

**A laboratory and glasshouse investigation on the effect of liming with
fly ash and processed stainless steel slag on two contrasting South
African soils**

By

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Submitted in fulfilment of the academic
requirements for the degree of
Master of Science in the
Discipline of Soil Science
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December 2008

PREFACE

The experimental work described in this dissertation was carried out in the Discipline of Soil Science of the School of Environmental Sciences, University of KwaZulu-Natal, Pietermaritzburg, from August 2006 to December 2008, under the supervision of Professor J. C. Hughes.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

Abstract

Soil acidity is a major land degradation problem that limits crop production globally. The high cost of traditional liming materials (calcitic limestone, dolomite etc.) and the vast areas of land that require liming have led to the exploratory utilisation of alkaline industrial by- products such as fly ash and stainless steel slag. The liming potential and effects of liming with fly ash (from the Duvha power station) and processed stainless steel slag (Calmasil) on two acid soils were investigated in this study.

The quality of fly ash and Calmasil as liming materials and their potential impacts on the soil quality and plant growth were investigated. The effects of liming with these materials on soil pH, EC, extractable Al, Mn, base cations and trace elements were investigated in an incubation experiment. A glasshouse trial was conducted to assess the effects of these materials on the growth of an acid intolerant crop, perennial rye grass. The incubation and glasshouse study were of a factorial design with two acid soils (the Avalon and Inanda soils), three materials (fly ash, Calmasil and lime); and five application rates of 0, 50, 100, 200 and 400% of the recommended optimum liming rate (OLR) for the growth of perennial rye grass.

Characterization of fly ash showed that the major elements (>5%) present (Si > Al > Fe) are not comparable to lime (Ca > Si > Mg) and that it has a low liming potential (calcium carbonate equivalence (CCE) of 9.6%) in comparison to lime. The chemical composition of Calmasil is comparable to lime with Ca > Si > Mg as the major elements and it has a very high liming potential (CCE = 97%). The incubation experiment showed that adding fly ash and Calmasil increased the pH of both soils. However, at the optimum liming rate (100% OLR), only the treatment with Calmasil in the Avalon soil attained pH levels within the desired pH range. Extractable Al and Mn decreased with addition of fly ash and Calmasil to levels comparable to lime in the incubated soils. Addition of fly ash and Calmasil also increased the extractable base cations of both soils. The yield-response of perennial rye grass to treatments in both soils was in the following order: fly ash > Calmasil > lime. Application of fly ash at > 200% OLR in the Avalon soil caused injury of ryegrass. Application of fly ash and Calmasil at lower rates has great agronomic potential in ameliorating soil acidity.

Declaration

I, declare that

1. The research reported in this dissertation, except where otherwise indicated, and is my original research.
2. This dissertation has not been submitted for any degree or examination at any other university.
3. This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
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Signed

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Date 5 June 2009

Signed

Professor J.C. Hughes

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Date 5 June 2009

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Acknowledgements

Many people have assisted and guided me in realising this project by providing me with emotional, moral and academic support. May the Lord continue to guide and bless them.

First, I would like to thank Professor J. C. Hughes for his supervision of this study. Your assistance, guidance and support have been much appreciated.

I would also like to extend thanks to Professor M. V. Fey for the research opportunity and assistance.

Eskom for their generous funding for the project.

Max Kane-Berman of Beestepan Boerdery Farm, Middelburg, Mpumalanga, South Africa for his hospitality and for providing the Avalon soil and Calmasil.

Louis Venter of Calmasil Pvt., Middelburg, Mpumalanga Province, South Africa for providing me with information on Calmasil.

The academic and technical staff in the Discipline of Soil Science at the University of KwaZulu-Natal for their assistance.

A note of thanks also goes to the School of Geological Sciences, School of Chemistry (Pmb) and the Centre of Electron Microscopy at the University of KwaZulu-Natal and the Soil Fertility and Analytical Services Laboratory, Cedara, KZN Department of Agriculture and Environmental Affairs for the analyses they carried out.

I would like to thank my family and friends for their abundant love and support.

A special thanks to God almighty for his abundant blessings and love.

General Introduction

Soil acidity is a major limiting factor for crop production globally (Sumner and Noble, 2003). In South Africa, it greatly affects the agricultural potential of Eastern Mpumalanga, Western Cape, Eastern Cape, KwaZulu-Natal and Limpopo Provinces (Beukes, 1997). The application of alkaline materials such as calcitic limestone, dolomite and slaked lime to improve crop production is common practice. In developed countries, the use of these materials over the past 50 to 100 years has led to marked decreases in soil acidity and improved crop production on acid soils under cultivation (Sumner and Noble, 2003). However, in most developing countries the high cost of commercial lime has resulted in their minimal use compromising soil fertility and crop production (Baligar and Fageria, 2006), and has prompted the need for alternative liming materials.

The alkaline nature and the need for sustainable and environmentally acceptable disposal options for fly ash (Tarkalson *et al.*, 2005, Renken *et al.*, 2006, Yunusa *et al.*, 2006) and metallurgical slag (Lopez *et al.*, 1995; Pinto *et al.*, 1995, Van der Waals and Claassens, 2003) have prompted their use as liming materials on acid agricultural soils. However, the major limitation of utilising these materials in agriculture is their high concentrations of potentially toxic elements, which may potentially contaminate the food chain. Of major concern with fly ash are trace elements such as B, Mo and Se (Adriano *et al.*, 1980). Chromium, Ni and Mo compounds are the main additives in the production of stainless steel (Pillay *et al.*, 2003; Shen *et al.*, 2004), and thus, are likely major elements of concern with processed stainless steel slag.

The comparison of fly ash and Calmasil to traditional liming materials such as limestone is imperative, as it will provide vital information on their efficacy as liming materials. However, due to their origin a comprehensive assessment of both the potential benefits and threats they may pose to the environment if used in liming programmes must be performed. The present research is a preliminary evaluation of the suitability of fly ash from Duvha power station and a processed stainless steel slag, Calmasil, commercially distributed by Calmasil Pvt. as liming materials for acid agricultural soils. The Duvha power station and Calmasil Pvt. are located in the Highveld of the Mpumalanga Province, one of the agricultural hubs of South Africa.

The area is characterised by acid soils under commercial crop production that require regular liming to attain their agronomic optimum (Van der Waals and Claassens, 2003). Soil acidity is also a major problem on land under commercial forest production, and in South Africa about 1.5 million hectares is under commercial forest plantation with about 41% of this planted area mainly in the Mpumalanga Province, 30% in KwaZulu-Natal Province and 11% in the Eastern Cape Province (Southern African Institute of Forestry, 2000). Soil acidity under both commercial crop production and forestry must be addressed to improve production.

The research will serve as a baseline study providing fundamental information for more comprehensive research on the utilisation of these materials in South African agriculture (in both crop production and forestry). The research aims are to evaluate the potential benefits of applying fly ash and processed stainless steel slag to acid agricultural soils in an attempt to improve soil quality with minimal negative impacts on the environment, thereby also providing an alternative disposal option.

Thus, the objectives of the research are to:

- physically and chemically characterise fly ash and processed stainless steel slag as potential liming materials for acid agricultural soils;
- assess the efficacy of fly ash and processed stainless steel slag in comparison to lime in ameliorating soil acidity by assessing the changes with time and application rate on soil pH, extractable Al, Mn and bases (Ca, Mg, K, Na) of treated acid agricultural soils in an incubation experiment;
- assess the major negative impacts of fly ash and processed stainless steel slag on soil quality by assessing changes with time and application rate on EC and extractable trace elements in treated acid agricultural soils in an incubation experiment; and
- assess the efficacy of fly ash and processed stainless steel slag in comparison to lime in improving the yield of perennial rye grass grown in treated acid soil in a glasshouse experiment.

The research study involved various laboratory experiments and a glasshouse experiment. A summary of the sequence of research work performed is given in

Figure (i). A review of the literature on soil acidity and the potential strategies for amelioration using fly ash and processed stainless steel slag is given in the next chapter. A synopsis of the research finding and recommendations for future research is given in the last chapter.

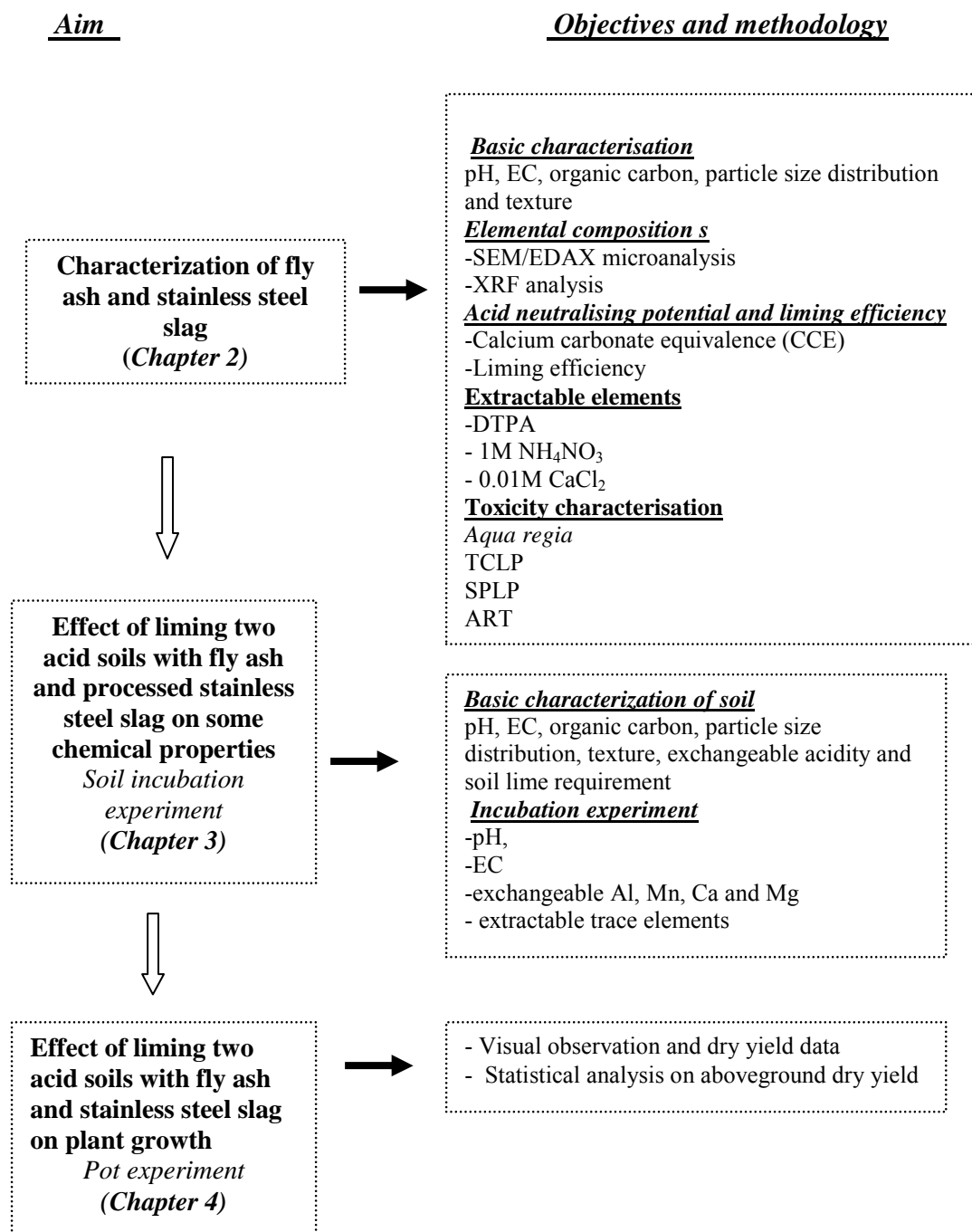


Figure (i). A flow diagram of the focus, objectives and some methods used in this study on the liming effect of fly ash and processed stainless steel slag on acid agricultural soils.

Chapter 1

Soil acidity and the potential strategies for amelioration using fly ash and processed stainless steel slag

1.1 Introduction

Soil acidity is a major limitation for crop production globally affecting over 30% of the topsoil of ice-free land area (Sumner and Noble, 2003), an estimated 4 billion ha⁻¹ of land (Baligar and Fageria, 2006). In South Africa, soil acidity induced infertility is a major problem with an estimated 5 million Ha of topsoil countrywide having a pH_(KCl) < 4.5 and severely acidic (Beukes, 1997).

The application of commercially available alkaline materials such as limestone, slaked lime and dolomite is common practice when ameliorating soil acidity (Fageria and Baligar, 2004). The use of these materials in developing countries over the past 50 to 100 years has led to a marked decrease in soil acidity and has also improved crop production on acid soils under cultivation (Sumner and Noble, 2003). However, the high material and transportation cost of these traditional liming materials has increased the need for an assured profitable economic response before advocating their use for crop production (Coventry *et al.*, 1989). With soil acidity increasingly becoming a problem globally (von Uexkull and Mutert, 1995; Pawlowski, 1997), Baligar and Fageria (2006) noted that economic constraints in developing countries at all scales of agricultural production (small-large scale) have resulted in the minimal use of traditional liming materials.

In South Africa, Buekes (1997) reported soil acidity as a major land degradation problem limiting crop production in both large and small-scale agriculture. The uneconomic nature of ameliorating soil acidity with traditional liming materials due to the vast areas of land affected has resulted in a need for cheaper and readily available alternative liming materials. The availability and alkali nature of some industrial by-products qualify them as potential alternatives for lime in agriculture and they include fly ash (Adriano *et al.*, 1980; Hodgson *et al.*, 1982; Bilski *et al.*, 1995) and metallurgical slag (Das *et al.*, 2006; Bhat *et al.*, 2007). The objectives of this chapter

are to outline soil acidity, its amelioration and to review research on the effects of liming acid soils with fly ash and metallurgical slag on soil properties and plant growth.

1.2 Soil acidity and its amelioration

1.2.1 Sources and nature of soil acidity

Acidification of soil results from both natural and anthropogenic activities and factors, and acid soils can be classified into two main groups, naturally occurring acid soils and anthropogenically derived acid soils (Sumner and Noble, 2003). Natural acidification of soils in pristine environments is a result of one or more of the following:

- i) intensive weathering as a result of acidic rainfall and / or high rainfall and temperature causing the leaching of base cations ;
- ii) deposition of acidic gaseous emissions of sulphur and nitrogen oxides in areas prone to volcanic activity;
- iii) oxidation of sulphide minerals to sulphuric acid in sulphur rich soils;
- iv) decomposition of organic matter in organic rich siliceous or base cation-poor parent material producing organic acids ; and the
- v) production of CO₂ by microbial and root respiration producing carbonic acid (Prasad and Power, 1997; Sparks, 2003; Sumner and Noble, 2003; Bloom *et al.*, 2005).

Anthropogenic activities are also increasingly contributing to soil acidity and soils with low buffering capacities are prone to acidity derived from such activities (Pawlowski, 1997). Acidic soils derived from anthropogenic activities are a result of one or more of the following:

- i) combustion of fossil fuels resulting in acidification of precipitation with sulphuric and nitric acids as the major acids;
- ii) mining activities that result in increased oxidation of sulphide minerals to sulphuric acid in soils;
- iii) nitrification following application of chemical fertilizer mainly nitrogen fertilizer (ammonium-based compounds such as ammonium sulphate,

ammonium nitrate and urea) in pasture systems and intensively managed row crop agriculture; and

- iv) removal of basic cations via crop harvesting and livestock rearing (Foth and Ellis, 1996; Prasad and Power, 1997, Sumner and Noble, 2003; Bloom *et al.*, 2005).

The introduction and / or the increase in H^+ in soil via the aforementioned natural and anthropogenic activities results in a decrease in soil pH consequently increasing the solubility of Al compounds (Pawłowski, 1997; Kabata-Pendias, 2001). Under soil conditions of elevated H^+ and Al^{3+} , Al^{3+} readily displaces exchangeable base cations reducing the acid neutralising capacity of the exchanger phase / soil exchange surface (Essington, 2004; Bloom *et al.*, 2005). This results in an increase in concentration of base cations in the soil solution and if they are leached, the acid neutralising capacity of the soil decreases and they become acidic. In addition to the aforementioned soil reactions the most detrimental acid generating chemical reactions are those related to the hydrolysis of Al^{3+} (Essington, 2004; Bloom *et al.*, 2005). The hydrolysis of ionic Al under acidic conditions generates protons increasing soil acidity.

1.2.2 Plant growth constraints on acid soils

The optimum pH range for the growth of most crops in soil is between 5.5 and 7.0, within which most plant nutrients are available (Prasad and Power, 1997; Yunusa *et al.*, 2006). Whereas, in most acid soils with pH levels lower than 5.5 the major plant growth limitations are due to elemental toxicity mainly arising from Al and / or Mn toxicity and deficiencies of mainly Ca and Mg (von Uexkull and Mutert, 1995; Prasad and Power, 1997; Menzies, 2003; Essington 2004). In addition to the aforementioned growth limitations some trace elements may pose a toxicity threat if present at elevated levels as their availability and mobility increases under acidic conditions (Pawłowski, 1997; Kabata and Pendias, 2001).

Aluminium toxicity is synonymous with acid soils and has been reported to affect crop production in India (Roy *et al.*, 1988), Australia (Aitken, 1992; Scott *et al.*, 2000; Zhang *et al.*, 2006), United States of America (Stevens *et al.*, 2001; Haby, 2002), China (Cifu *et al.*, 2004), Brazil (Fageria *et al.*, 2004) and South Africa (Farina *et al.*,

2000). High levels of phytoavailable Al in soil impacts plant physiological and biochemical process, in turn resulting in toxicity that is characterised by the inhibition of root and shoot growth and uptake of some plant macronutrients such as Ca, Mg, K and N (Kinraide and Parker, 1987; Fageria *et al.*, 1988; Prasad and Power, 1997; Postma, 2003).

Manganese is an essential plant nutrient; however, at elevated levels in soil or other growth mediums it retards plant growth by interfering with normal cellular metabolic activities (Le-Bot *et al.*, 1990; Prasad and Power, 1997). Elevated Mn levels are characteristic of acid soils of pH 5.5 or lower as a decrease in pH increases its bioavailability (Kabata-Pendias, 2001). Toxicity symptoms of Mn are characterised by leaf / blade chlorosis, necrotic spots and puckering (Foth and Ellis, 1996; Prasad and Power, 1997; Kabata-Pendias, 2001).

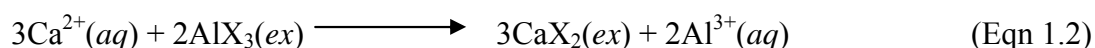
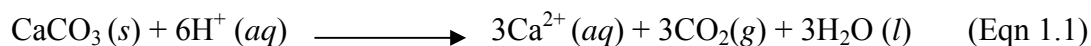
Calcium and Mg are essential plant nutrients and at low concentration levels their nutrient deficiencies symptoms are realised (Foth and Ellis, 1996; Prasad and Power, 1997). Low base cation (mainly Ca and Mg) levels are characteristic of acid soils due to their high leaching in areas with high rainfall and / or acid parent material that is not enriched in base cations (e.g. granite) (Prasad and Power, 1997).

1.2.3 Liming materials and the amelioration of soil acidity

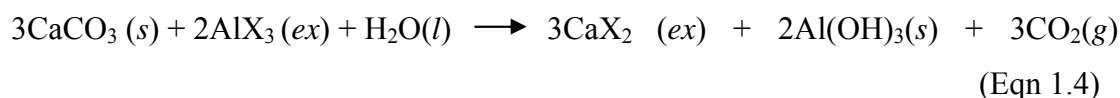
The application of traditional liming materials such as limestone, dolomite and burnt lime to acid soils for the amelioration of acidity consequently improving crop production is common practice (Foth and Ellis, 1996; Prasad and Power, 1997; Troeh and Thompson, 2005). In addition to limestone, the mineralogy and chemical composition of some alkali industrial by-products suggest that they can be utilised as liming materials. These include metallurgical slag such as basic slag, steel slag and stainless steel slag (Van der Waals and Claassens, 2003; Das *et al.*, 2006; Yusiarni *et al.*, 2007), and fly ash (Adriano *et al.*, 1980; Bilski *et al.*, 1995, Yunusa *et al.*, 2006).

Amelioration of soil acidity is a process that involves the increase in pH and exchangeable bases (Ca and Mg) of soil, and a decrease in availability of Al and Mn in soil through a series of acid neutralisation reactions (Kinraide and Parker, 1987;

Essington, 2004; Troeh and Thompson, 2005). The two major neutralisation reactions are those that involve the dissolution of alkaline materials as they consume protons and consequently polymerise and precipitate ionic Al and Mn. The neutralisation of acidity by calcite (a major mineral in limestone) is shown in equations 1.1 - 1.4 (Essington, 2004). The initial reaction (equation 1.1) results in a rapid increase in soil pH and ionic Ca, as the active acidity is neutralized. As soil pH and ionic Ca increases the retention of Ca on the soil exchange complex is favoured and Al^{3+} is expelled into the soil solution (equation 1.3). The expelled Al^{3+} undergoes hydrolysis transforming to less available forms at higher pH. The protons generated as Al^{3+} undergoes hydrolysis are consumed as calcite continues to dissociate.

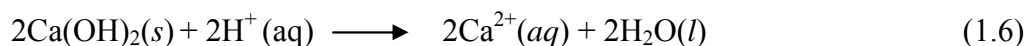
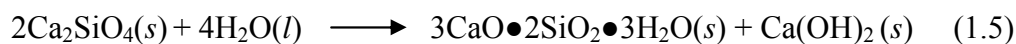


Overall equation

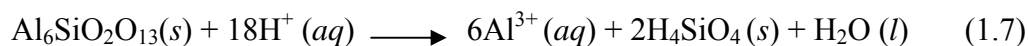


Alkaline industrial by-products have a more complex mineralogy in comparison to lime due to their origin and their neutralisation reactions are likely to involve minerals other than Ca and Mg oxides, hydroxides and carbonates. Some alkaline industrial by-products are also enriched in Ca and Mg silicates and aluminosilicate minerals and these include metallurgical slag (Shen *et al.*, 2004; Das *et al.*, 2006) and fly ash (Adriano *et al.*, Yunusa *et al.*, 2006). Yan *et al.* (2000); Essington (2004); Yunusa *et al.* (2006) state that in theory, the dissociation of Ca and Mg silicates and aluminosilicate minerals consumes protons and may potentially neutralize acidity.

The neutralisation of acidity by calcium silicate minerals is driven by the hydration of the minerals as it produces slaked lime that increases alkalinity (Yan *et al.*, 2000). The hydration and acid neutralizing process of calcium silicates are shown in equations 1.5 and 1.6.



The neutralisation of acidity by an aluminosilicate e.g. mullite as proposed by Yunusa *et al.* (2006) is shown in equation 1.7.



In addition to the acid neutralizing processes shown in equation 1.5- 1.7); research studies on the use of Si in agriculture have shown it to be beneficial to plant grown on acid soils (Gascho, 2001; Chen *et al.*, 2000; Pereira *et al.*, 2004). Liang *et al.* (2005), reported increases in the soil pH and the yield of maize grown in a highly weathered acid soil contaminated with Cd (spiked at rates of 20 and 40 mg kg⁻¹) treated with Si at 400mg kg⁻¹. The alleviation and / or reduction of Al toxicity has also been reported on acid soils treated with Si. Laboratory and field experiments have shown that increase in soil Si effectively reduces Al toxicity (Ma *et al.*, 2002; Morikawa and Saigusa, 2002). Ma *et al.* (2002) reported a decrease in the concentration of Al³⁺ as the concentration of silicic acid increased in solution and attributed this to the formation of non-toxic Al-Si complexes. Ma *et al.* (2006) highlighted the enhanced resistance and / or tolerance to biotic and abiotic stress of plants grown in soils with high available Si. Tuna *et al.* (2008) reported improved yield of wheat grown in a saline nutrient solution treated with Si. These findings on the effect of Si on soil properties and plant growth suggests that Si potentially ameliorates acidity and improves plant growth. However, some researchers preclude the role of Si in ameliorating soil acidity, stating it is the consequence of the alkali nature of the source of Si such as basic slag, stainless steel slag etc. (Morikawa and Saigusa, 2002; Bhat *et al.*, 2007). This may be true for Si applied in the form of alkali slag; however, findings by Ma *et al.* (2002) and Tuna *et al.* (2008) using Si in solution have shown it to decrease available Al and improve plant yield, which are both key factors in the amelioration of soil acidity on agricultural soils.

1.2.4 The efficiency of liming materials

In view of the economic constraints associated with the utilisation of lime as discussed in Section 1.1, the efficacy of liming materials is a key factor in determining its utilisation as profitable crop yield must be realised. The efficiency of a liming material is determined by its acid neutralising potential, particle size distribution, availability and convenience of spreading (Barber, 1984; Scotti *et al.*, 1992; Foth and Ellis, 1996).

Various terms are used when describing the efficiency of liming materials, and commonly used terms are relative neutralizing value (RNV), effective neutralising value (ENV) and effective calcium carbonate equivalence (ECCE) (Synder and Leep, 2007). Most methods for determining the quality and efficiency of liming materials are based on the neutralising value (NV) and particle size distribution and various formulas have been developed (Foth and Ellis, 1996; McFarland *et al.*, 2001; Troeh and Thompson, 2005; Snyder and Leep, 2007). The NV is determined by the chemical composition and the mineralogy of the liming material and is a measure of the amount of acid neutralising compounds expressed as the percentage of calcium carbonate equivalence (CCE), with pure calcium carbonate rated 100% (Barber, 1984; Foth and Ellis, 1996; McFarland *et al.*, 2001). The efficiency of liming material is determined by its effective calcium carbonate equivalence (ECCE), an estimation of the effectiveness represented as percentage and is the product of CCE and the fineness factors of the various particle size fractions (Foth and Ellis, 1996; McFarland *et al.*, 2001; Troeh and Thompson, 2007).

In addition to the efficiency of a liming material its efficacy (amount of material required to adjust soil pH to the desired level for profitable crop production) depends on the liming potential of the material, initial soil pH, clay content and buffer capacity of the soil (Foth and Ellis, 1996; Troeh and Thompson, 2005; Snyder and Leep, 2007). Studies on the effect of particle size on soil pH and crop yield (Scott and Cullis, 1992; Hodge and Lewis, 1994; Huang *et al.*, 2007) have shown that liming with finer liming materials results in increments in soil pH over shorter time periods, and generally higher soil pH and crop yields. The higher pH was possibly a result of the rapid reaction of lime with acidity as smaller particles have a greater surface area

in contact with soil consequently improving soil conditions in a shorter period, thus promoting plant growth. The amelioration of soil acidity and the efficiency of liming materials as discussed in subsection 1.2.3 and in this subsection (1.2.4) suggest that the key factors in determining the efficiency of a liming material are its chemical composition and particle size distribution.

1.3 Fly ash

1.3.1 Production, characteristics and disposal

Fly ash is a combustion by-product that is produced during the combustion of coal at thermal power stations during the generation of electricity. Coal power stations are the main source of electricity in most developing countries and remain a source of electricity in some developed countries. Fly ash is the non-combustible material that is produced when coal that is fed into a boiler following a pulverisation undergoes combustion (Figure 1.1). As coal undergoes combustion in the boiler, it heats up water producing steam that turns turbines generating electricity. The non-combustible by-products either settle at the bottom of the boiler (bottom ash) or rise up with the flue gases (fly ash).

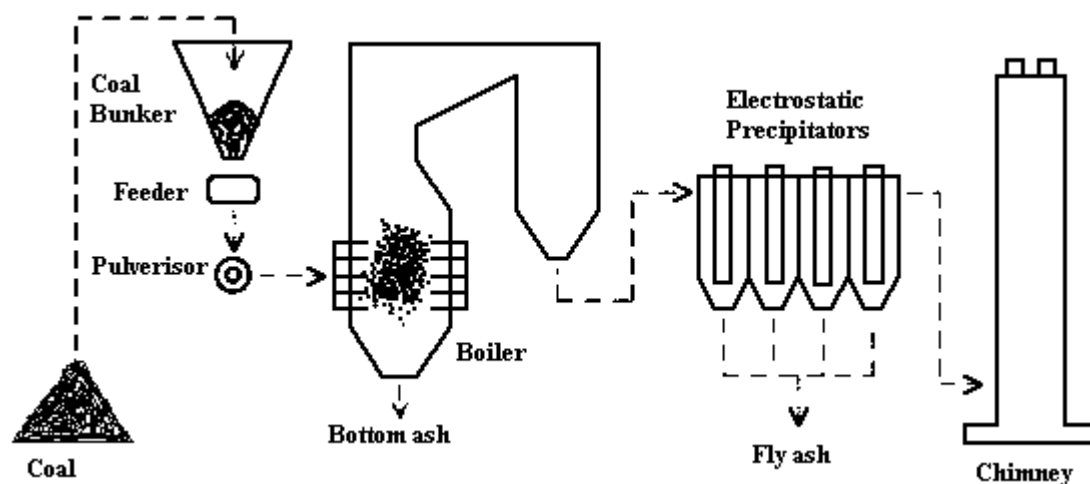


Figure 1.1 Schematic showing the production of fly ash in coal-fired power station (modified after Pflughoef *et al.*, 2000; Rocktron, 2008)

It is estimated that by 2030, global energy consumption will increase by at least two-thirds of the current consumption; developing countries are likely to become the largest consumers with their consumption exceeding that of the industrialized world (Dorian *et al.*, 2006). Currently fossil fuels are the main sources of energy globally with coal as the main source of energy at most thermal power stations; hence increases in energy consumption in the future will result in an increase in the volumes of by-products over time.

It is estimated that approximately 600 million tons of fly ash is produced globally every year out of which only 20 to 25% is utilised in the construction industry largely as a replacement of cement for concrete production, fill material for embankments and as grout (Shafiq *et al.*, 2007). South Africa produces approximately 28 million tons of fly ash annually (Reynolds *et al.*, 2002), the majority of the fly ash produced is disposed of in dams and dumps on land dedicated sites adjacent to the power stations with some utilised in the construction industry (Kruger, 1997; Van den Berg *et al.*, 2001). With such large volumes of fly ash that require disposal the anticipated increase in the energy consumption predicted by Dorian *et al.* (2006) suggests that the production of by-products such as fly is likely to increase, posing a greater disposal challenge in the future.

The physical and chemical properties of fly ash are variable and greatly depend on the type of coal used, boiler collector set up, efficiency, and the particle size of the fly ash (Adriano *et al.*, 1980; Daniels *et al.*, 2002; Jala and Goyal, 2006). Fly ash is generally characterised by silt loam textured particles that are primarily composed of spherical glassy particles with amorphous mineral structures (Adriano *et al.*, 1980; Van der Berg *et al.*, 2001; Daniels *et al.*, 2002; Yunusa *et al.*, 2006).

Mineralogical and crystallographic studies on fly ash suggests that it primarily consists of amorphous ferro-alumino silicate minerals and crystalline solid phases of quartz, mullite, magnetite, maghemite, lime, cristobalite, and haematite (Ural, 2005; Jankowski *et al.*, 2006; Goodarzi, 2006; Kutchko and Kim, 2006). The studies have also shown that major elements present in fly ash are Si, Al, and Fe with minor concentrations of Ca, Mg, K, Na, Ti and S and varying quantities of trace elements (Ural, 2005; Jankowski *et al.*, 2006; Kutchko and Kim, 2006).

Generally, trace elements such as As, B, Cd, Cr, Cu, Mo, Mn, Pb, Se, V and Zn are enriched in most fly ash (Adriano *et al.*, 1980; Daniels, 2002; Jankowski *et al.*, 2006). Some fly ash materials are pozzolanic, exhibiting cementitious properties when exposed to water and an activator (Adriano *et al.*, 1980; Daniels *et al.*, 2002). The elemental composition of fly ash suggests that it contains essential plant nutrients at levels exploitable for agronomic purposes (Tripathi and Sahu, 1997; Daniels *et al.*, 2002; Mittra *et al.*, 2005; Jankowski *et al.*, 2006). However, the high concentration levels of salts and trace elements are a major concern and limit the potential of utilising fly ash outside of the construction industry. The enrichment of major (Ca, Mg, K and Na) and trace elements (As, B, Cr, Cd, Mg, Se, Mo, Hg, Mo, Ni, Sb and V) in fly ash leachates has been reported by Beck *et al.*(2007); Manoharan *et al.*(2007) and Skodras *et al.*(2007). This suggests that the utilization of fly ash in industries that allow for its dissolution into the different spheres of the environment might compromise the environment.

Fly ash is disposed of either in a wet or dry state using wet or dry disposal methods (Van den Berg *et al.*, 2001; Daniels *et al.*, 2002; Jala and Goyal, 2006). Dry methods of disposal involve dumping of dry fly ash on landfills or dedicated land disposal (DLD) sites. In wet methods, water is used as a transportation medium, flushing out fly ash and disposing it as a slurry onto DLD sites or artificial lagoons. These disposal practices have resulted in huge dumps around power stations and increased pressure on municipal landfills. In South Africa, fly ash is disposed of using dry methods in most of the power stations built after 1985 and wet disposal methods are used at the older power stations (Van den Berg *et al.*, 2001) and is disposed of on dams and dumps at dedicated land disposal sites adjacent to the power stations (Kruger, 1997; Van den Berg *et al.*, 2001).

1.3.2 Effect of fly ash on some soil properties

The chemical composition of fly ash suggests that it has agronomic benefits as it can potentially supply plant nutrients, increase the pH, improve soil texture and water holding capacity of soils. However, due to its origin fly ash has some undesirable properties which may negatively impact crop production and they include; its

pozzalanic nature, high EC, trace elements and Al concentrations (Adriano *et al.*, 1980; Bilski *et al.*, 1995; Jala and Goyal, 2006; Yunusa *et al.*, 2006).

The increased need for an alternative disposal option for fly ash has led to exploratory research on its utilization in agriculture with emphasis on its potential to lime acid soils. Increases in the pH of acid soils treated with fly ash have been reported in pot experiments by Khan and Khan (1996), Sale *et al.* (1996), Clark *et al.* (1999), Matsi and Keramidas (1999), McCallister *et al.* (2002) and Spark and Swift (2008); and under field conditions by Adriano *et al.* (2002), Pathan *et al.* (2003), Stevens and Dunn (2004) and Tarkalson *et al.* (2005). The increase in pH of the treated soils may be attributed to the alkaline nature of some fly ash and the absorption of H during the dissolution of non-alkaline compounds (Adriano *et al.*, 1980; Seoane and Leiros, 2001; Yunusa *et al.*, 2006).

Increase in soil EC is synonymous with application of fly ash to acid soils (Adriano *et al.*, 1980; Bilski *et al.*, 1995; Sajwan *et al.*, 2003; Jala and Goyal, 2006; Yunusa *et al.*, 2006). Matsi and Keramidas (1999) reported an increase in EC with application rate in acid soils treated with fly ash at rates of 0, 5, 20 and 50 g kg⁻¹ (equivalent to 0, 0.5, 2 and 50% (w/w)) in a pot experiment. Under field conditions Adriano *et al.* (2002) reported similar findings in the cultivated layer (0-15cm) of acid soils treated with fly ash in the first year of a three year experiment. However, after three years the EC in the cultivated layer had decreased as the salts migrated down the soil profile. Sajwan *et al.* (2003) demonstrated that the application of fly ash to acid soil at rates of 0, 280, 560 and 1250 Mg ha⁻¹ did not compromise the quality of the soil and groundwater with respect to pH, and trace element contamination (As, B, Cd, Cr, Ni, Pb, Fe, Mo and Se) under field conditions, although soil EC increased. The contradictory nature of the results of the pot and field experiments suggests that high EC in soil following the application of fly ash may be a short-term limitation under field conditions. Hence, fly ash may require weathering prior to its utilisation for crop production especially under glasshouse conditions.

The neutralisation of acidity in soil by aluminosilicates, major minerals in fly ash, as proposed by Yunusa *et al.* (2006) for mullite in equation (1.4.5) releases ionic Al. Ionic Al is the major driver of soil acidity as its hydrolysis releases H⁺ (Essington,

2004) potentially decreasing soil pH and exacerbating soil acidity. McCallister *et al.* (2002) reported increases in the levels of exchangeable Al on acid soils treated with fly ash.

Wright *et al.* (1998) reported a decrease in exchangeable Al in acid soil treated with fly ash at rates of 0, 1.25, 2.5, 5, 10, 20 and 40 g kg⁻¹ (0, 0.125, 0.25, 0.5, 1, 2 and 4% (w/w)). The concentration levels of exchangeable Al decreased to 0 cmol kg⁻¹ at application rates of 10 g kg⁻¹ and greater. The decrease was attributed to the liming effect of fly ash. In this view the differences in extractable Al in the treated soils is possibly due to differences in application rates as low rates will not release large quantities of Al.

1.3.3 The effect of fly ash on plant growth

The effect of fly ash on plant growth on treated acid soils has shown variable growth response. Improved plant growth and yield on acid soils treated with fly ash at low rates has been demonstrated in pot experiments (Wright *et al.*, 1998; Matsi and Keramidas, 1999; Spark and Swift, 2008). Wright *et al.* (1998) did not report any negative effects on the growth of wheat following the treatment of acid soil with fly ash at rates of 0, 1.25, 2.5, 5, 10, 20 and 40 g kg⁻¹ equivalent to 0, 0.125, 0.25, 0.5, 1, 2 and 4% (w/w). Matsi and Keramidas (1999) reported similar findings on the yield of perennial rye grass grown on acid soil treated with fly ash at 0, 5, 20 and 50 g kg⁻¹ equivalent to 0, 0.5, 2 and 5% (w/w), respectively. Spark and Swift (2008) demonstrated a similar trend with maize grown on acids treated with fly ash at rates of 0, 1, 2, 3 and 5% (w/w). The improved plant growth was attributed to the amelioration of soil acidity by fly ash in the three experiments.

In some pot experiments the treatment of acid soils with fly ash at higher application rates has demonstrated that it is phytotoxic. Kuiker *et al.* (1994) reported an increase in the yield of corn grown on acid soil treated with fly ash at 0.0, 3.1, 6.3, 12.5, 25, 50, and 100 g kg⁻¹ as the application rate increased reaching a maximum at 50 g kg⁻¹, followed by a decrease at higher application rates. Khan and Khan (1996) reported a similar finding in a glasshouse experiment with tomatoes grown on acid soils treated with fly ash at rates of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100%. Their results

demonstrated that fly ash was beneficial to the growth of tomato up to a rate of 60%, above which it had a negative effect. Sale *et al.* (1996) also demonstrated an increase in the yield of barley grown on acid soil treated with fly ash at rates of 0, 6.25, 12.5, 25, 50, 75 and 100%(v/v). However, at rates of 50% and greater, it was detrimental to growth. Generally, the negative effect of fly ash on plant growth at high rates greater than 50% has been attributed to B toxicity as it generally contains high levels of B salts (Bilski *et al.*, 1995).

The effect of fly ash on plant growth in field experiments on acid soils have shown trends similar to the glasshouse and pot experiments in the short-term and has proved not to be detrimental to plant growth even at high rates over longer periods of time. Stevens and Dunns (2004) demonstrated this with cotton grown on acid soil treated with fly ash (at rates of 0, 3.4, 6.7 and 10.1 Mg ha⁻¹) over two years. The yield of the cotton lint decreased in the first year following the application of fly ash. However, the yield of cotton lint in the same fields increased in the second year. The decrease in the first year was also attributed to B toxicity. This result suggests that under field conditions B toxicity decreases with time, as it is leached from the root zone. This supports the view of Adriano *et al.* (2002) that B toxicity to plants grown on soils treated with fly ash is probably a short-term plant growth limitation as leaching of B over time will decrease its concentration levels and toxicity.

The pozzolanic nature of fly ash suggests that it may promote the cementation of soil and may impede root development in some soils after application at very high rates (Carlson and Adriano, 1993). Tripathi *et al.* (2004) reported inhibited root growth of lamk grown in a soil treated with fly ash at rates of 50 % and 100% (w/w). The reduced growth of roots in the treatments with fly ash was attributed to compaction and Al toxicity. However, at relatively low rates fly ash is not expected to negatively affect the physical properties of soil (El-Mogazi *et al.*, 1988).

1.3.3 Conclusions

The current literature shows that the application of fly ash results in an increase in soil pH and probably ameliorates soil acidity. The phytotoxic threat posed by fly ash on crops such as rye grass, cotton, wheat, barley and maize depends on the application

rate and may be realised at higher rates. There is immense potential in the utilisation of fly ash as a liming material at low application rates on acid agricultural soils as it will not only increase soil pH, but may also improve the physical properties of soil and act as source of plant nutrients. The utilisation of fly ash in agriculture may also provide a much needed viable and sustainable disposal option for fly ash.

1.4 Processed stainless steel slag

1.4.1 Production, characteristics and disposal

Stainless steel slag is a by-product of the production of stainless steel which involves the melting of scrap metal and metal alloys with limestone in an electric arc furnace, followed by decarbonising in a converter (Argon Oxygen Decarbonisation (AOD)) producing molten stainless steel as shown in Figure 1.3 (Shen *et al.*, 2004 ; SSINA, 2008). Stainless steel and its derivatives contain significantly high concentrations of Fe, Cr and Ni, alkaline oxides and hydroxides, and silicates (Pillay *et al.*, 2003; Shen *et al.*, 2004; Dominguez *et al.*, 2008).

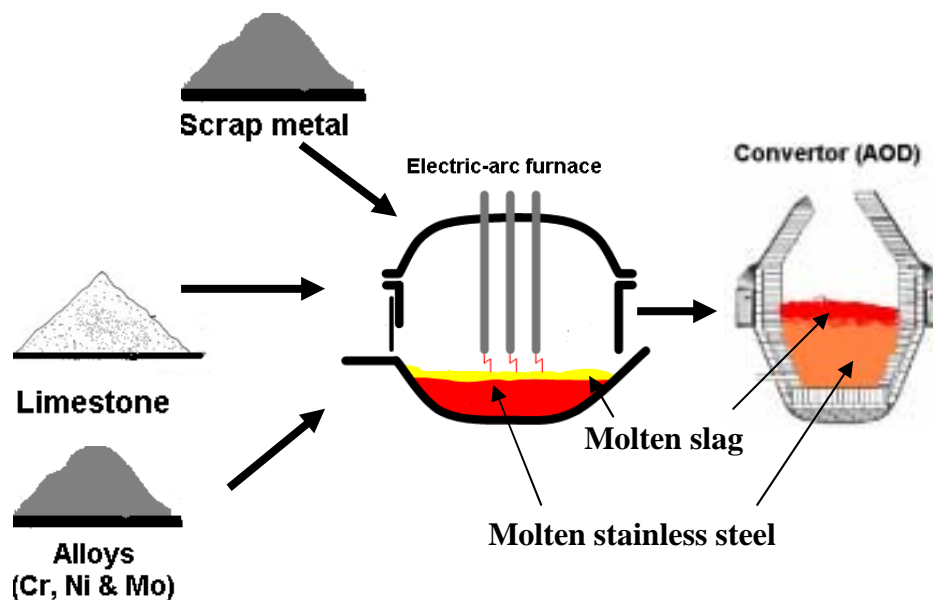


Figure 1.2 Schematic showing the production of molten stainless steel and slag (modified after Speciality Steel Industry of North America (SSINA, 2008).

The mineralogical composition and crystallographic structure of stainless steel slag and its derivatives suggests that it primarily consists of metal alloy grains (phases of Fe-Ni, Fe-Cr, Fe-Cr-Ni and Ni-Cr-Fe); crystalline solid phases of calcium silicate, larnite, quartz, calcite, magnetite, lime, chromite, periclase, fluorite; and amorphous silicates of Ca, Mg, Al, and Cr (Pillay *et al.*, 2003; Shen *et al.*, 2004). Processed stainless steel slag has pozzolanic properties (Shen *et al.*, 2004), exhibiting cementitious properties when exposed to water and an activator. However, unlike fly ash, the particle size distribution and texture of stainless steel slag and its derivatives are determined by the grinding system used prior to disposal and / or beneficial utilisation.

The stainless steel industry produces the largest amount of slag in the alloy steel industry, producing 1 tonne of slag for every 3 tonnes of stainless steel produced (Shen *et al.*, 2004). In 2007 approximately 27 836 million tonnes of stainless steel was produced globally and production is expected to increase in 2008 (International Stainless Steel Forum, 2008). Hence, approximately 9.27 million tonnes of stainless steel slag was produced in 2007. The commonly used disposal method for stainless steel slag is application into landfills as it contains high Cr and Ni (Pillay *et al.*, 2004; Shen *et al.*, 2004) posing a potential environmental threat.. However, other metallurgical slag such as steel slags, are utilised in the construction industry and agriculture as Si and / or P fertiliser (Geiseler, 1996; Motz and Geiseler, 2001; Pereira *et al.*, 2004; Das *et al.*, 2006). This suggests that metallurgical slag and its derivatives have other agronomic purposes.

1.4.2 Effect of processed stainless steel slag on soil properties and plant growth

Documented information on research studies into the use of stainless steel slag as a liming material on agricultural soil is not readily available. Shen *et al.* (2004) emphasized that limited research studies have been carried out on stainless steel slag and its derivatives. Despite the limited literature on the utilisation of processed stainless steel slag as lime in agriculture, the results from research conducted on the use of other metallurgical slags such as basic slag, Linz - Donawitz (LD) slag and converter slag on acid soils as lime have been very encouraging. Rodriguez *et al.* (1994) reported increases in soil pH, exchangeable Ca and Mg and decreases in

exchangeable Al on acid pasture soils treated with LD slag at rates of 0, 1, 2, 3, 4, 5, 6 and 7 Mg ha⁻¹. Pinto *et al.* (1995) reported similar findings with LD slag on pastures with acid soils at rates of 0, 1, 1.5, 3, 5 and 7.5 Mg ha⁻¹. The application of basic slag to acid soil showed a trend similar to LD slag increasing soil pH and exchangeable cations, and improving the yield of wheat (Bhat *et al.*, 2007; Shamim *et al.*, 2008). Ali and Shamir (2007) reported similar changes in soil pH and exchangeable cations. In the same experiment, converter slag also improved the dry matter yield of maize with increasing application rate reaching a maximum at the 2% rate followed by a decrease at 4%.

In South Africa, metallurgical slag and other metal industry by-products have been used on the Highveld, Mpumalanga Province of South Africa as lime for acid soils since the 1980's, but the results remain confidential (Van der Waals and Claassens, 2003). Generally, most metallurgical slag contain high concentrations of alkali base metals mainly Ca and Mg in the form of oxides, hydroxides and carbonates, and may be used as a replacement for limestone in the liming of acid agricultural soils (Van der Waals and Claassens, 2003; Das *et al.*, 2006; Yusiarni *et al.*, 2007).

The high concentrations of Cr, Ni, Mo and other trace elements in stainless steel slag (Pillay *et al.*, 2003; Shen *et al.*, 2004) may pose an environmental threat and potentially limit their use as a liming material in agriculture. However, Van der Waals and Claassens (2003) reported low levels of bioavailable and exchangeable Cr, Ni and V on acid agricultural soils treated with a total of approximately 20 tonnes of metallurgical slag over a period of 10 years. Thus, the environmental risk of utilising these materials may be minimal.

1.4.3 Conclusions

Current literature shows that the application of metallurgical slag increases the pH of acid soil and possibly ameliorates soil acidity. Although limited studies have been carried out on the effect of liming with metallurgical slag on acid soils, their potential as liming materials cannot be discounted. Thus, processed stainless steel slag may potentially ameliorate soil acidity and improve plant growth.

1.5 Legal implications of liming acid agricultural soils with fly ash and processed stainless steel slag

In South Africa, the Department of Water Affairs and Forestry (DWAF) is responsible for establishing and implementing appropriate management and disposal procedures for waste (DWAF, 2006). Fly ash, stainless steel slag, and its derivatives such as processed stainless steel slag are classified as hazardous waste because of their origin in terms of the Minimum Requirements for the Handling, Classification and Disposal of Hazardous Wastes (DWAF, 2006).

The Minimum Requirements are guidelines developed to prevent and minimise water pollution and to protect human health and the environment when disposing of waste. The disposal of waste into the environment is also governed by the National Water Act, 1998; Environmental Conservation Act, 1989; National Environmental Management Act (Act 107 of 1998); National Environment Management: Air quality Act (Act 39 of 2004); Constitution of the Republic of South Africa Act 108 of 1996, Section 24; and local by-laws or regulations.

The large scale utilization of fly ash and processed stainless steel slag as liming materials on acid soil requires special permission or delisting by DWAF, in terms of the Environmental Conservation Amendment Act, 2003 (Act 50 of 2003). The application of industrial by-products on soil requires thorough evaluation of the effects of the materials on soil quality, vegetation and ground and surface water quality (Ghodrati *et al.*, 1995). The major concerns associated with applying industrial wastes on soil are the toxicity threats posed by the leachable constituents such as trace elements and salts (Hansen *et al.*, 2002). The mobility of trace elements is of great concern in agro-ecosystems as their accumulation in plants grown on soils treated with industrial waste may pose a toxic hazard to the food chain, and their leaching may compromise groundwater quality. The hazard posed by trace element additions in soil is not only determined by their total concentration as a result of addition of a waste material, but by factors which include soil physico-chemical properties, agronomic practices, geopedoclimatic conditions and plant tolerance (He *et al.*, 2005).

Extremely alkaline groundwater with high concentrations of heavy metals and salts develops in areas in close proximity to fly ash and metallurgical slag dumps (Van den Berg *et al.*, 2001; Roadcap *et al.*, 2005). Highly alkaline environments perturb the soil processes posing a phytotoxic and / or zootoxic threat. The origin of fly ash and processed stainless steel slag suggests that their trace elements and salt content may pose an environmental threat. However, since liming involves the application materials onto land at lower quantities in comparison to landfilling and disposal on DLD sites, the environmental threat they pose may be minimal.

Assessing the environmental impact of waste is vital as it determines its suitability for application on land for beneficial agronomic purposes. The toxicological potential of wastes can be determined using chemical tests on waste materials and the treated soils (Wilke *et al.*, 2007). Batch leaching tests serve to establish and quantify the mobility of organic and inorganic constituents of waste materials disposed of in landfills with the underlying assumption that if constituents leach out from the waste, they may pose a threat to the environment, especially to groundwater. The Toxicity Characteristic Leaching Procedure (TCLP), Acid Rain Test (ART) and Synthetic Precipitation Leaching Procedure (SPLP) leaching tests are used to characterise the hazard posed by a waste material (USEPA, 1996; DWAF, 2006; Townsend, 2006).

Single extraction procedures are used to assess the trace element status of soil providing vital information on the environmental threat posed if enriched in soil due to anthropogenic activities. The status of elements in the different soil/media fractions can be divided into three main categories, the pseudo-total (non-active and potentially active), mobilisable (potentially bioavailable and leachable) and mobile (bioavailable, easily leachable and exchangeable) using different extraction solutions (Ure *et al.*, 1995; Gupta *et al.*, 1996; Ure, 1996).

1.6 General conclusions

The composition of fly ash (chemical and mineralogical) and particle size distribution suggests that it can be used as a liming material for agronomic purposes. The phytotoxic threat it appears to pose at high application rates may require it to be applied at low rates for agronomic purposes. Although there is limited literature on

the utilisation of processed stainless steel slag as lime in agriculture, its chemical and mineralogical composition suggests that it has the potential to ameliorate soil acidity. The positive liming effects reported for other metallurgical slags suggest that processed stainless steel slag may potentially have similar effects on acid soils. The application threshold at which fly ash and processed stainless steel slag pose a toxicity threat when liming must be established. The effects of liming with fly ash and processed stainless steel slag for agronomic purposes still have to be established in South Africa. A preliminary investigation thus is needed to assess the potential of these materials as alternatives to lime on acid agricultural soils in South Africa.

Chapter 2

Characterisation of fly ash and processed stainless steel slag

2.1 Introduction

The characterisation of fly ash and processed stainless steel slag as liming materials is a very important step in determining their utilisation on acid agricultural soils. Unlike traditional liming materials such as limestone that are natural rocks, fly ash and processed stainless steel slag contain additional elements, essential for plant growth such as Fe, P, K, S, Zn and Mo (Adriano *et al.*, 1980; Shen *et al.*, 2004; Jala and Goyal, 2006; Yunusa, 2006). However, due to their origin the materials potentially contain toxic elements at elevated levels such as Al, As, Cr, Cd, Ni, Pb, Se and V (Chapter 1). Thus, due to their chemical composition they must undergo characterisation as per hazardous material requirements for the determination of appropriate disposal and/or beneficial utilisation options.

This chapter aims to characterise fly ash and a processed stainless steel slag, Calmasil as liming materials and to assess their suitability for application on acid agricultural soils. The primary objectives of this chapter were to:

- i) determine some chemical and physical properties of fly ash and processed stainless steel slag;
- ii) determine the acid neutralizing potential of fly ash and processed stainless steel slag; and
- iii) investigate the potential benefits and toxicity of elements present in fly ash and stainless steel slag in comparison to a conventional agricultural liming material.

2.2 Materials and methods

Fly ash was collected from the precipitators at Dhuvha power station on the Highveld of Mpumalanga Province, South Africa. A processed stainless steel slag was sourced from a farm in Middelburg, Mpumalanga Province, South Africa. The processed stainless steel slag is a commercial liming material packaged and distributed by Calmasil Pvt. Middelburg, Mpumalanga Province, South Africa. The terms “processed stainless steel slag” and “Calmasil” will both be used when referring to

this material in this and subsequent chapters. Agricultural lime (dolomitic limestone with 85% CaCO_3 and MgCO_3) was sourced from Mthimkhulu Quarries in KwaZulu-Natal Province, South Africa. The fly ash, Calmasil, and agricultural limestone were air-dried, crushed, sieved to $< 2\text{mm}$, and stored in polyethylene bags in a laboratory under ambient conditions.

2.2.1 General characterisation of fly ash, Calmasil and lime

Measurements of pH in 1M KCl were carried out on 1:2.5 (10g in 25cm^3) solid-liquid ratio; the mixture was initially stirred and allowed to stand for an hour before measurements were taken. Electrical conductivity (EC) measurements were carried out in distilled water on a 1:2.5 (10g in 25cm^3) solid-liquid ratio; the mixture was initially stirred and allowed to stand for an hour before measurements were taken. This was followed by pH (distilled water) measurements in the same solution. Particle size distribution was determined using the pipette method (Gee and Bauder, 1986). Sample density was determined by scooping samples using a 5ml scoop and weighing them, followed by computation of density. This was repeated 10 times and the average value was recorded as the sample density. Texture was determined using the procedure of the Soil Classification Working Group (1991). The morphology of particles was determined using Scanning electron microscopy (SEM). X-ray fluorescence spectrometry (XRF) and energy dispersive X-ray (EDX) microanalysis were used to determine the major elements present in the materials. All procedures were carried out in triplicate except the XRF and EDX analysis.

2.2.2 Acid neutralising potential of fly ash, Calmasil and lime

Pure calcium carbonate has a CCE of 100% and is used as the benchmark to which all other liming materials are compared (Foth and Ellis, 1996; McFarland *et al.*, 2001; Troeh and Thompson, 2005). The acid neutralizing potential of the materials was determined as CCE using a procedure by Jackson (1958). The quality of fly ash and Calmasil as liming materials was determined using procedures by McFarland *et al.* (2001) and OMAFRA (2002).

2.2.3 Extractable elements in fly ash, Calmasil and lime

Extractable major elements (P, K, Ca, Mg, Na, S, Al) and trace elements (As, Cd, Cr, Cu, Fe, Mo, Mn, Ni, Pb, Se, V and Zn) were extracted using three solutions i.e., 0.01M CaCl₂ (Houba *et al.*, 2000), 1M NH₄NO₃ (DIN, 1997) and DTPA (Lindsay and Norvell, 1978). Although these methods were not developed for materials such as lime, which contain a large amount of easily soluble elements, they have been used for a wide variety of wastes that contain lime and are used here to allow some comparison with other published data. The ammonium nitrate method in particular is recommended in the DWAF (2006) guidelines for disposal of wastewater sludge, a material that may contain high amounts of such easily soluble elements. Elemental concentrations were determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), the elemental detection limits lie in the range of 10⁻¹ – 10⁻⁴ mg l⁻¹. All extraction procedures included a blank and were carried out in triplicate. Statistical correlations of the elemental concentrations of the trace elements extracted with the three extraction methods (DTPA, 1M NH₄NO₃, and 0.01M CaCl₂) were determined using Pearson's correlation test (two-tailed), SPSS Version 15.

2.2.4 Hazard characterisation of fly ash, Calmasil and lime

The environmental hazards posed by applying fly ash and Calmasil onto acid agricultural soils was characterised by comparing leachable and extractable elements to regulatory limits for the agronomic application of wastewater / biosolids on soil (USEPA, 1994; DWAF, 2006) and suitability for landfilling (USEPA, 1996). Comparison of some heavy metals present in fly ash and Calmasil (extracted with *aqua regia*) to the limits for heavy metals in wastewater by DWAF (2006) and EPA Part 503 Biosolids Rule (40 CFR Part 503) (USEPA, 1994) was performed. The *aqua regia* extraction was performed using the procedure of the ISSO (1995) and elemental concentrations were determined using ICP-OES, the elemental detection limits lie in the range of 10⁻¹ – 10⁻⁴. *Aqua regia* is a common digestion solution deemed to extract the pseudo-total elements in soils and sludge (Alloway, 1995). For the purposes of this study, a comparison of the *aqua regia* extractable heavy metals of inorganic industrial by-products to the limits for biosolids/wastewater was deemed acceptable because similar limits for their agronomic utilisation are currently not available in

South Africa. Thus, the results of the comparison of elements present in an inorganic material to the limits for organic materials will only serve as a reference in evaluating the suitability of fly ash and Calmasil for application on agricultural land and are by no means conclusive.

The leachability of potentially hazardous trace elements was determined using three batch leaching procedures namely the toxicity characterization leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP) and acid rain test (ART). These batch leaching tests serve to establish and quantify the mobility of organic and inorganic constituents of waste materials disposed of in landfills with the underlying assumption that if constituents leach out from the waste they may pose a threat to the environment, especially to groundwater. The TCLP, SPLP and ART are recommended procedures for the characterisation of hazardous waste material (USEPA, 1996; DWAF, 2006; Townsend, 2006).

The TCLP (Method 1311) developed by the USEPA (1996) simulates the leaching patterns of the inorganic and organic constituents of materials disposed of in a sanitary landfill. The leaching of the elements out of the material is presumed to be a result of its contact with organic acids (primarily acetic acid) following the decomposition of the organic component of domestic refuse. The SPLP (Method 1312) also developed by the USEPA (1996) simulates leaching patterns of waste materials in an unlined mono-disposal landfill following contact with natural precipitation presumed to be enriched in sulphuric and nitric acid. The ART used by DWAF (2006) simulates the leaching patterns of waste materials in mono-disposal sites following contact with precipitation presumed to be enriched with carbonic acid. Elemental concentrations of the leachates were determined using ICP-OES. Comparison of the TCLP leachable elements of the materials to the TCLP limits was also performed to characterise the hazardous nature of the materials. The three tests were chosen because the conditions they simulate are likely to exist under natural conditions, though at different magnitudes. Statistical correlations of the elemental concentrations of the trace elements leached using the three tests (TCLP, SPLP and ART) were determined using Pearson's correlation test (two-tailed), SPSS Version 15.

2.3 Results and discussion

2.3.1 Some chemical and physical properties of the materials

The pH of fly ash, Calmasil and lime was alkaline in both distilled water and 1M KCl (Table 2.1). The fly ash used in this study possessed a typical pH value within the range reported in review articles on the utilization of fly ash by Adriano *et al.* (1980) and Jala and Goyal (2006). Adriano *et al.* (1980) attributed the alkaline pH of fly ash to the dissolution of Ca and Mg compounds. The alkaline pH levels of Calmasil are in accordance with the results for processed stainless steel slag reported by Shen *et al.* (2004). Shen *et al.* (2004) attributed the alkaline pH of processed stainless steel slag to the dissolution of Ca and Mg carbonates, oxides and hydroxides. The EC of both fly ash and Calmasil were high (Table 2.1).

The particle size distribution of a liming material is a very important because smaller particles have greater reactive surface areas making them more reactive when exposed to acid. Hence, liming materials with higher percentage of finer particles are deemed more suitable for agriculture. Fly ash contains the highest percentage of fine particles (53% clay + silt). Hence, it potentially has the highest reactive surface area. The high silt content of fly ash (Table 2.1) supports the common view that its dominant particles are silt-sized (Adriano *et al.*, 1980; Ghodrati *et al.*, 1995; Daniels *et al.*, 2002; Pathan *et al.*, 2003).

Table 2.1 Some chemical and physical properties of fly ash, Calmasil and lime.

Property		Fly ash	Calmasil	Lime
pH	H ₂ O	11.01	11	8.76
	KCl	12.7	12.38	9.63
Electrical conductivity (dS m ⁻¹)		2.5	4.7	0.8
Sample density (g cm ⁻³)		0.8	1.8	1.65
Particle size distribution (%)				
Clay (<0.002mm)		6	3.8	4
Fine Silt (0.002 - 0.25mm)		36	7.6	5
Coarse Silt (0.025 - 0.05mm)		11	9	5
Very fine Sand (0.05 - 0.10mm)		32	21.6	14
Fine Sand (0.10 - 0.25mm)		14	29	25
Medium Sand (0.25 - 0.50mm)		1	15	25
Coarse Sand (0.500 - 2.0mm)		0	14	22
Texture		sandy loam	loamy sand	sand

The low sample density and the texture of fly ash suggest that its handling and application in a dry state may pose a challenge, as dust suppression mechanisms might be required. The SEM analysis of fly ash, Calmasil and lime showed variation in their morphology. Fly ash consists mainly of particles with an irregular shape and a few that are spherical, and generally showed minor cementation (Figure 2.1).

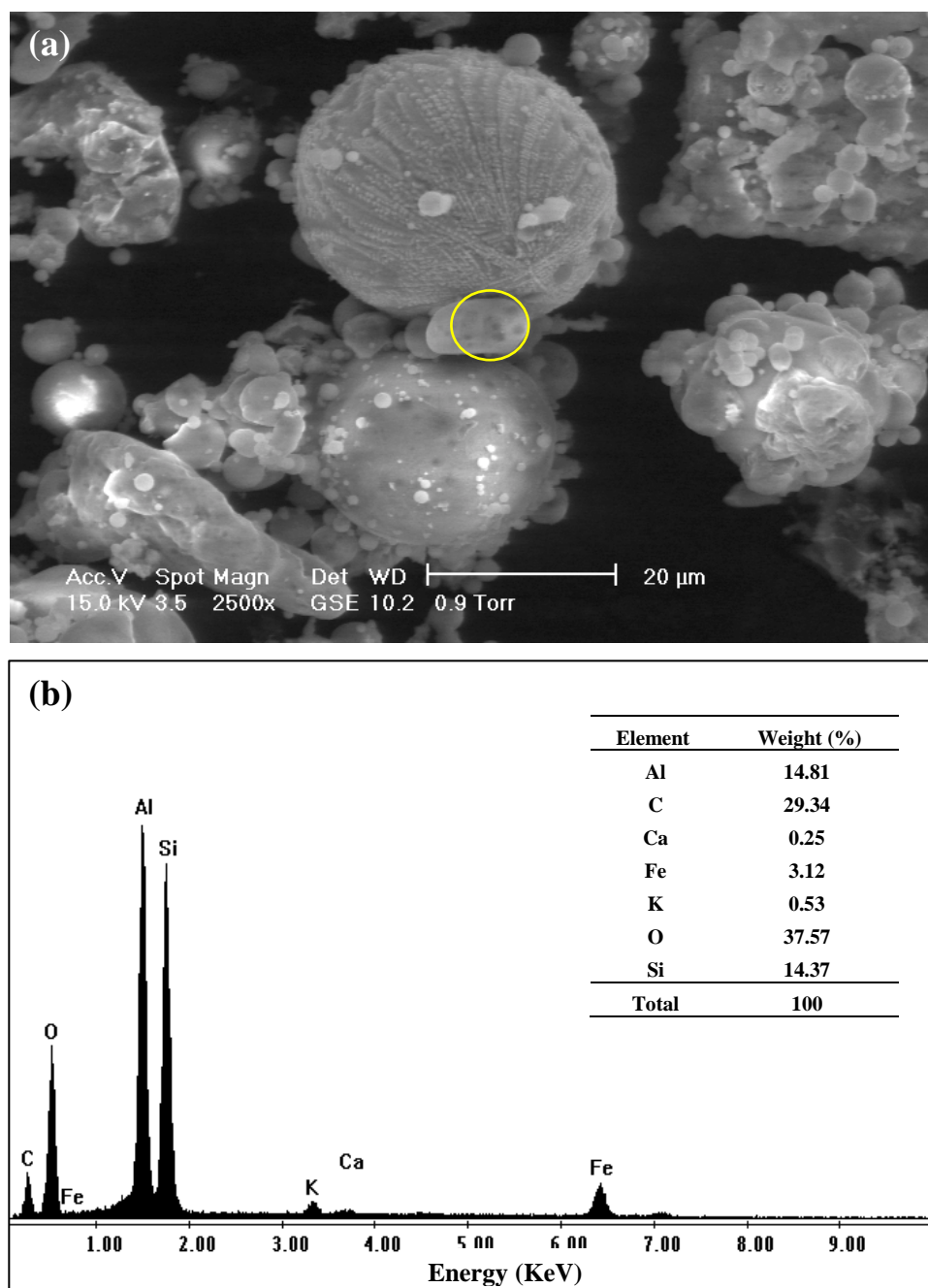


Figure 2.1 (a) Scanning electron microscopy (SEM) images of fly ash and (b) Energy dispersive X-ray spectroscopy (EDX) of the circled area.

The differences in the morphology of the particles of fly ash used in this study are in accordance with results reported by Foner *et al.* (1999), Daniels *et al.* (2002) and Smichowski *et al.* (2008). Calmasil primarily consisted of particles with an irregular shape showing notable cementation (Figure 2.2), and its morphology was comparable to other metallurgical slags produced in South Africa reported by Engelbrecht (1983).

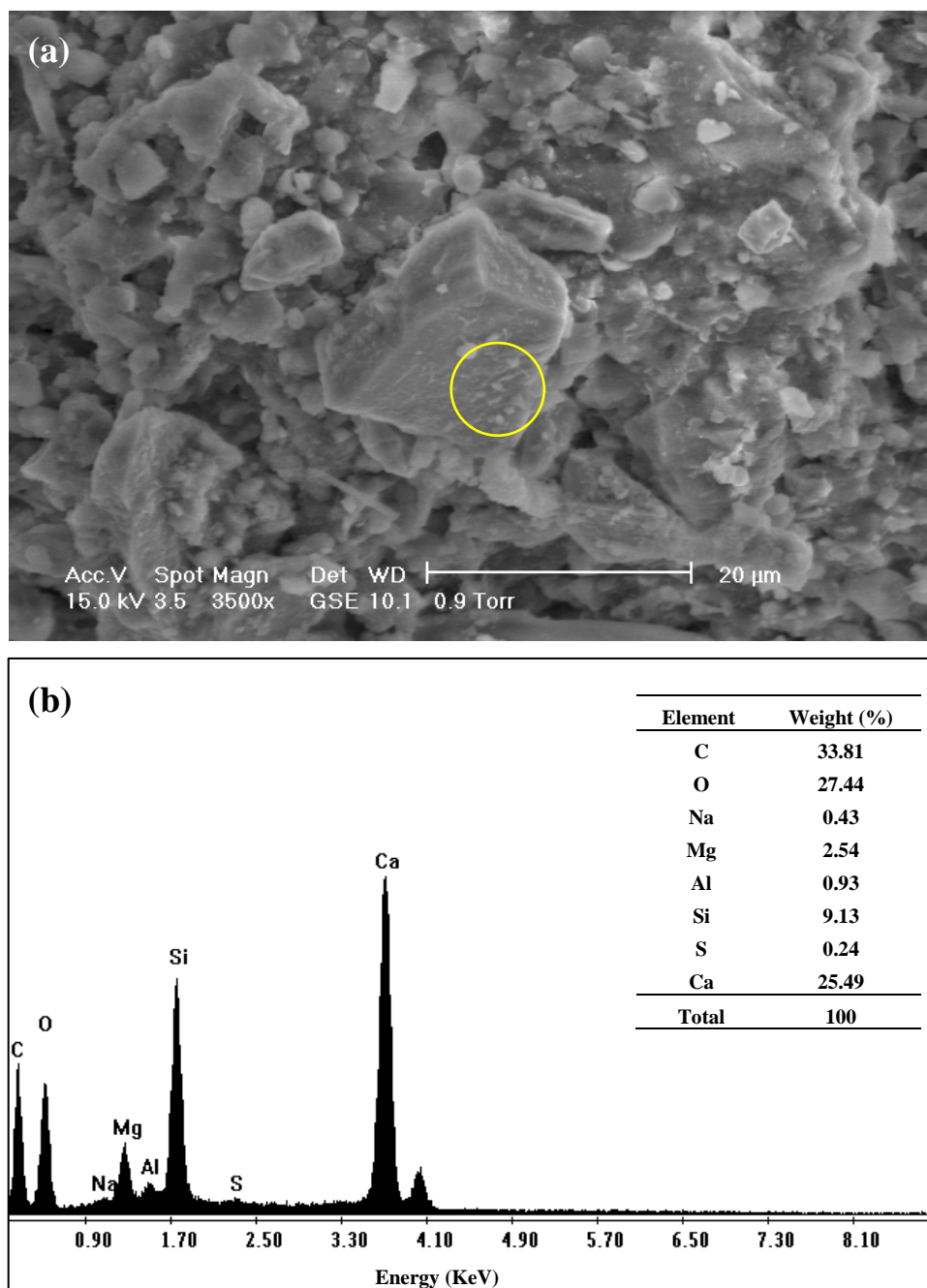


Figure 2.2 (a) Scanning electron microscopy (SEM) images of Calmasil and (b) Energy dispersive X-ray spectroscopy (EDX) of the circled area.

Calmasil is disposed of as a as slurry and this possibly results in the cementation of the particles. Lime primarily consisted of regular shaped particles and showed no cementation (Figure 2.3). The cementation exhibited by fly ash and Calmasil was possibly a result of their pozzolanic nature as has been reported for some fly ash (Adriano *et al.*, 1980; Daniels *et al.*, 2002) and processed stainless steel slag (Shen *et al.*, 2004).

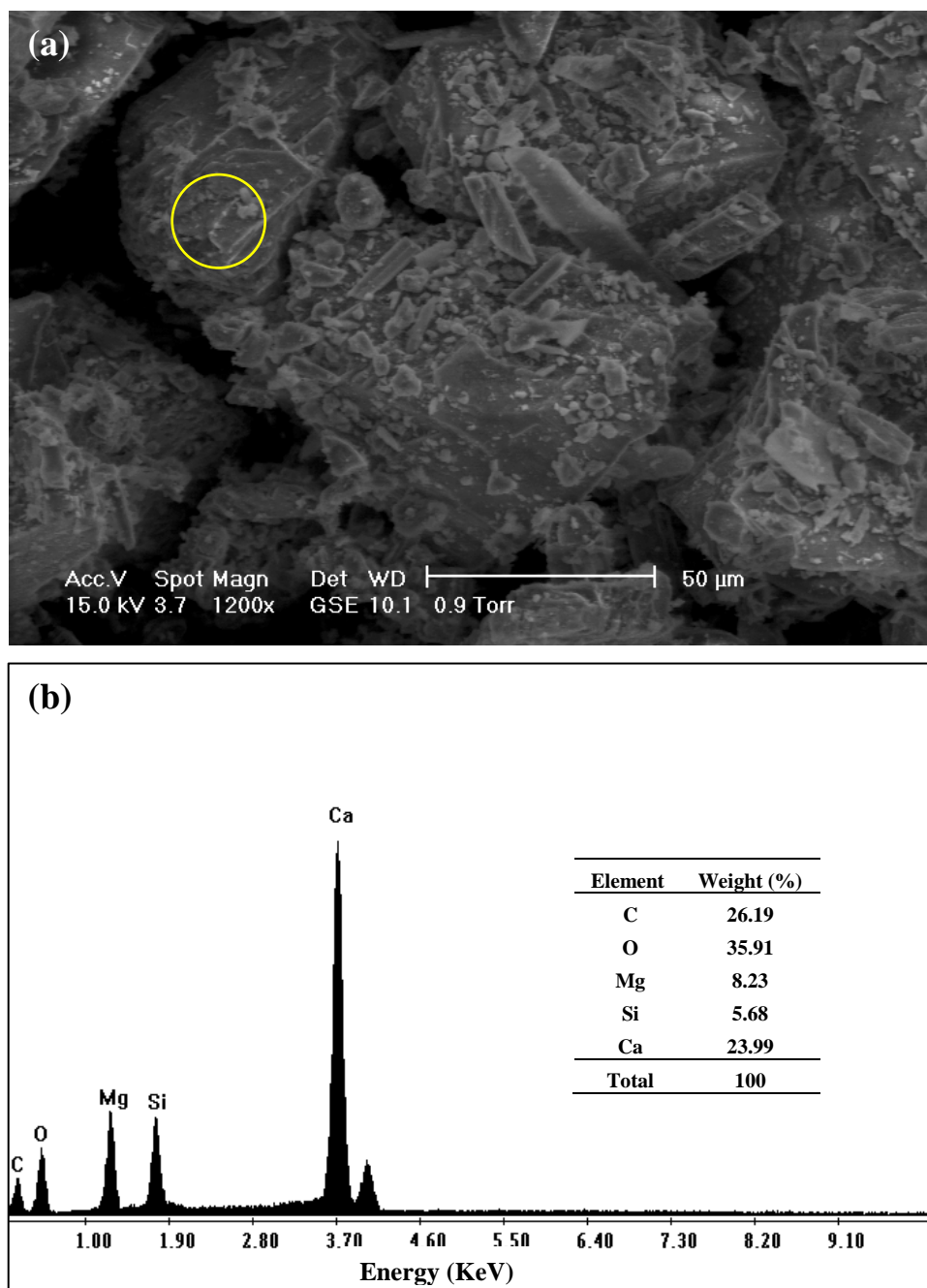


Figure 2.3 (a) Scanning electron microscopy (SEM) images of lime and (b) Energy dispersive X-ray spectroscopy (EDX) of the circled area.

2.3.2 Elemental composition of the materials

Lime contains the highest levels of Ca and Mg oxides, together with very low amounts of other oxides except SiO₂ (Table 2.2). Fly ash showed a different trend with the major matrix element oxides of Si, Al and Fe, together with very low levels (<5%) of Ca and Mg oxides. The low Ca and Mg in fly ash (approximately 13-fold lower than Calmasil and lime) suggests that it contains low levels of acid neutralizing minerals and compounds such as Ca and Mg oxides, carbonates and hydroxides that are characteristic of lime.

Table 2.2 Major elemental composition of fly ash, Calmasil and lime as expressed as oxides determined by X-ray fluorescence spectroscopy.

Major oxides (%)	Fly ash	Calmasil	Lime
Al ₂ O ₃	27.55	3.36	0.22
Fe ₂ O ₃	5.69	3.31	0.11
MnO	0.04	0.62	< 0.01
CaO	3.63	45.44	49.12
MgO	1.06	12.15	23.9
Na ₂ O	0.03	0.14	0.14
K ₂ O	0.82	0.07	0.05
Cr ₂ O ₃	0.03	2	0.02
NiO	0.01	0.21	<0.01
P ₂ O ₅	0.6	0.03	0.01
SiO ₂	59.01	32.08	26.53
TiO ₂	1.64	0.88	0.03

The high Si, Al and Fe oxides observed in the fly ash used in this study are comparable to the results reported in previous research (Adriano *et al.*, 1980; Pathan *et al.*, 2003; Jankowski *et al.*, 2006; Portgieter-Vermaark *et al.*, 2006). The elemental content of this fly ash (Table 2.2) affirms the general view that it dominantly consists of aluminosilicates as reported in previous research (Tripathi and Sahu, 1997; Jankowski *et al.*, 2006; Daniels *et al.*, 2002). The high Al levels in fly ash might be a

cause for concern, as they can potentially counteract the effect of liming in treated acid soils if the soil pH decreases over time, possibly reacidifying and/or exacerbating acidity by increasing the levels of ionic Al following dissolution.

The elemental composition of Calmasil showed a trend similar to lime suggesting that they are chemically comparable. Shen *et al.* (2004) reported similar findings for processed stainless steel slag that contained high levels of Ca and Mg. The elemental content of Calmasil suggests that the dominant acid neutralising compounds are comparable to lime. However, the higher Si content of Calmasil also suggests that calcium silicates are likely to be present in notable quantities in accordance with Shen *et al.* (2004).

Calmasil contains the highest levels of Ni, Cr and Mn oxides, comparable to similar findings for processed stainless steel slag (Shen *et al.*, 2004). The high levels of Ni and to a lesser extent Cr and Mn are major limitations to the disposal options of stainless steel slag and its derivatives (Pillay *et al.*, 2003; Shen *et al.*, 2004). The levels of these elements and the high levels of Al in Calmasil suggest that its application onto acid soils might pose a toxicity threat and potentially counteract the efforts to ameliorate soil acidity, respectively.

The elemental composition of fly ash determined using EDX (Figure 2.1) supports the XRF results (Table 2.2). Skodras *et al.* (2007) reported a similar composition for South African fly ash (from Kromdraai power station) and Colombian fly ash using EDX. The elemental composition of Calmasil determined using EDX (Figure 2.2) is comparable to the results determined using XRF (Table 2.2). The additional major elements present in fly ash (K and Fe) and Calmasil (S) at notable levels in comparison to lime might be of nutritional benefit to plant growth if applied to soils with a low fertility status.

2.3.3 Acid neutralizing potential of the materials

Upon addition of acid (1N HCl) to the materials during the determination of CCE only Calmasil and lime effervesced. This result supports previous results (Section 2.3.2) that the acid neutralizing compounds in Calmasil are comparable to lime and are likely to be Ca and Mg carbonates. The behaviour of Calmasil upon addition of

acid is in accordance with reports for processed stainless steel slag by Shen *et al.* (2004). Shen *et al.* (2004) attributed the effervescence to the dissolution of Ca and Mg carbonates, oxides and some silicates. The behaviour of fly ash upon addition of acid suggests that the dominant acid neutralizing compounds are not comparable to those present in Calmasil and lime. This is possibly due to the low content of Ca and Mg (Table 2.1 and Figure 2.1); and the low solubility of other neutralising compounds possibly aluminosilicates and calcium silicates.

The low CCE or NV of fly ash in comparison to Calmasil and lime suggests that its liming potential is low (Table 2.3 and 2.4). The CCE of fly ash used in this investigation is within the range reported by Schumann and Sumner, (2000).

Table 2.3 The quality of fly ash, Calmasil and lime as per the standards for liming materials as determined using the procedure of McFarland *et al.* (2001)

Property	Fly ash	Calmasil	Lime
Calcium carbonate equivalence (CCE) (%)	9.63	97.00	76.75
Fineness efficiency rating (%)	99.86	94.2	90.6
Effective calcium carbonate equivalence (%)	9.62	91.4	69.55

Although Calmasil and lime had higher CCE they had lower fineness efficiency rating (Table 2.3) and fineness rating (Table 2.4), fly ash had the highest fineness efficiency rating and fineness rating. The results suggest that fly ash is likely to react more rapidly due to its larger surface area if all the materials are applied in quantities of equivalent CCE.

Table 2.4 The quality of fly ash, Calmasil and lime as per the standards for lime determined using the procedure of the Ontario Ministry of Agriculture, Food and Rural affairs (OMAFRA), (OMAFRA, 2002).

Property	Fly ash	Calmasil	Lime
Neutralizing value (NV) (%)	9.630	97.00	76.75
Fineness rating (%)	99.58	82.60	71.80
Agricultural index (%)	9.590	80.12	55.12

The results suggest that Calmasil and lime are likely to have a lower liming efficiency if applied to acid soil due to their coarser particle size distribution. Hence, higher

quantities of the materials would be required to produce a liming effect equivalent to their CCE or neutralizing value (NV) in the short-term.

Assuming that fly ash is an inferior liming material in comparison to Calmasil and lime solely based on the CCE is questionable. This is because the standard method by Jackson (1958) used for determining CCE was designed for limestone and other natural liming rocks. Thus, the method might underestimate the liming potential of other materials with major acid neutralising compounds that are not carbonates, hydroxides and oxides of Ca and Mg as other compounds such as aluminosilicates and calcium silicates also consume H^+ ions when weathering (Yan, 2000; Essington, 2004; Yunusa *et al.*, 2006). Recent studies have also shown that the addition of compounds high in Si to acid soils increased their pH and ameliorated soil acidity. Liang *et al.* (2005) reported an increase in pH and plant biomass in Si treated soil. In this view, if the anticipated neutralisation by Si compounds (Chapter 1) is taken into account the effect of the low CCE of fly ash and fineness rating/fineness of Calmasil may be minimised.

2.3.4 Extractable elements in the materials

Single extraction procedures are designed to dissolve a phase whose element content can be correlated with availability of the element in the soil solution and/or to plants grown in soil, mimicking its availability the soil environment (Rauret, 1998). Thus, the extractability patterns of the various elements with single extraction solutions might be indicative of their release of the elements from the materials into the soil environment.

The major elements in fly ash that were determined using XRF and EDX were easily extractable by the three solutions (DTPA, 0.1M NH_4NO_3 and 0.01 $CaCl_2$) showing high concentration levels with the exception of Al which was detected at very low concentration levels (Appendix 2.1). The low levels show that Al is present in fly ash in compounds that are not readily soluble. Other plant nutrients such as K, P, Na, S, Fe and Mo were present in small amounts.

The major elements determined using XRF and EDX of Calmasil were easily extractable by the three solutions (DTPA, 0.1M NH_4NO_3 and 0.01 $CaCl_2$) showing a

trend similar to fly ash (Appendix 2.1). Calmasil had the highest levels of extractable Na and this might be cause of concern as it potentially poses a salinity threat to plants grown on treated acid soils. Other plant nutrients such as K, P, Na, S, Fe and Mo were present in small amounts.

The extractable sulphur levels of fly ash were generally comparable to Calmasil although the XRF and EDX analysis did not show that it was a major element in fly ash. The high S in both fly ash and Calmasil suggest that it is present in the materials in forms that are readily soluble possibly as sulphate and may be of nutritional benefit. Chromium is a major element of environmental concern with fly ash (Adriano *et al.*, 1980; Narukawa *et al.*, 2007) and stainless steel slag materials and their derivatives (Pillay *et al.*, 2003; Shen *et al.*, 2004) such as Calmasil, respectively. However, Pillay *et al.* (2003) concluded that the environmental risk posed by Cr in stainless steel slag might be minimal as its mobilisation is unlikely under ambient atmospheric conditions following disposal. However, the levels of extractable Cr in fly ash were comparable to lime suggesting that it may not be an element of environmental concern when utilising fly ash.

The results of the extraction elements present in fly ash, Calmasil and lime showed that the overall extraction of elements by the 1M NH_4NO_3 solution was not statistically significant to either the DTPA or the 0.01 M CaCl_2 extraction methods, hence, uncorrelated (Appendix 2.2, Table B2.2.1, Table B2.2.2 and Table B2.2.3, respectively). However, the results of the overall extraction elements present in fly ash, Calmasil and lime by the DTPA and the 0.01 M CaCl_2 solutions were statistically significant, hence, correlated (Appendix 2.2, Table B2.2.1, Table B2.2.2 and Table B2.2.3, respectively). Generally, the levels of extractable plant nutrients in fly ash and Calmasil were higher than lime. Hence, fly ash and Calmasil may be a source of plant nutrients and the application to acid soils may improve their fertility status.

2.3.5 Hazard characterisation of the materials

Pseudo-total concentrations of As and Cr in fly ash and Calmasil were comparable, and were above the DWAF (2006) Class A limits (Table 2.5). The Ni concentration levels of Calmasil are comparable to both DWAF (2006) and USEPA (1994) limits.

The results suggest that treatment of soil with Calmasil might elevate levels of potentially environmentally available Ni posing an environmental threat. As per the DWAF (2006) and USEPA (1994) regulations, the trace element contents of the regulated elements present in fly ash and Calmasil suggest that they are suitable for application on land for agricultural purposes or otherwise.

Table 2.5 Comparison of the total levels of some potentially toxic metals present in fly ash and Calmasil to the metal limits for the agricultural utilization of wastewater sludge (DWAF, 2006) and EPA Part 503 Biosolids Rule (USEPA, 1994).

Trace element mg kg ⁻¹	Fly Ash	Calmasil	DWAF(2006)*			USEPA(1994) [#]
			Class A	Class B	Class C	
As	66.3	67.2	<40	40-75	>75	75
Cd	Nd	nd	<40	40-85	>85	85
Cr	28.3	30.2	<1200	1200-3000	>3000	3000
Ni	20.7	396.4	<420	420	>421	420
Pb	Nd	33.62	<300	300-840	>840	840

Generally, the concentrations of trace elements in the TCLP extracts of fly ash, Calmasil and lime were lower than the TCLP limits with the exception of As and Se in fly ash (Table 2.6).

Table 2.6 Comparison of trace element levels in fly ash, Calmasil and lime in TCLP leachates to TCLP limits (USEPA, 1996).

Trace element mg l ⁻¹	FA	Calmasil	Lime	TCLP limits (USEPA,1996)
As	39.5	nd	nd	5
Cd	nd	nd	nd	1
Cr	1.76	1	nd	5
Mo	10.9	6.34	nd	NA
Ni	1.53	0.86	0.86	NA
Pb	nd	0.04	0.01	5
Se	1.67	0.03	<0.01	1
V	41.6	0.06	0.14	NA

nd: not detected.

NA: Not available.

Although TCLP limits for V and Mo are currently not available, the high levels of V and Mo in fly ash and Mo in Calmasil may be a cause of environmental concern if they are applied to soil. The levels of As and Se in the TCLP leachate of fly ash exceeded the TCLP limits and would be characterized as hazardous waste. Thus, its handling and disposal must be regulated. The levels of Ni in the TCLP leachate of Calmasil are comparable to lime suggesting that Ni may not be of great environmental concern as proposed earlier (Chapter 1).

The trace element concentration levels in the SPLP leachates are generally low (Table 2.7). The As level in the SPLP leachate of fly ash were notably lower than that detected in the TCLP leachates, suggesting the As bearing minerals and compounds are more readily soluble in the organic acid rich TCLP solution. The SPLP leachate levels of Mo in fly ash and Calmasil are high but are lower comparable to lime. This suggests that Mo levels in the fly ash and Calmasil used in this study might be of minimal environmental concern.

Table 2.7 SPLP extractable trace elements in fly ash, Calmasil and lime.

Trace element mg l ⁻¹	FA	Calmasil	Lime
As	2.38	nd	0.33
Cd	nd	nd	nd
Cr	3.05	2.44	nd
Mo	9	8.42	12.7
Ni	0.05	1.39	1.39
Pb	nd	nd	nd
Se	2.54	0.12	0.04
V	0.8	0.05	0.2

nd: not detected

Lead was detected in the *aqua regia* extract of Calmasil (Table 2.5) but not detected in the SPLP leachates. This suggests that Pb present in Calmasil will not readily leach out in environments rich in sulphuric and nitric acid. The Ni levels of Calmasil and lime in the SPLP leachates are comparable, suggesting that although *aqua regia* extractable Ni (Table 2.5) concentrations were high it might not readily leach in an environment dominated by sulphuric and nitric acid.

Generally, the levels of trace elements in ART leachates of fly ash, Calmasil and lime are low with the exception of As, V and Mo in fly ash (Table 2.8). The levels of most of the trace elements in the ART leachates of fly ash are similar to the TCLP leachates (Table 2.6).

Table 2.8 ART extractable trace elements in fly ash, Calmasil and lime.

Trace element mg l ⁻¹	FA	Calmasil	Lime
As	37.24	nd	nd
Cd	nd	nd	nd
Cr	0.22	1	nd
Mo	16.2	10	0.35
Ni	0.25	2.24	2.24
Pb	nd	0.04	nd
Se	3.96	0.03	nd
V	58.7	0.06	0.107

nd: not detected

The high levels of As, Mo and Se in the leachates of the fly ash used in this study are in accordance with Jankowski *et al.* (2006) for alkaline fly ash. The generally, low levels of extractable trace elements present in Calmasil suggest that the low application rates intended for liming might pose a threat to the environment. Van der Waals and Claassens (2003) demonstrated this on an acid soil previously limed cumulatively with 20 tonnes of metallurgical slag over a period of 10 years.

The results of the leaching of fly ash and lime showed that the overall leachable elements using the SPLP leaching test were not statistically significant to TCLP or ART leaching test results, hence, uncorrelated (Appendix 2.3, Table C2.3.1 and Table C2.3.3, respectively). However, the estimated correlation coefficients of the TCLP and ART results were statistically significant, hence, correlated. The results of the leaching of Calmasil showed that the overall leachable elements using the three leaching tests were statistically significant, hence, correlated (Appendix 2.3, Table C2.3.2). Generally, the concentrations of trace elements in the SPLP leachate of fly ash were lower than the TCLP and ART leachates. Calmasil leachate showed a different trend with trace elements in SPLP leachate generally higher than the TCLP

and ART leachates. The difference in the leaching behaviour of fly ash and Calmasil is possibly due to differences in their chemical behaviour noted earlier (Chapter 2).

2.4 Conclusions

Some of the physical and chemical properties of the fly ash and processed stainless steel slag used in this investigation are comparable to lime. The fly ash and Calmasil used contain acid neutralising compounds and have great potential as liming materials. The acid neutralizing behaviour of fly ash might not be comparable to Calmasil and lime if applied to acid soil due to differences in their acid neutralizing compounds. Although, fly ash is an inferior liming material in comparison to lime and processed stainless steel slag due to its low CCE. This might be overcome higher levels of equivalent CEC to Calmasil and lime if to be utilised. The concentrations of some plant nutrients present in fly ash and processed stainless steel slag are higher than lime, though generally low. The elevated EC and the availability of Al, As, Mo, Cr, Mn, Se, and V in fly ash, and Cr, Mo, Ni, Se and V in Calmasil, are a potential cause of concern in agro-ecosystems if the materials are to be applied at high application rates. Fly ash is a potentially hazardous material because of the high levels of As and Se. Generally, the application of fly ash and processed stainless steel slag onto acid soils might potentially ameliorate soil acidity and improve their fertility promoting plant growth in degraded or nutrient-poor soils. Additional laboratory (Chapter 3) and glasshouse (Chapter 4) investigations were undertaken in an attempt to investigate these findings.

Chapter 3

The effect of fly ash and processed stainless steel slag on soil pH, EC, extractable Al, Mn, base cations and trace elements

3.1 Introduction

Several studies have shown that applying alkaline industrial waste to acid soils can be an effective substitute for conventional agricultural lime in ameliorating soil acidity (Adriano *et al.*, 1980; McCallister *et al.*, 2002; Bhat *et al.*, 2007). However, the application of fly ash and processed stainless steel slag poses a potential environmental threat due to their origin (Chapter 1). Thus, it is important to assess the fate of these potentially toxic trace elements inherently in fly ash and Calmasil after treating acid soils.

This chapter reports an investigation on the amelioration of soil acidity and availability of potential toxic elements in two acid soils limed with fly ash and processed stainless steel slag. Changes in soil pH, extractable Al, Mn, base cations (Ca, Mg, K and Na) and trace elements (As, Cd, Cr, Mo, Ni, Pb, Se and V) with loading and time are monitored and assessed.

3.2 Materials and methods

3.2.1 Liming materials and soils

Fly ash, processed stainless steel slag (Calmasil) and lime, characterised and discussed in Chapter 2, were used to treat two contrasting acid topsoils (0-20cm) of the Avalon and Inanda forms (Soil Classification Working Group, 1991). The Avalon soil was collected from a recently cleared fallow plot on a farm on the outskirts of Middelburg, Mpumalanga Province, South Africa. The Inanda soil was collected from a forest plantation at World's View on the outskirts of Pietermaritzburg, KwaZulu-Natal Province, South Africa. Collected soils were air-dried, ground, sieved to < 2mm and stored in polyethylene bags in a laboratory under ambient conditions.

Some physical and chemical characteristics of the Avalon and Inanda soils were determined as follows:

- i) pH measurements was carried out in distilled H₂O and 1M KCl on 1:2.5 (10g in 25cm³) solid-liquid ratio with initial stirring after one hour;
- ii) EC measurements were carried out in distilled H₂O on 1:2.5 (10g in 25cm³) solid-liquid ratio with initial stirring after one hour;
- iii) exchangeable acidity by titrating a 1M KCl solution extract of 5g of soil in 50cm³ with 1M NaOH, using a procedure of the Non-Affiliated Soil Analysis Work Committee (1990);
- iv) organic carbon using the procedure by Walkley (1947) ;
- v) sample density by scooping samples using a 5ml scoop and weighing them followed by computation of density. This was repeated 10 times and the average value was recorded as sample density;
- vi) particle size distribution was determined using the pipette method (Gee and Bauder, 1986);
- vii) soil texture using the procedure of the Soil Classification Working Group (1991);
- viii) the optimum lime requirements using the procedure of Manson *et al.* (2004) as per the requirements for the growth of an acid intolerant crop, namely perennial rye grass (*Lolium perenne L.*). Perennial rye grass is a pasture and forage grass that achieves optimum growth at soil pH levels of between 5 and 8 (Balasko *et al.*, 2003), and thus its lime requirements were deemed suitable for the purposes of this investigation. The optimum liming requirement for each soil was determined as per limestone of 75% CCE. The optimum liming rates for the three materials were determined as follows:

$$\text{Optimum application rate} = \frac{75\%}{\text{CCE\% of material}} \times \text{Lime requirement} \quad (\text{after Mason } et al., 2004)$$

3.2.2 Soil incubation experiment

The experimental design was a factorial with two acid soils (the Avalon and Inanda), three liming materials (fly ash, Calmasil and lime); five application rates of 0, 50, 100, 200 and 400% of the optimum lime requirement (OLR) for the growth of

perennial rye grass. The application rates were equivalent to the rate for lime with 75% CCE at the OLR for an incorporation depth of 15cm per hectare of land. Composite samples of Avalon (1.2 kg) and Inanda (0.9 kg) soils were treated with fly ash, Calmasil and lime at the aforementioned application rates. The soil and liming material mixtures were shaken manually in plastic bags for 10 minutes to promote the even distribution of materials. The mixtures were then moistened to field capacity. Field capacity was determined using standard pressure pot and plate apparatus (Moodley, 2001). The moist mixtures were placed in opaque plastic buckets with lids. The incubation experiment was run in a laboratory over a period of 112 days under ambient conditions. The incubation pots were opened regularly to promote and maintain aerobic conditions.

Sub-samples were collected after 0, 3, 5, 7, 14, 28, 42, 56, 84, and 112 days for laboratory analysis. Measurements of pH in distilled water were carried out on all sub-samples. Sub-samples collected on Days 0, 14, 28, 56 and 112 were extracted for Al and Mn using 0.01M CaCl₂ (Houba *et al.*, 2000) and the elemental concentration levels were determined using ICP-OES, elemental detection limits lie in the range of $10^{-1} - 10^{-4}$.

Measurements of EC and base cations (Ca, Mg, K and Na) extracted using 1M NH₄NO₃ (DIN, 1997) were carried out on sub-samples collected on Day 112. Exchangeable or bioavailable trace elements were extracted on sub-samples collected on Day 0 and 112 using two unbuffered neutral salt solutions of 1M NH₄NO₃ (DIN, 1997) and 0.01M CaCl₂ (Houba *et al.*, 2000), and a buffered organic complexing solution, DTPA (Lindsay and Norvel, 1978). Elemental concentration levels were determined using ICP-OES, elemental detection limits lie in the range of $10^{-1} - 10^{-4}$.

3.3 Results and discussion

3.3.1 Characterisation of the soils

The Inanda soil had a notably higher exchangeable acidity and lime requirement in comparison to the Avalon soil, yet their pH in KCl were comparable (Table 3.1). The differences in exchangeable acidity and the lime requirement for the two soils is possibly due to the higher buffering capacity of the Inanda soil as it has a higher clay

and organic matter content. The low clay and exchangeable acidity of the Avalon soil used is characteristic of many soils in the Highveld of Mpumalanga Province which generally have a low buffering capacity as they are derived from predominantly sandstone parent material (Van der Waals and Claassens, 2003). The lime requirement for the Avalon soil is consistent with the value of 1.5 Mg ha⁻¹ reported for sandy soils in the Mpumalanga Province by Van der Waals and Claassens (2003) and Kane-Berman (*personal communication*, 2007). The amount of Calmasil required for liming the Avalon soil is in accordance with recommended rates reported by Kane-Berman (*personal communication*, 2007) for the same soil.

Table 3.1 Some physical and chemical properties of the Avalon and Inanda soils

Property	Avalon	Inanda
pH		
H ₂ O	4.48	3.84
1M KCl	3.64	3.60
Electrical Conductivity (dS m ⁻¹)	0.51	0.84
Exchangeable acidity (cmol ₊ kg ⁻¹)	0.17	4.70
Organic Carbon (%)	0.87	9.60
Sample density g cm ⁻³	1.40	0.75
Particle size distribution (%)		
Clay	16.2	28.2
Silt	4.8	26.1
Sand	79	45.7
Texture	sandy loam	clay loam
Optimum lime requirement 100% OLR (Mg ha ⁻¹)	1.5	17.5
Fly ash equivalent of 100% OLR (Mg ha ⁻¹)	11.7	136
Calmasil equivalent of 100% OLR (Mg ha ⁻¹)	1.16	13.5
Lime equivalent of 100% OLR (Mg ha ⁻¹)	1.47	17.1

The very high levels of fly ash required for both soils may limit its utilisation under field conditions possibly due to economic constraints, as more equipment and labour will be required.

3.3.2 Changes in pH, and extractable Al and Mn availability with time in the treated soils

The Avalon soil treated with fly ash, Calmasil and lime showed an increase in soil pH as the application rate increased and with time (Figure 3.1). The treatments with fly ash in the Avalon soil at the two highest application rates of 200% and 400% OLR showed an increase to the desired range for the growth of perennial rye grass of

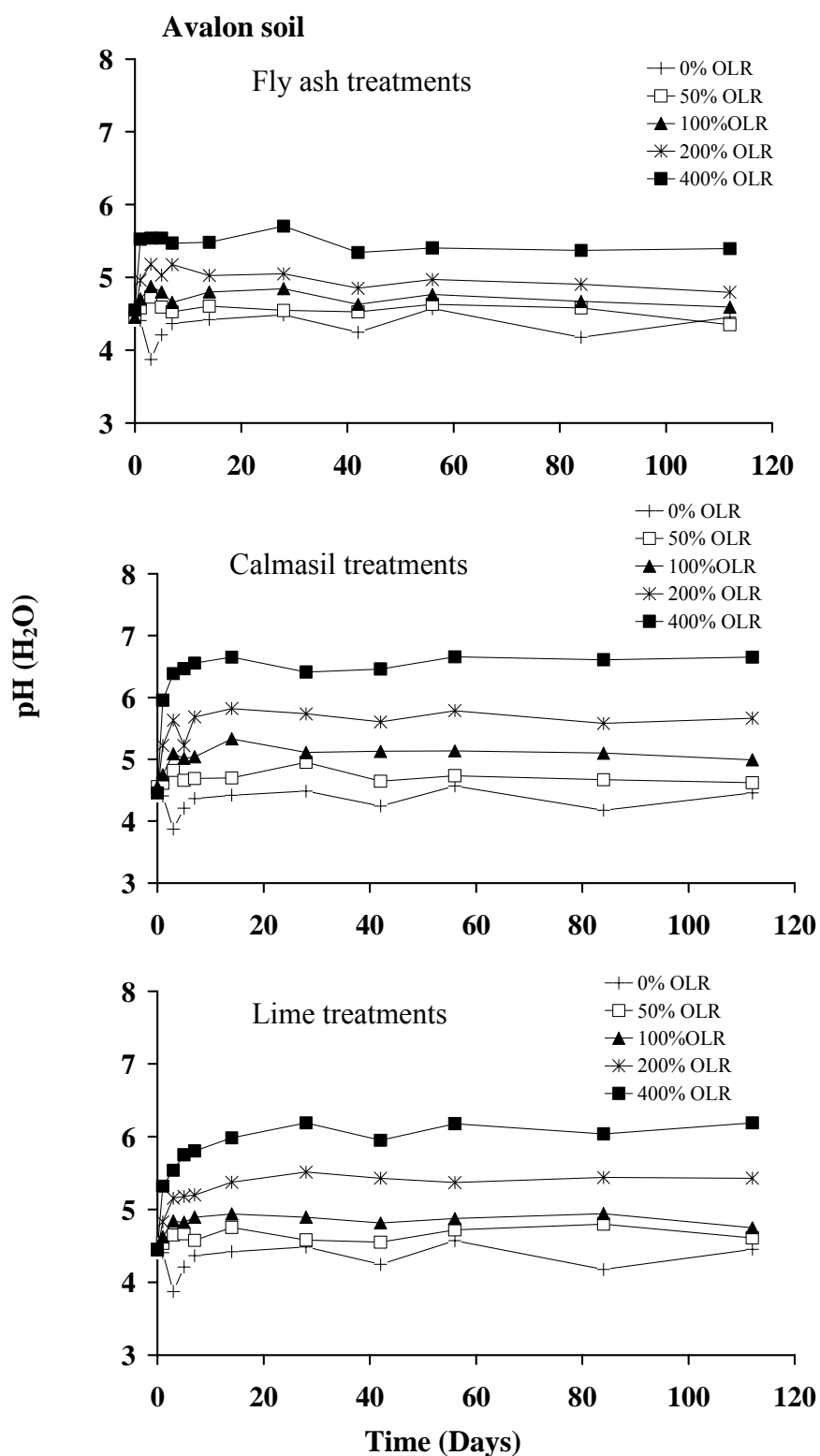


Figure 3.1 Changes in pH (H₂O) with time in the incubated Avalon soil treated at 0, 50, 100, 200 and 400% of the optimum liming rate (OLR) with equivalent rates of fly ash at 0, 5.85, 11.7, 23.4 and 46.8 Mg ha⁻¹; Calmasil at 0, 0.58, 1.16, 2.32 and 4.64 Mg ha⁻¹; and lime at 0, 0.735, 1.47, 2.94 and 5.88Mg ha⁻¹.

between 5 and 8. The pH of the treatments with fly ash at 50% and 100% OLR showed a decrease upon termination of the experiment with the treatment at 100% OLR showing pH levels comparable to the 0% OLR treatment. The decrease in soil pH at the lower rates of fly ash suggest reacidification of the Avalon soil at these rates, possibly due to a decrease in neutralisation activity with time. The decrease in activity is likely due to low solubility of the fly ash and / or the hydrolysis of Al released by fly ash.

The treatments with Calmasil in the Avalon soil showed an increase in soil pH to the desired range, for the three higher rates of 100%, 200% and 400% OLR (Figure 3.1). The highest increase to a soil pH of 6.65 was at 400% OLR and was the highest for all the treatments. The increase was 2.20 units greater than the lowest pH at the application rate of 0 Mg ha⁻¹ (0% OLR). The pH of the treatments with Calmasil at 50% and 100% showed a decrease with time after 42 days with the pH of the treatments at 50% OLR equivalent to the treatments at 0% OLR. The decrease in pH shown in the treatments with Calmasil at these rates is comparable to similar treatments with fly ash (Figure 3.1). The decrease in pH of the Avalon soil at the lower rates of Calmasil was possibly due to the aforementioned reasons for similar treatments with fly ash. The lime treatments in the Avalon soil showed a trend similar to the fly ash treatments, and it was possibly a result of the same reasons proposed for fly ash.

The pH in the Inanda soil treated with fly ash, Calmasil and lime showed an increase in as the application rate increased and with time (Figure 3.2). The treatments with fly ash in the Inanda soil showed an increase in soil pH to the desired pH of between 5 and 8 only at the highest application rate of 400% OLR (Figure 3.2). The results suggests that all the neutralising compounds were consumed at the lower rates of fly ash possibly due to the higher buffering capacity of the Inanda soil as it contains high clay and organic carbon (Table 3.1). The pH of the treatments with Calmasil showed an increase to the desired range at the two higher application rates of 200% and 400% OLR, a trend similar to the lime and fly ash treatments in the Avalon soil. The highest increase in pH in the Inanda soil was to 7.12 shown in the treatment with Calmasil at the highest rate. The increase was about 4.0 units higher than the lowest pH at the lowest application rate of 0% OLR).

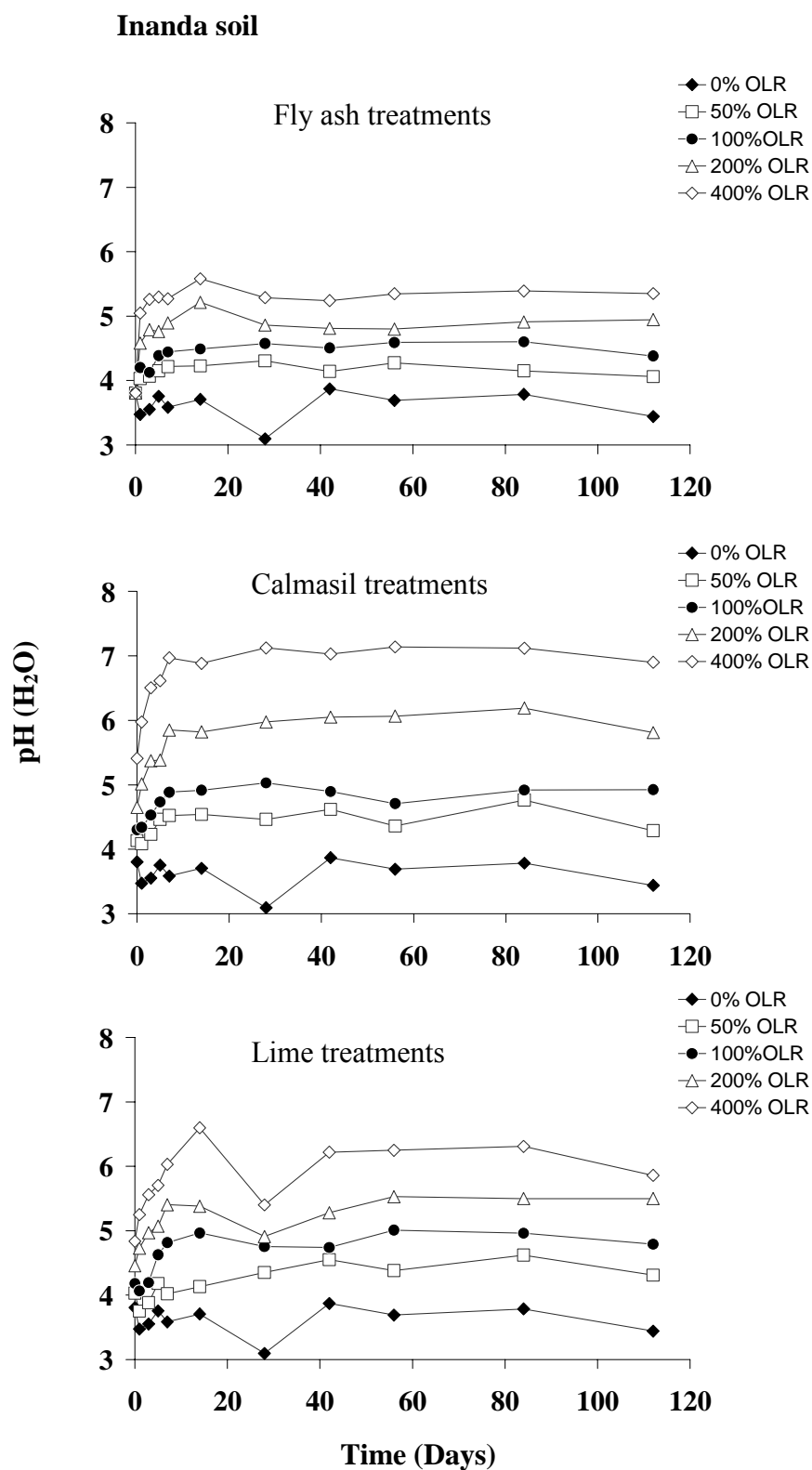


Figure 3.2 Changes in pH (H₂O) with time in the incubated Inanda soil treated at 0, 50, 100, 200 and 400% of the optimum liming rate (OLR) with equivalent rates of fly ash at 0, 68, 138, 272 and 544 Mg ha⁻¹; Calmasil at 0, 6.77, 13.54, 27.08 and 54.16 Mg ha⁻¹; and lime at 0, 8.55, 17.1, 34.2 and 68.4 Mg ha⁻¹.

The increase in pH of the treatments with fly ash in both soils was probably a result of the dissolution of Ca, Mg and Si compounds as suggested by previous researchers (Adriano *et al.*, 1980; Seone and Leiros, 2001; Daniels *et al.*, 2002). The lower than expected increase in the pH of the treatments with fly ash in both soils appear contrary to the expected results as the CCE at the different rates were equal to the other materials. Hence, it was expected to perform better than the other materials as it also had the highest fineness rating (Chapter 2, Table 2.3 and 2.4) suggesting that it would be the most reactive under acidic soil conditions. The inferior performance was possibly due to the low solubility of fly ash (Kim *et al.*, 2003). This in accordance to Stevens and Dunns (2004) who reported increases in the pH of acid soil treated with fly ash to desired levels only after the first year in a two-year field experiment where fly ash was used as a liming agent. Thus, the pH of both soils treated with fly ash at 100% OLR could well increase to the desired range over a longer period as the dissolution of acid neutralising compounds is likely to increase due to continuous changes in the soil environment.

The notable increase in the pH of both soils resulting from the addition of Calmasil suggests that it is the most soluble liming material with the highest levels of readily reactive alkalinity. The increase in the pH of the treatments with Calmasil was probably a result of the dissolution of Ca, Mg and Si compounds resulting in the neutralisation of acidity. The increases in the pH of treatments with Calmasil in both soils is in accordance with results for LD Slag (Rodriguez *et al.*, 1994; Pinto *et al.*, 1995), Basic slag (Bhat *et al.*, 2007) and calcium silicate slag (Chen *et al.*, 2000; Liang *et al.*, 2005, Nanayakkara *et al.*, 2008). The lower increase in pH shown in the treatments with lime in both soils is possibly a result of the relatively low solubility of lime (Foth and Ellis, 1996; Troeh and Thompson, 2005) and finesses efficiency rating /finesses rating reported earlier (Chapter 2, Tables 2.3 and 2.4). The differences in the response of the acid soils to the liming materials were not a result of differences in the CCE of the materials as this was factored into the experimental design.

Generally, the unamended soils showed cyclic changes in soil pH with time possibly a result of the changes in soil microbial activity (respiration, decomposition of organic matter and mineralization of C and N) controlling the release of H^+ (Bloom *et al.*, 2005). However, at higher application rates of all the materials marked changes with

time were not observed, suggesting buffering of the soil acidifying reactions by fly ash, Calmasil and lime.

The extractable Al in the treatments with fly ash, Calmasil and lime in the Avalon soil and Inanda soil showed a decrease with increasing application rate and with time (Figures 3.3 and 3.4). The extractable Al in the treatments of the Avalon soil showed a decrease after 14 days followed by an increase peaking at 28 days (Figure 3.2). After 28 days, extractable Al showed a general decrease with time. The treatments with fly ash in the Avalon at the two higher application rates (100 and 400% OLR) did not show a decrease in extractable Al to zero levels at the end of the incubation experiment as was shown by Calmasil and lime at the same application rates. This was possibly due to the release of Al from the fly ash as some acid neutralising compounds such as aluminosilicates dissociated, as they are the main drivers of the neutralisation of acidity by fly ash (Seone and Leoris, 2001; Yunusa *et al.*, 2006). These results are in accordance with McCallister *et al.* (2002) who reported an increase in extractable Al in acid soil treated with fly ash. The treatments with Calmasil and lime at the two higher application rates of 100% OLR and 400% OLR showed a marked increase in extractable Al to levels greater than the treatment at 0% OLR at 28 days.

The marked increase in the levels of extractable Al in these treatments was possibly due to the development of transitory acidic conditions suitable for the release of bound Al. The development of these conditions is possibly a result of a flush of CO₂ in the soil creating acidic conditions. This is possibly a result of two parallel processes i.e., a non-biological cause such as the reaction of Ca and Mg carbonate compounds with soil particles; and biological processes such as increased microbial activity after wetting of the soil. This is because the addition of water to dry soil results in an initial flush of microbial activity (respiration, decomposition of organic matter and mineralization of C and N) commonly known as the Birch process producing CO₂ and organic acids that gradually decline to a basal rate with time during soil incubation (Franzluebbers *et al.*, 2000). In the presence of lime, the production of CO₂ after the addition of water to soil increases greatly with increasing application rate (Fuentes *et al.*, 2006).

Avalon soil

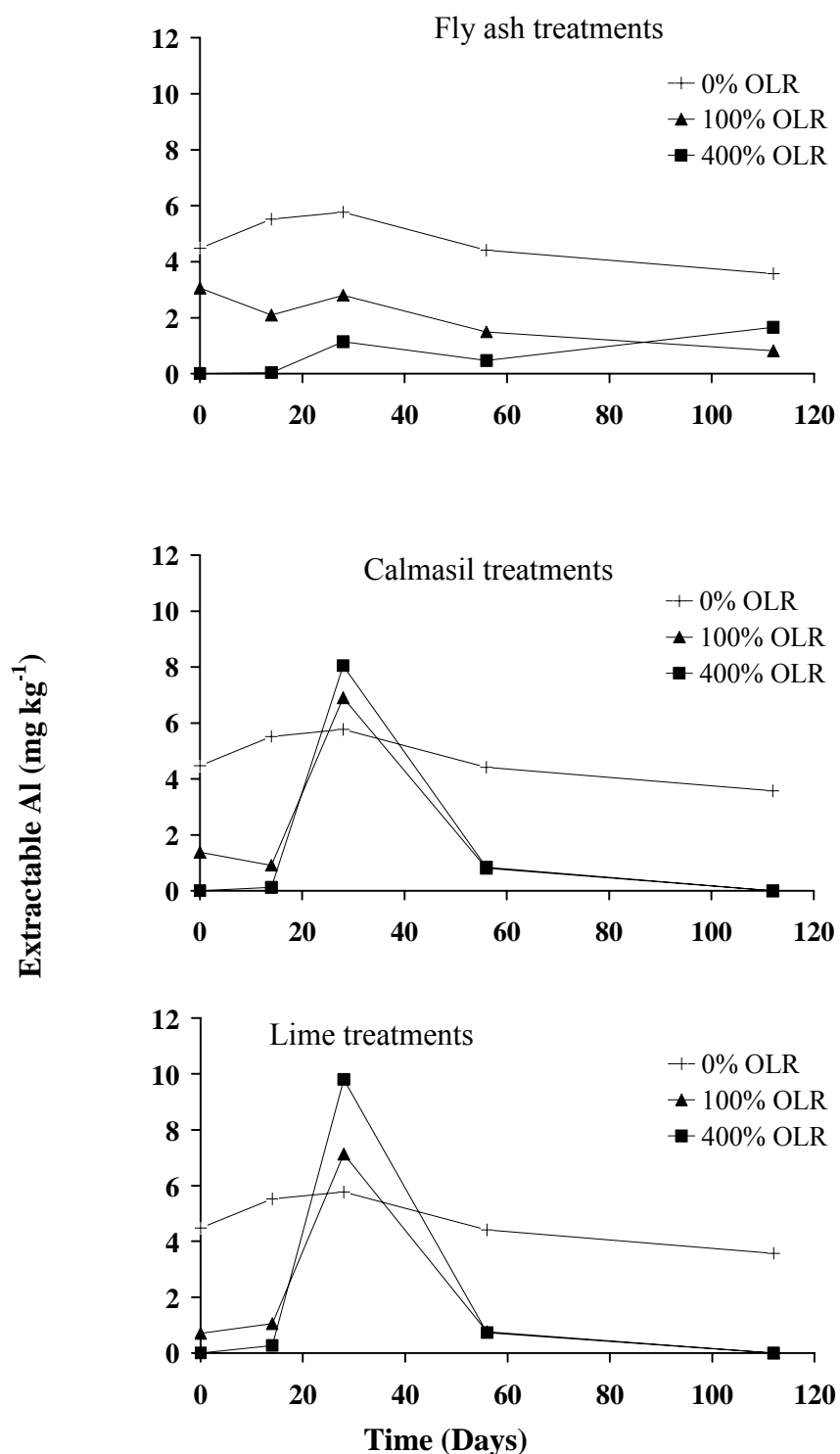


Figure 3.3 Changes in 0.01 M CaCl₂ extractable Al with time in the incubated Avalon soil treated at 0, 100 and 400% of the optimum liming rate (OLR) at equivalent rates with fly ash at 0, 11.7 and 46.8 Mg ha⁻¹; Calmasil at 0, 1.16 and 4.64 Mg ha⁻¹; and lime at 0, 1.47 and 5.88Mg ha⁻¹.

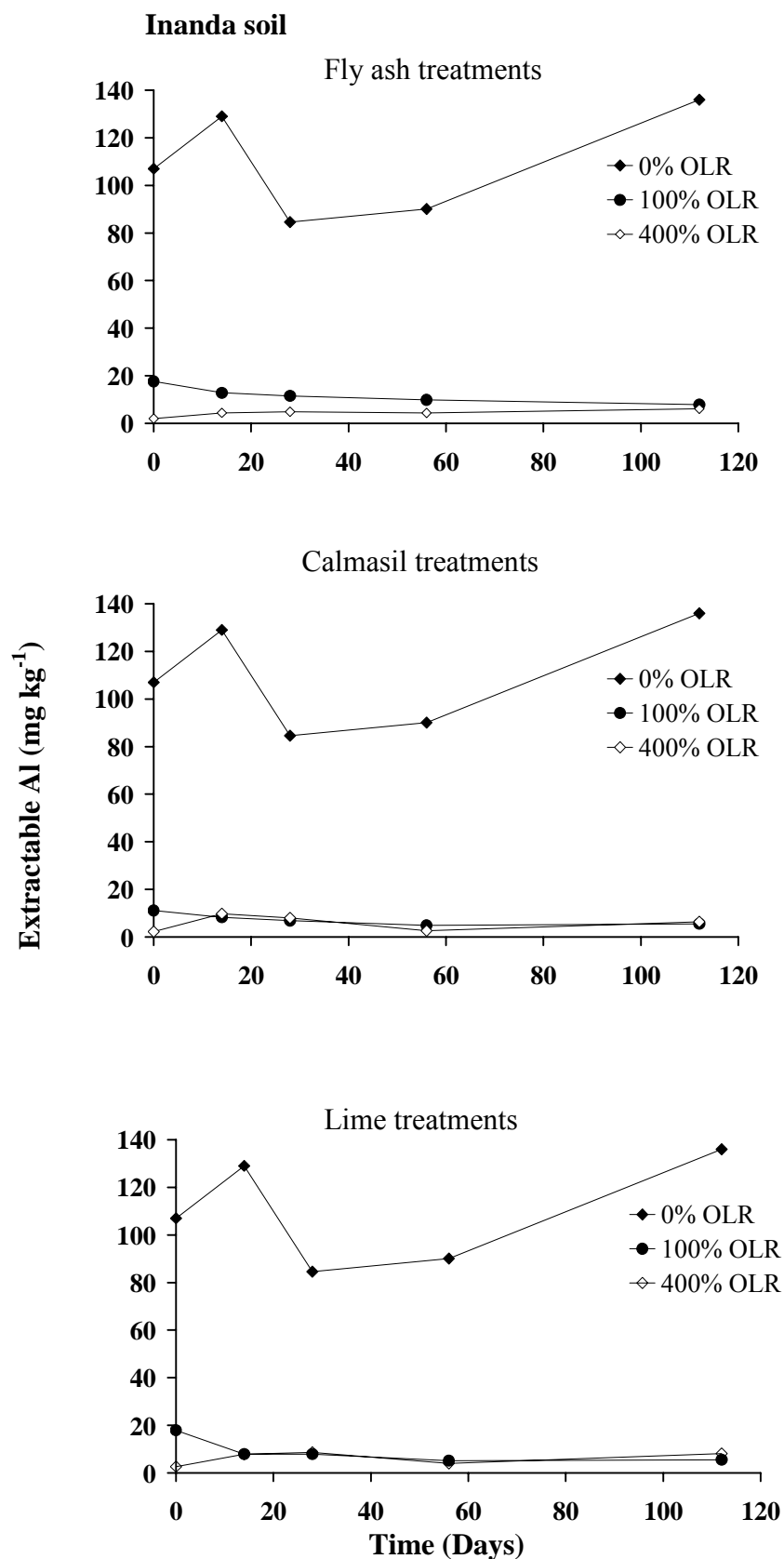


Figure 3.4 Changes in 0.01M CaCl₂ extractable Al with time in the incubated Inanda soil treated at 0%, 100% and 400% of the optimum liming rate (OLR) at equivalent rates with fly ash at 0, 138 and 544 Mg ha⁻¹; Calmasil at 0, 13.54 and 54.16 Mg ha⁻¹; and lime at 0, 17.5 and 70 Mg ha⁻¹.

The gradual decrease that followed in the treatments with Calmasil and lime in the Avalon soil would then be due to decreases in the production CO_2 by both processes and the increased consumption of carbonate compounds. These changes conditions in the incubated soils were probably conducive for the transformation of Al to forms that not easily extractable.

The extractable Al at the two higher application rates of 100% and 400% OLR in the treatments with fly ash, Calmasil and lime of the Inanda soil were notably lower than zero rate (Figure 3.4). The results show a trend different from the Avalon soil with the same treatments. The increased transformation of extractable Al into forms that were not readily extractable was possibly due to development of conditions conducive for the transformation of Al via reactions with both inorganic (carbonates, oxides etc.) and organic compounds as organic matter decayed following liming. The cyclic changes in the extractable Al in the zero treatments were possibly due the “birch process” coupled with incubation conditions that might have been conducive for the development of secondary flushes in CO_2 as the organic matter decayed.

The general decrease in extractable Al in the higher treatments with fly ash in both soils with increasing application and with time is in accordance with Wright *et al.* (1998). The decreases in extractable Al in the treatments with Calmasil showed a trend comparable to the results for acid soils treated with LD slag reported by Pinto *et al.* (1995). The decrease in extractable Al in all the treatments was probably due to the dissolution of acid neutralizing compounds and formation of compounds promoting the hydrolysis, polymerization and precipitation of ionic Al (Kabata-Pendias, 2001; Essington, 2004).

The levels of extractable Mn decreased with increasing application rate and with time in the treatments with fly ash, Calmasil and lime in both the Avalon and Inanda soils (Figures 3.5 and 3.6). The extractable Mn was not readily extractable in any of the higher treatments in the Avalon soil. The zero treatment in the Avalon soil A also showed a decrease in the extractable Mn with time. The decrease in all the treatments was possibly due to the oxidation of Mn through both biological and non-biological processes.

Avalon Soil

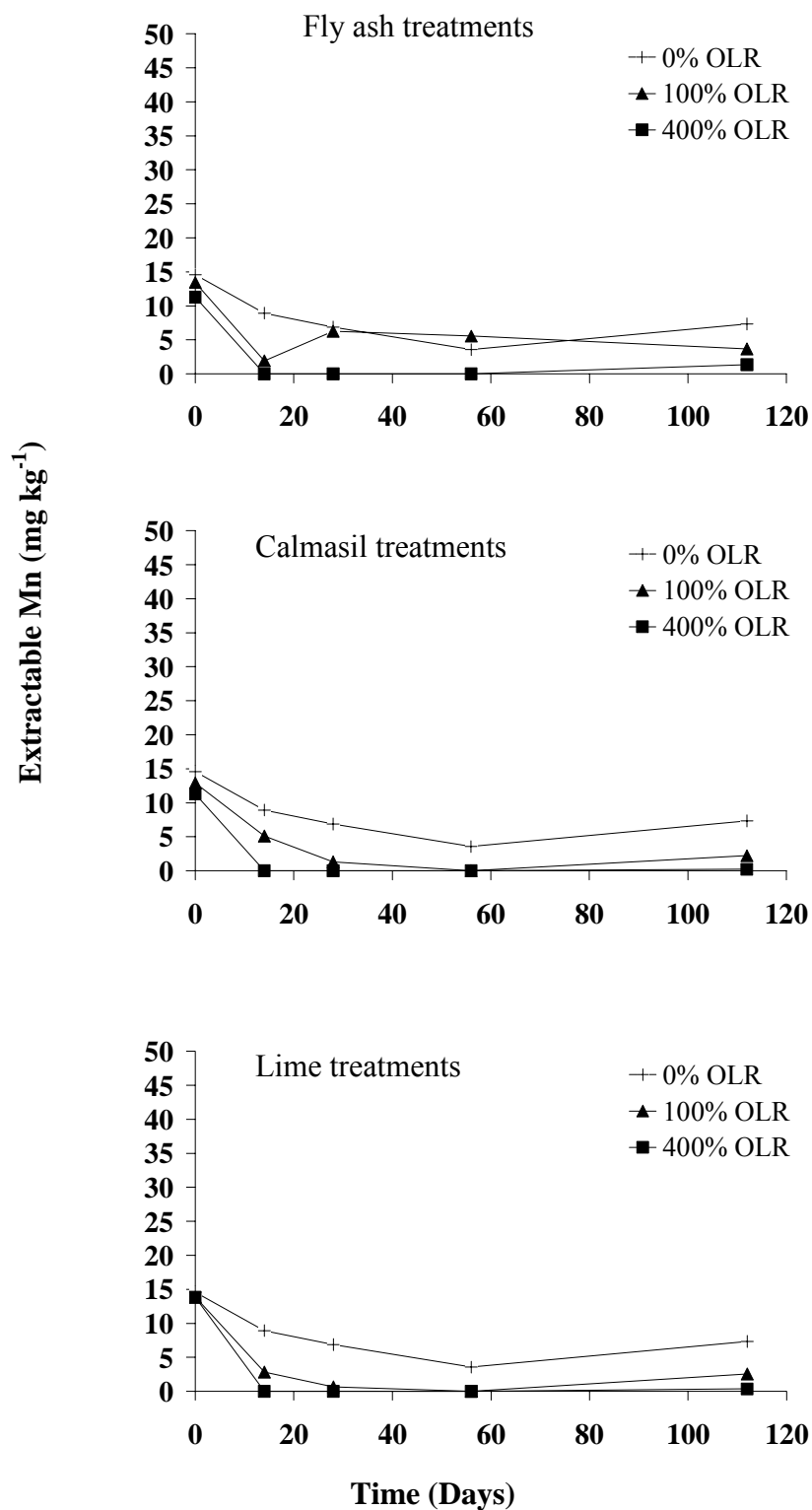


Figure 3.5 Changes in 0.01M CaCl_2 extractable Mn with time in the incubated Avalon soil treated at 0%, 100% and 400% of the optimum liming rate (OLR) with equivalent rates of fly ash at 0, 11.7 and 46.8 Mg ha^{-1} ; Calmasil at 0, 1.16 and 4.64 Mg ha^{-1} ; lime at 0, 1.47 and 5.88 Mg ha^{-1} .

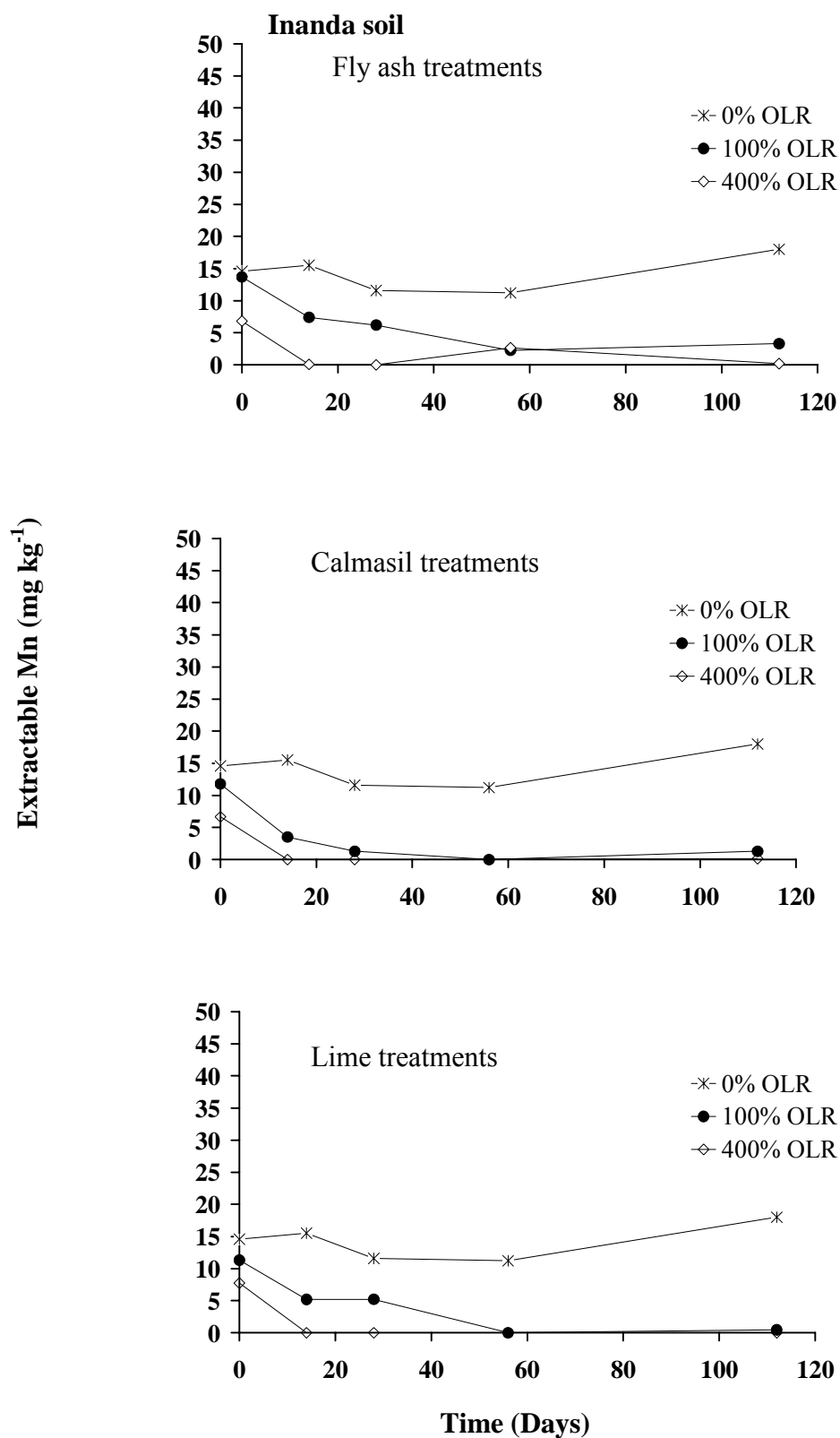
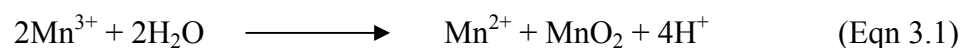


Figure 3.6 Changes in 0.01M CaCl₂ extractable Mn with time in the incubated Inanda soil treated at 0, 100 and 400% of the optimum liming rate (OLR) with equivalent rates of fly ash at 0, 138 and 544 Mg ha⁻¹; Calmasil at 0, 13.54 and 54.16 Mg ha⁻¹; and lime at 0, 17.5 and 70 Mg ha⁻¹.

The oxidation of Mn via biological processes in soils has been reported to be a major driver for the oxidation of Mn in soils (van Veen, 1973; Bromfield, 1976; Levan and Riha, 1986). Manganese is oxidised through non-biological processes forming relatively stable oxides upon addition of moisture as ionic Mn reacts with water to produce MnO_2 and H^+ (equations 3.1 and 3.2) (Bartlett and Ross, 2005).



In the presence of alkali materials, an increase in soil pH promotes the fixation of hydrolysis and precipitation ionic Mn (Kabata-Pendias, 2001; Essington, 2004; Bartlett and Ross, 2005). In view of the aforementioned factors the increased transformation of extractable Mn in the higher treatments in both soils was likely a results of combination of these factors. Manganese oxide in soil is relatively stable and insoluble (Barlett and Ross, 2005), and this may have resulted in its complete immobilisation in both soils.

3.3.3 The effect of fly ash, Calmasil and lime on EC and exchangeable Ca, Mg, K and Na

The treatments with fly ash, Calmasil and lime in the Avalon and Inanda soils showed notable increases in soil EC with increase in the amount of material added upon termination of the incubation experiment (Tables 3.2 and Table 3.3).

Table 3.2 EC and extractable Ca, Mg, K, Na after 112 days of incubated in the Avalon soil treated at 0,100 and 400% OLR with equivalent rates of fly ash at 0, 11.70 and 46.80 Mg ha^{-1} ; Calmasil at rates of 0, 1.16 and 4.64 Mg ha^{-1} and lime at rates of 0, 1.47 and 5.88 Mg ha^{-1}

Property	Control	Fly ash		Calmasil		Lime	
Rate (% OLR)	0	100	400	100	400	100	400
EC ($dS m^{-1}$)	0.01	0.11	0.15	0.11	0.21	0.10	0.15
Ca ($mg kg^{-1}$)	126	129	234	251	365	163	279
Mg ($mg kg^{-1}$)	25.6	30	45.30	44	80.20	40.10	71.1
K ($mg kg^{-1}$)	37.4	38	40.70	39.10	40.80	37.4	40.9
Na ($mg kg^{-1}$)	1.06	2.51	1.87	2.51	2.19	1.80	1.70

The changes in EC of some of the treatments with lime of both soils are contrary to the expected increase in EC of the treatments with fly ash and Calmasil because of their origin. The results suggest the effect of fly ash and Calmasil at 100% OLR and the extreme rate of 400% OLR on the EC of treated acid soils may not pose a salinity threat.

Table 3.3 EC and extractable Ca, Mg, K and Na after 112 days of incubated in the Inanda soil treated at 0, 100 and 400% OLR with equivalent rates of fly ash at 0, 136 and 544 Mg ha⁻¹; Calmasil at 0, 13.6 and 54.4 Mg ha⁻¹, and lime at rates 0, 17.10 and 68.4 Mg ha⁻¹.

Property	Control	Fly ash		Calmasil		Lime	
Rate (% OLR)	0	100	400	100	400	100	400
EC ($dS m^{-1}$)	0.32	0.45	0.66	0.53	0.91	0.61	1.28
Ca ($mg kg^{-1}$)	106	411	619	903	992	816	1084
Mg ($mg kg^{-1}$)	20.7	74.5	94.8	133	135	133	131
K ($mg kg^{-1}$)	32.4	43.2	19.9	45.2	50.6	44.9	64.10
Na ($mg kg^{-1}$)	1.04	9.11	6.72	21.1	24.2	14.1	16.00

The extractable Ca and Mg of the treated soils increased with the addition of fly ash, Calmasil and lime (Tables 3. 2 and Table 3.3). Extractable K showed the lowest increase with increasing application rate in both soils and showed a marked decrease at the highest rate of fly ash in the Inanda soil. The net decrease in extractable K was possibly due to low levels of K in fly ash (as reported in Chapter 2), the fixation of K released due to the liming effect (Foth and Ellis, 1996) and adsorption on aluminosilicates formed during the breakdown of fly ash (Zevenbergen *et al.*, 1999).

Extractable Na showed a notable increase in all the treatments at the two higher rates. The increase in soil EC and extractable Ca and Mg in the treatments with the fly ash is in agreement with previous findings (Adriano *et al.*, 1980; Elseewi *et al.*, 1980; Matsi *et al.*, 1999; Manoharan *et al.*, 2007). The increase in soil EC and extractable Ca, Mg, K with the treatments with Calmasil showed a trend similar to acid soils treated with LD slag (Rodriguez *et al.*, 1994; Pinto *et al.*, 1995).

3.3.4 The effect of fly ash, Calmasil and lime on the availability of trace elements

Generally, the DTPA extractable trace elements in the treatments with fly ash, Calmasil and lime in the Avalon and Inanda soils showed a decrease with time, with the exception of V that showed an increase in all the treatments with fly ash (Appendix 3.1 and 3.2). The 1M NH_4NO_3 and 0.01M CaCl_2 extractable trace elements in the treatments with fly ash, Calmasil and lime of both soils showed a trend similar to the DTPA extractions (Appendix 3.1 and 3.2). The general increase in V in the soils suggests that it exists as an anion that is probably mobile in soils as it has a negative charge. Liming increases the negative charge of the soil as it increases the cation exchange capacity (CEC) (Foth and Ellis, 1996) and possibly this also contributed to the increase in the availability of V in the treated soils. The increase in V in the control soils over time may be partially due to the former reason although other, at this stage unknown, causes may be also involved.

Arsenic was not detected in the two higher treatments with fly ash upon termination of the experiment, suggesting that it was not readily extractable as soils generally have a high attenuation capacity for As. The results are contrary to the expected increase in As in the soils treated with fly ash as the results of the *aqua regia* and TCLP extractions (Chapter 2; Table 2.5 and 2.6) showed notably high levels As that showed that it was highly soluble and would have been potentially extractable under acidic conditions. The Ni in the treatments with Calmasil of both soils showed a similar trend to As in the fly ash treatments. The low levels of these elements at the end of the incubation experiment were possibly due to the low solubility of As and Ni bearing compounds and/or the dilution effect following the application to soil.

Contrary to the earlier leaching and extraction results of fly ash, Calmasil and lime, the extraction results of the treated incubated soils showed that trace elements were not readily extractable following the incorporation of the materials into soil. More trace elements were detected in the untreated soils in comparison to the treated soils. The differences in the trace element status of the treated and untreated soils suggest that the application of the fly ash, Calmasil and lime generally decreased the mobility of trace elements present in soil. The decreased extractability of trace elements in the treated soil suggests that addition of fly ash and Calmasil to soil possibly increased

adsorption and /or precipitation of the trace elements to low levels. Kumpiene *et al.* (2008) and Iyer and Scott (2001) showed similar findings in contaminated soils treated with alkaline industrial waste, and reported a decrease in the mobility of trace elements in the contaminated soil. The general decrease observed in the treatments with fly ash is in accordance with results reported by Bilski *et al.* (1995) that demonstrated that addition of fly ash at 50% (w/w) did not result in the leaching of heavy metals (Cr, Pb, Mn, Se). The trace element status of the treatment with Calmasil in both soils is in accordance with results for slag reported by Van der Waals and Claassens (2003).

The effects of fly ash, Calmasil and lime on the availability of trace elements were notable for the 0.01M CaCl₂ and 1M NH₄NO₃ extraction in comparison to DTPA. Burgos *et al.* (2008) demonstrated a similar trend with 0.01M CaCl₂ and EDTA (organic complexing agent comparable to DTPA) in extracts from treated mine-spill-contaminated soil (clay loam soil) treated with biosolid compost, sugar beet lime, and a combination of leonardite plus sugar beet lime. The effect of the treatments on the availability of some metals was more evident with the 0.01M CaCl₂ extracts than the EDTA extracts. However, a decrease in soil pH under field conditions due to agronomic practices may possibly result in an increase in the availability of trace elements with time.

3.4 Conclusions

The application of fly ash and Calmasil to the Avalon and Inanda soils increased soil pH to levels comparable and higher than lime, respectively. However, increases to the desired pH at the optimum application rate were only attained in the Avalon soil with Calmasil. Extractable Al and Mn in both soils decreased with addition of fly ash and Calmasil to levels comparable to lime. Fly ash and Calmasil did not increase the levels of extractable Al and Mn. Soil acidity was not exacerbated only at the optimum application rate and higher with both materials. Addition of fly ash and Calmasil increased exchangeable Ca, Mg, K and Na, and improved the fertility status of both soils.

The trace element status of both the soils was not greatly impacted by the application of fly ash and Calmasil. The major trace elements of concern highlighted earlier

(Chapter 1) present in fly ash (As, Cr, Mo, Ni, Se) and Calmasil (Cr, Mo and N) are not liable to leach into the soil environment after incorporation through liming. However, V may be of concern. The Cr, Mo and Ni present in Calmasil are not liable to leach into the soil environment after incorporation. Thus, fly ash and Calmasil ameliorated soil acidity to levels comparable to lime and the trace elements in the treated soil did not show a marked increase and were not readily available in the treated soils. However, it is possible that with time and under normal agronomic practice the pH may decline and some of the heavy metals may become more readily available. Further experimentation would be necessary to examine this effect.

Chapter 4

The effect of liming with fly ash and processed stainless steel slag on plant growth: a preliminary glasshouse investigation with perennial rye grass

4.1 Introduction

The general positive response of crops to liming is principally a response to an increase in soil pH and factors such as alleviation of Al and Mn toxicity, and Ca, Mg Mo and B deficiencies (Hall, 1983, Arshard and Gill, 1996; Prasad and Power, 1997). The overall ability of a plant to grow in soil is dependent on many factors, which include climatic conditions and soil properties (chemical and physical). Changes in soil properties under controlled conditions arising from the addition of fertilizer, manure, lime etc. can be qualitatively assessed using plant growth patterns as they are indicative of changes in soil quality.

Recent studies have shown improved plant growth on acid soils treated with fly ash (Matsi and Keramidas, 1999; Mittra *et al.*, 2005; Yunusa *et al.*, 2008) and metallurgical slag (Rodriguez *et al.*, 1994; Carvalho-Pupatto *et al.*, 2004; Ali and Shahram, 2007; Bhat *et al.*, 2007). In view of these studies, the growth response of an acid intolerant plant species can be used to assess the liming ability of a potential liming material. This chapter reports a preliminary investigation on the effect of liming two acid soils with fly ash and Calmasil on the emergence, early growth, and establishment of an acid intolerant grass, perennial rye grass (*Lolium perenne L.*).

4.2 Materials and Methods

4.2.1 Soils and liming materials

Fly ash, Calmasil and lime with characteristics that were investigated and discussed in Chapters 2 and 3, were used to treat two contrasting acid topsoils (0-20cm) of the

Avalon and Inanda forms (Soil Classification Working Group, 1991) investigated in Chapter 3.

4.2.2 Glasshouse experiment

Perennial rye grass, commonly used for forage and reclamation was used. The liming rates determined in Chapter 3 were used in this investigation. Composite samples of 1.2kg of the Avalon and Inanda soils were treated with fly ash, Calmasil and lime at rates of 0, 50, 100, 200 and 400% Optimum liming rate (OLR). A basal application of 5:1:5 fertilizer was applied at a rate equivalent to the optimum N requirement for perennial rye grass as recommended by Manson *et al.* (2004) to all the treatments to provide the necessary macronutrients. The application of N fertilizer allowed for the investigation of the liming effect of fly ash and Calmasil under conditions with possible acidification due to chemical fertilizer, typical of fertilized agricultural soils.

Soil, liming materials and fertilizer were thoroughly mixed to promote the even distribution of the materials. The mixtures were added to 20cm-diameter plastic pots underlain with unperforated saucers to prevent any nutrient and water loss. About 20 seeds of perennial rye grass were sown in each pot at a depth of between 0.15 and 0.20cm. Each treatment had three replicates and pots were arranged in a complete randomized block design. The pots were watered regularly with distilled water. The pot experiment was run under natural lighting conditions in a glasshouse for 70 days.

Seedlings were thinned to five plants per pot 14 days after planting and after 70 days, the aboveground biomass was cut at about 1.5cm above the soil surface for all the treatments. The harvested material was oven dried at 60°C for 48hrs before being weighed. Yield data (g pot^{-1}) were recorded and analysis of variance (AVOVA) was carried out to determine the effects of interactions of soil type, treatment and application rate on the dry biomass yield using GenStat-9.1 (Lawes Agricultural Trust, Rothamsted Experimental Station). Transformation to mg pot^{-1} and to \log_{10} was performed to normalize the data where they were skewed and the coefficient of variance of the original data was greater than 20%. If the F statistic was significant the LSD comparisons of the mean yields at 5% level of significance were performed.

4.3 Results and Discussion

Germination of perennial rye grass germinated and emergence in all the treatments 7 days after sowing in both soils shows that the soil conditions were suitable. All the treatments with Calmasil at rates greater than 0% OLR had efflorescence on the surface 14 days after sowing. This was due to the precipitation and / or crystallisation of salts. The efflorescence observed on the surface of all the treatments with Calmasil suggest high levels of soluble salt in Calmasil and supports results in Chapter 2 that showed that Calmasil had a high EC and extractable Na in comparison to fly ash and lime (Tables 2.2, 2.4 and 2.5). However, growth constraints associated with high EC and Na were not observed in these treatments and this suggests that salts posed a minimal salinity threat to rye grass.

All the treatments with fly ash in the Inanda soil at the two higher rates of 200 and 400% OLR showed yellowing of leaves and drying out of the tips of leaves 18 days after sowing. The symptoms were not visible upon termination of the experiment after 70 days. The symptoms are characteristic of chlorosis and necrosis possibly a result of nutrient deficiencies for S, Fe, Zn and Cu and toxicities of Ni and B (Prasad and Power, 1997). Sale *et al.* (1996) reported similar symptoms on the leaves of barley grown on acid soil treated with fly ash at high rates of 75 and 100% (v/v). The symptoms were attributed to B toxicity and the symptoms observed on rye grass in the higher treatments in the present study were possibly also due to B toxicity. The severity of the injury symptoms on rye grass in the treatments with fly ash of the Inanda at higher rates showed a decrease after 18 days to levels where they were not detected after 70 days. Adriano *et al.* (2002) suggested that B toxicity symptoms on plants grown on soils treated with fly ash were temporary and only evident in the short term as B exists as an anion and is likely to be readily leached. Thus, the decrease in the injury symptoms on rye grass with time was possibly due to movement of B from the upper section of the pots to below rooting depth.

The treatments with lime in the Avalon soil showed stunted growth (Figure 4.1). This was possibly due to the decreased availability of essential nutrients due to liming, coupled with the low nutritional value of lime in comparison to the other liming materials.

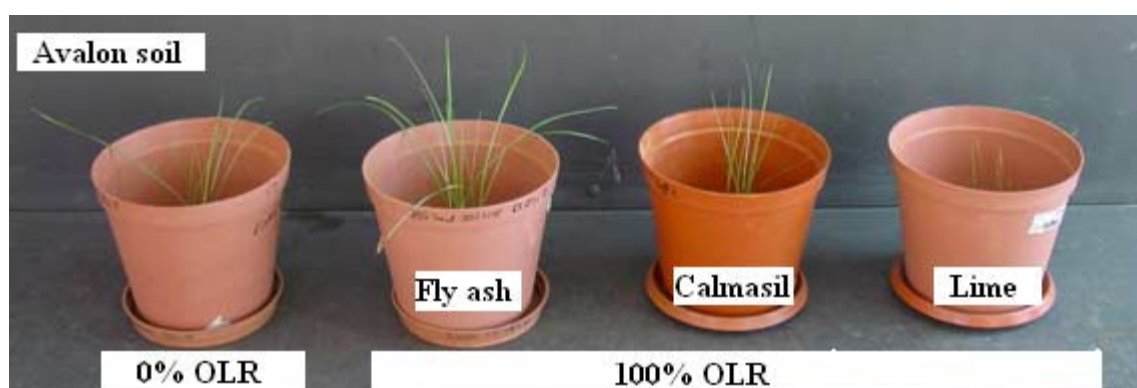


Figure 4.1 Growth of perennial rye grass (70 days) in Avalon soil treated at 0 and 100% optimum liming rate (OLR) with equivalent rates of fly ash at 0 and 5.85 Mg ha^{-1} ; Calmasil at 0 and 0.58 Mg ha^{-1} ; and lime at 0 and 0.735 Mg ha^{-1} .

The zero treatments of the Inanda soil (0% OLR) showed stunted growth and minor purpling and yellowing of leaves (Figure 4.2). The symptoms are characteristic of Al toxicity in young plants (Prasad and Power, 1997) and were not observed on the rye grass grown at higher application rates of fly ash, Calmasil and lime.

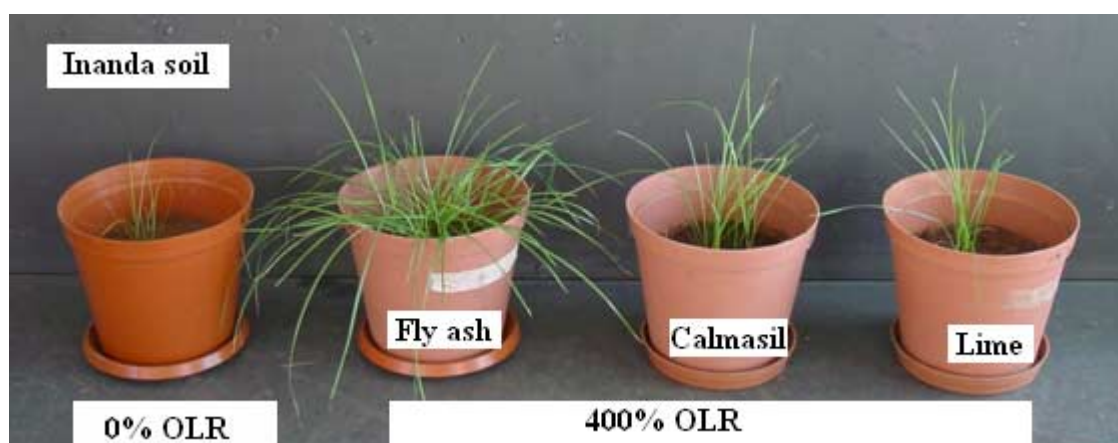


Figure 4.2 Growth of perennial rye grass (at 70 days) in Inanda soil treated at rates of 0 and 400% optimum liming (OLR) with equivalent rates of fly ash at 0 and 545 Mg ha^{-1} , Calmasil at 0 and 54.16 Mg ha^{-1} ; and lime at 0 and 68.4 Mg ha^{-1} .

The observations suggest that the application of fly ash, Calmasil and lime alleviated Al toxicity. Generally, the treatments with fly ash, Calmasil and lime in the Inanda soil showed improved growth in comparison to the same treatments in the Avalon

soil. Improved growth of rye grass in the treatments of the Inanda soils were possibly due to its higher nutritional status (Table 3.1).

The highest dry biomass yield in the treated Avalon soil was in the treatments with fly ash and lowest in the treatments with lime, the trend was generally in the following order: fly ash > Calmasil > lime (Figure 4.3). The treatments had a significant effect on the yield of perennial rye grass grown on the Avalon soil ($p < 0.001$) (Appendix 4, Table A4.1) The application rate of the treatments and the interaction of treatments and the application rate did not have significant effect on the yield of rye grass ($p > 0.05$). The yield of the treatments with fly ash showed an increase up to the rate of 23.4 Mg ha^{-1} , followed by a decrease at the highest application rate (Figure 4.3).

Karla *et al.* (1998) demonstrated a similar trend for the yield of maize, mustard and wheat grown on acid soil treated with fly ash under field conditions reporting an increase in the crop yield to a maximum followed by a decrease as the application rate of fly ash increased. Gupta *et al.* (2007) also demonstrated a similar trend for the yield of dry beans grown on acid soil with higher levels of organic carbon (3%) treated with fly ash at 10% (w/w) and 25% (w/w). Although, the application rates used in this experiment (0, 50, 100, 200, 400 OLR, equivalent to 0, 0.27%, 0.54%, 1.08% and 2.16% (w/w)) are lower than the rates used by Gupta *et al.*, (2007) the trends with yield are comparable. This suggests that the negative impact of fly ash treatments on crops grown in treated acid soils probably depends on the amount of organic carbon present in the soil. Hence, the yield of crops grown on acid soils treated with fly ash is likely to reach a maximum at different application rates as per amount of organic carbon.

The dry yield of rye grass showed an increase with increasing rate of Calmasil reaching a maximum at 1.16 Mg ha^{-1} , followed by a decrease at higher application rates (Figure 4.3). The treatments with Calmasil showed a yield trend similar to the treatments with fly ash.

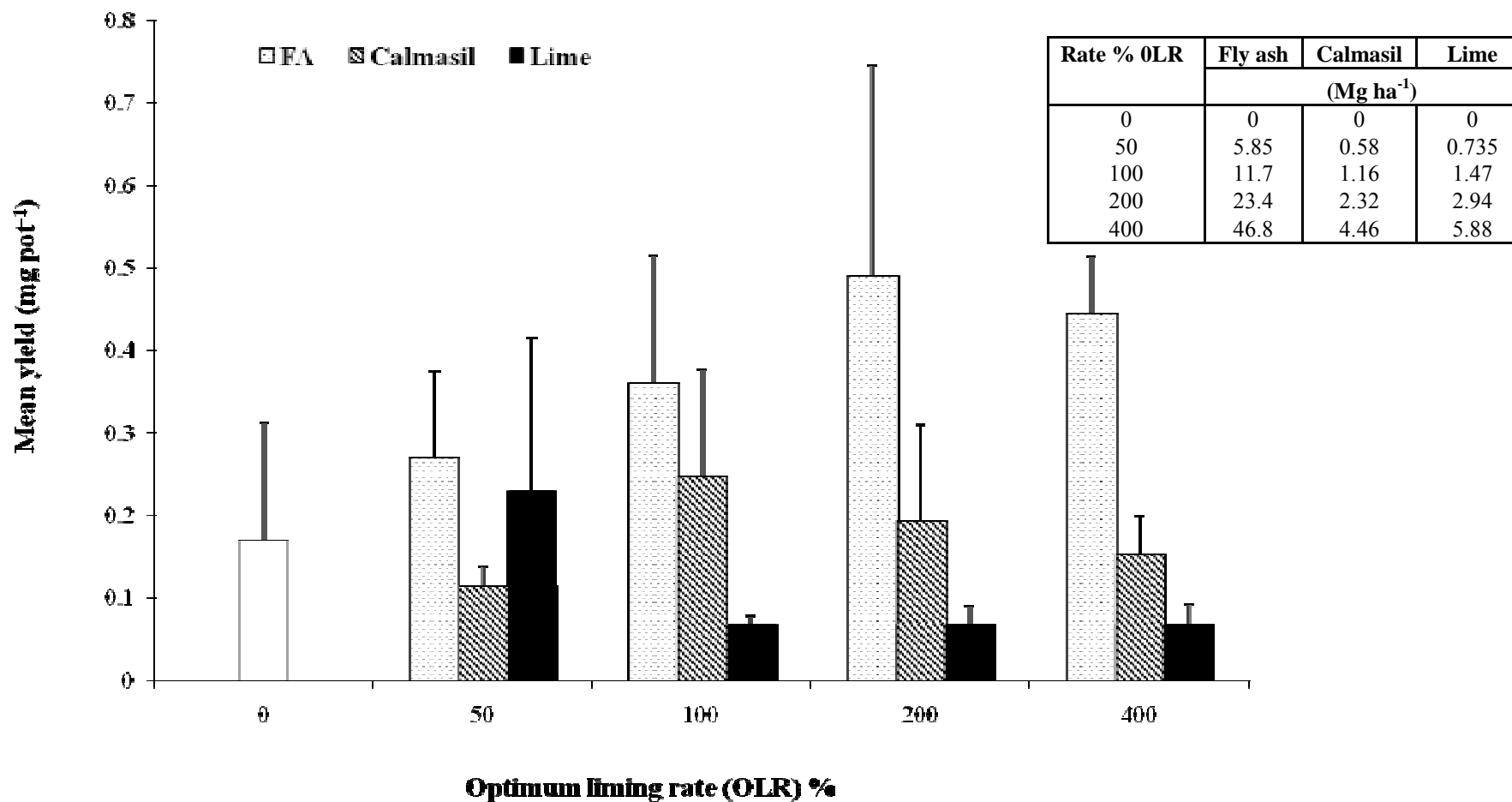


Figure 4.3 Dry biomass yield of perennial rye grass grown in the Avalon soil treated at 0, 50, 100, 200 and 400% optimum liming rate (OLR) with equivalent rates of fly ash at 0, 5.85, 11.7, 23.4 and 46.8 Mg ha⁻¹; Calmasil at 0, 0.58, 1.16, 2.32 and 4.46 Mg ha⁻¹; and lime at 0, 0.735, 1.47, 2.94 and 5.88 Mg ha⁻¹.

The trend shown by the yield of perennial grass grown in the treatments with Calmasil is in accordance with results for maize grown in soil treated with converter slag by Ali and Shahram (2007), who reported an increase in the dry yield of maize with increasing application rate reaching a maximum at 2% (w/w), followed by decreased at the highest rate of 4% (w/w). Although, the application rates used in this experiment (0, 50, 100, 200, 400 OLR, equivalent to 0, 0.27%, 0.54%, 1.08% and 2.16% (w/w)) are lower than the rates used by Ali and Shahram (2007) the trends with yield were comparable. This is probably a result of the differences in the chemical composition of the materials which depends on the source although the composition of major elements is likely to be akin. Hence, the yield of crops grown on acid soils treated with slags such as is likely to reach a maximum at different application rate depending on the slag used.

The improved growth of perennial rye grass with Calmasil at rates of 100 and 200% OLR (Figure 4.3) is in accordance with reports by Kane-Berman (*personal communication*, 2007) of improved commercial production of maize and potatoes grown on the Avalon soil treated with Calmasil at 3 Mg ha⁻¹ biannually. The yield of rye grass in the treatments with lime showed a trend different from the yield with fly ash and Calmasil, with the highest yield at the lowest application rate of 50% OLR followed by a decrease to a constant yield for the subsequent three higher application rates. The highest yield with Calmasil was at the optimum application rate in the treated Avalon soil, suggesting an accurate estimation of the application rate. However, the lower yield in the treatments of the Avalon soil with fly ash and lime at the 100% OLR are possibly due to the lower ameliorating effect, as both fly ash (Kim *et al.*, 2003) and lime (Foth and Ellis, 1996; Troeh and Thompson, 2005) have relatively low solubility.

The yield of rye grass grown on the treated Inanda soil was generally in the following order: fly ash > Calmasil > lime (Figure 4.4). The three treatments, the application rate and their interaction all had a significant effect on the yield of perennial rye grass grown on the Inanda soil ($p < 0.05$) (Appendix 4, Table A.4.2).

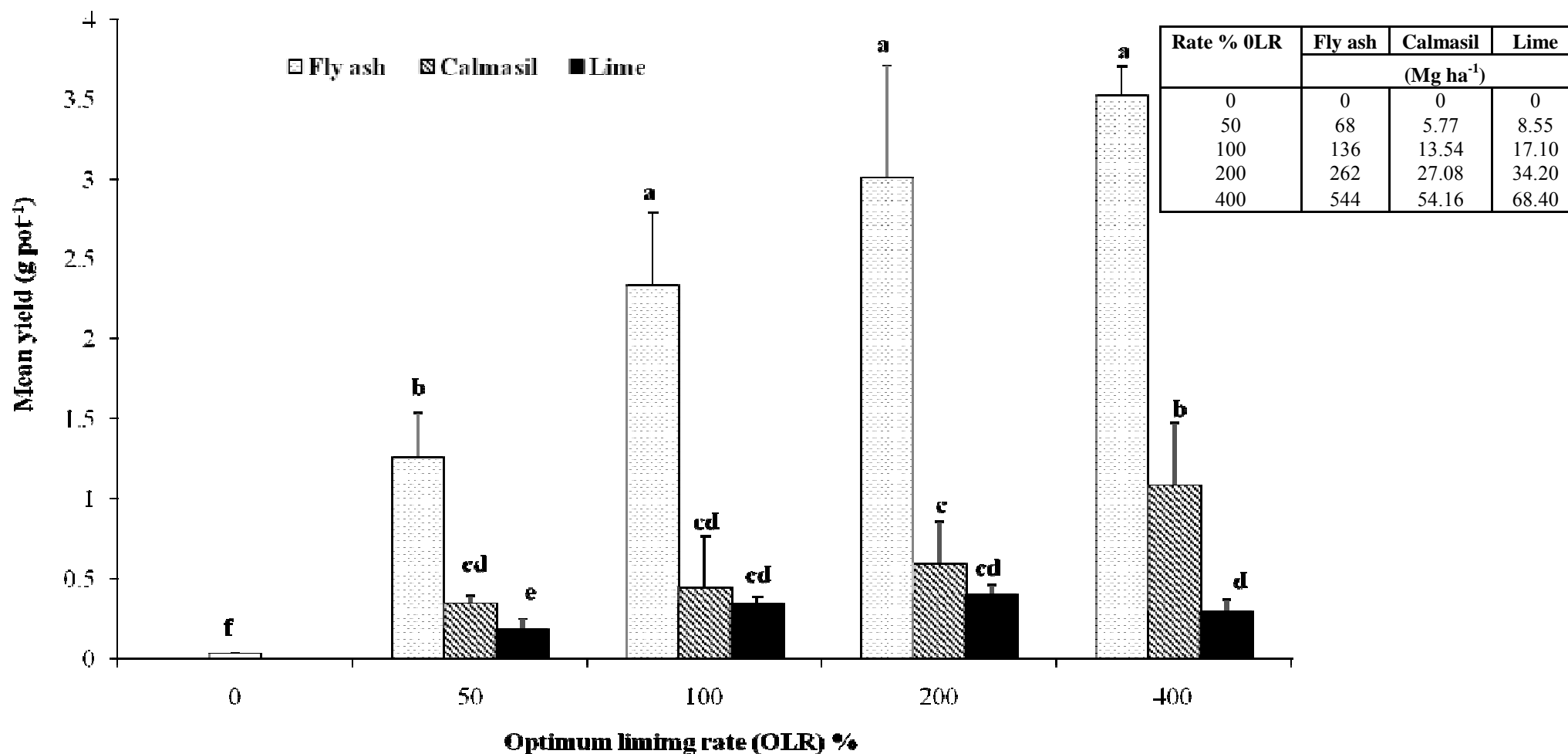


Figure 4.4 Dry biomass yield of perennial ryegrass grown in the Inanda soil treated at 0, 50, 100, 200, 400% optimum liming rate (OLR) with equivalent rates of fly ash at 0, 68, 136, 272 and 544 Mg ha⁻¹; Calmasil at 0, 6.77, 13.54, 27.08 and 54.16 Mg ha⁻¹; and lime at 0, 8.55, 17.1, 34.2 and 68.4 Mg ha⁻¹.

The yield of rye grass grown on the Inanda soil treated with fly ash showed an increase as the application rate increased reaching a maximum at the highest application rate (Figure 4.4). Fly ash, its application rate and their interaction all had a significant effect on the yield on the Inanda soil ($p < 0.05$).

The yield with Calmasil showed a linear increase with increasing application rate reaching a maximum at the highest application rate (Figure 4.4). The yield response of rye grass grown on the Inanda treated with fly ash and Calmasil showed a trend different from the Avalon soil. The yield of perennial rye grass was at the highest rate was significantly different from the lower rates. The increase in yield at the higher application rates shown by the treatments in the Inanda soil were possibly due to the fixation and transformation of potentially toxic elements by the clays and organic matter reducing their availability and toxicity possibly due to its likely higher buffering capacity (Table 3.1). Matsi and Keramidas (1999) demonstrated a similar trend for two acid agricultural soils (with organic C of 6.2 and 6.9 g kg⁻¹, and clay content of 15 and 26%) treated with fly ash showing an increase in application resulted in an increase in the yield of perennial rye grass.

The difference in the yield of rye grass in the treatments with the liming materials at equivalent rates indicates that the ameliorating effect on soil acidity is material specific. This is due to differences in chemical characteristics of the materials and their interaction with the acid soil. The general increase in the yield of rye grass with increasing application rate of fly ash and Calmasil to levels higher than with lime suggests that the increase in yield was not solely a result of the amelioration of soil acidity. Improved plant growth in the treatments with fly ash and Calmasil of both soils was possibly due to an increase in the supply of plant nutrients as they have a higher nutritional value (Chapter 2). The generally improved growth of perennial rye grass in both soils treated with fly ash is in accordance with results for maize (Plank *et al.*, 1975; McMurphy *et al.*, 1996; Schumann and Sumner, 1999), rice (Rautaray *et al.*, 2003; Mittra *et al.*, 2005), peanuts (Mittra *et al.*, 2005), perennial rye grass (Matsi and Keramidas, 1999) and tomatoes (Khan and Singh, 2001).

The improved growth and yield of rye grass on the treatments with Calmasil of both soils is in accordance with results for rice (Carvalho-Pupatto *et al.*, 2004; Gupta *et al.*,

2007), wheat (Bhat *et al.*, 2007), corn (Wang and Cia, 2006) and pasture grasses such as rye grass, cocksfoot and white clover (Pinto *et al.*, 1992; Rodriguez *et al.*, 1994; Lopez *et al.*, 1995). Introduction of Si to soil has shown to be beneficial to plant growth and development (Pereira *et al.*, 2004; Ma and Yamaji, 2006). Thus, the high concentrations of Si in fly ash and Calmasil (Figure 2.4) may have also played a role in improving the growth of rye grass in the treated acid soils.

A positive growth response is not necessarily indicative of a low toxicity threat posed by fly ash and Calmasil, as rye grass may accumulate trace elements without showing prevailing elemental toxicity effects. Though it was not investigated here the accumulation of potentially toxic elements (B, Ni, Pb, Co, Zn, Mn, Cr, Cu, Mo and Se) has been reported for barley (Sale *et al.*, 1996), maize (Clark *et al.*, 1999; Schumann and Sumner, 1999), and perennial rye grass (Matsi and Keramidias, 1999). The accumulation of potentially toxic elements can also be anticipated in plants grown on soils treated with Calmasil because of its origin.

4.4 Conclusions

Generally, the results obtained from the pot experiment are encouraging as the application of fly ash and Calmasil improved the growth of rye grass at the optimum rate and higher in comparison to lime in both soils. However, the application of fly ash at rates higher than 100% OLR possibly resulted in nutrient deficiencies and / or elemental toxicities (possibly B) during the early development and establishment of perennial rye grass. The soil type greatly influences the growth response of rye grass grown in acid soils amended with fly ash and Calmasil. Thus, very high application rates may result in plant growth constraints in soils with low buffering capacities. Also with such application rates of fly ash over time the amounts of potentially toxic elements may become significant, even though their short-term solubilities are low. The utilization of fly ash and Calmasil to ameliorate soil acidity is a feasible liming option for acid agricultural soils. However, the growth response of perennial rye grass to fly ash and Calmasil is not necessarily indicative of a low toxicity threat. There is a need therefore for the development of guidelines and standards for the utilization of fly ash and Calmasil on acid soil agricultural soil at high application rates.

5. General conclusions and recommendations

5.1 Conclusions

The main objectives of this investigation were to characterise fly ash and Calmasil as liming materials and to evaluate their effect on soil pH, EC, extractable Al, Mn, base cations (Ca, Mg, K and Na), extractable trace elements, and plant growth.

Characterisation of fly ash showed that it is an alkaline sandy loam (with 47% silt) material of low CCE (9.6%) with high EC. X-ray fluorescence and EDX analysis showed that the major elements (>3%) in fly ash are Si, Al, Fe and Ca. Scanning electron microscopy analysis of fly ash showed that it consists mainly of particles with an irregular shape showing minor cementation. Calmasil showed that it is an alkaline loamy sand material with a high CCE (97%) and EC. The XRF analysis of Calmasil showed that the major elements (>3%) were Ca, Si, Mg, Fe and Al. The morphology of Calmasil was comparable to fly ash showing notable cementation. The heavy metal content of fly ash and Calmasil were lower than the regulatory limits of DWAF (2006) and USEPA (1994) for the application of wastewater / biosolids for agricultural purposes. However, TCLP leachates of fly ash showed that the levels of As were above the limits recommended for landfilling waste.

Fly ash increased the pH of the Avalon and Inanda soils with increasing application rate. However, at the optimum liming rate (100% OLR) the pH was not raised to the desired range of between 5 and 8. Calmasil increased the pH of the Avalon and the Inanda soil with increasing application rate and at the 100% OLR soil pH was raised to the desired range only in the Avalon soil treatments. Generally, extractable Al decreased with amount added and time and was completely immobilised only in the Calmasil and lime treatments of the Avalon soil. Extractable Mn decreased with increasing application rate and time, and was completely immobilised in all the higher treatments by the termination of the incubation experiment. Generally, extractable base cations increased with increasing application rate so improving the fertility status of the soil.

Perennial rye grass grew in all the pots treated with fly ash, Calmasil and lime even at rates greater than the optimum liming rate. Fly ash and Calmasil improved the growth of perennial rye grass at the optimum liming rate and higher to levels greater than lime in both soils. Application of fly ash and Calmasil at higher rates in the Avalon with low organic carbon and clay may pose a phytotoxic threat. However, plant growth constraints posed by the phytotoxic threat of fly ash may not be realised under field conditions. The investigation has shown that liming the Avalon and Inanda soils with fly ash and Calmasil improved the growth of perennial rye grass. It has also affirmed that fly ash and Calmasil are suitable for application on land for agricultural purposes or otherwise as per DWAF (2006) and USEPA (1994) regulatory limits for the application of wastewater / biosolids for agricultural purposes.

This investigation has provided an insight into the effects of these materials under laboratory and glasshouse conditions and has shown some of the potential benefits and limitations. It has shown there is enormous potential in the utilisation of alkaline fly ash and processed stainless steel slag as liming materials for acid agricultural soils. However, further investigations must be performed to increase our understanding of the current findings especially under field conditions. This will allow for the delisting of the materials as hazardous waste and the developments of guidelines for their sustainable utilisation in agriculture.

5.2 Recommendations

This research was an initial investigation and various avenues exist for further extensive research. Long and short-term investigations on the neutralisation of acidity by fly ash and its weathering patterns may provide insights on its acid neutralising potential. These aspects can be examined by means of acid-base reactions, leaching tests and incubation studies under a variety of controlled conditions. Such investigations will aid in the development of suitable methods for the determination of the liming potential of fly ash and possibly stainless steel slag that take into account all the major acid neutralising compounds and minerals.

Generally, the soil pH of the treatments with fly ash increased, although the levels were lower than the desired range at the optimum liming rate possibly due to its low

solubility. A decrease in soil pH under field conditions due to agronomic practices may possibly result in an increase in the availability of trace elements with time. Hence, a trace element specific approach should be taken into consideration when assessing the availability and mobility of trace elements in fly ash and stainless steel slag treated soils, as some elements exist in various forms and states each with characteristic environmental impacts. The utilisation of fly ash and stainless steel slag in agriculture as liming agents must also take the effect of soil type and the long-term enrichment of trace elements in soil into consideration when recommending the materials, as liming is an ongoing process.

Perennial rye grass is a commonly used forage grass and the differences in the growth response of perennial rye grass to the traditional liming material showed that fly ash and stainless steel slag might have nutritional benefits. Similar extensive glasshouse and field investigations are proposed with cereal crops such as maize, wheat, barley and forage grasses. The accumulation of elements to determine their potential beneficial and toxic effect should also be taken into consideration.

A better understanding of the complex processes involved in acidification and amelioration strategies of fly ash and Calmasil requires long-term laboratory, glasshouse and field experiments that encompass all the highlighted recommendations. This will also allow the assessment of environmental risk and economic feasibility of their utilisation on acid agricultural soils. Their utilisation should also be explored in areas such as reclamation of mine lands, maintenance of sports fields and similar applications where aesthetic appearance of the landscape are important rather than their nutritional value for crops.

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Appendices

Appendix 2.1 DTPA, 1M NH_4NO_3 , 0.01M CaCl_2 extractable elements in fly ash, Calmasil and lime.

Table A 2.1 DTPA extractable elements of fly ash, Calmasil and lime.

Element (mg kg^{-1})		Fly ash	Calmasil	Lime
Major	P	0.41	0.01	0.09
	K	11.92	40	6.88
	Ca	ND	ND	ND
	Mg	17.32	nd	40
	Na	2.82	138	4.31
	S	233	102	3.82
Trace	Al	0.77	1.06	nd
	As	nd	nd	nd
	Cd	0.01	nd	nd
	Cr	1.76	1.02	nd
	Cu	0.31	0.22	nd
	Fe	15.1	2.81	nd
	Mo	0.86	0.48	nd
	Mn	0.98	nd	0.11
	Ni	0.17	0.12	nd
	Pb	0.03	0.04	0.01
	Se	0.28	0.03	0
	V	1.44	0.06	0.14
	Zn	nd	nd	nd

ND: not determined

nd: not detected

Table A 2.2 1M NH₄NO₃ extractable elements in fly ash, Calmasil and lime.

Element (mg kg⁻¹)		Fly ash	Calmasil	Lime
Major	P	0.41	0.01	0.09
	K	41	133	2.98
	Ca	4656	8918	686
	Mg	72.14	11.38	14.92
	Na	2.82	138	4.31
	S	233	102	3.82
Trace	Al	nd	nd	nd
	As	1.48	nd	nd
	Cd	nd	nd	nd
	Cr	0.82	2.58	nd
	Cu	0.29	0.67	nd
	Fe	nd	nd	nd
	Mo	1.42	1.1	nd
	Mn	5.49	nd	nd
	Ni	0.27	0.46	nd
	Pb	nd	nd	nd
	Se	0.37	0.08	nd
	V	1.61	0.77	0.11
	Zn	nd	nd	nd
ND: not determined				
nd: not detected				

Table A2.3 0.01M CaCl₂ extractable elements in fly ash, Calmasil and lime.

Element (mg kg ⁻¹)		Fly ash	Calmasil	Lime
Major	P	nd	nd	nd
	K	16.63	72.8	11.7
	Ca	ND	ND	ND
	Mg	nd	nd	62.9
	Na	3.97	685	7.03
	S	357	162	3.4
	Al	12.9	0.58	nd
	Fe	nd	nd	nd
Trace	As	0.2	0.21	0.19
	Cd	nd	nd	nd
	Cr	0.24	2.43	nd
	Cu	nd	nd	nd
	Mo	1.71	1.21	0.01
	Mn	nd	nd	nd
	Ni	nd	0.1	nd
	Pb	nd	nd	nd
	Se	0.6	0.12	0.03
	V	nd	0.05	0.19
	Zn	nd	nd	nd

ND: not determined
nd: not detected

Appendix 2.2 Correlation matrix for DTPA, 1M NH_4NO_3 , and 0.01M CaCl_2 estimated correlation coefficients using Persons two-tailed test for fly ash, Calmasil and lime.

Table B2.2.1 Correlation matrix for DTPA, 1M NH_4NO_3 , and 0.01M CaCl_2 estimated correlation coefficients using Persons two-tailed test for fly ash.

		DTPA	1M NH_4NO_3	0.01M CaCl_2
DTPA	Pearson Correlation	1	-.011	.996(**)
	Sig. (2-tailed)		.962	.000
	N	20	20	20
1M NH_4NO_3	Pearson Correlation	-.011	1	-.011
	Sig. (2-tailed)	.962		.963
	N	20	20	20
0.01M CaCl_2	Pearson Correlation	.996(**)	-.011	1
	Sig. (2-tailed)	.000	.963	
	N	20	20	20

** Correlation is significant at the 0.01 level (2-tailed).

Table B2.2.2 Correlation matrix for DTPA, 1M NH_4NO_3 , and 0.01M CaCl_2 estimated correlation coefficients using Persons two-tailed test for Calmasil.

		DTPA	1M NH_4NO_3	0.01M CaCl_2
DTPA	Pearson Correlation	1	-.074	.906(**)
	Sig. (2-tailed)		.762	.000
	N	19	19	19
1M NH_4NO_3	Pearson Correlation	-.074	1	-.057
	Sig. (2-tailed)	.762		.817
	N	19	19	19
0.01M CaCl_2	Pearson Correlation	.906(**)	-.057	1
	Sig. (2-tailed)	.000	.817	
	N	19	19	19

** Correlation is significant at the 0.01 level (2-tailed).

Table B2.2.3 Correlation matrix for DTPA, 1M NH₄NO₃, and 0.01M CaCl₂ estimated correlation coefficients using Persons two-tailed test for lime.

		DTPA	1M NH ₄ NO ₃	0.01M CaCl ₂
DTPA	Pearson Correlation	1	-.055	.999(**)
	Sig. (2-tailed)		.824	.000
	N	19	19	19
1M NH ₄ NO ₃	Pearson Correlation	-.055	1	-.053
	Sig. (2-tailed)	.824		.828
	N	19	19	19
0.01M CaCl ₂	Pearson Correlation	.999(**)	-.053	1
	Sig. (2-tailed)	.000	.828	
	N	19	19	19

** Correlation is significant at the 0.01 level (2-tailed).

Appendix 2.3 Correlation matrix for TCLP, SPLP, and ART estimated correlation coefficients using Persons two-tailed test for fly ash, Calmasil and lime.

Table C2.3.1 Correlation matrix for TCLP, SPLP, and ART estimated correlation coefficients using Persons two-tailed test for fly ash.

		TCLP	SPLP	ART
TCLP	Pearson Correlation	1	.051	.970
	Sig. (2-tailed)		.905	.000***
	N	8	8	8
SPLP	Pearson Correlation	.051	1	.070
	Sig. (2-tailed)	.905		.869
	N	8	8	8
ART	Pearson Correlation	.970	.070	1
	Sig. (2-tailed)	.000***	.869	
	N	8	8	8

*** Statistical significance at 1% probability level (2 tailed).

Table C2.3.2 Correlation matrix for the TCLP, SPLP, and ART estimated correlation coefficients using Persons two-tailed test for Calmasil.

		TCLP	SPLP	ART
TCLP	Pearson Correlation	1	.991(**)	.993(**)
	Sig. (2-tailed)		.000	.000
	N	8	8	8
SPLP	Pearson Correlation	.991(**)	1	.978
	Sig. (2-tailed)	.000		.000
	N	8	8	8
ART	Pearson Correlation	.993(**)	.978	1
	Sig. (2-tailed)	.000	.000	
	N	8	8	8

*** Statistical significance at 1% probability level (2-tailed).

Table C2.3.3 Correlation matrix of the TCLP, SPLP, and ART estimated correlation coefficients using Persons two-tailed test for lime.

		TCLP	SPLP	ART
TCLP	Pearson Correlation	1	-.068	.978
	Sig. (2-tailed)		.874	.000***
	N	8	8	8
SPLP	Pearson Correlation	-.068	1	.110
	Sig. (2-tailed)	.874		.796
	N	8	8	8
ART	Pearson Correlation	.978	.110	1
	Sig. (2-tailed)	.000***	.796	
	N	8	8	8

*** Statistical significance at 1% probability level (2-tailed).

[illegible]

Table A3.2 1M NH₄NO₃ extractable trace elements (mg kg⁻¹).

	Control	Fly ash		Calmasil		Lime	
Rate (Mg ha ⁻¹)	0	11.7	46.8	1.16	4.64	1.47	5.88
As							
Day 0	nd	nd	nd	nd	nd	nd	nd
Day 112	nd	nd	nd	nd	nd	nd	nd
Cd							
Day 0	nd	nd	nd	nd	nd	nd	nd
Day 112	nd	nd	nd	nd	nd	nd	nd
Cr							
Day 0	nd	<0.01	0.01	nd	<0.01	<0.01	nd
Day 112	<0.01	<0.01	nd	nd	nd	nd	nd
Mo							
Day 0	nd	<0.01	nd	nd	<0.01	nd	nd
Day 112	nd	nd	nd	nd	<0.01	nd	<0.01
Ni							
Day 0	0	<0.01	0.01	nd	nd	nd	nd
Day 112	0.03	0.03	nd	nd	nd	nd	nd
Pb							
Day 0	nd	nd	nd	nd	nd	nd	nd
Day 112	nd	nd	nd	nd	nd	nd	nd
Se							
Day 0	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.02
Day 112	nd	nd	nd	nd	nd	nd	nd
V							
Day 0	nd	0.03	0.07	0.09	0.19	0.03	0.09
Day 112	nd	0.02	0.13	0.16	0.25	0.10	0.21

nd: not detected

Table A3.2.1 DTPA extractable trace elements (mg kg⁻¹).

	Control	Fly ash		Calmasil		Lime	
Rate (Mg ha ⁻¹)	0	136	544	1.16	4.64	17.1	68.4
As							
Day 0	nd	3.11	0.33	nd	0.47	3.78	nd
Day 112	1.09	0.27	nd	4.02	1.37	nd	nd
Cd							
Day 0	nd	nd	nd	nd	nd	nd	nd
Day 112	nd	nd	nd	nd	nd	nd	nd
Cr							
Day 0	1.29	2.27	6.35	2.87	6.23	0.16	0.53
Day 112	3.13	2.11	1.34	2.62	4.17	1.81	2.06
Mo							
Day 0	nd	nd	10	nd	nd	10.2	nd
Day 112	nd	nd	nd	nd	nd	nd	nd
Ni							
Day 0	11.3	15.4	16.3	11.2	11.3	4.59	6.66
Day 112	22.5	25.1	17.7	30.3	26.1	19.5	14.2
Pb							
Day 0	130	138	112	123	113	87.4	108
Day 112	119	141	85.6	161	72.2	146	120
Se							
Day 0	nd	nd	nd	nd	nd	0.27	nd
Day 112	nd	nd	nd	nd	nd	nd	nd
V							
Day 0	2	10.1	11.2	1.83	4.59	1.33	0.43
Day 112	4.4	5.05	4.28	3.21	3.18	2.28	2.4

Table A3.2.2 M NH₄NO₃ extractable trace elements (mg kg⁻¹).

[illegible]

[illegible]

Appendix 4. ANOVA tables for yield of perennial rye grass grown in the Avalon and Inanda soils treated at rates of 0, 50, 100, 200 and 400% of the optimum liming rate (OLR) with fly ash, Calmasil and lime.

Table A4.1 ANOVA tables for yield of perennial rye grass grown on the Avalon soil treated at rates of 0, 50, 100, 200 and 400% of the optimum liming rate (OLR) with equivalent rates of fly ash at 0, 68, 136, 272, and 544 Mg ha⁻¹; Calmasil at rates 0, 6.77, 13.54, 27.08 and 54.16 Mg ha⁻¹; and lime at rates of 0, 8.55, 17.1, 34.2 and 68.4 Mg ha⁻¹.

Source variation	d.f	SS	MS	VR	F probability
Treatment	2	2.05373	1.02687	14.44	<0.001
Rate	4	0.0732	0.0183	0.26	0.0903
Treatment.Rate	8	1.09857	0.13732	1.93	0.093
Residual	28	1.99178	0.07114		
Total	44	5.28416			
Coefficient of variation %	12.1				

Table A4.2. ANOVA table for yield of perennial rye grass grown on Inanda soil treated at rates of 0, 50, 100, 200 and 400% of the optimum liming rate (OLR) with equivalent rates of fly ash at 0, 68, 136, 272, and 544 Mg ha⁻¹; Calmasil at rates 0, 6.77, 13.54, 27.08 and 54.16 Mg ha⁻¹; and lime at rates of 0, 8.55, 17.1, 34.2 and 68.4 Mg ha⁻¹.

Source variation	d.f	SS	MS	VR	F Probability
Treatment	2	4.2373	2.11865	104.66	<0.001
Rate	4	1.061132	3.65283	180.45	<0.001
Treatment.Rate	8	1.29467	0.16183	7.99	<0.001
Residual	30	0.60728	0.02024		
Total	44	20.75057			
Coefficient of variation %	5.5				