Currently across Australia environmental agencies within each state regulate use of industrial by-products and are responsible for approving licenses for their limited re-use (Bossilkov, 2008). There are no national formalised frameworks or standardised methodologies for industry to follow that would promote the widespread use of industrial by-products interstate or encourage international marketing of these materials. Individual state government agencies have attempted to establish their own guidelines for re-using industrial by-products (EPA Queensland, 1999; EPA Queensland, 2000; EPA Victoria, 2009).

Industry associations, such as the Ash Development Association of Australia (ADAA) and Australasian Slag Association (ASA), have been the driving force behind promoting acceptable re-use of fly ash (EPA Queensland, 1999), and have established their own
assessment criteria (ADAA, 2007). More recent progress has been made by the Environmental Protection and Heritage Council (EPHC), through the initiation of the Primary Industries Ministerial Council (PIMC), towards a national approach for assessing industrial by-products for land uses (EPHC, 2006). Through this initiative, a defined methodology and national guidelines has been developed for assessing contaminants in fertilisers and fertiliser ingredients, including industrial residues (Sorvani et al., 2008).

Typically guidelines and assessments developed in Australia have placed a lot of emphasis on the compositional components in a material which potentially lead to an overly conservative estimate of risk. Further to this, $K_d$ values (partition coefficients) are commonly used as a means of assessing a material’s susceptibility to leach in a given environment (e.g. a fertiliser or by-product in an agricultural soil). The greater the $K_d$ value, the less likely a chemical will leach or contribute to runoff (US EPA, 2009)). The $K_d$ parameter is a factor related to the partitioning of a contaminant between the solid and aqueous phases and is defined as the ratio of the quantity of the adsorbate adsorbed per mass of solid to the amount of the adsorbate remaining in solution at equilibrium.

For the reaction

$$A + C_i = A_i$$

the mass action expression for $K_d$ is

$$K_d = \frac{\text{Mass of Adsorbate Sorbed}}{\text{Mass of Adsorbate in Solution}} = \frac{A_i}{C_i}$$

where:

- $A =$ free or unoccupied surface adsorption sites
- $C_i =$ total dissolved adsorbate remaining in solution at equilibrium
- $A_i =$ amount of adsorbate on the solid at equilibrium.

An investigation by Staunton (2004) reported that $K_d$ values can change in different soil profiles and at different pH, and do not account for changes in soil properties (which could occur over time). Applying one set of $K_d$ values for conducting assessments on industrial by-products, for example as a soil amendment in soils, should therefore be exercised with caution as this could lead to inaccurate interpretation, and subsequent rejection of a by-product that may otherwise be acceptable for re-use.
2.4.2 International

Countries with a high utilisation of industrial by-products have corresponding well established frameworks. Such countries include the USA, New Zealand, Netherlands, Denmark, Germany and Sweden (Bossilkov et al., 2008). These frameworks encompass extensive environmental risk assessments that assess the potential leaching of contaminants from a material under a range of scenarios (including pH). One example is the European standard BS12920:2006, which outlines a step-wise methodology for characterising a ‘waste’ material under specific conditions. The methodology in its entirety allows ‘waste’ materials, such as industrial by-products, to be assessed for an intended re-use application or for appropriate disposal. Following the outlined methodology ensures that the material is comprehensively characterised, the scenario is fully defined and that the parameters influencing leaching behaviour over a specified time frame are identified. The final steps in the methodology include geochemical modelling of leach data which assists in predicting the long term leaching behaviour of the material (British Standards, 2008).

Leaching assessment methodologies from a scenario risk-based assessment framework developed by the Energy Research Centre of the Netherlands (ECN), in collaboration with Vanderbilt University, USA (Kosson et al., 2002; van der Sloot et al., 2006), are currently being considered by the International Aluminium Institute (IAI) as best practise methodology in the aluminium industry for assessing the use of bauxite residue (van der Sloot and Kosson, 2010).

The scenario risk-based assessment uses leach data from a range of standard leach tests (also developed by ECN and Vanderbilt University) to determine the leaching characteristics of a granular material based on pH, liquid:solid ratio and mass transfer rate. These tests are designed to illustrate the effect of leaching from materials in contact with rainfall at low and fast flow rates, in different pH environments and when materials are compacted. The series of leach tests are:

- pH dependent leach test (CEN, 2005);
- Up flow percolation column test (CEN, 2004); and
- Dynamic monolithic leaching test (CEN, 2012).

‘Waste’ can be referred to as an industrial by-product being assessed for an intended re-use application or for appropriate disposal.
Leach data collected using these tests, combined with LeachXS™ geochemical modelling, has been a useful tool for performing a comprehensive environmental assessment on by-products for different re-use scenarios (van der Sloot and Kosson, 2010). Acceptance of this methodology by the aluminium industry, regulators and communities is anticipated to encourage industry investment for developing bauxite residue into marketable commodities for use in agriculture and construction applications and provide more confidence in large scale industrial by-product re-use.

The US EPA has been supporting the development of alternative leaching procedures, in conjunction with Vanderbilt University, for applications where the standard Toxicity Characteristic Leaching Protocol (TCLP) is not required. Method procedures for the aforementioned three leach tests - pH dependent test, up-flow percolation (column) test and the monolith (tank) leach test - have been prepared at Vanderbilt University by the leaching assessment research group, known as the Leaching Environmental Assessment Framework (LEAF). Currently inter-laboratory comparisons are being conducted to validate LEAF methods 1313, 1314, and 1315 respectively (Vanderbilt University, 2011), for implementation into the US as standard leach tests (van der Sloot and Kosson, 2010).

2.5 Leach test procedures

Regulatory bodies from different countries have adopted their own standard leach tests in which to assess and characterise industrial by-products for re-use or for waste management. As a result, this has led to the development of a wide range of single and sequential extraction leach tests, that differ in method parameters such as particle size, liquid:solid ratio, extractant, extraction time and temperature, and pH conditions. Some examples are listed in Table 2-2.

---

9 Materials excluded from consideration as a hazardous waste under the Resource Conservation and Recovery Act (RCRA).
<table>
<thead>
<tr>
<th>Leach test</th>
<th>Extractant</th>
<th>L/S ratio</th>
<th>pH</th>
<th>Extraction time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘Availability’ test</td>
<td>Deionised water with addition of nitric acid</td>
<td>1st step 100:1</td>
<td>Controlled</td>
<td>1st step 3hr</td>
<td>(Nordtest, 1995)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2nd step 100:1</td>
<td>1st step 7</td>
<td>2nd step 18hr</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sequential Extraction Leach test</td>
<td>1st step: acetic acid</td>
<td>1st step 40:1</td>
<td>No pH control</td>
<td>1st step 16hr</td>
<td>(Ure et al., 1993)</td>
</tr>
<tr>
<td></td>
<td>2nd step: Hydroxylammonium chloride</td>
<td>2nd step 40:1</td>
<td></td>
<td>2nd step 16hr</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3rd step: ammonium acetate</td>
<td>3rd step 50:1</td>
<td></td>
<td>3rd step 16hr</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Demineralised water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Australian Standard Leaching Protocol (ASLP)</td>
<td>Demineralised water, sodium acetate buffer solution</td>
<td>20:1</td>
<td>No pH control</td>
<td>18hr</td>
<td>(Standards Australia, 1997)</td>
</tr>
<tr>
<td>Toxicity Characteristic Leaching Procedure (TCLP)</td>
<td>sodium hydroxide and sodium acetate buffer solution</td>
<td>20:1</td>
<td>No pH control</td>
<td>18hr</td>
<td>(US EPA, 1992)</td>
</tr>
<tr>
<td>pH dependent leach test</td>
<td>Demineralised water, nitric acid and sodium hydroxide</td>
<td>10:1</td>
<td>pH range 4-12 or controlled at selected pH</td>
<td>48hr</td>
<td>(CEN, 2005).</td>
</tr>
</tbody>
</table>
Single extraction leach tests for soil can be conducted using a range of extractants. Examples include strong acids (aqua regia, nitric or hydrochloric acids), un-buffered salt solutions (calcium chloride, sodium nitrate or ammonium nitrate), buffered salt solutions (ammonium acetate/acetic acid) and complexing agents (EDTA). Since these types of leach tests do not account for pH in the data interpretation, the measured leach data can be influenced by the efficiency of the extractant towards the individual elements. This can lead to variability in leaching data, depending on which extraction solution is used in the test. The changes in leaching behaviour of species using different extractants has led countries to adopt different solutions for a range of single extraction tests for specific objectives (van der Sloot et al., 1997). Examples being the use of EDTA for determining the availability of copper, hot water for extraction of boron and calcium chloride for measuring mobility of heavy metals in polluted soils.

A comparison of different leach tests investigated by Brunori et al. (1999) showed that of the variations in method parameters used, pH had the greatest influence on leaching. This observation was also reported by van der Sloot (2002), highlighting the importance of controlling final pH when measuring leaching and the significance of pH environment when assessing by-products materials for re-use. Hence a pH dependent leach test was developed to assist in assessing granular materials (amended soils, sludges and treated biowaste) under a range of different exposure scenarios (van der Sloot et al., 2004).

2.6 ASLP and TCLP leach tests for assessing re-use of Alkaloon® and Red Lime™
The Australian Standard Leaching Procedure (ASLP) (Standards Australia, 1997) is currently recognised as a standard leach test in Western Australia for assessing a material’s leaching characteristics against environmental guidelines, for the purpose of waste management (DEC, 1996; DEC, 2003; DEC, 2004). The ASLP was originally based on the United States (US) Toxicity Characteristics Leaching Procedure (TCLP10), US EPA method 1311 (US EPA, 1992), a procedure designed to simulate leachate from industrial wastes co-disposed in acidic landfill (Graham, 2004). The extractants used in the TCLP method are acetic acid and acetic acid/sodium hydroxide buffer solution which are used to measure leaching from a waste material at an initial pH of 2.88 or 4.93 respectively, depending on whether the material reacts in acid or alkaline (Gerritse, 2000).

The ASLP method was later developed to incorporate the use of reagent water as an additional leaching medium, to allow for leaching measurements in non-putrescible mono-

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10 Standard leach test used in other Australian states.
fill systems and for measurement in contaminated soils under *in-situ* conditions (Graham, 2004). Although the ASLP test is applicable for leaching in non-putrescible systems and putrescibles, the TCLP is the more broadly adopted leach test in Australia.

The TCLP was used for monitoring leaching of heavy metals from Alkaloam® in the DAFWA broad scale agricultural field trials (section 2.3). The reliability of the TCLP data was questioned by Gerritse (2000) regarding its suitability for predicting leaching behavior in highly alkaline materials, such as Alkaloam®.

The TCLP can be suitable for approximating concentrations leached from a material in a field situation, as long as the extracting solution remains acidic (pH 2.88 or pH 4.93). Since Alkaloam® is highly alkaline, the pH of the extracting solution and the final leachate solution from the TCLP is therefore critical for correct interpretation of the data.

No final pH data were reported in the environmental monitoring report, giving some doubt to the validity of the leach data, in particular for predicting leaching during the high application rates (250t/ha) at the initial stages of the trials. Since the ASLP is very similar in procedure to the TCLP, the appropriateness of applying this leach test to alkaline materials may also be inappropriate.

Understanding the leaching behaviour of an industrial by-product in different pH environments is an important factor when assessing these materials for a range of re-uses applications, as the environment pH is not likely to be the same for each field application, or may change over time. For example, if Alkaloam® is to be considered for use as a soil amendment, assessment of its leaching characteristics when amended in soils across a range of pH environments would allow predictions to be made on how metal mobility may change if the soil pH environment changes. This information would be valuable in predicting whether any measured leachables from Alkaloam® amelioration are likely to cause detriment to a receiving environment and hence whether use of the material in a specific scenario is feasible.

The TCLP and ASLP are limited in that they only provide leach data at two or three pH values respectively, and therefore do not provide information on the long-term leaching behaviour of the material being tested (van der Sloot, 1996). Use of these leach tests for assessing industrial by-products for a range of re-use scenarios are therefore not likely to be appropriate unless the pH of the re-use scenario is representative of the pH values used in these tests.
2.7 pH dependent leach test for the assessment of industrial by-products for re-use

The pH dependent leach test, a standard European Union leach test (CEN, 2005), has been demonstrated as being applicable for characterising leaching behaviour in a range of granular materials such as fly ash, soils, asphalt, cement mortar and compost, in addition to evaluating waste (van der Sloot et al., 2006). This leach test is encompassed in the scenario risk-based assessment methodology discussed in section 2.4 and is designed to characterise the leaching behaviour of a material as a function of pH (van der Sloot, 2002).

The pH dependent leach test has been successfully used for assessment of materials in a range of applications: e.g. for assessing leaching in contaminated soils (Dijkstra et al., 2004); assessing the carbonation of a by-product for carbon dioxide sequestration (Huijgen et al., 2006); and for characterising leaching behaviour in a range of bauxite residues from Alcoa’s alumina refineries (Carter et al., 2005).

The test provides information on how the leaching of species from a material may change across a specific pH range, as well as the available concentration for leaching, with this concentration being typically less or equal to the total concentration. An example of a pH dependent leaching profile is illustrated in Figure 2-3 for the leaching of iron from Alkaloam®. The natural pH of Alkaloam® is denoted by * on the chart.

![Figure 2-3: pH dependent leaching of iron from Alkaloam®](image)

**Figure 2-3: pH dependent leaching of iron from Alkaloam®**
This leach data is an important input into environmental assessments as it allows predictions to be made on what species are likely to be mobile in a specific pH environment and what species could potentially accumulate in the material over time. Evaluation of this information would be a major step forward in conducting more thorough environmental assessments on industrial by-products than the current ASLP and TCLP, and is likely to provide more accurate predictions of leaching behaviour in a re-use scenario due to better representation of pH in the field.

Application of pH dependent leach data to geochemical modelling software, such as LeachXS™, can provide further insight into the mechanisms controlling leaching and the chemical speciation formed in the solid and liquid phases over varying pH environments (Figure 2-4). This information would compliment environmental assessments and assist in determining the speciation of any leachables. Understanding the mechanisms controlling leaching also allows modifications to reduce leaching from industrial by-products to be better targeted: e.g. if copper leaching is an issue, then organics that are controlling leaching should be targeted.

Examples of the use of geochemical modelling with LeachXS have been used to predict leaching from Municipal Solid Waste Incinerators (MSWI) (Astrup et al., 2006), evaluate
the impact of stabilised waste disposal (Van der Sloot et al., 2007), and characterise untreated and neutralised bauxite residue for improved waste management (Carter et al., 2008).

van der Sloot (2002) reported that;

“The pH dependent leach test has been proven to be one of the most useful methods to characterise a material’s behaviour under a variety of exposure and treatment conditions, and provides a comparison for almost any other existing leaching test, with the exception of EDTA extraction.”

This suggests that the pH dependent leach test could be used alongside leach tests already adopted in Australia, such as the ASLP and TCLP, and provide further improvements to the validity of environmental impact assessments on by-products.

This thesis will assess comparisons of ASLP and pH dependent leach tests for application on the alkaline materials, Alkaloam® and Red Lime™ to determine the appropriateness of the two methods for assessing these types of materials. Comparisons will also be made to determine the feasibility of using the pH dependent leach test alongside the ASLP for the purposes of assessing industrial by-products for re-use and assist in their development as marketable commodities.

An investigation by Carter et al., (2009) showed that the pH dependent leach test can be used for evaluating leaching behaviour of residue by-products when amended into a WA agricultural soil. This thesis will expand on the work to assess leaching of Alkaloam® and Red Lime™ amended in a range of WA agricultural soils and a Swan Coastal Plain soil, and demonstrate potential benefits from soil amelioration in each of these soils. Application of the pH dependent leach test to a wider range of WA soils will determine whether this test can be used as a suitable predictive tool for evaluating leaching at different application rates of Alkaloam® and Red Lime™ to the range of soils. Geochemical modelling will be applied to the leach data to further understand the release controlling mechanisms in these materials.

pH dependent leach data for Alkaloam® will also be used to help address the uncertainty around the TCLP data reported for the DAFWA agricultural field trials and demonstrate that WA soils (agricultural and Swan Coastal Plain) amended with Alkaloam® do not leach heavy metals at the natural pH environment of these soils.
Chapter 3

SAMPLES AND METHODS

This chapter outlines the methodologies and description of samples used in this thesis.

3.1 Samples

3.1.1 Alkaloam®

Alkaloam® is the fine red mud fraction of Alcoa’s bauxite residue (<75µm) that has been atmospherically or forced carbonated and is stored on residue drying beds. The carbonation process converts residual entrained sodium hydroxide (caustic) in the red mud to sodium carbonate, effectively decreasing the alkalinity\(^{11}\) and converting the mud to a benign product suitable for re-use. Whilst Alkaloam® is traditionally the term given to Alcoa’s atmospherically carbonated red mud, forced carbonation may also be used (Cooling et al., 2002; Cooling et al., 2005).

Alkaloam® samples analysed for this thesis were sub-sampled from a batch provided to DAFWA. This batch was used for conducting soil amendment field trials on agricultural soil in the Peel-Harvey Catchment and wheatbelt areas (DoA, 2002). The Alkaloam® was originally sourced from Alcoa’s Kwinana residue site.

3.1.2 Red Lime™

During the production of alumina via the Bayer process, carbon dioxide is captured and converts some of the sodium hydroxide critical to the refining process to sodium carbonate. Slaked lime (calcium hydroxide) is used to convert the sodium carbonate back to sodium hydroxide by way of a process step known as causticisation. The residual products from the causticisation process are calcium carbonate, tri-calcium aluminate (TCA6) and tri-calcium aluminate monocarbonate, as shown by the equations in 1.01, 1.02 and 1.03 respectively.

\[
\begin{align*}
\text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 &= \text{CaCO}_3 + 2\text{NaOH} \\
3\text{Ca(OH)}_2 + \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} &= 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} \\
3\text{Ca(OH)}_2 + \text{CaCO}_3 + \text{Al}_2\text{O}_3 + 8\text{H}_2\text{O} &= 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}
\end{align*}
\]

These by-products are collectively referred to as causticiser residue. The coarse fraction of causticiser residue has been named Red Lime™.

\(^{11}\) A corresponding decrease in pH from pH13 to pH<10.5.
Red Lime™ is incorporated into the bauxite residue stream and constitutes up to 5% of the total mass of residue. Red Lime™ represents the solid alkaline component of the residue.

Samples of Red Lime™ analysed for this thesis were sub-sampled from a lime pilot plant located at the Alcoa Kwinana refinery. The causticiser residue from the pilot plant was separated and washed to obtain the coarse fraction and then solar dried to produce Red Lime™. This material was also supplied to DAFWA for conducting lime trials on agricultural soil in the Peel Harvey Coastal Catchment and wheatbelt areas (DoA, 2002).

3.1.3 Soil samples
A range of West Australian (WA) agricultural soils and a Swan Coastal plain soil were characterised to determine the ambient levels of elements already present in WA soil. Corresponding data for Alkaloam® and Red Lime™ were compared to natural soils for context and to identify any elements that may require further investigation.

3.1.3.1 Agricultural soils
The agricultural soils were sampled from three sites that participated in the DAFWA lime and soil amendment field trials in the Peel-Harvey Catchment, Southern Coastal and wheatbelt areas. The region of these sites is illustrated in Figure 3-1.

The Peel-Harvey Catchment area covers the hydrological catchments of the Murray, Harvey and Serpentine rivers, which exit at the mouth of the Peel Inlet and Harvey Estuary as shown in Figure 3-2.
Figure 3-1: (a) Geographical illustration of the wheatbelt and Swan coastal areas within Western Australia (courtesy of Australian Native Seeds Online), (b) the location of the Peel Harvey Catchment within the Swan coastal region (courtesy of Johnson, 2008)
Figure 3-2: The Peel Harvey Coastal Catchment illustrating the hydrological catchments of the Harvey, Murray and Serpentine

Extensive agricultural farming with the overuse of phosphate fertilisers, in addition to increased urban development in this catchment, has drawn significant interest and much debate over the condition of the three river systems and the future fate of the Peel inlet and Harvey estuary. The soils sampled from the farms ranged from deep sandy soils to clay loam soils, and have been classified using the WA soil classification described in Table 3-1.
Table 3-1: Classification and description of agricultural soils (Clarendon et al., 2010)

<table>
<thead>
<tr>
<th>Agricultural Soils</th>
<th>Sample Location</th>
<th>Soil Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manning Heavy</td>
<td>Sabina Vale Farm, Busselton</td>
<td>Sodic Kurosolic Redoxic Hydrosol (clay loam soil)</td>
</tr>
<tr>
<td>Manning Light</td>
<td>Sabina Vale Farm, Busselton</td>
<td>Fragic Sesquic Semiaquic Podosol (sandy soil)</td>
</tr>
<tr>
<td>Merredin (Wheatbelt region)</td>
<td>Merredin Dryland Research Station, Great Eastern Hwy, Merredin</td>
<td>Ferric-Acidic Mesotrophic Yellow Kandosol (sandy soil)</td>
</tr>
<tr>
<td>Newdegate (Wheatbelt region)</td>
<td>50 Stubbs Street, Lake Grace Newdegate</td>
<td>Basic Ferric Petroferric Orthic Tenosol (sandy soil)</td>
</tr>
</tbody>
</table>

3.1.3.2 Swan Coastal Plain soils

The Swan Coastal Plain soils were sampled west of the Darling Scarp, near Yarloop, encompassing an area of the Peel-Harvey Catchment. The Coastal plain soils typically found in this area are the Pinjarra Plain and the three dune systems, Bassendean, Spearwood and Quindalup coastal dunes, as illustrated in Figure 3-3.

Soil was sub-sampled at various geographic locations alongside Johnston Road in Yarloop, to obtain soil from each of the Pinjarra Plain, Bassendean and Spearwood dune regions. Pinjarra Plain soils are referred to as duplex soils, consisting of recent alluvial loams and older acid sandy top soils overlying a clay B-Horizon (Allen et al., 2009).

Bassendean soils are the most heavily leached of the coastal plain soils. These soils are high drainage sands with very little water holding capacity, and have low natural fertility due to their poor nutrient retention properties. Bassendean soils are typically characterised by their low capacity to retain phosphorus (Allen et al., 2009).

The Spearwood soils are considered the central sands that form ‘ridges’ parallel to the coast. These soils consist of “a coarse to medium grained calcarenite composed largely of fossil (shell) skeletal fragments... and various amounts of quartz sand” (DEC Atlas, 1980). Spearwood soils have a moderate capacity to adsorb phosphorus.
The Swan Coastal Plain soils have been classified using the Australian Soil Classification (Isbell, 2002) and are summarised in Table 3-2.

**Table 3-2: Classification and description of Swan Coastal Plain soils**

<table>
<thead>
<tr>
<th>Swan Coastal Plain Soils</th>
<th>Sample Location</th>
<th>Soil Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinjarra Plain</td>
<td>Johnston Road, Yarloop</td>
<td>Brown Kandosol or brown Dermosol (sandy loam soil)</td>
</tr>
<tr>
<td></td>
<td>(Peel Harvey Catchment)</td>
<td></td>
</tr>
<tr>
<td>Bassendean</td>
<td>Johnston Road, Yarloop</td>
<td>Redoxic or Oxyaquic</td>
</tr>
<tr>
<td></td>
<td>(Peel Harvey Catchment)</td>
<td>Hydrosol (sandy soil)</td>
</tr>
<tr>
<td>Spearwood</td>
<td>Johnston Road, Yarloop</td>
<td>Yellow-Orthic Tenosol</td>
</tr>
<tr>
<td></td>
<td>(Peel Harvey Catchment)</td>
<td></td>
</tr>
</tbody>
</table>
3.1.4 Amending soils with Alkaloam® and Red Lime™

A WA coastal plain soil (Bassendean soil) and the agricultural soils were amended with Alkaloam® and Red Lime™ at application rates of 6.25g/kg and 1.6g/kg respectively. These application rates were representative of amendment rates used in the liming field trials conducted by Clarendon et al. (2010). Red Lime™ has a neutralisation capacity four to five times higher than that of Alkaloam®; therefore the application rate for Red Lime™ and Alkaloam® were normalised based on their neutralisation capacities. Alkaloam® and Red Lime™ blend rates for each soil were determined based on the dry weights (see section 3.3.1), a soil density of 1.6g/cm³ and a soil depth of 10cm. The contents were mixed on a rotating oscillating mixer for 1 hour to homogenise the sample. The amended soil samples were then stored in the dark at room temperature.

3.1.5 Construction and natural materials

Conventional construction materials and natural materials were analysed for comparative purposes and as contextualising data for evaluating Alkaloam® and Red Lime™ as marketable commodities. The construction materials were randomly selected from different sites throughout the Perth Metropolitan area, as described in Table 3-3. Natural beach sand and quarried limestone were also sampled from local sources.

Table 3-3: Description of construction and natural materials

<table>
<thead>
<tr>
<th>Construction and Natural Materials</th>
<th>Sample Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue metal</td>
<td>Coyne Road</td>
</tr>
<tr>
<td>Road Gravel</td>
<td>Lyon Road</td>
</tr>
<tr>
<td>Road Base</td>
<td>Coyne Road</td>
</tr>
<tr>
<td>Beach sand</td>
<td>Monkey Mia and Secret Harbour beaches</td>
</tr>
<tr>
<td>Yellow Sand</td>
<td>Building site on Corinthian Road, Rossmoyne</td>
</tr>
<tr>
<td>Quarry Limestone</td>
<td>Limestone quarry at Kwinana residue</td>
</tr>
</tbody>
</table>
3.2 Analytical methods

3.2.1 Moisture content
Sub-samples of soil (20-40g) were accurately weighed onto crucibles or glass dishes before drying at 110°C overnight. The dry soil samples and crucible/dish were then reweighed and the moisture content calculated using the following calculation:

\[
\%\text{moisture} = \left[ \frac{(m_c + m_{ws}) - (m_c + m_{ds})}{m_{ws}} \right] \times 100
\]

where:
\(m_c\) = weight of dry crucible/dish
\(m_{ws}\) = weight of wet soil
\(m_{ds}\) = weight of dry soil

3.2.2 Total composition
Samples were analysed for compositional analysis by Ultratrace Geoanalytical Laboratories. All samples were pulverised using a vibrating disc pulveriser and extracted for compositional analysis using either a mixed acid digest, sodium peroxide fusion or aqua regia digest. All chemical reagents were Analytical Reagent (AR) grade.

For the mixed acid digest, the pulverised sample was digested and refluxed in a solution of nitric, perchloric, hydrochloric and hydrofluoric acids and then analysed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES)\(^{12}\) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)\(^{13}\). Due to the high sodium content present in Alkaloam® and Red Lime™, radial ICP instruments were used to ensure easily ionised elements, such as lithium and potassium, did not exaggerate high intensities that can lead to high instrumental inaccuracies. The ICP scan methods provided compositional data for most species, with the exception of some refractory minerals.

Refractory minerals were analysed using the sodium peroxide fusion method, in which samples were fused with sodium peroxide and the subsequent melt dissolved in hydrochloric acid for analysis by ICP-OES\(^{14}\) and ICP-MS\(^{15}\).

---

12 Analytes were Cu, Zn, Co, Ni, Mn, P, Sc, V, Al, Ca, Na, K, S and Al.
13 Analytes were As, Ag, Ba, Be, Bi, Cd, Ga, Li, Mo, Pb, Sb, Sn, Sr, W, Ta, Y, Hf, Zr, Nb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Se, Rb, In, Te, Cs, Re and Tl.
14 B, Cr, Si, Fe, Mg, Ti.
15 Ge.
Aqua regia digest (mixture of hydrochloric and nitric acids) was used to extract mercury with analysis by ICP-MS. Chlorine was determined colorimetrically and fluoride determined using a Selective Ion Electrode (SIE)\textsuperscript{16}. Fluoride concentration could not be measured in samples containing aluminium at concentrations greater than 3mg/L due to limitations with the SIE methodology.

3.2.3 Radionuclides
The radionuclides uranium and thorium were analysed by Ultratrace Geoanalytical Laboratories. The analysis method involved fusing the sample with sodium peroxide and dissolving the resultant melt in dilute hydrochloric acid for analysis by ICP-MS.

An interlaboratory study conducted by Carter (2005a) showed that the sodium peroxide fusion method compared well to analyses by Delayed Neutron Activation (DNA) and Neutron Activation Analysis (NAA), the nuclear techniques recommended by the Australian Nuclear Science and Technology Organisation (ANSTO).

3.2.4 X-Ray diffraction
All the materials were analysed by X-Ray Diffraction (XRD) to determine the crystalline mineral phases present in their composition. The analysis was conducted by Alcoa’s Technology Delivery Group, in accordance with their in-house methods (Taylor, 2007; Taylor, 2009). Samples were prepared by micronising the material in a grinding jar with ethanol and then drying on a warm hot plate under an infra-red lamp.\textsuperscript{17} The dried micronized sample was then pressed into a disc using a Herzog press and analysed for crystalline mineralogical content using a PANalytical X’Pert Pro MPD X-Ray Diffractometer. Traces and PCPDFWIN auxiliary software were used for accessing the International Centre for Diffraction Data (ICDD) databases to assist in the identification of the mineralogical phases.

3.2.5 pH
Soil pH was measured in accordance with Rayment (1992), unless otherwise indicated. The method involved adding an accurately weighed amount (dry weight) of material to demineralised water at an L/S ratio of 5:1, at ambient temperature. The samples were

\textsuperscript{16} Also referred to as Specific Ion Electrode.

\textsuperscript{17} Samples cannot be dried in a conventional oven due to accumulation of ethanol vapour (a potential fire hazard). Drying was carried out using infra-red lamps with a warm hot plate in a fume cupboard.
mechanically shaken for 15 minutes and then left to settle for 10 minutes before measuring the pH of the supernatant.

The pH of certain soils referenced in this thesis was measured in calcium chloride (0.01M) solution (Rayment, 1992). The calcium chloride method is the preferred method by soil scientists for conducting pH on soils as it provides more stable pH measurement over extended time periods. Soil pH can fluctuate from season to season, due to changes in salt levels from addition of nitrogen and potassium fertilisers, decomposition of organic matter and minerals, or from leaching of salts during rainfall. Calcium chloride can be used to simulate the salts normally present in soils and account for these fluctuations (Clemson, 2004).

A relationship has been determined between soil pH measured in water and in calcium chloride (Little, 1992; Clemson, 2004), allowing comparisons to be made in cases where different methods have been used.

3.2.6 Phosphorus retention index
Phosphorus Retention Index (PRI) measurements were used to determine a soil’s capacity to adsorb phosphorus and to establish if adsorption capacity could be improved using Alkaloam® or Red Lime™ as a soil amendment. The PRI was measured for all samples, in accordance with a method developed at the Chemistry Centre WA (Allen et al., 1990).

A sample of soil was equilibrated in a solution of potassium chloride (0.02M) containing phosphorous (10µg/mL), by shaking the mixture end over end for 16 hours at 23°C. A subsample of the equilibrated solution was then centrifuged at 3,500rpm and the phosphorus concentration measured by spectrophotometric analysis.

The PRI was expressed as the ratio of $P_{\text{ads}}:P_{\text{eq}}$, where $P_{\text{ads}}$ is the concentration of phosphorus adsorbed by soil and $P_{\text{eq}}$ is the concentration of phosphorus in solution. The PRI measurements were conducted by the Chemistry Centre, WA.

3.2.7 Acid neutralisation capacity (ANC)
This analysis is a measure of the buffering capacity or inherent neutralising capacity of a material. The ANC curve for each material was generated from pH dependent leach test data. From this data the buffering capacities of each material were assessed and compared for discussion.
3.2.8 Sample preparation for leach testing

In accordance with the pH dependent leach test methodology (CEN, 2005) for sample preparation; leach testing should be carried out on a material that constitutes particle size of 95%w/w less than 1mm. If oversized material exceeds 5% w/w, the oversized fraction should be crushed and added to the sample. All root and vegetative matter that do not form an inherent part of the sample should be removed.

All samples were air dried or placed in a 30 ºC oven for 2 days. The samples were screened through a 4.75mm and 1.7mm sieve to separate oversize material and any vegetative matter from the rest of the sample. The total weight of the soil sample and the large particulate matter were then individually recorded. For the majority of soils, more than 95%w/w of the sample was less than 1mm in particle size and therefore crushing was not necessary. Bassendean, Manning Heavy and Manning Light soils all contained some root matter which was added back into the sample. Road gravel, quarry limestone and blue metal were all crushed using a jaw crusher to achieve a sample of <1mm particle size. Following sieving, the samples were passed through a splitter to homogenise the sample, and then stored in polypropylene bulk containers in the dark at room temperature.

3.2.9 Leach tests

3.2.9.1 Australian Standard Leaching Procedure

All samples were leach tested according to the Australian Standard Leaching Protocol (ASLP) (Standards Australia, 1997). Samples were leached in pH 2.9 and pH 5 solutions, and in deionised water to represent leaching at its natural pH. AR grade acetic acid and AR grade sodium hydroxide were used to prepare solutions at pH 2.9 and pH 5.

Leach testing was conducted at a liquid to solid ratio (L/S) of 20L/kg for 18 hours at ambient temperature, after which time the final pH of the solution was measured. After 18 hours the samples were filtered, and the leachate solutions analysed for a range of major, minor and trace metals using ICP-OES and ICP-MS. The ASLP analyses were conducted by Genalysis Laboratory Services.

This test assumes that all leaching and reactions at the liquid/solid interface are close to equilibrium after 18 hours under these test conditions.
3.2.9.2 pH Dependent Leach Test (with centrifugation)

pH dependent leach testing was conducted by the Technology Delivery Group at Alcoa on samples of Alkaloam® and Red Lime™, the agricultural soils, a WA Coastal Plain soil and their corresponding amended soils. The test was conducted in accordance with European Standard method CEN/TS 14429 (CEN, 2005), with the use of centrifugation rather than vacuum filtration for achieving solid/liquid separation before collecting the eluates. Centrifugation was used in preference to vacuum filtration to improve solid/liquid separation in clay type soils, such as Alkaloam®, Red Lime™ and Manning Heavy soil. Effects from use of centrifugation is discussed in Chapter 5

The pH dependent leach test involves leaching the sample over a pH range of 4 to 12 (including the material’s natural pH) at an L/S ratio of 10L/kg (dry weight) for 48 hours at 20°C. It was assumed that all leaching and reactions at the liquid/solid interface were close to equilibrium after 48 hours under these conditions (Dijkstra, 2006a). This was confirmed by ensuring that the pH of the leachate solutions after 44 hours and 48 hours did not vary by more than 0.3 pH units.

The pH dependent leach tests conducted for this thesis were carried out over an extended pH range of 0.5 to 12 to determine the available leaching concentration of each species. The available leaching concentration is defined as the total concentration of the species available for reacting. This is often taken as being the leachable concentration of an element at extreme high or low pH since most metals exhibit their maximum solubility under these pH conditions. It should be noted however, that some metals may exhibit their maximum solubility at neutral pH (van der Sloot et al., 1997).

Eight eluate solutions were prepared using demineralised water, AR grade nitric acid (15.6M) and/or sodium hydroxide (2M) to achieve final pH values that are approximately evenly spaced in the range of pH 0.5 to 12 after 48 hours of leaching. A dry mass of 15g ± 1.5g of sample was individually weighed into 8 x 250mL polypropylene (PP) bottles. One third of an eluate solution was added to each bottle, and the solutions equilibrated for 30 minutes in a rotating water bath (20°C, 10rpm). After 30 minutes another third of the eluate solution was added to the bottle. The solution was equilibrated for a further 90 minutes before the last portion of eluate solution was added. The sample was then allowed to equilibrate under continuous rotation for a total of 48 hours. The solution pH was measured at 3, 44 and 48 hours after the initial eluate addition. From the amounts of acid or base added to reach the target pH, the acid neutralisation capacity (ANC) was calculated.
At the end of the 48 hour equilibration period the bottles were centrifuged at 10,000 rpm for 15 minutes\(^{18}\) and then filtered through a 45µm membrane filter. The pH of the solutions at 44 and 48 hours did not vary by more than 0.3 pH units for any sample, satisfying the condition for approaching equilibrium. The filtered eluate solutions were analysed for a range of major, minor and trace elements using ICP-OES or ICP-MS. Chloride was analysed by colorimetric analysis, fluoride by SIE measurement. These analyses were conducted by Ultratrace Geoanalytical Laboratories.

The pH dependent leach test has good repeatability for a variety of soil and soil-like materials, such as sediments, sludge and bio-waste (van der Sloot, 2002) and for heterogeneous materials, such as bottom ash from municipal solid waste incinerators (Dijkstra et al., 2006a)

### 3.2.10 Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC)

The eluates from the pH dependent leach test were also analysed for TOC using an OI Analytical Model 1010 Wet Oxidation TICTOC analyser. This analysis was conducted by Alcoa’s Technology Delivery Group in accordance with their in-house methods (Donnovan, 2009; Formentin, 2009).

Previous experiments have indicated that Alcoa residue samples, containing high concentrations of carbonate, can produce artificially inflated TOC results due to the carry over of carbonate species (Carter, 2006). To minimise this interference, all TOC analyses were carried out after the Total Inorganic Carbon (i.e. bicarbonate, carbonate etc.) had been extracted and purged from the sample.

The TICTOC analytical procedure requires dilution of the eluates using a Gilson autosampler prior to analysis. The diluted solutions were injected into a heated reaction chamber where the sample was acidified with phosphoric acid to dissociate all inorganic carbon species to carbon dioxide, before removal by sparging with an inert gas. Following TIC removal, the remaining organic carbon (TOC) was quantified by addition of persulphate to the sample and heating to 96°C to oxidise the organic carbon to carbon dioxide.

\(^{18}\)Standard method involves filtering under vacuum. Centrifugation was carried out to improve solid/liquid separation for clay type soils, Alkaloam® and Red Lime™.
3.2.11 Optimised pH dependent leach test method for assessing agricultural soils, Alkaloam® and Red Lime™ and for determining nitrate leaching

Method development was carried out on the standard pH dependent leach test in order to optimise the procedure for assessing leaching in clay type soils, and for determining nitrate leaching in soils. A discussion of the method development is discussed in Chapter 5

The optimised pH dependent leach test procedure is in accordance with the standard method, with the following exceptions;

(i) The samples were centrifuged at 10,000rpm for 15 minutes and then filtered under vacuum. This was to improve the liquid/solid separation for collecting eluates from clay type soils.

(ii) Hydrochloric acid was used as an alternative extractant to nitric acid for determining nitrate leaching in soils. Due to the differences in molar concentration of the two acids, the hydrochloric acid volume was adjusted accordingly to provide the same mol H⁺/kg soil when preparing the leaching solutions.

3.2.12 Nitrate analysis

Nitrate analyses were conducted on the pH dependent test eluates by Ultratrace Geoanalytical Laboratories in accordance with APHA 4500 NO3-B (APHA, 2005a). Nitrate analyses were determined by colorimetric analysis using a Perkin-Elmer Lambda 2 UV-VIS spectrometer at wavelengths of 220nm and 275nm.

Further nitrate analyses were conducted by Chemcentre, WA in accordance with the APHA 4500 NO3-I method (APHA, 2005b). A sample was filtered through a 0.45um cellulose acetate membrane prior to analysis. Nitrate analyses were determined by automatic flow injection using a copper coated cadmium column to reduce nitrate to nitrite. The total nitrite (reduced nitrate and original nitrite in sample) was then quantified by diazotization with sulphanilamide under acidic conditions to form a diazonium ion, and then complexed with N-(1-naphthyl)-ethylenediamine dihydrochloride. The resulting pink dye absorbs at wavelength 540 nm. A correction was made for any nitrite present by analysing without the reduction step. Analyses were conducted on a Lachat Flow Injection Analyser (FIA).

3.2.13 Clay content

Samples of Alkaloam®, Red Lime™ and Bassendean, Manning Heavy and Merredin soils were analysed for their clay content, which was then used as an input parameter for geochemical modelling of leaching behaviour (Section 3.4). The clay analysis involved
treating the sample with hydrogen peroxide to oxidise organic material, and then with hydrochloric acid to remove carbonates. The sample was dried and then passed through a 35μm sieve. The <35μm particles were separated according to a settling experiment, and periodical time and depth fractions collected to enable the mass percentage of clay to be calculated according to Stokes Law. Clay analyses were conducted by ECN, Research Centre of the Netherlands, in accordance with a standard hydrometer test, NEN 5753 (2006).

3.2.14 Reactive iron and aluminium (hydr)oxide content
The concentrations of reactive (amorphous and crystalline) iron and (amorphous) aluminium oxides and hydroxides were determined in Alkaloam®, Red Lime™, and Bassendean, Manning Heavy and Merredin soils. These were considered to be important sorbing phases in these materials and therefore were required as an input parameter for use in geochemical modelling (Section 3.4).

Amorphous iron oxides and hydroxides were extracted using an ascorbate extraction at a liquid to solid ratio of 20:1 for 24 hours at room temperature. A dithionate extraction was used to extract the amorphous and crystalline iron oxides and hydroxides at a liquid to solid ratio of 20:1 for four hours at 60°C, and an oxalate extraction was used at a liquid to solid ratio of 100:1 for four hours at room temperature, to extract the amorphous aluminium oxides and hydroxides. The iron extraction methods are described in Kostka and Luther (1994) and the aluminium extraction method in Blakemore et al., (1987). These analyses were conducted by ECN, Research Centre of the Netherlands.

The information on the extracted iron and aluminium (hydr)oxides was used to calculate the amount of active iron and aluminium surfaces available in a sample for adsorption reactions. This total amount was expressed in terms of hydrous ferric oxide (FeOOH) and was referred to as “HFO” for input into the modelling software. Since no current database model systems exist for aluminium adsorption reactions, all aluminium (hydr)oxides were converted to hydrous ferric oxide (FeOOH) equivalents. For a description and justification of this approach, see Djikstra, et al., (2004) and Meima and Comans (1998).

3.2.15 Solid humic and fulvic acid content
Alkaloam®, Red Lime™ and Bassendean, Manning Heavy and Merredin soils were analysed for solid humic and fulvic acid content. This was considered to be the reactive solid organic matter in a material. The humic and fulvic acid concentrations were combined as one input parameter for geochemical modelling (section 3.4). The combined
concentration was referred to as Solid Humic Acid (SHA) in the model. The samples were analysed by ECN using a batch method, based on the method of Swift (1996), and is described by van Zomeren and Comans (2007).

3.3 Geochemical modelling

Analytical leach data from the pH dependent leach testing of materials used in this thesis were compared to geochemical modelling predictions. Geochemical modelling was also conducted to predict chemical speciation and to determine the mechanisms controlling leaching of different species\(^{19}\) in the materials across the pH environment of 0.5 to 12. The partitioning of free ions and complexed metal species in solution, as well as partitioning of elements in the solid and solution phases were predicted.

Geochemical modelling was carried out using ORCHESTRA, a JAVA based modelling framework, embedded in the database/expert system LeachXS\(^{2}\) interface (van der Sloot et al., 2003). Geochemical modelling predictions were based on the solubility of minerals, sorption to reactive hydr(oxide) minerals and reactive humic and fulvic acid in the solid and solution phase. The ORCHESTRA modelling framework was used to calculate mineral saturation indices (SI’s) of eluate data generated by the pH dependent leach test, solution speciation, mineral solubility and sorption processes, based on a number of adsorption and speciation models incorporated in the software.

The adsorption and speciation models were as follows:

Solution speciation was calculated using thermodynamic data from the MINTEQA2 (Allison et al., 1991) database, version 3.11, with some modifications (see Dijkstra et al., 2002, for a description of these changes). Additional minerals from Lothenbach and Winnefeld (2006), such as tricalcium aluminate hexahydrate, were also included in the database. The Davies equation was used to calculate species activities (Appelo et al., 2005). The (NICA)-Donnan approach was used to model adsorption of metal species to organic matter (Kinniburgh et al., 1999), which used the generic parameters for proton (Milne et al., 2001) and metal ((Milne et al., 2003) complexation. The Diffuse Layer Model of Dzombak and Morel (1990) and recommended ‘generic’ parameters were used for adsorption to HFOs. A Donnan model was used to calculate adsorption to permanently charged clay surfaces, assuming a charge density of 0.25 equivalent kg\(^{-1}\) and a fixed Donnan volume of 1L/kg, which may be considered as average values for illitic clay minerals (McBride, 1994).

\(^{19}\) E.g. incorporation within a mineral, sorption to organic material or DOC, precipitation etc.
Sample input parameters required for the geochemical modelling were;

(i) the amount of reactive solid surfaces; these being the concentration of clay, HFO and SHA.
(ii) the concentration of dissolved reactive organic material (dissolved humic and fulvic acids).
(iii) the available leaching concentrations for elements.
(iv) the solubility controlling minerals.
(v) the sum of pH + pE; an indication of the redox state of the soil sample (low pE being reduced state and high pE being oxidised state).

In cases where the HFO and SHA had not been measured directly for a soil, estimates were used based on the measured values of similar soils.

The dissolved reactive organic material for Alkaloam® and Red Lime™ was considered to be 20% of the dissolved organic carbon (DOC). This was based on fractionation studies at Alcoa that have calculated the soluble organic material present in the Bayer liquor to be 19% fulvic acids and 0.7% humic acids (unpub. data). For soil samples, the percentage of DOC considered to be reactive varied with pH. This is based on results from preliminary fractionation work conducted by ECN (Carter et al., 2009) using the fractionation method described in van Zomeren and Comans (2007). At acidic pH approximately 25% of the DOC was considered to be reactive, progressively decreasing to 15% reactive at pH 5 and 6 and then progressively increasing to 95% of the DOC being reactive at alkaline pH.

The identified mineral phases determined in the soils and ameliorants using XRD analysis were not considered suitable for use in geochemical modelling of leach data. The XRD data represents the mineral phases on a bulk material, whereas leaching is based on the assessment of mineral phases at the surface of particles, which can often be different. Solubility controlling mineral phases used for the geochemical modelling were selected from an initial base set of minerals provided by Dr Hans van der Sloot. The modelling process was then used to identify possible solubility controlling minerals from this set, based on their solubility indices and ability to provide a reasonable prediction of leaching against actual data. Any minerals showing obvious deviations from the expected leaching were discarded from the selection.

The available leaching concentration was assumed to be the maximum concentration that is available for extraction under the conditions of the leach test. This is commonly observed at
the extreme acid or alkaline pH for elements. The available carbonate concentration was estimated for input into the modelling. This is because at acidic pH carbonate is lost from the system and therefore its available concentration cannot be determined from extract measurements. The available carbonate concentration was based on the total inorganic carbon (carbonate) in the solid and from the available calcium concentration, since calcium carbonate is a predominant species in the amendments. This value was estimated at 1.5 times the available calcium concentration and then optimised based on the modelling outcomes.

The sum of pH + pE was assumed to be 15 for oxidised materials and pH + pE = 11 for mildly reducing materials.

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20 Some elements can exhibit their maximum leaching at neutral pH.
Chapter 4

METHOD DEVELOPMENT

4.1 Introduction

The properties of Alkaloam® and Red Lime™ suggest that environmental benefits could be derived from use of these materials in applications such as agricultural soil amelioration, treatment of acid sulphate soils and use in infiltration barriers to improve water quality. Determining the feasibility of using Alkaloam® and/or Red Lime™ in such applications would first require a detailed environmental risk assessment to ensure no adverse impacts will arise from incorporation of these materials.

An environmental assessment would need to include extensive characterisation of the material as well as a fundamental understanding of the material’s leaching behaviour in environments representative of the proposed application. Any perceived changes in the environment over time would also need to be considered, as well as an indication of how these changes may influence leaching behaviour and subsequent impact to the surrounding environment.

The leaching properties of materials are predominantly influenced by pH as most metals exhibit a noticeable increase in solubility at both low and high pH (van der Sloot et al., 1997). An understanding of the leaching behaviour of Alkaloam® and Red Lime™ in a range of pH environments would assist in assessing these products for different re-use applications.

The ASLP test, whilst recognised in Australia as the standard method for measuring leaching in materials for waste disposal or recycling, is limited in that it only provides information on the leachability of a material at three given pH environments, namely pH 2.9, pH 5 and at the material’s natural pH. If Alkaloam® or Red Lime™ were to be considered for re-use in alternative pH environments to these values, an environmental impact assessment using the ASLP could not be achieved with any confidence. A similar case would also be true using the US TCLP methodology described in Chapter 3.

In contrast, the pH dependent leach test, recognised by the European Union as a standard leach test for granular materials, is designed to provide information on the leaching behaviour of a material across a wide range of pH environments. Used with appropriate geochemical modelling, this test can predict the mechanisms controlling leaching, provide
insight into the chemical speciation present and allow predictions to be made on how a materials leaching behaviour could potentially change as the environment pH changes.

This test was developed and recommended by ECN, the Energy Centre for the Netherlands, in collaboration with Vanderbilt University in the US, for characterising waste materials for environmental impact assessments (van der Sloot et al., 2006) and could similarly be applied to characterising industrial by-products for assessing environmental impacts for a range of potential re-use applications.

For the purposes of assessing Alkaloam® and Red Lime™ as suitable re-use products, in particular as soil amendments, the pH dependent test required the following process optimisation to the standard CEN/TS 14429 (CEN, 2005) procedure.

4.1.1 Optimisation to assess nitrate leaching
The standard pH dependent leach test method prescribes the use of nitric acid for preparation of leaching solutions. The use of nitric acid prevents the accurate measurement of nitrate leaching in the samples, and therefore restricts the use of this method when environmental risk assessments based on nitrate mobility are required. Measuring nitrate leaching in Alkaloam® and Red Lime™ for the purposes of assessing their ability to retain nitrate, as well as phosphate, would be desirable. An alternative acid to nitric acid was therefore investigated to determine if nitrate leaching could be measured whilst maintaining the same extractants of other major, minor and trace elements measured using the conventional method.

4.1.2 Optimisation to improve solid/liquid separation in clay type soils
The eluates produced from leaching of Alkaloam® and clay type soils (Manning Heavy) in the alkaline pH range could not be filtered effectively using vacuum filtration conditions, as per the standard CEN/TS 14429 (CEN, 2005) method. This was due to the presence of a dark brown gel substance that blocked the filter membranes. Studies by Kučerík et al. (2007) suggest that humic acid may aggregate at low concentration in alkaline pH to form micellular humates and other colloidal species. It is hypothesised that these colloidal formations were present as a viscous ‘gel’ substance in the eluates, which prohibited the solutions from filtering under standard vacuum conditions. Alternative solid:liquid separation techniques were therefore investigated to optimise this separation process.

The procedural and analytical variability of the optimised pH dependent leach test was determined for different soils so that leach data discussed in this thesis could be accurately
interpreted. The variability of the optimised pH dependent leach test was assessed based on
the procedure being manually conducted by Alcoa’s Technology Delivery Group.

4.2 Use of Hydrochloric acid as an alternative extractant in the pH dependent leach test

4.2.1 Introduction

Use of nitric acid as an extractant in the standard pH dependent leach test procedure does not
allow nitrate leaching to be assessed. Since nitrates and phosphates are introduced into
agricultural soils through the application of fertilisers, these species are likely to be of
particular interest for assessing the benefits of agricultural soil amendments that could
prevent or reduce the magnitude of nitrate and/or phosphorus leaching from the treated soil.

The major cause of toxic algal blooms frequently observed in the Peel-Harvey Estuarine
system are reported to be caused by leachable phosphates, through overuse of fertilisers in
extensive agricultural farming and from increased urban development (Birch, 1982). Nitrates commonly found in fertilisers are also likely to threaten this water system, producing more highly toxic algal blooms than the phosphates. Lantzke (1997) has reported that high to very high nitrate concentrations commonly occur in the shallow groundwater beneath horticultural properties of the sandy soils of the Swan Coastal Plain. These levels are often in excess of the World Health Limit (WHL) for drinking water (10mg/L NO₃-N).

The abstraction of groundwater for irrigation from dams and shallow production bores in
these areas are of concern due to the recycling of nutrient rich water that could have a toxic
effect on crops. Nitrogen levels in the Peel-Harvey stormwater drains and groundwater
bores were monitored as part of the EPA monitoring program for the DAFWA field trials. Some sampling locations were found to contain levels above ANZECC levels (Rivers, 1997).

Nitrate algal blooms typically only develop in the absence of phosphates and therefore are
not likely to be present in the Peel-Harvey Estuarine system unless phosphate levels are
significantly depleted, or removed. Recently there has been growing interest in using soil
amendments, such as Alkaloam®, as a remedy for cleaning up the Peel-Harvey Estuarine
system of phosphorus algal blooms (EPA, 2008). Should this prove successful, nitrate algal
blooms could potentially develop if nitrate is not retained by soil amendments as effectively
as the phosphates, particularly with the levels reported being so high. Assessment of nitrate
leaching in amended agricultural soils is therefore important to understand the potential of
this occurring.
The majority of research on the use of Alkaloam® as a soil amendment has centred on its ability to retain phosphorus. Research by Ho et al. (1991a) and (1991b), Philips (1998) and McPharlin (1994) suggests Alkaloam® also has the benefit of retaining nitrogen, in the form of ammonium-nitrogen (NH₄⁺), when amended in Bassendean associated sands. Nitrate-nitrogen (NO₃⁻) retention however was not observed using Alkaloam® amended with gypsum (Red mud gypsum - RMG) up to doses of 256t/ha RMG (McPharlin, 1994). The charge of the nitrogen speciation and the net surface charge of the amended soil particles are likely to influence whether the matrix can retain nitrogen.

Hydrochloric acid was investigated as an alternative extractant to nitric acid in the pH dependent leach test. This was to determine if there were any differences in the leachability of metal species using the two extractants and whether hydrochloric acid could be used for assessing nitrate leaching in the soil amendments, Alkaloam® and Red Lime™, and the amended soils across a pH of 0.5-12.

Hydrochloric acid is a strong inorganic monoprotic acid, similar to nitric acid. Its acid dissociation constant (Kₐ) is higher than nitric acid (1.3 x 10⁶ vs 2.4 x 10¹) indicating that it is the strongest acid of the two extractants. Although hydrochloric acid is not a chelating agent, the chloride ions released from the strong acid may be susceptible to forming water soluble chloride complexes with cations from an insoluble salt. Any effected cations will therefore show increased leaching when extracted with hydrochloric acid comparative to nitric acid.

4.2.2 Results and discussion

4.2.2.1 Differences in leachability of species using hydrochloric and nitric acid in the pH dependent leach test

(i) Alkaloam® and Red Lime™

pH dependent leach tests were performed on Alkaloam® and Red Lime™ using hydrochloric acid and nitric acid extractants. Figures 4-1 to 4-3 show the leaching data of Alkaloam® and Red Lime™ using both acids, for a range of major, minor and trace elements. The charts are plotted on a logarithmic scale, in units of mg/kg, to illustrate the availability of elements leaching and to correct for minor variations in sample weights. The leaching concentrations of some key elements typically monitored in environmental studies, such as mercury, cadmium, antimony and lead were below analytical detection limits in these materials, and therefore are not included. Charts for the full suite of elements analysed are in Appendix A.
The natural pH of the materials is denoted as * on the charts. Nitric and hydrochloric acid extractants were used to generate leaching pH values up to the materials natural pH. Any differences in leaching concentration between the two sets of pH dependent leach data up to the natural pH will be attributed to the differences in extractants.

A Comparison of the pH dependent leach data for Alkaloam® and Red Lime™ indicate that the leachability of the majority of elements from these materials was similar using nitric acid or hydrochloric acid as the extractant. This was particularly the case for arsenic, beryllium, calcium, chromium, iron (for Red Lime™) potassium, magnesium, molybdenum, sodium, phosphorus, silicon (for Alkaloam®), sulphur, strontium and vanadium.

Differences between the two extractants were noted however for aluminium, iron and manganese from Alkaloam®, with leaching concentrations being approximately half an order of magnitude higher when extracted using hydrochloric acid. This occurred in particular across the acidic pH range. Selenium, in contrast was lower by almost half an order of magnitude. For the leaching of Red Lime™, the extraction of aluminium, DOC, selenium and zinc were all lower using hydrochloric acid, with zinc showing differences of half an order of magnitude between the two extractants. Only silicon showed slightly higher leaching from Red Lime™ using hydrochloric acid.
Figure 4-1: pH dependent leaching of species from Alkaloam® and Red Lime™ using nitric and hydrochloric acid extractants
Figure 4-2: pH dependent leaching of species from Alkaloam® and Red Lime™ using nitric and hydrochloric acid extractants.
Figure 4-3: pH dependent leaching of species from Alkaloam® and Red Lime™ using nitric and hydrochloric acid extractants

The leachability of iron and manganese from Alkaloam® at the acidic pH range showed a positive bias in leach data when extracted using hydrochloric acid, as illustrated in Figure 4-4.

Figure 4-4: Leachability of iron and manganese in Alkaloam® and Red Lime™ using nitric and hydrochloric acid extractants

LeachXSTM geochemical modelling predicted that the processes controlling the solubility of these elements in both extractants was the same across the acidic pH range, i.e. iron is controlled by sorption to clay and goethite mineral; manganese is controlled by sorption to
clay and organics. The increased leachability of manganese is not likely to be due to association with soluble organics since the DOC measured using hydrochloric acid extractant was slightly lower than that measured using nitric acid extractant. The solubility of iron and manganese from soils is readily increased in the presence of high concentrations of chlorides, nitrates and sulphates at low pH (Nádaská et al., 2012). Dissolution of goethite is also assisted by the formation of Fe-Cl surface complexes (Sidhu et al., 1981). In light of these findings and the fact that hydrochloric acid is a stronger acid than nitric acid, it is postulated that the high bias leaching concentrations of iron and manganese using hydrochloric acid extractant are likely to be associated with the dissolution of goethite and desorption from clay to form soluble iron (II) and manganese (II) chlorides.

Whilst hydrochloric acid is not classed as a chelating agent, it can provide a source of chloride ions that may complex with heavy metals, such as cadmium, cobalt, nickel and copper, to form soluble metal-chloride complexes (Doner, 1978). The formation of soluble inorganic complexes mobilise metals that may otherwise be immobilised in a soil and therefore produce a positive bias in the leach data. Cadmium is reported to be strongly affected by the presence of chloride, forming highly soluble anionic cadmium-chloride complexes (CdCl$_4^{2-}$) (van der Sloot, 2002).

The leaching concentrations of cadmium, cobalt, nickel and copper in Alkaloam®, Red Lime™ and the WA agricultural soils were close to or below the analytical detection limit in both extractants, suggesting that these elements are not of concern in these materials.

(ii) WA Agricultural Soils (Manning Heavy and Manning Light soil)

pH dependent leach tests were also carried out on two WA agricultural soils, Manning Heavy (clay) soil and Manning Light (sandy) soil in nitric acid and hydrochloric acid extractants. The pH dependent leach data using nitric acid was plotted across a pH range of 0.5 to 12 (which included the sodium hydroxide extraction at pHs above the natural soil pH). This data was compared against corresponding leach data using hydrochloric acid. Since hydrochloric acid was only required for producing acidic eluates in the range of pH 0.5 to 4, only these data points have been plotted for comparison.

The leachable concentrations measured using both extractants were found to be very similar for the majority of major, minor and trace elements, illustrated in Figures 4-5 to 4-8. This provides further evidence that hydrochloric acid can be used as a suitable alternative to nitric acid for determining the pH dependent leaching of most analytes in these soils. Elements
lower than their analytical detection limits are not presented below; a full suite of elements can be found in Appendix B.

Figure 4-5: pH dependent leaching of species from Manning Heavy (clay soil) using nitric and hydrochloric acid extractants
Figure 4-6: pH dependent leaching of species from Manning Heavy (clay soil) using nitric and hydrochloric acid extractants

Figure 4-7: pH dependent leaching of species from Manning Light (sandy soil) using nitric and hydrochloric acid extractants
A high bias was observed at approximately pH 2 for the leaching of arsenic, molybdenum, selenium and thorium from Manning Heavy soil using hydrochloric acid extractant, as shown in Figure 4-9. It is postulated that the high concentration of chloride ions are destabilising the adsorption surface of these elements, similar to that observed in
Alkaloam®, and increasing their solubility through the formation of soluble cation-chloride complexes.

![Graphs showing pH dependent emission of As, Mo, Se, and Th](image)

**Figure 4-9:** pH dependent leaching of arsenic, molybdenum, selenium and thorium from Manning Heavy soil using hydrochloric and nitric acid extractants

### 4.2.2.2 Nitrate leaching in Alkaloam® and Red Lime™ using hydrochloric acid extractant in the pH dependent leach test

The pH dependent leach test was conducted on Alkaloam® and Red Lime™ using hydrochloric acid to measure nitrate leaching from these materials across a pH range of 0.5 to 12. The eluates were analysed for nitrate by colorimetric analysis as described in section 3.3.12 and are shown in Figure 4-10.

Leaching of nitrate from Alkaloam® and Red Lime™ produced different profiles. In Alkaloam® a broad ‘U’ curve was observed, with maximum solubility occurring at extreme acidic and alkaline conditions. This process is due to the nitrate-sorbing surface solubilising at low pH, and at high pH the surface charge of particles becoming progressively negative, repelling negatively charged nitrate ions and increasing their solubility.
In Red Lime™, maximum solubility occurred at extreme acidic pH and decreased progressively with increasing pH. This trend suggests that nitrate mobility in Red Lime™ is not being influenced by changes to the surface charge of particles with change in pH, but rather is dependent on the precipitation of a mineral species. It is postulated that nitrate ions are being sorbed by the zeolite mineral, laumonite, or calcite (calcium carbonate) mineral present in Red Lime™. This postulation is based on previous studies by Mažeikienė et al. (2008) that have shown nitrate ions can be removed from solution using natural zeolites, and studies by Singh and Sekhon (1978) that have shown nitrate can adsorb to calcite (calcium carbonate). Supporting this postulation is the pH dependent leaching behaviour of silicon and calcium in Red Lime™, which was also consistent with the leaching behaviour of nitrate. Further investigations are required to determine the mineral sorption process involved.

The detection limit of the colorimetric analysis method used for quantifying nitrate was high (10mg/L; equivalent to 100mg/kg for the pH dependent leach test), limiting the ability to measure nitrate leaching in the agricultural or the Swan Coastal Plain soils, and leaching in Alkaloam® in the mid pH range. Further leach tests were therefore conducted using an alternative nitrate analysis method (automatic flow injection using a copper-coated cadmium column) with a detection limit two orders of magnitude lower than the colorimetric analysis.
4.2.2.3  **Comparison of nitrate leaching in a WA Swan Coastal Plain soil with and without Alkaloam® amendment**

Bassendean soil was selected to assess the impact of Alkaloam® amendment on nitrate leaching due to its very poor nutrient retention capacity. Previous research using column tests has reported that Alkaloam® blended with gypsum did not retain nitrate-nitrogen in a Gavin sand\(^{21}\) spiked with high amounts of ammonium nitrate to simulate extremes of irrigated vegetable production on the Swan Coastal Plain (McPharlin, 1994). The pH of the sand amended with varying amounts of Alkaloam® amended gypsum was between pH 5 and 7\(^{22}\) before addition of ammonium nitrate, therefore nitrate leaching was only measured within this pH range.

A pH dependent leach test was conducted on Bassendean soil spiked with nitrate, to measure nitrate leaching in this type of soil across a wider pH range of 0.5 to 12. A comparison was made against the corresponding Bassendean soil amended with Alkaloam® to determine if any increase in nitrate retention could be achieved within the same pH range.

A 1kg subsample of air-dried Bassendean soil was spiked with a nitrate solution and mixed thoroughly to ensure homogeneity. The nitrate source\(^{23}\) was from a hydroponic solution that contained potassium nitrate and calcium nitrate at a total nitrate concentration of 2.7%w/v. The nitrate solution was prepared by diluting 1.9mL of the hydroponic solution into 30mL deionised water and then added in full to the air-dried soil. The preparation was conducted in a stainless steel tray and the soil manually mixed for 20 minutes. The prepared Bassendean soil was then split into two equal portions of which one was further dosed with Alkaloam® at an application rate of 6.25g/kg and mixed to ensure the Alkaloam® was homogenously incorporated throughout the soil.

A pH dependent leach test using hydrochloric acid was conducted on the amended and unamended prepared Bassendean soil and the eluates analysed for nitrate using the automatic flow injection technique. Leach data from this investigation are shown in Figure 4-11.

The data illustrate that Alkaloam® has the potential to retain nitrate in Bassendean soil between the pH range 2 to 12. Maximum retention occurred at approximately pH 2.3 with

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\(^{21}\) A Bassendean associated sand.

\(^{22}\) 1:5 pH in water.

\(^{23}\) Direct nitrate was spiked into the soil rather than a nitrogen source, such as urea, to ensure that nitrate would be present in the soil for assessing any leaching.
68% nitrate retained. Across a typical WA agricultural soil pH range of 5 to 8, an average of 55% nitrate was retained.

Figure 4-11: Comparison of nitrate leaching from a nutrient enriched Bassendean soil with and without Alkaloam® amendment

Studies conducted by McPharlin (1994) showed that Alkaloam® did not retain nitrate from a Gavin sand (Bassendean associated sand) when amended with gypsum. Strahm and Harrison (2007) reported that the capacity for soils to sorb macronutrient anions, such as nitrate, is in the preferential order of PO$_4^-$ > SO$_4^{2-}$ > NO$_3^-$. Since gypsum addition (CaSO$_4$) introduces sulphate ions to the soil matrix, it is therefore likely that these anions will preferentially compete with nitrate ions for the sorption sites of the particles and subsequently prevent or reduce nitrate adsorption. Further investigations are recommended to confirm if amending Alkaloam® with gypsum reduces the capacity to retain nitrate in Bassendean soil.

At alkaline pH (pH >8) the data indicate that Alkaloam® does not retain nitrate in Bassendean soil. This is believed to be due to the negatively charged particle surfaces present at high pH that would not favour adsorption of anionic ions, such as nitrate (NO$_3^-$). This is consistent with observations reported by Krupka and Serne (2002) that anionic adsorption to mineral surfaces becomes less favourable as alkalinity increases.

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24 Also known as Red Mud gypsum (RMG).
The pH dependent leach test can be used to assess benefits of nitrate retention from soil amelioration. This could be a valuable tool for improving nitrogen management and optimising fertiliser use in WA soils.

4.2.2.4 Use of pH dependent leach testing for assessment of nitrate leaching in WA soils
Nitrogen management in WA assumes that WA soils contain negligible or no positive charge and therefore are unable to retain nitrate against leaching. Research by Wong and Wittner (2009) have challenged this assumption, based on the clay mineralogy in highly weathered soils of the WA Wheatbelt area being predominately kaolinite and iron/aluminium (hydr)oxides. Kaolinite and iron/aluminium hyd(oxide) minerals are said to have variable charged surfaces, with positive charge density (measured as anionic exchange capacity (AEC) increasing at lower pH. The research studies by Wong and Wittner (2009) reported that soils across a wide area of the WA wheatbelt did in fact measure positive charge and anionic exchange capacity (AEC) that delayed nitrate leaching in these soils.

In light of this finding, it is recommended that pH dependent leaching of nitrate be assessed on the WA Wheatbelt soils, (e.g. Merredin soil) to determine the extent of nitrate retention in these soils at different environment pH.

4.2.3 Conclusion
Leachable concentrations for the majority of major, minor and trace elements in Alkaloam®, Red Lime™ and a sandy and clay agricultural WA soil (Manning Light and Manning Heavy soils) were similar using hydrochloric acid and nitric acid as two different extractant acids. This indicates that hydrochloric acid is suitable as an alternative extractant to nitric acid for carrying out the pH dependent leach test in these materials.

Some caution is recommended when investigating the leaching of elements that are strongly affected by the presence of chloride, such as cobalt and cadmium, as soluble chloride complexes could produce positive bias in the data. In the case of the aforementioned materials, these elements were below the analytical detection limits in the materials analysed, and therefore were not a concern in this investigation. A positive bias was observed for the leachability of manganese and iron in Alkaloam® at acidic pH range using hydrochloric acid as the extractant. At pH 2 the dissolution of arsenic, molybdenum, selenium and thorium in Manning Heavy soil also increased using hydrochloric acid. This suggests that these elements are potentially affected by the presence of chloride ions.
Hydrochloric acid can be used as an alternative to nitric acid in the pH dependent leach test for evaluating nitrate leaching in materials. The pH dependent leaching behaviour of nitrate from Alkaloam® was characterised by a shallow ‘U’ curve, with maximum solubility occurring at extreme acidic and alkaline pH. Nitrate solubility was influenced by changes in the surface charge of particles with changing pH.

The pH dependent leaching of nitrate from Red Lime™ decreased with increasing pH. Unlike Alkaloam®, nitrate mobility in Red Lime™ is not influenced by changes to the surface charge of particles with change in pH, but is dependent on the precipitation of a mineral species. It is postulated that nitrate ions are being sorbed by the zeolite mineral, laumonite, or calcite (calcium carbonate) mineral present in Red Lime™, based on previous research and consistencies in the pH dependent leaching profiles of calcium and silicon with nitrate.

Alkaloam® has the potential to retain nitrate in Bassendean soil in the pH range of 2 to 8. Across a typical WA soil pH range of 5 to 8, Alkaloam® was shown to retain an average of 55% nitrate when amended in a Bassendean soil dosed with 50ppm nitrate.

The pH dependent leach test could be used as a useful tool for assessing nitrate retention in WA soils and for assessing benefits of nitrate retention from soil amelioration.

4.2.4 Recommendations
It is recommended that hydrochloric acid be used as an alternative extractant to nitric acid for determining the pH dependent leaching of nitrate from soil type materials.

It is recommended that further investigations be conducted to determine whether the presence of gypsum will change the nitrate retention properties of Alkaloam®.

In light of research by Wong and Wittner (2009) that reports positive charge density and AEC being measured in WA Wheatbelt soils delay nitrate leaching (retain nitrate), it is recommended that pH dependent leach test studies be conducted on these soils to determine the extent of the nitrate retention across a range of soil pH.

It is recommended that the pH dependent leach test be evaluated for assessing nitrate retention in a range of WA soils from different cropping areas to determine if it can be used as a tool for improving nitrogen management and optimising fertiliser use in WA soils.
4.3 Solid/liquid separation by centrifugation in fine particulate and clay type soils

4.3.1 Introduction

Eluates produced from the pH dependent leach tests at alkaline pH conditions (pH ≥10) were dark brown in colour. The colour intensity of the solution increased with increasing pH, which is typically evident of dissolved humics. These solutions were difficult to filter under vacuum filtration with a 0.45µm membrane (standard method conditions), due to the formation of a dark brown gelatinous film collecting on the surface of the filter membrane. Filtration times often exceeded 12 hours to collect the alkaline eluates, or required excessive replacement of spent filter membranes, jeopardising the integrity of the sample. It is believed that adsorption of metal ions within the gelatinous film are susceptible to being lost at this stage of the leach test procedure, and may produce lower concentrations in the final filtered eluate than expected. The formation of the gelatinous film was noticeably more prevalent in materials containing fine particulates or clay, in particular the Bassendean soil, Manning Heavy soil, Alkaloam® and Red Lime™. This was consistent with work conducted by Barrington (2005). The gelatinous substance was initially believed to be the formation of micellular or colloidal humic material in alkaline solution. Studies reported by (Kučerík et al., 2007) have shown that fine humates can aggregate at low concentration (as low as 0.001g/L) at pH 7 and 12 and at high ionic strength.

Alternative separation techniques were considered for improving the solid/liquid separation in these types of materials and to avoid unnecessary replacement of expensive filter membranes. Preliminary tests using pressurised filtration were unsuccessful, and so centrifugation was assessed as an alternative separation technique.

Centrifugation has been used for separating suspensions of gas works soil and asphalt granulate for assessing the pH dependent leaching of TOC and its effect on the leaching of polyaromatic hydrocarbons (PAHs). In these studies, higher leaching concentrations of PAHs were obtained using centrifugation than by vacuum filtration using a range of filter membranes (Comans, 2011). Leaching concentrations may have been higher due to the very high centrifugation speed and length of centrifugation time used (27000rpm, 30mins) however, this was not ascertained. Very little development work has been reported on leach test methods using centrifugation and the effect on leaching concentration with respect to centrifuge speed and time.

This section reports on whether centrifuge speed will change the leaching concentration of major, minor and trace metals than previously reported and whether this separation technique can be optimised for improving solid/liquid separation of eluates.
4.3.2 Experimental conditions
The pH dependent leach test was carried out on Manning Heavy soil, with and without centrifuging, to determine if the solid/liquid separation process could be optimised without compromising the leaching behaviour in the equilibrated soil solution, or without changing the measureable concentrations of the elements.

pH dependent leach testing was carried out on replicate 15g (dry weight) sub-samples of Manning Heavy soil to produce eluates with final pH values of 2.2 (acidic pH), 5.6 (natural pH) and 9.7 (alkaline pH) after leaching for 48 hours. At each pH, solid/liquid separation was carried out by centrifuging the samples at speeds of 10,000rpm, 15,000rpm or 20,000rpm for 15 minutes, followed by vacuum filtration through a 0.45µm membrane. Eluates at each pH were also collected by vacuum filtration through the 0.45µm membrane without using centrifugation. These were considered a control for comparative purposes. All eluates were submitted to Ultratrace Laboratories for analysis of a suite of elements.

4.3.3 Results and discussion
Eluates centrifuged prior to vacuum filtration displayed a decrease in solution colour intensity and very little or no colloidal humic material collected on the filter membranes (depending on the pH of the eluate), compared to samples that were not centrifuged. The surface of the membranes did not block or require frequent replacement to collect a suitable volume of filtered eluate for analysis. In contrast, eluates filtered under vacuum without centrifugation took approximately seven hours to filter due to the surface of the membrane being blocked. The filter membrane had to be changed three times to collect sufficient volume of eluate for analysis.

Figures 4-12 to 4-14 shows the effect of centrifugation and centrifugation speed on the leaching concentration of elements from Manning Heavy (clay) soil in acidic pH (2.2), natural pH (5.6), and alkaline pH (9.7) environments. The data are plotted on a logarithmic scale. Other elements were analysed, however concentrations were too low to determine if any changes were apparent from the use of centrifugation, and therefore were not presented in the charts. A full suite of the experimental data is listed in Appendix C.
Effect of centrifugation and Centrifugation Speed on Leaching of trace elements in Manning Heavy clay soil at pH 2.2

Effect of centrifugation and Centrifugation Speed on Leaching of trace elements in Manning Heavy clay soil at pH 5.6

Effect of centrifugation and Centrifugation Speed on Leaching of trace elements in Manning Heavy clay soil at Natural pH (pH 9.7)

Figure 4-12: Effect of centrifuge speed on leaching of constituents from Manning Heavy soil at pH = 2.2

Figure 4-13: Effect of centrifuge speed on leaching of constituents from Manning Heavy soil at natural pH = 5.6

Figure 4-14: Effect of centrifuge speed on leaching of constituents from Manning Heavy soil at pH = 9.7
4.3.3.1 Effect of Centrifugation on leaching concentrations

There were no measurable differences in the leachable concentrations of elements at acidic pH (2.2) with or without centrifugation of the samples prior to filtration, as illustrated in Figure 4-12. With the exception of sulphur and chloride, the plotted elements exhibit maximum solubility at extreme acidic pH and therefore are likely to be unaffected being already fully dissolved in solution (see chapter 7).

Following centrifugation, there were no fine particulates or colloidal species visibly present in the eluates and the solutions were weaker in colour intensity. The eluates filtered very easily without replacement of the filter membranes, therefore there was no potential loss of metals through adsorption onto the gelatinous film.

Leachable concentrations of aluminium, iron, and silicon measured in eluates from Manning Heavy soil at natural pH (5.6) and alkaline pH (9.7) were lower when samples were not centrifuged, compared to samples that had been centrifuged prior to filtration (Figures 4-11 and 4-12). It is postulated that without centrifugation these metal ions are being lost by adsorption to the colloidal humic species layer collecting on the surface of the filter membrane. On replacement of the spent membranes, these species are then subsequently removed from the sample. Differences in the leachable concentrations with and without centrifuging were most prominent when the soil was leached at alkaline pH (9.7), which is when the highest amount of gelatinous humic layer was formed and the highest number of filter membranes were replaced. The largest change in concentration was observed for silicon, with an order of magnitude increase in the leachate concentration for the centrifuged sample.

Carter et al. (2008) reported that the dominant process controlling solubility in Busselton soil (Manning Light soil), typically found in the Swan Coastal plain, was adsorption to particulate organic matter, specifically humic and fulvic acids. This suggests that the presence of humic in the eluates is likely to play a significant role in adsorption of cationic species, such as iron, aluminium and silicon, and therefore decrease element concentrations when the gelatinous layer is present. This is in agreement with the observations shown. Other heavy metal cations likely to be susceptible to adsorption onto organic particulates are copper, lead, nickel, cobalt, manganese and zinc (van der Sloot et al. 1997). These elements were also expected to show lower measured concentrations when no centrifugation was used, however the concentrations were either too low or below detection limit.
Eluates from leach testing of Manning Heavy soil at natural pH were less intense in colour than the eluates at alkaline pH, with the dark gelatinous layer of colloidal material still visible on the filter membranes, but at much smaller quantity than when just vacuum filtration was used. The membranes were not as susceptible to clogging up with colloidal organic material and therefore were not replaced as frequently in comparison to the alkaline pH. Since the membranes were replaced less frequently, a lower concentration of elements adsorbed to the organic colloidal material would have been lost when replacing the membranes. This trend is highlighted in Figures 4-13 and 4-14, where the difference in concentration between eluates centrifuged vs non-centrifuged are not as significant at natural pH as at alkaline pH.

4.3.3.2 Effect of Centrifugation speed on leaching concentrations

With the exception of magnesium, increasing the centrifuge speed from 10,000rpm to 15,000rpm or 20,000rpm did not change the leaching concentration (Figures 4-12 to 4-14) of the analytes. Data suggest that a centrifuge speed of 10,000rpm would be sufficient to provide suitable solid/liquid separation for a sample, any further increase in speed would be unnecessary.

4.3.4 Conclusions

Concentrations of metals such as aluminium, silicon and iron in eluates not centrifuged prior to vacuum filtration were lower than when the eluates were centrifuged. The eluates contained fine precipitates or colloidal species that were not removed from solution unless centrifugation was used. The colloidal species are postulated to be micellar humics that could adsorb metals such as aluminium, silicon and iron effectively, and trap them on the filter membrane during filtration.

The differences between concentrations of centrifuged and non-centrifuged eluates were greatest for eluates at alkaline pH. This appears to be due to greater losses incurred from adsorption of metals onto the colloidal humic layer and subsequent removal from frequent replacement of the blocked filter membranes. Incorporation of centrifugation prior to vacuum filtration consolidated the fine particulates and colloidal species, producing a clear solution that allowed efficient filtration and minimised losses of metals in the filtrate.

The loss of aluminium, iron and silicon during filtration without centrifugation compromises the integrity of the leaching data. Centrifugation followed by vacuum filtration is therefore recommended as the optimum methodology for solid/liquid separation using the pH dependent leach test.
Increasing centrifuge speed from 10,000rpm to 15,000rpm and 20,000rpm did not change the leaching concentrations for most elements, indicating that a centrifuge speed of 10,000rpm would be sufficient for optimising solid/liquid separation during leach testing.

4.3.5 Recommendations

It is recommended that centrifugation be used to improve solid/liquid separation when conducting the pH dependent leach test on granular materials that contain clay particulates. This will improve the leach data precision for elements such as aluminium, iron, silicon, phosphorus, chloride, TOC, calcium, potassium, magnesium, sodium and sulphur, in addition to reducing the sample preparation time.

These findings have been incorporated into a new method for pH dependent leach testing of clay type soils, as reported in Chapter 3 section 3.2.11.
Chapter 5

COMPARISON OF ASLP AND pH DEPENDENT LEACH TESTS

5.1 Introduction
This chapter reports on the comparisons between two standard leach tests, the ASLP (Australian Standard Leaching Procedure) and the pH dependent leach test (a European Union standard leach test).

The pH dependent leach test has been recognised as a method that allows mutual comparison of alternative leach tests. Comparisons between a range of single extraction leach tests using different extraction solutions (e.g. CaCl$_2$, NaNO$_3$, acetic acid) conducted on a contaminated river sediment and a soil amended with sewerage sludge compare well when plotted in relation to the pH dependent leach test (van der Sloot, 2004). Since ASLP reflects a single extraction leach test using acetic acid, it is anticipated that this leach test may also correlate well with the pH dependent leach test.

Leach testing was conducted on Alkaloam®, Red Lime™, the WA agricultural soils and amended agricultural soils to determine if leach data correlates well between the two leach test methodologies, and to determine if either test is suitable for conducting environmental assessments on Alkaloam® and Red Lime™ for re-use applications, in particular as soil ameliorants. A description of the procedures for the ASLP and pH dependent leach tests is outlined in Chapter 3 section 3.3.9.

A comparison of the method parameters for the ASLP and pH dependent leach tests, listed in Table 5-1, show that the leach tests differ in respect to extraction solution, contact time of the solid phase with the extractant, pH, liquid:solid ratio and particle size.
Table 5-1: Differences between standard parameters for ASLP and pH Dependent Leach tests

<table>
<thead>
<tr>
<th></th>
<th>ASLP</th>
<th>pH Dependent Leach Test</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
<td>pH 2.9, pH 5 and natural pH</td>
<td>pH 4(^{25}) to 12 (including natural pH)</td>
</tr>
<tr>
<td><strong>pH controlled</strong></td>
<td>No</td>
<td><em>Two modes</em></td>
</tr>
<tr>
<td></td>
<td>i) Controlled final pH at end of leaching period</td>
<td>i) Controlled final pH at end of leaching period</td>
</tr>
<tr>
<td></td>
<td>ii) Constant pH over entire leaching period</td>
<td>ii) Constant pH over entire leaching period</td>
</tr>
<tr>
<td><strong>Extractant</strong></td>
<td>Glacial acetic acid solution</td>
<td>Nitric acid solution</td>
</tr>
<tr>
<td></td>
<td>Glacial acetic acid/sodium hydroxide solution.</td>
<td>Sodium hydroxide solution.</td>
</tr>
<tr>
<td></td>
<td>Deionised water for natural pH.</td>
<td>Deionised water (DW) for natural pH.</td>
</tr>
<tr>
<td><strong>Addition of extractant</strong></td>
<td>Added as one portion</td>
<td>Controlled final pH: Added in 3 progressive portions.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Constant pH controlled: Continuous addition of extractant throughout the leach test period.</td>
</tr>
<tr>
<td><strong>Particle size</strong></td>
<td>&lt;2.4mm</td>
<td>&lt;1mm</td>
</tr>
<tr>
<td><strong>Liquid: Solid ratio</strong></td>
<td>20:1</td>
<td>10:1</td>
</tr>
<tr>
<td><strong>Leaching Conditions</strong></td>
<td>18 hours @ ambient temp (~ 21°C to 24°C)</td>
<td>48 hours at 20°C</td>
</tr>
<tr>
<td><strong>Application</strong></td>
<td>Simulates leaching of a material placed in putrescible landfill</td>
<td>Simulates leaching in single material system at different pH environments</td>
</tr>
</tbody>
</table>

The ASLP test was based on the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP), originally developed to measure the leachability of wastes co-disposed in putrescible landfills (Graham, 2004). Leaching is measured under initial pH conditions of pH 2.9, pH 5 and the materials natural pH. Acidic pH extraction solutions are prepared from

\(^{25}\) Standard pH range is pH 4 to 12 however leach studies in this thesis were conducted in the pH range 0.5 to 12.
acetic acid and acetic acid/sodium hydroxide to simulate decomposing putrescible matter in landfill. Deionised water is used as an extractant to simulate in-situ conditions in landfill (Graham, 2004). The solid material is in contact with the extraction solution for 18 hours after which the eluate is collected by filtration and analysed for a range of species. An assumption is made that all reactions influencing leaching have approached equilibrium at 18 hours. Following the leaching period, the final pH of the solution should be reported, as this is likely to differ from the initial pH due to reactions occurring between the extractant and species in the soil. However this is not always performed.

The pH dependent leach test measures the leaching behaviour of a material over a longer time period and a wider pH range than the ASLP. Leaching is measured after 48 hours (as opposed to 18 hours with ASLP), and at eight pH values over a final leaching pH range of 4 to 12 (as opposed to three initial pH values). Whilst the standard method is designed to assess leaching across a pH range of 4 to 12, the leach studies in this thesis were conducted across a final pH range of 0.5 to 12. This was to ensure that the maximum concentration available for leaching for each element was measured, which occurs at extreme acidic or alkaline pH for the majority of elements (van der Sloot, 1997).

The pH dependent leach test is conducted by direct addition of pre-selected amounts of acid or base (CEN, 2005) to achieve a desired final pH on completion of the 48 hour leaching period. The extractant is added to a material in three progressive portions to ensure a change in the pH of the solid/liquid matrix does not occur too rapidly (Carter, 2005b). A gradual change in pH allows slow reactions from interaction of the extractant with species in the soil to occur prior to leaching, as would be representative of conditions in the field. Too rapid a change in pH may prevent some species forming if the precursor constituents become highly mobile and are leached from the matrix before the extractant has time to react.

The pH dependent leach test can also be conducted under continuous pH control conditions. In this mode the leaching can be assessed at constant pH conditions over the entire 48 hour leaching period. This is performed by continuous pH measurement and automatic addition of acid or base (CEN, 2006). The leaching investigations conducted for this thesis were not carried out using this mode since a wider pH range of exposure scenarios were required for the studies. In both modes the pH dependent test aims to approach equilibrium at the end of the leaching period.

In contrast, ASLP does not allow leaching to be measured under controlled pH conditions, therefore leach data assessed using this test can be potentially misinterpreted, depending on
whether the final pH or initial pH of the leaching solutions are used for the evaluation. In addition, any changes in pH between the initial and final solutions, from the effects of dissolution and precipitation reactions occurring during contact of the material with the extractant, will not be accounted for in the data interpretation. In the ASLP test, prepared leaching solutions are added in one full measure to the material, rather than proportionally as conducted in the pH dependent leach test.

The required particle size of the test material is smaller in the pH dependent leach test than that used in the ASLP, providing a larger surface area of the material for leaching. Smaller particle size has been shown to enhance the mobility of metals as a result of increased surface area (Al-Abed, 2006), and is expected to move more rapidly to steady state leaching conditions (Dijkstra, et al., 2006a).

Acetic acid, the extraction solution used in the ASLP test, is an effective chelating agent used in industry (Schlumberger, 2009), and has the ability to complex with cations to form soluble acetate complexes. Heavy metal cations, such as copper, cobalt, nickel, lead and zinc have been reported to be susceptible to chelation (Jones, 1981). Studies by Essaku et al. (2003) confirm this, reporting that the solubility of lead and zinc are enhanced through interaction with acetic acid, and give rise to higher extraction efficiencies in leach tests. Metals susceptible to chelation with acetic acid therefore may produce higher leaching concentrations using the ASLP test, relative to the pH dependent leach test, which uses a non-chelating extractant, nitric acid. Using non-chelating extractants in leach tests will minimise reactions between the extraction solution and material and therefore the data generated will be more representative of the materials leaching behaviour.

The limitations and deficiencies of the ASLP outlined above are significant flaws in the method and therefore do not give confidence to the user that ASLP test data can provide a representative evaluation of a materials leaching properties. Given that the ASLP is the only standard leach test recognised in Australia for environmental related assessments, it is imperative that other leach tests be considered and validated as soon as possible to offer a more thorough and accurate evaluation process for assessing by-product materials for re-use.

A series of investigations were conducted using pH dependent leach testing and ASLP to investigate differences between the procedures and to look at the effect of leaching under particular pH environments.
5.2 Results and Discussion

5.2.1 Comparison of information provided by ASLP and pH dependent leach tests

ASLP and pH dependent leach testing was conducted on Alkaloam®, Red Lime™ and Manning Light sandy soil, with and without 1.6g/kg Alkaloam® amendment. Comparisons were made between the two sets of leach data for a range of constituents in order to illustrate the differences in information provided from the ASLP and pH dependent leach test.

A typical example of the differences in leaching information provided from the ASLP and pH dependent leach test can be seen using the leach data for magnesium from Alkaloam® and Red Lime™, and Manning Light (sandy) soil with and without 1.6g/kg Alkaloam® amendment (Figures 5-1 and 5-2).

The total concentration for magnesium has been added to the charts for reference but was not obtained from the leach tests. On the ASLP charts, the initial pH of the leachate solutions (pH 2.9, pH 5 and pH 7.06) has been reported to illustrate the differences between the initial and final leaching pH values that were measured, and highlight the importance of reporting final pH for evaluating leach data.

Figure 5-1: Comparison of ASLP and pH dependent leach test data for magnesium from Alkaloam® and Red Lime™
Figure 5-2: Comparison of ASLP and pH dependent leach test data for magnesium from Manning Light soil with and without 1.6g/kg Alkaloam® amendment

5.2.1.1 Influence of pH on leaching

Figures 5-1 and 5-2 illustrate the limitations of the ASLP leach test method in that it only provides information on the leaching of constituents from a material at three pH values, which if not applicable to the pH environment being investigated would be of limited use for environmental assessments. This is consistent with observations reported by URS Australia (2009) that ASLP is not representative of the actual conditions that occur for a fertiliser applied to agricultural land. In contrast, the corresponding data obtained from the pH dependent leach test data provides information on how pH will influence the leaching of constituents across a pH range of 0.5 to 12, allowing predictions to be made on leaching behaviour as an environment’s pH changes. Since the test measures leaching at extreme acidic and alkaline pH, at which most metals exhibit their maximum solubility, the available leaching concentration of a constituent can also be determined26 (van der Sloot et al., 1997).

The maximum concentration of a constituent available for leaching can be less than or equivalent to the total concentration present in a material. Differences between the available leaching concentration and total concentration are indicative that some of the species is bound in the solid phase; through an adsorption or complexation process, or may be

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26 Often different from the total concentration.
incorporated within a mineral phase (See Chapter 7). This information cannot be obtained using the ASLP test.

5.2.1.2 Leaching of high buffering capacity materials

The initial pH and final pH of the leaching solutions in the ASLP test were significantly different for Alkaloam® and Red Lime™ (Figure 5-1). This is attributed to the high buffering capacity of these materials and their natural alkaline pH. High buffering capacity materials can resist changes to their natural pH on addition of acid or base. Red Lime™, having a higher buffering capacity than Alkaloam®, showed the most significant difference with the initial leaching pH of 2.9 and 5 producing eluates with a final leaching pH of 10.1 and 12 respectively. Alkaloam® produced a final leaching pH of 5.2 and 6.6 respectively. This is a significant limitation in the ASLP test.

Differences in the initial pH and final pH, if not reported, can be open to considerable misinterpretation of leach data, depending on whether the measured leaching concentrations are taken as occurring at pH 2.9 and 5 or at their final leaching pH. In the case of the DAFWA Alkaloam® field trial monitoring, the leaching data reported from the ASLP testing did not include the final leaching pH (Rivers, 1997) and therefore could be misinterpreted, depending on the extent of the differences. This is in agreement with comments made by Gerritse (2000).

In addition, the final pH values of the ASLP are often different to the start pH, and cannot be controlled. This does not allow the data to be compared to other samples because the solutions are at different pH values, and pH is the major parameter that determines the ability of contaminants to leach.

Using ASLP for monitoring leaching from Alkaloam® amended soils in paddocks with high application rates of Alkaloam® (>20t/ha) are potentially at more risk of being misinterpreted than at lower rates, where the pH change will be less significant. The ASLP is unreliable for assessing leaching in high buffering capacity materials, in particular for those materials with naturally high alkaline pH, such as Alkaloam® and Red Lime™ and other industrial by-products of this nature.

Low buffering capacity soils such as Manning Light soil showed little change between the initial and final leaching pH, as illustrated in Figure 5-2. Therefore, data interpretation from ASLP testing is less likely to be misinterpreted for these types of samples.
The final pH measured for Manning Light soil amended with Alkaloam® also showed little change from the initial pH (Figure 5-2), indicating that the amendment rate of Alkaloam® (6.25g/kg\textsuperscript{27}) was not high enough for the buffering capacity to change the pH of the leaching solution.

5.2.1.3 *Comparison of leaching between different materials*

The final pH values for the ASLP data were noticeably different between each of the materials at the three pH levels tested, preventing direct comparison of leach data between samples. For example, the ASLP test conducted using pH 5 extractant on Manning Light soil had a final pH of 5, pH 6.6 for Alkaloam® and pH 12 for Red Lime™. In contrast, direct comparisons of leach data could be made between materials using the pH dependent leach test due to the full pH range included in the test (Figure 5-3).

![Figure 5-3: Comparison of magnesium leaching from Alkaloam®, Red Lime™ and Manning Light soil with and without Alkaloam® amendment, using pH dependent leach test data](image)

5.2.1.4 *Identifying constituents exhibiting solubility or availability controlled leaching behaviour*

The leaching of constituents from a material is influenced by fundamental processes occurring between the soil and extractant that control their solubility. Examples of processes that can occur are; complexation of metals to other species to form soluble complexes that

\textsuperscript{27} Equivalent to 10t/ha at 1cm soil depth.
mobilise otherwise immobile constituents, re-precipitation or sorption processes that immobilise initially dissolved constituents back into the solid phase, or the formation of soluble and insoluble mineral phases that in turn will control solubility of constituents. The leaching of constituents from a material that are influenced by these fundamental processes is described as being “solubility controlled”, and can be identified using geochemical modelling (Astrup et al., 2006; van der Sloot et al., 2007 and Dijkstra et al., 2004). pH is a key variable that can affect these fundamental processes and therefore has a significant impact on the leaching behaviour of a material.

The leaching of some constituents can be independent of pH or solubility controlling processes. These species are highly soluble and their leaching concentration is only limited by the total amount present in the material, rather than by solubility controlling mechanisms. Species with this type of leaching behaviour are described as being “availability controlled” and are characterised by having similar concentrations across a wide pH range (van der Sloot et al., 1997).

The pH dependent leaching profile of elements from a material can be used to identify whether species exhibit “availability controlled” or “solubility controlled” leaching behaviour in a matrix. For example, Figure 5-4 shows the leaching profile of potassium and sodium from Red Lime™. These species are exhibiting availability-controlled behaviour since their leaching concentration is independent of pH and remains consistent across the pH range.

The pH dependent leaching profile of sodium from Alkaloam® exhibits availability controlled behaviour from pH 0.5 to 4.7, and then becomes solubility controlled up to its natural pH of 10.6 (Figure 5-5). In contrast, ASLP generates insufficient leach data (blue dots) to facilitate identification of availability and solubility controlled processes.

**Figure 5-4: Potassium and sodium - availability controlled metals in Red Lime™**

The pH dependent leaching of sodium from Alkaloam® exhibits availability controlled behaviour from pH 0.5 to 4.7, and then becomes solubility controlled up to its natural pH of 10.6 (Figure 5-5). In contrast, ASLP generates insufficient leach data (blue dots) to facilitate identification of availability and solubility controlled processes.
5.2.1.5 Prediction of mechanisms controlling leaching behaviour with the aid of geochemical modelling

pH dependent leach data, with the aid of LeachXSTM geochemical modelling, can facilitate prediction of the processes controlling leaching of constituents from a material, and the elemental partitioning between dissolved and particulate species across the pH range tested. Specific sample input parameters are required to conduct the modelling, which include the concentration of reactive solid material (e.g. concentration of clay, solid organic and iron and aluminium (hydr)oxides within the sample), the concentration of dissolved organic material, the available leaching concentration of elements, and the mineral phases believed to be controlling solubility (described in Section 3.3). The ASLP procedure yields insufficient data to conduct geochemical modelling.

Figure 5-6 illustrates the pH dependent leaching of calcium from Alkaloam® across the pH range of 1-12, and the predicted partitioning of the element between the solid and liquid phases over this pH range using geochemical modelling. The red dots on the chart are pH dependent leach data for calcium and the dashed line is the predicted leaching calculated by the LeachXSTM geochemical software.
The geochemical modelling output predicts the solubility of calcium to be predominantly controlled by the mineral calcite and to a lesser degree, tricalcium aluminate (TCA6), and sorption processes such as adsorption to iron hydr(oxide) surfaces and particulate organic matter at pH >7. As the pH increases from 7 to 12, calcium becomes progressively less mobile as it is bound with the aforementioned species. At pH<7, the most important process controlling solubility of calcium is its adsorption to clay, and to a lesser extent sorption to insoluble organics (specifically humic and fulvic acids). At pH<7 calcium is predicted to be predominantly mobile and is available in solution as free cations rather than bound in the solid phase.

![Diagram](image)

**Figure 5-6: Predicted solubility and solid:liquid phase partitioning of calcium from Alkaloam® at varying pH**

Prediction of processes controlling leaching behaviour, and the partitioning of these constituents between the solid and liquid phases across a wide pH range, are critical input parameters for comprehensive environmental assessments on potential industrial by-products such as Alkaloam® and Red Lime™. The inability to generate robust geochemical modelling data using ASLP inputs again reinforces the need to use the pH dependent leach test procedure where comprehensive environmental assessments are required.
Discussion and interpretation of pH dependent leach data using geochemical modelling for Alkaloam®, Red Lime™ and the WA agricultural soil samples is described in Chapter 7.

5.2.2 Correlation of ASLP and pH dependent leach data

Investigations by van der Sloot (2004) report that the pH dependent leach test is a method that allows mutual comparison between leach tests. To determine if the ASLP test is mutually comparable with the pH dependent leach test the two sets of leach data were overlaid for a range of elements. For the purpose of comparing data the leaching concentrations were expressed in terms of mg/L rather than mg/kg, to account for the differences in liquid:solid ratios used in the procedures.

Charts in this section compare the ASLP and pH dependent leach test data for a selected suite of leached constituents from Alkaloam®, Red Lime™ and Manning Light and Newdegate agricultural soils. Leaching concentrations less than the detection limit of the analysis have been plotted as half the detection limit. In some samples (e.g. Red Lime™ and Manning Light soil), the detection limit was not the same for all eluates analysed; in such cases the highest detection limit has been plotted on the chart. The symbol * on the charts denotes the natural pH of the soil. The complete set of data is in Appendix D.

5.2.2.1 Correlation of ASLP and pH dependent leach data from Alkaloam®

Figure 5-7 includes leach data obtained from ASLP and pH dependent leach testing of Alkaloam®. With the exception of aluminium, leaching concentrations using the two methodologies were similar for most elements, despite differences in the method parameters, such as liquid:solid ratio, particle size, extractant and extraction time. This indicates that pH is the controlling parameter influencing leaching, and that other method parameters have less impact on the leaching behaviour. The strong influence of pH on leaching reinforces the importance of recording and reporting final pH when using the ASLP methodology.
The leach data from both tests correlated well irrespective of the leaching concentration. This is illustrated with the leaching of selenium, magnesium and silicon having comparable leaching concentrations at 0.1mg/L, ~10mg/L and 100mg/L respectively.
The ASLP leaching concentration for aluminium at a final pH of 5.2 (using the pH 2.9 extraction solution) was higher than the corresponding leaching concentration from the pH dependent leach test. This observation is consistent with differences in aluminium leaching reported by Carter et al. (2003) from Alcoa residue samples collected from the Point Comfort refinery. It is postulated that aluminium has undergone dissolution from the mineral gibbsite on contact with acetic acid. This has implications on the interpretation of aluminium leaching data for environmental assessments of Alkaloam® when acetic acid is used as an extractant. The pH dependent leach test would be more suitable for by-product re-use scenarios since leaching with acetic acid is not a representative field condition.

5.2.2.2 Correlation of ASLP and pH dependent leach data from Manning Light and Newdegate agricultural sandy soils

Figure 5-8 shows the leach data generated from the ASLP and pH dependent leach testing of Manning Light sandy soil. The two sets of data correlated well for most elements, illustrating again that pH, rather than other method parameters, is the main factor controlling the mobility of constituents.

Exceptions to this were observed for phosphorus and zinc (Figure 5-9) with ASLP concentrations being higher than the pH dependent leaching concentrations. Phosphorus leaching was higher at a final pH of 3.2 (using the pH 2.9 extraction solution) and zinc leaching higher at all three pH values measured. The higher ASLP concentrations for zinc are believed to be due to chelation effects and the formation of soluble zinc-acetate complexes.

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28 Alcoa residue from Point Comfort refinery contains predominantly red mud (Alkaloam®).

29 Acetic acid is appropriate for assessing leaching under putrescible waste conditions as the method was originally designed for.
Figure 5-8: Correlation of ASLP and pH dependent leach test data for Manning Light sandy soil
A comparison of leach data generated from the ASLP and pH dependent leach testing of Newdegate sandy soil did not correlate as well as Manning Light soil, as shown in Figures 5-10 and 5-11. Differences in the leach data suggests that the acetic acid extractant has a stronger influence on leaching in this soil (in addition to pH).
Figure 5-11: Correlation of ASLP and pH dependent leach test data for Newdegate sandy soil

5.2.2.3 Correlation of ASLP and pH dependent leach data from Red Lime™

ASLP and pH dependent leach tests were conducted on Red Lime™. Due to the high buffering capacity of Red Lime™ and lack of pH control using the ASLP methodology, comparisons could only be made in the alkaline pH range 10 to 12.5 (Figure 5-12). This reinforces the limitations associated with using the ASLP for conducting leach testing on high buffering capacity materials, in particular at natural high alkaline pH. Leach data over the limited pH range of pH 10-12.5 correlated well for the two tests, irrespective of leaching concentrations (0.05mg/L to 1000mg/L).
Figure 5-12: Correlation of ASLP and pH dependent leach test data for Red Lime™
5.2.3 Chelation effects from use of acetic acid as an extraction solution

Previous studies have reported that copper, cobalt, nickel, lead and zinc are susceptible to chelation (Jones, 1981) and (Essaku et al., 2003) The leaching concentrations of copper, cobalt and lead in Alkaloam®, Red Lime™ and the sandy agricultural soils were at or below the analytical detection limit, therefore the impact of chelation on these species could not be determined. For nickel and zinc, higher ASLP leaching concentrations were measured in Newdegate and Manning Light sandy soils respectively, indicating that chelation has occurred with the acetic acid extractant (Figure 5-13) in these materials.

Iron and manganese also have the potential to complex with acetic acid (Jones, 1981). ASLP and pH dependent leaching concentrations of these constituents however were similar for Alkaloam® and Manning Light soil, suggesting that acetic acid has not chelated with iron and manganese in these materials. In contrast, ASLP concentrations were higher in Newdegate soil, indicating that acetic acid is in fact increasing the mobility of these elements in this soil (Figure 5-14).

![Figure 5-13: High bias ASLP leaching concentrations due to chelation effects from use of acetic acid extractant](image-url)
Figure 5-14: Leaching of manganese and iron from the WA agricultural soils and Alkaloam® using the ASLP and pH dependent leach tests

In summary, leach data generated from the ASLP and pH dependent leach testing of Alkaloam® and Manning Light sandy soil correlated well for the majority of elements. This suggests that despite differences in the methodology and parameters of the two tests (e.g. the extractant, particle size, L:S ratio etc.), pH is the dominant factor affecting leaching. Using the pH 2.9 extraction solution in the ASLP test liberated higher leaching concentrations for phosphorus from Manning Light soil and for aluminium from Alkaloam®, relative to the pH dependent leach test. This has implications on the interpretation of aluminium and phosphorus leaching data for environmental assessments of Alkaloam® and Manning Light soil when acetic acid is used as an extractant. Differences were observed between the leach data generated from the ASLP and pH dependent leach testing of Newdegate soil for a range of elements, highlighting that the acetic acid extractant has an impact on leaching in this soil.
Using non-chelating extractants in leach tests will minimise reactions between the extraction solution and material and therefore generate leach data that will be more representative of a materials leaching behaviour. For this reason, the pH dependent leach test is likely to generate leach data more representative of field conditions than the ASLP test.

For Alkaloam® and Manning Light soil, the results described above were in agreement with van der Sloot (2002), which reported single extractions using acetic acid (similar to ASLP and TCLP) and other extraction solutions exhibited leaching behaviour dependent on pH and independent of the extraction solution. This is not in agreement for Newdegate soil.

5.2.4 Comparison of ASLP and pH dependent leach testing for assessment of industrial by-products for re-use

The pH dependent leach test has been shown to provide information on changes in leachability of constituents from a material across an extensive pH range (see section 5.2.1). In comparison, the ASLP provides limited leach data, which is susceptible to misinterpretation, particularly for high buffering capacity materials with natural alkaline pH or if the final pH values at the end of the leaching period are not reported. For assessing industrial by-products, such as Alkaloam® and Red Lime™ for re-use, the pH dependent leach test provides more representative leach data than the ASLP test, and hence will provide more confidence in evaluating impacts of a material on a receiving environment.

Conducting the pH dependent leach test on industrial by-products as an input to a detailed environmental assessment will provide insight into whether constituents are likely to be mobile from the by-product at a pH environment representative of a re-use application being considered, and whether mobility of some constituents are likely to increase if the pH environment should change. This is critical for assessing by-product re-use for applications where the environment is susceptible to pH changes, and will allow any foreseeable issues to be assessed in the feasibility assessments.

Using pH dependent leach testing with LeachXS™ geochemical modelling provides information on the mechanisms or sorption processes likely to be controlling leaching in the field, and partitioning of species between the solid and liquid phase at a given pH (see Chapter 7 for details on Alkaloam®, Red Lime™ and the WA agricultural soils). ASLP data is not suitable for such applications due to the limited pH values tested. Therefore a detailed

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30 With the exception of the complexation agent EDTA.
environmental assessment of Alkaloam® and Red Lime™ for re-use applications should use pH dependent leach test data in preference to ASLP data.

As an example, Figure 5-15 shows the aluminium and phosphorus leaching from Alkaloam® using ASLP and pH dependent leach testing. The pH dependent leach test data (blue line) show that Alkaloam® leaches the least amount of aluminium in a pH range of 6.3 to 8. Outside of this range aluminium leaching increases rapidly as the environment becomes more alkaline or acidic. The data also show that approximately one tenth of the total aluminium concentration is unavailable for leaching.

The corresponding ASLP data (red line) also suggest that leaching increases rapidly below pH 6.3, however due to insufficient data generated using the ASLP methodology, the continued immobilisation of aluminium up to pH 8 cannot be determined. Inaccurate interpretation of leach data due to insufficient information from the ASLP test could lead to rejecting an industrial by-product for re-use that may otherwise prove to be a beneficial commodity.

The pH dependent leach test data in Figure 5-15 also illustrate that the amount of phosphorus leaching from Alkaloam® across the pH range of 4.7 to 7.9 is less than the detection limit of the analysis. This suggests that within this pH range the phosphorus is bound in the soil matrix, and therefore is unavailable for leaching. Outside the pH range of 4.7 to 7.9, phosphorus leaching increases. The corresponding ASLP analysis was unable to determine phosphorus leaching in Alkaloam® due to the high analytical detection limit. In light of the good correlation between data from the two leach tests in Alkaloam®, as illustrated in section 5.2.2, it is anticipated that the concentrations would be similar using ASLP, however

Figure 5-15: Assessment of aluminium and phosphorus leaching in Alkaloam® using ASLP and pH dependent leach testing

The pH dependent leach test data in Figure 5-15 also illustrate that the amount of phosphorus leaching from Alkaloam® across the pH range of 4.7 to 7.9 is less than the detection limit of the analysis. This suggests that within this pH range the phosphorus is bound in the soil matrix, and therefore is unavailable for leaching. Outside the pH range of 4.7 to 7.9, phosphorus leaching increases. The corresponding ASLP analysis was unable to determine phosphorus leaching in Alkaloam® due to the high analytical detection limit. In light of the good correlation between data from the two leach tests in Alkaloam®, as illustrated in section 5.2.2, it is anticipated that the concentrations would be similar using ASLP, however

31 By adsorption to reactive iron or aluminium (hydr)oxide sites as described in Chapter 7.
it is recommended that the ASLP test be repeated for analysis of phosphorus using lower detection limits to confirm this.

Figure 5-16 illustrates the ASLP and pH dependent leaching of aluminium and phosphorus from Red Lime™. Due to the high alkalinity and high buffering capacity of Red Lime™, the ASLP test can only measure leaching from this material at a final leaching pH ≥10.

The ASLP is suitable for the original purpose it was designed for, that is assessing materials under scenarios where there is no pH control, such as co-disposal in a putrescible landfill, or where the final leaching pH is irrelevant, such as assessment against environmental regulations with clearly defined ASLP criteria. The ASLP test however will not provide sufficient information to determine any changes in leachability for scenario exposures outside this scope. By comparison, the pH dependent leach test can be pH controlled, and therefore leaching can be assessed across the pH range 0.5 to 12 (Figure 5-16).

5.2.5 Comparison of ASLP and pH dependent leach testing for assessment of Alkaloam® and Red Lime™ as soil ameliorants

The major cause of eutrophic rivers and waterways in the South West of WA, in particular along the Swan Coastal Plain, has been reported to be due to fertiliser phosphorus leaching from infertile sandy soils (Summers et al., 1996a; Birch, 1982). Use of soil ameliorants, such as Alkaloam® and Red Lime™, to improve the phosphorus retention properties of these soils, has been identified as the most significant land management solution for reducing phosphorus leaching, and subsequently reducing eutrophication in the contaminated
rivers. (Summers et al., 1996b; EPA WA, 2008\textsuperscript{32}). Using pH dependent leach testing to assess phosphorus retention benefits from Alkaloam\textsuperscript{®} and/or Red Lime\textsuperscript{TM} amelioration in agricultural sandy soils would prove useful, given the extensive leaching information the test provides. Some examples are illustrated in the following sections.

5.2.5.1 Assessment of Alkaloam\textsuperscript{®} and Red Lime\textsuperscript{TM} amended in a Swan Coastal Plain Soil (Bassendean soil)

Figure 5-17 shows the pH dependent leaching of phosphorus from a Bassendean soil enriched with 1.2g/kg Triple Super Phosphate (TSP) and 0.625g/kg urea, and the corresponding effect of amending the enriched soil with 1.6g/kg Red Lime\textsuperscript{TM} or 6.25g/kg of Alkaloam\textsuperscript{®}. The Bassendean soil was spiked with TSP to elevate the concentration of phosphorus within the soil for investigating changes in phosphorus leaching. Application rates of the ameliorants were calculated to represent an application rate of 2.56t/ha Red Lime\textsuperscript{TM} and 10t/ha Alkaloam\textsuperscript{®} to the top 10cm depth of Bassendean soil. The application rate of Alkaloam\textsuperscript{®} was selected based on previous laboratory and field trials (Summers, 2001), while the Red Lime\textsuperscript{TM} application rate was optimised based on its buffering capacity at the Busselton farm trial site and “district practice” being used at Merredin and Newdegate agricultural farms (Clarendon et al., 2010).

![Figure 5-17: Effect of pH on Phosphorus leaching in a TSP and urea enriched Bassendean soil with and without 6.25g/kg Alkaloam or 1.6g/kg Red Lime amendment](image)

\textsuperscript{32} Alkaloam is termed ‘bauxite residue’ in this literature
The data illustrate that Alkaloam® and Red Lime™ ameliorants retain phosphorus in Bassendean soil at an optimum pH range of 5 to 6. At the amendment rates used (Red Lime™: 1.6g/kg and Alkaloam®: 6.25g/kg), both ameliorants show a similar degree of phosphorus retention. The pH dependent leach data for Alkaloam® suggests phosphorus leaching may increase relative to the unamended soil across the pH range of 7 to 10, however further investigation is recommended to confirm this observation.

LeachXST™ geochemical modelling results predict phosphorus mobility in Alkaloam® and Red Lime™ as being predominantly controlled by adsorption to iron and aluminium hydr(oxide) surfaces at pH<8 (see chapter 7 for more details). An example of this can be seen in Figure 5-18 for the geochemical modelling of phosphorus from Alkaloam® amended Bassendean soil.

![Figure 5-18: Predicted partitioning of phosphorus species bound in the Alkaloam® amended Bassendean soil matrix or free in solution across the pH range 1 – 14](image)

At pH<6 the predicted leaching of phosphorus generated from the geochemical modelling was lower than the actual leach data, indicating that the amount of phosphorus sorbed to the iron/aluminium (hydr)oxide sites in the Alkaloam® matrix is lower than that predicted.

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33 MilliQ water used in leach test therefore pH measurement is based on milliQ water, not CaCl₂.
through the modelling. It is postulated that not all of the iron/aluminium hydr(oxide) sites in the Alkaloam® are active for sorption of the phosphorus ions, which would be assumed in the modelling.

5.2.5.2 Assessment of Alkaloam® and Red Lime™ amended in a WA agricultural sandy soil (Manning Light soil)

Figure 5-19 illustrates the ASLP and pH dependent leaching of magnesium and phosphorus in Manning Light soil with and without 6.25g/kg Alkaloam® amendment. The pH dependent leach data for magnesium indicate that mobility does not change considerably between the amended and unamended soil, across the pH range 0.5 to 12. This suggests that the 6.25g/kg amended rate of Alkaloam® would have little influence on the leaching of magnesium irrespective of the pH conditions in the field. The data also suggest that magnesium is least mobile in the amended soil matrix at a pH range of 7 to 8.

The ASLP data in contrast only predict magnesium leaching within a limited soil pH range of 3.2 to 5.9, and fail to predict the pH environment at which minimum leaching will potentially occur. If the field conditions are outside this pH range or if environmental conditions were to cause a change in soil pH, the ASLP test would not provide sufficient information to allow a valid assessment.

The pH dependent leach data for phosphorus in Figure 5-19 indicate that phosphorus leaching from Manning Light soil could be reduced across a soil pH range of 4.4 to 7.7, if the soil is amended with 6.25g/kg Alkaloam®. Corresponding ASLP data also indicate that a reduction in phosphorus leaching could be achieved in this soil due to Alkaloam® amelioration. However, the pH envelope in which ASLP leaching is measured is restricted
to a soil pH range of 3.2 to 6.3, consequently any phosphorus retention benefits achieved from Alkaloam® amelioration outside this pH environment would have gone undetected.

In light of the investigations discussed above, the pH dependent leach test is considered a far superior leach test to the ASLP for conducting scenario based environmental assessments on industrial by-products, such as Alkaloam® and Red Lime™, for use as soil amendments.

5.3 Conclusions

The ASLP is limited in that it only provides information on the leaching of constituents from a material at three pH values. If industrial by-products are being considered for re-use in applications that are not representative of these pH values, this leach test would be of limited use for input into environmental assessments.

ASLP does not allow leaching to be measured under controlled pH conditions, therefore assessment of leach data using this test can be misinterpreted depending on whether the final pH or initial pH of the leaching solutions are used in the evaluation.

The pH dependent leach test provides information on changes in leachability of constituents from a material across a pH range of 0.5 to 12. The final leaching pH values are controlled and therefore any changes in pH from reactions occurring during the leaching period are accounted for in the test.

ASLP is not suitable for assessing by-products that have a high buffering capacity and natural alkaline pH, such as Alkaloam® and Red Lime™. Since the final pH values are controlled in the pH dependent leach test, this method can assess leaching in high buffering capacity materials.

Acetic acid, the extraction solution used in the ASLP test, is an effective chelating agent that is susceptible to forming soluble or insoluble complexes with cations. Chelation effects occurring in a leach test are not likely to be representative of what would occur under field conditions in a soil matrix. In contrast, the pH dependent leach test uses a non-chelating inorganic acid (nitric acid) as the extractant. Non acid-base reactions between the extraction solution and material are therefore minimised and hence provide a more accurate representation of a materials leaching behaviour.
Conducting the pH dependent leach test on industrial by-products as part of an in depth environmental assessment process would provide insight into whether constituents are likely to be mobile at a pH representative of applications being considered, and whether mobility of constituents are likely to increase if the pH environment should change. This would be valuable information if the by-products were to be used in environments susceptible to pH changes and would allow any foreseeable issues to be considered in feasibility assessments.

Since the final pH values in the ASLP are not controlled and will be specific for each material tested, this prevents direct comparisons of leach data being made between materials. In contrast, direct comparisons of leach data can be made between materials using the pH dependent leach test.

The pH dependent leach test can determine whether the mobility of constituents from a material exhibit “availability controlled” leaching behaviour or solubility controlled leaching behaviour.

pH dependent leach data, with the aid of LeachXST™ geochemical modelling, is capable of predicting the processes controlling leaching of constituents from a material, and determining the speciation partitioned between the solid and liquid phase of the matrix across a defined pH range. A fundamental understanding of the species present in the liquid and solid phase would enable more accurate environmental assessments to be conducted (e.g. determine whether a species is present in a different form and whether this species is bound in the solid phase or in solution).

The pH dependent leach provides more representative fundamental information on leaching than the ASLP and hence more confidence for evaluating the impact of a material on the receiving environment. This test is superior for conducting scenario based environmental assessments on industrial by-products, such as Alkaloam® and Red Lime™ for re-use applications.

Leach data obtained from the ASLP and pH dependent leach test correlated well for most elements in Alkaloam®, Red Lime™ and Manning Light soil, despite differences in method parameters. pH is the dominant factor controlling leaching, and method parameter differences such as particle size, extraction solution and extraction time have less impact on the leaching behaviour in these materials.
Comparison of leach data from the ASLP and pH dependent leach testing of Newdegate soil showed noticeable differences in the concentrations for a range of elements. This highlights that acid-base reactions are occurring between the acetic acid extractant and soil material and is influencing the mobility of species in this soil (in addition to pH).

5.4 Recommendations

It is recommended that the pH dependent leach test be considered as an alternative to ASLP for conducting more accurate environmental assessments on industrial by-products for re-use applications.

Conduct validation tests on the pH dependent leach test alongside ASLP to determine whether this test can be recognised as a standard leach test in Australia.
Chapter 6

CHARACTERISATION OF ALKALOAM AND RED LIME

6.1 Introduction
This chapter reports on some of the physical and chemical properties of Alkaloam®, Red Lime™ and the WA agricultural soils. A suite of analyses were conducted on the materials to determine their full composition, radionuclide content, phosphorus retention capability and natural buffering capacity. The characteristic properties of each material were used to assist in the interpretation of their leach data (as discussed in chapter 7).

The properties of Alkaloam® and Red Lime™ were compared against natural WA soils (Swan Coastal Plain and Darling Range), the WA agricultural soils and some construction materials to contextualise key differences between the materials.

6.2 Composition
6.2.1 Alkaloam® and Red Lime™
Tables 6-1 to 6-3 lists the chemical and mineralogical composition of Alkaloam®, Red Lime™, WA agricultural soils, WA beach sands and a range of construction materials.
<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Alkaloam</th>
<th>Red Lime™</th>
<th>Pinjarra Plain Soil</th>
<th>Bassendean soil</th>
<th>Spearwood Soil</th>
<th>Manning Light</th>
<th>Manning Heavy</th>
<th>Merredin</th>
<th>Naradgellaneous</th>
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<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
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<td>&lt;1</td>
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<td>75</td>
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<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;20</td>
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<td>&lt;20</td>
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<td>15.7</td>
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<td>210</td>
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Blue shaded font indicates the highest concentrations for each element across the range of natural materials.
Table 6-2: Composition of beach sands and construction materials for comparison with Alkaloam® and Red Lime™

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<tr>
<th>Sample Name</th>
<th>Secret Harbour sand Feb 06</th>
<th>Monkey Mia beach sand</th>
<th>Quarry limestone</th>
<th>Blue metal Coyne Road</th>
<th>Road base - Coyne Rd</th>
<th>Road Gravel - Lyons Road</th>
<th>Yellow sand</th>
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<tr>
<td>Natural pH</td>
<td></td>
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<tr>
<td>Fe (%)</td>
<td>0.26</td>
<td>0.44</td>
<td>0.28</td>
<td>5.6</td>
<td>3.83</td>
<td>17.8</td>
<td>0.7</td>
</tr>
<tr>
<td>K (%)</td>
<td>0.58</td>
<td>0.02</td>
<td>0.3</td>
<td>2.99</td>
<td>2.95</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Mg (%)</td>
<td>1.43</td>
<td>0.06</td>
<td>0.52</td>
<td>1.86</td>
<td>1.95</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Na (%)</td>
<td>0.39</td>
<td>0.04</td>
<td>0.13</td>
<td>2.29</td>
<td>1.88</td>
<td>0.13</td>
<td>0.02</td>
</tr>
<tr>
<td>Si (%)</td>
<td>9.02</td>
<td>43.6</td>
<td>18.7</td>
<td>27.3</td>
<td>31.5</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>Ti (%)</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.55</td>
<td>0.4</td>
<td>0.67</td>
<td>0.13</td>
</tr>
<tr>
<td>Ag (mg/kg)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>As (mg/kg)</td>
<td>6</td>
<td>2</td>
<td>8</td>
<td>2</td>
<td>&lt;1</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td>B (mg/kg)</td>
<td>20</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>20</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Ba (mg/kg)</td>
<td>151</td>
<td>10</td>
<td>85</td>
<td>2130</td>
<td>732</td>
<td>54</td>
<td>110</td>
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<tr>
<td>Cd (mg/kg)</td>
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<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Co (mg/kg)</td>
<td>6.9</td>
<td>2.5</td>
<td>6.8</td>
<td>158</td>
<td>61.1</td>
<td>11.5</td>
<td>8.3</td>
</tr>
<tr>
<td>Cr (mg/kg)</td>
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<td>500</td>
<td>200</td>
<td>200</td>
<td>300</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Cu (mg/kg)</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>20</td>
<td>14</td>
<td>5</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Cs (mg/kg)</td>
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<td>50</td>
<td>&lt;50</td>
<td>250</td>
<td>&lt;50</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>Cs (mg/kg)</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.7</td>
<td>2.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Cu (mg/kg)</td>
<td>2</td>
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<td>2</td>
</tr>
<tr>
<td>F (mg/kg)</td>
<td>600</td>
<td>100</td>
<td>300</td>
<td>800</td>
<td>400</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>Ga (mg/kg)</td>
<td>1</td>
<td>1</td>
<td>1.2</td>
<td>20.4</td>
<td>17.6</td>
<td>43.8</td>
<td>2.6</td>
</tr>
<tr>
<td>Hg (mg/kg)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<tr>
<td>La (mg/kg)</td>
<td>3.7</td>
<td>1.2</td>
<td>4</td>
<td>91</td>
<td>35</td>
<td>3.7</td>
<td>3.1</td>
</tr>
<tr>
<td>Li (mg/kg)</td>
<td>2.5</td>
<td>4.5</td>
<td>2.5</td>
<td>13</td>
<td>8</td>
<td>3.5</td>
<td>7</td>
</tr>
<tr>
<td>Mn (mg/kg)</td>
<td>45</td>
<td>26</td>
<td>33</td>
<td>744</td>
<td>437</td>
<td>126</td>
<td>58</td>
</tr>
<tr>
<td>Mo (mg/kg)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>1</td>
<td>1</td>
<td>5.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Ni (mg/kg)</td>
<td>4</td>
<td>6</td>
<td>&lt;1</td>
<td>41</td>
<td>20</td>
<td>32</td>
<td>9</td>
</tr>
<tr>
<td>Pb (mg/kg)</td>
<td>340</td>
<td>20</td>
<td>220</td>
<td>1160</td>
<td>420</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>Pb (mg/kg)</td>
<td>5</td>
<td>10</td>
<td>4</td>
<td>21</td>
<td>34</td>
<td>18</td>
<td>7</td>
</tr>
<tr>
<td>Rb (mg/kg)</td>
<td>16.8</td>
<td>1</td>
<td>10.4</td>
<td>93.4</td>
<td>147</td>
<td>10.2</td>
<td>14</td>
</tr>
<tr>
<td>S (mg/kg)</td>
<td>1720</td>
<td>120</td>
<td>500</td>
<td>1340</td>
<td>260</td>
<td>500</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Sb (mg/kg)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Sc (mg/kg)</td>
<td>0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>15</td>
<td>11.5</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>Se (mg/kg)</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Sn (mg/kg)</td>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>2</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Sr (mg/kg)</td>
<td>1980</td>
<td>184</td>
<td>977</td>
<td>367</td>
<td>139</td>
<td>22.5</td>
<td>11</td>
</tr>
<tr>
<td>Th (mg/kg)</td>
<td>0.8</td>
<td>0.3</td>
<td>0.6</td>
<td>24.2</td>
<td>21</td>
<td>72.5</td>
<td>1.1</td>
</tr>
<tr>
<td>U (mg/kg)</td>
<td>1.1</td>
<td>0.4</td>
<td>0.8</td>
<td>3.2</td>
<td>7.4</td>
<td>7.5</td>
<td>0.4</td>
</tr>
<tr>
<td>V (mg/kg)</td>
<td>8</td>
<td>8</td>
<td>26</td>
<td>146</td>
<td>104</td>
<td>1130</td>
<td>12</td>
</tr>
<tr>
<td>Zn (mg/kg)</td>
<td>7</td>
<td>9</td>
<td>1</td>
<td>68</td>
<td>54</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>Zr (mg/kg)</td>
<td>50</td>
<td>90</td>
<td>70</td>
<td>220</td>
<td>130</td>
<td>500</td>
<td>150</td>
</tr>
</tbody>
</table>

Blue shaded font indicates the highest concentrations for each element across the range of natural materials.
Alkaloam® is rich in iron and aluminium (~21% and ~10% respectively), and contains approximately 10% quartz. The (hydr)oxides of aluminium and iron present in Alkaloam® are known to adsorb phosphorus and are the source of the high phosphorus retention properties exhibited for this material (section 6.4). This has made Alkaloam® attractive as a potential soil ameliorant for poor nutrient retaining sandy soils in WA (Summers, 2001; Ward and Summers, 1993).

XRD analysis of Alkaloam® (Table 6-3) indicates that the aluminium is present in the mineral form of gibbsite, and iron in the mineral forms of hematite and goethite. Alkaloam® contains similar amounts of calcium to the Pinjarra Plain and Bassendean soils of the Swan Coastal Plain, and is in the form of calcite. The sodium content in Alkaloam® is high comparative to the other materials, which originates from entrained caustic used in the alumina refining process.
Heavy metals, such as arsenic, gallium, chromium, copper, lead, manganese, strontium, uranium and vanadium were measured in the natural WA soils and typical construction materials. The majority of these metals were also measured in Alkaloam®, with concentrations comparable or lower to the natural background levels measured in the Darling Range soils and the construction materials (in particular blue metal, road base and road gravel) (Table 6-1 and 6-2).

Concentrations of arsenic and manganese analysed in the Darling Range soils were measured at three times and twenty six times the concentrations measured in Alkaloam® respectively. The concentration of total chromium in Bassendean soil was also elevated by comparison, with a concentration of 450ppm compared to Alkaloam® at 200ppm, consistent with that reported by Wendling et al. (2008). Uranium, strontium and phosphorus concentrations in Alkaloam® were comparable with the Darling Range soil, Bassendean soil and Manning Heavy soil respectively, and sulphur levels were in the same order of magnitude as beach sand. Trace metals analysed in Alkaloam®, such as barium, cadmium and cobalt were also lower or similar in concentration to blue metal. Analysis of typical construction materials used in WA indicated that the vanadium concentration in road gravel is approximately two times the concentration analysed in Alkaloam®, the barium concentration in blue metal is one order of magnitude higher than in Alkaloam® and fluorine levels were similar to blue metal.

The concentrations of arsenic and sulphur/sulphate in Alkaloam® are sufficiently elevated to trigger the Ecological Investigation Levels (EILs) of the DEC Contaminated Sites guidelines (DEC, 2010). However, due to the naturally high metal concentrations in the WA soils and some construction materials (i.e. blue metal and road base), these materials would also exceed the guidelines (Table 6-4). Context with natural materials is required if industrial by-products, such as Alkaloam®, are to be environmentally assessed for re-use applications. An assessment of WA soils amended with 20t/ha Alkaloam® indicates that the concentration of all elements are well below the EIL trigger values (URS Australia, 2009).
Table 6-4: Assessment of Alkaloam®, Red Lime™, WA soils and construction materials against the EILs of the DEC Contaminated Sites guidelines 2010

<table>
<thead>
<tr>
<th>Metal/Metalloid</th>
<th>Ecological Investigation Levels (EIL)</th>
<th>Soil Amendments</th>
<th>Agricultural land used for Lime Field Trials</th>
<th>Swan Coastal Plain Soils</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Red Lime</td>
<td>Alkaloam</td>
<td>Manning Light</td>
</tr>
<tr>
<td>Antimony</td>
<td>20</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Arsenic</td>
<td>20</td>
<td>12</td>
<td>12</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Barium</td>
<td>300</td>
<td>52</td>
<td>218</td>
<td>85</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Chromium III</td>
<td>400</td>
<td>&lt;50</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Chromium VI</td>
<td>1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Cobalt</td>
<td>50</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Copper</td>
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<td>18</td>
<td>3</td>
</tr>
<tr>
<td>Lead</td>
<td>600</td>
<td>29</td>
<td>28</td>
<td>31</td>
</tr>
<tr>
<td>Manganese</td>
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<td>155</td>
<td>129</td>
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<td>Mercury</td>
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<td>0.03</td>
<td>0.04</td>
<td>0.01</td>
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<tr>
<td>Molybdenium</td>
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<td>5</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>Nickel</td>
<td>50</td>
<td>6</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Tin</td>
<td>50</td>
<td>16</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>Vanadium</td>
<td>50</td>
<td>1120</td>
<td>850</td>
<td>32</td>
</tr>
<tr>
<td>Zinc</td>
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<td>21</td>
<td>28</td>
<td>21</td>
</tr>
<tr>
<td>Sulphur</td>
<td>600</td>
<td>1400</td>
<td>1660</td>
<td>220</td>
</tr>
<tr>
<td>Sulphate</td>
<td>2000</td>
<td>4260</td>
<td>5360</td>
<td>860</td>
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</table>

<table>
<thead>
<tr>
<th>Metal/Metalloid</th>
<th>Ecological Investigation Levels (EIL)</th>
<th>Darling Range Soils</th>
<th>Beach Sand</th>
<th>construction materials</th>
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<td></td>
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<td>Fine fraction</td>
<td>Intermediate Fraction</td>
<td>Coarse Fraction</td>
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<td>&lt;0.2</td>
<td>&lt;0.5</td>
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<tr>
<td>Arsenic</td>
<td>20</td>
<td>12</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>Barium</td>
<td>300</td>
<td>52</td>
<td>218</td>
<td>85</td>
</tr>
<tr>
<td>Cadmium</td>
<td>3</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Chromium III</td>
<td>400</td>
<td>300</td>
<td>300</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Chromium VI</td>
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<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Cobalt</td>
<td>50</td>
<td>20</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Copper</td>
<td>100</td>
<td>16</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>Lead</td>
<td>600</td>
<td>32</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Manganese</td>
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<td>4260</td>
<td>4260</td>
<td>4610</td>
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<td>NA</td>
<td>NA</td>
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<tr>
<td>Molybdenium</td>
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<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Nickel</td>
<td>50</td>
<td>15</td>
<td>15</td>
<td>15</td>
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<tr>
<td>Tin</td>
<td>50</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Vanadium</td>
<td>30</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Zinc</td>
<td>200</td>
<td>52</td>
<td>52</td>
<td>52</td>
</tr>
<tr>
<td>Sulphur</td>
<td>600</td>
<td>100</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>Sulphate</td>
<td>2000</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
</tbody>
</table>

NA = Not analysed. *Sb2O3 expressed as Sb Total Chromium values reported against Chromium III
Red Lime™ is predominantly composed of calcium minerals in the form of calcite, hydrotalcite, tricalciumaluminate monocarbonate and tricalcium aluminate (TCA6) (Table 6-3). Red Lime™ exhibits high buffering capacity due to the high calcium content (section 6.5) and high phosphorus retention capabilities (section 6.4). These properties make Red Lime™ an attractive alternative to conventional liming materials in agricultural practices, and as a soil ameliorant for improving phosphorus retention in WA sandy soils (Clarendon et al., 2010).

The compositional analysis of Red Lime™ shows elevated concentrations of fluorine and selenium relative to the natural soils and construction materials (Table 6-1 and 6-2). Other metals with elevated concentrations in Red Lime™, such as arsenic, phosphorus, sulphur, strontium and vanadium were comparable to concentrations measured in some construction materials, beach sand and the Darling Range soils. Phosphorus is also present in Red Lime™, which is incorporated during the lime causticisation stage of the alumina refining process.

The concentrations of arsenic, vanadium and sulphur/sulphate in Red Lime™ are sufficiently elevated to trigger the EILs (Table 6-4). In comparison, the concentrations of these metals in the natural Darling Range soils and beach sand are also elevated to trigger the EILs. The concentration of analytes in the WA soils when amended with 1.6g/kg of Red Lime™ were calculated based on the effective contribution from the Red Lime™ and the concentration already present in the soil. Assessment of these concentrations against the EILs indicates that analytes are well below the EIL trigger values in these soils using a 1.6g/kg Red Lime™ amelioration rate (Table 6-5).
Table 6-5: Assessment of WA soils amended with 1.6g/kg Red Lime™ against the EILs of the DEC Contaminated Sites guidelines 2010

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Ecological Investigation Levels (EIL) (mg/kg)</th>
<th>Calculated total concentration of analyte in Newdegate soil amended with 1.6g/kg Red Lime™ (mg/kg)</th>
<th>Calculated total concentration of analyte in Merredin soil amended with 1.6g/kg Red Lime™ (mg/kg)</th>
<th>Calculated total concentration of analyte in Manning Light soil amended with 1.6g/kg Red Lime™ (mg/kg)</th>
<th>Calculated total concentration of analyte in Manning Heavy soil amended with 1.6g/kg Red Lime™ (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>20</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Arsenic</td>
<td>20</td>
<td>2.3</td>
<td>2.3</td>
<td>&lt;1</td>
<td>3.3</td>
</tr>
<tr>
<td>Barium</td>
<td>300</td>
<td>36.1</td>
<td>22.1</td>
<td>85.1</td>
<td>100.1</td>
</tr>
<tr>
<td>Cadmium</td>
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<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>Chromium III</td>
<td>400</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>Chromium VI</td>
<td>1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Cobalt</td>
<td>50</td>
<td>10.0</td>
<td>5.0</td>
<td>&lt;2</td>
<td>2.0</td>
</tr>
<tr>
<td>Copper</td>
<td>100</td>
<td>10.0</td>
<td>14.0</td>
<td>3.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Lead</td>
<td>600</td>
<td>6.0</td>
<td>7.0</td>
<td>31.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Manganese</td>
<td>500</td>
<td>38.0</td>
<td>38.0</td>
<td>139.0</td>
<td>185.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>1</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>40</td>
<td>1.0</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>60</td>
<td>20.0</td>
<td>14.0</td>
<td>9.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Tin</td>
<td>50</td>
<td>1.0</td>
<td>1.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Vanadium</td>
<td>50</td>
<td>5.1</td>
<td>4.1</td>
<td>34.1</td>
<td>60.1</td>
</tr>
<tr>
<td>Zinc</td>
<td>200</td>
<td>8.0</td>
<td>6.0</td>
<td>21.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td>600</td>
<td>52.3</td>
<td>102.3</td>
<td>222.3</td>
<td>422.3</td>
</tr>
<tr>
<td>Sulphate</td>
<td>2000</td>
<td>156.8</td>
<td>306.8</td>
<td>666.8</td>
<td>1266.8</td>
</tr>
</tbody>
</table>

NA = not analysed
6.2.2 Swan Coastal Plain soils and WA agricultural soils

The Swan Coastal Plain soils vary in pH across a range of 6.8 to 8.4\textsuperscript{34}, with Spearwood soil the most acidic (pH 6.85) and Bassendean soil the least acidic (pH 8.43). Bassendean and Spearwood soils contain approximately 40% silica, indicative of high quartz content in these soils. Pinjarra Plain soil contains the highest levels of aluminium and iron (5% and 3.5% respectively), present in the mineral forms of gibbsite and haematite. The high aluminium and iron levels in this soil are indicative of the high phosphorus retention properties in comparison to the other soils of the Swan Coastal Plain. Conversely, the Bassendean soil contains significantly lower concentrations of aluminium and iron (approximately 1.2% and 0.7% respectively), resulting in poor phosphorus retention properties that typically characterise this soil (section 6.4).

The Swan Coastal Plain soils contain naturally high ambient levels of chromium, with Bassendean soil containing the highest concentration at 450ppm. Bassendean and Pinjarra Plain soils showed similar amounts of calcium (approximately 2.7% and 2.9% respectively), providing some buffering capacity to these soils (Allen et al., 2009). Spearwood soil contains very low calcium concentration (0.23%), which is reflected in the low acid neutralisation capacity (ANC) of this soil (see section 6.5).

The WA agricultural soils are moderately acidic with Manning Heavy (clay) and Manning Light (sandy) soils measuring the lowest pH at 5.2 and 5.9 respectively. The soils are composed predominantly of quartz (40-50%) at similar levels to those in the Swan Coastal Plain soils.

Chlorine levels were elevated in both Manning Heavy and Manning Light soils relative to Alkaloam®, Red Lime™ and the Swan Coastal Plain soils. The trace metal concentrations analysed in the agricultural Newdegate and Merredin soils were very low, suggesting that these soils contained very little nutrient value at the time they were sampled.

The phosphorus concentration in Manning Heavy soil was noticeably high relative to the other agricultural soils and Swan Coastal Plain soils. This is indicative of the high phosphorus retention capacity of the soil that would be typically expected in clay type materials (see section 6.4).

\textsuperscript{34} pH measured in water.
6.3 Radionuclides

Alkaloam®, like many other construction materials, such as concrete, cement, natural building stone, limestone and gravel contain radionuclides (Cooper, 2005; Baxter, 1993).

The Darling Range contains naturally occurring radionuclides, uranium and thorium, in the activity range of 0.022 to 0.110 Bq/g for U$^{238}$ and 0.053 to 0.5Bq/g for Th$^{232}$ (Alach et al, 1996). Background radiation in the Darling Range is due to a number of factors from altitude to granite formations. Bauxite deposits sourced from the Darling Range, used for the extraction of alumina, will similarly contain these elements, as does gravel and granite (Baxter, 1993). Since Alkaloam® is the fine fraction of bauxite residue remaining after alumina has been extracted; it too will contain these elements commonly found in the Darling Range.

The radionuclide activity for uranium, thorium and potassium, present in the bauxite residue products, Alkaloam®, Red Lime™ and Red Sand$^{35}$, was calculated and compared to that of the natural soil sampled from the Darling Range. The activities were calculated based on the total concentration of the radionuclides analysed in each material (Table 6-6).

<table>
<thead>
<tr>
<th>Material</th>
<th>U (Bq/g)</th>
<th>Th (Bq/g)</th>
<th>K (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Lime</td>
<td>0.08</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Alkaloam</td>
<td>0.19</td>
<td>1.11</td>
<td>0.10</td>
</tr>
<tr>
<td>Darling Range Soil</td>
<td>0.19</td>
<td>0.78</td>
<td>0.01</td>
</tr>
<tr>
<td>Wagerup washed carbonated Red Sand™</td>
<td>0.12</td>
<td>0.56</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The data in Table 6-6 show that the specific radionuclide activity of uranium in Alkaloam® is comparable to that of the Darling Range soil. The thorium and potassium activity by comparison is higher. The remaining bauxite residue products, Red Lime™ and Red Sand™, contain lower uranium and thorium activity than the Darling Range soil. The radionuclide activity of potassium is slightly higher in Red Lime™ relative to the Darling Range soil.

$^{35}$ The remaining course fraction of bauxite residue.
The calculated specific activities for each radionuclide were consistent with values reported for red mud in studies by Cooper (2005) and Cooper et al. (1995), which concluded that there was no significant increase in radionuclide levels in vegetable crops grown in the Swan Coastal Plain sands in the application range of 0 to 480t/ha. The specific activities are also consistent with those reported in URS (2009), which concluded that application rates of 20t/ha Alkaloam® would result in above background dose rates much less than the public incremental γ dose limit of 1mSv/yr. An amendment rate of 1500t/ha Alkaloam® would need to be applied for the 1mSv/yr incremental γ dose exposure for the general public to be reached for 100% occupancy (Summers et al., 1993b). Since the optimum amendment rate of Alkaloam® is 20t/ha, application rates up to 1500t/ha are unrealistic and will not be typically used in the field.

Radionuclide activity reported in Alach et al (1996) for the Darling Range is slightly lower than levels calculated in this investigation. This may be attributed to differences in the techniques used to measure the radionuclide activity.

### 6.4 Phosphorus Retention Properties

A soil’s capacity to adsorb phosphorus can be measured in terms of its Phosphorus Retention Index (PRI). The PRI of surface soils can vary depending on the extent of leaching of calcium carbonate, the amount of organic matter in the soil and the phosphate fertiliser history (Allen et al., 2001). Aluminium and iron, particularly in the hydr(oxide) form, are also known to adsorb phosphorus and will also influence soil phosphorous retention capacity.

Table 6-7 shows the PRI for Alkaloam® and Red Lime™ at natural pH. Both materials exhibit elevated PRI; Red Lime due to the high calcium carbonate (calcite) and aluminium content, and Alkaloam® due to the high iron and aluminium content.

<table>
<thead>
<tr>
<th>Material</th>
<th>PRI (mL/g)</th>
<th>Natural pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaloam</td>
<td>56</td>
<td>10.6</td>
</tr>
<tr>
<td>Red Lime</td>
<td>&gt;1000</td>
<td>12.4</td>
</tr>
</tbody>
</table>

A direct comparison of the PRI for Alkaloam® and Red Lime™ initially suggests that Red Lime™ has a higher capacity to adsorb phosphorus than Alkaloam®. However, pH
differences can significantly influence phosphorus leaching and subsequently phosphorus retention. PRI is typically measured at a soil's natural pH, therefore if the maximum phosphorus retention for a soil does not occur at its natural pH, then the phosphorus retention properties of a material measured in the laboratory could be lower than that potentially observed in the field.

To demonstrate the effect of pH on phosphorus retention, a pH dependent leach test was conducted on Alkaloam® and Red Lime™ to illustrate the phosphorus leaching profile of these materials over a pH range of 0.5 to 12 (Figure 6-1).

![Graph showing pH dependent emission of phosphorus from Alkaloam® and Red Lime™](image)

* denotes natural pH on the charts

**Figure 6-1**: pH dependent leaching of Alkaloam® and Red Lime™ across a pH range 0.5 to 12

The data show that the minimum leaching of phosphorus (i.e. maximum phosphorus retention) for Alkaloam® occurs in the approximate pH range of 4.5 to 8, and at pH>8 for Red Lime™. This suggests that the maximum PRI values for Alkaloam® and Red Lime™ should be measured at these pHs respectively. Since their natural pH is highly alkaline (pH 10.6 for Alkaloam® and pH 12.8 for Red Lime™) the PRI reported in Table 6-7 is the maximum for Red Lime™, but could be higher for Alkaloam® if it were measured at a lower pH. This is supported by Barrow (1982), who reported that phosphorus adsorption in red mud can be affected by modifying pH.\(^{36}\) It is therefore important that the pH of any PRI measurement be reported.

Further investigations into assessing PRI of materials at different pH is recommended to determine how PRI relates to the phosphorus retention capacity of the material and whether PRI can be used to estimate capacity.

\(^{36}\) Maximum Phosphorus adsorption of red mud in Barrow (1982) was reported at pH6.8.
PRIs for the Swan Coastal Plain soils and WA agricultural soils are reported in Table 6-8. Subsequent changes in their PRI following amendment with Alkaloam® and Red Lime™ at application rates typically representative of what would be used in the field are also reported.

Table 6-8: Changes in PRI measured for the Swan Coastal Plain soils and WA agricultural soils when amended with Alkaloam® or Red Lime™

<table>
<thead>
<tr>
<th>Material</th>
<th>PRI (mL/g)</th>
<th>PRI (mL/g)</th>
<th>final pH of solution</th>
<th>PRI (mL/g)</th>
<th>PRI (mL/g)</th>
<th>final pH of solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pj Plain soil</td>
<td>79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bassendean</td>
<td>3</td>
<td>4.1</td>
<td>8.2</td>
<td>4.4</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>Spearwood</td>
<td>8.1</td>
<td>9.2</td>
<td>6.9</td>
<td>12</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>Manning Light (sandy)</td>
<td>4.9</td>
<td>10</td>
<td>5.7</td>
<td>7.8</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>Manning Heavy (clay)</td>
<td>110</td>
<td>98</td>
<td>5.3</td>
<td>230</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Merredin</td>
<td>5.0</td>
<td>6.3</td>
<td>7.2</td>
<td>6.2</td>
<td>7.34</td>
<td></td>
</tr>
<tr>
<td>Newdegate</td>
<td>4.3</td>
<td>6.8</td>
<td>7.42</td>
<td>6</td>
<td>7.66</td>
<td></td>
</tr>
</tbody>
</table>

(<2mL/g = poor P adsorption; 2-20mL/g = moderate P adsorption, >20 strongly adsorbing phosphorus)

The lowest PRIs were measured in the three sandiest soils, namely Bassendean soil, Manning Light and Newdegate soil. Of these soils, Bassendean soil measured the lowest PRI, confirming its very poor phosphorus retention properties. These soils are infertile, containing low iron and aluminium hydr(oxide) minerals, carbonate minerals and organic content that would otherwise retain phosphorus. Excessive use of highly soluble phosphorus fertilisers on the Bassendean soils, predominantly located in the Peel Harvey Catchment and Swan coastal plain, have been identified as the main cause for the eutrophication and poor water quality observed in the Peel inlet and Harvey estuarine systems (Ritchie et al., 1993).

Now fast becoming a significant environmental concern, the state and federal governments have initiated a Peel Harvey Catchment Water Quality Improvement Plan (WQIP) to reduce phosphorus loading to the catchment by 50% relative to current levels (EPA WA, 2008)³⁷. Whilst implementation of low solubility phosphorus fertilisers is anticipated to reduce loadings by 10%, a significant reduction is believed to be achievable using soil amendments with high phosphorus retention capacities, such Alkaloam®.

³⁷ EPA target to reduce phosphorus loadings from current 140tP/Ha to 75tP/Ha.
Data in Table 6-8 indicate that amending the WA soils with Alkaloam® at a soil amendment rate of 6.25g/kg (equivalent to 10t/ha field rate) increased the PRI in the sandy soils but not in the Manning Heavy clay soil. Manning Light sandy soil showed the greatest increase in PRI when amended with Alkaloam®, and will gain the most benefit if Alkaloam® soil amelioration is used.

Bassendean sand amended with Alkaloam® was expected to show a greater increase in PRI relative to the unamended soil than was measured, since this soil exhibits a lower PRI than Manning Light soil (Table 6-8). Figure 6-2 illustrates the pH dependent leaching of phosphorus from Bassendean soil with and without 6.25g/kg Alkaloam® amendment. The data indicate that Alkaloam® amendment increases phosphorus retention (decrease phosphorus leaching) in this soil at an optimum soil pH of approximately 3.6 to 6. Since the natural pH of the Alkaloam® amended soil is outside this optimum pH range (i.e. pH 8.2) the PRI gain from amelioration will not be significant. To gain maximum phosphorus retention benefit in this sandy soil, sufficient Alkaloam® amendment would need to be applied to reduce the pH of the amended soil into the range of pH 3.6 to 6.

This illustration suggests that greater phosphorus retention benefits from Alkaloam® amendment are likely to occur in agricultural areas where sandy soils are more acidic from fertiliser use.

![Figure 6-2: pH dependent leaching of phosphorus from Bassendean sand with and without 6.25g/kg Alkaloam® amendment](image-url)
A decrease in PRI was measured for Manning Heavy clay soil when amended with Alkaloam®. The soil’s high PRI value suggests that the material already exhibits high phosphorus retention capabilities that would negate any additional effect from amendment with Alkaloam®. Soils with a PRI of >20mL/g are considered to have strongly adsorbing phosphorus capabilities (Allen et al., 2001) and rarely respond to phosphorus fertiliser applications. High PRI soils therefore are not likely to benefit from the use of Alkaloam® soil amendment. These would include clay-type soils and soils containing naturally high levels of iron or aluminium oxide minerals.

The Pinjarra Plain soil in the Swan Coastal Plain is naturally high in iron (Table 6-1), reflecting a very high PRI for a WA sandy soil. Whilst the PRI of this soil was not measured when amended with Alkaloam® or Red Lime™, it is postulated that the soil’s PRI, and its phosphorus retention properties, would not improve with Alkaloam® amelioration. Alkaloam® amendment is also not likely to provide any benefit from increasing soil pH to increase nutrient availability (liming) since the natural pH of this soil is already near neutral.

With the exception of Merredin and Newdegate soils, there was no measurable change in the pH of the soils when amended with 6.25g/kg Alkaloam®. This was consistent with observations reported in the liming and soil amendment field trials (Clarendon et al., 2010). This suggests that for acidic soils to benefit from liming practices using Alkaloam® amelioration, much higher application rates are required to increase the pH of the soil.

PRI data reported in Table 6-8 suggest that using 1.6g/kg Red Lime™ amendment could improve the PRI of naturally high phosphorus retaining soils, such as Manning Heavy soil and moderately high phosphorus retaining soils, such as Pinjarra Plain soil. PRI improvements from sandy soils amended with Red Lime™ are likely to exhibit similar or slightly less benefits in phosphorus retention than using Alkaloam®.

6.5 Acid Neutralisation Capacity (ANC)/Buffering Capacity
The acid/base neutralisation curves for Alkaloam® and Red Lime™ are illustrated in Figure 6-3. Data from these curves were used to determine the buffering capacity of the materials. The acid buffering capacity is a measurement of how much resistance a material has to changes in pH on addition of acid.
Both materials are believed to exhibit good buffering capacity due to calcium (in the form of calcite and tricalcium aluminate) and sodalite present in the materials (Snars and Gilkes, 2010). The acid neutralisation curves illustrate that to reduce the pH of Alkaloam® from pH 8 to 5 requires 1.91 molH⁺/kg. In contrast, Red Lime™ requires 7.94 molH⁺/kg, which illustrates that Red Lime™ has a higher buffering capacity of the two by-products.

The buffering capacity of Alkaloam®/Red Mud has been reported to be different based on the different bauxite deposits and refinery processes used. However similar buffering capacities have been observed where the same bauxite deposits and similar refinery processes are used, for example; from the three Alcoa refineries Kwinana, Pinjarra and Wagerup (Snars and Gilkes, 2010).

The buffering capacity of the WA soils was also determined using the acid/base neutralisation capacity curve generated from the pH dependent leach test for each soil material. Table 6-9 shows the amount of acid required to acidify the Swan Coastal Plain soils and WA agricultural soils from pH 8 to pH 5, and the amount required to make the same change in pH after amending the soils with 6.25g/kg Alkaloam® and 1.6g/kg Red Lime™.
Table 6-9: Buffering capacity of the Swan Coastal Plain soils and WA agricultural soils and changes due to soil amelioration with 6.25g/kg Alkaloam® and 1.6g/kg Red Lime™

<table>
<thead>
<tr>
<th>Soil</th>
<th>Soil amended with 6.25g/kg Alkaloam®</th>
<th>Soil amended with 1.6g/kg Red Lime™</th>
<th>Increase in soil's buffering capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinjarra plain soil</td>
<td>1.345</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spearwood soil</td>
<td>0.072 0.126 0.101 0.750 0.403</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bassendean soil</td>
<td>0.8 1.244 1.494 0.555 0.868</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manning Heavy soil</td>
<td>0.072 0.13 0.103 0.806 0.431</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manning Light soil</td>
<td>0.018 0.101 0.069 4.611 2.833</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Merredin</td>
<td>0.057 0.115 0.06 1.018 0.053</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Newdegate</td>
<td>0.041 0.031 0.037 -0.244 -0.098</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The WA agricultural soils measured lower buffering capacity than the Swan Coastal Plain soils. Of the agricultural soils analysed, Manning Light sandy soil exhibited the lowest buffering capacity, with only 0.018mol/kg acid required to acidify the soil from pH 8 to pH 5. Manning Heavy clay soil exhibited the highest buffering capacity, with 0.072mol/kg acid required to acidify the soil down three pH units. The buffering capacity of Manning Heavy soil was comparable with Spearwood soil of the Swan Coastal Plain.

Agricultural soils with low buffering capacity present significant environmental issues in that their pH is susceptible to change with seasonal variation and soil weathering. As the soil pH becomes more acidic or alkaline, some species in the soil, in particular phosphorus, can become more mobile, transporting into nearby waterways via run-off or through leaching into groundwater. Improving a soils buffering capacity can therefore assist in stabilising species in the soil and reducing negative impacts to the surrounding environment.

With the exception of Newdegate soil, amending the WA agricultural soils with Alkaloam® and Red Lime™ at application rates of 6.25g/kg and 1.6g/kg respectively improved the buffering capacity of the soils by a factor of 0.8 to 4.6 (Alkaloam®) and 0.1 to 2.8 (Red Lime™). Although Red Lime™ has higher buffering capacity than Alkaloam®, the data in Table 6-9 suggests that an ameliorant rate of 1.6g/kg Red Lime™ does not increase a soil’s buffering capacity as much as an ameliorant rate of 6.25g/kg Alkaloam®. A higher optimum amendment rate of 2.5g/kg (equivalent to 4t/ha) Red Lime™ is expected to increase a soils buffering capacity similar to or slightly higher than using an amendment rate of 6.25g/kg Alkaloam®.

No change in the PRI of Newdegate soil was observed when amended with Alkaloam® or Red Lime™. The composition of this soil (Table 6-1) indicates very low calcium concentrations, the predominant species that provides buffering capacity in a soil. It is
believed that higher soil amendment rates would be required to increase the calcium content in this soil to a level where increased buffering capacity could be measured.

6.6 Conclusions

Alkaloam®, like many other construction materials, such as concrete, cement, natural building stone, limestone and gravel contain natural radionuclides.

The total concentration of uranium and its specific radionuclide activity in Alkaloam® is comparable to that of the Darling Range soil. The remaining bauxite residue products, Red Lime™ and Red Sand™ contain lower uranium and thorium activity than the Darling Range soil. The specific radionuclide activities for Alkaloam® are consistent with those reported in other literature.

Naturally high metal concentrations measured in WA soils and construction materials, such as blue metal and road base, are elevated enough to trigger the Ecological Investigation levels (EILs) of the DEC Contaminated Sites guidelines (DEC, 2010). Alkaloam® and Red Lime™ also trigger these guidelines. Further assessment of Alkaloam® and Red Lime™ as soil amendments, at top dressed application rates of 10t/ha to 20t/ha (Alkaloam®) and 2.56t/ha (Red Lime™) used in liming trials, are well below the EIL trigger values.

Of the WA Swan Coastal Plain soils, Pinjarra plain soil exhibited the highest PRI and Bassendean soil the lowest PRI. This is related to the levels of aluminium and iron present in these soils (Pinjarra Plain containing highest levels and Bassendean containing lowest levels).

Leaching of phosphorus from granular materials is influenced by pH. PRI is typically measured at natural pH. Unless a material exhibits maximum phosphorus retention capability at its natural pH, the maximum PRI may not be measured. Making comparison of by-products based on PRI to determine their suitability as soil amendments therefore may lead to misinterpretation.

Of the WA soils investigated for this thesis, the lowest PRIs were measured in the three sandiest soils, namely Bassendean soil, Manning Light and Newdegate soil. PRIs for all the WA sandy soils improved when amended with 6.25g/kg Alkaloam®. Manning Light sandy soil showed the greatest increase in PRI when amended with Alkaloam®, and therefore is likely to gain the most benefit in the field if broad scale Alkaloam® soil amelioration is used. The more acidic the pH of the sandy soil the greater the improvement in PRI was
observed from Alkaloam® amendment. In light of this observation, it is proposed that in agricultural areas where sandy soils are likely to be most acidic from fertiliser use, the greater phosphorus retention benefits from Alkaloam® amendment are likely to occur.

Amending WA sandy soils with 1.6g/kg Red Lime™ showed similar or slightly less PRI improvements than using 6.25g/kg Alkaloam® in the sandy soils.

Alkaloam® did not increase the PRI of soils that already exhibiting naturally high PRI, such as Manning Heavy clay soil. In light of this observation, it is anticipated that Alkaloam® will also be ineffective at increasing the PRI of Pinjarra Plain soil. The PRI of these types of soils however were improved when amended with Red Lime™.

The WA agricultural soils measured lower buffering capacity than the Swan Coastal Plain soils. Manning Light sandy soil exhibited the lowest buffering capacity and Manning Heavy clay soil the highest buffering capacity. The buffering capacity of Manning Heavy soil was comparable to Spearwood soil from the Swan Coastal Plain.

Red Lime™ has a higher buffering capacity than Alkaloam® due to the higher calcite content in the material.

Amending the WA agricultural soils with 6.25g/kg Alkaloam® and 1.6g/kg Red Lime™ improved the buffering capacity of the soils by a factor of 0.8 to 4.6 (Alkaloam®) and 0.1 to 2.8 (Red Lime™). A higher amendment rate of 2.5g/kg Red Lime™ is expected to improve the buffering capacity of the WA soils similar to or slightly higher than that observed using 6.25g/kg Alkaloam®.

No change in the PRI of Newdegate soil was observed when amended with Alkaloam® or Red Lime™ at application rates of 1.6g/kg Red Lime™ or 2.56g/kg Alkaloam®. It is anticipated that higher amendment rates would be required to increase the calcium content in this soil to measure an increase in the soils buffering capacity.

### 6.7 Recommendations

Phosphorus retention is influenced by pH; therefore it is recommended that the pH of the solution be reported for PRI measurements.
Further investigations into assessing PRI of materials at different pH are also recommended to determine how phosphorus retention properties relate to the pH of the material and whether PRI can be used to estimate capacity.
Chapter 7

pH DEPENDENT LEACHING OF ALKALOAM®
RED LIME™ AND WA SOILS

7.1 Introduction
This chapter discusses the pH dependent leaching of a range of species from Alkaloam®, Red Lime™ and the WA soils across a pH range of 0.5 to 12. Geochemical modelling using LeachXS™ has been applied to the pH dependent leach data to predict speciation and the mechanisms controlling leachability. The partitioning of free ions and complexed metal species in solution, as well as partitioning of elements in the solid phase and liquid phase, are also predicted.

LeachXS™ geochemical modelling was used to fit up to 24 elements simultaneously and assumed all sites and conditions in the soil were at a state of equilibrium. The geochemical modelling required an iterative approach, with the selection of mineral phases and other estimated input parameters modified after each run to improve the modelling. The modelling results presented in this chapter were considered the best fit against actual leach data for the majority of species and provide a good prediction of the processes controlling leaching in the by-products and WA soils.

Input parameters required for the geochemical modelling and related assumptions are detailed in Chapter 3: Methodology Section 3.4.

7.2 pH dependent leaching of Alkaloam®
PpH dependent leach testing was performed on a sample of Alkaloam® used in the agricultural field trials, and the resulting leachates analysed for major, minor and trace metals and anionic species. Figures 7-1, 7-2 and 7-3 illustrate the pH dependent leaching profiles for a range of analytes. The total composition has been plotted, where available, to illustrate the quantity of each species that is available for leaching. The full suite of species analysed can be found in Appendix E.

38 E.g. incorporation within a mineral, sorption to solid organic material, complexation to DOC, precipitation etc.
Figure 7-1: pH dependent leaching of a range of species from Alkaloam®
Figure 7-2: pH dependent leaching of a range of species from Alkaloam®
Figure 7-3: pH dependent leaching of a range of species from Alkaloam®

Concentrations of some heavy metal species such as antimony, cadmium, mercury, lithium and lead were below the analytical detection limit. Within the noise of the measurements, no changes in leaching behaviour with respect to pH could be ascertained for these elements. Leaching concentrations for arsenic were also below the detection limit except at extreme alkaline pH.

The pH dependent leaching profile is specific for each element and is influenced by different processes controlling its solubility. The leaching of aluminium, iron, phosphorus and vanadium from Alkaloam® show a characteristic ‘V’ shaped profile, as illustrated in Figures 7-1 to 7-3. The mobility of these species is most prominent at extreme acidic and alkaline pH, with the least mobility being exhibited at near neutral pH. The ‘V’ shaped leaching profile is typical of amphoteric elements that have undergone inorganic complexation reactions such as hydrolysis or complexation with carbonate (Meima and Comans, 1997).

The maximum available leaching concentration of aluminium, calcium, sodium and strontium from Alkaloam® was equivalent to its total concentration, with maximum dissolution occurring at low pH extremes. These elements were predicted to be dissociated from clay and made available as free cations (section 7.3) under these pH conditions. Although this implies that these elements could be fully released into a receiving
environment should Alkaloam® be exposed to such low pH environments, this is unlikely to occur due to the alkaline nature of this material.

For the majority of analytes, the maximum available concentration for leaching was less than its total concentration in Alkaloam®. This indicates that a portion of the analytes are permanently bound up in the Alkaloam® matrix and will not be available for leaching, irrespective of the pH conditions. The processes binding these analytes are discussed in section 7.3.

Figure 7-4 shows the pH dependent leach data measured for chloride, potassium and sodium from Alkaloam®, and the availability controlled and solubility controlled behaviour exhibited by these elements across a specific pH range.

Due to the high solubility properties of chloride, potassium and sodium, the leaching behaviour of these analytes was expected to show availability controlled behaviour across the full pH range. However, solubility controlled behaviour was observed across a pH range.

---

39 leaching concentration is independent of pH.
specific to each element. Geochemical modelling predicted that the solubility controlling process for these elements was adsorption to clay (section 7.3.2).

Calcium, magnesium, silicon and strontium showed similar leaching profiles, exhibiting maximum leaching at extreme acidic pH and decreased leaching with increased pH (Figure 7-5). This leaching profile is indicative of cationic species in solution at extreme acidic pH conditions followed by the formation of a precipitate or mineral phase as the pH environment increases. Geochemical modelling predictions of these precipitated phases are discussed in section 7.3.1.

![Figure 7-5: Leaching of metals that exhibit maximum mobility at extreme acidic pH and decreased leaching with increased pH](image)

Figure 7-6 shows the pH dependent leaching data for uranium from Alkaloam®. The data show that uranium consistently leaches across a pH range of approximately 6 to 10.5, which is believed to be due to formation of soluble uranyl carbonate species. This is followed by a sudden decrease in leaching at extreme alkaline pH. It is postulated that the uranyl carbonate species no longer become mobile, but are adsorbed to ferrihydrite surfaces, as reported by Waite et al. (1994). This is supported by a corresponding decrease in leaching of iron at the same pH, also illustrated in Figure 7-6.
The presence of carbonate is known to influence the mobility of uranium at alkaline pH (Duff and Amrhein, 1996; Elless and Lee, 1998). Uranium mobility is increased due to the speciation of dissolved uranium (VI) that readily complexes with carbonate to form a range of soluble uranyl carbonate complexes. The nature of these complexes is pH dependent, and complexes are present in the following forms with increasing pH: $\text{UO}_2(\text{OH})_2^{+}$, $\text{UO}_2(\text{CO}_3)^{2-}$, $\text{UO}_2(\text{CO}_3)^{3-}$, $\text{UO}_2(\text{CO}_3)(\text{OH})_3^-$. (Ioppolo-Armanios, 2011).

![Figure 7-6: pH dependent leaching of iron and uranium from Alkaloam®](image)

At the natural pH of typical agricultural soils (pH 4.8 to 8), the leaching concentrations of most species in Alkaloam®; antimony, arsenic, barium, cadmium, copper, fluoride, gallium, iron, lead, lithium, mercury, phosphorus, titanium, thorium and vanadium, were below the detection limit of the analysis. The leaching concentrations of other species, such as aluminium, cobalt, chromium, manganese and molybdenum were also very low in this pH range. The low leachable characteristics of this material suggest that Alkaloam® is not likely to be a significant concern to the environment should it be used as a soil amendment. This is further discussed in chapter 8.

**7.3 Solubility controlling processes influencing leaching of species from Alkaloam®**

Geochemical modelling using LeachXS™ was applied to the pH dependent leach data of Alkaloam® to determine the processes likely to be controlling leaching for a range of constituents across the pH range tested. The modelling was also used to predict speciation across the solid and liquid phases of the matrix and the association of the species as free ions or complexed ions in the liquid phase.

The geochemical input parameters used for modelling leach data for Alkaloam® are presented in Table 7-1. The clay content could not be determined for Alkaloam® due to poor solids flocculation during the analysis, therefore this value was estimated as half of the...
clay content measured in Red Lime™. This was based on there being 50% difference for clay measured for Alkaloam® than Red Lime™, reported in Carter et al. (2009).

**Table 7-1: Input parameters for geochemical modelling of Alkaloam®**

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaloam_Field_Trial_180906 (P,1,1)</td>
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<td></td>
</tr>
<tr>
<td>Solved fraction DOC</td>
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<td></td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
<td></td>
</tr>
<tr>
<td>L/S</td>
<td>9.9999 l/kg</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>7.207E-01 kg/kg</td>
<td></td>
</tr>
<tr>
<td>HFO</td>
<td>1.250E-02 kg/kg</td>
<td></td>
</tr>
<tr>
<td>SHA</td>
<td>9.943E-04 kg/kg</td>
<td></td>
</tr>
<tr>
<td>CO3 = 0.36 times Ca conc</td>
<td></td>
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</tbody>
</table>

The modelled leach data for Alkaloam® best compared with actual leach data when reactive aluminium/iron hydr(oxide) surfaces (HFO) were input in the model at 20% of the amount quantified in the Alkaloam® sample. This indicates that <100% of the surfaces of the aluminium and iron hydr(oxide)s were active in the material.

The minerals; barite, tricalcium phosphosphate (TCP), tricalcium aluminate hexahydrate (TCA6: 3CaOAl2O3.6H2O), albite, calcite, gibbsite, fluorite, CO3-hydrotalcite, goethite, ferrihydrite, strontianite and zinc silicate (ZnSiO3) provided the best solubility predictions and modelling fit against actual leach data. These solubility controlling mineral phases identified for Alkaloam® are discussed in the following section.

**7.3.1 Minerals controlling solubility in Alkaloam®**

The following geochemical charts provide a comparison of pH dependent leach data (red dots) with modelled data (red dashed line) for a range of species. The charts also illustrate the solubility behaviour and the partitioning of species across the solid and liquid phases that are predicted to control leaching.

**Aluminium:** The leaching of aluminium was predicted to be predominantly controlled by the solubility of gibbsite and an aluminosilicate mineral, albite, across the full pH range tested (Figure 7-7). Albite also modelled well in place of albite, inferring that these two aluminosilicate minerals are likely to be surrogate materials for the Desilication Product (DSP) present in Alkaloam®. The minerals tricalcium aluminate hexhydrate (TCA6:
3CaO·Al₂O₃·6H₂O) and CO₃-hydrotalcite were predicted to also control aluminium solubility, but to a much lesser extent.

![Graphs showing [Al⁺³] as function of pH and Partitioning liquid-solid, [Al⁺³]](image)

Figure 7-7: Predicted and measured leaching of aluminium from Alkaloam® and the predicted speciation in the solid and liquid phase controlling solubility

**Iron**: The leaching of iron from Alkaloam® was predicted to be predominantly controlled by the solubility of two minerals, goethite and ferrihydrite (Figures 7-8 and 7-9). Iron is incorporated within these minerals in the Alkaloam® matrix and becomes mobile via solubilisation of goethite across an approximate pH range of 2 to 8 (Figure 7-8), and from the solubility of ferrihydrite across an approximate pH range of 8 to 12 (Figure 7-9). In addition to goethite, adsorption to solid humic and fulvic acids was also predicted to control solubility of iron in the acidic pH range.
Figure 7-8: Predicted and measured leaching of iron from Alkaloam® at pH<8 and the predicted speciation in the solid phase controlling solubility.

Figure 7-9: Predicted and measured leaching of iron from Alkaloam® in the pH range 8 to 12 and the predicted speciation in the solid phase controlling solubility.
Calcium: Leaching of calcium from Alkaloam® was predicted to be predominantly controlled by the mineral calcite in the pH range of 7 to 13 (Figure 7-10). Sorption to clay, and to a lesser extent, to insoluble humic and fulvic acids and fluorite, was predicted to reduce the leaching of calcium across the pH range of 2 to 6.5. Tricalcium aluminate modelled calcium as well as TCA6. Since both minerals are present in Alkaloam®, this suggests that either of the tricalcium aluminate minerals could be controlling the leaching of calcium.

Silicon: The leaching of silicon was predicted to be solely controlled by the solubility of an aluminosilicate mineral. The predicted data modelled well using albite (Figure 7-11) or analbite. Since neither of these phases has been identified in Alkaloam® by XRD analysis, it is postulated that these minerals are likely to be surrogate materials to the desilication product present in Alkaloam®. This is consistent with observations reported in Carter et al (2009).
**Figure 7-11: Predicted and measured leaching of silicon from Alkaloam® and the predicted speciation in the solid phase controlling solubility**

**Other species:** Magnesium, barium, strontium and zinc were partly controlled by minerals and adsorption to clay, iron/aluminium (hydr)oxides or insoluble humic and fulvic acids (illustrated as POM-particulate organic matter on the geochemical speciation charts). The leaching profiles of these species were different by comparison, but with minimum leaching occurring when the species was incorporated within the associated mineral. This is illustrated in Figure 7-12.

Magnesium was predicted to be controlled by magnesite and CO3-hydrotalcite minerals at the alkaline pH range. Barium was controlled by barite at the acidic pH range, strontium was controlled by the mineral strontianite at alkaline pH, and zinc by the mineral zinc silicate.
Figure 7-12: Predicted and measured leaching of magnesium, barium, strontium and zinc from Alkaloam® and the predicted speciation in the solid phase controlling solubility
Fluoride: Leaching of fluoride from Alkaloam® was predicted to be controlled by the solubility of fluorite mineral at neutral pH, and by adsorption to clay at alkaline and acidic pH (Figure 7-13).

![Figure 7-13: Predicted and measured leaching of fluoride from Alkaloam® and the predicted speciation in the solid phase controlling solubility](image)

7.3.2 Adsorption to clay

Several species in Alkaloam® were partly adsorbed to clay. Metals such as aluminium, silicon, iron and copper were predicted to be adsorbed to clay at extreme acidic and alkaline pH.

Other species, such as calcium, magnesium, strontium and manganese were controlled by clay in the acidic pH range only. The alkali elements, chloride and potassium, were highly soluble in Alkaloam® at pH<5 but became progressively immobilised in the matrix due to clay sorption, as the pH became more alkaline (Figure 7.14).
7.3.3 Adsorption to iron and aluminium (hydr)oxides

Adsorption to iron and aluminium (hydr)oxides (HFOs) was predicted to be a predominant process controlling leaching for many species in Alkaloam®, due to the high concentration of iron and aluminium (hydr)oxides present in the matrix. This observation is consistent with previous work reported in Carter et al. (2008), that HFOs\textsuperscript{40} are a major factor controlling element mobility in bauxite residues sourced from different Alcoa refineries.

Geochemical modelling predictions indicated that this sorption process controls the mobility of phosphorus, magnesium, strontium, manganese, molybdenum and lead. Barium was also predicted to be controlled by HFOs but within the alkaline pH range only.

The leaching of phosphorus was controlled solely by adsorption to HFOs, with the anions being freely available in solution at alkaline pH (Figure 7-15).

\textsuperscript{40} Referred to as IAH in the Carter et al. (2008) report.
The mobility of copper and chromium was controlled in part by adsorption to HFOs as well as insoluble organics, as shown in Figures 7-16 and 7-17 respectively. The dissolution of these metals was associated with complexation to dissolved organic carbon at a pH range of 6 to 11 (for copper) and 4 to 8 (for chromium). For copper, the leaching of free metal ions ($\text{Cu}^{2+}$) and soluble inorganic complexes are assumed to be the most toxic and bioavailable forms that can negatively impact on aquatic ecosystems (Karlsson et al., 2006). Hence in the pH range of 6 to 11, copper mobility was predicted to be in a less bioavailable form, as a result of its association with soluble organics.

**Figure 7-15:** Predicted and measured leaching of phosphorus from Alkaloam® and the predicted speciation controlling solubility

**Figure 7-16:** Predicted and measured leaching of copper from Alkaloam® and the predicted speciation controlling solubility
7.3.4 Adsorption to organics (soluble and insoluble humic and fulvic acids)
Thorium and uranium leaching from Alkaloam® was predicted to be controlled by organics (Figure 7-18). The metal species were associated with adsorption to insoluble humic and fulvic acids, and complexation with soluble humic and fulvic acids. For both elements the modelling results indicated that the SHA concentration for Alkaloam® was too low to accurately reflect the leach data. This anomaly was identified as being due to competitive adsorption effects of cationic species for the active organic sites that could not be accurately modelled in soil matrices. A detailed discussion of this effect is reported later in this chapter under sections 7.5.4 and 7.7.4.
7.4 pH dependent leaching of Red Lime™

pH dependent leach testing was performed on Red Lime™ used in the agricultural field trials. During the 48 hour leaching period an increase in pressure inside the sample bottles was observed, presumably caused by the liberation of carbon dioxide, due to the reaction of carbonate species present in the Red Lime™. Figures 7-19 to 7-21 show the pH dependent leaching of a range of species analysed from the eluates. The full suite of species analysed is in Appendix E.

Concentrations of antimony, copper, mercury and lead were close to or below the detection limit of the analysis. Within the noise of the measurements, no changes in leaching behaviour with respect to pH could be ascertained for these elements.

As noted for Alkaloam®, the leaching profiles of analytes from Red Lime™ were also specific to each element, and were influenced by different processes controlling leachability. With the exception of calcium and silicon, the majority of species in Red Lime™ exhibited different pH dependent leaching profiles to those measured in Alkaloam®. This is due to different processes controlling leaching of the constituents in the two materials, as predicted...
using geochemical modelling. Differences in the processes controlling leachability in the two residue materials was believed to be due to the calcium minerals and higher organic content measured in Red Lime™ having a greater influence on the solubility of species. This is discussed further in section 7.5.

Figure 7-19: pH dependent leaching of a range of species from Red Lime™
Figure 7-20: pH dependent leaching of a range of species from Red Lime™
The maximum available concentration for leaching for all species in Red Lime™ occurred at extreme acidic pH. This was contrary to that observed for molybdenum in Alkaloam®, where the maximum available leaching concentration occurred at alkaline pH.

At the natural pH of typical agricultural soils (pH 4.8 to 8), the leaching concentrations of arsenic, cadmium, chromium, fluoride, iron, phosphorus, lead and thorium from Red Lime™ were below the detection limit of the analysis (Figures 7-19 to 7-21). Other species, such as aluminium, barium, calcium, cobalt, magnesium, manganese, molybdenum and nickel displayed some leaching behaviour in this pH range. An assessment of the leaching concentrations from an agricultural soil amended with Red Lime™ were therefore compared...
against DEC regulatory waste guidelines to determine whether an ameliorant rate of 1.6g/kg could be used without adverse impact to the environment. This is discussed in Chapter 9.

The highly soluble chloride and sodium species were availability controlled across the majority of the pH range tested (Figure 7-22). The leaching of chloride decreased at extreme alkaline pH, suggesting that a sorption process or mineral is likely to be controlling leachability in this environment. Geochemical modelling predicted that adsorption to clay is the controlling process influencing the decreased leachability.

The pH dependent leach data for potassium suggested that this species is solubility controlled in Red Lime™ across the pH range 0.1 to 12.5. This was unexpected due to the high solubility of potassium. Solubility was predicted to be controlled by adsorption to clay, similar to the process observed in Alkaloam®.

Figure 7-22: pH dependent leaching of salts from Red Lime™
7.5 Solubility controlling processes influencing leaching of species from Red Lime™

The geochemical input parameters and minerals used for modelling leach data for Red Lime™ are presented in Table 7-2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red_Lime_Field_Trial_190906 (P,1,1)</td>
<td></td>
</tr>
</tbody>
</table>

- **Solved fraction DOC**: 0.2
- **Sum of pH and pe**: 15.00
- **L/S**: 10.0000 l/kg
- **Clay**: 1.320E+00 kg/kg
- **HFO**: 3.530E-02 kg/kg
- **SHA**: 1.926E-02 kg/kg
- **CO3 = 0.3 x Ca conc**

The solid humic acid (SHA) was quantified higher in Red Lime™ compared to Alkaloam® (19258mg/kg vs 994.29mg/kg). The carbonate concentration was estimated for the modelling, and the final input value was determined from the best fit between the actual and predicted leach data. This was estimated to be 20% of the available calcium concentration.

The predicted leach data for Red Lime™ using geochemical modelling compared well to actual data when a 50% lower concentration of aluminium/iron (hydr)oxide surfaces (HFOs) was entered into the model. This is believed to be due to the surfaces of the HFOs not all being active in the material, which is the assumption made in the modelling software. The inclusion of the minerals barite, tricalcium phosphate (TCP), tricalcium aluminate hexahydrate (TCA6 - 3CaOAl2O3.6H2O), laumonite, calcite, amorphous aluminium hydroxide, fluorite, CO3-hydrotalcite, ferrihydrite, strontianite and iron vanadate gave good solubility predictions. Speciation and processes controlling leachability of the metals was similar to Alkaloam®, with the exception of some different minerals for aluminium, silicon and iron that are discussed in section 7.5.1.

7.5.1 Minerals controlling solubility in Red Lime™

The following geochemical charts illustrate the actual pH dependent leach data (red dots) of Red Lime™ against modelled behaviour (red dashed line) for a range of species. The charts also illustrate the solubility behaviour and the partitioning of species across the solid and liquid phases that are predicted to be controlling leaching.
Aluminium: The leaching of aluminium from Red Lime™ was predicted to be controlled by several minerals; amorphous aluminium hydroxide, CO₃-hydrotalcite, laumonite and TCA₆ (Figure 7-23). Of these mineral phases, amorphous aluminium hydroxide was predicted to be the dominant mineral phase controlling solubility of aluminium, with minimum leaching occurring across the pH range of 4 to 12 due to incorporation of aluminium within this mineral. Attempts were made to model the data using gibbsite mineral as predicted for Alkaloam®, however this did not model as well as amorphous aluminium hydroxide. Tricalcium aluminate hexhydrate (TCA₆) and CO₃-hydrotalcite were predicted to also control aluminium leaching at alkaline pH, but to a much lesser extent.

![Graph of aluminium leaching](image)

**Figure 7-23: Predicted and measured leaching of aluminium from Red Lime™ and the predicted speciation controlling solubility**

Iron: The leaching of iron was controlled by different speciation in Red Lime™ to that in Alkaloam®. Iron vanadate mineral was predicted to partly control iron mobility at the acidic pH range and the solubility of ferrihydrite controlled iron at the alkaline pH range (Figure 7-24). Unlike Alkaloam® (section 7.3.1), the data modelled poorly at pH 10 to 13 when goethite was included into the model. This suggests that goethite is not likely to be

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41 Also controlled by adsorption to organics, discussed in section 7.5.4.
present in Red Lime™. This is backed up by the low iron concentration measured in Red Lime™ relative to Alkaloam® (Chapter 6).

![Graph showing [Fe+3] as function of pH and Partitioning liquid-solid, [Fe+3]](image)

**Figure 7-24: Predicted and measured leaching of iron from Red Lime™ and the predicted speciation controlling solubility**

**Calcium:** the predominant mineral controlling calcium leachability in Red Lime™ was calcite (Figure 7-25). A portion of the calcium species were predicted to be incorporated within the minerals laumonite and fluorite within the acidic pH range of 3 to 6, however the most dominant controlling process in acidic environments was adsorption to clay (see section 7.5.2).

At extreme alkaline pH calcium was predicted to be incorporated within TCA6 in the solid phase. The formation of these mineral phases was predominantly influenced by the high carbonate content present in Red Lime™.

**Silicon:** The calcium aluminosilicate mineral, laumonite, modelled the leach data for silicon in Red Lime™ more closely than the sodium aluminosilicate minerals, analbite and albite, previously determined to control leaching of silicon from Alkaloam® (Figure 7-26). The presence of laumonite would account for the additional calcium present in Red Lime™ relative to Alkaloam®.
Figure 7-25: Predicted and measured leaching of calcium from Red Lime™ and the predicted speciation controlling solubility.

Figure 7-26: Predicted and measured leaching of silicon from Red Lime™ and the predicted speciation controlling solubility.
Phosphorus: Geochemical modelling of leach data for phosphorus predicted TCP as the mineral controlling leaching in the alkaline pH range (Figure 7-27). In contrast, Alkaloam® was controlled solely by adsorption to HFOs. Due to the high calcium content in Red Lime™, the formation of TCP provided an important role for release of phosphate in alkaline pH environments.

Figure 7-27: Predicted and measured leaching of phosphorus from Red Lime™ and the predicted speciation controlling solubility

Fluoride: Leaching of fluoride from Red Lime™ was predicted to be strongly controlled by the mineral fluorite across the pH range of 5 to 13. Upon leaching from Red Lime™, the anions were predicted to be freely available in solution (Figure 7-28).

Magnesium: Magnesium was predicted to be partly controlled by the mineral CO₃-hydrogencarbonate across the alkaline pH range (Figure 7-29). In an acidic pH environment the cationic species were freely available in solution. The factors controlling magnesium leaching in Red Lime™ were similar to that predicted in Alkaloam®, with the exception of the additional mineral magnesite (section 7.3.1).
Other species: The leaching of barium and strontium was controlled by the solubility of barite and strontianite respectively, the solubility controlling minerals also present in Alkaloam®. Uranium was predicted to be controlled by the solubility of schoepite at alkaline pH.

7.5.2 Adsorption to clay
The adsorption of species to clay was an important process controlling the solubility of many species from Red Lime™ in the acidic pH range; namely aluminium, calcium, silicon, magnesium and fluoride. Species such as cadmium, manganese, lead, zinc and nickel were partly controlled by adsorption to clay, in addition to insoluble humic and fulvic acids.
7.5.3 Adsorption to iron and aluminium (hydr)oxides

Many species were partly controlled by adsorption to iron and aluminium (hydr)oxides, but by varying amounts specific to the element. Examples of this can be seen from the reduced leaching of manganese, lead, zinc, nickel and cadmium in Figures 7-30 and 7-31 at neutral to alkaline pH due to this adsorption process.

For manganese, lead and nickel, adsorption to iron and aluminium (hydr)oxides was predicted to be the most dominant factor controlling their solubility (Figure 7-30).

![Graphs showing pH dependent leaching of manganese, lead, and nickel](image)

Figure 7-30: Predicted and measured pH dependent leaching of manganese, lead and nickel from Red Lime™ controlled predominantly by adsorption to iron and aluminium (hydr)oxides
For zinc and cadmium, adsorption to insoluble humic and fulvic acids was the more
dominant process controlling solubility, with adsorption to iron and aluminium (hydr)oxides
only partially controlling their solubility (Figure 7-31).

Phosphorus was also controlled by iron and aluminium (hydr)oxides, but only across the
acidic pH range, as previously illustrated in Figure 7-27.

7.5.4 Adsorption to organics (soluble and insoluble humic and fulvic acids)
The solubility of thorium, uranium and chromium in Red Lime™ was predicted to be
controlled by organics. These metals were associated with adsorption to insoluble humic
and fulvic acids in the solid phase and complexation with soluble humic and fulvic acids in
solution, illustrated as ‘POM bound’ and ‘DOC bound’ on the charts in Figure 7-32.
The predicted leach data (dotted lines) for chromium and uranium showed poor correlation with actual leach data (red dots) at pH>9 and pH 4 to 8 respectively. A comparison of the predicted and actual leach data implies that the SHA concentration used in the modelling was too low to provide accurate predictions for these elements. Conversely using the same SHA value in the model, the predicted leach data for zinc and cadmium implies that the SHA value is too high to correlate well with actual leach data (Figure 7-31).

The differing proportions of SHA required to model each element suggests that competitive adsorption of cationic species for the active organics sites is occurring. The affinity of a
species to adsorb to organics is based on the valency of the species\textsuperscript{42}, its hydrated radius\textsuperscript{43} and the surface charge density of the organic particles. The Non-ideal Competitive Adsorption (NICA) Donnan model incorporated into the LeachXSTM software does not account for this variability in the metal species binding properties (Groenenberg et al., 2010) and therefore is unable to provide exact correlation of predicted to actual data for all elements at once. In addition, LeachXSTM assumes that all soil particles are in a state of equilibrium with each other, which is not likely to be the case in true field conditions.

7.6 pH dependent leaching of a Swan Coastal Plain soil (Bassendean soil)
Figures 7-33 to 7-35 illustrate the pH dependent leaching behaviour for a range of species in Bassendean soil (Appendix E contains data for the full suite of analytes). The solution pH interfered with analytical methodology, whereby the low pH solution increased detection limit relative to the high pH solutions. This creates an artefact within the graphical analysis as the data moves from one baseline to another for samples at or below detection limit.

Arsenic, cadmium, cobalt, chromium, copper, fluoride, gallium, mercury, lithium, lead, antimony, selenium, tin, thorium, titanium and vanadium were measured close to or below the detection limit of the analysis, and any changes in leaching behaviour for these elements could not be ascertained. Geochemical modelling however was capable of predicting the speciation responsible for preventing leaching of some of these metals from the soil matrix, and these results are discussed herein.

\textsuperscript{42} Divalent species have a higher affinity than monovalent species.

\textsuperscript{43} Species with smaller hydrated radius has a higher affinity towards exchange sites as it can approach the organic surface easier.
Figure 7-33: pH dependent leaching of a range of species from Bassendean soil
Figure 7-34: pH dependent leaching of a range of species from Bassendean soil
As reported for Alkaloam® and Red Lime™, the pH dependent leaching profiles for species in Bassendean soil were specific for each element, and were influenced by soluble mineral phases and adsorption processes discussed in section 7.7. Less leachables were noted in Bassendean soil than in Alkaloam® and Red Lime™. This can be explained by the extensive weathering and leaching processes the soils from the Bassendean dunes have undergone, resulting in negligible leachable metal content remaining in the material.

The pH dependent leaching profile of phosphorus from Bassendean soil indicates that this species leaches across an approximate pH range of 1.5 to 6 (Figure 7-34). Since the Bassendean soil has a natural pH of 8.4 (Chapter 4), phosphorus leaching is unlikely to occur unless the environment pH becomes more acidic, such as soils used for agricultural purposes.

The pH dependent leaching profile of DOC in Figure 7-33 suggests that insoluble organic carbon is predominantly present in the soil across a pH range of 2 to 9. Under extreme acidic and alkaline soil conditions the organic carbon is believed to become more soluble as shown by increased leaching at these pH environments.
Potassium, chloride and sodium did not show availability controlled leaching behaviour (Figure 7-36), inferring that solubility controlling processes are likely to be influencing the mobility of these species. LeachXSTM geochemical modelling predicted that these elements were controlled by adsorption to clay (section 7.7.2).

![Figure 7-36: pH dependent leaching of chloride, potassium and sodium from Bassendean soil](image)

**7.7 Solubility controlling processes influencing leaching of species from Bassendean soil**

The geochemical input parameters used for modelling leach data for Bassendean soil are presented in Table 7-3.
Table 7-3: Input parameters for geochemical modelling of Bassendean soil

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<tr>
<td>HFO</td>
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<td>SHA</td>
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<tr>
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</table>

The predicted leach data for Bassendean soil using geochemical modelling compared well to actual data when 25% of the quantified reactive aluminium/iron hydr(oxide) surfaces (HFOs) was used in the model. This is likely due to the surfaces of the aluminium and iron hydr(oxide)s not being 100% active in the soil, which is the assumption made in the modelling software. The inclusion of the minerals analbite, calcite, amorphous aluminium hydroxide and ferrihydrite gave good solubility predictions. The carbonate concentration was estimated based on a fraction of the calcium concentration that would provide the best fit to actual data.

The geochemical charts in the following sections illustrate the actual pH dependent leach data (red dots) of Bassendean soil against modelled behaviour (red dashed line) for a range of species. The charts also illustrate the solubility behaviour and the partitioning of species across the solid and liquid phases that are predicted to be controlling leaching.

7.7.1 Solubility controlling minerals in Bassendean soil

An XRD analysis of the soil sample indicated the presence of silicon, aluminium calcium and iron mineralogical structures within the Bassendean soil (See Chapter 3: Methodology). Using geochemical modelling the following solubility controlling mineralogical phases were predicted to be controlling the leaching of these elements at different pH ranges.

Aluminium: The leaching of aluminium from Bassendean soil was predicted to be controlled by the solubility of an aluminosilicate mineral analbite and amorphous aluminium hydroxide within the pH range of 5 to 11 (Figure 7-37). The leach data did not model well when gibbsite or boehmite was input into the model.
Although gibbsite is thermodynamically more stable than amorphous aluminium hydroxide, this mineralogical phase will preferentially precipitate, in accordance with the Ostwald Step Rule. This states that the more soluble, less stable phase will precipitate first followed sequentially by increasingly less soluble more stable phases.

Kinetics for the precipitation of gibbsite is very slow, therefore short-term solubility controlling processes for aluminium are likely to be controlled by the amorphous aluminium hydroxide mineral. Assessment of long-term leaching of aluminium, where gibbsite or boehmite minerals are likely to have precipitated over time, should be modelled to provide more accurate predictions (Amira International, 2007).

**Calcium**: the solubility controlling mineral phase for calcium was predicted to be calcite in Bassendean soil (Figure 7-38). Incorporation of calcium within the calcite mineral is the most important factor reducing calcium leaching across a pH range of 7 to 12. Adsorption processes, such as adsorption to clay and insoluble humic and fulvic acids were predicted as less significant controlling mechanisms in this soil matrix.
Iron: The mineral that gave the best solubility prediction for iron was ferrihydrite in Bassendean soil. This mineral controls the solubility of iron across a pH range of 8 to 12, with this being the predominant controlling factor at the extreme alkaline pH 11 and 12 (Figure 7-39).

Silicon: The dominant process controlling the leachability of silicon in Bassendean soil across the pH range of 5 to 11 was the solubility of the aluminosilicate mineral, analbite (Figure 7-40). Inclusion of kaolinite clay mineral to the model in replace of analbite produced an overestimated prediction of the silicon being retained in the matrix and therefore was not used for the modelling.

Figure 7-38: Predicted and measured pH dependent leaching of calcium from Bassendean soil and the partitioned speciation controlling solubility
Figure 7-39: Predicted and measured pH dependent leaching of iron from Bassendean soil and the partitioned speciation controlling solubility

Figure 7-40: Predicted and measured pH dependent leaching of silicon from Bassendean soil and the partitioned speciation controlling solubility
7.7.2 Adsorption to clay

With the exception of thorium, the solubility of all species analysed were partly controlled by clay, but within a pH range specific to each element. For example, clay adsorption was predicted to be an important factor controlling the solubility of aluminium, nickel, selenium and zinc across high acidic and alkaline pH range, as illustrated in Figure 7-41 for selenium and zinc.

![Figure 7-41: Clay adsorption controlling the solubility of selenium and zinc in Bassendean soil at high acid and alkaline pH](image)

Iron was controlled by the presence of clay at high alkaline pH and conversely silicon was controlled at high acidic pH conditions (previously illustrated in Figures 7-39 and 7-40 respectively). Whilst copper and chromium were predominantly controlled by organic particulates in Bassendean soil, these species were also shown to be influenced by clay adsorption at extreme alkaline pH. However, this soil pH is unlikely to occur in the environment; therefore these species will be dominated by the presence of organic material in these types of soil matrices.

Clay adsorption was noted to be a dominant process controlling the solubility of magnesium and strontium across the full pH range tested. The modelled leaching predictions were
overestimated for these elements (Figure 7-42) due to the competitive adsorption effects for organics not accounted for in the modelling.

Clay modelled chloride, potassium and sulphate poorly, even when a superficially high concentration was included in the model. Their pH dependent leaching profiles indicated solubility controlling behaviour; however the processes responsible could not be ascertained.

This leaching behaviour was found to be different to that observed in the WA agricultural soils, where leaching of these constituents progressively increased with increasing pH due to the variable surface charge characteristics of the soil with change in pH (see section 7.9.2, 7.12.4 and 7.13.4).

### 7.7.3 Adsorption to iron and aluminium (hydr)oxides

Reactive iron and aluminium (hydr)oxide surfaces within Bassendean soil were predicted to partially control the solubility of manganese, nickel, and silicon at alkaline pH, and zinc at neutral pH.
This adsorption process was the dominant mechanism controlling solubility of selenium and phosphorus across the majority of the pH range tested, as shown previously in Figure 7-41 and below in Figure 7-43 respectively. Geochemical modelling predicted arsenic and molybdenum were also controlled by this process, however the predicted leaching did not correlate well with leach data.

![Figure 7-43: Predicted and measured pH dependent leaching of phosphorus from Bassendean soil and the speciation controlling solubility](image)

7.7.4 Adsorption to organics (soluble and insoluble humic and fulvic acids)
Organics in the Bassendean soil played a predominant role in controlling the solubility of most constituents in this soil. Leaching of the majority of metals was partially or predominantly controlled through adsorption to insoluble humic and fulvic acids, or by complexation to soluble organic acids.

The solubility of thorium, uranium, chromium and copper were predominantly controlled by adsorption to insoluble humic and fulvic acids across the pH range of 1 to 10.

Some leaching was observed for these elements across the full pH range, with the partitioning of these species in the liquid phase being associated as free cations in solution or complexed with soluble humic and fulvic acids (DOC bound). These varied for each element (Figure 7-44). For example, the mobilisation of thorium from Bassendean soil across the full pH range was predicted to be associated with formation of soluble complexes with humic and fulvic acids. In the case of copper leaching, the cationic species were predicted to be available in solution at high alkaline and acidic environments, and bound in the form of a soluble organic complex at pH 8 to 10. Copper in the form of an organic complex has been reported to be less bioavailable and much less toxic than free copper ions (Steenbergen et al., 2005).
This example highlights that the ability to predict speciation in solution for potentially toxic metals, such as copper, can prove highly beneficial for assessing the likely bioavailability and subsequent environmental impacts of a material being tested in specific scenarios.

Figure 7-44: Organic speciation in the solid and liquid phase predicted to be controlling leaching of a range of species in Bassendean soil
The concentration of insoluble organic material (SHA) measured in the Bassendean soil modelled well against leaching data for uranium and thorium, but the results indicated the concentration was overestimated for chromium and copper (Figure 7-44). In contrast, other species such as manganese and magnesium were found to be underestimated and would require a higher value of SHA to improve the modelling results (Figure 7-45). The different amount of SHA required to model each element is indicative of competitive adsorption effects occurring between the metals for the active organic sites, as previously discussed in section 7.5.4. This effect cannot be accounted for due to the limitation of the Non-Ideal Competitive Adsorption (NICA) Donnan model incorporated into the LeachXSTM software.

Figure 7-45: Organic speciation in the solid and liquid phase predicted to be controlling leaching of manganese and magnesium in Bassendean soil

7.8 pH dependent leaching of Manning Light and Manning Heavy agricultural soils
Figures 7-46 to 7-48 illustrate pH dependent leach data for a range of analytes in Manning Light and Manning Heavy agricultural soils. The total concentration for each analyte has been plotted to provide a baseline concentration for the total amount available for leaching44. A full suite of analytes measured for these soils can be found in Appendix E.

44 With the exception of Dissolved Organic Content (DOC), where this was not available.
Several constituents were measured close to or below the detection limit of the analysis in these soils and therefore any changes in leaching behaviour for these elements could not be determined. For both soils these included arsenic, boron, fluoride, mercury, molybdenum, lead and tin. Additional elements in Manning Light soil included cobalt, chromium, copper, gallium, lithium, antimony, selenium, uranium and vanadium.

Figure 7-46: pH dependent leaching of a range of species from Manning Light and Manning Heavy soils
Figure 7-47: pH dependent leaching of a range of species from Manning Light and Manning Heavy soils
Figure 7-48: pH dependent leaching of a range of species from Manning Light and Manning Heavy soils

A comparison of the leaching profiles for the two agricultural soils shows that the leaching behaviour is relatively similar for most species, but with higher leaching concentrations obtained in the more clay type Manning Heavy soil. Geochemical modelling on these soils...
(section 7.9.4 and 7.10.3) predicted that the mechanisms controlling leaching for the majority of species was the same for both soils, and that this was associated with adsorption to insoluble organics and complexation with soluble organics (specifically humic and fulvic acids).

The pH dependent leaching of DOC in Figure 7-47 shows that there is consistently more soluble organics leaching from Manning Heavy than Manning Light soil (note that the chart is on a logarithmic scale, therefore a small difference in leaching illustrated on the chart is significant). This would account for the higher leaching concentrations in Manning Heavy soil as species are being mobilised through complexation with the dissolved organic acids.

Different pH dependent leaching profiles were observed for uranium and cobalt for the two soils. For uranium, this was believed to be due to the different mechanisms controlling its mobility, in particular across the alkaline pH, where increased leaching was observed in Manning Heavy soil (Figure 7-48). At alkaline pH, uranium was predicted to be controlled by adsorption to clay in Manning Heavy soil (section 7.9.2) and adsorbed to insoluble organics in Manning Light soil (section 7.10.4). Although mobility of uranium was through complexation to soluble organics in the solution phase for both soils, the higher partition coefficient ($K_d$) of uranium with clay compared to organics (US EPA, 1999), in addition to the higher concentration of soluble organics available to potentially complex with uranium, are likely to have accounted for the higher leachability of uranium in the Manning Heavy soil.

Mechanisms controlling the leachability of cobalt could not be determined using LeachXSTM geochemical modelling since cobalt is not available as a reactive constituent in the LeachXS software. Based on a report by WHO (2006), it is understood that the different pH dependent leaching characteristics for cobalt in the two soils is related to differences in the available humic acids and anions present in the soil matrix. It is recommended that cobalt be added as a reactive constituent in the LeachXSTM geochemical modelling to allow speciation and partitioning across the solid and liquid phases to be predicted.

The pH dependent leaching behaviour of DOC from Manning Light and Manning Heavy soils (Figure 7-47) indicate that most organics are present as insoluble species at the natural pH of the soils. In both soils, these organics become more soluble as the pH increases from its natural pH environment. Hence other species present in these soils, which have an affinity to complex with organics, are likely to also become mobile as the pH increases. This
was confirmed by geochemical modelling and is discussed further in sections 7.9.4 and 7.10.4.

The maximum concentrations available for leaching for cobalt, chloride, phosphorus and sulphur were measured higher than their total concentration in the soil. This anomaly may originate from the methodology used for analysing composition, inferring that not all elements were successfully extracted from the soil during the mixed acid digest. For the majority of species the maximum concentration available for leaching was lower than the total concentration of the element. Therefore, total composition is not recommended as key criteria for assessing a material’s impact on the environment as this will lead to an overly conservative evaluation and may unjustly dismiss a material as being unsafe.

The pH dependent leaching of phosphorus in the two soils (Figure 7-49) indicated that Manning Heavy has higher phosphorus retention properties than Manning Light soil across a pH range 2 to 7, which includes their natural pH. This is indicative of the PRI values measured for these soils (section 6.6, Table 6-7), assuming that the PRI value has been reported at its natural pH or within this pH range.

![Figure 7-49: pH dependent leaching of phosphorus from Manning Light and Manning Heavy soils](image)
7.9 Solubility controlling processes influencing leaching of species from Manning Heavy soil

Geochemical modelling using LeachXS™ was applied to leach data to determine the processes likely to be controlling leaching for a range of species across the pH range tested, and to predict the speciation in the liquid and solid phases of the matrix associated with leaching.

The geochemical input parameters used for modelling leach data for Manning Heavy soil are presented in Table 7-4.

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<th>Solved fraction DOC</th>
<th>Varied with pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>9.9991 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>1.350E+00 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>1.160E-02 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>1.650E-03 kg/kg</td>
</tr>
<tr>
<td>CO₃=0.75XCa conc.</td>
<td></td>
</tr>
</tbody>
</table>

The values used in the model were all measured values, with the exception of the carbonate concentration that was estimated. Modelling was conducted using estimated carbonate concentrations in the range of 10% to 150% of the calcium concentration, however the carbonate concentration was found not have any impact on the modelling of calcium, irrespective of the value inputted into the model. An arbitrary value of 0.75 times the calcium concentration was used for completeness.

The following geochemical modelling charts illustrate the actual pH dependent leach data (red dots) of Manning Heavy soil against modelled predicted behaviour (red dashed line) for a range of species. The charts also illustrate the solubility behaviour and the partitioning of species across the solid and liquid phases that are predicted to be controlling leaching.
7.9.1 Solubility controlling minerals in Manning Heavy soil

Very few mineralogical phases were predicted to control the leaching of species from Manning Heavy soil. The high amount of clay present in this soil was initially thought to be kaolinite, however the solubility of this mineral did not model well against the leach data.

The mineral quartz was predicted to control solubility of silicon across the pH range 1 to 11 (Figure 7-50). Whilst the modelled leaching for silicon did not correlate well with the leach data, the omission of silicon minerals from the model produced very poor predictions, indicating that mineralogical processes were indeed present. Of the range of silicon minerals modelled, quartz gave the best prediction.

![Figure 7-50: Mineralogical phases predicted to control solubility of silicon from Manning Heavy soil](image)

7.9.2 Adsorption to clay

Modelling indicated that clay controlled the solubility of most elements in this soil. Adsorption to clay was the predominant process controlling leaching for some elements, including barium, calcium, fluoride, potassium, magnesium, manganese and strontium. For other elements, such as nickel, copper and zinc, adsorption to insoluble humic and fulvic acids and HFOs were also important solubility controlling processes (Figure 7-51). Other species, such as uranium and thorium were controlled by clay and adsorption to insoluble humic and fulvic acids (section 7.9.4)
The predicted leaching of chloride and sulphate could not be modelled accurately with clay adsorption (Figure 7-52). The leaching profiles of these species showed a similar linear trend of increased leaching with increased pH, rather than an availability controlled behaviour predicted by the model. This observation indicates that the solubility of chloride and sulphate in Manning Heavy soil is being influenced by the change in surface charge characteristics of the soil with changing pH. At acidic pH when the surface charge of particles is positive these anions favour adsorption; conversely as the pH increases, the surface charge of particles becomes more negative such that these anions will not be readily adsorbed (Wong and Wittner, 2009).
7.9.3 Adsorption to iron and aluminium (hydr)oxides

In Manning Heavy soil, the mobility of phosphate was predicted to be controlled by adsorption to iron/aluminium (hydr)oxides across the acidic pH range, with maximum adsorption occurring at pH 4.5 to 5. At alkaline pH, phosphorus leached from the soil as free ions in solution (Figure 7-53).

Figure 7- 52: Predicted and measured pH dependent leaching of chloride and sulphate from Manning Heavy soil

Figure 7- 53: Phosphorus solubility controlled by adsorption to iron and aluminium (hydr)oxides in Manning Heavy soil
7.9.4 Adsorption to organics (humic and fulvic acids)

The majority of species were predicted to be complexed with soluble humic and fulvic acids when mobilised from Manning Heavy soil. Although clay adsorption appeared to be an important factor controlling some species in the solid phase of the matrix, complexation with dissolved organics played the most important factor in the liquid phase.

The solubility of aluminium and iron were predominantly controlled by adsorption to clay in the solid phase, with a small portion being controlled by adsorption to insoluble humic and fulvic acids (indicated as POM – particulate organic matter on the geochemical speciation charts). Predicted leaching however indicated that the amount of insoluble humic and fulvic acids (SHA) input in the model was underestimated for this soil (Figure 7-54). Geochemical modelling predicted that a concentration of thirty times the SHA measured in this soil would be required to give a good comparison of predicted and actual leach data. This deficiency was also noted for uranium and thorium, with concentrations of ten times the actual SHA measured in the soil being required to model the leach data well (Figure 7-55).

The different concentrations of insoluble organics required to model each element indicate that competitive adsorption of cationic species exists for the active organics sites. The affinity of a cation to adsorb to organics is based on its valency45, its hydrated radius46 and the surface charge density on the organic particles. The Non-Ideal Competitive Adsorption (NICA) Donnan model incorporated into the LeachXS™ software does not account for this variability in the metal species binding properties (Groenenberg et al., 2010) and is believed to be a limitation in the modelling process.

45 Divalent species have a higher affinity than monovalent species.
46 Species with smaller hydrated radius has a higher affinity towards exchange sites as it can approach the organic surface easier.
Figure 7-54: Predicted and measured pH dependent leaching of aluminium and iron from Manning Heavy soil with predicted partitioning of speciation.

Figure 7-55: Predicted and measured pH dependent leaching of uranium and zinc from Manning Heavy soil with predicted speciation controlling solubility.
7.10 Solubility controlling processes influencing leaching of species from Manning Light soil

Geochemical modelling was carried out on the pH dependent leach data for Manning Light soil. Input parameters for the modelling were estimated for all the reactive solid surfaces (i.e. HFO, SHA (particulate organic matter) and clay content). The estimated values were initially based on those reported in Carter et al. (2009) for Busselton soil, and then optimised to give the best fit against actual data. Input parameters for the modelling are presented in Table 7-5.

Table 7- 5: Input parameters for geochemical modelling of Manning Light soil

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>Solved fraction DOC</td>
<td>varied with pH</td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>9.9968 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>2.000E-03 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>1.300E-03 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>9.000E-03 kg/kg</td>
</tr>
<tr>
<td>CO3=0.2XCa conc.</td>
<td></td>
</tr>
</tbody>
</table>

7.10.1 Solubility controlling minerals in Manning Light soil

Geochemical modelling of the leach data indicated that quartz was the only solubility controlling mineral present in Manning Light soil, which influenced the mobility of silicon. For the majority of species, adsorption processes associated with organics were predicted to be the most dominant factor controlling leaching, as was the case for Manning Heavy soil. The reactive solid surfaces (clay, HFO and SHA) that best modelled the leach data for this soil were noticeably lower than the concentrations measured in other WA soils that were modelled. This is indicative of the poor metal retention characteristics of Manning Light soil, comparative to the other soils tested.

7.10.2 Adsorption to clay

Clay adsorption was not considered an important process for controlling solubility in Manning Light soil. Species such as aluminium, iron, phosphorus, chromium, zinc, copper and molybdenum were predicted to be adsorbed to clay at highly alkaline conditions (pH>11), however it is unlikely that these conditions will exist in the field.
7.10.3 Adsorption to iron and aluminium (hydr)oxides

Phosphorus was predominantly controlled by adsorption to iron and aluminium (hydr)oxides in the solid phase (Figure 7-56). This adsorption process was most prominent in the soil matrix at pH 4.5. This process was also an important factor for the leaching of molybdenum, selenium and antimony, specifically across the pH range 3 to 11.

![Figure 7-56: Predicted and measured pH dependent leaching of phosphorus from Manning Light soil and the predicted speciation controlling solubility](image)

7.10.4 Adsorption to organics (humic and fulvic acids)

Key species, such as aluminium, barium, cadmium, calcium, chromium, iron, lead, magnesium, manganese, potassium, uranium, thorium, and zinc, were all predominantly controlled by organics.

The predicted leaching modelled well against actual data for iron, copper, thorium and zinc, however for other elements the modelled leaching was underestimated or overestimated using the same SHA input value presented in Table 7-5. Examples of this can be seen in Figure 7-57 for cadmium, copper, manganese and zinc.

The predicted leaching was underestimated for cadmium and copper, indicating that the SHA value was too high. Conversely, the predicted leaching for manganese was overestimated, but correlated well with actual leach data for zinc. This again highlights the competitive adsorption effects occurring between the cations for the active organic sites that are not accounted for in the LeachXST™ geochemical modelling.

It is recommended that further research be conducted towards improving the NICA Donnan model in the LeachXST™ software to accommodate for the different binding properties of cations to active organic sites.
Figure 7- 57: Predicted and measured pH dependent leaching of cadmium, copper, manganese and zinc from Manning Light soil and the predicted speciation controlling their solubility.
7.11 pH dependent leaching of Merredin and Newdegate agricultural soils

The pH dependent leaching behaviour for a range of species from Merredin and Newdegate soils from the Wheatbelt area of WA are illustrated in Figures 7-58 to 7-61. A full suite of analytes measured for these soils can be found in Appendix E. The analytical detection limits for all species analysed in the two soils were the same, with the exception of aluminium, boron, barium, cobalt lithium, nickel and zinc, where the detection limit was higher in the Newdegate soil.

Several species were measured close to or below the detection limit of the analysis in these soils and therefore any changes in leaching behaviour for these elements could not be determined. For both soils, this included arsenic, cadmium, mercury, lithium, molybdenum, antimony, selenium, and tin, and nickel for Merredin soil. Leaching concentrations of lead and fluoride were also below the detection limit of the analysis, except at extreme acidic pH conditions and extreme alkaline pH conditions respectively.

Figure 7-58: pH dependent leaching of a range of species from Merredin and Newdegate soils
Figure 7-59: pH dependent leaching of a range of species from Merredin and Newdegate soils
Figure 7-60: pH dependent leaching of a range of species from Merredin and Newdegate soils
Figure 7-61: pH dependent leaching of a range of species from Merredin and Newdegate soils

For the majority of species, the pH dependent leaching profiles in Merredin soil were comparative to Newdegate soil, but with consistently higher leaching concentrations. This is likely due to the higher soluble organics present in Merredin soil being available for complexing and mobilising species from the soil matrix. This was confirmed by the higher DOC leaching concentrations from Merredin soil, comparative to Newdegate soil (Figure 7-59). In contrast, copper and zinc produced higher leaching concentrations in the Newdegate sample.

Phosphorus leaching from Merredin soil was shown to be higher than Newdegate soil at their natural pH (data point denoted by * on the chart) (Figure 7-60). This observation was unexpected due to the slightly higher PRI for Merredin soil compared to the Newdegate soil (section 6.4, Table 6-7). This highlights that the PRI measured for a soil may not always reflect the maximum phosphorus retention capability of the soil unless the PRI is measured at the optimum pH for maximum retention, as appears to be the case for Newdegate soil.

Leaching of sodium in both soils was shown to be availability controlled, as shown in Figure 7-62. The increase in sodium leaching in the alkaline pH range was due to the addition of sodium hydroxide to the leaching solutions to achieve the final alkaline pH eluates in the test.
7.12 Solubility controlling processes influencing leaching of species from Merredin soil

LeachXSTM geochemical modelling was applied to the pH dependent leach data of Merredin soil to determine the processes likely to be controlling leaching for a range of species, and to predict the speciation in the liquid and solid phases of the matrix across the pH range tested.

The geochemical input parameters used for modelling are presented in Table 7-6.

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<td>L/S</td>
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<td>Clay</td>
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The values used in the model were all measured values with the exception of the carbonate concentration, which was estimated. Merredin soil was classified as a kandasol (Chapter 3;
methodology), which is categorised as being non-calcerous throughout its soil profile\(^{47}\) (based on *The Australian Soil Classification* by Isbell, 2002), and therefore does not contain carbonate. This was confirmed by the varying the carbonate concentration, which did not affect the modelling of calcium, irrespective of the concentration that was input in the model. An arbitrary value of 0.75 times the calcium concentration was used for completeness.

The following geochemical modelling charts illustrate the actual pH dependent leach data (red dots) of Merredin soil against modelled predicted behaviour (red dashed line) for a range of species. The charts also illustrate the solubility behaviour and the partitioning of species across the solid and liquid phases that are predicted to be controlling leaching.

**7.12.1 Solubility controlling minerals in Merredin soil**

Quartz and zinc silicate were predicted to be the solubility controlling minerals influencing the leaching of silicon and zinc respectively (Figures 7-63 and 7-64). The presence of quartz in Merredin soil constitutes approximately 40% of the soil, hence the solubility of this mineral dominated the leachability of silicon. Zinc silicate was shown partly control the solubility of zinc, and this was predicted to occur in the approximate pH range of 8.5 to 12.

![Figure 7-63: Predicted and measured pH dependent leaching of silicon from Merredin soil and predicted speciation controlling solubility](image)

\(^{47}\) Or to a depth of 0.2m if the A1 horizon is weakly developed.
7.12.2 Adsorption to clay

Clay adsorption was the dominant process controlling the solubility of potassium and lithium from Merredin soil across the pH range 1 to 12. For the majority of other species this adsorption process played an important role in addition to other controlling processes, such as adsorption to inorganic humic and fulvic acids and/or aluminium/iron hyd(roxides).

Most species were controlled by the three adsorption processes, but to varying degrees depending on the element, as shown by example with calcium (Figure 7-65), magnesium, barium, manganese and strontium (Figure 7-66).

Figure 7-64: Predicted and measured pH dependent leaching of zinc from Merredin soil and the predicted speciation controlling solubility

Figure 7-65: Predicted and measured pH dependent leaching of calcium from Merredin soil and the predicted speciation controlling solubility
Figure 7-66: Predicted and measured pH dependent leaching of magnesium, barium, manganese and strontium from Merredin soil and the predicted speciation controlling solubility

For other species, such as aluminium, iron and uranium, the adsorption processes controlling leaching were associated with clay and insoluble humic and fulvic acids.
7.12.3 Adsorption to iron and aluminium (hydr)oxides

Phosphorus, molybdenum and selenium were predicted to be predominantly controlled by adsorption to iron and aluminium (hydr)oxide surfaces, across the majority of the pH range tested. Clay adsorption was predicted to play an important role at acidic and alkaline pH conditions as shown in Figure 7-67.

Figure 7-67: Predicted and measured pH dependent leaching of molybdenum, phosphorus and selenium from Merredin soil and the predicted speciation controlling solubility
7.12.4 Adsorption to organics (humic and fulvic acids)
Chromium, iron, uranium and thorium were predominantly controlled by adsorption to organic particulates. Leaching was associated with complexation to soluble humic and fulvic acids in the solution phase across the full pH range for thorium. For chromium, iron and uranium, the cationic metals were predicted to be freely available in solution or complexed with soluble humic and fulvic acids, dependent on the pH. Species predicted to be partly controlled by adsorption to insoluble humic and fulvic acids were aluminium, calcium, magnesium, barium, manganese, nickel, strontium and zinc.

7.12.5 Leaching influenced by changes in surface charge of soil particles
The leaching of chloride and sulphate linearly increased with increasing pH in Merredin soil, similar to Manning Heavy and Manning Light soils. It is believed that the solubility of chloride and sulphate is being influenced by the change in surface charge characteristics of the soil with changing pH, as discussed in section 7.9.2. This behaviour could not be predicted using the geochemical modelling parameters used.

7.13 Solubility controlling processes influencing leaching of species from Newdegate soil
Geochemical modelling using LeachXS™ was applied to the pH dependent leach data of Newdegate soil to determine the processes likely to be controlling leaching for a range of species across the pH range tested, and to predict the speciation in the liquid and solid phases of the soil matrix across the pH range.

The geochemical input parameters used for modelling leach data for Newdegate soil are presented in Table 7-7.

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<table>
<thead>
<tr>
<th>Input specification</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Solved fraction DOC</td>
<td>Varied with pH</td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>5.500E-01 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>2.550E-04 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>7.040E-03 kg/kg</td>
</tr>
<tr>
<td>CO3=0.75XCa conc.</td>
<td></td>
</tr>
</tbody>
</table>
Input values for the reactive solid surfaces listed in the above table were estimated for the modelling. Clay was estimated to be 3.6% of its dry weight based on a report by McGhie and Posner (1981) that stated Newdegate soil was approximately 4%; and that the clay content in Newdegate soil reported in the soil amendment pot trials in Clarendon et al. (2010) was slightly lower than Merredin soil (which had been measured to be 4.4% of its dry weight).

The HFO content was estimated as half that used for modelling Merredin soil. This was based on the iron oxide content measured in Newdegate soil being approximately 50% that measured in Merredin soil. The SHA value (which relates to the insoluble humic and fulvic acid in the soil) was estimated to be the same as that used for modelling Merredin soil. Estimations for carbonate concentration were modelled using equivalent to 10% to 150% of the calcium concentration, however the carbonate concentration did not have any impact on the modelling of calcium, irrespective of the value inputted into the model. An arbitrary value of 0.75 times the calcium carbonate concentration was used in the model for completeness.

The following geochemical modelling charts illustrate the actual pH dependent leach data (red dots) of Newdegate soil against modelled predicted behaviour (red dashed line) for a range of species. The charts also illustrate the solubility behaviour and the partitioning of species across the solid and liquid phases that are predicted to be controlling leaching.

The mechanisms predicted to be controlling leaching of particular constituents from Newdegate soil were very similar to the predictions for Merredin soil. This was expected since their leaching profiles were similar in shape, but with higher leaching concentrations for Merredin soil due to the association of more soluble humic and fulvic acids complexing with species and mobilising them from the solid phase.

7.13.1 Solubility controlling minerals in Newdegate soil
Quartz was predicted to control the solubility of silicon in Newdegate soil. This was the only solubility controlling mineral predicted to be present.
7.13.2 Adsorption to clay
As was the case for Merredin soil, adsorption to clay was also an important process controlling leaching behaviour for the majority of species in Newdegate soil. Potassium was predominantly controlled by clay across the full pH range tested. Some species were partly controlled by other adsorption processes; namely adsorption to humic and fulvic acids and/or reactive aluminium hydr(oxide) surfaces. For example, magnesium, manganese, nickel and lead were controlled by adsorption to clay, organics and iron/aluminium hydr(oxide surfaces). Aluminium, calcium, iron and strontium were controlled by adsorption to clay and organics. These are discussed further in section 7.13.3 and 7.13.5 below.

7.13.3 Adsorption to iron and aluminium (hydr)oxides
The dominant factor predicted to be controlling leaching of phosphorus from Newdegate soil was adsorption to reactive aluminium/iron (hydr)oxide sites. This sorption process, in addition to clay, was also predicted to control the mobility of selenium (Figure 7-68), molybdenum, phosphorus and antimony (Figure 7-69).

Figure 7-68: Speciation predicted to be controlling leaching of selenium and molybdenum from Newdegate soil
Figure 7-69: Speciation predicted to be controlling leaching of molybdenum, phosphorus and antimony from Newdegate soil

7.13.4 Chloride and sulphate leaching

The leaching of chloride from Newdegate soil, shown in Figure 7-70, was consistent with trends observed in the other WA agricultural soils. The solubility of chloride is believed to be controlled by the change in surface charge of the soil particles with change in pH.

Figure 7-70: Increased leaching of chloride with increasing pH
7.13.5 Adsorption to organics (humic and fulvic acids)
In addition to clay, adsorption to organics was also predicted to be an important factor controlling most species in Newdegate soil. This can be seen from the geochemical speciation of aluminium, calcium, iron and strontium (Figure 7-72).

Figure 7-71: Cations controlled by adsorption to organics and clay in Newdegate soil
Conclusions

The pH dependent leach test allows the user to determine whether potential leachables from a material are likely to be a concern in different pH environments. Applying LeachXS geochemical modelling to the pH dependent leach data allows predictions to be made on the speciation of elements, as well as the partitioning of the species across the solid and liquid phases. The ability to predict speciation in solution for potentially toxic metals, such as copper, can prove highly beneficial for assessing the likely bioavailability and hence potential impact a material is likely to have on its surrounding environment.

The maximum concentration of an element available for leaching was found to be less than its total concentration for the majority of species in the soil materials. Total concentration is therefore not recommended as key criteria for assessing a materials impact on the environment as this will lead to an overly conservative evaluation and may unjustly dismiss materials as being unsafe for re-use.

The leaching behaviour of species from Alkaloam®, Red Lime™ and the WA soils were specific for each element across the pH range 0.5 to 12. Elements were predicted to be controlled by incorporation within mineral phases or by adsorption processes, such as adsorption to clay, organics and iron/aluminium (hydr)oxides.

The amount of iron/aluminium (hydr)oxides required to model the leach data well was less than the total amount analysed. This is likely due to the surfaces of the aluminium and iron hydr(oxide)s not being 100% active in the soil matrices, which is the assumption made in the modelling software.

For species controlled by adsorption to organics, it was noted that different SHA values would be required to accurately model leach data for each element in the soils. Using a single SHA value in the model generated underestimations for some elements, and overestimations for others. This limitation was believed to be due to competitive adsorption of cationic species for the active organic sites that could not be accounted for using the Nonideal Competitive Adsorption (NICA) Donnan model incorporated in the LeachXS software. This discrepancy was found to be most prevalent in the agricultural soils where most elements were controlled by organics.

Geochemical modelling of the actual leach data for Alkaloam®, Red Lime™ and the WA soils predicted the following speciation to be controlling leaching;

187
**Alkaloam®:**

Adsorption to iron/aluminium (hydr)oxides was predicted to be the predominant factor controlling leaching of phosphorus, magnesium, strontium, manganese, molybdenum, and lead from Alkaloam®.

Chloride was availability controlled in the acidic pH range and controlled by adsorption to clay at neutral to alkaline pH range.

Thorium and uranium were controlled by adsorption to organics.

The leaching of some elements in Alkaloam® was predicted to be controlled by the following solubility mineral phases:

<table>
<thead>
<tr>
<th>Element</th>
<th>Controlling Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>Gibbsite, TCA6, Albite or Analbite (surrogates for DSP) and CO3-Hydrotalcite</td>
</tr>
<tr>
<td>Barium</td>
<td>Barite</td>
</tr>
<tr>
<td>Calcium</td>
<td>Calcite, TCA (minor – Fluorite and TCP)</td>
</tr>
<tr>
<td>Silicon</td>
<td>Albite or Analbite (surrogates for DSP)</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Fluorite</td>
</tr>
<tr>
<td>Magnesium</td>
<td>CO3-Hydrotalcite, Magnesite</td>
</tr>
<tr>
<td>Strontium</td>
<td>Strontianite</td>
</tr>
<tr>
<td>Iron</td>
<td>Goethite (pH2-8) &amp; Ferrihydrite (pH&gt;8)</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zinc Silicate</td>
</tr>
</tbody>
</table>

Albite and analbite modelled silicon well, but were believed to be surrogates of the desilication product (DSP) present in Alkaloam®.

The majority of species in Alkaloam® were partly controlled by adsorption to clay at the extreme acidic and/or alkaline pH. Potassium was predominantly controlled by clay in both Alkaloam® and Red Lime™.

**Red Lime™**

With the exception of calcium and silicon, the leaching behaviour for the majority of species in Red Lime™ showed different profiles to that in Alkaloam®. This was believed to be due to the additional calcium minerals and higher organic content present in Red Lime™.
Manganese, lead, zinc, nickel and cadmium were predicted to be controlled by adsorption to organics and iron/aluminium (hydr)oxides.

Chromium, thorium and uranium were controlled by organics.

The leaching of some elements in Red Lime™ was predicted to be controlled by the following solubility mineral phases:

<table>
<thead>
<tr>
<th>Element</th>
<th>Controlling Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium:</td>
<td>Amorphous Aluminium Hydroxide, TCA, Laumonite and CO3-Hydrrotalcite</td>
</tr>
<tr>
<td>Barium:</td>
<td>Barite</td>
</tr>
<tr>
<td>Calcium:</td>
<td>Calcite, Laumonite, Fluorite, TCA (minor –TCP)</td>
</tr>
<tr>
<td>Silicon:</td>
<td>Laumonite</td>
</tr>
<tr>
<td>Fluoride:</td>
<td>Fluorite</td>
</tr>
<tr>
<td>Phosphorus:</td>
<td>TCP</td>
</tr>
<tr>
<td>Magnesium:</td>
<td>CO3-Hydrrotalcite</td>
</tr>
<tr>
<td>Strontium:</td>
<td>Strontianite</td>
</tr>
<tr>
<td>Iron:</td>
<td>Ferrihydrite</td>
</tr>
</tbody>
</table>

Iron was controlled by goethite and ferrihydrite in Alkaloam® and only ferrihydrite in Red Lime™. This is likely to be due to the higher concentration of organics inhibiting the formation of goethite in Red Lime™.

The adsorption of species to clay was an important process controlling the solubility of many species from Red Lime™ in the acidic pH range; namely aluminium, calcium, silicon, magnesium and fluoride.

Chloride was availability controlled in Red Lime™.

**Bassendean soil:**
Bassendean soil exhibited minimum phosphorus leaching at the soils natural pH, but potentially leached phosphorus across the acidic pH range. Phosphorus leaching is therefore not likely to be an issue in this soil unless its environment becomes more acidic, for example, if used for agricultural farming.
The pH dependent leaching of organics from Bassendean soil suggests that insoluble organic carbon is predominantly present in the soil across a pH range 2 to 9. At extreme acidic and alkaline pH the organic carbon becomes increasingly mobile.

The leaching of some elements in Bassendean soil was predicted to be controlled by the following solubility mineral phases;

<table>
<thead>
<tr>
<th>Element</th>
<th>Controlling Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium:</td>
<td>Amorphous aluminium hydroxide, Analbite</td>
</tr>
<tr>
<td>Calcium:</td>
<td>Calcite</td>
</tr>
<tr>
<td>Silicon:</td>
<td>Analbite</td>
</tr>
<tr>
<td>Iron:</td>
<td>Ferrihydrite</td>
</tr>
</tbody>
</table>

Phosphorus and selenium were predominantly controlled by adsorption to iron/aluminium (hydr)oxides in Bassendean soil.

Leaching of the majority of species from Bassendean soil was controlled by adsorption to clay and adsorption to organics (insoluble humic and fulvic acids).

The pH dependent leaching behaviour of chloride and potassium in Bassendean soil was noticeably different to that in the agricultural soils. In Bassendean soil, chloride exhibited a ‘V’ shaped profile across the pH range 1 to 12. In the agricultural soils the leaching of chloride increased linearly with increasing pH, suggesting that solubility was controlled by the variable surface charge on the soil particles with changing pH. Leaching of potassium from Bassendean soil decreased with increasing pH up to pH 8 and then increased at extreme alkaline conditions. The speciation controlling solubility of potassium in this soil could not be ascertained, and did not model well using clay adsorption when predicted as a controlling process. In the agricultural soils however, potassium was controlled by adsorption to clay.

Copper, chromium, uranium and thorium were controlled by adsorption to insoluble organics in the solid phase with association with soluble organics in the liquid phase.

Manning Heavy soil:

With the exception of cobalt and uranium, the leaching of most species in Manning Heavy soil exhibited similar behaviour to that observed in Manning Light soil, but at higher leaching concentrations. This was believed to be due to the higher amount of soluble organics present in Manning Heavy soil that were potentially available for complexing and
mobilising species from the soil. This was confirmed by corresponding higher DOC leaching concentrations measured in Manning Heavy soil.

Due to the high clay content, the majority of species in Manning Heavy soil were controlled by adsorption to clay in the solid phase; e.g. barium, calcium, fluoride, potassium, magnesium, manganese and strontium. Adsorption to organics also played an important role but to a lesser extent. In the solution phase the mobility of most species were associated with complexation to soluble humic and fulvic acids, rather than being available as free ions. Uranium, copper and zinc were controlled predominantly by adsorption to organics in Manning Heavy soil.

Phosphorus was predominantly controlled by adsorption to iron/aluminium (hydr)oxides.

Quartz was the only solubility controlling mineral phase present in Manning Heavy and Manning Light soil. This controlled the leachability of silicon.

**Manning Light soil:**
The reactive solid surfaces that best modelled the leach data for the Manning Light soil were noticeably lower than the concentrations measured in the other WA soils modelled. This was indicative of the poor metal retention properties of Manning Light soil, comparative to the other soils tested.

Adsorption to organics was the most dominant factor controlling leaching for the majority of species from Manning Light soil.

Clay adsorption was not an important process for controlling solubility of species in Manning Light soil.

Phosphorus was predominantly controlled by adsorption to iron/aluminium (hydr)oxides across the pH range of 0.5 to 9. Molybdenum was controlled by this adsorption process across the pH range 3 to 11.

**Merredin soil:**
The pH dependent leaching behaviour of most species in Merredin soil exhibited similar profiles to that in Newdegate soil, but at higher leaching concentrations. This was believed to be due to the higher amount of soluble organics present in Merredin soil that were
potentially available for complexing and mobilising species from the soil. This was confirmed by corresponding higher DOC leaching concentrations measured in Merredin soil.

Phosphorus leaching was measured to be higher in Merredin soil than Newdegate soil at their natural soil pH. This observation was in contrast to the PRI values measured for these soils (Merredin measured a slightly higher PRI than Newdegate, implying a higher phosphorus retention capability).

The mineral phases quartz and zinc silicate were predicted to control the solubility of silicon and zinc respectively from Merredin soil. Zinc silicate partially controlled zinc across the pH range of approximately 8.5 to 12.

Clay adsorption was the dominant process controlling the solubility of potassium and lithium across the full pH range 0.5 to 12. For the majority of other species, clay adsorption partly controlled solubility in addition to other adsorption processes. Aluminium, iron and uranium were controlled by adsorption to clay and organics. Calcium, magnesium, barium, manganese and strontium were controlled by adsorption to clay, organics and iron/aluminium (hydr)oxides.

Phosphorus, was predominantly controlled by adsorption to iron/aluminium (hydr)oxides. Molybdenum and selenium were predominantly controlled by adsorption to iron/aluminium (hydr)oxides across a pH range 2 to 10 and adsorption to clay at high acidic and alkaline pH.

Chromium, iron, uranium and thorium were predominantly controlled by adsorption to organics.

The solubility of chloride and sulphate was influenced by the variable surface charge of the soil particles with changing pH (anion adsorption will be favoured under more acidic conditions due to the particle surface being more positively charged. Anion adsorption will be repelled under more alkaline conditions due to the more negatively charged particle surface). This was shown by a linear increase in leaching concentrations with increased pH. This leaching behaviour could not be predicted using LeachXS™ geochemical modelling.

**Newdegate soil:**
Quartz was the only solubility controlling mineral phase in Newdegate soil, which controlled the solubility of silicon.
Clay adsorption was a dominant factor controlling solubility of the majority of species from Newdegate soil, as was the case for Merredin soil. Other adsorption processes partly controlled some species. For example, manganese and magnesium nickel, lead and zinc were controlled by adsorption to clay, organics and iron/aluminium (hydr)oxides. Aluminium, calcium, iron and strontium were partly controlled by adsorption to clay and organics. Molybdenum, selenium and antimony were partly controlled by adsorption to clay and iron/aluminium (hydr)oxides.

Copper, chromium, uranium and thorium were predominantly controlled by organics.

Phosphorus was controlled by adsorption to iron/aluminium (hydr)oxides across the full pH range 0.5 to 12.

Chloride and sulphate leaching showed similar behaviour to Merredin soil, and was influenced by the variable surface charge of the soil particles with changes in pH.

### 7.15 Recommendations

Determine what processes are controlling the leaching of potassium and chloride in Bassendean soil.

Optimise the geochemical modelling for vanadium and selenium in both Alkaloam® and Red Lime™ to determine the processes controlling the leaching of these elements.

Determine whether the NICA Donnan model in the LeachXS™ software can be improved to accommodate the different binding properties of cations to active organic sites.

Optimise the geochemical modelling to predict leaching of species influenced by the variable surface charge of particles with changes in pH to correlate well with actual leach data.

Include cobalt as a reactive constituent in the LeachXS™ software to allow geochemical speciation modelling to be conducted on this element in different soils.
Chapter 8

Changes in Leaching of WA Soils when Amended with Alkaloam®

8.1 Introduction

The sandy soils located along the West Australian Swan Coastal Plain and some of the agricultural soils in the WA Wheatbelt and Peel Harvey region are renowned for their poor nutrient retention properties, providing challenges for agricultural farmers to appropriately manage these soils while preventing overuse of fertilisers. Extensive field studies on the use of soil amendments, such as Alkaloam®, have demonstrated that the nutrient retention properties of these soils can be improved with adequate amelioration (Summers et al., 1996b; Summers, 2001).

Studies have shown that economic and environmental benefits can be gained from soil amelioration, through increased pasture growth and reduced nutrient mobility into groundwater (Summers et al., 1987; Summers et al., 1996a). However very little is known about how Alkaloam® amelioration will change the leaching characteristics of different species within the soil and how these changes may be influenced by changes in soil pH. Research conducted by Summers and Pech (1997) reported that there were no differences detected in the water quality of catchments amended with 20t/ha Alkaloam® and comparable catchments based on the heavy metals analysed. This suggests that there were negligible changes in the leaching behaviour for the soils amended in this trial. This chapter investigates changes to the leaching characteristics of a range of species in the WA soils when amended with 6.25g/kg Alkaloam® (equivalent to a 10t/ha top dressed application rate) at varying pH.

pH dependent leach test data for soils from the WA Swan Coastal Plain and agricultural soils were each compared against the corresponding soil amended with 6.25g/kg Alkaloam® to illustrate differences in leaching behaviour. A combination of pH dependent leach test data and LeachXS™ geochemical modelling was used to predict the partitioning of major, minor and trace elements in these amended soils, particularly in relation to the release of a range of key elements, phosphorus retention capability and adsorption of organic matter. The geochemical modelling involved fitting up to 24 elements simultaneously.

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48 Ag, Al, As, Cu, Cr, Hg, P, Pb, N, Se.
49 LeachXS™ geochemical modelling assumes all sites and conditions in the soil are at equilibrium.
The modelling required an iterative approach, with the selection of mineral phases and other estimated input parameters modified after each run to improve the fit against measured leach data. The modelling results presented in this chapter were considered the best fit against actual leach data for the majority of species and provide a best case prediction of the processes controlling leaching in the soils.

Table 8-1 shows the natural pH of the WA soils and the change in soil pH on amending with 6.25g/kg Alkaloam®. The differences in pH reflect anticipated changes in soil pH in the top 1cm of soil.

<table>
<thead>
<tr>
<th>soil</th>
<th>Unamended pH</th>
<th>Amended with 6.25g/kg Alkaloam® 10t/Ha</th>
<th>pH increase in soil due to Alkaloam® amendment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manning Light</td>
<td>5.89</td>
<td>6.453</td>
<td>0.563</td>
</tr>
<tr>
<td>Manning Heavy</td>
<td>5.55</td>
<td>6.01</td>
<td>0.46</td>
</tr>
<tr>
<td>Merredin</td>
<td>6.79</td>
<td>7.2</td>
<td>0.41</td>
</tr>
<tr>
<td>Newdegate</td>
<td>6.08</td>
<td>7.42</td>
<td>1.34</td>
</tr>
<tr>
<td>Bassendean</td>
<td>8.43</td>
<td>8.51</td>
<td>0.08</td>
</tr>
<tr>
<td>Spearwood</td>
<td>6.85</td>
<td>7.62</td>
<td>0.77</td>
</tr>
</tbody>
</table>

An approximate increase of 0.4 to 0.6 pH units was observed in Manning Light, Manning Heavy and Merredin soils when amended with 6.25g/kg (10t/ha equivalent) Alkaloam®. With the exception of Newdegate soil, these increases were consistent with pH differences observed in the soil amendment field trials (Clarendon et al., 2010) in the 2nd year of the trial. The increase in pH from amending Newdegate soil was almost double that reported for the field trials. The pH increase was however consistent with the third growing season of the corresponding pot trials. Lower pH changes in the field, relative to the laboratory data, may have been due to the drought conditions experienced at the Newdegate trial site.

The leaching behaviour of some species may change due to the pH differences from Alkaloam® amelioration, in addition to the effect of Alkaloam® itself. In the case of

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50 Pot trials conducted due to insufficient data obtained from Newdegate field trial as a result of very dry weather conditions.
Bassendean soil, where very little pH change was observed between the amended and unamended soil, any differences in leaching behaviour will be attributed to the effect of Alkaloam®.

8.2 Changes in leaching of Bassendean soil when amended with 6.25g/kg Alkaloam®

Figures 8-1 and 8-2 illustrate the pH dependent leaching behaviour of Bassendean soil with and without 6.25g/kg Alkaloam® amendment for a range of elements (green and blue lines) and their comparison against leaching in Alkaloam® (red line). The natural pH of these materials is denoted as * on the charts. The pH dependent leaching profiles for the full suite of analytes measured is in Appendix G.

Some heavy metals and other species such as arsenic, beryllium, cadmium, cobalt, copper, chromium, fluoride, gallium, mercury, lithium, molybdenum, lead, antimony, selenium, tin, vanadium and uranium were detected in both the soil and amended soil extracts at concentrations close to or below the analytical detection limit. Within the noise of the measurements, no change in leaching behaviour from a 6.25g/kg Alkaloam® amelioration rate could be ascertained for these species.

It is important to note that the solution pH impacted upon analytical methodology detection limits, whereby increased detection limits were recorded for low pH solutions. This creates an artefact within the graphical analysis as the data moves from one baseline to another. This anomaly only occurred with samples at or below detection limit.
Figure 8-1: pH dependent leaching of Bassendean soil amended with 6.25g/kg Alkaloid® and comparison with the individual matrices.
Ameliorating Bassendean soil with 6.25g/kg Alkaloam® did not significantly change the leaching behaviour of the majority of species in the amended soil. Leachability appeared to be higher in the amended soil across the acidic pH range, in particular at pH 2. This corresponded with an increase in DOC at the same pH (Figure 8-1), suggesting that increased mobility of metals in the amended soil at pH 2 are likely to be associated with complexation to DOC.

Silicon showed the greatest impact from amending the soil with Alkaloam®, with leaching increasing by half an order of magnitude in an approximate pH range of 2 to 6. The higher leaching concentration of silicon in the amended soil was attributed to the additional silicon
present in Alkaloam®. Increased leaching of this element with decreasing pH was due to dissolution of the mineral albite, as predicted by geochemical modelling.

Magnesium, strontium, calcium and manganese showed similar leaching profiles, with increased leaching at extreme acidic pH environments. Using geochemical modelling these species were predicted to be controlled by similar sorption processes; namely adsorption to organics and aluminium/iron (hydr)oxides, with the exception of calcium. Calcium was predicted to be predominantly controlled by the mineral calcite.

The pH dependent leaching profiles of chloride and molybdenum were noticeably different in Bassendean soil and Alkaloam® (Figures 8-1 and 8-2). The leaching behaviour of these elements in the amended soil reflected similar behaviour to the soil itself, and appeared not to be influenced by additional concentrations introduced from the Alkaloam® amendment. This was despite the high leaching properties of chlorine and molybdenum at pH>6.5 in Alkaloam®.

Geochemical modelling predicted that at pH>6.5 the mechanisms controlling leaching of molybdenum and chloride in Alkaloam® and Bassendean soil were different. In Bassendean soil molybdenum was bound in the soil matrix by adsorption to insoluble organics. In Alkaloam® molybdenum leached out and was associated as free ions in the solution phase (see Chapter 7; section 7.3.3 and section 7.7.3 for Alkaloam® and Bassendean soil respectively). Chloride was controlled by adsorption to clay in Alkaloam® and by changes in the surface charge of the soil particles with pH in Bassendean soil (see Chapter 7; section 7.3.2 and section 7.7.2 respectively).

The leaching behaviour of manganese, zinc and iron in the amended Bassendean soil were significantly different compared to the individual matrices. The leaching concentrations measured for manganese and zinc were higher across the acidic pH range, and higher across the full pH range for iron (Figure 8-3).
The increased mobilisation of these elements corresponded with increased leaching of dissolved organic carbon (DOC) in the amended soil, indicating that some of the organic acids present in the matrix are forming soluble complexes with these cationic species. This was backed up by geochemical speciation modelling that confirmed these elements are adsorbed to organics across the pH range in question (Figure 8-4).

Other species predicted to be controlled by adsorption to organics, such as copper, chromium, uranium and thorium did not show increased leaching in the amended soil relative to the individual matrices. This indicates that soluble organic acids favour complexation with specific cations, making them more susceptible to dissolution than other species.
A comparison of the pH dependent leach test data for phosphorus in Alkaloam® amended and unamended Bassendean soil (Figure 8-5) illustrates that Alkaloam® can increase the phosphorus retention properties in this soil type across an approximate pH range of 3 to 6 at a 6.25g/kg amelioration rate.

The pH of acidic WA agricultural soils lie typically in this pH range, consequently soils with characteristics similar to the Bassendean sandy soil (e.g. Manning Light) are likely to benefit from Alkaloam® amelioration at this application rate.
8.3 Solubility controlling processes influencing leaching of species from Bassendean Soil with and without 6.25g/kg Alkaloam® amendment

The geochemical input parameters used for modelling the actual leach data for Alkaloam® amended Bassendean soil are presented in Table 8-2. Input values into the model were based on the same data used for modelling Bassendean sand (Chapter 7, Section 7.7) and 0.625% of that inputted for Alkaloam®.

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solved fraction DOC</td>
<td>Varied with pH</td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>1.488E-01 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>3.528E-03 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>1.985E-03 kg/kg</td>
</tr>
<tr>
<td>CO3 conc 8063mg/kg</td>
<td></td>
</tr>
</tbody>
</table>

Mineral phases that were predicted to be controlling species in the individual matrices were also added to the model. Carbonate concentration was estimated based on the data used for the unamended soil and a proportional amount included due to Alkaloam® amelioration.
8.3.1 Minerals controlling solubility in Bassendean soil amended with 6.25g/kg Alkaloam®

The following geochemical modelling charts illustrate the actual pH dependent leach data (red dots) against predicted leaching behaviour (red dashed line) for a range of elements. The charts also illustrate solubility behaviour and the partitioning of species across the solid and liquid phases predicted to be controlling leaching for particular elements.

With the exception of iron, the leaching of Bassendean soil amended with 6.25g/kg Alkaloam® modelled well with the same mineral solubility as the unamended soil. These were albite and amorphous aluminium hydroxide (Al(OH)₃) for aluminium, calcite for calcium and albite for silicon (Figure 8-6). This indicates that the solubility controlling minerals, Gibbsite, CO₃-hydrotalcite and TCA6 in Alkaloam®, did not influence leaching of these species at the ameliorant rate of 6.25g/kg.

Figure 8-6: Predicted mineral phases controlling leaching of aluminium, calcium and silicon from Bassendean soil amended with 6.25g/kg Alkaloam®
The leaching of iron was predicted to be controlled by adsorption to insoluble organics (in particular humic and fulvic acids) in the Alkaloam® amended Bassendean soil. In contrast, iron was also controlled by the mineral ferrihydrite in the individual matrices (Figure 8-7).

Figure 8-7: Predicted speciation in the solid phase controlling the leaching of iron from Bassendean soil amended with 6.25g/kg Alkaloam® and the individual matrices

Phosphorus leaching was predicted to be controlled by the solubility of tricalcium phosphate (TCP) mineral at alkaline pH>9 in Alkaloam® amended Bassendean soil (Figure 8-8). In contrast, this mineral did not control phosphorus in the unamended soil, indicating that the mineral has been introduced from the Alkaloam®.
For the majority of the pH range tested, the dominant process controlling phosphorus was adsorption to aluminium/iron (hydr)oxides.

Zinc was predicted to be predominantly controlled by the mineral zinc silicate at alkaline pH (Figure 8-9). Like TCP, this mineral phase has also been introduced with Alkaloam®, since zinc was controlled by organics in the unamended soil.
8.3.2 Adsorption to clay

Despite very little clay being present in Bassendean soil (approximately 1%), the majority of species were partly controlled by adsorption to clay, in addition to other sorption processes, such as adsorption to aluminium/iron (hydr)oxides and/or adsorption to insoluble organics. This indicates that clay sorption strongly controls the mobility of constituents in this soil.

Figures 8-10 and 8-11 illustrate the pH dependent leaching of magnesium, barium, manganese, nickel and strontium, highlighting the influence of clay sorption at different extents, in addition to other aforementioned sorption processes.

Overestimated leaching predictions based on the solid organic model inputs (illustrated as POM on the geochemical charts) were observed for manganese, barium and strontium, reflecting the competitive adsorption effects of the cations for active organic sites not accounted for in the modelling. This was discussed in Chapter 7.

![Graphs showing pH dependent leaching of magnesium, barium, manganese, nickel and strontium in Bassendean soil amended with 6.25g/kg Alkaloam®](image-url)

Figure 8-10: Influence of clay sorption controlling solubility of magnesium and barium in Bassendean soil amended with 6.25g/kg Alkaloam®
Clay adsorption was predicted to also control the solubility of potassium, however modelling output was a poor fit with the leach data and would require further investigation to confirm this process was an important factor for this species.

**8.3.3 Solubility controlled by surface charge of particles**
The solubility of chloride increased with increasing pH, similar to the unamended soil. This leaching behaviour suggests that the mobility of chloride is controlled by changes to the surface charge of the soil particles with changes in pH.
8.3.4 Adsorption to Iron/aluminium (hydr)oxides

The predicted mobility of antimony, selenium, molybdenum and fluoride was controlled by adsorption to aluminium/iron (hydr)oxides as well as clay (Figure 8-12). This was consistent with the mechanisms controlling these species in the unamended soil. Phosphorus was also controlled by this process at pH<9. This has been discussed previously in Section 8.3.1.

Figure 8-12: Leaching of species from Bassendean soil amended with 6.25g/kg Alkaloam® controlled by adsorption to aluminium/iron (hydr)oxides
8.3.5 Adsorption to organics (humic and fulvic acids)

The solubility of thorium, uranium, copper and chromium from the Alkaloam® amended Bassendean soil was predominantly controlled by adsorption to insoluble humic and fulvic acids. Their mobilisation from the solid phase was strongly associated with complexation to soluble organic acids (Figure 8-13 and Figure 8-14). The organic acids complexing with these metals were not believed to be associated with the increased DOC observed in the amended soil\textsuperscript{51}, because their leaching concentrations were very similar to those in the individual matrices. It is likely that they are complexing with similar organic acids present in the individual matrices.

The predicted leaching for chromium was shown to be underestimated based on the value of organic material inputted into the model (Figure 8-14). Dissolution via soluble humic and fulvic acids therefore may be more significant than illustrated on the geochemical chart.

Adsorption to insoluble humic and fulvic acids was also predicted as an important process for many other species in the amended soil, such as magnesium, barium, manganese, nickel, strontium, lead and vanadium. This occurred at the amended soils natural pH and at varying pH ranges specific to the element.

Figure 8- 13: Predicted and measured leaching of thorium from Bassendean soil amended with 6.25g/kg Alkaloam® controlled by association with soluble organics

\textsuperscript{51} These were complexed with manganese, zinc and iron, as previously discussed.
Figure 8-14: Predicted and measured leaching of uranium, copper and chromium from Bassendean soil amended with 6.25g/kg Alkaloam® controlled by association to organics

8.4 Changes in leaching of Manning Light soil when amended with 6.25g/kg Alkaloam®

Figures 8-15 to 8-17 illustrate the pH dependent leaching of a range of analytes in Manning Light soil amended with 6.25g/kg Alkaloam® and the pH dependent leaching of the individual matrices, for comparison. The total concentration of analytes in Manning Light soil are also plotted to illustrate the relative amount remaining bound in the soil matrix. The natural pH of the materials is denoted as * on the charts.
Some heavy metals such as arsenic, boron, barium, beryllium, cadmium, cobalt, chromium, gallium, mercury, lithium, molybdenum, lead, antimony, selenium, tin, vanadium and uranium were detected in both the soil and amended soil extracts at concentrations close to or below the analytical detection limit. Within the noise of the measurements, no changes in leaching behaviour from Alkaloam® amelioration could be ascertained for these species. 

For some analytes the low pH solutions had a higher detection limit than the high pH solutions, which was due to the analytical methodology. For analytes measured at or below the detection limit, this created an artefact within the graphical analysis as the data moves from one baseline to another. Only significant concentration changes are therefore described hereafter; however a full suite of the species measured can be found in Appendix G.

The maximum concentration available for leaching for all species, except chloride and sulphur, in Manning Light soil was less than the corresponding total concentration (Figures 8-15 and 8-16). This indicates that a portion of each species is permanently bound in the soil matrix and will not be available for leaching. Environmental assessments based on total concentration can be a conservative estimation of what will leach in the field, and therefore are unlikely to accurately assess whether a material could adversely impact on the environment. Total concentration is not recommended as a sole basis for assessing industrial by-products for re-use as it may lead to unjustly rejecting materials that may otherwise be suitable and safe to use.

Data in Figures 8-15 to 8-17 illustrate that the leaching behaviour for the majority of species in Alkaloam® amended Manning Light soil reflect that of the unamended soil, suggesting that an Alkaloam® amelioration rate of 6.25g/kg is insufficient to significantly impact on leachability in this soil. This was particularly of interest for species such as calcium, magnesium, manganese, molybdenum, silicon and thorium, where the leaching profiles for the individual matrices were significantly different.
Figure 8-15: pH dependent leaching of a range of species from Manning Light soil amended with 6.25g/kg Alkaloam® and comparison to the individual matrices.
Figure 8-16: pH dependent leaching of a range of species from Manning Light soil amended with 6.25g/kg Alkaloam® and comparison to the individual matrices
Figure 8-17: pH dependent leaching of a range of species from Manning Light soil amended with 6.25g/kg Alkaloam® and comparison to the individual matrices

Exceptions to this were noted for copper, iron, silicon and zinc. A significant increase in the leaching concentrations of these elements was observed in the Alkaloam® amended soil, relative to the individual matrices (Figure 8-18). This corresponded with an increase in DOC (Figure 8-17), indicating that increased mobility of these species is likely to be associated with complexation to soluble organics that exhibit increased availability in the amended soil matrix. LeachXSTM geochemical modelling confirmed this, with silicon being the only exception. Silicon was predicted to be controlled by the solubility of quartz in both Alkaloam® and the soil. Hence the dissolution of additional quartz from Alkaloam® amendment was believed to contribute to the higher leaching concentration of silicon in the Manning Light amended soil.
Figure 8-18: Increased leaching concentrations in Manning Light soil amended with 6.25g/kg Alkaloam®, relative to the individual components

Due to the different detection limits reported for the pH dependent testing of the amended and unamended soil, it was difficult to ascertain whether a 6.25g/kg Alkaloam® amelioration rate would be capable of increasing the retention of metals.

The distinctive increase in PRI measured for this soil as a result of ameliorating with 6.25g/kg Alkaloam® however (reported in Chapter 6) suggests that phosphorus retention can be improved at this ameliorant rate. It is recommended that this investigation be repeated with standardised detection limits to determine if benefits from the retention of other species can be achieved at this ameliorant rate.
8.5 Solubility controlling processes influencing leaching of species from Manning Light Soil amended with 6.25g/kg Alkaloam®

Geochemical modelling was carried out on the pH dependent leaching data for Manning Light soil amended with 6.25g/kg Alkaloam® to determine the mechanisms controlling leaching and to determine the speciation present in the solid and liquid phases at the solid: liquid interface.

Input concentrations for the reactive solid surfaces (clay, HFO; iron/aluminium (hydr)oxides, SHA; organic content) were estimated based on the concentrations modelled for the unamended soil and Alkaloam® proportionately. The carbonate concentration was also estimated based on the concentrations used for modelling the unamended soil and the proportional concentrations added from amendment with Alkaloam®.

The geochemical input parameters used for modelling the actual leach data for Alkaloam® amended Manning Light soil are presented in Table 8-3.

Table 8-3: Input parameters for geochemical modelling of Manning Light soil amended with 6.25/kg Alkaloam®

<table>
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<th>Material</th>
<th>Input specification</th>
</tr>
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<td>Manning_Light_Alkaloam_100907 (P,1,1)</td>
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</table>

<table>
<thead>
<tr>
<th>Input specification</th>
<th>Value</th>
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<td>Solved fraction DOC</td>
<td>varied with pH</td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>6.500E-03 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>2.500E-03 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>8.950E-03 kg/kg</td>
</tr>
<tr>
<td>CO3 conc</td>
<td>122mg/kg</td>
</tr>
</tbody>
</table>

The amount of HFO required to achieve good predictions of the leach data for phosphorus in the amended soil was slightly higher than the sum of the proportional amounts calculated for those used to model the individual matrices. In the case of Alkaloam®, not all of the iron/aluminium sites were believed to be active. It is believed that these sites were activated due to a change in the soil matrix when amended into the Manning Light soil. This would account for slightly higher HFO being required to model the amended soil.
8.5.1 Minerals controlling solubility in Manning Light soil amended with 6.25g/kg Alkaloam®

The modelled data compared well with actual data for mineral phases that were present in the individual matrices. The solubility controlling mineral phases included quartz, calcite and manganese hydrogen phosphate (MnHPO₄) that modelled silicon, calcium, manganese and phosphorus respectively. Mineral phases in Alkaloam®, such as gibbsite, albite, TCP, TCA, barite, strontianite, magnesite and fluorite were not predicted to have any impact on the soil when a 6.25g/kg amelioration rate was used.

Silicon: Figure 8-19 compares the speciation in the solid phase controlling the solubility of silicon in Manning Light soil, Alkaloam® and Manning Light soil amended with 6.25g/kg Alkaloam®. The processes controlling leaching of silicon were similar for the amended and unamended soil, with the dominant process being associated with the solubility of quartz mineral.

Albite, the solubility mineral phase controlling silicon in Alkaloam®, did not control silicon leaching in the amended soil. This suggests that the amelioration rate was too low for this mineral to have an impact.

At high alkaline pH range, sorption to aluminium and iron hydr(oxide) surfaces was predicted to control solubility. Although this occurred in all three matrices, the amended soil closely resembled that of the unamended soil.

Calcium: Figure 8-20 shows the differences in speciation controlling leaching of calcium from Manning Light soil, Alkaloam® and Manning Light soil amended with 6.25g/kg Alkaloam®.

The mineral calcite was predicted to control calcium in the Alkaloam® amended Manning Light soil, and adsorption to organics and iron/aluminium hydr(oxide) in the unamended soil. This indicates that the calcite mineral controlling solubility of calcium in the amended soil is influenced by the addition of Alkaloam® to the soil.
Figure 8-19: Predicted and measured pH dependent leaching of silicon from Manning Light soil, Alkaloam® & Manning Light soil amended with 6.25g/kg Alkaloam® and the speciation controlling leaching.
Manganese and phosphorus: Figures 8-21 and 8-22 illustrate the speciation controlling manganese and phosphorus solubility respectively in Alkaloam® and Manning Light soil with and without 6.25g/kg Alkaloam® amendment. The charts indicate that the solubility controlling mineral manganese phosphate (MnHPO₄) is introduced to the soil through Alkaloam® amelioration. This mineral phase partially controlled the solubility of manganese and phosphorus in the amended soil.
Figure 8-21: Predicted and measured pH dependent leaching of manganese from Manning Light soil, Alkaloam® & Manning Light soil amended with 6.25g/kg Alkaloam® and the speciation controlling leaching
Figure 8-22: Predicted and measured pH dependent leaching of phosphorus from Manning Light soil, Alkaloam® & Manning Light soil amended with 6.25g/kg Alkaloam® and the speciation controlling leaching

8.5.2 Adsorption to clay

Adsorption to clay was predicted to partially control solubility in addition to other sorption processes for most species in Manning Light soil amended with 6.25g/kg Alkaloam®. Clay adsorption controlled solubility predominantly under highly alkaline and/or highly acidic pH environments in the amended soil. This process is therefore not likely to be a significant controlling factor under normal field conditions, which are typically around neutral soil pH.
Unsuccessful attempts were made to model the actual data using kaolinite, suggesting that the kaolin clay mineral is not a dominant sorption process controlling the leaching of species in this soil.

The leach data for chloride and sulphate could not be modelled accurately using clay (Figure 8-23), as was initially predicted to be the controlling process. Chloride and sulphate leaching linearly increased with increasing pH, indicating that their mobility is being influenced by the variable surface charge on the soil particles with changing pH (i.e. at acidic pH the surface charge of particles is positive and anions will favour adsorption; conversely as pH increases the surface charge of particles becomes more negative and anions will not be readily adsorbed) (Wong and Wittner, 2009).

![Figure 8-23: Predicted and measured pH dependent leaching of sulphate and chloride from Manning Light soil amended with 6.25g/kg Alkaloam®](image)

### 8.5.3 Adsorption to iron/aluminium (hydr)oxides

Phosphorus, molybdenum, selenium and antimony were predominantly controlled by adsorption to active iron/aluminium (hydr)oxide surfaces, indicating that these species are likely to be retained if Alkaloam® amelioration is used in this type of soil. At an ameliorant rate of 6.25g/kg of Alkaloam® the leaching concentrations of these metals were the same as the unamended soil (Figure 8-24) and therefore are unlikely to impact on the retention of these metals at this application rate. If application rates above 6.25g/kg are to be used, further investigation is required to evaluate if molybdenum and selenium supplements are necessary for cattle grazing on Alkaloam® amended paddocks.

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52 Essential nutrients for livestock (Parish and Rhinehart, 2008).
Figure 8-24: Comparison of pH dependent leaching concentrations of molybdenum, selenium, antimony and phosphorus in Manning Light soil, Alkaloam® and Manning Light soil amended with 6.25g/kg Alkaloam®

Figure 8-25 shows the actual and predicted leaching of molybdenum, selenium, phosphorus and antimony in Manning Light soil amended with 6.25g/kg Alkaloam® across a pH range 0.5 to 12. This adsorption process was predicted to control these species across the majority of the pH range tested.

The speciation profiles illustrated in the charts were identical to the predicted profiles of the unamended Manning Light soil, with the exception of phosphorus. This indicates that the additional amount of iron/aluminium hydroxide introduced to the soil from the Alkaloam® amelioration did not desorb molybdenum, selenium and antimony from the insoluble organics present in the soil.
Figure 8-25: Predicted speciation controlling solubility of molybdenum, selenium, phosphorus and antimony from Manning Light soil amended with 6.25g/kg Alkaloam®
8.5.4 Adsorption to organics (humic and fulvic acids)

Geochemical modelling indicated that the majority of metals in Manning Light soil amended with 6.25g/kg Alkaloam® were predominantly or partially controlled by insoluble humic and fulvic acids. Aluminium, calcium, chromium, copper, iron, nickel, strontium, thorium, uranium and zinc were fully controlled by insoluble humic and fulvic acids. Magnesium, manganese, potassium, molybdenum and lead were partially controlled by this adsorption process, as well as adsorption to aluminium/iron (hydr)oxides at high acidic and high alkaline pH. Some examples of the metals partially controlled by adsorption to humic and fulvic acids are shown in Figure 8-26.

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Figure 8-26: Solubility and speciation of humic and fulvic acids partially controlling the mobility of manganese, magnesium and lead in Manning Light soil amended with 6.25g/kg Alkaloam®

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Examples of metals dominated by adsorption to humic and fulvic acids are shown in Figure 8-27. At neutral pH all of the species were controlled by humic and fulvic acids.

Figure 8-27: Solubility and speciation of humic and fulvic acids dominating the mobility of copper, iron, thorium and zinc in Manning Light soil amended with 6.25g/kg Alkaloam®
The solubility and speciation profiles in the solid and liquid phase in the Alkaloam® amended soil were very similar to predicted profiles for the unamended Manning Light soil (see section 7.10).

8.6 Changes in leaching of Manning Heavy soil when amended with 6.25g/kg Alkaloam®

Figures 8-28 to 8-31 show a comparison of the pH dependent leaching behaviour of Manning Heavy soil with and without 6.25g/kg Alkaloam® amendment for a range of species. The corresponding pH dependent leaching from Alkaloam® is also plotted for comparison. The measured natural pH for these materials is denoted as * on the charts. A full suite of the analytes analysed for the Alkaloam® amended Manning Heavy soil can be found in Appendix G.

Arsenic, mercury, antimony and tin were detected in both the soil and amended soil extracts at concentrations close to or below the analytical detection limit, therefore changes in leachability due to amelioration could not be ascertained for these metals.

Figure 8-28: pH dependent leaching of species from Manning Heavy soil, Alkaloam® and Manning Heavy soil amended with 6.25g/kg Alkaloam®
Figure 8-29: pH dependent leaching of species from Manning Heavy soil, Alkaloam® and Manning Heavy soil amended with 6.25g/kg Alkaloam®
Figure 8-30: pH dependent leaching of species from Manning Heavy soil, Alkaloam® and Manning Heavy soil amended with 6.25g/kg Alkaloam®
For the majority of constituents, the leaching concentrations in the amended soil reflected similar values to that in the unamended Manning Heavy soil across the full pH range 0.5 to 12. An exception to this was the leaching of cobalt, phosphorus and sulphur.

Leaching of cobalt in the amended soil was found to be noticeably lower than in the unamended Manning Heavy soil, across the full pH range tested (Figure 7-28). This was due to the “dilution effects” from the presence of Alkaloam® (i.e. resulting from the lower leaching of cobalt seen in Alkaloam®). Sulphur leaching increased slightly in the amended Manning Heavy soil in the pH range of 2 to 6 (Figure 8-30).

Phosphorus leaching increased in the range of pH 2 to 4.5 when Manning Heavy soil was ameliorated with 6.25g/kg Alkaloam® (Figure 7-30). This is indicative of the decreased PRI value measured for the amended soil compared with the unamended soil as discussed in Chapter 4; section 6.4. Alkaloam® amelioration is therefore not recommended for improving phosphorus retention in clay type soils similar to Manning Heavy soil.
8.7 Solubility controlling processes influencing leaching of species from Manning Heavy Soil amended with 6.25g/kg Alkaloam®

Geochemical modelling was carried out on the pH dependent leach data for Manning Heavy soil amended with 6.25g/kg Alkaloam®. Input concentrations for the reactive solid surfaces (clay, HFO;iron/aluminium (hydr)oxides, SHA;organic content) were estimated based on the quantities modelled for the unamended soil and Alkaloam®. The final quantity of HFO used for modelling the amended Manning Heavy soil was slightly less than the sum of the proportional amounts from the individual matrices. This was selected based on the best prediction of phosphorus leach data against actual leach data. The carbonate concentration was also estimated based on the amount used for modelling the unamended soil and the proportional amount added from amendment with Alkaloam®.

The geochemical input parameters used for modelling the actual leach data for Alkaloam® amended Manning Heavy soil are presented in Table 8-4.

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<th>Material</th>
<th>Input specification</th>
<th>Manning_Heavy_Alkaloam_240707 (P,1,1)</th>
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<tr>
<td>Solved fraction DOC</td>
<td>varied with pH</td>
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</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
<td></td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
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</tr>
<tr>
<td>Clay</td>
<td>1.346E+00 kg/kg</td>
<td></td>
</tr>
<tr>
<td>HFO</td>
<td>8.000E-03 kg/kg</td>
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</tr>
<tr>
<td>SHA</td>
<td>1.646E-03 kg/kg</td>
<td></td>
</tr>
<tr>
<td>CO3 conc 550.5mg/kg</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The modelling output provided good predictions of the leach data using the above parameters, with the exception of some species that were strongly controlled by adsorption to organics (SHA). In the case of aluminium, iron and uranium, the predicted leaching was overestimated compared to the actual data. An increased SHA value of 20 to 30 times would be required to provide a good fit with actual leach data for these species. This shortfall in SHA is a consequence of the shortfall measured in the Manning Heavy soil, as discussed in Section 7.9.4.
8.7.1 Minerals controlling solubility in Manning Heavy soil amended with 6.25g/kg Alkaloam®

Quartz was predicted to be the only solubility controlling mineral phase in Manning Heavy soil amended with 6.25g/kg Alkaloam®, which controlled the mobility of silicon across the pH range of 1 to 12. This suggests that the 6.25g/kg Alkaloam® amelioration rate is too low for the other mineral phases present in Alkaloam® to have any influence on leaching in the soil (e.g. calcite, gibbsite, TCA, CO₃-hydrotalcite, strontianite, magnesite, barite etc.).

8.7.2 Adsorption to clay

Modelling indicated that the majority of species were controlled by adsorption to clay. In some species this adsorption process was predicted to be the dominant factor controlling mobility, as was the case for aluminium, iron, calcium and barium, lithium, strontium and potassium. For other species, this process was partially controlled by other factors, such as adsorption to iron/aluminium (hydr)oxide surfaces and/or adsorption to humic and fulvic acids. For example, manganese, magnesium molybdenum and antimony were partially controlled by clay and iron/aluminium (hydr)oxides; cadmium, copper and nickel were partially controlled by clay, humic and fulvic acids and iron/aluminium (hydr)oxides.

8.7.3 Adsorption to iron/aluminium (hydr)oxides

The increased amount of active iron/aluminium hydr(oxide) sites introduced to the soil matrix from Alkaloam® amelioration was predicted to partially control the solubility of magnesium, copper and manganese (Figures 8-32 to 8-34 respectively).

Magnesium, which was controlled by clay in the unamended soil, was predicted to be controlled by active iron/aluminium (hydr)oxides across the pH range 8 to 14 when amended with 6.25g/kg Alkaloam® (Figure 8-32).

Figures 8-33 and 8-34 illustrate the increased effect of iron/aluminium (hydr)oxides active sites on the solubility of manganese and copper respectively, following amendment of Manning Heavy soil with 6.25g/kg Alkaloam®.
Figure 8-32: Predicted and measured leaching of magnesium controlled by adsorption to aluminium/iron (hydr)oxides in Manning Heavy soil when amended with 6.25g/kg Alkaloam®

Figure 8-33: Influence of iron/aluminium (hydr)oxides on the solubility of copper in Manning Heavy soil with and without 6.25g/kg Alkaloam® amendment
8.7.4 Adsorption to organics (humic and fulvic acids)

Species controlled by association with insoluble and soluble humic and fulvic acids were similar in the amended and unamended Manning Heavy soil. The quantity of solid humic and fulvic acid input into the model was predicted to be an underestimate for aluminium, iron and uranium with an estimated increase of 20-30 times the concentration required to provide a good fit against actual data, depending on the element. The predicted leach data at acidic pH for manganese, cadmium and copper improved slightly on increasing the organic content approximately 10 to 20 times. This effect could be caused competitive adsorption of the cationic metals for the active organic sites.

Aluminium, iron, chromium, cadmium, copper, nickel, lead, uranium and thorium were predicted to be partially controlled by adsorption to insoluble humic and fulvic acids, across different pH ranges, specific to the element. Other adsorption processes for these species have been discussed in sections 8.5.1.2 and 8.5.1.3.
8.8 Changes in leaching of Merredin soil when amended with 6.25g/kg Alkaloam®

A comparison of the pH dependent leach behaviour for Merredin soil with and without 6.25g/kg Alkaloam® amendment is illustrated in Figures 8-35 to 8-38 for a range of species. The corresponding pH dependent leach data for Alkaloam® is also plotted for comparison. The natural pH of these materials is denoted as * on the charts. A full suite of the analytes measured can be found in Appendix G.

Arsenic, cadmium, fluoride, mercury, molybdenum, antimony, selenium, and tin were detected in the amended soil extract at concentrations close to or below the analytical detection limit. No change in leaching behaviour from a 6.25g/kg Alkaloam® amelioration rate could be ascertained for these species.

![Graphs showing pH dependent emission of Al, Ca, Cd, and Cl for Merredin soil, Alkaloam®, and Merredin soil amended with 6.25g/kg Alkaloam®](image)

Figure 8-35: pH dependent leaching of a range of species from Merredin soil, Alkaloam® and Merredin soil amended with 6.25g/kg Alkaloam®
Figure 8-36: pH dependent leaching of a range of species from Merredin soil, Alkaloam® and Merredin soil amended with 6.25g/kg Alkaloam®
Figure 8-37: pH dependent leaching of a range of species from Merredin soil, Alkaloam® and Merredin soil amended with 6.25g/kg Alkaloam®
Figure 8-38: pH dependent leaching of a range of species from Merredin soil, Alkaloam® and Merredin soil amended with 6.25g/kg Alkaloam®

Consistent with observations for the other WA soils, the pH dependent leaching for the majority of species in Alkaloam® amended Merredin soil reflected that of the unamended soil. Differences between the amended and unamended soil were observed in the leaching of aluminium, cobalt and gallium. These differences were not believed to be associated with organics since the DOC leaching concentrations were similar in both soil matrices.

The mobility of aluminium decreased in the Alkaloam® amended Merredin soil in the pH range 4 to 7 (Figure 8-35) relative to the untreated soil. The speciation modelling of aluminium in the solid and liquid phase across the pH range 1 to 12 was predicted to be the same in the amended and unamended soil matrices, despite differences in the leaching concentrations. The processes predicted to be controlling mobility were adsorption to clay and organics. Since the leaching concentrations of DOC are the same in both soils, reduced aluminium leaching in the amended soil must be due to additional clay adsorption.

Gallium leaching also decreased between the pH range of 3 to 6.5 (Figure 8-36) but increased above pH 8. Cobalt also increased at pH>8 in the amended Merredin soil (Figure 8-36). Geochemical modelling could not be conducted on these elements as they are not
available in the reactive species list of the LeachXS™ software. It is recommended that these reactants be added to allow evaluations to be made on these species.

The chart illustrating the pH dependent leaching of copper in Figure 8-36 displays increased leaching at pH 8 in the amended soil. This trend was an artefact caused by differing detection limits in the analysis of the low and high pH eluates.

8.9 Solubility controlling processes influencing leaching of species from Merredin soil amended with 6.25g/kg Alkaloam®

Geochemical modelling was carried out on the pH dependent leach data for Merredin soil amended with 6.25g/kg Alkaloam®. Input values for the reactive solid surfaces (clay, HFO; iron/aluminium (hydr)oxides and SHA; organic content) were estimated based on the quantity modelled for the unamended soil and Alkaloam® proportionately. The carbonate concentration used in the model was the contribution from Alkaloam® only.

The geochemical input parameters used for modelling the actual leach data for Alkaloam® amended Merredin soil are presented in Table 8-5.

Table 8-5: Input parameters for geochemical modelling of Merredin soil amended with 6.25/kg Alkaloam®

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<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solved fraction DOC</td>
<td>Varied with pH</td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>6.645E-01 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>2.400E-03 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>7.046E-03 kg/kg</td>
</tr>
<tr>
<td>CO3 conc = 62.5mg/kg</td>
<td></td>
</tr>
</tbody>
</table>

The amount of HFO required to achieve good predictions of the leach data for phosphorus and other species in the amended soil was slightly lower (80%) than the sum of the proportional amounts used to model the individual matrices. It is believed that some of the iron/aluminium hydroxide surfaces may not all be active in the amended soil matrix.
8.9.1 Minerals controlling solubility in Merredin soil amended with 6.25g/kg Alkaloam®

Quartz was predicted to be the only solubility mineral phase in Merredin soil amended with 6.25g/kg Alkaloam®, which controlled the mobility of silicon across the pH range 1 to 12. Consistent with observations noted for other WA soils, this indicates that the 6.25g/kg Alkaloam® amelioration rate is too low for other mineral phases present in Alkaloam® to have any influence on leaching in this soil. (e.g. calcite, gibbsite, TCA, CO₃-hydrotalcite, strontianite, magnesite, barite etc.).

8.9.2 Adsorption to clay

Adsorption to clay was predicted to be an important factor for controlling the solubility of most species in Merredin soil amended with 6.25g/kg Alkaloam®. This adsorption process was the dominant factor controlling mobility of aluminium, strontium, calcium, barium, lithium and potassium across the full pH range tested. Other adsorption processes also controlled these species but to a lesser extent. Examples of this are shown for barium, calcium and strontium in Figure 8-39.

Magnesium and manganese were also dominated by adsorption to clay at pH<8, but in the alkaline pH range were dominated by adsorption to iron/aluminium (hydr)oxides and insoluble humic and fulvic acids.

All three adsorption processes influenced the mobility of the remaining metals (adsorption to clay, insoluble organic acids and active iron/aluminium (hydr)oxides. This occurred at different pH ranges specific to the element. Examples were cadmium, copper, manganese, magnesium, nickel, lead and zinc.
Figure 8-39: Predicted and measured leaching of barium, calcium and strontium from Merredin soil amended with 6.25g/kg Alkaloam® and the speciation controlling their mobility

8.9.3 Adsorption to iron/aluminium (hydr)oxides

The solubility of phosphorus from Merredin soil amended with 6.25g/kg Alkaloam® was predicted to be predominantly controlled by adsorption to active iron/aluminium (hydr)oxides. Molybdenum, arsenic, antimony and selenium were also partially controlled by this adsorption process, in addition to adsorption to clay, as shown in Figure 8-40.
8.9.4 Adsorption to organics (humic and fulvic acids)

Adsorption of iron, cadmium, chromium, copper, uranium, thorium and zinc to insoluble organic acids was predicted to be the dominant process controlling solubility of these metals in Merredin soil amended with 6.25g/kg Alkaloam®.

Competitive adsorption of the cations to active organic sites, based on their adsorption affinities\textsuperscript{53}, was noted during the modelling and was consistent with observations in other

\textsuperscript{53} The affinity of a species to adsorb to organics is based on the valency of the species, its hydrated radius and the surface charge density of the organic particles.
WA soils. The modelling showed that the amount of insoluble humic and fulvic acids in the matrix was too low to provide a good fit of predicted leach data against actual data for aluminium and iron. Conversely, modelling barium, cadmium, copper, nickel, lead and chromium showed the amount of insoluble humic and fulvic acids to be too high. This effect has been discussed previously in chapter 7. Examples of this effect are shown for thorium (good prediction), aluminium (overestimation of leaching) and chromium (underestimation of leaching) in Figure 8-41.

Figure 8-41: Predicted and measured leaching of thorium, aluminium and chromium from Merredin soil amended with 6.25g/kg Alkaloam®
8.10 Changes in leaching of Newdegate soil when amended with 6.25g/kg Alkaloam®

Figures 8-42 to 8-44 show a comparison of the pH dependent leach behaviour for Newdegate soil with and without 6.25g/kg Alkaloam® amendment for a range of species. A full suite of the analytes measured can be found in Appendix G.

Figure 8-42: pH dependent leaching of a range of species from Newdegate soil, Alkaloam® and Newdegate soil amended with 6.25g/kg Alkaloam®
Figure 8-43: pH dependent leaching of a range of species from Newdegate soil, Alkaloam® and Newdegate soil amended with 6.25g/kg Alkaloam®
Figure 8-44: pH dependent leaching of a range of species from Newdegate soil, Alkaloam® and Newdegate soil amended with 6.25g/kg Alkaloam®
The pH dependent leaching of species from Newdegate soil amended with 6.25g/kg Alkaloam® showed some differences compared to the unamended soil. An example is the decreased leaching of copper and DOC in the Alkaloam® amended soil, highlighting that mobilisation of this metal is via formation of soluble copper-organic complexes in this soil matrix. This was confirmed by geochemical modelling, as discussed in section 8.7.1.4.

Leaching concentrations increased for calcium, chloride, iron, potassium, magnesium, strontium, sulphur, silicon and vanadium in Newdegate soil when ameliorated with 6.25g/kg Alkaloam®. Dissolution of these elements was believed to be due to desorption from clay, since clay adsorption was predicted to be an important factor controlling leaching (see section 8.7.1.2). The extent of the increased leaching in the amended soil and the pH at which this occurred was specific for each analyte.

The most significant increase in leaching was observed for silicon, with concentrations increasing by one order of magnitude at pH 8 to 12 in the Alkaloam® amended Newdegate soil. This was believed to be due to the release of silicon from the dissolution of the aluminosilicate mineral (albite) and quartz from Alkaloam® and Newdegate soil respectively. Note. The leaching profiles of silicon from Newdegate soil and Alkaloam® are distinct due to the different minerals controlling solubility.

8.11 Solubility controlling processes influencing leaching of species from Newdegate soil amended with 6.25g/kg Alkaloam®

Geochemical modelling was carried out on the pH dependent leach data for Newdegate soil amended with 6.25g/kg Alkaloam®. Input concentrations for the reactive solid surfaces (clay, HFO;iron/aluminium (hydr)oxides and SHA;organic content) were estimated based on the quantities modelled for the unamended soil and Alkaloam® proportionately. The carbonate concentration used in the model was the contribution from Alkaloam® only.

The geochemical input parameters used for modelling the actual leach data for Alkaloam® amended Merredin soil are presented in Table 8-6.
Table 8-6: Input parameters for geochemical modelling of Merredin soil amended with 6.25/kg Alkaloam®

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newdegate_Alkaloam_170407 (P,1,1)</td>
<td></td>
</tr>
<tr>
<td>Solved fraction DOC</td>
<td>0.2</td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>5.535E-01 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>8.587E-04 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>7.046E-03 kg/kg</td>
</tr>
<tr>
<td>CO3 conc = 289mg/kg</td>
<td></td>
</tr>
</tbody>
</table>

The amount of HFO required to achieve good predictions of the leach data for phosphorus and other species in the amended soil was slightly lower (75%) than the sum of the proportional amounts calculated for those used to model the individual components. Some of the iron/aluminium hydroxide surfaces may not be active in the amended Newdegate soil matrix.

The adsorption processes controlling specific species in Newdegate soil were consistent with those observed in the unamended soil and are discussed herein.

8.11.1 Minerals controlling solubility in Newdegate soil amended with 6.25g/kg Alkaloam®

Geochemical speciation modelling predicted that the solubility of Quartz controlled the mobility of silicon in Alkaloam® amended Newdegate soil. This was consistent with observations noted for Merredin amended soil. No other minerals were determined to control leaching in this amended soil.

8.11.2 Adsorption to clay

Adsorption to clay was an important factor controlling solubility of most species in Newdegate soil amended with 6.25g/kg Alkaloam®. This adsorption process was predicted to be the dominant factor controlling mobility of aluminium, potassium, lithium, strontium, and calcium across the whole pH range tested, and for magnesium and barium at pH<8. For other constituents, other adsorption processes, in addition to clay, played an important role in controlling leaching. This is summarised in Table 8-7.
Table 8- 7: Adsorption process controlling leaching of constituents from Alkaloam® amended Newdegate soil

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sorption processes controlling solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium and lithium</td>
<td>Adsorption to clay only</td>
</tr>
<tr>
<td>Antimony and selenium</td>
<td>Adsorption to clay and active iron/aluminium (hydr)oxides (HFOs)</td>
</tr>
<tr>
<td>Aluminium, iron, barium, copper</td>
<td>Adsorption to clay and insoluble organics and strontium</td>
</tr>
<tr>
<td>Calcium, magnesium, cadmium,</td>
<td>Adsorption to clay, active iron/aluminium (hydr)oxides and</td>
</tr>
<tr>
<td>manganese, lead and zinc</td>
<td>insoluble organics</td>
</tr>
</tbody>
</table>

The significance of clay adsorption on the mobility of species is illustrated by examples in Figure 8-45 for potassium (dominant process) and antimony (controlled by aluminium/iron (hydr)oxides and clay) and Figure 8-46 for barium (controlled by organics and clay) and magnesium (controlled by aluminium/iron (hydr)oxides, organics and clay).

Figure 8- 45: Clay sorption controlling solubility of potassium and antimony in Newdegate soil amended with 6.25g/kg Alkaloam®, in addition to other adsorption processes
8.11.3 Adsorption to iron/aluminium (hydr)oxides

The solubility of phosphorus from Newdegate soil amended with 6.25g/kg Alkaloam® was controlled by adsorption to iron and aluminium (hydr)oxide surfaces across the full pH range tested. This process appears to be the key factor controlling phosphorus in all the WA agricultural soils, the Swan Coastal Plain soil and the two amendments.

Arsenic and antimony were partially controlled by this process in addition to adsorption to clay. The contributing effect of the additional active iron and aluminium sites introduced to the soil through Alkaloam® amelioration is therefore expected to improve retention of these elements in the amended soil. Leaching concentrations of arsenic and antimony were below the detection limit of the analysis therefore any improved retention of these elements could not be ascertained.

Figure 8-46: Clay sorption controlling solubility of barium and magnesium in Newdegate soil amended with 6.25g/kg Alkaloam®, in addition to other adsorption processes.
### 8.11.4 Adsorption to organics (humic and fulvic acids)

The majority of species were controlled by insoluble humic and fulvic acids in Newdegate soil amended with 6.25g/kg Alkaloam®.

Uranium, thorium, iron, cadmium and copper were dominated by this adsorption process across the full pH range 1 to 12 tested, indicating their strong association to organics in the soil. Lead was also controlled by adsorption to organics in the pH range of approximately 1 to 6. These species were mobilised into the solution phase through the formation of soluble cation-organic complexes or as free ions, depending on the pH of the soil environment. Examples of this are shown in Figure 8-47 for chromium, thorium and uranium.

![Figure 8-47: Complexation of humic and fulvic acids with cations in the liquid and solid phase controlling solubility of chromium, thorium and uranium in Newdegate soil amended with 6.25g/kg Alkaloam®](image-url)
Decreased DOC leaching observed in Newdegate soil due to Alkaloam® amelioration corresponded with decreased leaching of chromium, copper and iron (Figure 8-42). This suggests that soluble organics responsible for mobilising these species in Newdegate soil are becoming immobilised as the organics become insoluble in the amended soil.

In the case of uranium and cadmium, leaching concentrations in the amended and unamended soil were at or below the detection limit of the analysis. Hence any affects due to decreased DOC mobility in the amended soil could not be ascertained. Although it is anticipated that a further reduction in leaching of uranium and cadmium may have been achieved, the very low leaching levels indicate that these species are already immobile in the amended soil.

Competitive adsorption effects were shown to be very prominent from the modelling of the amended Newdegate soil. Reasons for this have been discussed previously (Chapter 7; section 7.5.4).

**8.12 Assessment of leach data against regulatory guidelines**

The pH dependent leaching concentrations were assessed against the European Union Landfill Directive to determine whether leaching concentrations from the WA agricultural soils and the Swan Coastal Plain soil amended with 6.25g/kg (10t/ha) Alkaloam® would exceed the criteria. These guidelines are more stringent than the WA contaminated sites guidelines and would provide a conservative assessment of any potential impacts to the environment.

All leaching concentrations were within the inert landfill criteria at the pH range representative of field conditions where Alkaloam® is proposed to be used (i.e. in agricultural acidic soils at an approximate range of pH 4.5 to 8). URS (2009) reported these findings and further assessed these concentrations against ANZECC water quality guidelines. URS (2009) reported that concentrations were within acceptable limits. Ameliorating these soils with 6.25g/kg therefore is not expected to be a detriment to the environment.
8.13 Process Development of Alkaloam® for use as a soil amendment at 6.25g/kg application rate

Alkaloam® is currently atmospherically carbonated or forced carbonated (using carbon dioxide) to effectively reduce the pH of the material\textsuperscript{34}. The material is rotary hoed whilst stored in residue drying beds to increase exposure to the atmosphere and hence the extent of the atmospheric carbonation. No further process development on Alkaloam® is deemed essential for the material to be used as a soil amendment in the WA agricultural soils and Coastal Plain soil at the application rate of 6.25g/kg (10t/ha equivalent in top 1cm soil). The pH of the soil does not change significantly at this amelioration rate and changes in leaching from Alkaloam® amelioration are within acceptable limits based on ANZECC water quality guidelines (ANZECC, 2000) and the highly stringent European Landfill Directive guidelines (European Union Council, 1999). Increased application rates up to 20t/ha Alkaloam® have also been reported to be within acceptable limits for regulations in Australia, Canada, UK and US (Summers, 2001), therefore this application rate is also likely to be environmentally acceptable.

8.14 Conclusions

The pH change in soils amended with 6.25g/kg (10t/ha equivalent) Alkaloam® in the laboratory was consistent with pH changes reported in the 2\textsuperscript{nd} year of the liming/soil amendment field trials.

Changes in leaching behaviour for Alkaloam® amended soils are attributed to pH changes from Alkaloam® amelioration, in addition to the presence of Alkaloam® in the matrix. One exception to this was observed for the Manning Heavy soil, where changes in leaching were solely attributed to the presence of Alkaloam® due to negligible change in pH post Alkaloam® amelioration.

Geochemical modelling predictions using LeachXS\textsuperscript{TM} software closely matched leaching behaviour for a range of species in different soils amended with 6.25g/kg Alkaloam®, using estimates for reactive surfaces based on the proportionate concentrations measured in the individual matrices.

\textsuperscript{34} Converting sodium hydroxide entrained in Alkaloam® to sodium carbonate.
Competitive adsorption effects of metals to insoluble organic acids in the Alkaloam® amended soil matrices could not be modelled using LeachXSTM. This is a limitation of the software.

The solubility of phosphorus in all the WA agricultural soils and the Swan Coastal Plain soil is controlled by adsorption to active iron/aluminium (hydr)oxide sites.

The pH dependent leaching concentrations of the WA agricultural soils and the Swan Coastal Plain soil when amended with 6.25g/kg Alkaloam® were assessed against the conservative European Landfill Directive. All concentrations are within the inert landfill criteria at the pH range representative of field conditions in agricultural acidic soils at an approximate range of pH 4.5 to 8.

**Bassendean soil amended with 6.25g/kg Alkaloam®**

Amending Bassendean soil with an Alkaloam® amelioration rate of 6.25g/kg (10t/ha equivalent) did not significantly change leaching behaviour. The greatest impact was observed for silicon where leaching increased by half an order of magnitude within an approximate pH range of 2 to 6.

The pH dependent leaching profiles for the majority of species in Alkaloam® amended Bassendean soil was similar to the unamended soil. This was despite high leaching concentrations of chloride and molybdenum from Alkaloam® in the acidic pH range.

The leaching behaviour of the amended soil was significantly different for manganese, iron and zinc compared to the individual matrices. Increased mobility of these species was due to complexation with DOC, which was confirmed by geochemical speciation modelling and a corresponding increase in the leaching of DOC in the amended soil.

Amending Bassendean soil with 6.25g/kg Alkaloam® has the potential to increase the phosphorus retention properties of this soil type over an extended pH range of 3 to 6 (this soil already exhibits phosphorus retention in the pH range 6 to 9). The pH of acidic WA agricultural soils typically lie in this pH range, consequently agricultural soils with characteristics similar to Bassendean sandy soils are likely to benefit from Alkaloam® amelioration at this application rate.

Solubility controlling mineral phases controlling leaching in Alkaloam® amended Bassendean soil were similar to the unamended soil, with the exception of TCP and Zinc
silicate, which were introduced into the soil from the Alkaloam® amendment. The mineral phases TCP and zinc silicate were predicted to partially control the mobility of phosphorus and zinc respectively in the amended soil. This occurred at alkaline pH. Iron was controlled by ferrihydrite in the individual matrices and adsorption to organics in the amended soil.

A summary of the mineral controlling phases in the amended Bassendean soil are:

<table>
<thead>
<tr>
<th>Element</th>
<th>Controlling Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>Amorphous aluminium hydroxide, Analbite</td>
</tr>
<tr>
<td>Calcium</td>
<td>Calcite</td>
</tr>
<tr>
<td>Silicon</td>
<td>Albite</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>TCP</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zinc silicate</td>
</tr>
</tbody>
</table>

Despite negligible clay concentrations in Bassendean soil (approximately 1%), the majority of species were partially controlled by adsorption to clay, in addition to other adsorption processes (i.e. adsorption to aluminium/iron (hydr)oxides and/or adsorption to insoluble organics). This indicates that clay adsorption strongly controls the mobility of constituents in this soil.

The solubility of chloride increased with increasing pH, similar to the unamended soil, suggesting that mobility of chloride is controlled by changes to the surface charge of the soil particles with changes in pH.

The mobility of antimony, selenium, molybdenum and fluoride was predicted to be controlled by adsorption to aluminium/iron (hydr)oxides and clay.

The solubility of copper, chromium, thorium and uranium from Alkaloam® amended Bassendean soil was predominantly controlled by adsorption to insoluble humic and fulvic acids. Their mobilisation from the solid phase was strongly associated with complexation to soluble organic acids.

Adsorption to insoluble organics was predicted as a dominant process for controlling mobility of magnesium, barium, manganese, nickel, strontium, lead and vanadium. This process occurred at the natural pH of the amended soil and across different pH ranges, specific for each element.
Manning Light soil amended with 6.25g/kg Alkaloam®

The maximum available leaching concentration for all species, except chloride and sulphur, in Manning Light soil were less than their corresponding total concentration, indicating that only chloride and sulphur (in the form of sulphate) will fully mobilise from the soil.

With the exception of iron, copper, silicon and zinc, the leaching concentrations for most species reflected that of the unamended soil, suggesting that the 6.25g/kg amelioration rate is insufficient for Alkaloam® to affect leaching. This was despite the leaching profiles of calcium, magnesium, manganese, molybdenum, silicon and thorium being significantly different for the individual matrices.

Leaching concentrations of iron, copper, silicon and zinc were higher in the Alkaloam® amended Manning Light soil relative to the individual matrices. This corresponded with increased DOC, indicating that the mobility of these cations has increased due to complexation with organics.

Geochemical modelling predicted a higher proportion of iron/aluminium hydr(oxide) active sites in Alkaloam® amended Manning Light soil than in the individual components.

A summary of the mineral controlling phases in the amended Manning Light soil are:

<table>
<thead>
<tr>
<th>Element</th>
<th>Controlling Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium:</td>
<td>Calcite (from Alkaloam®)</td>
</tr>
<tr>
<td>Silicon:</td>
<td>Quartz (from the soil)</td>
</tr>
<tr>
<td>Manganese and Phosphorus:</td>
<td>Manganese hydrogen phosphate (from Alkaloam®)</td>
</tr>
</tbody>
</table>

Mineral phases in Alkaloam®, such as gibbsite, analbite, TCP, TCA, barite, strontianite, magnesite and fluorite did not have an impact on the mobility of constituents in the amended soil when a 6.25g/kg amelioration rate was used.

Clay sorption is not a significant controlling factor for leaching in Alkaloam® amended Manning Light soil at natural pH field conditions. Chloride and sulphate leaching linearly increased with increasing pH, suggesting that their mobility is influenced by the variable surface charge on the soil particles with changing pH.

No phosphorus retention was measured from ameliorating Manning Light soil with 6.25g/kg Alkaloam®.
The majority of metals were either partially or fully controlled by adsorption to insoluble organics (humic and fulvic acids). Magnesium, manganese, potassium, molybdenum and lead were partially controlled by this adsorption process; aluminium, calcium, chromium, copper, iron, nickel, strontium, thorium, uranium and zinc were fully controlled by this process across the pH range 1 to 12.

**Manning Heavy soil amended with 6.25g/kg Alkaloam®**

With the exception of phosphorus, cobalt and sulphur, the leaching concentrations of the majority of constituents from Manning Heavy soil amended with 6.25g/kg Alkaloam® were similar to the unamended soil.

Cobalt leaching decreased across the pH range 1 to 12 when amended with Alkaloam®, while sulphur leaching increased slightly in the pH range 2 to 6.

Phosphorus leaching increased in the range pH 2 to 4.5. This is indicative of the decreased PRI measured for the Alkaloam® amended soil relative to the unamended soil.

Quartz is the only solubility controlling mineral phase in Alkaloam® amended Manning Heavy soil (at 6.25g/kg amelioration rate).

The leaching of the majority of species were controlled by adsorption to clay. This was the dominant process for aluminium, iron, calcium and barium, lithium, strontium and potassium. For other species such as magnesium, molybdenum, antimony, cadmium, copper and nickel, this process partially controlled mobility.

The additional iron/aluminium hydr(oxide)s incorporated into the soil due to Alkaloam® amelioration were predicted to compete with clay sites for the adsorption of copper, manganese and magnesium.

**Merredin soil amended with 6.25g/kg Alkaloam®**

Consistent with observations for the other WA soils, the pH dependent leaching for the majority of species in Alkaloam® amended Merredin soil reflected that of the unamended soil. The exception was aluminium, where leaching decreased across the pH range of 4 to 7 due to additional clay adsorption.

The concentration of HFO required to predict measured leach data for phosphorus and other species in the amended soil was slightly lower than the sum of the proportional amounts used
to model the individual matrices (80% used). This could result from some of the iron/aluminium hydroxide surfaces not being 100% active in the amended soil matrix.

Quartz is the only solubility controlling mineral phase in Alkaloam® amended Merredin soil (at 6.25g/kg amelioration rate).

Adsorption to clay is an important factor controlling most species in the amended soil. This is the dominant process controlling solubility of aluminium, strontium, calcium, barium, lithium and potassium in the amended soil.

The dominant factor controlling solubility of iron, cadmium, chromium, copper, uranium, thorium and zinc in the amended Merredin soil is adsorption to insoluble organics.

**Newdegate soil amended with 6.25g/kg Alkaloam®**

Ameliorating Newdegate soil with 6.25g/kg Alkaloam® altered the leaching behaviour compared to the unamended soil.

The leaching of copper decreased in the amended soil, due to a corresponding decrease in solubility of organics (lower DOC).

Leaching concentrations of calcium, chloride, iron, potassium, magnesium, strontium, sulphur, silicon and vanadium increased in Newdegate soil when ameliorated with 6.25g/kg Alkaloam®. Dissolution of these elements was believed to be due to desorption from clay, since clay sorption was predicted to control leaching.

The leaching of silicon increased by one order of magnitude within the pH range 8 to 12 in the amended Newdegate soil, which is likely due to the release of silicon on dissolution of quartz in the amended soil matrix.

The concentration of HFO required to predict actual leach data was slightly lower than the sum of the proportional HFO concentrations used to model the individual matrices (75% used). This may be caused by some inactivity on the iron/aluminium hydroxide surfaces in the amended Newdegate soil matrix.

Quartz was the only solubility controlling mineral present in the Alkaloam® amended Newdegate soil, which controlled the solubility of silicon.
The leaching of the majority of species from Newdegate soil amended with 6.25g/kg Alkaloam® was controlled by insoluble humic and fulvic acids. Uranium, thorium, iron, cadmium and copper were dominated by this adsorption process across the full pH range 1 to 12. Lead was controlled by this process in the pH range 1 to 6.

Adsorption to clay was also an important factor controlling the solubility of most species in Newdegate soil amended with 6.25g/kg Alkaloam® as follows;

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sorption processes controlling solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium and lithium</td>
<td>Adsorption to clay only</td>
</tr>
<tr>
<td>Antimony and selenium</td>
<td>Adsorption to clay and active iron/aluminium (hydr)oxides (HFOs)</td>
</tr>
<tr>
<td>Aluminium, iron, barium, copper</td>
<td>Adsorption to clay and insoluble organics</td>
</tr>
<tr>
<td>and strontium</td>
<td></td>
</tr>
<tr>
<td>Calcium, magnesium, cadmium,</td>
<td>Adsorption to clay, active iron/aluminium (hydr)oxides and insoluble organics</td>
</tr>
<tr>
<td>manganese, lead and zinc</td>
<td></td>
</tr>
</tbody>
</table>

Modelling results indicated that competitive adsorption effects were dominant in Newdegate soil amended with Alkaloam®.

No process development on Alkaloam® is deemed essential for the material to be used as a soil amendment in Manning Light, Merredin, Newdegate and Bassendean soils at the application rate of 6.25g/kg (10t/ha equivalent in top 1cm soil). This is supported by insignificant change in soil pH at this amelioration rate, and that changes in leaching post-Alkaloam® amelioration are within acceptable limits based on ANZECC water quality guidelines and the highly stringent European Landfill Directive guidelines.

8.15 Recommendations

Determine if LeachXS™ can be used to predict leaching of species at different application rates of Alkaloam® by comparing predicted data against actual data.

Repeat the pH dependent analysis of Manning Light soil amended with 6.25g/kg using consistent detection limits to ascertain whether benefits of retaining other metals in addition to phosphorus can be achieved at this amelioration rate.
Alkaloam® amelioration is not recommended for clay type soils such as Manning Heavy soil.

Gallium and cobalt should be added to the list of available reactive species in LeachXS™ so that geochemical speciation modelling can be predicted for these elements.

Total concentration does not correlate with leaching behaviour of most elements in the Alkaloam® amended soils and therefore composition is not recommended for conducting environmental assessments on Alkaloam® as a soil ameliorant in WA soils.


9.1 Introduction

‘Liming’ is a common agricultural practise, used to neutralise acidity of agricultural soils and in turn improve the uptake of major plant nutrients, such as potassium, nitrogen and phosphorus, for plants growing in acidic soils. Agricultural lime materials are composed predominantly of calcium carbonate; which improves the buffering capacity of soils, and provides a source of calcium.

Alcoa Red Lime™, primarily comprising calcium carbonate, has been investigated as an alternative liming agent to conventional agricultural lime materials (Clarendon et al., 2010). Studies investigated the effectiveness of Red Lime™ to changes in soil pH, increased buffering capacity, nutrient availability and plant yield. Very little research was conducted on the leaching behaviour of the soils following amendment with Red Lime™, and whether any changes in leaching behaviour may impact on the environment.

This chapter investigates the pH dependent leaching characteristics for four WA agricultural soils following amendment with 1.6g/kg Red Lime™ (equivalent to a top dressed application of 2.56t/ha). The pH dependent leach data was compared against the corresponding unamended soils to determine any changes in leaching from amelioration, and if so, whether these changes are likely to be a concern or provide benefit to the environment. Where applicable, the results have been compared against outcomes from the liming trials reported in Clarendon et al. (2010).55

A combination of pH dependent leach test data and LeachXS™ geochemical modelling was used to predict the partitioning of major, minor and trace elements in the Red Lime™ amended soils. The geochemical modelling required an iterative approach, with a selection of mineral phases from both Red Lime™ and the agricultural soil, and other estimated input parameters, modified after each run to fine tune the modelling. The modelling results presented in this chapter represent the best fit against actual leach data for the majority of species, and provide a good prediction of the processes controlling leaching in the soils.

55 Discussions referring to Manning Light soil and Manning Heavy soil in this chapter are referred to as “Busselton sand” and “Busselton loam” in the liming trial report.
LeachXS™ geochemical modelling assumes all sites and conditions in the soil are at equilibrium.

9.2 Effect of 1.6g/kg Red Lime™ amelioration on agricultural soil pH
Table 9-1 shows the natural pH of the WA agricultural soils and the change in soil pH after amendment with 1.6g/kg Red Lime™

<table>
<thead>
<tr>
<th>soil</th>
<th>pH Difference due to Red Lime™ amendment</th>
<th>pH (1:10 DI Water) from pH dependent leach tests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unamended</td>
<td>Amended with 1.6g/kg Red Lime™ (2.56t/Ha)</td>
</tr>
<tr>
<td>Manning Light</td>
<td>5.89</td>
<td>6.39</td>
</tr>
<tr>
<td>Manning Heavy</td>
<td>5.55</td>
<td>5.635</td>
</tr>
<tr>
<td>Merredin</td>
<td>6.79</td>
<td>7.34</td>
</tr>
<tr>
<td>Newdegate</td>
<td>6.08</td>
<td>7.66</td>
</tr>
<tr>
<td>Bassendean</td>
<td>8.43</td>
<td>9.27</td>
</tr>
<tr>
<td>Spearwood</td>
<td>6.85</td>
<td>8.44</td>
</tr>
</tbody>
</table>

The pH of Manning Light soil and Merredin soil measured an increase of 0.5 pH units when amended with 1.6g/kg Red Lime™. Soil amendment/liming field trials conducted by Clarendon et al. (2010) reported a slightly higher increase of 1.45 and 0.7 pH units respectively using similar Red Lime™ amelioration rates (2.56t/ha equivalent rate). Newdegate soil recorded the highest change in soil pH from 1.6g/kg Red Lime™ amelioration, which was consistent with the pH of the soil recorded in the third growing season of the liming trials.

The pH of Manning Heavy soil did not change significantly when ameliorated with 1.6g/kg Red Lime™. This was believed to be due to the natural high buffering capacity of Manning Heavy soil relative to the other soils, as discussed in Chapter 6; Section 6.5.

Since pH is a dominant factor controlling leaching, any changes in pH to the agricultural soil from Red Lime™ amelioration may influence the leaching behaviour, in addition to any leaching that is specific to the ameliorant.
9.3 Changes in leaching of Manning Light soil when amended with 1.6g/kg Red Lime™

The pH dependent leach test was carried out on Manning Light soil amended with 1.6g/kg Red Lime™. The leach data was compared against data for Red Lime™ and Manning Light soil. A full suite of the analytes measured is in Appendix H.

The pH dependent leaching behaviour for the majority of species in the Red Lime™ amended Manning Light soil reflected similar profiles to that of the corresponding unamended soil, irrespective of the differences in leaching characteristics of the individual Red Lime™ and Manning Light soil matrices. In addition, leaching concentrations for the majority of elements did not increase using a Red Lime™ amelioration rate of 1.6g/kg. Exceptions to this were calcium, magnesium, copper, phosphorus and sulphur as discussed below.

Calcium: Calcium leaching increased slightly in the amended soil across the pH range of 1 to 10. This was expected due to additional calcium in the Red Lime™ being introduced to the soil matrix (Figure 9-1).

Copper: Copper leaching increased at pH<2 and pH >8 when ameliorated with 1.6g/kg Red Lime™ (Figure 9-2). Leaching concentrations of copper at the soils’ natural pH (denoted by * on the chart) were below or at detection limit in both the amended and unamended soil matrices. This suggests that copper is likely to remain immobile in the Red Lime™ amended soil under natural field conditions, unless external factors introduce a highly acidic...
or alkaline environment to the soil. Importantly, the detection limit for copper analysis in the amended soil was higher than that for the unamended soil. It is recommended that the analysis be repeated in the amended soil using the lower detection limit to confirm that copper will remain immobile.

**Figure 9-2: pH dependent leaching of copper from Red Lime™, Manning Light soil and Manning Light soil amended with 1.6g/kg Red Lime™**

**Sulphur:** A comparison of the pH dependent leach data for sulphur in the amended and unamended soil indicates that leaching concentrations increased consistently by half an order of magnitude across the pH range 1 to 12 after Red Lime™ amelioration (Figure 9-3). This infers that the increased leaching of sulphur in this soil matrix is independent of pH. Increased leaching is believed to be due to the net negative surface charge of the soil particles increasing from the addition of Red Lime™, making adsorption of negatively charged sulphate less favourable.
Magnesium: The leaching concentrations of magnesium were higher in the Red Lime™ amended Manning Light soil across the pH range 4 to 8, including the soils natural pH (Figure 9-4). Increased leachability of magnesium from agricultural soils may have the potential to lead to magnesium deficiencies in crops, indicative of poor growth and yellow leaves. No reports of magnesium deficiency were noted in the liming trial studies, suggesting that the increased magnesium leaching at this amelioration rate may not cause detrimental impacts to the crops.
Phosphorus: Leaching of phosphorus increased by a factor of two, from 5mg/kg to 10mg/kg, in Manning Light soil at pH 2.18, following amelioration with 1.6g/kg Red Lime™ (Figure 9-5). Although this is considered a significant increase, the extreme acidic pH environment is not likely to occur under typical field conditions for this soil. Highly acidic soils (e.g. acid sulphate soils) neutralised with Red Lime™ would need to be thoroughly assessed to ensure phosphorus leaching does not increase in these treated soils, in particular over time, in case the pH of the soil becomes progressively acidic once again.

At the natural pH of Manning Light soil, no measurable change in phosphorus leaching was detected at a 1.6g/kg Red Lime™ amelioration rate, suggesting that phosphorus is not mobile at natural field conditions. This was consistent with no phosphorus deficiencies reported in the plant tissue analyses of crops grown in Red Lime™ amended Manning Light soil at a similar amelioration rate in the pothouse and field liming trials.

![pH dependent Emission of P](image)

**Figure 9- 5: pH dependent leaching of phosphorus from Red Lime™, Manning Light soil and Manning Light soil amended with 1.6g/kg Red Lime™**

9.4 Solubility controlling processes influencing leaching of species from Manning Light Soil amended with 1.6g/kg Red Lime™

Geochemical modelling was carried out on the pH dependent leach data for Manning Light soil amended with 1.6g/kg Red Lime™. Input values for the reactive solid surfaces (clay, HFO; iron/aluminium (hydr)oxides and SHA; organic content) were estimated based on the concentration modelled for the unamended soil and Red Lime™ proportionately. The carbonate concentration was estimated based on the concentration used for modelling the
unamended soil and the proportional concentration added from amendment with Red Lime™.

The geochemical input parameters used for modelling the actual leach data for Red Lime™ amended Manning Light soil are presented in Table 9-2.

### Table 9-2: Input parameters for geochemical modelling of Manning Light soil amended with 1.6/kg Red Lime™

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Manning Light with Red Lime (P,1,1)</td>
</tr>
<tr>
<td>Solved fraction DOC</td>
<td>0.2</td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>4.112E-03 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>2.495E-03 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>9.031E-03 kg/kg</td>
</tr>
</tbody>
</table>

The amount of HFO required to obtain a good prediction of the leach data for phosphorus in the amended soil was slightly lower than the sum of the proportional concentrations used to model the individual components. This is believed to be due to some of the iron/aluminium hydr(oxide) sites in the amended soil not being active.

### 9.4.1 Minerals controlling solubility in Manning Light soil amended with 1.6g/kg Red Lime™

Geochemical speciation modelling of Manning Light soil amended with 1.6g/kg Red Lime™ indicated that the mineralogical phases in Red Lime™ had a strong influence on the solubility of elements in the amended sandy soil, despite the amelioration rate of the Red Lime™ being very low. Table 9-3 shows a list of the solubility controlling mineral phases attributed from Red Lime™ amelioration and the corresponding element(s) controlled by the mineral. In the unamended soil, these elements were controlled by organics. Quartz was also predicted to be a solubility controlling mineral phase (for silicon), which was already present in the soil itself.
Table 9-3: Mineral phases controlling solubility of elements in Manning Light soil amended with 1.6g/kg Red Lime™

<table>
<thead>
<tr>
<th>Controlling Mineral Phase from Red Lime™ amelioration</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_3$-hydrotalcite</td>
<td>Magnesium and Aluminium</td>
</tr>
<tr>
<td>TCA6</td>
<td>Aluminium and Calcium</td>
</tr>
<tr>
<td>Calcite</td>
<td>Calcium</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>Iron</td>
</tr>
<tr>
<td>Manganese Hydrogen Phosphate</td>
<td>Manganese and Phosphorus</td>
</tr>
</tbody>
</table>

9.4.2 Adsorption processes controlling solubility of elements from Manning Light soil amended with 1.6g/kg Red Lime™

A comparison of the geochemical modelling data for the Red Lime™ amended soil with unamended soil indicated that adsorption processes controlling the solubility of specific elements in the two soil matrices were the same. This suggests that only the mineralogical phases in Red Lime™ are in sufficient quantity at the 1.6g/kg amelioration rate to influence changes to the mobility of constituents in the soil matrix.

9.4.3 Adsorption to clay

Clay adsorption was insignificant at controlling solubility in the amended or unamended soil. This was anticipated due to the low clay content in this soil type, relative to the other WA agricultural soils.

9.4.4 Adsorption to iron/aluminium (hydr)oxides

The solubility of phosphorus, molybdenum, selenium and antimony was predicted to be controlled by adsorption to active iron/aluminium hydr(oxide) surfaces. Consequently, increasing Red Lime™ amelioration rates to Manning Light soil is expected to increase the retention of these elements, as the amount of iron/aluminium (hydr)oxides introduced into the soil increase. This is consistent with observations reported for phosphorus and selenium in the pothouse and field liming trials; where phosphorus retention was measured at a 2.56t/ha equivalent Red Lime™ application rate and above; and higher selenium levels were measured in plant tissue and seed using equivalent of 4t/ha Red Lime™ and 10t/ha Alkaloam® (Clarendon et al., 2010). Red Lime™ amelioration is therefore likely to be beneficial to the environment through retention of phosphorus, and for maintaining health and production of grazed livestock by increasing selenium levels in crops used as a feedstock for cattle.
The extent of molybdenum retention in the soil would require further investigation if higher Red Lime™ amelioration rates are to be used, since high levels of molybdenum may affect the health of livestock. The lime field studies did not report on any changes to molybdenum levels in soil or plant tissue using Red Lime™ or Alkaloam® amendments.

9.4.5 Adsorption to insoluble organics
The majority of elements in Red Lime™ amended Manning Light soil were predicted as being dominantly controlled by organics across the pH range 1 to 12 for barium, cadmium, chromium, copper, strontium, thorium, uranium and zinc. Aluminium, calcium, iron, magnesium and manganese were partly controlled by adsorption to organics, in addition to other controlling processes (i.e. adsorption to iron/aluminium (hydr)oxides and/or incorporation within a mineral phase).

9.5 Changes in leaching of Manning Heavy soil when amended with 1.6g/kg Red Lime™

pH dependent leach testing was carried out on Red Lime™ amended Manning Heavy soil. Leaching concentrations of the analytes were compared against those measured in the unamended soil to determine if leaching properties were influenced by Red Lime™ amelioration. The full suite of the analytes is listed in Appendix H.

The pH dependent leaching profiles for all elements measured in the Red Lime™ amended soil reflected that of the soil itself, irrespective of the significant differences in leaching profiles of the two individual matrices. This was consistent with observations reported for Alkaloam® amelioration in this soil (Chapter 8).

Comparison of the pH dependent leach data for the amended and unamended Manning Heavy soil indicate that a 1.6g/kg Red Lime™ amelioration rate has the potential to reduce leaching of cobalt and potassium in this soil across a pH environment 1 to 12 (Figure 9-6).

---

56 Excessive molybdenum intake induces secondary copper deficiency in cattle by combining with copper and sulphur to form copper thiomolybdate, known as molybdenosis (Dept. of Agriculture, 2007).
Cobalt and potassium are essential nutrients for maintaining the health of livestock and crops respectively; hence the ability to retain these elements in the soil, through use of amendments, may be beneficial for agricultural farming, providing they are made available for plant uptake. In the liming trials, the potential benefit of higher crop yields from retention of potassium could not be determined due to fluctuations in yields across the growing seasons for each treatment investigated. Further investigation using higher Red Lime™ amelioration rates is recommended to ascertain the benefits from retaining these elements in the soil.

Leaching concentrations for cobalt and potassium in the Red Lime™ amended Manning Heavy soil were noticeably lower than the concentrations of the individual matrices, suggesting that a more dominant adsorption process is likely to be retaining these elements in the amended soil. Geochemical modelling predicted that the solubility of potassium was controlled by clay adsorption. However in the case of cobalt, no predictions could be made due to its absence from the LeachXS™ geochemical speciation model.

Leaching of DOC also decreased in Manning Heavy soil when ameliorated with 1.6g/kg Red Lime™, across a pH range 1 to 8 (Figure 9-7). Changes to the DOC leaching properties did not appear to influence changes to the leaching of other elements in the ameliorated soil, as was observed in some soils ameliorated with Alkaloam®. This is because the speciation of most elements in the liquid phase within the pH range 1 to 8 is present as free ions in solution, rather than complexes with DOC. Elements associated with complexation to DOC in the liquid phase mostly occurred at pH>8 where DOC leaching was the same in the amended and unamended soil.
Elements predicted to be strongly dominated by complexation to soluble organics at pH 1 to 8 in this soil, such as uranium and thorium, showed indications of reduced leaching, because of the reduced DOC mobility. However, detection limits used for the analysis of these elements in the amended and unamended soils were different. Further analyses are required to confirm if the lower mobility is a consequence of reduced DOC leaching.

9.6 Solubility controlling processes influencing leaching of species from Manning Heavy Soil amended with 1.6g/kg Red Lime™

Geochemical modelling was carried out on the pH dependent leach data for Manning Heavy soil amended with 1.6g/kg Red Lime™. Input values for the reactive solid surfaces (clay, HFO; iron/aluminium (hydr)oxides and SHA; organic content) were estimated based on the concentration modelled for the unamended soil and Red Lime™ proportionately. The carbonate concentration was estimated based on the concentration used for modelling the unamended soil and the proportional concentration added from amendment with Red Lime™.

The geochemical input parameters used for modelling the actual leach data for Red Lime™ amended Manning Heavy soil are presented in Table 9-4.
Table 9-4: Input parameters for geochemical modelling of Manning Heavy soil amended with 1.6/kg Red Lime™

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manning Heavy with Red Lime (P,1,1)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solved fraction DOC</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>1.352E+00 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>8.028E-03 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>1.681E-03 kg/kg</td>
</tr>
</tbody>
</table>

The amount of HFO required to obtain a good prediction of the leach data for phosphorus in the amended soil was slightly lower than the sum of the proportional concentrations used to model the individual components. This is believed to be due to some of the iron/aluminium hydr(oxide) sites in the amended soil not being active.

9.6.1 Minerals controlling solubility in Manning Heavy soil amended with 1.6g/kg Red Lime™

Mineralogical phases in Red Lime™ did not have a strong influence on the solubility of elements in the amended clay soil, with the exception of calcite, that controlled the solubility of calcium at alkaline pH (Figure 9-8).

Figure 9-8: Influence of calcite controlling the solubility of calcium in Manning Heavy soil when ameliorated with 1.6g/kg Red Lime™
9.6.2 Adsorption processes controlling solubility of elements from Manning Heavy soil amended with 1.6g/kg Red Lime™

In Manning Heavy soil, most elements were controlled by adsorption to clay. On ameliorating the soil with 1.6g/kg Red Lime™, adsorption to iron/aluminium (hydr)oxides became an important process controlling the solubility of most elements. Examples can be seen for magnesium, manganese and nickel (Figures 9-9 to 9-11).

Figure 9-9: Predicted and measured leaching of magnesium controlled by adsorption to iron/aluminium (hydr)oxides in Manning Heavy soil when amended with 1.6g/kg Red Lime™
Figure 9-10: Predicted and measured leaching of manganese controlled by adsorption to iron/aluminium (hydr)oxides in Manning Heavy soil when amended with 1.6g/kg Red Lime™

Figure 9-11: Predicted and measured leaching of nickel controlled by adsorption to iron/aluminium (hydr)oxides in Manning Heavy soil when amended with 1.6g/kg Red Lime™
The leaching concentrations of magnesium and manganese were higher in the amended Manning Heavy soil than the unamended soil. This could be due to the change in adsorption processes controlling these elements.

9.7 Changes in leaching of Merredin and Newdegate soils when amended with 1.6g/kg Red Lime™

The pH dependent leach test was conducted on Merredin and Newdegate soils following their amelioration with 1.6g/kg Red Lime™. A full suite of analytes measured can be found in Appendix I and J.

A comparison of the leach data for the amended and unamended soils indicate that Red Lime™ amelioration has the potential to increase mobility of some analytes but decrease the mobility of others. For example, higher leaching concentrations were measured for calcium, manganese, nickel and strontium in the Red Lime™ amended Merredin and Newdegate soils (Figures 9-12 and 9-13). In addition, leachability of chromium, copper and zinc increased in amended Merredin soil and potassium, magnesium, silicon and vanadium increased in amended Newdegate soil.

Figure 9-12: Increased leaching of calcium and manganese from Merredin and Newdegate soils due to amelioration with 1.6g/kg Red Lime™
Figure 9-13: Increased leaching of nickel and strontium from Merredin and Newdegate soils due to amelioration with 1.6g/kg Red Lime™

Leach data for the Red Lime™ amended Merredin and Newdegate soils at their natural pH were assessed against DEC environmental guidelines to determine if the increased leachability is of concern.

Leaching concentrations for the Red Lime™ amended soils were well below the 2010 Landfill Waste guidelines for all analytes except nickel (Table 9-5). Assessment against the ANZECC freshwater guidelines indicated that the leaching of aluminium, copper and nickel however were above the 80% criteria level for both amended soils. A further assessment into what impact this would have on the receiving environment is recommended should Red Lime™ amelioration be used in these soils.

---

57 ASLP leach data had to be used to assess against the criteria for Landfill waste guidelines.
<table>
<thead>
<tr>
<th>element (mg/L)</th>
<th>DEC 1996 Landfill Waste classification by WA ASLP Criteria</th>
<th>Merredin amended with 1.6g/kg Field trial Red Lime ASLP leachate concentrations (mg/L)</th>
<th>Newdegate amended with 1.6g/kg Field trial Red Lime ASLP leachate concentrations (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inert Landfill</td>
<td>Putrescible landfill</td>
<td>Secure Landfill</td>
</tr>
<tr>
<td>Final pH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.5</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.1</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Chromium (VI)</td>
<td>0.5</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>Lead</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.01</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.5</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.2</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Silver</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Fluoride</td>
<td>15</td>
<td>15</td>
<td>150</td>
</tr>
</tbody>
</table>
The total concentration of analytes expected to be present in the Red Lime™ amended soils were also assessed against Ecological Investigation Levels (EILs) and Health Investigation Levels (HILs) of the DEC Contaminated Sites regulatory guidelines (Tables 9-6 and 9-7). Calculated concentrations (based on the proportional sum of the total concentrations measured for the individual components) were well below the EIL and HIL regulatory criteria for all elements. Increased concentrations of elements in the soil from Red Lime™ amelioration at this application rate are not likely to cause environmental concern.

Table 9-6: Calculated concentrations of analytes in Red Lime™ amended Newdegate and Merredin soils and their assessment against EILs

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Ecological Investigation Levels (EIL) (mg/kg)</th>
<th>Calculated total concentration of analyte in Newdegate soil amended with 1.6/kg Red Lime™ (mg/kg)</th>
<th>Calculated total concentration of analyte in Merredin soil amended with 1.6/kg Red Lime™ (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>20</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Arsenic</td>
<td>20</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Barium</td>
<td>300</td>
<td>36.1</td>
<td>22.1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>3</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Chromium III</td>
<td>400</td>
<td>&lt;50</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Chromium VI</td>
<td>1</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Cobalt</td>
<td>50</td>
<td>10.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Copper</td>
<td>100</td>
<td>10.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Lead</td>
<td>600</td>
<td>6.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Manganese</td>
<td>500</td>
<td>38.0</td>
<td>38.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>1</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>40</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>60</td>
<td>20.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Tin</td>
<td>50</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Vanadium</td>
<td>50</td>
<td>5.1</td>
<td>4.1</td>
</tr>
<tr>
<td>Zinc</td>
<td>200</td>
<td>8.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td>600</td>
<td>52.3</td>
<td>102.3</td>
</tr>
<tr>
<td>Sulphate</td>
<td>2000</td>
<td>156.8</td>
<td>306.8</td>
</tr>
</tbody>
</table>
Table 9-7: Calculated concentrations of analytes in Red Lime™ amended Newdegate and Merredin soils and their assessment against HILs

<table>
<thead>
<tr>
<th>Analyte</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>Calculated total concentration of analyte in Newdegate soil amended with 1.6/kg Red Lime™ (mg/kg)</th>
<th>Calculated total concentration of analyte in Merredin soil amended with 1.6/kg Red Lime™ (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>31</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>820</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Arsenic</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>400</td>
<td>200</td>
<td>500</td>
<td>2.26</td>
<td>2.26</td>
</tr>
<tr>
<td>Barium</td>
<td>15000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>190000</td>
<td>36.15</td>
<td>22.15</td>
</tr>
<tr>
<td>Beryllium</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>40</td>
<td>100</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>Cadmium</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>40</td>
<td>100</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Chromium I1</td>
<td>120000</td>
<td>-</td>
<td>-</td>
<td>480000</td>
<td>240000</td>
<td>600000</td>
<td>&lt;50</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Chromium VI</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>400</td>
<td>200</td>
<td>500</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Cobalt</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>400</td>
<td>200</td>
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<td>5.00</td>
</tr>
<tr>
<td>Copper</td>
<td>1000</td>
<td>-</td>
<td>-</td>
<td>4000</td>
<td>2000</td>
<td>5000</td>
<td>10.01</td>
<td>14.01</td>
</tr>
<tr>
<td>Lead</td>
<td>300</td>
<td>-</td>
<td>-</td>
<td>1200</td>
<td>600</td>
<td>1500</td>
<td>6.05</td>
<td>7.05</td>
</tr>
<tr>
<td>Manganese</td>
<td>1500</td>
<td>-</td>
<td>-</td>
<td>6000</td>
<td>3000</td>
<td>7500</td>
<td>38.05</td>
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</tr>
<tr>
<td>Methyl Mercury</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>20</td>
<td>50</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Mercury</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>60</td>
<td>30</td>
<td>75</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>390</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5100</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>Nickel</td>
<td>600</td>
<td>-</td>
<td>-</td>
<td>2400</td>
<td>600</td>
<td>3000</td>
<td>20.01</td>
<td>14.01</td>
</tr>
<tr>
<td>Tin</td>
<td>47000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>610000</td>
<td>1.03</td>
<td>1.03</td>
</tr>
<tr>
<td>Vanadium</td>
<td>550</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7200</td>
<td>5.11</td>
<td>4.11</td>
</tr>
<tr>
<td>Zinc</td>
<td>7000</td>
<td>-</td>
<td>-</td>
<td>28000</td>
<td>14000</td>
<td>35000</td>
<td>8.01</td>
<td>6.01</td>
</tr>
<tr>
<td>boron</td>
<td>3000</td>
<td>-</td>
<td>-</td>
<td>12000</td>
<td>6000</td>
<td>15000</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>
Some analytes became less mobile in Merredin and Newdegate soil when amended with 1.6g/kg Red Lime™, specifically at the natural pH of the amended soil. Lower leaching concentrations were measured for chloride, iron, gallium, silicon, titanium and thorium in Red Lime™ amended Merredin soil (Figure 9-14) relative to the unamended soil.

Geochemical modelling predicted that the retention of these elements was controlled by different adsorption processes (to clay and organics) and soluble mineral phases (quartz), rather than a single mechanism controlling all elements. DOC leaching did not change significantly across the pH range 1 to 12, suggesting that the increased retention was
therefore likely to be due to additional clay surfaces and quartz made available in the soil from Red Lime™ amelioration, rather than adsorption to organics.

In Newdegate soil, Red Lime™ amelioration reduced the leaching of chloride, copper, gallium and DOC at the amended soil’s natural pH (Figure 9-15). The slight decrease in DOC leaching did not impact on the leaching of other elements.

![Figure 9-15: pH dependent leaching of chloride, copper, gallium and DOC from Newdegate soils with and without 1.6g/kg Red Lime™ amendment](image)

The pH dependent leach data for phosphorus in both the amended Merredin and Newdegate soils indicated that a 1.6g/kg Red Lime™ amelioration rate is not likely to increase phosphorus retention (Figure 9-16). This was consistent with observations reported in the Clarendon et al., (2010) liming trials. Higher amelioration rates of 4t/ha also reported no phosphorus retention in Merredin soil.
9.8 Solubility controlling processes influencing leaching of species from Merredin soil amended with 1.6g/kg Red Lime™

The geochemical input parameters used for modelling leach data for Merredin soil amended with 1.6g/kg Red Lime™ are presented in Table 9-7. Input values used in the model were based on proportional values used for modelling the individual matrices.

Table 9-8: Input parameters for geochemical modelling of Merredin soil amended with 1.6g/kg Red Lime™

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merredin_Red_Lime_080507 (P,1,1)</td>
<td>0.2</td>
</tr>
<tr>
<td>Solved fraction DOC</td>
<td>0.2</td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
</tr>
<tr>
<td>Clay</td>
<td>6.621E-01 kg/kg</td>
</tr>
<tr>
<td>HFO</td>
<td>2.075E-03 kg/kg</td>
</tr>
<tr>
<td>SHA</td>
<td>7.071E-03 kg/kg</td>
</tr>
</tbody>
</table>

Mineral phases that were predicted to be controlling species in the individual matrices were also added to the model. Carbonate concentration was estimated based on the concentration estimated in the unamended soil and the proportional amount added from Red Lime™ amendment.
9.8.1 Minerals controlling solubility in Merredin soil when amended with 1.6g/kg Red Lime™

Of all the mineralogical phases present in Red Lime™, only calcite had an impact on the solubility of calcium in Merredin soil when ameliorated with Red Lime™. This occurred across the alkaline pH range (Figure 9-17). This suggests that the 1.6g/kg ameliorant rate may be too low for other mineral phases in Red Lime™ to control leaching in this soil matrix.

![Figure 9-17: Predicted and measured leaching of calcium from Merredin soil with and without 1.6g/kg Red Lime™ amendment and the speciation in the solid phase controlling solubility](image)

Quartz controlled the solubility of silicon in both the amended and unamended Merredin soil.

9.8.2 Adsorption processes controlling solubility of elements from Merredin soil amended with 1.6g/kg Red Lime™

Adsorption processes controlling the solubility of elements in Merredin soil, such as adsorption to clay, organics and iron/aluminium (hydr)oxides were similar in the Red Lime™ amended Merredin soil.
9.9 Solubility controlling processes influencing leaching of species from Newdegate soil amended with 1.6g/kg Red Lime™

The geochemical input parameters used for modelling leach data for Newdegate soil amended with 1.6g/kg Red Lime™ are presented in Table 9-8. Input values used in the model were also based on proportional values used for modelling the individual matrices.

Table 9- 9: Input parameters for geochemical modelling of Newdegate soil amended with 1.6g/kg Red Lime™

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newdegate_Red_Lime_080507 (P,1,1)</td>
<td></td>
</tr>
</tbody>
</table>

| Solved fraction DOC | 0.2 |
| Sum of pH and pe   | 15.00 |
| L/S                 | 10.0000 l/kg |
| Clay                | 5.521E-01 kg/kg |
| HFO                 | 4.671E-04 kg/kg |
| SHA                 | 7.071E-03 kg/kg |

9.9.1 Minerals controlling solubility in Newdegate soil amended with 1.6g/kg Red Lime™

No mineralogical phases from Red Lime™ controlled the solubility of elements in Newdegate amended soil. Only quartz controlled the solubility of silicon in this matrix, which was present in the original soil matrix.

9.9.2 Adsorption processes controlling solubility of elements in Newdegate soil amended with 1.6g/kg Red Lime™

Adsorption processes controlling the solubility of elements in Newdegate soil were similar in the Red Lime™ amended Newdegate soil.

9.10 Changes in leaching of Bassendean soil when amended with 1.6g/kg Red Lime™

The pH dependent leach test was conducted on Bassendean soil amended with 1.6g/kg Red Lime™ (2.56t/ha top dressed equivalent rate). The leaching profiles for the full suite of analytes is in Appendix K.
pH dependent leaching profiles for most analytes measured in Red Lime™ amended Bassendean soil reflected that of the unamended soil, irrespective of the distinct differences in leaching of some elements in the individual matrices. A comparison of the leaching concentrations from the Red Lime™ amended and unamended Bassendean soil were very similar across the pH range 1 to 12, suggesting that an amelioration rate of 1.6g/kg is not high enough to make any significant changes to the soil’s leaching characteristics.

An exception to this was observed at pH 2 for barium, calcium, magnesium, manganese, silicon, strontium and zinc, where the leaching concentration in the unamended soil was lower than in the amended Bassendean soil (Figure 9-18 and Figure 9-19). The lower leaching concentration for these elements was shown to correspond with lower leaching of DOC, inferring that these elements are likely to be adsorbed to more insoluble organics at pH 2 in the unamended soil.

Figure 9-18: pH dependent leaching of species from Red Lime™, Bassendean soil and Bassendean soil amended with 1.6g/kg Red Lime™
Some heavy metal species and other species of potential concern such as cadmium, chromium, copper, fluoride, mercury, lead, antimony, selenium, tin, and thorium were detected in both the soil and amended soil extracts at concentrations close to or below the analytical detection limit. Within the noise of the measurements, no change in leaching behaviour from a 1.6g/kg Red Lime™ amelioration rate could be ascertained for these species.

The pH dependent leaching of sodium from Red Lime™ amended and unamended Bassendean soil represented solubility controlled behaviour (Figure 9-20). Using geochemical modelling, the processes predicted to be controlling mobility of sodium was adsorption to clay and organics in the amended and unamended soil. In contrast, the leaching of sodium from Red Lime™ exhibited availability controlled behaviour.

Figure 9-19: pH dependent leaching of species from Red Lime™, Bassendean soil and Bassendean soil amended with 1.6g/kg Red Lime™
9.11 Solubility controlling processes influencing leaching of species from Bassendean Soil amended with 1.6g/kg Red Lime™

The geochemical input parameters used for modelling the leach data for Bassendean soil amended with 1.6g/kg Red Lime™ are presented in Table 9-9. Input values used in the model were based on proportional values used for modelling the individual matrices.

Table 9-10: Input parameters for geochemical modelling of Bassendean soil amended with 1.6g/kg Red Lime™.

<table>
<thead>
<tr>
<th>Material</th>
<th>Input specification</th>
<th>Input specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bassendean_Lime_111006 (P,1,1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solved fraction DOC</td>
<td>Varied with pH</td>
<td></td>
</tr>
<tr>
<td>Sum of pH and pe</td>
<td>15.00</td>
<td></td>
</tr>
<tr>
<td>L/S</td>
<td>10.0000 l/kg</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>1.464E-01 kg/kg</td>
<td></td>
</tr>
<tr>
<td>HFO</td>
<td>3.510E-03 kg/kg</td>
<td></td>
</tr>
<tr>
<td>SHA</td>
<td>2.000E-03 kg/kg</td>
<td></td>
</tr>
</tbody>
</table>

Mineral phases that were predicted to be controlling species in the individual matrices were also added to the model. Carbonate concentration was estimated based on the concentration estimated in the unamended soil and the proportional amount added from Red Lime™ amendment.
9.11.1 Minerals controlling solubility in Bassendean soil amended with 1.6g/kg Red Lime™

The carbonate associated minerals in Red Lime™ were determined to control the solubility of some species in the Red Lime™ amended Bassendean soil.

For example, laumonite, the mineral phase partially controlling aluminium, silicon and calcium in Red Lime™, also controlled these metals in the amended Bassendean soil, in addition to amorphous aluminium hydroxide and calcite minerals already present in the soil itself. Ferrihydrite was predicted to be the solubility controlling mineral for iron in both the amended and unamended soil.

Other solubility controlling mineral phases, such as manganese hydrogen phosphate, calcite and amorphous aluminium hydroxide, were consistent in both the amended and unamended soil.

9.11.2 Adsorption to clay

The proportion of additional clay introduced into Bassendean soil from ameliorating with 1.6g/kg Red Lime™ was higher than the additional iron/aluminium (hydr)oxides (HFO). Despite this, the HFO surface sites were noticeably more active than the clay sites. An example can be seen for the geochemical speciation of fluoride in the amended and unamended soil, shown in Figure 9-21.
Figure 9-21: Predicted and measured leaching of fluoride controlled by adsorption to clay and iron/aluminium (hydr)oxides in Bassendean soil with and without 1.6g/kg Red Lime™ amendment

9.11.3 Adsorption to organics and active iron/aluminium (hydr)oxide surfaces

The leaching of the majority of species in Red Lime™ amended Bassendean soil were controlled by adsorption to active insoluble organics, such as barium, chromium, copper, magnesium, lead, strontium, thorium, uranium. Other species, such as cadmium, magnesium, nickel, and zinc were partially controlled by adsorption to organics and/or iron/aluminium (hydr)oxide surfaces. This was consistent with observations reported for the unamended soil.

Leaching concentrations of those species partially controlled by active iron/aluminium (hydr)oxides in Bassendean soil did not decrease further when the soil was ameliorated with Red Lime™. This suggests that the application rate of Red Lime™ was too low to provide sufficient additional iron/aluminium (hydr)oxide sites for decreasing leaching, despite the sites being more controlling than adsorption to clay.

Competitive adsorption effects were also noted in the Red Lime™ amended Bassendean soil, as discussed in Chapter 7 and 8.
9.12 Process development of Red Lime™ for use as a soil amendment or liming agent at 1.6g/kg application rate

Red Lime™ is currently produced by taking a side stream of the causticiser residue from the Bayer circuit, and washing and separating out the course fraction. The material is then solar dried and made available for re-use. Further treatment of the material would be desirable to selectively reduce the total concentration of aluminium, copper and nickel in Red Lime™, prior to it being solar dried for use as a liming agent or soil amendment in Merredin and Newdegate soils. This additional treatment would reduce the risk of increased leaching of these elements in the Red Lime™ ameliorated soils, and lower concentrations below the ANZECC freshwater guidelines for the 80% criteria level at the 1.6g/kg amelioration rate.

9.13 Conclusions

The pH dependent leaching profile for the majority of elements in all the amended soils reflected similar profiles to the corresponding unamended soil, despite significant differences in the leaching behaviour of the individual components.

*Manning Light soil amended with 1.6g/kg Red Lime™*

The mineralogical phases in Red Lime™ had a strong influence in controlling the solubility of aluminium, calcium, magnesium, manganese, iron and phosphorus in amended Manning Light soil, despite the 1.6g/kg amelioration rate being very low. In the unamended soil these elements were controlled by organics, with the exception of phosphorus, which was controlled by HFOs.

Ameliorating the WA agricultural soils with 1.6g/kg Red Lime™ increased the natural pH of Newdegate soil by 1.58 pH units, and Manning Light and Merredin soil by 0.5 units. This liming rate did not change the pH of the Manning Heavy soil, due to the soil’s high buffering capacity.

In Manning Light soil, leaching concentrations of calcium and sulphur increased across the pH range 1 to 12 when ameliorated with 1.6g/kg Red Lime™, with sulphur concentrations increasing by one order of magnitude. This was concluded as being due to the net negative surface charge of the soil particles increasing from the addition of Red Lime™. Phosphorus leaching increased between pH 1 to 6 and copper leaching increased at pH<2 and pH>8. Leaching of these elements however remained unchanged at the soil’s natural pH.
Magnesium leaching increased in the pH range 4 to 8. No reports of magnesium deficiency were noted in the pothouse and field liming trials, suggesting that the increased magnesium leaching due to the 1.6g/kg amelioration rate may not be sufficient to cause detrimental effects to crops.

The solubility of phosphorus, molybdenum, selenium and antimony was predicted to be controlled by adsorption to active iron/aluminium hydr(oxide) surfaces. Consequently, increasing Red Lime™ amelioration rates in Manning Light soil may increase the retention of these elements, as the amount of iron/aluminium (hydr)oxides introduced into the soil increases.

The dominant process controlling solubility of barium, cadmium, chromium, copper, strontium, thorium, uranium and zinc across the pH range of 1 to 12 was adsorption to humic and fulvic acids. Other species, such as aluminium, calcium, iron, magnesium and manganese, were partially controlled by adsorption to organics, in addition to other controlling processes (i.e. adsorption to iron/aluminium (hydr)oxides and/or incorporation within a mineral phase).

**Manning Heavy soil amended with 1.6g/kg Red Lime™**

Ameliorating Manning Heavy soil with 1.6g/kg Red Lime™ reduced the leaching of cobalt and potassium across the pH range 1 to 12, with concentrations being noticeably lower in the amended soil than each of the individual matrices. These retention properties may be beneficial in agricultural farming for this soil type, providing the elements are made available for plant uptake. The leaching concentrations for cobalt and potassium in the Red Lime™ amended Manning Heavy soil were also noticeably lower than the concentrations of the individual matrices. Potassium was strongly controlled by adsorption to clay. The process controlling cobalt could not be predicted due to the reactant species not being available in the LeachXS™ geochemical speciation modelling.

DOC leaching also decreased, across the pH range 1 to 8. Uranium and thorium were strongly controlled by organics and showed a corresponding decrease in leaching due to the reduced DOC mobility. Changes to the DOC leaching properties did not influence any changes to the leachability of other elements in the ameliorated soil.

**Merredin and Newdegate soils amended with 1.6g/kg Red Lime™**

pH dependent leach data suggest that amending Merredin and Newdegate soils with 1.6g/kg Red Lime™ has the potential to increase leaching of calcium, manganese, nickel and
strontium across a pH range 4 to 10. Mobility of chromium, copper and zinc also increased in the amended Merredin soil and potassium, magnesium, silicon and vanadium increased in the amended Newdegate soil.

Leaching concentrations for the Red Lime™ amended Merredin and Newdegate soils were determined to be well below the 2010 Landfill Waste guidelines for all analytes, except nickel. Assessment against the ANZECC freshwater guidelines indicated that leaching of aluminium, copper and nickel were above the 80% criteria level for both amended soils. Further investigation (e.g conceptual site modelling) is required to assess whether these elements are a potential risk to environmental receptors.

The total concentration of analytes expected to be present in Merredin and Newdegate soil when amended with 1.6g/kg Red Lime™ were well below the Ecological Investigation Levels (EILs) and Health Investigation Levels (HILs) of the DEC Contaminated Sites regulatory guidelines.

Red Lime™ amelioration reduced the leaching of chloride, iron, gallium, silicon, titanium and thorium in Merredin soil at the soil’s natural pH and across the pH range 4 to 8. For the majority of these elements the increased retention was due to additional clay surfaces and quartz made available in the soil from Red Lime™ amelioration. In Newdegate soil, Red Lime™ amelioration reduced the leaching of chloride, copper, gallium and DOC at the amended soil’s natural pH.

The pH dependent leach data indicate that ameliorating Merredin and Newdegate soils with 1.6g/kg Red Lime™ did not increase the phosphorus retention properties of these soils across the whole pH range 1 to 12. This implies that higher amelioration rates would be required if Red Lime™ is to be used as a soil amendment for retaining nutrients, in addition to a liming material.

_Bassendean soil amended with 1.6g/kg Red Lime™_

Measured leaching concentrations from the Red Lime™ amended and unamended Bassendean soil were very similar across the pH range 3 to 12, suggesting that an amelioration rate of 1.6g/kg is not high enough to make any significant changes to the soil’s leaching characteristics.

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58 ASLP leach data had to be used to assess against the criteria for Landfill waste guidelines
At pH 2 leaching of barium, calcium, magnesium, manganese, silicon, strontium and zinc were lower in Bassendean soil than the Red Lime™ amended soil. This was due to less DOC release which would typically mobilise these elements at this pH.

The pH dependent leaching of sodium from Red Lime™ amended and unamended Bassendean soil represented solubility controlled behaviour. Using geochemical modelling, the processes predicted to be controlling mobility of sodium was adsorption to clay and organics in the amended and unamended Bassendean soil. In contrast, the leaching of sodium from Red Lime™ exhibited availability controlled behaviour.

The mineral, laumonite, was introduced into the Bassendean soil matrix on amendment with 1.6g/kg Red Lime™. Laumonite was predicted to partially control the solubility of aluminium, silicon and calcium in the amended soil.

The proportion of additional clay introduced into Bassendean soil from ameliorating with 1.6g/kg Red Lime™ was higher than the additional iron/aluminium (hydr)oxides (HFO). Despite this, the HFO surface sites were noticeably more active than the clay sites. Leaching concentrations of those species partially controlled by active HFOs in Bassendean soil did not decrease further when the soil was ameliorated with Red Lime™. This suggests that the application rate of Red Lime™ was too low to provide sufficient additional active HFO sites for decreasing leaching, despite the sites being more controlling than adsorption to clay.

9.14 Recommendations
Detection limits for the analysis of some species in the agricultural soils were lower than those in the corresponding Red Lime™ amended soil. As a consequence, interpretation of changes in leach data between the amended and unamended soils was limited. Repeat analysis of some analytes using consistent detection limits for each amended and unamended soil would allow further interpretation of leach data and changes due to Red Lime™ amelioration.

Using consistent and lower detection limits, determine the extent of copper immobilisation in Manning Light soil due to amelioration with 1.6g/kg Red Lime™.

Using consistent and lower detection limits, confirm that uranium and thorium leaching decreases as a result of decreased DOC leaching in Manning Heavy soil amended with 1.6g/kg Red Lime™.
Add cobalt as an available reactant to LeachXS™ to enable geochemical modelling to be conducted – specifically with this being an essential nutrient for ongoing health and production of livestock.

Conduct environmental scenario assessments on Merredin and Newdegate soil amended with 1.6g/kg Red Lime™ to determine what impact the increased leachables may have on a receiving environment.

Determine whether increased Red Lime™ amelioration rates will increase the phosphorus retention properties in Merredin and Newdegate soil.

Investigate opportunities for process development of Red Lime™ to selectively reduce the total concentration of aluminium, nickel and copper in the material.
Chapter 10

OVERALL CONCLUSIONS

10.1 Introduction
The aim of this study was to assess the leaching behaviour of bauxite residue products, Alkaloam® and Red Lime™ in various environments. The purpose of the study was to assess their suitability as re-use products and to determine if any process development would be required to assist in their development as sustainable marketable commodities.

Five major objectives were set to meet this aim;

1. Compare ASLP and pH dependent leach tests for application on the alkaline Bayer residue products, Alkaloam® and Red Lime™, to determine the appropriateness of these two methods for assessing by-products for re-use and to assist in their development as marketable commodities.
2. Develop a method on the pH dependent leach test to assess Bayer residue products.
3. Assess the leaching behaviour of Alkaloam® and Red Lime™ and determine whether these materials are safe for use, based on their leaching properties.
4. Determine changes in leaching from WA soils when Alkaloam® and Red Lime™ are applied as ameliorants at an application rate of 6.25g/kg and 1.6g/kg respectively. Using LeachXS™ geochemical modelling, determine the processes controlling leaching for a range of species.
5. Determine if any process development is required on Alkaloam® and Red Lime™ to be considered as raw material commodities.

10.2 ASLP vs pH dependent leach testing for assessing industrial by-products, Alkaloam® and Red Lime™ for re-use
A comparison of the ASLP and pH dependent leach test data for Alkaloam®, Red Lime™ and a WA agricultural soil (chapter 5) illustrates that the pH dependent leach test provides more representative fundamental information on leaching than the ASLP, and hence more confidence for assessing the impact of a material on a receiving environment.

The pH dependent leach test provides information on changes in leachability of constituents from a material across a pH range 0.5 to 12. The final leaching pH values are controlled and therefore any changes in pH from reactions occurring during the leaching period are
accounted for in the test. ASLP does not allow leaching to be measured under controlled pH conditions, therefore assessment of leach data using this test can be misinterpreted depending on whether the final pH or initial pH of the leaching solutions are used in the evaluation.

ASLP is not suitable for assessing by-products that have a high buffering capacity and natural alkaline pH, such as Alkaloam® and Red Lime™. The leaching of Red Lime™ using ASLP could only be measured in the alkaline pH region, since the final leaching pH values were uncontrolled and all above pH 10. Differences between the initial and final leaching pH were significant, with the start pH being 2.9 and 5 compared to the final leaching pH values of 10.3 and 12 respectively. Such a significant difference is open to misinterpretation of leach data if concentrations are assessed based on their initial pH values as opposed to the final leaching pH. Final pH values are controlled in the pH dependent leach test and therefore this method, in contrast, is capable of assessing leaching in high buffering capacity alkaline materials.

Conducting the pH dependent leach test on industrial by-products as part of an in depth environmental assessment process can provide insight into whether constituents are likely to be mobile at a pH representative of applications being considered, and whether mobility of constituents are likely to increase if the environment pH changes. This would be valuable information if by-products are to be used in environments susceptible to pH changes and would allow any foreseeable issues to be considered in feasibility assessments.

The pH dependent leach test can determine whether the mobility of constituents from a material exhibit “availability controlled” or “solubility controlled” leaching behaviour. The test also determines the maximum concentration available for leaching for each species in the matrix, which is considered a more accurate assessment for determining potential impacts to the environment than total composition.

pH dependent leach data, with the aid of LeachXSTM geochemical modelling, is capable of predicting the processes controlling leaching of constituents from a material, and determining the speciation partitioned between the solid and liquid phase of the matrix across a defined pH range. A fundamental understanding of the species present in the liquid and solid phase could potentially identify whether the more toxic forms of a constituent are present in the matrix at a given pH (e.g. mobilisation of copper through the formation of soluble complexes with organics is in a less toxic form than freely available copper ions in solution).
ASLP and pH dependent leach data correlated well for most elements in Alkaloam®, Red Lime™ and Manning Light soil, despite differences in the method parameters. This highlights that pH is the dominant factor controlling leaching, and that method parameter differences such as particle size, extraction solution and extraction time have less impact on the leaching behaviour in these materials.

The pH dependent leach test with LeachXS™ geochemical speciation modelling is an effective tool that could be adopted as part of environmental assessments for evaluating the use of industrial by-products for re-use, in particular for evaluating their use as soil amendments. This process will also assist in determining whether any process development is required to develop a sustainable product for re-use. This test is considered more superior to the ASLP for scenario based environmental assessments.

10.3 Method development on pH dependent leach test
Incorporation of a centrifugation step (10,000rpm;15mins) prior to vacuum filtration in the pH dependent leach test improved solid/liquid separation for soils with a high clay content. The centrifugation also consolidated colloidal species (micellular humics) from the alkaline eluates and improved settling. This prevented filter membranes blocking up from the build up of a gelatinous colloidal layer and subsequent loss of metals through adsorption to the gel. Centrifugation improved the leach data accuracy for elements, in addition to reducing the sample preparation time.

Increasing the centrifuge speed from 10,000rpm to 15,000rpm and 20,000rpm did not change the leaching concentrations for most elements, indicating that a centrifuge speed of 10,000rpm would be sufficient for optimising solid/liquid separation during leach testing.

Nitric acid can be used as an alternative extractant to hydrochloric acid for determining nitrate leaching in Alkaloam®, Red Lime™ and the WA soils.

The pH dependent leaching behaviour of nitrate from Alkaloam® was characterised by a shallow ‘U’ curve, with maximum solubility occurring at extreme acidic and alkaline pH. Nitrate solubility was influenced by changes in the surface charge of particles with changing pH.

The pH dependent leaching of nitrate from Red Lime™ decreased with increasing pH, and was controlled by the precipitation of a mineral species. It is proposed that nitrate ions are
being adsorbed by the zeolite mineral laumonite, or calcite, present in Red Lime™, based on previous research and consistencies in the pH dependent leaching profiles of calcium and silicon with nitrate.

Alkaloam® has the potential to retain nitrate in Bassendean soil in the pH range 2 to 8 when applied at 6.25g/kg amelioration rate. At alkaline pH>8 Alkaloam® does not retain nitrate in this soil.

The pH dependent leach test can be used to assess benefits of nitrate retention from soil amelioration. This could be a valuable tool for improving nitrogen management and optimising fertiliser use in WA soils.

The leaching concentrations for the majority of elements analysed from Alkaloam®, Red Lime™, Manning Light and Manning Heavy (clay soil) WA agricultural soil were similar using hydrochloric acid and nitric acid extractants. A positive bias in leaching was observed using hydrochloric acid extractant for those elements strongly affected by the presence of chloride ions, in particular in the acid pH range.

10.4 Leaching of Alkaloam® and Red Lime™

The minimum leaching of antimony, aluminium, arsenic, barium, cadmium, cobalt, chromium, DOC, copper, gallium, iron, lead, lithium, mercury, molybdenum, phosphorus, uranium, thorium and zinc from Alkaloam® occurred within the natural pH range of WA agricultural soils (i.e. pH 4 to 7.59). This indicates that Alkaloam® amelioration has the potential to retain metals in these soils.

Red Lime™ also showed minimum leaching in this pH range for antimony, arsenic, cadmium, chromium, copper, DOC, fluoride, iron, gallium, lead, lithium, mercury, molybdenum, phosphorus, tin, thorium and zinc.

The leaching behaviour of species from Alkaloam®, Red Lime™ and the WA soils were specific for each element across the pH range 0.5 to 12. Elements were predicted to be controlled by incorporation within mineral phases or by adsorption processes, such as adsorption to clay, organics and iron/aluminium (hydr)oxides. Specific details of processes controlling leaching in these materials are provided in Chapter 7.

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59 pH range is with respect to measurements in water, pH measurements in CaCl₂ solution will be lower.
With the exception of calcium and silicon, the leaching behaviour for the majority of species in Red Lime™ showed different profiles to that in Alkaloam®. This was believed to be due to the additional calcium minerals and higher organic content present in Red Lime™.

Iron was controlled by goethite and ferrihydrite in Alkaloam® and only ferrihydrite in Red Lime™. This is likely to be due to the higher concentration of organics inhibiting the formation of goethite in Red Lime™.

Chloride was availability controlled across the full pH range in Red Lime™ and only in the acidic pH range in Alkaloam®. In the neutral to alkaline pH range chloride was controlled by adsorption to clay in Alkaloam®.

The amount of iron/aluminium (hydr)oxides required to model leach data well was less than the total amount analysed. This is likely due to the surfaces of the aluminium and iron hydr(oxide)s not being 100% active in the matrices, which is the assumption made in the modelling software.

10.5 Affect of Alkaloam® and Red Lime™ amelioration on the pH dependent leaching in WA soils
The pH change in the soils when amended with 6.25g/kg (10t/ha equivalent) Alkaloam® in the laboratory was found to be consistent with pH changes reported in the 2nd year of the liming/soil amendment field trials.

Ameliorating the WA agricultural soils with 1.6g/kg Red Lime™ increased the natural pH of Newdegate soil by 1.58 pH units, and Manning Light and Merredin soil by 0.5 units. This liming rate did not change the pH of the Manning Heavy soil, due to the soil’s high buffering capacity.

The leaching behaviour of species from Alkaloam® and Red Lime™ amended WA soils were specific for each element across the pH range 0.5 to 12. Specific details of processes controlling leaching in these materials are provided in Chapter 8 and 9.

With the exception of Merredin and Newdegate soil, the leaching concentrations for the majority of elements in the WA soils were similar with or without amelioration with Alkaloam® and Red Lime™. Exceptions to this using Alkaloam® amelioration were
increased leaching of silicon and decreased leaching of phosphorus in Bassendean soil, increased leaching of iron, copper, silicon and zinc in Manning Light soil, increased leaching of phosphorus and sulphur in Manning Heavy soil and decreased leaching of cobalt in Manning Heavy soil. Exceptions to this using Red Lime™ amelioration were increased leaching of calcium, sulphur and magnesium in Manning Light soil.

The leaching of several species from Newdegate soils were impacted greatly from amelioration with 6.25g/kg Alkaloam®. Copper leaching decreased due to a corresponding decrease in soluble organics. The leaching of calcium, chloride, iron, potassium, magnesium, strontium, sulphur, silicon and vanadium increased due to desorption from clay and dissolution of quartz (for silicon).

Amending Merredin and Newdegate soils with 1.6g/kg Red Lime™ increased the leaching of calcium, manganese, nickel and strontium. Mobility of chromium, copper and zinc also increased in the amended Merredin soil and potassium, magnesium, silicon and vanadium in amended Newdegate soil.

Amending Merredin and Newdegate soils with 1.6g/kg Red Lime™ reduced the leaching of chloride, iron, gallium, silicon, titanium and thorium in Merredin soil and reduced the leaching of chloride, copper, gallium and DOC in Newdegate soil at their natural pH.

Leaching concentrations of some metals in the amended soils were higher than in the individual matrices. This was due to increased complexation with soluble organics (DOC).

With the exception of Manning Light soil, the amount of HFO required to model data for the amended WA soils was lower than the proportional sum of the concentrations used to model the individual matrices. This indicates that the HFOs present in the amended soils are not 100% active. In Alkaloam® amended Manning Light soil a higher concentration of HFO was required, indicating that more HFOs are active in this amended soil than the individual matrices.

No phosphorus retention was measured from ameliorating Manning Light soil with 6.25g/kg Alkaloam®. Higher amelioration rates may need to be considered.

Ameliorating Manning Heavy soil with 1.6g/kg Red Lime™ decreased leaching of cobalt and potassium across the full pH range 0.5 to 12. This may be beneficial in agricultural
farming providing the elements are made available for plant uptake. DOC leaching also decreased.

Solubility controlling mineral phases in Alkaloam® did not control leaching of the majority of constituents in the amended soils. Exceptions to this were zinc sulphite and TCP, that partially controlled zinc and phosphate in Bassendean soil, and calcite, and manganese hydrogen phosphate, that partially controlled calcium, manganese, and phosphate in Manning Light soil.

The mineralogical phases in Red Lime™ had a strong influence in controlling the solubility of aluminium, calcium, magnesium, manganese, iron and phosphorus in amended Manning Light soil, despite the 1.6g/kg amelioration rate being very low.

The mineral, laumonite, was introduced into the Bassendean soil matrix on amendment with 1.6g/kg Red Lime™. This mineral was predicted to partially control the solubility of aluminium, silicon and calcium in the amended soil.

The solubility of phosphorus in the Alkaloam® and Red Lime™ amended WA soils is controlled by adsorption to active iron/aluminium (hydr)oxide sites.

Competitive adsorption effects of metals to insoluble organic acids in the Alkaloam® and Red Lime™ amended soil matrices could not be accounted for in the LeachXS™ geochemical speciation modelling. This is a limitation in the software.

Chloride leaching in the amended WA soils was controlled by the variation in surface charge on the soil particles with changes in pH.

10.6 Process development of Alkaloam® and Red Lime™

Some metals in Alkaloam® are above the Ecological Investigation Level trigger values in terms of total concentration, but indicated very low leachability. When used as a soil ameliorant in the WA soils at the application rate of 6.25g/kg (10t/ha equivalent in top 1cm soil), the heavy metals were measured well below all Ecological Investigation Levels and Health Investigation Levels. This was due to the dilution effects of the soil.

Leaching concentrations in the Alkaloam® ameliorated soils at 6.25g/kg application rate are within acceptable limits based on ANZECC water quality guidelines and within the inert
landfill criteria for the highly stringent European Landfill Directive guidelines at the pH range representative of field conditions.

No process development on Alkaloam® is therefore deemed necessary for the material to be used as a soil amendment in Manning Light, Merredin, Newdegate and Bassendean soils at the application rate of 6.25g/kg.

The total concentration of analytes expected to be present in the Red Lime™ amended soils (at 1.6g/kg application rate) were well below the EIL and HIL regulatory criteria for all analytes. Leaching concentrations were determined to be well below the 2010 Landfill Waste guidelines 60 for all analytes except nickel 61, and below the 80% ANZECC freshwater guidelines for all analytes, except aluminium, copper and nickel.

Process development of Red Lime™ to selectively reduce the total concentration of aluminium, nickel and copper would be desirable prior to its use as a liming agent or soil amendment in Merredin and Newdegate soils. In particular if these soils are located close to receiving waters.

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60 ASLP leach data had to be used to assess against the criteria for Landfill waste guidelines.
61 On the border of the criteria.
Chapter 11

OVERALL RECOMMENDATIONS

It is recommended that;

The pH dependent leach test be considered as an alternative to ASLP for conducting more accurate environmental assessments on industrial by-products for re-use applications.

Validation tests be conducted on the pH dependent leach test alongside ASLP to determine whether this test can be recognised as a standard leach test in Australia.

Further investigations be conducted to determine if LeachXS™ geochemical modelling can be used to accurately predict leaching behaviour for Alkaloam® and Red Lime™ amended agricultural soils, at different amelioration rates.

Centrifugation (10,000rpm; 15mins) be incorporated into the pH dependent leach test, prior to filtration, to improve solid/liquid separation on soils that contain clay particulates. This will improve the leach data accuracy for elements such as aluminium, iron, silicon, phosphorus, chloride, TOC, calcium, potassium, magnesium, sodium and sulphur, in addition to reducing the sample preparation time.

Hydrochloric acid is used as an alternative extractant to nitric acid for assessing the pH dependent leaching of nitrate in soil materials.

The pH dependent leach test be evaluated for assessing nitrate retention in a range of WA soils from different cropping areas to determine if it can be used as a tool for improving nitrogen management and optimising fertiliser use in WA soils.

Further research be conducted to determine whether the NICA-Donnan model in the LeachXS™ software can be improved to accommodate the different binding properties of cations to active organic sites. An alternative solubility model may need to be considered if this is not feasible.

Gallium and cobalt be added to the list of available reactive species in LeachXS™ so that geochemical speciation modelling can be predicted for these elements in soil matrices.
Column leach testing be performed on Alkaloam® and Red Lime™ amended agricultural soils to determine the cumulative release of constituents as a function of cumulative Liquid:solid ratio.

It is not recommended that;

Hydrochloric acid be used for assessing leaching of constituents from soils, other than nitrate. This is because some elements are strongly affected by the presence of chloride ions and can produce a high bias in leaching.

Alkaloam® amelioration be applied to clay type soils such as Manning Heavy soil. This soil naturally exhibits high PRI and therefore will not benefit from amelioration. In addition, phosphorus leaching increases in the pH range 2 to 4.5 as a result of Alkaloam® amelioration in this soil.

Total concentration be used as key criteria for assessing a materials impact on the environment. This is because the maximum concentration of an element available for leaching was found to be less than its total concentration for the majority of species in the WA soils and amendments. Using total concentration in assessments will lead to an overly conservative evaluation and may unjustly dismiss materials as being unsafe for re-use.
Chapter 12

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