THE AMENDMENT OF ACID SOIL WITH AN ETTRINGITIC WASTE AND ITS EFFECTS ON PLANT GROWTH

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PREFACE

The experimental work described in this thesis was carried out in the Department of Geological Sciences, University of Cape Town, from August 1994 to December 1994, under the supervision of Dr Martin Fey and Associate Professor James Willis.

These studies represent original work by the author and have not been submitted for degree purposes to another university. Where use has been made of the work of others, it has been duly acknowledged in the text.

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ABSTRACT

Associated with ESKOM's ash water beneficiation programme is the precipitation of an ettringitic waste from highly alkaline, saline water. The waste is dominated by ettringite ($Ca_{12}Al_4(OH)_{24}(SO_4)_6.52H_2O$) with calcite ($CaCO_3$) as a minor phase (17.7% for the sample used in this study). Apart from the presence of calcite, the ettringite itself is alkaline due to the presence of OH ions. Following a submission that the waste had potential as an ameliorant of acid soil, research into this possibility was initiated.

Following the determination of a calcium carbonate equivalent (HCl-CCE) value of 78% using the HCl back titration method of Horwitz (1980), an incubation experiment was initiated using three acid soils of contrasting characteristics: a so-called Silvermine sand, Kranskop A and Kranskop B soils. The effects on soil acidity of ettringitic waste were compared with analytical grade calcite. Soils (50g samples) were incubated with the two alkaline amendments for two weeks, following which pH(KCl), pH(H_2O) and KCl-extractable acidity were determined. Ettringitic waste led to apparently lower levels of acidity neutralization for corresponding treatments set on an HCl-CCE basis. This difference was minimized with the highly buffered, sesquioxide and organic-rich Kranskop A soil which could be attributed to the greater reactivity of the ettringitic waste with organically-complexed acidity together with the "self-liming" effect of SO_4 in sesquioxide-rich soils (*sensu* Reeve & Sumner, 1972). The waste showed progressively less neutralization with Kranskop B and Silvermine soils apparently in response to a decline in buffering capacity of these soils.

CCE determined on the basis of incubation showed a variation (depending on soil type) of 37-63% or 45-64% based on extractable acidity and pH(KCl) respectively. It was shown that in terms of constituents of ettringitic waste, ettringite itself contributes to neutralization of soil acidity (54-66% of acidity; 61-78% of pH(KCl)), the reactivity increasing with soil buffering capacity.

A second component of the research involved a plant growth experiment under controlled, phytotron conditions using *Zea mays* L. (maize) as a bio-indicator. The aim was to demonstrate, by comparison with calcite and gypsum, the effect of ettringitic waste on parameters of soil chemistry and subsequently on nutrient availability. It was anticipated that ettringitic waste would exhibit an intermediate response between calcite and gypsum due to the presence of both OH and SO_4 ions. Silvermine sand was used as the growth medium due to its exceptionally low pH(KCl) of 3.50. The experiment consisted of a completely randomized 3 x 5 factorial design giving 45 combinations.

In comparison with calcite, ettringitic waste induced significantly less change in pH for corresponding treatment levels but this was not reflected in acidity *per se*, a phenomenon which could be attributed to the low acidity status of the soil. The excessive application of P was inferred to have induced certain anomalous soil chemical features, with decreases in K, NH_4, Cl and NO_3 being attributed to the possible precipitation of a crandallite-type mineral. MINTEQA2 speciation predicted supersaturation of the soil solution with hydroxyapatite indicated the thermodynamic feasibility for precipitation of this mineral. This provided a plausible explanation for the decrease in solution concentration of Ca in the case of calcite and ettringitic waste treatments. Enhanced CEC may have been an additional explanation for the observed trends for Ca together with the other major cations in respect of calcite treatments. Ettringitic waste, by virtue of the addition of other impurities resulted in less adsorption of Na, K, NH_4, Mg and Ca relative to calcite treatments, for a given pH. In contrast, the consistently observed trends for gypsum treatments were attributed to an increase in anion exchange capacity (AEC) which lead to an initial shift of PO_4, Cl and NO_3 to the exchangeable phase but suppressed this uptake at higher treatment levels, possibly due to displacement by high concentrations of SO_4. Cation concentrations increased with an decline in pH under gypsum applications probably in response to a similar shift in CEC.

Increases in plant dry mass with incremental additions of calcite and ettringitic waste were paralleled by similar trends in plant height, with dry mass not being significantly different for corresponding treatment levels of these amendments. Although yield responses to nutritional or toxic effects of the amendments were difficult to interpret, a major parameter influencing plant growth may have been a nutrient imbalance due to excessive P. Visual symptoms associated with lower yields included chlorosis and interveinal chlorosis which might have been attributable to Cu deficiency while necrotic symptoms may have reflected B toxicity. Plants grown at the highest level of ettringitic waste exhibited no deficiency or toxicity symptoms, with the implication that available metal concentrations of this product were not excessively high.

In addition to nutrient supply at suitable levels for maize, the ettringitic waste exhibits a CCE close to that of a range of other liming materials studied by Engelbrecht (1983), and its use as agricultural lime would provide a productive means of disposal.

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INTRODUCTION

Waste by-products generated by industrial processes in many cases require disposal in suitable containments in order to prevent environmental pollution. In some instances, however, such products may be used for more productive purposes. The disposal of liquid effluents in land treatment systems for the enhancement of primary productivity is a typical case in point and is central to the present investigation.

Associated with ESKOM's coal power plant operations is the transportation of pulverized ash to adjacent ash dams in the form of a slurry. While recycling of water is an integral part of this system of waste ash disposal, the generation of a positive water balance associated primarily with excessive precipitation, necessitates the improvement of water quality prior to being returned to the natural environment. As a result of saturation with calcium hydroxide and calcium sulphate, ash water is exceptionally alkaline and saline. Beneficiation of disposable water is accordingly required in order to comply with legal requirements regarding entry of industrial effluents into natural waters. The addition of calcium aluminate facilitates the precipitation of an "ettringitic" waste, so named because of its principal constituent, ettringite ($Ca_{12}Al_4(OH)_{24}(SO_4)_6.52H_2O$). The only other phase present is calcite ($CaCO_3$) which occurs as a minor constituent. The result of this process is a reduction in pH and salinity of the water, to a more acceptable level for environmental disposal.

It was initially anticipated that the waste product would be disposed of on ash dams. However, a more productive means of disposal was subsequently proposed by Fey during 1993. It was submitted that the product exhibited potential for use as a liming amendment of acid soil due to its observed intense reactivity with strong acid. The presence of calcite (a recognized liming agent) combined with the occurrence of Ca and OH ions (which are recognized constituents involved in acid soil neutralization) in the ettringite mineral, were viewed as potential ameliorants of soil acidity. Furthermore, due to the "self-liming" effect of SO_4 ions in sesquioxide-rich subsoil horizons (*sensu* Reeve & Sumner 1972), the presence of this ion was viewed as being of additional relevance. Based on these premises and following a proposal for research into the use of the ettringitic waste as a potential liming agent, the current project was initiated.

The objectives of the present investigation were consequently as follows:

(a) to compare the liming potential of the ettringitic waste with respect to calcium carbonate using three soils of contrasting characteristics;

(b) to investigate, by comparison with calcite ($CaCO_3$) and gypsum ($CaSO_4.2H_2O$), the effect of the ettringitic waste on soil properties;

(c) to assess by comparison with $CaCO_3$, the effects of the waste on plant growth by virtue of its neutralization of soil acidity and induced pH change;

(d) to differentiate by comparison with $CaSO_4.2H_2O$, the effects of the waste on plant growth due to a liming effect from those due to nutrient addition.

CHAPTER 1

A LITERATURE REVIEW OF THE NATURE AND CONSEQUENCES FOR PLANT GROWTH OF SOIL ACIDITY AND ITS ALLEVIATION BY SOIL AMENDMENTS

1.1 The nature of soil acidity

The pH is the most widely used criterion to judge the degree of soil acidity, with the pH of soils ordinarily ranging from around 4 to 7 (Thomas & Hargrove, 1984), although serious problems associated with soil acidity are seldom encountered above a pH value of 5.5 (Sumner *et al.*, 1991). While values above pH 7 would indicate alkalinity, appreciable amounts of soil acidity may exist above this value (Thomas & Hargrove, 1984). The use of soil pH as an acidity index should accordingly be regarded as more empirical than otherwise.

It is well established that acid soils behave as though they have two components of acidity. Exchangeable acidity is that portion of the soil acidity that can be replaced with a neutral, unbuffered salt such as KCl, $CaCl_2$, or NaCl. Unbuffered salts are used since buffered salts may lead to precipitation of Al ions as hydroxide. Exchangeable acidity in soils is due almost entirely to monomeric Al^{3+} ions but also includes exchangeable H ions which was first shown by Veitch (1904). The exact amount of exchangeable Al^{3+} is difficult to determine because it tends to increase with extraction volume (Kissel *et al.*, 1971). Furthermore, no neutral salt extraction gives very exact results for Al or H due to hydrolysis of Al^{3+} and subsequent dissolution of more Al^{3+} as the extraction proceeds.

Non-exchangeable acidity is determined from the total acidity by difference with exchangeable acidity. Total acidity can be measured by titrating a soil suspension up to a high pH (normally about pH 8), the amount of acidity in the soil being equivalent to the NaOH used (Rowell, 1988). Empirically, a pH of 8 to 9 appears to correspond to complete neutralization of adsorbed Fe and Al ions (Coleman & Thomas, 1964). The non-exchangeable acidity is in the form of protons which can be released from the surfaces as the pH rises, or as non-exchangeable Al. It has no direct effect on plant growth but has to be neutralised as the pH is raised (Rowell, 1988). There are three main sources of protons being derived from pH dependent hydrolytic reactions involving hydroxy-Al, organic matter, and hydrated oxides of Al and Fe (Coleman & Thomas, 1964).

As a result of Al or Fe oxide accumulation as surface coatings on clays, the proportion of exchangeable Al^{3+} to total acidity is reduced, as has been shown for montmorillonite (e.g. Coleman *et al.*, 1964). The exchangeable acidity as a proportion of the total acidity varies with the nature of the soil and the percent base saturation, being highest for montmorillonite, intermediate for dioctahedral vermiculites, and lowest for the kaolinite minerals.

In organic soils, it is apparent that much of the H ion concentration arises from the hydrolysis of Al^{3+} that is difficult to replace with KCl and indeed the proportion of exchangeable acidity is very low for reasons reviewed by Thomas and Hargrove (1984). First, most of the acidity is ionized only by raising the pH. Second, in acid soils much of the ionised CEC of organic matter is countered by Al, Fe, or both, which are not easy to exchange. These metals probably are present as hydroxy-metal-organic complexes that are difficult or impossible to replace.

In soils with practically no organic matter but containing large quantities of hydroxy-Al, similar results to organic matter are obtained with the production of the H ion through hydrolysis of non-replaceable hydroxy-Al (Kissel *et al.*, 1971).

1.2 Causes of soil acidity

A recent monograph on soil acidity by Fey *et al.* (1990), provides a useful perspective on acidification of the pedosphere. The phenomena which combine to render a soil acidic are complex and may appear in two distinct ways. The first involves a predominantly microbiological (and agriculturally accelerated) generation of nitric, sulphuric and carbonic acids within the pedosphere. A second results from atmospheric fallout of these acids and although this is a natural process it is intensified anthropogenically through the combustion of fossil fuels to produce acid rain. The relationships between these master variables are complex, however, and too detailed to be described concisely.

Acid soils are associated with areas of high rainfall but differences do arise in these areas due to chemical variation of parent materials (which may, for example, be impoverished in bases and/or facilitate leaching by virtue of a sandy texture), topographic position (bases are leached from higher areas and accumulate in low-lying areas) and vegetation (certain species remove bases at a more rapid rate, while different vegetation types vary in respect of their control of the soil-water balance). While these are the master variables, a complex interaction of numerous secondary factors is involved in the control of soil acidity.

Acidification only materializes with the removal of a soluble base by leaching or plant uptake. Such bases are removed from soil colloids by acidic anions, the most fundamental reaction being hydrolytic dissociation of bases, although similar reactions will occur with other acid anions such as HCO_3. In effect, acidification results as much from the availability of acid anions (HCO_3, NO_3 or SO_4) to accompany the removal of basic cations as it does from the availability of H ions (Reuss & Johnson, 1986).

While acidity is a natural feature of many landscapes, in many instances acidification is altered by human agencies. Apart from the soil acidification effects of increased CO_2, NO_x and SO_x levels in the atmosphere due to fossil fuel combustion and other industrial processes, the accelerated acidification of soils under agriculture is well known. Reasons for increased acidity under agriculture have been described by Fey *et al.* (1990) as an interaction of the following processes: enhanced aeration increases the oxidation rate of organic compounds with a net production of acid; oxidation of ammoniacal fertilizers which leads to the production of nitric and in some cases sulphuric acid; and, the removal of basic nutrients - Ca, K and Mg - in harvested crops.

1.3 Consequences of soil acidity for plant growth

1.3.1 *Soil acidity and nutrient status*

Nutrient toxicity and deficiency problems of acid soils have been reviewed by several authors for different regions. Two particularly valuable contributions are those for soils of the southern USA (Adams, 1984) and a more general treatment of the subject by Sumner *et al.* (1991). The latter authors have emphasised the effect of pH on solution activity of nutrient elements, providing a useful compilation of reactions and solution activities from data provided by Lindsay (1972, 1979).

While a nutrient may be soluble in the soil solution at levels sufficient for plant nutrition, it may nevertheless be unavailable due to the antagonistic effects of other elements which prevent it from being absorbed by roots. The levels of many of the essential and toxic elements in soils are determined by desorption from, or the solubilities of one or other solid phase, with changes in acidity causing marked shifts in the equilibria. For others, the soil solution concentrations are governed by organic transformations (Sumner *et al.*, 1991). It is accordingly for this reason that the status of various macro- and micronutrients will be considered with respect to soil pH in turn.

1.3.1.1 Nitrogen

Soil pH has long been recognised as affecting soil microbial activities related to N but significant inhibition of microbial activities probably only occurs in strongly acidic soils (pH < 5) since most microbial populations in soils are active over a rather wide pH range (Adams, 1984). Some of the current concepts of soil pH and nitrogen availability which have been summarized by Adams and Martin (1984) include the following: mineralization of organic nitrogen decreases below pH 6.0 to 6.5; nitrification rate is optimal at pH 6.6 to 8.0 and progressively decreases below this value becoming negligible below pH 4.5; optimum pH for denitrification by soil microbes is 7.0 to 7.5, the rate being much slower below pH 5.0; nitrogen fixation is highly pH dependent for some legume-*Rhizobium* associations.

1.3.1.2 Phosphorus

Much controversy has surrounded the availability of P with change in pH, with reports that the lowering of soil pH may increase, decrease or not affect P availability and uptake by plants (Sumner & Farina, 1986). In reviewing this topic, Sumner *et al.* (1991) have contended that this ambiguity could be attributed to the neglect of certain factors involved. Most published reports on solution P availability and uptake have provided a maximum P content between pH 5 and 6.5 (e.g. Juo & Uzu, 1977; Bolan & Hedley, 1990). However, some researchers (e.g. Muurmann & Peech, 1969; Krogstad, 1991) have reported a trend of opposite nature with total phosphate showing a minimum over this pH range, coinciding with the zone of minimum Al solubility. Sumner *et al.* (1991) have quoted Haynes (1984) as contending that this latter behaviour is probably a transient feature of acid soils with large amounts of soluble Al, which given sufficient time will lead to hydroxy-Al cation desorption and recrystallization to form gibbsite. These authors have accordingly concluded that P availability to plants is largely determined by equilibrium desorption/ solubility considerations.

1.3.1.3 Potassium

Adams (1984) has reported that for soils in the Southern US, an increase in pH leads to an important shift of solution K to the exchangeable phase due to an increase in pH dependent CEC. Similar results have been reported by Haynes and Ludecke (1981) in New Zealand and by Juo and Uzu (1977) for soils in Nigeria where acidity results in more K being in solution and less on exchange sites. The negative aspect associated with this low pH condition would be potential K loss through downward leaching.

1.3.1.4 Calcium and magnesium

Changes in solution and exchangeable Ca with pH show an increase in concentrations of these components (Haynes & Ludecke, 1981) which would be expected since all liming materials contain Ca and should result in increased availability of this nutrient in the soil solution. With regards to Mg, Juo and Uzu (1977) have shown an increase in solution concentration with a decrease in exchangeable content as pH decreases, due to a reduction in variable charge. This high solution concentration can lead to potential leaching loss while at the same time liming may induce Mg deficiency, probably due to adsorption on exchange sites or precipitation (Sumner *et al.*, 1978).

1.3.1.5 Sulphur

In an attempt to account for all the observations made regarding anion adsorption in soils, Chang and Thomas (1963) proposed a mechanism for sulphate adsorption whereby aluminium replacement or hydrolysis leads to the production of H ions. Simultaneously SO_4 replaces OH ions on Fe or Al hydroxide coatings, whereafter replaced OH ions react with H ions. It was further noted that sulphate adsorption is increased as pH is lowered because the replaced OH ions are more effectively neutralized. Adams and Rawajfih (1977) have provided an alternative explanation for uptake of sulphate in the solid phase at low pH being due to precipitation of Al and Fe sulphates. Elkins and Ensminger (1971) noted that increasing pH through liming resulted in increased sulphate in solution and enhanced uptake by plants. This was attributed to a sharp decline in retention of adsorbed sulphate at higher pH values due to surface charge becoming less positive. Such an increase in solution content is responsible for sulphate deficiency due to leaching, as reported by these authors for many portions of the southeastern USA.

1.3.1.6 Micronutrients

With regards to micronutrients and soil acidity, elements whose essentiality is not universal are not considered in the present contribution. Only those elements which are essential to plants, as listed by Sposito (1989), will be discussed.

Although soluble Cu is negatively correlated with pH (Sumner *et al.*, 1991) and liming to about pH 7 has been reported to reduce the availability of toxic levels of Cu (Spencer, 1966), this situation may only be serious under regimes of Cu application, due to the low availability of this element in strongly to moderately acidic soils (Sillanpoa, 1987).

Zinc activity rapidly increases with decreasing pH (Lindsay, 1972) although differential uptake has been reported even between cultivars of species (Clark, 1978). Liming has been shown to remove Zn from the available organic to unavailable hydrous metal oxide and crystalline sesquioxide forms (Tagwira *et al.*, 1992). In the case of metal oxides, this has been attributed to adsorption through the medium of polyvalent phosphate ions (Stanton, 1964).

Manganese availability is controlled by many factors, including soil Mn content, soil pH, redox potential, organic ligands and plant genetics. Manganese complex formation is usually favoured at high pH because more functional groups (e.g. COOH, OH) on organic ligands are ionized. On the other hand, low pH conditions and an abundance of electrons (reducing environment) will lead to solid Mn dissolution (Vega *et al.*, 1992). Tolerance to Mn will be dependent on plant species genetics although these authors have reported that even acid tolerant species such as cowpea are known to be sensitive.

Conditions of Fe deficiency in "Fe efficient" *Lupinus albus* are known to induce a greater concentration of H ions, reductants and chelating agents in the vicinity of its roots, with a resultant increase in extractable Fe (Gardner *et al.*, 1982). Römheld *et al.* (1982) have contended that an increase in reducing capacity of roots is an essential step in the enhanced uptake and transport of Fe under Fe deficient conditions. This capacity for increased reduction of Fe (III) is strongly promoted by a high H ion concentration at the reduction site on the outer surface of the plasmalemma.

Boron availability to plants is a function of both soil texture and pH with availability per unit of water soluble B increasing with the coarseness of soil texture (Wear & Patterson, 1962). Bester (1993) illustrated a similarity in adsorption-pH functions exhibited by three soils types. Adsorption was shown to decrease from approximately pH 2 to about pH 4.5 whereafter an increase occurred to a maximum between pH 8 and 9. A further decline in B has been shown to occur above this level (Bingham *et al.*, 1971). The availability of boron to plants and hence toxicity problems would accordingly be expected to follow the opposite trend with maxima coinciding with minimum adsorption.

In contrast to the aforementioned micronutrients, Mo deficiency symptoms occur under low pH conditions, due to the enhanced adsorption of this anionic nutrient with an increase in anion exchange capacity. Since Mo is required in the process of symbiotic nitrogen fixation as well as other physiological processes (Evans, 1956), adequate availability of this element for plant growth may be ensured by increasing soil pH provided that sufficient insoluble concentrations are present (Gammon *et al.*, 1954). This has been shown to increase nodule efficiency in legumes (e.g. Doerge *et al.*, 1985) as well as the Mo content in plant tissue (e.g. De Roton *et al.*, 1991).

1.3.2 *Toxicity problems in acid soils*

Soil acidity may induce the aforementioned toxicity or deficiencies of various nutrients (Mn being the most important with respect to toxicity) which appears to be due primarily to nutrient imbalance (Sumner *et al.*, 1991). In addition to these nutrients, other cations which are responsible for toxicity problems include hydrogen and aluminium. While aluminium can sometimes enhance plant growth (Foy *et al.*, 1978), toxicity of this element is probably the most important growth-limiting factor for plants in most strongly acid soils (Foy, 1984).

1.3.2.1 Hydrogen toxicity

In order to separate the direct effects of the H ion from the indirect effects associated with solubility and availability of various nutrients, emphasis has been placed on solution-culture experiments. Islam *et al.* (1980) have concluded that the two primary effects of H on growth include: (i) injury to roots such as suppression of lateral root development and leakiness of membranes and, (ii) decreased uptake of cations.

1.3.2.2 Aluminium toxicity

The effect of Al toxicity is largely manifested as a malformation as well as a malfunction of the root system, a syndrome which is exacerbated by Ca deficiency characterised by growth reductions of the meristematic tissue (Foy, 1984). Apart from the direct effects of low pH and its effect on deficiencies and toxicities of metal ions, this parameter does not provide a good indication of potential Al toxicity. Indeed the critical soil pH at which Al becomes soluble or exchangeable in toxic concentrations depends on many soil factors including the dominant clay minerals, organic matter levels, ionic concentration and the plant species or cultivar (Foy, 1984). The level of KCl-extractable Al is dependent on the most soluble phase present and on pH, but not necessarily on the magnitude of CEC or its supposed degree of saturation with Al, since background dissolution of solid phase Al occurs during extraction (Sumner *et al.*, 1991). Such extractable or soluble Al levels are further modified by the presence of solid phase, organic-Al complexes (Bloom *et al.*, 1979) and toxicity of a particular Al concentration is reduced considerably by organic compounds (Hue *et al.*, 1986). Based on considerations of solubility equilibria of sparingly soluble solids, Sumner *et al.* (1991) have contended that solubility of Al is enhanced by increased levels of ionic strength irrespective of whether pH is decreased or not, a condition which is intensified by water stress.

1.4 Amendment of acid soils with liming materials

1.4.1 *The process of soil acidity neutralization*

Liming is the addition to soil of any calcium or calcium- and magnesium-containing compound that is capable of reducing the activity of acid cations of the soil solution due to the presence of basic anions. Neutralization of acid cations ultimately results in their precipitation as $Al(OH)_3$ and $Fe(OH)_3$, followed by displacement on exchange sites with Ca and other basic cations (Tisdale *et al.*, 1985).

While the activity of liming materials is largely restricted to the plough layer in an agricultural context, the use of gypsum ($CaSO_4.2H_2O$) to ameliorate acidity in sesquioxide-rich subsoil horizons due to the mobility of the SO_4 ion is well established. Reeve & Sumner (1972) originally proposed a "self-liming" effect of gypsum to account for a reduction in exchangeable Al. In reviewing the literature, Shainberg *et al.* (1989) have listed the mechanisms underlying the "self-liming" reaction which include: (1) ligand exchange of SO_4 for OH ions on sesquioxide surfaces, (2) adsorption of acid cations in preference to Ca on sesquioxide surfaces which have been charged by specific adsorption of SO_4, and/or (3) a partial conversion of hydroxy Al minerals into a basic Al sulphate solid and $Ca(OH)_2$.

1.4.2 *Types and neutralising values of liming materials*

In considering the value of materials as liming agents, it is necessary to determine their ability to neutralize soils. Pure $CaCO_3$ is the standard against which other liming materials are measured with calcium carbonate equivalent (CCE) being defined as the acid neutralizing capacity of a liming material expressed as a weight percentage of $CaCO_3$ (Tisdale *et al.*, 1985).

In reviewing the literature, Barber (1984) recognised four categories of liming materials *viz.* agricultural limestone, marl, slag and miscellaneous materials. Limestone, the main liming material used, is usually a mixture of calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] which requires crushing to a sufficiently fine level in order to react readily with the soil. In contrast, the use of hydrated lime [$Ca(OH)_2$], burnt lime (CaO), marl (an unconsolidated powdery $CaCO_3$ deposit) and miscellaneous liming materials have apparently decreased in recent years. This is apparently due to the overall quantity of such materials being rather limited (Barber, 1984), although the respective neutralizing values of these materials are 136%, 179% and 70 to 90%.

Several types of materials are classed as slags, three of which are important agriculturally, consisting mainly of Ca or Mg aluminosilicates but with small amounts of other elements being present (Barber, 1984; Tisdale *et al.*, 1985). Blast-furnace slag is used mainly to neutralize soil acidity and supply Ca and Mg, with a CCE of 75 to 90%. Basic slag was in previous years generally applied because of its P content but because of its neutralizing value (CCE = 60 to 70%), it is also a good liming material. Openhearth slag is used mainly because of its high Mn content for Mn depleted soils in addition to its liming effect (Barber, 1984).

Other miscellaneous materials that are used as liming agents in localized areas include fly ash from coal-burning power generating plants, sludge from industrial water treatment plants, lime or flue dust from cement manufacturing, sugar lime, pulp mill lime, carbide lime, acetylene lime, packinghouse lime, shells etc. (Tisdale *et al.*, 1985).

1.4.3 *Ettringitic waste as a potential liming agent*

Many of the miscellaneous liming materials mentioned above are waste products of industrial processes. An additional industrial by-product which has the potential of being used as a liming agent, as mentioned in the introduction to this thesis, is an ettringitic waste produced by ESKOM's newly proposed water beneficiation programme.

The chemical conditions for the formation of this ettringitic waste are probably similar to those reported in numerous papers on cement research. The formation of ettringite by the hydration of tricalcium aluminate ($3CaO.Al_2O_3$) in the presence of $Ca(OH)_2$ and gypsum ($CaSO_4$) is well established (e.g. Van Aardt & Visser, 1968; Punzet & Ludwig, 1974; Akiba & Iwasaki, 1976; Bonin & Cariou, 1980). This formation has similarly been shown for calcium aluminate ($CaO.Al_2O_3$), whereby Ca and SO_4 liberated from $Ca(OH)_2$ and gypsum react to produce ettringite and simultaneously consume $Al(OH)_4^-$ eluted from $CaO.Al_2O_3$ (Tsuyuki & Kasai, 1982). In order to form ettringite, 2 moles of $Al(OH)_4^-$ are required against 3 moles of Ca^{2+}. The presence of $Ca(OH)_2$ has been shown to retard ettringite formation in the presence of tricalcium aluminate (Akiba & Iwasaki, 1976; Bonin & Cariou, 1980) while in the case of other calcium aluminates, $Ca(OH)_2$ is involved in the reaction as a reagent, inducing an increase in the kinetics (Bonin & Cariou, 1980).

As aforementioned, ettringitic waste produced from alkaline ash waters contains a major mineral phase in the form of ettringite ($Ca_{12}Al_4(OH)_{24}(SO_4)_6.52H_2O$) with an additional minor quantity of calcite. The presence of calcite in the ettringitic waste may partially be explained by the presence of CO_2 which leads to decomposition of ettringite (Jambar & Zivica, 1985; Nishikawa *et al.*, 1992). However, ettringitic waste precipitated from acid mine drainage is unlikely to contain calcite due to low pH conditions unfavourable for the formation of this mineral.

Apart from the presence of $CaCO_3$, the use of this waste as a liming material exhibits further potential due to the presence of constituent OH and SO_4 ions in ettringite, as mentioned in the introduction to this thesis. Should the liming potential of this product be realized in practice, it would provide a marketable commodity while simultaneously eliminating a potential waste product. It is accordingly the subject of the present thesis to assess the consequences of this ettringitic waste product for soil acidity and plant growth.

CHAPTER 2

THE LIMING EFFECT OF ETTRINGITIC WASTE ON THREE SOILS

2.1 Introduction

A large number of liming materials are currently available in agriculture. While the majority of these are natural carbonates, industrial alkaline by-products have become increasingly available (Engelbrecht, 1983). As mentioned in the introduction to this thesis, it has been suggested that ettringitic waste may be a potentially useful ameliorant of acid soils for agricultural purposes. Apart from the presence of a minor phase of calcite which is a recognised liming material, the ettringite mineral itself shows potential for acid soil amendment.

By virtue of both the alleviating effect of Ca, which would rectify a Ca deficiency and/or lessen the severity of Al toxicity (Foy, 1984), and the neutralizing effect of OH, the ettringite mineral would aid in the liming of acid soils. The additional advantage of using a sulphate containing compound (i.e. ettringite) is the high mobility of the sulphate radical which would readily penetrate the subsoil and thereby potentially increase the depth of acid soil neutralization (Reeve and Sumner, 1972; Shainberg *et al.*, 1989).

The aim of this study was to assess, by means of an incubation experiment with three soils, the effects of the ettringitic waste on soil acidity. As calcite is the standard against which all potential liming materials are compared, it was expedient to compare the effects of both of these materials concurrently. This would permit an assessment of the calcium carbonate equivalent (CCE) of the waste product.

2.2 Materials and methods

2.2.1 *Soil characterization*

Due to variation in soil characteristics exhibited by different soil types, it was decided that for a representative study of liming potential, incubation of the ettringitic waste should be carried out with a variety of soils exhibiting contrasting attributes. To this end, three soils were selected: a Kranskop A horizon, which is rich in organic matter and sesquioxides in the clay fraction; a Kranskop B horizon which exhibits an abundance of clay minerals and sesquioxides; and an orthic A horizon from a sandy soil which has been colloquially named "Silvermine sand". As characterization of the Kranskop A and B horizons was not possible due to a shortage of soil sample, selected physical and chemical properties from the work of Smith and Fey (1994) have been tabulated in Table 1. The Silvermine sand which was sampled within the Silvermine Reserve on the Cape Peninsula, was obtained in sufficient quantity for characterization purposes, detailed results of which are provided in Appendix 1; selected properties are summarised in Table 1.

Particle size distribution was established by sedimentation and screening (Non-Affiliated Soil Analysis Working Committee, 1990). For the analysis of clay minerals, the clay fraction was isolated by dispersion in dilute Na_2CO_3 solution and repeated collection of the supernatant after settling of the $>2\mu m$ fraction. The clay was flocculated with NaCl, dialysed against distilled water and a $2cm^3$ aliquot of the suspension was pipetted onto a glass slide and allowed to dry at room temperature. The specimen was scanned through a range of 5° to $30°2\theta$ with a Philips PW 1390 X-ray diffractometer using Cu $K\alpha$ radiation; a diffractogram of the scan is provided in Appendix 2. Organic carbon content was determined by the Walkley-Black wet oxidation method (Non-Affiliated Soil Analysis Working Committee, 1990). Elemental composition was determined using wavelength-dispersive X-ray fluorescence spectroscopy with the following spectrometers and primary radiation tubes: (1) Siemens SRS-303AS, Rh tube for major elements, Mo, Nb, Zr, Y, Sr, U, Rb, Th and Pb; (2) Philips PW 1400, Au tube for Zn, Cu and Ni; and W tube for Co, Mn, Cr and V.

2.2.2 *Treatment levels and incubation conditions*

Analytical grade $CaCO_3$ was used in the present study while ettringitic waste was obtained from ESKOM in the form of a slurry and had been precipitated from alkaline ash water associated with waste ash at one of ESKOM's coal power plants. Chemical composition of the ettringitic waste sample as determined by X-ray fluorescence spectroscopy is provided in Appendix 3.

In assessing the effectiveness of a liming agent in terms of its ability to neutralize acids, reference is invariably made to calcium carbonate ($CaCO_3$) in order to establish the calcium carbonate equivalent (CCE). CCE is defined as the acid neutralizing capacity of an agricultural liming material expressed as a weight percentage of calcium carbonate (Tisdale *et al.*, 1985). While numerous techniques have been established, the HCl-CCE back titration method (Horwitz, 1980) has been reported to be a poor indicator of CCE due to large discrepancies between values determined with this technique relative to incubation results (Engelbrecht, 1983). For purposes of the present study, however, it was employed to establish an approximate neutralizing value for the ettringitic waste due to its rapidity. The use of a more reliable technique such as the NH_4Cl method (Engelbrecht, 1983) was not feasible due to a lack of suitable equipment.

To establish the levels of application to be employed in the subsequent experiment, the determination of a $CaCO_3$ versus pH curve was necessary. Based on typical lime application levels on acid soils, the amount of lime to be applied to a 50g sample of the Silvermine sand was determined as 0.2g. The following $CaCO_3$ levels, above and below this value, were selected for incubation with the sandy soil: 0.25, 0.05,

Table 1. Selected physical and chemical properties of the soils used for incubation with calcite and ettringitic waste

Soil texture *	Silvermine sand	Kranskop A	Kranskop B
Clay %	2.1	60	66
Silt %	13.6	32	30
Sand %	85.2	8	4
Clay fraction mineralogy *			
Kaolinite	-	60	74
Vermiculite	-	20	3
Gibbsite	-	20	14
Hematite	-	-	9
Quartz	100	-	-
Organic carbon % *	1.29	5.42	2.14
$pH(H_2O)$	4.72	5.80	5.92
pH(KCl)	3.50	4.37	4.27
KCl-extractable Ca ($mmol_c.kg^{-1}$) *	14.97	8.00	3.80
KCl-extractable Mg ($mmol_c.kg^{-1}$) *	8.00	10.2	6.66
KCl-extractable acidity ($mmol_c.kg^{-1}$)	6.00	18.0	20.0

* Data for Kranskop A and Kranskop B soils were obtained from Smith and Fey (1994).

0.1, 0.2 and 0.4g. Based on the pH(H_2O) change associated with the application of these levels of lime (Figure 1), and with due consideration to the negligible increase in pH associated with higher levels of lime, it was decided to adjust the levels of $CaCO_3$ to be used in subsequent incubation to the following values: 0.025, 0.05 and 0.1g. Based on the HCl-CCE value of 78%, the following equivalent levels of ettringitic waste were determined: 0.032, 0.064 and 0.128g. Due to the variation in speed of reactivity of different size fractions of lime (Engelbrecht, 1983; Tisdale *et al.*, 1985), both the ettringitic waste and calcite were ground to pass a 180μm sieve.

For the three soil types, 50g samples were taken for the incubation of individual levels of liming materials; samples had been passed through a 2mm sieve to standardize particle size for soil-lime reaction during incubation. Due to a shortage of sample, replication of different lime levels was not conducted with the Kranskop A and Kranskop B horizons. In contrast, two replicates were established for the Silvermine sand to assess

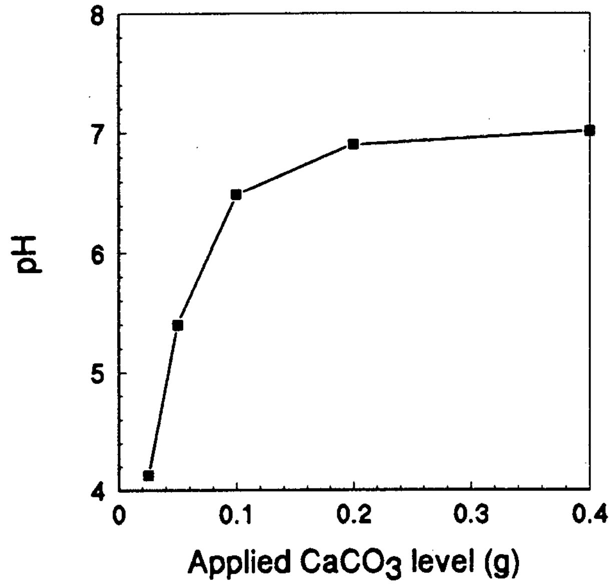

Figure 1. Liming curve showing the relationship between soil pH and $CaCO_3$ application in the Silvermine sand.

repeatability of results. Field moisture capacity (FMC) was established by bringing subsamples of soil to saturation point with a measured volume of water and halving this value. Soils were incubated in bottles at a constant temperature of 20.5°C, with FMC being maintained by addition of water to compensate for evaporative loss on a daily basis. Bottles were kept open during incubation to prevent CO_2 saturation of the atmosphere, which would in turn lead to suppression of the neutralization reaction. Incubation was conducted in a closed box to reduce light levels and prevent algal growth.

2.2.3 *Acidity determinations*

Based on minimal change in indices of acidity after a two week period of incubation as shown by Engelbrecht (1983) for a range of liming materials, an incubation period of two weeks was decided upon. At the culmination of this period, all three soils were analyzed for pH(H_2O), pH(KCl) and KCl-extractable acidity (Non-Affiliated Soil Analysis Working Committee, 1990). However, in contrast to the recommended method of mixing 10g dried soil with 25ml solution and allowing the suspension to stand for a period of time, 2.5g soil were mixed with 25ml solution. While the latter ratio was erroneously selected at the commencement of soil analysis, tests showed that little difference occurred between the two extraction ratios. Suspensions were subsequently shaken on a reciprocal shaker for four minutes, whereafter samples were centrifuged for 5 minutes at 6000rpm. Measurements of pH were made with a CRISON 2001 pH meter, by inserting the electrode in the supernatant solution. Samples suspended in KCl were filtered through Whatman no. 1 filter paper. Aliquots (10ml) of these extracts were subsequently titrated with 0.01M NaOH to a phenolphthalein end-point.

2.2.4 *Relative contributions of ettringite and calcite to neutralization of soil acidity*

To assess the relative contributions of calcite and ettringite in the ettringitic waste to changes in pH(KCl) and acidity, it was necessary to establish the proportions of these two components in the sample of waste product used in the present study. It was convenient to determine the amount of calcite using the so-called "Karbonat-bomb" apparatus following the procedure of Birch (1981). A calibration curve of applied $CaCO_3$ level versus pressure (KPa) (Figure 2) was generated by digesting 0.5 and 1.0g samples of calcite in concentrated HCl, while the corresponding manometer readings were

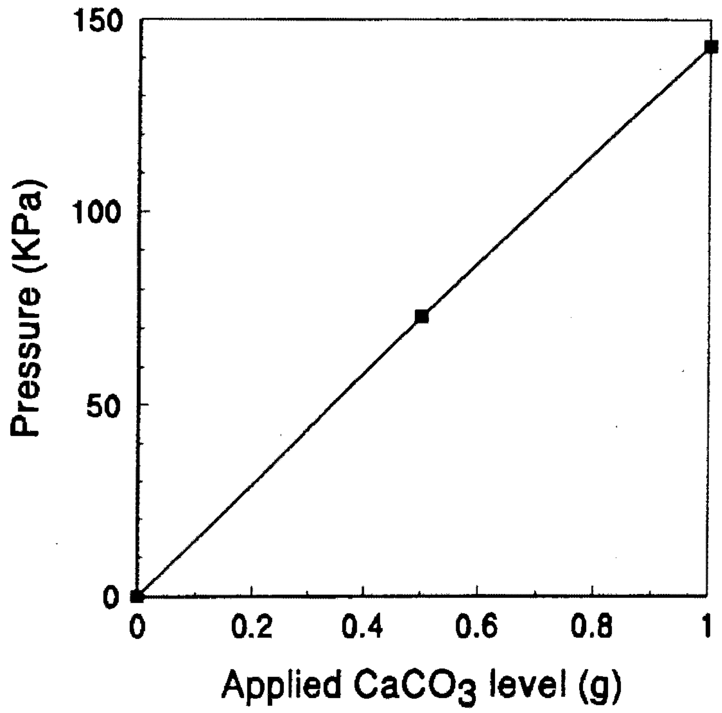

Figure 2. Karbonat bomb calibration-curve for the determination of calcite concentration in the ettringitic waste.

recorded. To obtain an accurate manometer reading for the ettringitic waste, it was necessary to digest a 5g sample in duplicate. Manometer readings were interpolated from the calibration curve to determine the mass% $CaCO_3$ contained within the waste product. The resultant value (17.7%) was used to determine the relative contribution to acidity neutralization of ettringite and calcite in the ettringitic material. An example of the procedure followed for this determination is provided in Figure 3. The second order polynomial equations describing the curves used to differentiate the contributions of these constituents to acidity neutralization are presented in Appendix 4.

Value (a), the mass of $CaCO_3$ contained within the 0.064g ettringitic waste application level, was used to determine its contribution to the neutralization of acidity, (b). Since point (d) represented the acidity corresponding to 0.064g of ettringitic waste, the respective contributions of calcite and ettringite to acidity neutralization were determined by the difference of (b) and (d)-(b) from the control treatment, (e), respectively. The acidities corresponding to calcite and ettringite were expressed as

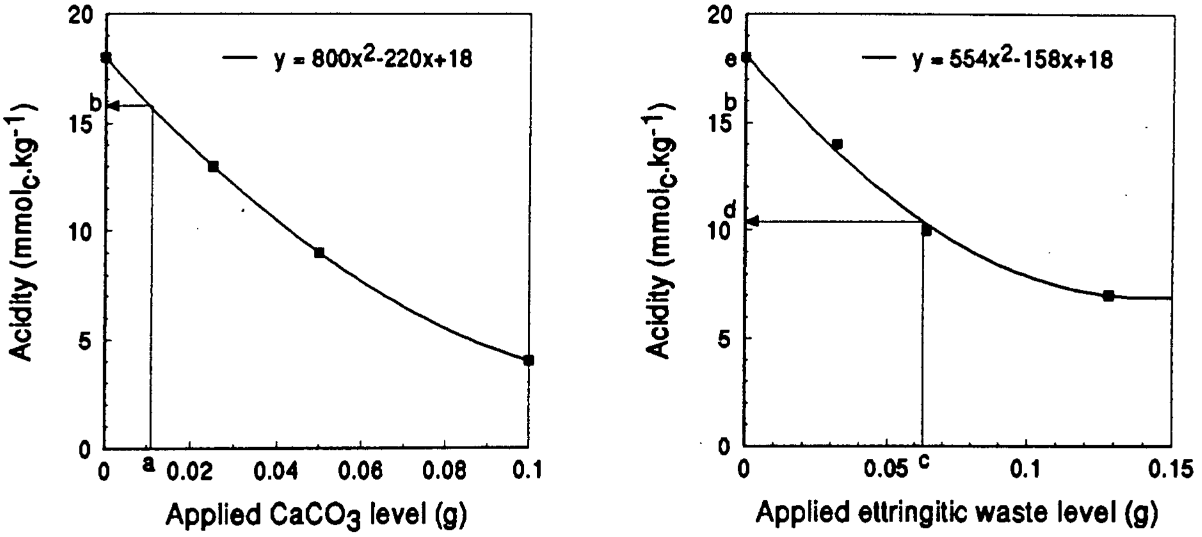

Figure 3. Acidity versus alkaline amendment level in the Kranskop A soil used to determine the relative contributions to acidity neutralization of calcite and ettringite within the ettringitic waste.

percentages of the acidity (d) to obtain the proportional contribution to acidity neutralization of these two constituents.

2.2.5 *Calcium carbonate equivalence of the ettringitic waste*

It would be expedient in evaluating the neutralization capacity of a new limingproduct to provide an accurate assessment of its CCE. By comparing changes in indices of acidity in the different soil types under investigation, the neutralizing capacity of the ettringitic waste in soils of markedly different characteristics could be assessed relative to $CaCO_3$. Apart from KCl-extractable acidity, the use of pH(KCl) was additionally chosen for this purpose, in preference to pH(H_2O) due to its more sensitive response to liming increments for the different soils.

For the sake of clarity, an example of the means of determining CCE is illustrated in Figure 4 which shows acidity as a function of amendment level in the Kranskop A soil. To determine CCE, the two liming agents had to be compared on a set mass basis for corresponding treatment levels. Hence where point (a) represented the lowest level of ettringitic waste (i.e. 0.032g), point (b) was the equivalent mass of the lowest calcite level

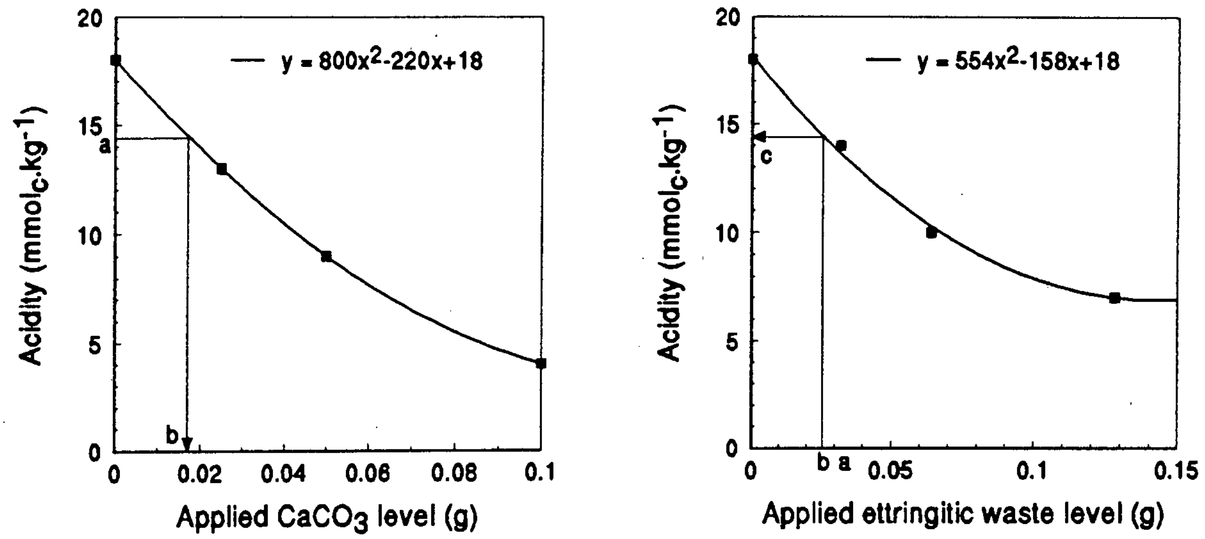

Figure 4. Contribution to acidity neutralization of incremental levels of calcite and ettringitic waste used to determine incubation-CCE.

(i.e. 0.025g). The contribution to acidity neutralization by a $CaCO_3$ equivalent mass of waste was found to be (c) by interpolation. Now to determine CCE, (c) was obtained from the $CaCO_3$ versus acidity curve to obtain a mass of $CaCO_3$ which would induce the observed acidity neutralization. CCE was determined by expressing (d) as a percentage of (e), the corresponding $CaCO_3$ application level to ettringitic waste level 0.032g. Equations used to determine CCE values are provided in Appendix 4.

2.3 Results and discussion

Incubation results for the change in pH(KCl), pH(H_2O) and KCl-extractable acidity with incremental addition of calcite and ettringitic waste are presented in Figures 5, 6 and 7, respectively. Original acidity data are provided in Appendix 5.

2.3.1 *Acidity changes in different soil types*

The much more substantial change in pH(H_2O) and pH(KCl) of the Silvermine sand (relative to the Kranskop soils) with incremental additions of liming materials, indicates that the former soil has a much lower buffering capacity. A less substantial decline in acidity of this unbuffered soil per incremental increase in lime level may

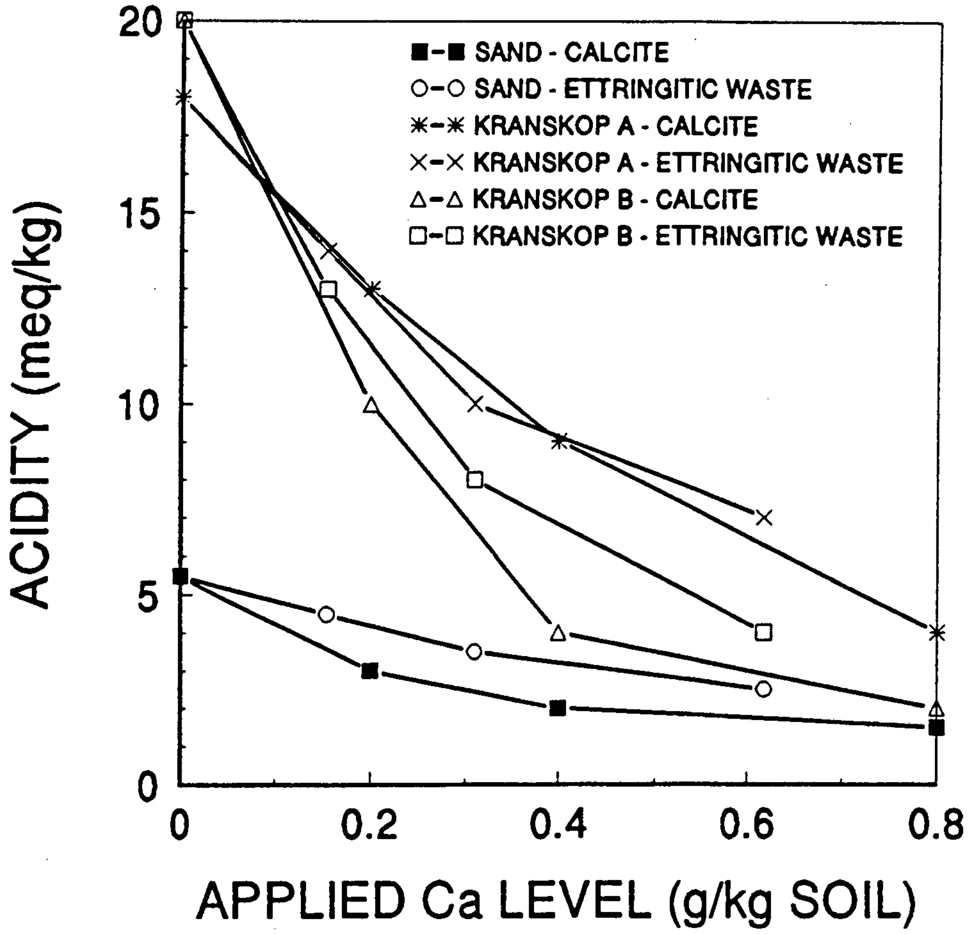

Figure 5. Change in KCl-extractable acidity as a function of increasing levels of soil amendments in contrasting soil types.

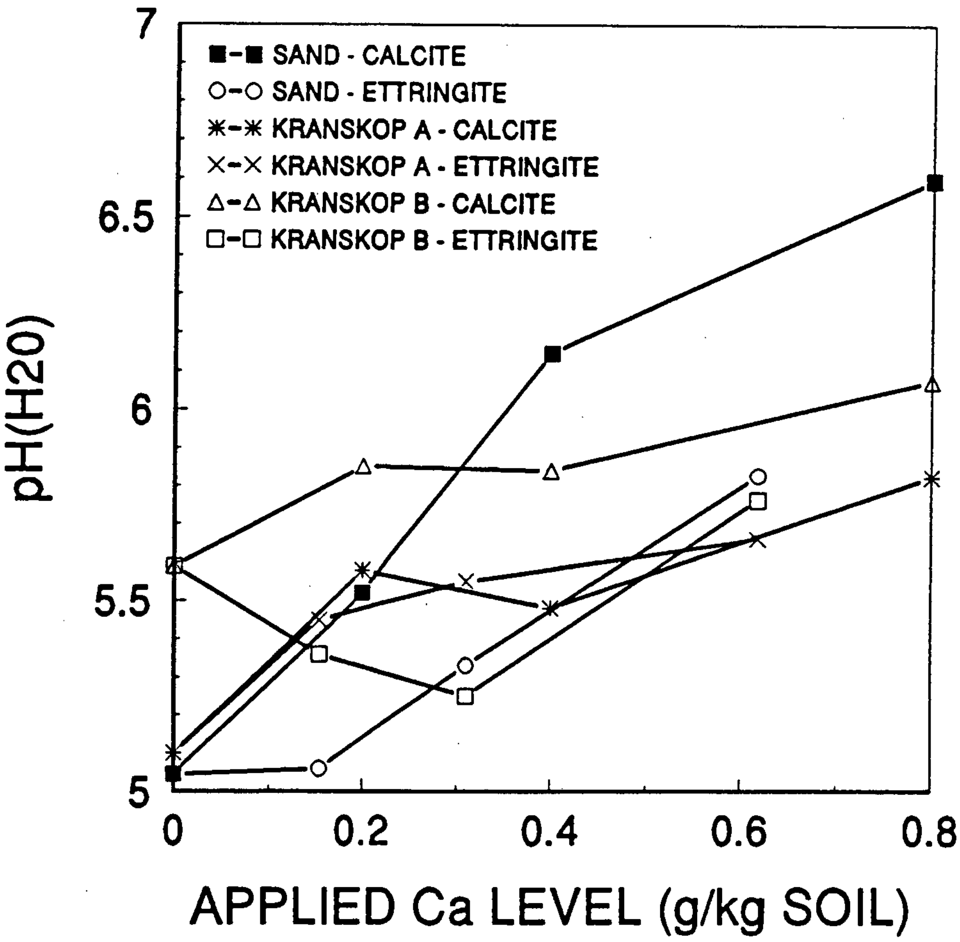

Figure 6. Change in pH(H_2O) as a function of increasing levels of soil amendments in contrasting soil types.

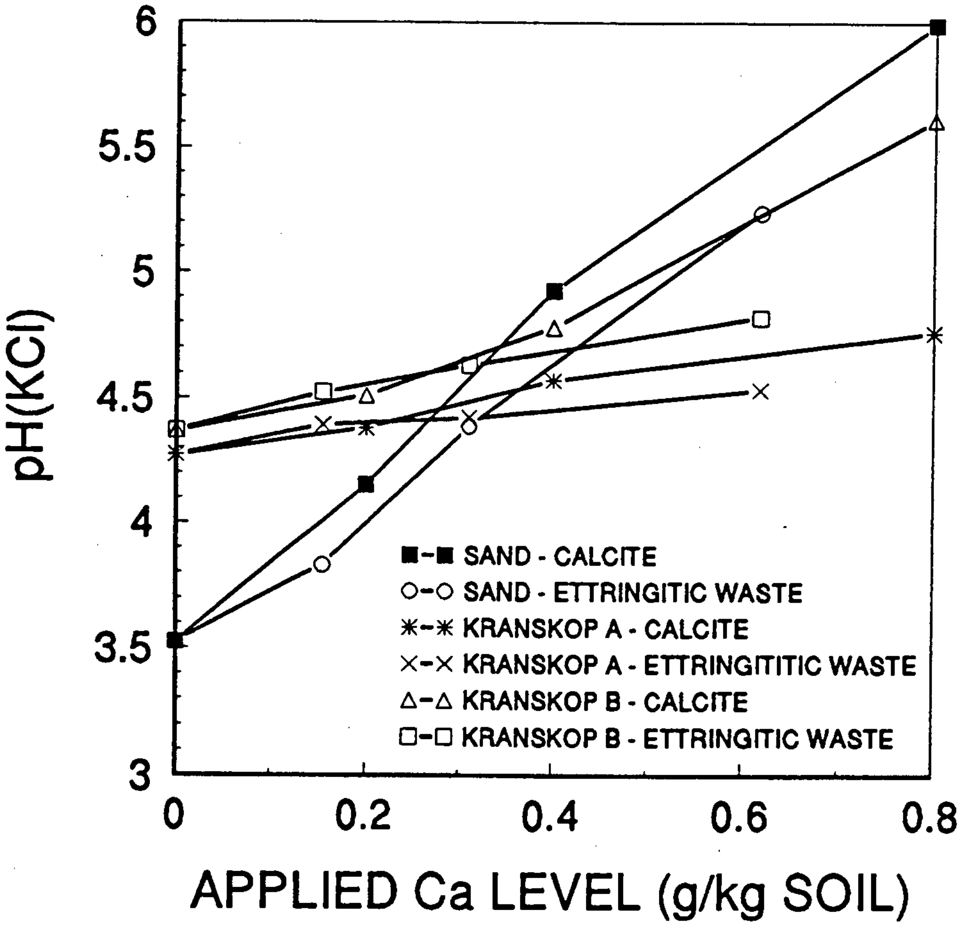

Figure 7. Change in pH(KCl) as a function of increasing levels of soil amendments in contrasting soil types.

possibly be attributable to a large proportion of acidity being in the non-exchangeable fraction, complexed by organic functional groups, as opposed to the KCl-extractable component (Rowell, 1988).

In assessing the different degrees of acidity change exhibited by the three soils, consideration should be given to soil properties (Table 1) especially with respect to the likely contribution to CEC by organic matter and different clay minerals. Since CEC is greatest for humic substances and represents the most important source of free protons, followed by hydrous oxides and 1:1 layer aluminosilicates (Sposito, 1989), it may be concluded that the Silvermine sand is poorly buffered due to both a low organic carbon percentage and a virtual absence of clay minerals and sesquioxides. Buffering capacity is correspondingly greater in the Kranskop B (rich in kaolinite and sesquioxides) and Kranskop A soils (rich in kaolinite, sesquioxides and organic matter).

2.3.2 *A comparison of liming potential of ettringitic waste relative to calcite*

Although it was not tested statistically because of insufficient replication, calcite generally results in superior neutralization of soil acidity mass for mass, than does the ettringitic waste (Figures 5 to 7). This may be attributable to the inappropriate CCE values determined for the latter with the HCl method of Horwitz (1980). However, the discrepancy in acid neutralization for the two materials apparently sequentially decreases for the Kranskop B and A soils, respectively. While the waste contains a certain amount of calcite, this is a minor component and the overall lower neutralization of the waste product may be attributed primarily to ettringite which is the product's only major phase present.

It is possible that in the sesquioxide-rich Kranskop A and B horizons, the contributions of the calcite impurity in the ettringitic product to changes in pH and exchangeable acidity may be greater than in the Silvermine sand, because of the higher buffer capacity of the former soils. In addition, it is probable that acidity changes are further induced by the presence of SO_4 ions from the ettringite. This is consistent with the "self-liming" reaction (Reeve & Sumner, 1972) of gypsum in sesquioxide-rich subsoils as has been discussed in Chapter 1 of this thesis. As possible confirmation of this line of thought, a more substantial contribution to neutralization of acidity was exhibited by the ettringitic waste in the sesquioxide-rich Kranskop A and B horizons, than in the

Silvermine sand. This could be inferred from the larger percentage ettringite contribution (or smaller calcite contribution) to changes in pH(KCl) and exchangeable acidity in the Kranskop soils compared with the Silvermine sand (Table 2).

These differences in the calcite and ettringite contributions to the change in indices of acidity between amendment levels may possibly be attributed to differences in the distribution of particle sizes of both the soil and liming materials. The rate at which the liming materials react is largely dependent on the surface area in contact with the soil. While soil particle size was standardized by screening through a 2mm sieve, the variation in particle size of this sieved fraction could contribute significantly to soil reactivity with liming agents. The effects of particle size of lime on reactivity is well established, with reports of as much as 70% of the variation in reactivity being due to particle size differences (Engelbrecht, 1983; Tisdale *et al.*, 1985). Indeed, Elphick (1955) concluded that particle size plays a greater role in limestone reactivity than type of

Table 2. Calculated contribution (%) of calcite and ettringite in the ettringitic waste to indices of soil acidity for different soil types.

Soil	Waste level(g/kg)	pH(KCl)		KCl-extractable acidity	
Silvermine sand		Ettringite	Calcite	Ettringite	Calcite
	0.64	54	46	72	28
	1.28	65	35	55	45
	2.56	64	36	34	66
	Average	61	39	54	46
Kranskop A					
	0.64	78	22	70	30
	1.28	59	41	70	30
	2.56	64	36	58	42
	Average	67	33	66	34
Kranskop B					
	0.64	84	16	63	37
	1.28	79	21	59	41
	2.56	71	29	43	57
	Average	78	22	55	45

material. While sieving of liming materials in the current investigation was made through a 180μm sieve, particle size variation within this fraction may have been substantial.

In accounting for smaller differences between the effects of calcite and ettringitic waste treatments in the Kranskop A compared with Kranskop B soil it could be argued that the higher buffer capacity of the former, due to its larger organic carbon content ensured a further degree of reaction by both liming materials during the period of incubation.

An assessment of the liming potential of a product would be incomplete without an accurate estimation of CCE. By incubating the ettringitic waste with different soil types, a more meaningful evaluation of neutralization value was gained (Table 3). It is apparent that in more buffered soils such as the Kranskop A and B, extractable acidity provides a more precise indication of CCE than does pH(KCl), while the reverse holds true for the Silvermine sand.

Table 3. Calcium carbonate equivalent (CCE) values (%) of ettringitic waste based on incubation in contrasting soil types.

Soil	Waste level (g/kg)	KCl-extractable acidity	pH(KCl)
Silvermine Sand			
	0.64	44	44
	1.28	36	44
	2.56	31	48
	Average	37	45
Kranskop A			
	0.64	64	56
	1.28	66	48
	2.56	59	41
	Average	63	48
Kranskop B			
	0.64	52	80
	1.28	52	64
	2.56	45	48
	Average	50	64

In respect of exchangeable acidity, the calculated CCE value ranged from 37% in the Silvermine soil to 63% in the highly buffered Kranskop A soil. The incubation CCE values of 39 liming materials in a highly buffered Wilgenhof soil assessed by Engelbrecht (1983), had an average value of 62.4% which falls close to that of the ettringitic waste obtained in the Kranskop A soil. It may be concluded that the optimal use of ettringitic material would be realized in highly buffered, sesquioxidic soils.

2.4 Conclusion

Based on CCE determinations established by means of the HCl back-titration method, discrepancies in acidity neutralization were obtained between the ettringitic waste and calcite following incubation in different soil types. This finding verifies the contention of Engelbrecht (1983) that this method provides a poor index of CCE. However, the discrepancy obtained between values of acidity parameters for calcite and ettringitic waste in different soil types becomes negligible in moving along the buffering capacity continuum from an unbuffered sandy soil (as in the Silvermine sand) to a highly buffered, organic-rich, sesquioxidic soil. It is contended that this may be attributed, firstly, to a greater reactivity of the ettringitic waste in soils which exhibit a larger component of non-exchangeable acidity in the form of organic matter. In addition, and possibly of equal significance, the "self-liming" effect of SO_4 ions in sesquioxide-rich soils will induce further neutralization of soil acidity. The latter point is substantiated by the elevated contribution of ettringite, a SO_4 containing mineral, to the change in acidity parameters in the Kranskop A and B soils.

The contributions of calcite and ettringite (as components of the ettringitic waste) to neutralization of soil acidity for given percentages of these components, provides baseline data upon which predictions acid neutralization in different soil types can be made with varying proportions of these minerals in the waste. Such prediction is important because the proportions of ettringite and calcite in the waste may vary, depending on the process by which the waste is generated.

Use of an incubation technique facilitated a more meaningful assessment of CCE than that provided by the HCl method. The variation in CCE values obtained using different amendment levels of the ettringitic waste may have been due to particle size variability of both the soils as well as liming materials employed. The presence of SO_4 ions may also have contributed to the variation in CCE values among different soil types, for a given particle size distribution and incubation period. The greatest reactivity of this waste was realized in the sesquioxidic, organic-rich Kranskop A horizon. In comparison with the average incubation CCE values obtained for a number of commercial liming materials by Engelbrecht (1983), the ettringitic waste provides a commensurate degree of acidity neutralization and therefore may be considered as having satisfactory properties for use as an alkaline amendment of acid soils.

CHAPTER 3

PLANT RESPONSES TO AN ACID SANDY SOIL AMENDED WITH DIFFERENT TREATMENT LEVELS OF ETTRINGITE, CALCITE AND GYPSUM

3.1 Introduction

The detrimental effects of acid soil infertility on plant growth, particularly those due to high levels of exchangeable aluminium and insufficient calcium, are well known (Foy, 1984). Moreover, the amelioration of aluminium toxicity problems by liming or application of gypsum (in respect of subsoil acidity) is well established (Tisdale *et al.*, 1984; Shainberg *et al.*, 1989).

Many soils contain sufficient quantities of most essential nutrients, but nutritional problems may arise due to desorption/ solubility/ organic transformation factors which affect availability (Sumner *et al.*, 1991). The principle governing the application of lime to induce improvements in soil fertility often involves the effect of changing pH on nutrient solubility.

The factors of acid soil infertility and consequent crop responses are complex, however, since not all soils which are acidic require lime, nor should all lime responsive soils be brought to the same pH (Frey *et al.*, 1984). Furthermore, management of acidic soils requires a consideration of both topsoil and subsoil horizons. While different strategies have been formulated to address this problem, the ameliorative effect of gypsum in acidic, sesquioxidic subsoil horizons, the explanation of which has been considered in Chapter 1, may have an important bearing on the present investigation due to the presence of SO_4 ions in the ettringite mineral.

While nutrients may be soluble in the soil solution at levels sufficient for plant growth, adsorption by plant roots may be affected by synergistic or antagonistic effects between elements. In providing an alternative perspective to soil acidity problems, Sumner *et al.* (1991) pointed out the importance of considering soil nutrient availability from the perspective of ion activities as opposed to concentrations, especially in respect of those nutrients for which the mobility is diffusion limited.

By means of a replicated pot experiment, the present study was aimed at investigating the effects of increasing levels of ettringitic waste on soil acidity parameters and nutrient status with concomitant effects on plant growth. Because the presence of Ca in ettringite is balanced by basic OH and acidic sulphate SO_4 ions, it was anticipated that the effects of the ettringitic waste on soil chemical properties and plant growth response would be intermediate between those of $Ca(OH)_2$ or $CaCO_3$, and $CaSO_4.2H_2O$. It was accordingly decided to compare this waste with both calcite and gypsum as a soil amendment.

3.2 Materials and methods

A variety of maize (*Zea mays* L.) exhibiting a high seed viability, PAN 6578, was used as a bio-indicator due to its rapid initial growth rate combined with familiar morphological features which would facilitate a qualitative comparison of plant responses to different treatments. For the purposes of the current experiment, the Silvermine sand, a detailed characterization of which was provided in Chapter 2, was employed as the growth medium due to its very low pH(KCl) of 3.50. Ettringitic waste was from the same sample used in the incubation experiment, while both calcite and gypsum were analytical grade reagents.

3.2.1 *Factorial treatment set*

A completely randomised factorial design was employed for the experiment which included five treatment levels, including a control of no treatment, for each soil amendment. The treatments were arranged in a 3 x 5 factorial design giving 45 combinations in total and which conformed to the requirements of sufficient degrees of freedom (Zar, 1974). Controls were provided for each soil amendment in order to assess the variability in plant growth associated with variation in environmental conditions. Treatment levels of calcite and ettringite were extrapolated from levels determined for a 50g sample in the incubation experiment (Chapter 2) to levels required for a 1200g pot mass. Gypsum quantities were determined on an equivalent Ca mass basis with those contained in the calcite treatment levels. The experimental layout is provided in Table 4.

Table 4. Experimental layout.

		mg/kg of soil
Calcite levels	0:	0.00
	1:	0.50
	2:	1.00
	3:	2.00
	4:	4.00
Ettringitic waste levels	0:	0.00
	1:	0.64
	2:	1.28
	3:	2.56
	4:	5.11
Gypsum levels	0:	0.00
	1:	0.86
	2:	1.72
	3:	3.43
	4:	6.87

3.2.2 *Growth environment*

Due to time constraints in the present investigation, the plant growth component was limited to a pot trial (as opposed to a field trial) under controlled phytotron conditions, the environmental parameters for which are specified in Table 5. The

Table 5. Phytotron environmental parameters.

Light regimes:	
Incandescent	06h00 - 08h00
	17h00 - 19h00
Metal halide and sodium	08h00 - 17h00
	08h00 - 09h00: gradual increase in intensity
	16h00 - 17h00: gradual decrease in intensity
Humidity:	47 - 68%
Temperature (sequence over 24h):	
18h00 - 08h00	20°C
08h00 - 09h00	gradual increase to 28°C
09h00 - 17h00	28°C
17h00 - 18h00	gradual decrease to 20°C

positioning of pots was varied rotationally to minimize any effects of environmental gradients within the growth chamber.

3.2.3 *Nutrient addition and soil treatments*

A sample of the Silvermine sand was screened through a 4mm sieve to remove organic debris and to standardise soil particle size range for subsequent soil-lime reaction. In order to supplement soil nutrient status for subsequent experimentation, a basal treatment of macro- and micronutrients was applied to the experimental soil. The following levels of macronutrients were applied per kilogram of soil following the scheme of Fey (1993, unpublished manual): 15mg Mg (as $MgSO_4.7H_2O$), 49mg K (as KCl) and 250mg N (as NH_4NO_3). The mass of soil required to bring a pot to full capacity was determined as 1200g. Since the experimental design included three replicates per treatment, 3600g (i.e. the amount of soil required for three pots) of soil was taken and the requisite amount for each treatment was added to the soil together with the following applications of micronutrients per kilogram of soil (Long Ashton nutrient solution, Hewitt, 1966): 1.5mg B (as H_3BO_3), 1.14mg Mn (as $MnSO_4.4H_2O$), 0.152mg Zn as ($ZnSO_4.7H_2$), 0.061mg Cu as ($CuSO_4.5H_2O$), 0.03mg Mo as $Na_2MoO.2H_2O$ and 18mg of Fe (as ferric sodium EDTA). The soil and additives were thoroughly blended before being divided into separate soil fractions for individual pots. Following potting of soil in plastic bags, 96mg of P (as H_3PO_4) was added to each pot and the bags were thoroughly shaken to ensure uniform mixing of applied phosphorus.

3.2.4 *Plant growth*

Eight seeds were sown per pot by planting at a depth of 1.5cm and covering with soil to ensure sufficient osmotic pressure for water uptake by the seeds. Prior to sowing, pots had been brought to field moisture capacity (FMC) by the addition of 185ml of water. Germination occurred about four days after planting and seedlings were thinned to four plants per pot after a further four days. Pots were maintained at FMC by daily addition of tap water and were systematically rotated to minimize the effects of variation in microclimate conditions such as temperature and light regimes. Symptoms of deficiency and toxicity were recorded during the course of growth.

While FMC may have represented a water level in excess of levels suitable for plant growth, it was nevertheless a practical water level due to a high evaporation rate from the Silvermine sand under hot conditions of the phytotron. Furthermore, while the use of tap water may have been unsuitable due to the introduction of dissolved solutes, tap water would probably have simulated water applied under field conditions more accurately and thereby be more representative of soil and plant responses under such conditions.

3.2.5 *Harvesting of plant material*

Harvesting was carried out after three and a half weeks by cutting at a height of 1 cm above soil level. Roots were removed from the soil and washed with water for subsequent qualitative comparison. Subsequent quantitative analysis of roots was not conducted due to both high costs of analysis and the difficulty of cleaning root material. Above-ground plant parts were dried to constant mass in a through-flow oven at 80°C, after which dry mass was recorded.

3.2.6 *Analytical methods*

Samples of oven-dried plant material were analyzed in the laboratories of the Elsenburg Agricultural Development Institute. Following milling of samples by means of a Falling Numbers mill, preweighed plant material was ashed at 480°C in porcelain crucibles overnight. Digestion of ashed samples was carried out by the addition of 5ml 1:1 HCl solution onto the grey ash in each crucible and then allowing to equilibrate for 30 minutes at 50°C. The mixture of HCl and ash was subsequently diluted by the addition of 35ml distilled water. Digested samples were analyzed for the following elements using a Beckman Spectrospan 5 multi-element Direct Coupled Plasma (DCP) spectrometer: P, Ca, Mg, Na, K, Mn, Cu, Zn, Fe and B.

Samples of soil which had been used for each treatment in the growth experiment were analyzed for the following parameters of acidity as outlined in Chapter 2: pH(H_2O), pH(KCl) and 1M KCl-extractable acidity. In addition, KCl extracts were submitted for the analysis of the basic cations, Ca and Mg, by means of atomic absorption spectroscopy (AAS) using a Spectra AA-30 Varian spectrometer. Concentrations of these elements were determined using N_2O/acetylene and air/acetylene flames, respectively. It was necessary to dilute samples by a factor of ten for the analysis of Ca, as this corresponded to the optimal range for Ca determination by virtue of Beer's law. The combination of extractable acidity and basic cations were summed to determine effective cation exchange capacity (ECEC), whereafter acid saturation was determined as: acidity x 100/ECEC.

In addition to the indices of acidity, extracts of saturated paste (Non-Affiliated Soil Analysis Working Committee, 1990) were prepared for two replicates of each treatment. Measurements of electrical conductivity of extracts were taken with a CRISON Micro CM 2201 meter for the determination of a dilution factor. Samples were diluted by a factor of 80 to reduce ionic concentrations into a range suitable for analysis (i.e. less than 100μS/cm) of the following major soil solution ions using a Dionex Suppressed Ion Chromatography system: Li, Ca, Mg, Na, K, NH_4, Cl, SO_4, NO_3, NO_2 and PO_4. Prior to analysis, samples were filtered through an On Guard P filter to remove particulates. Cations were analyzed using an Ionpac CS 12 column with methane-sulfonic acid as the eluent while anions were analyzed by means of an AS 4A column and a combined mmol conc. $Na_2CO_3/NaHCO_3$ eluent. Due to over-dilution combined with a poor calibration curve for PO_4, it was necessary to determine concentrations of this ion using the Murphy and Riley spectrophotometric method (Murphy & Riley, 1962). In addition, due to its significance as a toxic element to plant growth, aluminium was determined with undiluted samples of the saturated pastes using the Chrome Azurol S spectrophotometric technique (Kennedy & Powell, 1986). To assess the quality of data by charge balance, it was necessary to determine HCO_3 by titration of a 10 ml aliquot from each saturated paste with 0.005M HCl to a screened methyl orange end-point.

3.2.7 *MINTEQA2 speciation*

Ionic concentration data obtained for saturated paste extracts using the aforementioned techniques were used as input for the equilibrium speciation model, MINTEQA2 (Allison *et al.*, 1991), for the determination of single ion activities and saturation indices of pertinent solid phases.

3.3 Results and discussion

The role of pH in altering the activities of various plant nutrients in the soil solution has been emphasised (Chapter 1). It is accordingly the aim of this section to assess the effects of the ettringitic waste relative to calcite and gypsum on soil acidity parameters due to fertility problems associated with acid soils. In addition, consideration is given to the effects of these amendments on soil fertility and consequently the bioavailability of various plant nutrients. As a basis for comparison between soil amendments, the concentration of Ca in each amendment has been employed in assessing the effect on soil chemical properties and plant growth.

3.3.1 *Soil acidity*

In order to shed greater light on the effects of different soil amendments, it would be instructive to compare the Silvermine sand with other acidic forest soils. The data of du Toit (1993) for a range of forest soils from Natal are plotted in Figure 8, which shows that most soils conform to the expected trend of an inverse relationship between acid saturation and pH(KCl) as shown by Coleman *et al.* (1967). The occurrence of distinct outliers from this trend are conspicuous, however, and notably include the Silvermine sand as well as samples S2 and G1 from du Toit's (1993) investigation. Acid saturation of the Silvermine sand is anomalously low in relation to pH value and there was no clear explanation when soil properties were compared with the outliers in du Toit's (1993) collection.

Change in parameters of acidity as a function of different amendments are presented in Figure 9 (p 36), with the original data being provided in Appendix 6. While increases in pH(KCl) and pH(H_2O) or, conversely, decreases in acidity or acid saturation associated with the addition of calcite and ettringitic waste have been considered in Chapter 2, replication in this experiment has permitted a statistical analysis of results. Differences in these parameters occur between corresponding treatment levels of calcite and ettringitic waste. The pH difference is only marginal, however, when the treatments are compared on the basis of equivalent Ca application, which may be expected in view of the predominance of basic OH anions balancing Ca and Al ions in ettringite ($Ca_{12}Al_4(OH)_{24}(SO_4)_6.52H_2O$). No significant differences ($p<0.05$) in KCl-extractable acidity were observed between corresponding amendment levels of the two alkaline ameliorants, whereas the differences between gypsum and both the liming agents were significant at most treatment levels. Significant differences in acid saturation between amendment treatments were observed for only one treatment level.

3.3.2 *Soil nutrient status*

Changes in soil nutrient status as a function of the addition of different amendment levels are presented in Figures 10 (p 37) and 11 (p 38), the original data for which are provided in Appendices 7 and 8 for cations and anions, respectively. The quality of data obtained by different analytical techniques is assessed by means of charge balance calculations in Appendix 9. While reasonable agreement occurs between cations and anions for ettringitic waste and gypsum treatments, this does not hold true for calcite.

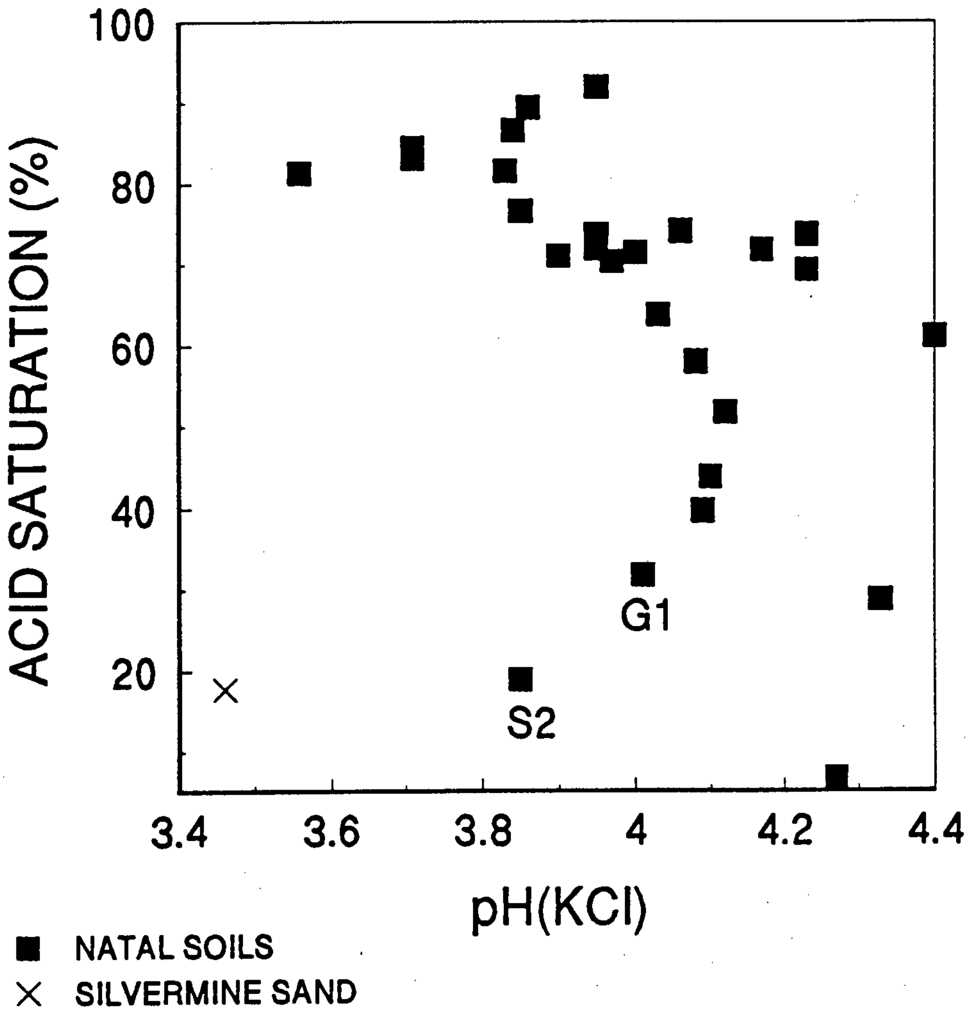

Figure 8. The relationship between pH(KCl) and acid saturation for different forest soils.

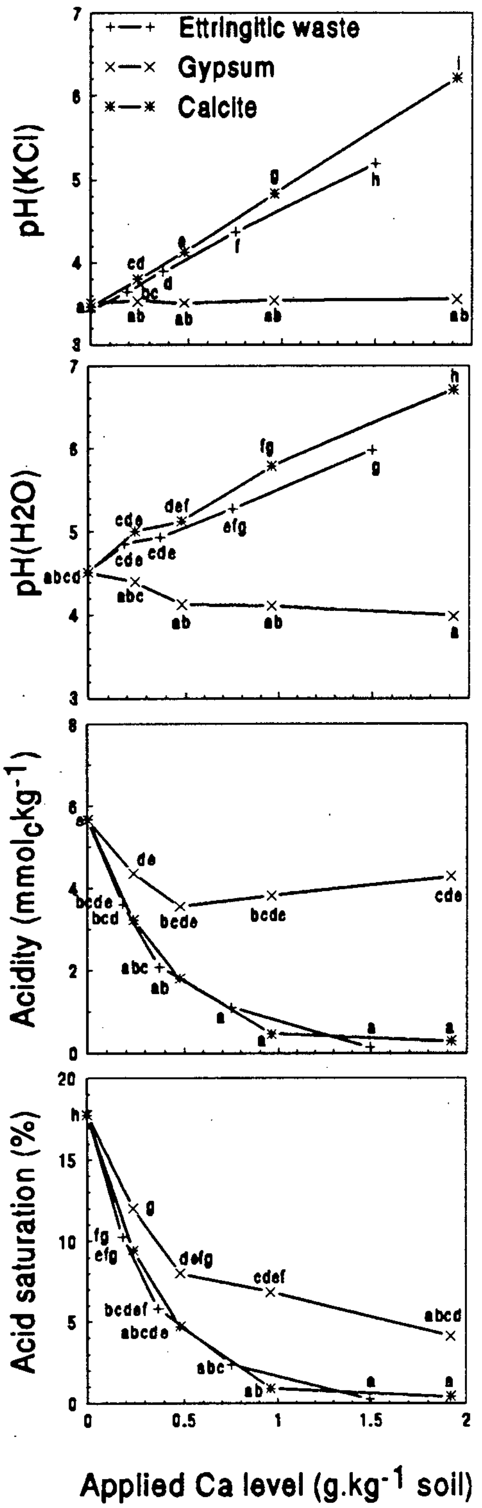

Figure 9. Change in acidity parameters of the Silvermine sand as a function of the application of Ca in different soil amendments. Alphabetic symbols indicate significant differences determined by a Tukey multiple range test at the 5% level. Letters held in common between treatments indicate a lack of significant difference.

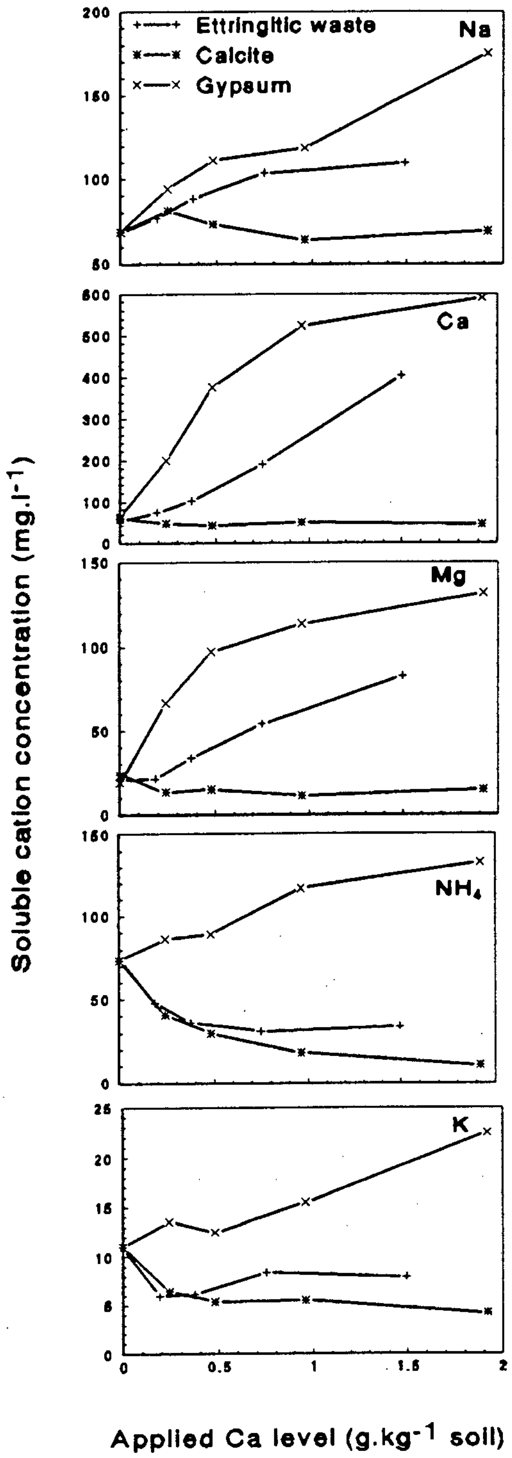

Figure 10. Change in solution concentration of major soil cations as a function of the application of Ca to 1200g Silvermine sand in the form of different amendments.

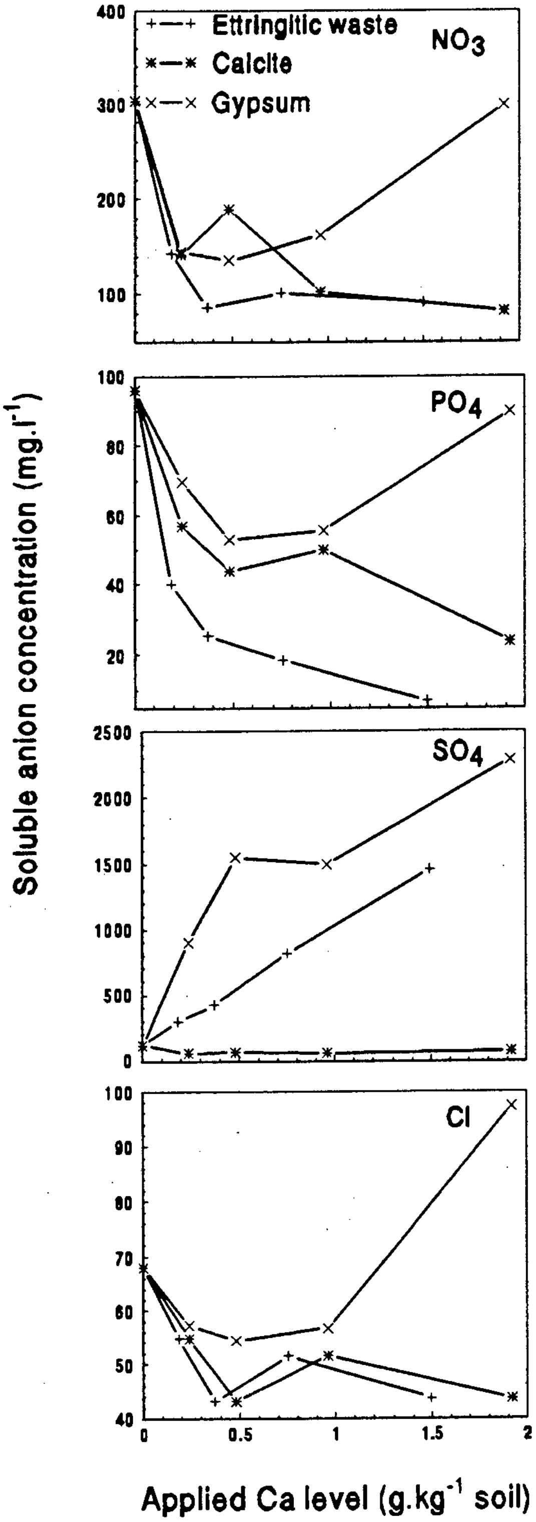

Figure 11. Change in solution concentration of major soil anions as a function of the application of Ca to 1200g of Silvermine sand in the form of different soil amendments.

Due to total charge being higher in the case of cations, it is believed that the discrepancy may be attributed to negatively charged dissolved organic matter.

3.3.2.1 Nitrogen

The effect of acidity on N availability operates largely in an indirect manner through its effect on soil microorganisms (Adams & Martin, 1984). Since ammonification is relatively insensitive to acidity over the pH range of most agricultural soils (Sumner *et al.*, 1991), whereas nitrification is markedly reduced below pH 6 and undetectable below pH 4.5 (Adams & Martin, 1984), it might be expected that the reduction in NH_4 concentration associated with a pH increase in the case of calcite and ettringitic waste (Table 6) would be matched by an equivalent increase in NO_3. The results for NH_4 (Figure 10, p 37) and NO_3 (Figure 11, p 38) are contrary to this expectation, however, and it may be argued that a reduction in the concentration of these nutrients has taken place in response to greater plant uptake with increased pH, in order to maintain internal nutrient balance. Indeed, NH_4 uptake by plants is depressed by increasing acidity (Tisdale *et al.*, 1985). Uptake of both NH_4 and NO_3 by the microbial biomass may also partially explain the decreased concentration of these ions.

Table 6. Equilibrium pH values recorded from saturated paste extracts

Treatment	Average pH
Control	4.26
Calcite 0.600g (1)	4.96
Calcite 1.200g (2)	5.32
Calcite 2.400g (3)	6.12
Calcite 4.800g (4)	7.38
Ettr. W 0.770g (1)	4.48
Ettr. W 1.540g (2)	4.73
Ettr. W 3.100g (3)	5.61
Ettr. W 6.200g (4)	6.07
Gypsum 1.032g (1)	3.92
Gypsum 2.064g (2)	3.71
Gypsum 4.128g (3)	3.72
Gypsum 8.257g (4)	3.78

Note: (1), (2), (3) and (4) represent corresponding treatment levels

An alternative explanation for the decline in concentration of these nutrients is the possibility that NH_4 and NO_3 could have been lost as gaseous emissions, N_2 and N_2O, due to the presence of anaerobic microsites. Although the sandy soil facilitated rapid evaporation, the maintenance of a high moisture content (FMC) might well have induced such microsites. Unfortunately, the lack of foliar N data make the interpretation of these results difficult.

The decline in concentration of NH_4 associated with incremental levels of the two alkaline amendments may, however, reflect an increase in CEC with pH. As a further possibility, the precipitation of an NH_4 based mineral seems plausible. The basal application of phosphorus (80mg P/kg soil) in the current experiment was erroneously high if compared with experimental applications of other studies ranging from 20 - 67mg P/kg soil (data adapted from Lindsay & Taylor, 1960). The addition of P in the form of H_3PO_4 under acid conditions, as in the present case, tends to form complex phosphates of Fe and Al (Tisdale *et al.*, 1985) due to the elevated activity of these ions under low pH conditions.

It was initially anticipated that in the light of likely reaction products following the application of common phosphatic fertilizers (Sample *et al.*, 1980), the precipitation of an NH_4-taranakite ($Al_5(NH_4)_3H_6(PO_4)_8.18H_2O$) type mineral seemed possible especially in light of the low pH of the soil which would be expected to contain large amounts of Al. Furthermore, the dissolution of ettringite would yield Al for this purpose. According to thermodynamic calculations, the precipitation of this mineral was plausible under control and gypsum treatments, although this did not hold true for the alkaline amendments, which exhibited an opposite trend to the solubility line for this mineral. Although it has not been verified by thermodynamic calculations, it is possible that precipitation of one of the crandallite group minerals, possibly crandallite ($CaAl_3(PO_4)_2(OH)_5.H_2O$), would account for the observed trend of NH_4 which is able to occupy a so-called third position in minerals of the plumbogummite subgroup of this group (Lindsay *et al.*, 1989). The precipitation of a mineral belonging to this subgroup would provide a plausible explanation for the reduction in solution concentration of NH_4 in response to an increase in pH and consequently in the scale of the nitrification reaction to produce NO_3.

The effect of gypsum on soil solution composition is known to induce an increase in the concentration of soluble NO_3^- (Shainberg *et al.*, 1989). In the present study, incremental addition of gypsum induced an increase in soil solution NH_4 concentration, while NO_3 exhibited an initial decline followed by an equivalent increase in concentration. It is interesting to note that this trend is reflected in other anions, notably Cl and PO_4, while other cations exhibit a similarity to NH_4. It is possible that an increase in anion exchange capacity (AEC) associated with a decrease in pH (Sposito, 1989) due to the application of gypsum leads to an initial enhanced uptake of NO_3. Since NO_3 is probably displaced by SO_4 ions due to specific adsorption of the latter (Shainberg *et al.*, 1989), the initial application of gypsum may induce an increase in uptake of NO_3 but the displacement of these ions at subsequent larger applications of gypsum would seem likely in light of the low buffer capacity of the Silvermine sand. This would account for the increased solution concentration of NO_3 at higher levels of gypsum application. In contrast the sequential increase in soil solution concentration of NH_4 may be attributed to a decrease in CEC combined with mass action displacement of ions by the addition of Ca (a further constituent of gypsum) on remaining CEC. This hypothesis concerning the effects of gypsum is considered to apply to all cations and anions in the current investigation and will not be reconsidered in subsequent sections.

The accumulation of NO_2 (26 ppm), was observed in the highest calcite treatment level. Nitrite is known to accumulate under conditions of alkalinity and high NH_4 levels due to the suppressive effect of the latter at alkaline soil pH values on the *Nitrobacter* groups of organisms (Tisdale *et al.*, 1985). While NH_4 levels are notably low at the highest calcite treatment level (Figure 10, p 37), a sufficient concentration of this cation would apparently account for NO_2 production at the pH concerned (Table 6, p 39).

3.3.2.2 Phosphorus

The decline in soil phosphate levels associated with increase in pH (Figure 11, p 38; Table 6, p 39), follows the inverse trend to that reported for most soils where PO_4 activity decreases above and below a pH value of about 5.5 (Sumner *et al.*, 1991). The observed trend in this investigation could be attributed to what Haynes (1984) has described as the transient nature of acid soils exhibiting large amounts of soluble Al. However, an alternative and possibly more plausible explanation would follow from the aforementioned possibility of crandallite precipitation. Evidence supporting this contention is the notably lower PO_4 concentration in the case of amendment with ettringitic waste. The provision of Al by ettringite (in addition to ambient Al levels) could possibly facilitate precipitation of greater amounts of taranakite. In addition, MINTEQA2 speciation predicted that at least in the case of calcite treatment levels three (2.4g) and four (4.8g), and ettringitic waste treatment level four (6.2g), a supersaturation of the soil solution with respect to hydroxyapatite ($Ca_5(PO_4)_3(OH)$) (Table 7), indicated the thermodynamic feasibility for precipitation of this mineral.

3.3.2.3 Potassium

It is important to consider the similarity in chemical behaviour of K to NH_4 in this study, with similar declines in concentrations for both nutrients following an increase in pH. The previously invoked formation of crandallite-type mineral to explain the observed decline in soil solution NH_4 concentrations may well apply in the case of K, which could occupy a similar third position (Lindsay *et al.*, 1989) to NH_4 in the mineral structure.

Table 7. Averaged saturation indices of selected minerals in the soil solution under the effect of differing amendments and amendment levels.

Treatment	Gibbsite	Jurbanite	Alunite	Hydroxyapatite	Gypsum
Control	-2.20	-1.76	-1.28	-9.53	-1.49
Calcite 0.600g				-5.44	-1.77
Calcite 1.200g				-3.55	-1.77
Calcite 2.400g				+2.66	-1.72
Calcite 4.800g				+8.41	-1.69
Ettr. W 0.770g	-0.98	-0.68	-0.17	-8.62	-1.10
Ettr. W 1.540g				-7.13	-0.77
Ettr. W 3.100g				-0.64	-0.35
Ettr. W 6.200g				+2.36	+0.14
Gypsum 1.032g	-3.34	-1.44	-1.98	-10.58	-0.33
Gypsum 2.064g	-3.86	-1.41	-2.70	-11.48	+0.03
Gypsum 4.128g	-3.77	-1.38	-2.48	-10.76	+0.11
Gypsum 8.257g	-3.75	-1.34	-2.14	-9.75	+0.27

As an alternative explanation, increased pH levels associated with the application of ettringitic waste and calcite (Table 6, p 39) induce a marginal decline in soluble K concentration which may be attributable to pH dependent CEC. The results confirm the findings of other workers (e.g. Haynes & Ludecke, 1981; Juo & Uzu, 1977). A higher solution concentration of K in the case of ettringitic waste treatments is attributed firstly to its lower neutralizing capacity (Chapter 2) relative to calcite, which would induce a greater CEC relative to ettringitic waste for corresponding application levels. Elevated CEC would facilitate the uptake of incremental additions of Ca as calcite, while in no way altering the capacity to hold K and other soil cations on the exchangeable phase. In addition, it is contended that the yield of Al from the dissolution of ettringite, as well as the presence of other components in the ettringitic waste are of further significance in explaining the observed difference in trend between calcite and ettringitic waste treatments.

Assuming that CEC of a particular soil is uniform for a given pH, then it would be expected that concentrations of soil solution cations would be uniform for the particular pH concerned. However, where equilibrium pH values are approximately equivalent for the third (3.1g) and fourth (2.4g) treatment levels of calcite and ettringitic waste, respectively (Table 6, p39), concentrations of the soil solution cations (Figure 10, p 37) corresponding to these levels are markedly different. It is probable that excessively high soil solution concentrations of these cations in the case of ettringitic waste applications are a result of the high concentrations of these elements in the waste (Appendix 3) relative to the pure quality calcite reagent which was used in this study. As the trend is observed with respect to Na, K, Ca and Mg, this will not be considered in subsequent sections relevant to these cations.

3.3.2.4 Calcium

Both gypsum and ettringitic waste application elevate the level of Ca in the soil solution, a trend which does not hold true for calcite treatments. In addition to the aforementioned effects of change in CEC which would partially account for the differences in Ca concentration in solution, speciation of results using MINTEQA2 indicated a supersaturation of the soil solution with respect to hydroxyapatite (Table 7). This would possibly be due to high concentrations of PO_4 from the basal nutrient treatment and OH from the liming reaction, providing a plausible means of Ca precipitation from the soil solution. The uptake of Ca in the aforementioned crandallite-type mineral is a further possible reason for the observed solution concentrations of Ca, being sustained even at high levels of calcite application.

Levels of Ca associated with ettringitic waste application are intermediate between gypsum and calcite treatments and probably represent a combination of the competition for cation exchange sites of cations contained within the ettringitic waste as well as the possibility of hydroxyapatite precipitation, as indicated by the positive saturation indices for this mineral at the highest ettringitic waste treatment level.

3.3.2.5 Magnesium

Magnesium is known to be a poor competitor for exchange sites relative to Ca (Sumner *et al.*, 1991), while large increases in pH may induce deficiencies of this element (Sumner *et al.*, 1978). Results reported here indicate that the trends for Mg follow those of Ca (Figure 10, p 37). Calcite application apparently has no effect on the soil solution concentration of Mg. It is probable that a large number of exchange sites generated from an increase in pH would be occupied by Ca added in the form of calcite, thereby preventing further adsorption of Mg from the solution. In addition, the postulated precipitation of Ca in hydroxyapatite would reduce competition for exchange sites which might otherwise have displaced Mg, leading to an increased solution concentration of the latter element. Hence deficiencies of Mg due to increased uptake on CEC are unlikely with the present soil due to its low buffering capacity, although loss of this element through competitive displacement and subsequent leaching cannot be ruled out.

3.3.2.6 Sulphur

The addition of sulphate in the form of ettringitic waste and gypsum leads to successively higher solution concentrations of this ion (Figure 11, p 38). Considering the composition of gypsum ($CaSO_4.2H_2O$) and ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$), it would be expected that due to the much higher proportional SO_4 content in gypsum, solution concentrations of this ion should be greater in respect of gypsum treatments. The absence of SO_4 in calcite amendments would account for the lack of change in associated soil solution concentrations for this ion.

3.3.2.7 Chlorine

The decrease in solution Cl concentration associated with the liming amendments (calcite and ettringitic waste) is difficult to explain in light of the expected decline in AEC associated with an increase in pH, which would presumably lead to a release of Cl into solution. The possibility of co-precipitation of Cl with some mineral such as the aforementioned hydroxyapatite or crandallite, cannot be ruled out. A possible explanation for change in Cl concentration with gypsum application, similar to that of NO_3, has also been suggested (section 3.3.2.1).

3.3.2.8 Aluminium

Aluminium concentrations in the soil solution in the present study may have been affected by mineral precipitation due to the large application of phosphorus. Nevertheless, the lack of measurable Al associated with most lime treatments (Appendix 10) implies the precipitation of Al, and/or its uptake by organic functional groups associated with an increase in pH. Organic functional group complexation is known to provide an important means of reducing Al concentration (Hue *et al.*, 1986).

Sumner *et al.* (1991) have contended that solid phase dissolution may be the overriding factor controlling Al levels in soil solution and have illustrated the dependence of Al^{3+} activity upon solution pH in equilibrium with various mineral phases. MINTEQA2 predictions of the undersaturation of gibbsite, alunite and jurbanite (Table 7, p 43) would imply that in the absence of precipitation of some other solid phase such as the aforementioned crandallite-type mineral, surface adsorption-desorption reactions would control soil solution concentration of this ion. This has been provided as an alternative hypothesis for the control of the solution composition in acid subsoils (Sumner *et al.*, 1987).

3.3.3 *Plant response to soil amendments*

The effect on soil chemical properties of the different amendments has been considered in some detail. However, the ultimate purpose underlying the liming of acid soils in an agricultural context, is to improve plant production. The following section therefore assesses the effects of the amendments on plant growth and foliar composition.

3.3.3.1 Shoot yield

The effects of the different soil amendments on plant dry matter production are presented in Figure 12. Based on the ANOVA results, no significant differences in dry mass were obtained between any of the gypsum treatments, although an apparent initial slight increase and subsequent decrease in dry mass was obtained for incremental additions of gypsum. While no significant differences were found between calcite and ettringitic waste at corresponding levels of application, growth was initially higher in treatments with the latter soil amendment. The highest treatment levels of both

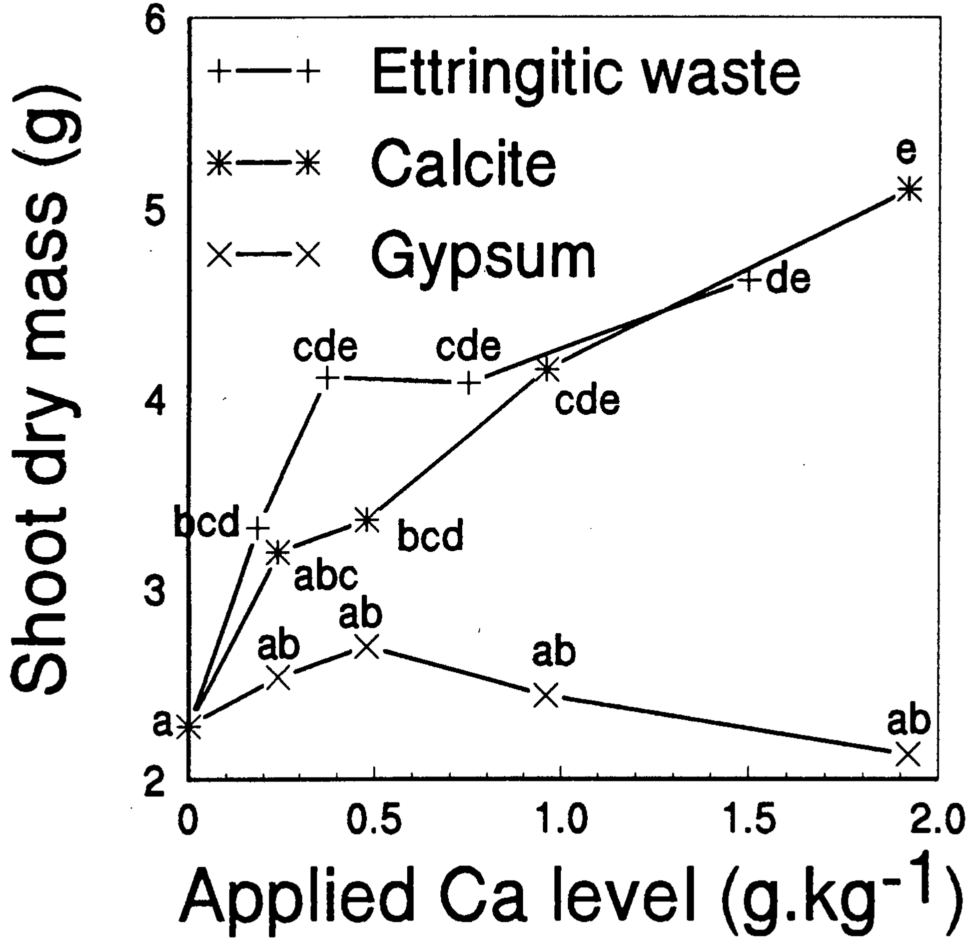

Figure 12. Dry mass increase as a function of incremental levels of soil amendments. Letters indicate significant differences determined by a Tukey multiple range test, with letters held in common indicating a lack of significant difference in plant dry mass at the 5% level.

ettringitic waste and calcite resulted in significantly greater dry mass production than the control treatment. It is interesting that the initially greater dry mass associated with lower levels of ettringitic waste, compared with corresponding levels of calcite, matches the initial increase associated with amendment by gypsum, possibly suggesting a nutritional effect of Ca and/or S (it should be noted in this respect that soluble Ca levels were elevated by both ettringitic waste and gypsum treatments but not significantly by calcite).

3.3.3.2 Qualitative observations

To the extent that the aforementioned yield responses can be explained by nutritional or toxic effects of the amendments, there is the possibility that these will produce visual symptoms which are sometimes quite specific and can therefore be of diagnostic value (Bennet, 1993).

With regard to roots, malformation of the root system is attributed to Al toxicity and this is exacerbated by low levels of soil Ca (Foy, 1984). The general qualitative trend of roots in this study appeared to be one of an increase in size of primary roots and general fibrousness of the root system associated with incremental additions of calcite and ettringitic waste. In contrast, increasing treatments of gypsum apparently result in impeded root development, being least fibrous at the highest treatment level. Since Al injured roots are characteristically stubby and brittle, with root tips and lateral roots being thickened (Foy, 1984), the trends observed with increasing lime amendment appear to indicate an elimination of Al toxicity. This may appear anomalous considering the exceptionally low pH of the unamended Silvermine sand at which free ion activity of Al approaches a maximum. However, the aforementioned exceptionally low acid saturation of this soil relative to other forest soils in Natal may indicate that Ca levels are sufficiently high to overcome the detrimental effects of Al, where Al is believed to exert its effect in the cell walls of roots possibly through decreased pore size (Blamey *et al.*, 1990; Blamey & Asher, 1994). While such a contention would require verification with analytical results of root matter from more acid saturated conditions, the observed superior trends in root development with successively higher lime treatments are probably due to more favourable fertility conditions. These in turn would lead to enhanced growth of above ground plant parts with subsequent carbohydrate allocation to root development.

With regards to above-ground plant parts, the main symptoms of deficiency or toxicity included chlorosis, interveinal chlorosis, necrosis and stunting as presented for different treatment levels in Table 8. Since the occurrence of these symptoms declines with increasing levels of the alkaline amendments, and to a lesser extent gypsum, the beneficial effects of these amendments on plant growth are apparent. However, no obvious explanation for these symptoms is available. In addition, the occurrence of leaf tip malformation and necrosis observed for certain treatments (e.g. ettringitic waste 3.1g), which is a manifestation of Ca deficiency possibly induced by Al toxicity (Foy, 1984), is difficult to explain in light of soil solution concentrations of these ions. In parallel with the trends of plant dry-mass production, incremental additions of gypsum coincided with a lack of change in plant height, while calcite and ettringitic waste treatments resulted in increased plant height (Plate 1, p 50).

Table 8. Averaged number of leaves per pot exhibiting deficiency and toxicity symptoms.

Treatment	Necrosis	Interveinal Chlorosis	Chlorosis
Control	13	15	11
Calcite 0.600g	15	11	5
Calcite 1.200g	16	11	6
Calcite 2.400g	13	5	0
Calcite 4.800g	1	0	0
Ettr. W 0.770g	15	9	7
Ettr. W 1.540g	12	6	4
Ettr. W 3.100g	14	2	2
Ettr. W 6.200g	0	0	0
Gypsum 1.032g	13	9	7
Gypsum 2.064g	15	9	7
Gypsum 4.128g	16	8	5
Gypsum 8.257g	15	7	4

3.3.4 *Foliar composition*

In order to interpret the visual diagnosis of deficiencies and toxicities, it is necessary to assess foliar composition and compare the analytical data with published critical values. Concentrations of different macro- and micro-nutrients in above-ground plant parts are compared graphically in Figures 14 (p 51) and 15 (p 52), respectively, while original data are provided in Appendix 11. Reference is made to the compilation of Voss (1993) for sufficiency ranges of plant nutrients in selected parts of maize plants at different stages of plant development (Table 10, p 53). Considering the age of plants at harvest in the present study as being beyond the 3- to 4- leaf stage but far from silk, nutrient concentrations should be compared in relation to both stages provided by Voss (1993).

While foliar N and S contents were not determined, the symptoms associated with deficiencies of these elements are in agreement with those observed in the present study. Both nitrogen and sulphur deficiency in young maize plants cause whole plants to be pale yellowish green and have spindly stalks. Interveinal chlorosis and stunting of plants are further manifestations of sulphur deficiency which tends to be favoured by acid, sandy soils (Voss, 1993). While basal S treatment was provided in the form of $MgSO_4$, the acid sandy conditions of the Silvermine sand may have induced a deficiency of this element due to lower SO_4 solubility under acidic conditions. The supply of SO_4 in the form of gypsum and ettringitic waste would serve to ameliorate this condition, however, and trends in plant growth are not paralleled by those of soil solution SO_4 content, implying that S nutrition is not the cause of the major trends observed in plant growth.

3.3.4.1 Phosphorus

Since P sufficiency spans the range of 0.2-0.8%, foliar P values obtained for all except the highest treatment levels of calcite and ettringitic waste in this study are considerably in excess of the sufficiency range and may present a problem in terms of nutrient imbalance, the manifestations of which are often seen as poor plant growth such as stunting (Bennett, 1993). The decline in foliar P content was indeed paralleled by an increase in plant height, while in respect of gypsum treatments, high foliar P contents coincide with an apparent lack of change in plant height.

The trends of soil PO_4 level under different soil amendments (Figure 11, p 38)

Plate 1. Trends of plant height associated with incremental additions of gypsum, calcite and ettringitic waste.

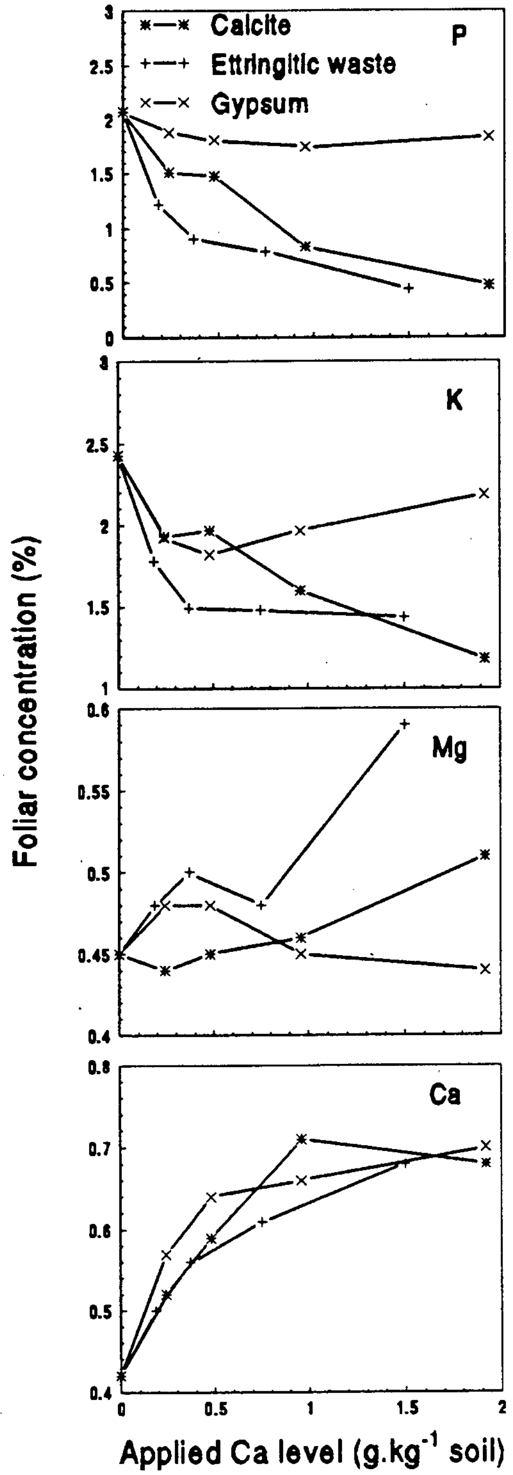

Figure 14. Macronutrient foliar composition as a function of the application of Ca to 1200g of Silvermine sand in the form of different soil amendments at varying levels.

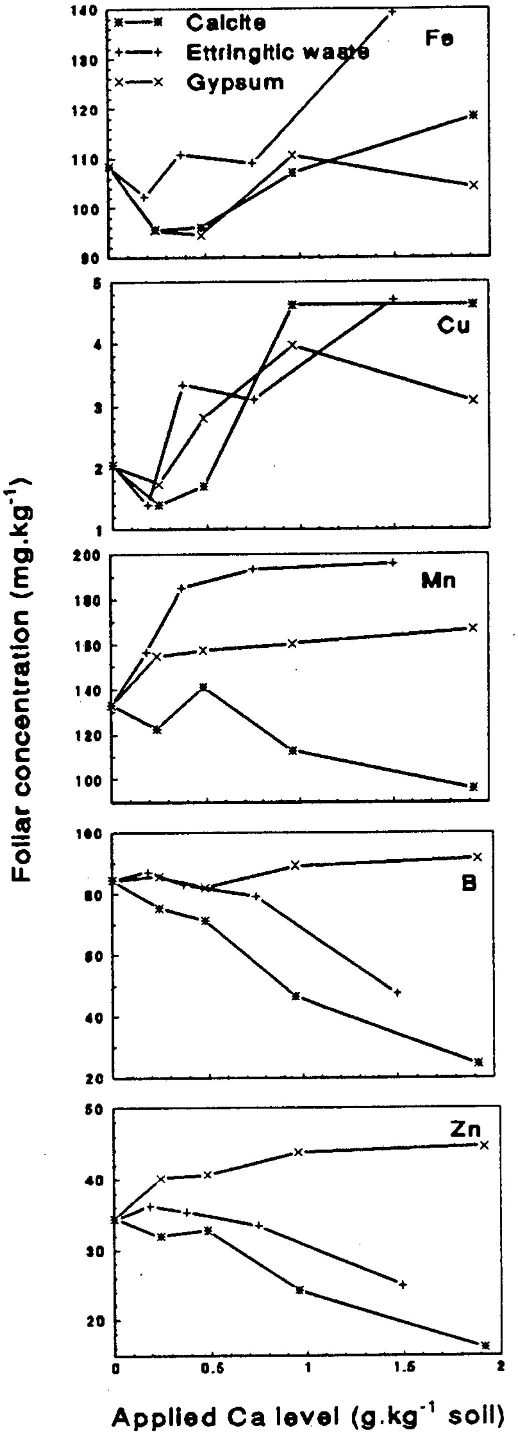

Figure 15. Micronutrient foliar composition as a function of the application of Ca to Silvermine sand in the form of different soil amendments at varying levels.

Table 10. Sufficiency ranges of nutrients in selected parts of maize plant

	Sufficiency ranges in plants	
Element	Ear leaf at silk	Whole plant, 3- to 4- leaf stage
N (%)	2.7-3.5	3.5-5.0
P (%)	0.2-0.4	0.4-0.8
K (%)	1.7-2.5	3.5-5.0
Ca (%)	0.2-1.0	0.9-1.6
Mg (%)	0.2-0.6	0.3-0.8
Fe (ppm)	21-250	50-300
Zn (ppm)	20-70	20-50
Mn (ppm)	20-150	50-160
Cu (ppm)	6-20	7-20
B (ppm)	4-25	7-25

appear to follow those of foliar P content, implying some direct relationship between soil solution concentration (or activity) and bioavailability.

3.3.4.2 Potassium

Potassium levels, which show a decline with increasing levels of calcite and ettringitic waste would appear to be deficient relative to the normal values supplied by Voss (1993). The greater incidence of necrosis associated with higher levels of foliar K at lower amendment levels implies that necrotic symptoms cannot be attributed to K deficiency. Leaf K content is also reduced by gypsum which is in agreement with previous findings (Shainberg *et al.*, 1989)

Both Ca and Mg are known to compete with K for entry into the plant, with availability being dependent on the concentration of K relative to Ca and Mg (Tisdale *et al.*, 1985). It is interesting that where soil concentrations of Ca, Mg and K are generally higher in response to ettringitic waste treatments than to calcite (Figure 10, p 37), foliar contents of K are generally lower in response to the former. This would appear to imply that the more competitive Ca and Mg ions associated with ettringitic waste treatments are preventing the uptake of K from solution.

3.3.4.3 Calcium

It is inferred from the similar foliar Ca values exhibited by plants grown in soils ameliorated with the different amendments that the Ca deficiency symptom of stunting (Voss, 1993) is probably of little significance in the present instance. In contrast to the other two amendments, plant height is unaltered with increasing foliar Ca levels in the case of gypsum (Plate 1, p 50).

In assessing the bioavailability of plant nutrients, increasing use has been made of ion activities and chemical potentials in soil solutions (Sumner *et al.*, 1991). Of interest is which expression of soil Ca availability provides the best indication of Ca uptake. In assessing this aspect with respect to Ca (Figure 16), it is apparent that in the case of calcite, both activity and concentration are poor indicators of foliar Ca, whereas KCl-extractable Ca provides an indication of bioavailability which is only marginally superior. Since in respect of both ettringitic waste and gypsum, activity and concentration are well correlated with plant available Ca, it is possible that the observed trend for calcite is due to its sparingly soluble nature. This contention is further supported by the clear relationship between foliar content and the level of Ca applied in the form of calcite. The trends observed for the former two amendments in respect of solution activity are supported by results presented by Sposito (1989) for a range of plant nutrients.

3.3.4.4 Magnesium

In reviewing the literature, Shainberg *et al.* (1989) have reported the invariable decline in foliar Mg associated with gypsum treatments, a trend which has not been observed in this study. However, in contrast with the alkaline amendments, foliar Mg levels do not exhibit an incremental increase in response to soil solution Mg levels under the amendment of gypsum. Due to the antagonism between Ca, K or NH_4 and Mg for plant uptake (Tisdale *et al.*, 1985), the high concentrations of these competitive ions in gypsum amended soil may well account for uptake of Mg below that which might have been expected. Nevertheless, Mg levels for all treatments are apparently within the sufficiency range for maize (Table 10, p 53) and it is possible that the observed interveinal chlorosis may have been due to some other cause.

3.3.4.5 Micronutrients

Foliar concentrations of micronutrients in response to the soil amendments are shown in Figure 15 (p 52). As with macronutrients, reference is made to the compilation

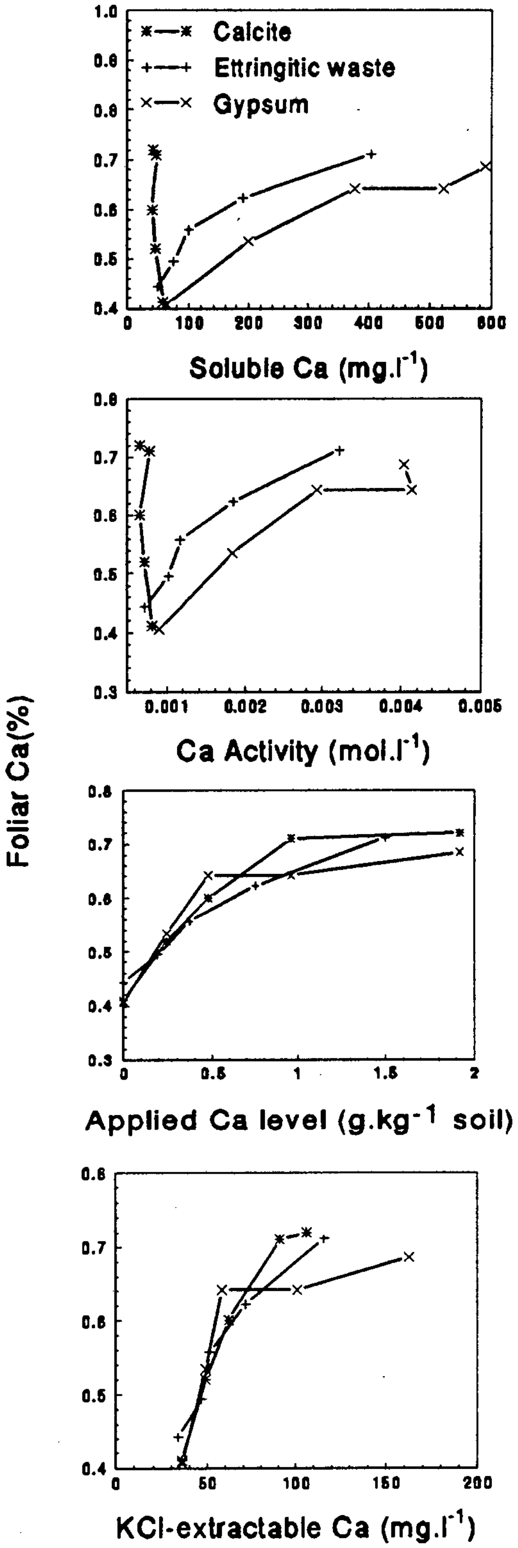

Figure 16. Foliar Ca concentration as a function of different parameters of soil calcium applied in the form of different amendments.

of Voss (1993) on sufficiency limits for plant nutrients in respect to maize (Table 10, p 53). A combination of impoverished soil, together with insufficient basal amendment with Cu, has led to a deficiency in all treatments, although this is apparently ameliorated to some degree by increasing levels of the different amendments. This is despite the known decrease in soil solution activity of Cu associated with increasing pH (Sumner *et al.*, 1991) which would be expected in respect of the two liming agents. However, the highly unbuffered nature of the Silvermine sand may favour the adsorption by soil solids of other ions in preference to copper. Since copper deficiency results in streaking of leaves and partial necrosis on the edges of older leaves (Voss, 1993), the observed symptoms of necrosis and interveinal chlorosis may possibly be due to a deficiency of this nutrient.

Zinc levels in the plant material are neither deficient nor in excess of the sufficiency range. Foliar Zn is reduced in parallel to the increase in soil solution pH in response to treatments with the liming agents while the opposite trend is observed for gypsum treatments.

Manganese toxicity, in the form of necrosis and crinkling of upper leaves (Bennett, 1993) is believed not to be manifested in the present study in spite of levels of Mn being in excess of sufficiency in response to ettringitic waste treatments. While necrotic symptoms were observed for different treatments, such symptoms did not coincide with the highest foliar Mn contents. It is possible that the elevated foliar Mn contents are a result of the high Mn content of the waste (Appendix 3) relative to background levels in the Silvermine sand (Appendix 1). While CEC would increase in response to the elevated pH generated by the waste, concentrations of this and other metal cations are probably well in excess of CEC, thereby producing elevated soil solution concentrations of Mn. A greater foliar Mn concentration was also observed in response to gypsum treatments which confirms the general finding that Mn uptake increases following gypsum application, apparently in response to an increase in soil solution Mn concentration (Shainberg *et al.*, 1989). The decrease in soil pH associated with gypsum treatments (Table 6, p 39), would also play a role since soil solution Mn solubility is determined by pH (Sumner *et al.*, 1991).

Foliar Fe concentrations are apparently sufficient for maize growth. The increase in foliar Fe content in response to the alkaline amendments exhibits a trend opposite to that which is generally reported (e.g. Gardner *et al.*, 1982). As with Cu, it is possible that preferential uptake of ions other than Fe on soil solid phases has taken place. Consequently, elevated soil solution concentrations of Fe would favour greater bioavailability. Higher foliar Fe contents in the case of ettringitic waste treatments relative to calcite may be attributed to the addition of this element in the former amendment.

Levels of foliar B could be responsible for some of the trends in maize growth. All treatments, with the exception of the highest calcite treatment exhibited foliar B levels well in excess of the sufficiency range of this element. While the observed levels do not necessarily imply toxicity, the range between deficiency and toxicity is nevertheless narrow for this element (Tisdale *et al.*, 1985) and the positive growth response to liming treatments may well have been due to reduction of B to a more favourable level. The pH-dependant nature of B availability is well known (Bester, 1993). Boron toxicity is known to induce necrotic edges in maize leaves (Voss, 1993). While such necrotic edges were not obviously evident, general leaf necrosis was prevalent, the cause of which might have been B toxicity.

3.4 Conclusions

The aim of this chapter has been to demonstrate the effect of soil amendment with an ettringitic waste on soil chemical properties and consequent nutrient availability and plant growth, in comparison with calcite and gypsum. The Silvermine sand, by virtue of its unbuffered character and acidic reaction, gave rise to soil and plant responses which in some cases were unusual. Although pH was exceedingly low, this was not matched by the degree of acid saturation which is surprisingly low. Not surprisingly, however, there was an absence of any obvious symptoms of toxicity in the maize roots.

In comparison with calcite, ettringitic waste induced significantly less change in pH for corresponding treatment levels but this was not reflected in acidity *per se*, a phenomenon which could be attributed to the low acidity status of the soil. Indeed, a more acid saturated soil may well have exhibited significant differences for the observed differences in pH between equivalent treatment levels. The high application of P as a basal treatment was inferred to have induced certain anomalous soil chemical features, notably the decrease in soluble NH_4, NO_3, Cl and PO_4 concentrations with an increase in pH. This was attributed to the precipitation of a crandallite-type mineral. Supersaturation of the soil solution with hydroxyapatite could have facilitated the decrease in solution concentration of Ca in the case of calcite and ettringitic waste treatments. This, together with enhanced CEC, could explain the observed trends in soil solution concentrations of Ca; K and Mg trends were similarly explicable in light of an increase in CEC. In contrast, the consistently observed trends for gypsum treatments were attributed to an increase in AEC which initially enhanced sorption of PO_4, Cl and NO_3 but suppressed this sorption at higher treatment levels due to displacement by high concentrations of SO_4. Cation concentrations decreased with CEC under gypsum applications.

The observed trends of plant dry mass were paralleled by plant height for different amendment levels. Dry mass was not significantly different for corresponding treatment levels of calcite and ettringitic waste, a feature which was tracked by various foliar nutrient levels. A decrease in plant height was associated with a reduction in excessive foliar P levels which might have reflected a trend towards more favourable nutrient balance. Cu deficiency may have led to the observed symptoms of chlorosis and interveinal chlorosis, while B toxicity might have induced necrotic symptoms.

Of additional interest were the increased foliar concentrations of Cu and Fe associated with an increase in pH in response to applications of the two liming agents. This anomalous feature was ascribed to the highly unbuffered nature of the Silvermine soil which facilitated displacement of these nutrients from exchange sites by more competitive ions. A similar increase in Mn in response to amendment with ettringitic waste was explicable in the light of the unbuffered nature of the soil combined with high concentration of this nutrient in the waste, relative to background levels.

CHAPTER 4

GENERAL DISCUSSION AND CONCLUSIONS

4.1 The effects of ettringitic waste on soil acidity

A primary objective of the present study was to assess the liming potential of ettringitic waste produced from alkaline ash water. The CCE is of special relevance in this respect. While the HCl back-titration method (Horwitz, 1980) produced a CCE of 78%, this provided a poor index of the neutralizing value in soil, as observed from the incubation-CCE which varied from 37-63% depending on soil type. The upper value of this CCE range, associated with a well-buffered Kranskop A soil, is comparable with an average incubation-CCE value of 62.4% for a range of materials studied by Engelbrecht (1983) using a highly buffered Wilgenhof soil.

Neutralizing capacity was lowest in the Silvermine sand, reflecting its low buffering capacity. The highest degree of neutralization by ettringitic waste was obtained in the organic-rich, sesquioxidic Kranskop A soil, apparently in response to its high buffering capacity combined with the "self-liming" effect of SO_4 (Reeve & Sumner, 1972), which is a constituent of ettringite, in sesquioxidic soils. These results indicated that it is both the organic matter content and sesquioxides which enhance soil acidity neutralization.

It was shown that in terms of the constituents of ettringitic waste, ettringite itself contributes to neutralization of soil acidity (54-66% of exchangeable acidity; 61-78% of pH(KCl)), the reactivity increasing in the order of Silvermine sand, Kranskop A and Kranskop B. Since the composition of ettringitic waste is likely to vary depending on the composition of the water from which it is precipitated, by establishing the concentration of ettringite itself, predictions of the relative neutralizing value of ettringitic waste could be made in soils of differing characteristics.

Considering the known ameliorative effect on acidity of gypsum on sesquioxidic subsoils due to the mobility of the SO_4 radical, combined with its "self-liming" effect, ettringitic waste could be of additional agricultural benefit in such soils. While historically, agronomists have addressed the problem of soil acidity in the context of the plough layer, acid conditions in subsoil horizons pose a major limitation to successful production of many important crop species (Shainberg *et al.*, 1989). While lime can be used to neutralise acidity of topsoil horizons, in many cases gypsum is incorporated to neutralize subsoil acidity. The combination of basic OH ions and SO_4 ions within ettringitic waste would function in the amelioration of acidity to a greater depth in sesquioxide-rich soils. The economic benefits of using a product containing both of these components could support the selection of ettringitic waste as a liming agent in such soils. The additional contribution to soil nutrient status of this product will be considered below.

While in the present investigation, experimentation was conducted under controlled conditions in small containers, the potential benefit of ettringitic waste as a liming agent would need to be verified in field conditions, especially in terms of its ability to neutralize acidity in sesquioxide-rich subsoils. Furthermore, the effects of applying the waste in its original slurry form would need to be assessed, since only powder application was considered in this study.

4.2 The consequences for soil chemistry of ettringitic waste application

It was originally anticipated that the effects of ettringitic waste on soil chemistry would be intermediate between $CaCO_3$ or $Ca(OH)_2$ and $CaSO_4.2H_2O$ due to the presence of both basic OH and neutral SO_4 ions. The results of the present study supported this expectation. Apart from the lower neutralization of acidity relative to calcite, application of ettringitic waste resulted in soil solution cation concentrations which were intermediate between the other amendments. While this could be attributed to enhanced CEC, the addition of other ionic constituents within the waste product were believed to compete for exchange sites in the exceptionally unbuffered Silvermine sand. This contention was based on the observation that for levels of the two liming agents which led to an equivalent change in pH, solution concentrations of different cations were markedly different.

Reports of a shift to the exchangeable phase of Mg (Sumner *et al.*, 1978) with an increase in pH were not supported by this study, apparently due to the low buffering capacity of the soil. While concentrations of K and NH_4 showed a decrease in concentration with liming due to enhanced CEC, the precipitation of a crandallite type mineral provided an alternative explanation. There was further evidence supporting this contention in the form of lower solution concentrations of PO_4 in response to ettringitic waste application. Since crandallite contains Al as a constituent, the supply of this element by ettringite would favour greater precipitation of such a mineral with concomitant removal of PO_4. Furthermore, mineral precipitation would have been favoured by high application of P as a basal nutrient treatment. Supersaturation of the soil solution with respect to hydroxyapatite, as determined by MINTEQA2 speciation, indicated the possibility for precipitation of Ca and PO_4 in this mineral. While the decrease in solution PO_4 content was attributed to precipitation of this mineral, this unusual trend over the pH range concerned could be due to a transient feature of acid soils with large amounts of soluble Al as described by Haynes (1984). To clarify which of these explanations is likely to be relevant, further experimentation with varying levels of applied P content would be necessary.

4.3 The consequences of ettringitic waste for plant growth and plant nutrient status

The real value of a liming agent is observed in terms of its effects on plant growth. While significant differences in pH were observed for corresponding levels of calcite and ettringitic waste, this was not reflected in plant dry mass. Indeed, although not significant, in the case of ettringitic waste treatments, plant dry mass initially exceeded that of calcite treatments. It is believed that apart from its liming effect, the addition of plant nutrients in ettringitic waste may have been responsible for this trend. The presence of other nutrients, especially Mg, would make the choice of this product additionally desirable as a liming agent. Tisdale *et al.* (1985) contend that in the choice of a liming material, the Mg content should be considered, since this element is deficient in many soils.

Foliar Mg, Fe and Mn levels were notably higher in respect of ettringitic waste treatments implying an increased availability, while K levels were generally below those recorded for calcite treatments despite higher K levels in the soil solution. Since both Ca and Mg are known to compete with K for uptake and since foliar Mg content is elevated in respect of ettringitic waste treatments, the antagonistic effect of Mg on K uptake is plausible. However, this effect may not occur in more buffered soils where Mg and Ca uptake on exchange sites is likely to be enhanced with a concomitant reduction in competition for uptake. While K deficiencies were observed for all treatments, this might be due to the precipitation of the hypothesised crandallite type mineral.

Evidence listed by Sposito (1989) indicates that free ion activity is invariably correlated with plant content for a number of different elements. In the present study, however, neither free ion concentration nor thermodynamic activity provided a good index of Ca uptake in respect of calcite, which is possibly attributable to the sparingly soluble nature of this liming agent. With regards to ettringitic waste and gypsum, however, these parameters were well correlated with plant uptake of Ca.

While the availability of Mg is often reduced due to the competition of Ca, K and NH_4 for plant uptake (Tisdale *et al.*, 1985), the solution concentration of Mg exceeds that of K but is approximately equal to that of NH_4, indicating that the concentration of Mg may have overcome the negative effects of competition with other nutrients.

With regard to the possibility of nutrients being present in toxic concentrations, the ettringitic waste resulted in the uptake of Mn in excess of sufficiency limits of this nutrient for maize, although toxicity symptoms were not observed. Manganese availability is likely to be reduced in more buffered soils due to adsorption of this metal. Although toxicities will therefore probably not be encountered in respect of maize, this will not necessarily hold true for other crop species. While the foliar contents of other metals not essential to plant growth were not considered, the lack of any toxicity symptoms at the highest application level of ettringitic waste would imply that additional constituents are not likely to be present in toxic concentrations. Furthermore, liming to a sufficient level is likely to reduce the uptake of cations, thereby mitigating the possibility of toxicities.

4.4 Conclusion

This dissertation provides ample evidence in support of the use of ettringitic waste as an agricultural lime. The observed trends for dry mass are likely to vary in response to soil type with the beneficial effects of nutrient addition being lessened in soils exhibiting greater buffer capacity due to increased adsorption on exchange sites. Verification of the beneficial effects of this product should be made with field trials, using both slurry and powder forms in different soils and with different crop species. Ultimately, the use of this product will be determined by economic incentives such as soil type, transport costs, available quantities and competition with other liming materials.

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APPENDIX 1

Soil description and analytical data.

Profile no.:	001
Locality:	Pine Plantation, Silvermine Nature Reserve, Cape Peninsula (34°5'S; 18°25'E)

Site description: The pit was sited on a south-westerly facing upper midslope (slope < 5°). Slight surface rill erosion was observed with no apparent microrelief features. Surface hard rock and boulders covered an area of 2-10%. The site had previously been covered in a fynbos/grassland mosaic and is presently under pine plantation.

Parent material:	Table Mountain Sandstone (local colluvium; residual)
Soil form:	unidentified
Soil family:	unidentified

Orthic A: Grey (5YR 6/1) when dry, dark grey (7.5 YR 4/1) when moist; apedal, single grained sand; loose when dry, friable when moist; non-sticky; non-plastic; porous (water absorption 0.5 seconds); very fine roots common.

Table A1. Analytical results for the Silvermine Sand.

Soil physical properties	Particle size distribution (%)
Coarse sand (0.5-2.0mm)	55.8
Fine sand (0.1-0.5mm)	24.5
V. fine sand (0.05-0.1mm)	4.9
Coarse silt (0.02-0.05mm)	0.5
Fine silt (0.002-0.02mm)	13.1
Clay (<0.002mm)	2.1

Note: X-Ray diffraction showed that the clay size fraction consisted almost entirely of quartz with the absence of any detectable clay minerals.

Soil chemical properties	
Organic carbon %	1.29
pH (H_2O)	4.72
pH (KCl)	3.50
KCl-extractable Ca ($mmol_c.kg^{-1}$)	14.97
KCl-extractable Mg ($mmol_c.kg^{-1}$)	8.00
KCl-extractable acidity ($mmol_c.kg^{-1}$)	6.00
Effective CEC ($mmol_c.kg^{-1}$)	28.97
Acid saturation (%)	20.71

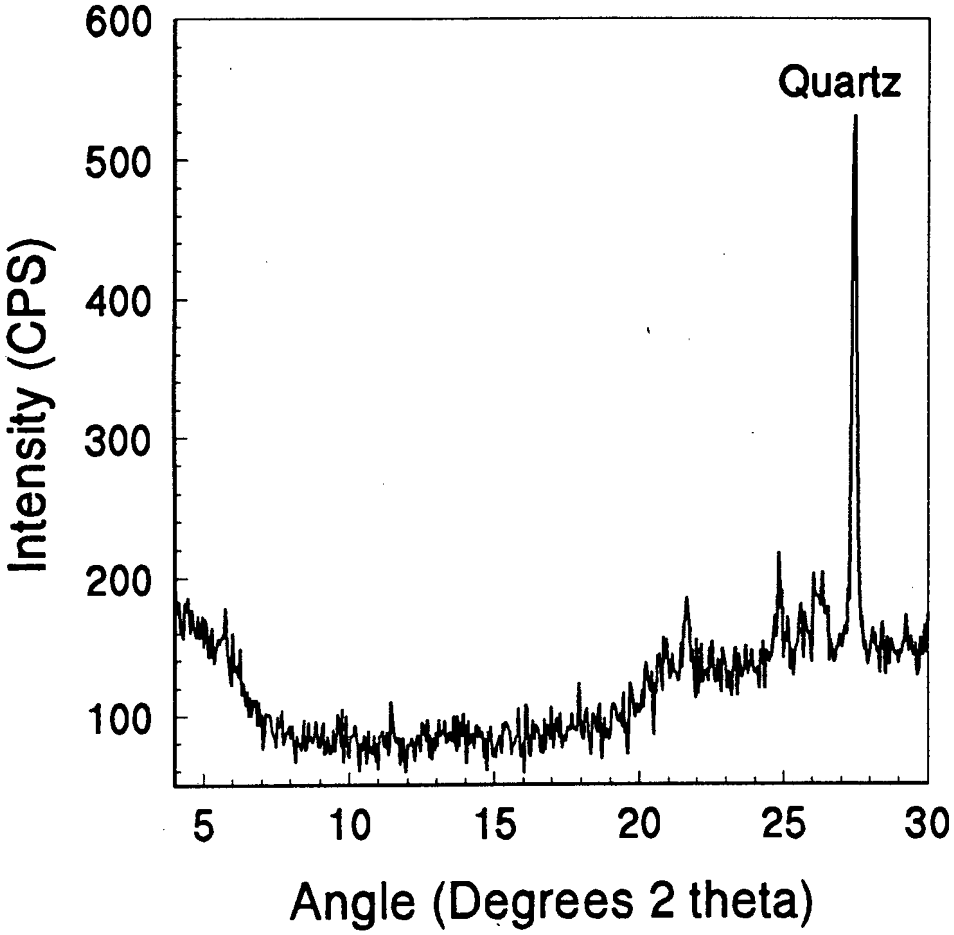
Table A2. Total elemental analysis of Silvermine sand

MAJOR ELEMENTAL ANALYSIS (%)	
SiO_2	93.71
TiO_2	0.15
Al_2O_3	0.28
Fe_2O_3	0.43
MnO	<0.01
MgO	0.03
CaO	0.06
Na_2O	0.03
K_2O	0.03
P_2O_5	0.01
H_2O	0.74
LOI	3.64
TOTAL	99.09
TRACE ELEMENTAL ANALYSIS (ppm)	
Mo	1.2
Nb	4.7
Zr	235.0
Y	5.8
Sr	7.4
U	<1.1
Rb	1.2
Th	<1.5
Pb	5.5
Zn	17.0
Cu	2.2
Ni	6.0
Co	<1.3
Mn	48.0
Cr	23.0
V	6.0

Elemental concentrations determined with wavelength-dispersive XRFS using the following spectrometers and primary radiation tubes: (1) Siemens SRS-303AS, Rh tube for major elements, Mo, Nb, Zr, Y, Sr, U, Rb, Th and Pb; (2) Philips PW 1400, Au tube for Zn, Cu and Ni; and W tube for Co, Mn, Cr and V.

APPENDIX 2

Clay mineralogy of the Silvermine sand.



APPENDIX 3

Total elemental analysis of the ettringitic waste product

MAJOR ELEMENTAL ANALYSIS (%)	
SiO_2	2.15
TiO_2	0.70
Al_2O_3	16.04
Fe_2O_3	0.94
MnO	0.36
MgO	0.92
CaO	34.61
Na_2O	0.28
K_2O	0.09
P_2O_5	0.02
H_2O	9.15
CO_2	7.79
SO_3	11.20
LOI	10.77
TOTAL	95.11

TRACE ELEMENTAL ANALYSIS (ppm)	
Mo	7.1
Nb	3.8
Zr	68.0
Y	4.9
Sr	707.0
U	<1.6
Rb	3.1
Th	3.2
Pb	5.4
Zn	33.0
Cu	9.9
Ni	113.0
Co	5.9
Mn	3163.0
Cr	936.0
V	65.0

Elemental concentrations determined with wavelength-dispersive XRFS using the following spectrometers and primary radiation tubes: (1) Siemens SRS-303AS, Rh tube for major elements, Mo, Nb, Zr, Y, Sr, U, Rb, Th and Pb; (2) Philips PW 1400, Au tube for Zn, Cu and Ni; and W tube for Co, Mn, Cr and V.

A total of 95% for all constituents within the waste is probably attributable to an inaccurately determined S concentration.

APPENDIX 4

Equations describing relationships between acidity and alkaline amendment level.

Soil Type	KCl-extractable acidity	pH(KCl)
1) Silvermine Sand		
Calcite	$y=5.88-121.54X+781.82X^2$	$y=3.50+29.99X-50X^2$
Ettringitic waste	$y=5.53-37.93X+110.9X^2$	$y=3.50+12.37X+9.98X^2$
2) Kranskop A		
Calcite	$y=18.00-220X+800X^2$	$y=4.26+6.47X-14.18X^2$
Ettringitic waste	$y=18.14-158.38X+554X^2$	$y=4.28+3.02X-8.43X^2$
3) Kranskop B		
Calcite	$y=19.95-462.91X+2836X^2$	$y=4.37+3.85X+85.82X^2$
Ettringitic waste	$y=20-250X+976.56X^2$	$y=4.37+4.71X-9.54X^2$

Note: X = level of calcite or ettringitic waste application
Y = KCl-extractable acidity or pH(KCl)

APPENDIX 5

Incubation experiment acidity data.

TREATMENT	pH(H_2O)	pH(KCl)	ACIDITY ($mmol_c.kg^{-1}$)
SILVERMINE SAND			
CONTROL	5.20	3.51	5
CALCITE 0.025g-1	5.57	4.17	3
CALCITE 0.025g-2	5.47	4.13	3
CALCITE 0.050g-1	6.21	4.90	2
CALCITE 0.050g-2	6.08	4.95	2
CALCITE 0.100g-1	6.59	5.72	2
CALCITE 0.100g-2	6.60	6.26	1
ETTR. W 0.032g-1	5.04	3.66	5
ETTR. W 0.032g-2	5.08	4.00	4
ETTR. W 0.064g-1	5.26	4.22	4
ETTR. W 0.064g-2	5.40	4.55	3
ETTR. W 0.128g-1	5.97	5.02	2
ETTR. W 0.128g-2	5.68	5.45	3
KRANSKOP A			
CONTROL	5.10	4.27	18
CALCITE 0.025g	5.58	4.38	13
CALCITE 0.050g	5.48	4.57	9
CALCITE 0.100g	5.82	4.76	4
ETTR. W 0.032g	5.45	4.57	14
ETTR. W 0.064g	5.55	4.42	10
ETTR. W 0.128g	5.66	4.63	7
KRANSKOP B			
CONTROL	5.59	4.37	20
CALCITE 0.025g	5.85	4.51	10
CALCITE 0.050g	5.84	4.78	4
CALCITE 0.100g	6.07	5.61	2
ETTR. W 0.032g	5.36	4.44	13
ETTR. W 0.064g	5.25	4.63	8
ETTR. W 0.128g	5.76	4.82	4

APPENDIX 6

Pot experiment acidity data.

* Units in mmol$_c$/kg ; ** Units in ppm; A.S. - Acid Saturation (%).

TREATMENT	pH(KCl)	pH(H_2O)	ACIDITY*	Mg*	Mg**	Ca*	Ca**	A.S.
CONTROL-1	3.43	4.50	6.20	8.45	10.3	16.00	31	20.23
CONTROL-2	3.37	4.24	5.48	8.09	9.8	18.00	35	17.35
CONTROL-3	3.46	4.79	4.65	6.61	8.0	17.00	34	16.45
ETTR.W 0.77g-1	3.67	4.77	4.00	7.17	8.7	23.00	46	11.71
ETTR.W 0.77g-2	3.59	4.92	3.43	6.98	8.5	24.00	48	9.95
ETTR.W 0.77g-3	3.66	4.88	3.35	8.14	9.9	25.50	51	9.06
ETTR.W 1.54g-1	3.89	4.95	1.93	7.50	9.1	25.50	51	5.51
ETTR.W 1.54g-2	3.84	4.89	1.98	6.75	8.2	25.00	50	5.86
ETTR.W 1.54g-3	3.93	4.96	2.35	7.20	8.8	29.00	58	6.10
ETTR.W 3.10g-1	4.45	5.09	1.10	9.11	11.1	35.00	70	2.43
ETTR.W 3.10g-2	4.38	5.50	1.05	8.43	10.3	36.50	73	2.28
ETTR.W 3.10g-3	4.29	5.25	1.13	8.84	10.8	37.50	75	2.37
ETTR.W 6.20g-1	5.17	5.80	0.00	8.28	10.1	65.50	131	0.00
ETTR.W 6.20g-2	5.14	6.09	0.35	6.66	8.1	50.50	101	0.61
ETTR.W 6.20g-3	5.25	5.86	0.15	8.39	10.2	66.50	133	0.13
CONTROL- 1	3.50	4.71	5.08	9.16	11.1	17.50	34	15.99
CONTROL- 2	3.53	4.74	3.73	9.46	11.5	18.50	37	11.76
CONTROL- 3	3.47	3.57	3.85	9.15	11.1	17.50	34	12.62
GYPSUM 1.03g-1	3.48	4.41	4.08	10.08	12.3	26.00	52	10.15
GYPSUM 1.03g-2	3.54	4.44	5.00	6.66	8.1	22.50	45	14.64
GYPSUM 1.03g-3	3.56	4.35	4.00	7.77	9.4	24.00	48	11.18
GYPSUM 2.06g-1	3.53	3.93	3.43	8.42	10.2	33.00	66	7.64
GYPSUM 2.06g-2	3.49	4.22	3.10	7.73	9.4	25.00	50	8.65
GYPSUM 2.06g-3	3.47	4.22	4.15	8.00	9.7	41.00	82	7.81
GYPSUM 4.13g-1	3.50	4.12	4.55	9.20	11.2	49.50	99	7.19
GYPSUM 4.13g-2	3.50	4.13	3.78	5.90	7.2	51.00	102	6.22
GYPSUM 4.13g-3	3.63	4.10	3.10	5.05	6.1	35.50	71	7.10
GYPSUM 8.26g-1	3.52	3.93	5.23	8.19	10.0	108.5	217	4.29
GYPSUM 8.26g-2	3.54	4.03	3.98	8.01	9.7	79.00	158	4.37
GYPSUM 8.26g-3	3.59	4.00	3.65	10.07	12.2	83.50	167	3.75
CONTROL- 1	3.44	5.07	8.65	5.88	7.2	20.50	40	24.69
CONTROL- 2	3.44	4.67	4.85	8.95	10.9	15.50	30	16.55
CONTROL- 3	3.48	4.34	8.63	7.99	9.7	19.00	37	24.22
CALCITE 0.6g-1	3.70	5.15	5.40	6.31	7.7	25.00	50	14.70
CALCITE 0.6g-2	3.93	5.06	2.03	5.84	7.1	3.50	47	6.46
CALCITE 0.6g-3	3.76	4.88	2.25	6.14	7.5	23.50	47	7.06
CALCITE 1.2g-1	4.13	5.05	1.98	6.32	7.7	30.50	61	5.09
CALCITE 1.2g-2	4.08	5.08	2.28	7.72	9.4	31.50	63	5.48
CALCITE 1.2g-3	4.15	5.24	1.15	5.05	6.1	27.00	54	3.46
CALCITE 2.4g-1	4.83	5.63	0.68	7.44	9.0	39.50	79	1.49
CALCITE 2.4g-2	4.87	5.87	0.33	5.80	7.1	51.00	102	0.57
CALCITE 2.4g-3	4.80	5.88	0.33	6.80	8.3	38.50	77	0.71
CALCITE 4.8g-1	6.22	6.62	0.30	4.38	5.3	54.00	108	0.51
CALCITE 4.8g-2	6.26	6.67	0.30	4.48	5.5	129.5	259	0.22
CALCITE 4.8g-3	6.18	6.85	0.25	4.48	5.4	52.00	104	0.44

APPENDIX 7

Saturated paste cation concentrations. Units in ppm .

TREATMENT	Li	Na	NH4	K	Mg	Ca
CONTROL 1	0.5	75.1	98.0	11.6	29.3	68.1
CONTROL 2	0.3	48.3	38.9	5.3	12.6	31.9
ETTR.W 0.77g	0.4	65.7	27.2	4.5	14.5	57.0
ETTR.W 0.77g	0.8	87.9	67.8	7.4	28.9	91.9
ETTR.W 1.54g	0.6	88.1	40.2	6.6	41.2	81.4
ETTR.W 1.54g	0.6	88.8	31.6	5.8	26.5	119.0
ETTR.W 3.10g	0.8	105.1	28.1	7.8	49.5	180.4
ETTR.W 3.10g	0.8	102.3	34.0	9.0	58.6	201.4
ETTR.W 6.20g	0.8	119.3	36.0	7.9	74.1	361.1
ETTR.W 6.20g	0.6	99.6	31.2	8.0	91.5	448.6
CONTROL 1	0.6	68.7	57.1	7.9	19.8	57.3
CONTROL 2	0.6	84.3	109.8	12.2	27.7	59.4
CALCITE 0.60g	0.0	88.9	28.4	7.0	12.9	40.8
CALCITE 0.60g	0.0	74.0	52.9	5.9	14.0	49.5
CALCITE 1.20g	0.4	69.2	26.2	5.4	14.9	39.0
CALCITE 1.20g	0.0	77.4	33.4	5.4	15.2	43.1
CALCITE 2.40g	0.0	57.4	23.1	5.2	13.0	49.5
CALCITE 2.40g	0.0	70.8	12.5	5.7	8.8	46.5
CALCITE 4.80g	0.4	68.0	6.8	4.5	13.7	41.4
CALCITE 4.80g	0.4	70.7	14.2	3.9	15.7	43.6
CONTROL 1	0.0	54.0	80.0	12.0	18.0	44.0
CONTROL 2	0.0	82.0	58.0	17.0	20.0	84.0
GYPSUM 1.03g	0.6	84.0	100.0	13.0	77.0	195.0
GYPSUM 1.03g	0.6	105.0	72.0	14.0	57.0	202.0
GYPSUM 2.06g	0.0	112.0	78.0	11.0	91.0	341.0
GYPSUM 2.06g	0.0	110.0	100.0	14.0	103.0	413.0
GYPSUM 4.13g	0.0	98.0	120.0	13.0	117.0	535.0
GYPSUM 4.13g	0.0	139.0	114.0	18.0	110.0	512.0
GYPSUM 8.26g	0.0	212.0	170.0	28.0	146.0	583.0
GYPSUM 8.26g	1.5	138.0	95.0	17.0	117.0	596.0

APPENDIX 8

Saturated paste anion concentrations. Units in ppm.
Murphy-Riley spectrophotometric method (PO_4^{3-}-MR).

TREATMENT	F	Cl	NO2	NO3	PO4-IC	PO4-MR	SO4
CONTROL 1	0.0	79.4	0.0	395.5	60.9	51.4	134.0
CONTROL 2	0.0	36.4	0.0	143.7	54.8	92.4	68.5
ETTR.W 0.77g	0.0	30.5	0.0	66.0	23.5	28.8	248.5
ETTR.W 0.77g	2.7	41.1	0.0	113.1	22.0	51.4	177.5
ETTR.W 1.54g	0.0	37.4	0.0	68.9	25.8	27.1	418.8
ETTR.W 1.54g	0.0	48.8	0.0	103.8	26.5	23.8	432.3
ETTR.W 3.10g	0.0	49.0	0.0	66.6	26.3	26.0	751.5
ETTR.W 3.10g	0.0	54.4	0.0	136.3	0.0	10.5	891.4
ETTR.W 6.20g	5.3	37.9	0.0	92.4	0.0	6.6	1444.9
ETTR.W 6.20g	0.0	49.3	0.0	89.3	0.0	7.3	1467.9
CONTROL 1	0.0	60.6	0.0	241.2	75.4	127.3	89.1
CONTROL 2	0.0	93.9	0.0	477.1	74.3	108.2	128.5
CALCITE 0.60g	0.0	32.3	0.0	114.3	37.1	65.8	49.3
CALCITE 0.60g	0.0	40.2	0.0	168.5	27.5	48.2	65.4
CALCITE 1.20g	0.0	39.8	0.0	186.3	24.0	32.8	54.3
CALCITE 1.20g	0.0	41.1	0.0	190.6	38.7	54.7	68.5
CALCITE 2.40g	0.0	32.0	0.0	121.0	33.3	57.9	56.9
CALCITE 2.40g	0.0	32.4	0.0	83.9	28.8	41.8	52.6
CALCITE 4.80g	0.0	25.7	27.0	55.0	22.0	27.1	84.7
CALCITE 4.80g	0.0	29.0	25.4	108.0	18.0	20.2	59.1
CONTROL 1	0.0	63.6	0.0	307.6	53.5	82.4	122.1
CONTROL 2	6.5	74.7	0.0	251.4	79.1	114.0	124.0
GYPSUM 1.03g	0.0	53.6	0.0	167.6	49.8	72.3	947.7
GYPSUM 1.03g	2.7	60.9	0.0	122.4	44.4	67.3	860.7
GYPSUM 2.06g	0.0	50.7	0.0	122.5	33.1	38.2	1487.5
GYPSUM 2.06g	0.0	58.3	0.0	147.7	48.0	67.6	1605.3
GYPSUM 4.13g	0.0	55.9	0.0	181.8	33.5	33.9	1869.8
GYPSUM 4.13g	3.6	57.6	0.0	145.0	34.2	76.9	1152.0
GYPSUM 8.26g	0.0	82.1	0.0	181.9	53.6	119.4	2140.1
GYPSUM 8.26g	0.0	87.0	0.0	191.0	53.0	60.1	2158.0

APPENDIX 9

Cation/anion charge balance. Units in mmol_c/kg.

CHARGE- CATIONS	Li	Na	NH4	K	Mg	Ca	TOTAL
CONTROL 1	0.07	3.27	5.44	0.30	2.41	3.40	14.89
CONTROL 2	0.04	2.10	2.16	0.14	1.04	1.59	7.07
ETTR.W 0.77g	0.06	2.86	1.51	0.12	1.19	2.84	8.58
ETTR.W 0.77g	0.12	3.82	3.77	0.19	2.38	4.59	14.86
ETTR.W 1.54g	0.09	3.83	2.23	0.17	3.39	4.06	13.77
ETTR.W 1.54g	0.09	3.86	1.76	0.15	2.18	5.94	13.97
ETTR.W 3.10g	0.12	4.57	1.56	0.20	4.07	9.00	19.52
ETTR.W 3.10g	0.12	4.45	1.89	0.23	4.82	10.05	21.56
ETTR.W 6.20g	0.12	5.19	2.00	0.20	6.10	18.02	31.62
ETTR.W 6.20g	0.09	4.33	1.73	0.20	7.53	22.39	36.27
CONTROL 1	0.09	2.99	3.17	0.20	1.63	2.86	10.94
CONTROL 2	0.09	3.67	6.10	0.31	2.28	2.96	15.41
CALCITE 0.60g	0.00	3.87	1.58	0.18	1.06	2.04	8.72
CALCITE 0.60g	0.00	3.22	2.94	0.15	1.15	2.47	9.93
CALCITE 1.20g	0.06	3.01	1.46	0.14	1.23	1.95	7.83
CALCITE 1.20g	0.00	3.37	1.86	0.14	1.25	2.15	8.76
CALCITE 2.40g	0.00	2.50	1.28	0.13	1.07	2.47	7.45
CALCITE 2.40g	0.00	3.08	0.69	0.15	0.72	2.32	6.96
CALCITE 4.80g	0.06	2.96	0.38	0.12	1.13	2.07	6.70
CALCITE 4.80g	0.06	3.08	0.79	0.10	1.29	2.18	7.49
CONTROL 1	0.00	2.38	4.48	0.31	1.49	2.20	10.86
CONTROL 2	0.00	3.58	3.23	0.44	1.65	4.22	13.12
GYPSUM 1.03g	0.09	3.68	5.58	0.35	6.38	9.75	25.82
GYPSUM 1.03g	0.09	4.58	4.01	0.38	4.71	10.10	23.87
GYPSUM 2.06g	0.00	4.89	4.38	0.29	7.56	17.04	34.16
GYPSUM 2.06g	0.00	4.82	5.59	0.38	8.50	20.63	39.92
GYPSUM 4.13g	0.00	4.29	6.67	0.35	9.64	26.71	47.66
GYPSUM 4.13g	0.00	6.06	6.36	0.47	9.10	25.59	47.58
GYPSUM 8.26g	0.00	9.21	9.44	0.74	12.03	29.14	60.56
GYPSUM 8.26g	0.22	6.00	5.28	0.43	9.60	29.76	51.29

APPENDIX 9
CONTINUED

ANIONS	F	CL	NO2	NO3	PO4- (MR)	SO4	HCO3-	TOTAL
CONTROL 1	0.00	2.24	0.00	6.38	1.59	2.81	0.24	13.26
CONTROL 2	0.00	1.03	0.00	2.32	2.86	1.43	0.13	7.76
ETTR.W 0.77g	0.00	0.86	0.00	1.06	0.89	5.17	0.31	8.30
ETTR.W 0.77g	0.14	2.23	0.00	3.53	1.59	7.13	0.10	14.73
ETTR.W 1.54g	0.00	1.05	0.00	1.11	0.84	8.72	0.13	11.85
ETTR.W 1.54g	0.00	1.38	0.00	1.67	0.74	9.00	0.20	12.98
ETTR.W 3.10g	0.00	1.38	0.00	1.07	0.80	15.65	0.37	19.28
ETTR.W 3.10g	0.00	1.53	0.00	2.20	0.32	18.56	0.17	22.79
ETTR.W 6.20g	0.28	1.07	0.00	1.49	0.20	30.08	0.34	33.46
ETTR.W 6.20g	0.00	1.39	0.00	1.44	0.23	30.56	0.36	33.97
CONTROL 1	0.00	1.71	0.00	3.89	3.94	1.85	0.06	11.45
CONTROL 2	0.00	2.65	0.00	7.70	3.35	2.68	0.10	16.46
CALCITE 0.60g	0.00	0.91	0.00	1.84	2.04	1.03	0.06	5.87
CALCITE 0.60g	0.00	1.13	0.00	2.72	1.49	1.36	0.13	6.83
CALCITE 1.20g	0.00	1.12	0.00	3.00	1.01	1.13	0.08	6.35
CALCITE 1.20g	0.00	1.16	0.00	3.07	1.69	1.43	0.59	7.94
CALCITE 2.40g	0.00	0.90	0.00	1.95	1.79	1.18	0.71	6.54
CALCITE 2.40g	0.00	0.91	0.00	1.35	1.29	1.10	0.87	5.53
CALCITE 4.80g	0.00	0.72	0.59	0.89	0.84	1.76	2.03	6.83
CALCITE 4.880g	0.00	0.82	0.55	1.74	0.62	1.23	0.34	5.30
CONTROL 1	0.00	1.79	0.00	4.96	2.55	2.54	0.06	11.90
CONTROL 2	0.34	2.11	0.00	4.05	3.53	2.58	0.08	12.69
GYPSUM 1.03g	0.00	1.51	0.00	2.70	2.24	19.73	0.00	26.18
GYPSUM 1.03g	0.14	1.72	0.00	1.97	2.08	17.92	0.00	23.84
GYPSUM 2.06g	0.00	1.43	0.00	1.98	1.18	30.97	0.00	35.56
GYPSUM 2.06g	0.00	1.64	0.00	2.38	2.09	33.42	0.00	39.54
GYPSUM 4.13g	0.00	1.58	0.00	2.93	1.05	38.93	0.00	44.49
GYPSUM 4.13g	0.09	1.62	0.00	2.30	1.19	23.53	0.00	28.73
GYPSUM 8.26g	0.00	3.17	0.00	6.72	1.86	50.58	0.00	62.33
GYPSUM 8.26g	0.00	2.32	0.00	2.93	3.69	44.55	0.00	53.50

APPENDIX 10

Soil solution aluminium concentrations.

TREATMENT	CONCENTRATION (ppm)
CONTROL	0.042
CONTROL	0.092
CONTROL	0.083
CONTROL	0.065
CONTROL	0.649
ETTR. W- 0.77g	0.191
GYPSUM - 1.03g	0.224
GYPSUM - 1.03g	0.193
GYPSUM - 2.06g	0.305
GYPSUM - 2.06g	0.399
GYPSUM - 4.13g	0.444
GYPSUM - 4.13g	0.368
GYPSUM - 8.26g	0.412
GYPSUM - 8.26g	0.364

APPENDIX 11

Foliar composition data.
Trace element data are (Cu, Zn, Mn, Fe and B) measured in mg/kg.

TREATMENT	P(%)	K(%)	Ca(%)	Mg(%)	Cu	Zn	Mn	Fe	B
CONTROL-1	1.84	2.35	0.407	0.433	2.4	34.4	128	120	66.5
CONTROL-2	1.67	2.01	0.479	0.476	1.6	33.8	145	135	75.9
CONTROL-3	1.92	2.32	0.444	0.437	1.1	33.7	140	151	84.3
ETTR.W 0.77g-1	1.16	1.84	0.496	0.486	2.9	35.3	150	112	81.2
ETTR.W 0.77g-2	1.38	1.97	0.493	0.471	0.3	37.4	152	84	91.4
ETTR.W 0.77g-3	1.13	1.53	0.503	0.490	1.0	35.9	168	110	88.3
ETTR.W 1.54g-1	0.90	1.53	0.583	0.521	3.0	38.7	194	110	87.4
ETTR.W 1.54g-2	0.92	1.51	0.532	0.484	3.8	34.7	169	120	81.9
ETTR.W 1.54g-3	0.87	1.44	0.577	0.507	3.2	32.8	193	102	79.3
ETTR.W 3.10g-1	1.05	1.45	0.667	0.496	2.2	32.0	201	107	88.6
ETTR.W 3.10g-2	0.69	1.54	0.579	0.488	3.8	36.2	184	110	76.1
ETTR.W 3.10g-3	0.63	1.45	0.578	0.460	3.3	32.4	195	110	72.5
ETTR.W 6.20g-1	0.44	1.49	0.705	0.583	5.5	26.1	204	151	43.8
ETTR.W 6.20g-2	0.45	1.52	0.719	0.604	4.5	24.7	207	134	44.0
ETTR.W 6.20g-3	0.43	1.27	0.625	0.586	4.1	23.8	176	133	54.5
CONTROL-1	2.46	2.55	0.416	0.462	2.5	37.9	127	240	88.9
CONTROL-2	2.21	2.53	0.396	0.419	1.0	32.9	129	101	86.0
CONTROL-3	2.06	2.58	0.408	0.449	1.4	33.4	127	85	99.4
GYPSUM 1.03g-1	2.06	2.10	0.546	0.450	2.1	40.7	149	104	83.8
GYPSUM 1.03g-2	1.65	1.79	0.524	0.496	2.2	37.4	146	96	81.5
GYPSUM 1.03g-3	1.94	1.88	0.626	0.479	0.9	42.3	169	85	91.2
GYPSUM 2.06g-1	1.49	1.77	0.645	0.465	3.6	38.9	156	97	77.6
GYPSUM 2.06g-2	2.14	1.95	0.638	0.477	0.8	39.7	152	91	85.0
GYPSUM 2.06g-3	1.81	1.74	0.645	0.493	4.0	43.5	164	252	83.0
GYPSUM 4.13g-1	1.85	2.12	0.609	0.403	4.7	43.4	146	123	83.0
GYPSUM 4.13g-2	1.85	1.90	0.674	0.490	3.4	44.0	161	109	93.5
GYPSUM 4.13g-3	1.56	1.88	0.683	0.444	3.8	44.1	174	98	91.4
GYPSUM 8.26g-1	1.63	1.80	0.677	0.483	2.8	42.3	166	105	93.6
GYPSUM 8.26g-2	2.10	2.68	0.695	0.397	3.3	46.9	164	100	94.9
GYPSUM 8.26g-3	1.78	2.09	0.736	0.434	3.1	44.7	170	106	86.2
CONTROL-1	2.21	2.38	0.400	0.460	0.7	32.8	133	88	94.0
CONTROL-2	1.84	2.29	0.416	0.459	0.9	32.9	130	91	79.0
CONTROL-3	2.39	2.86	0.403	0.420	6.7	38.2	140	109	87.0
CALCITE 0.6g-1	1.79	2.01	0.534	0.423	1.0	32.6	124	84	67.9
CALCITE 0.6g-2	1.26	1.68	0.505	0.467	1.7	31.3	127	94	81.8
CALCITE 0.6g-3	1.49	2.11	0.522	0.434	1.5	31.9	116	108	76.4
CALCITE 1.2g-1	1.42	1.89	0.560	0.450	1.2	33.9	131	101	76.0
CALCITE 1.2g-2	1.62	2.29	0.646	0.433	2.7	34.2	157	99	65.9
CALCITE 1.2g-3	1.38	1.73	0.573	0.480	1.2	30.2	136	87	71.9
CALCITE 2.4g-1	0.98	1.70	0.741	0.447	4.3	25.0	114	109	44.2
CALCITE 2.4g-2	0.96	1.54	0.671	0.471	4.6	24.8	102	103	48.9
CALCITE 2.4g-3	0.54	1.55	0.726	0.454	5.0	22.9	121	109	46.3
CALCITE 4.8g-1	0.46	1.08	0.722	0.480	3.6	14.4	95	105	25.7
CALCITE 4.8g-2	0.47	1.20	0.712	0.517	4.8	15.6	102	111	26.6
CALCITE 4.8g-3	0.51	1.26	0.605	0.521	5.5	18.3	91	139	20.9