SLAGS AS AGRICULTURAL LIMES: REACTIVITY AND HEAVY METAL AND PHOSPHORUS BIO-AVAILABILITY

By

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DECLARATION

These studies have not been submitted in any form to another university and, except where acknowledged in the text, are the results of my own work.

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SUMMARY (ENGLISH)

Steel industry by-products (slags) are regularly used as agricultural limes on the South African Highveld where the soils are prone to natural and anthropogenic acidification. These materials are the products of a purification process aimed at extracting phosphorus and silica from iron (or related) ores. In the process several impurities such as heavy metals are incorporated into the slag. In certain quarters concern is being voiced about the environmental impact of these heavy metals.

Two pot experiments were conducted to test the heavy metal and phosphorus bioavailability from several commercial slags. Pot experiments differ from field experiments and heavy metal uptake is usually exaggerated in plants grown in pots. Furthermore, soil pH influences the mobility of heavy metals in soils. The limes were therefore applied to similar pH levels and the limes with high and low metal concentrations were compared.

The Resin Suspension Method (RH-value) was used as a reactivity parameter of the limes and a $Ca(OH)_2$ equilibration method was used to determine the lime requirement of the soils. Twelve limes were collected with the aid of the Registrar of Fertilisers and applied in the heavy metal experiment to obtain pH values of 5.8, 6.8, and 7.8. A further experiment to determine phosphorus availability was conducted using four slags to obtain pH values of 5.5, 6.0, and 6.5.

The heavy metal uptake was tested using spinach as test crop. The concentrations in the plants were high. There were no significant differences between the high and low metal containing limes. Spinach accumulates high concentrations of trace elements and therefore aggravates metal uptake compared to most other crops. The conclusion is that the use of slags poses little threat in the short term. Due to the nature of the experiments trial it is not possible to comment on the desirability of long-term slag use. Further research is required to determine the impact if soil heavy metal concentrations are increased and management practices lead to acidification.

The RH-value proved to be the most accurate reactivity indicator when compared to the Calcium Carbonate Equivalent (CCE) in HCl. Two different soil to solution ratios (1:1 and 1:2.5) in the $Ca(OH)_2$ determinations were used and compared with the pH at the end of the pot experiment. The 1:2.5 ratio combined with the RH-value gave pH predictions closest to the actual pH values. Although all the methods were relatively close to the actual values, the CCE HCl parameter led to wider variation in results. In limes with a small difference between the CCE HCl and RH values the predicted pH values also had a small difference. In the limes where the CCE HCl and RH values differed widely there was a corresponding large difference in predicted pH values.

In determining the P-availability from the slags it appeared as though the Si in the slags influenced the P-concentrations in the plants (spinach). In a soil with a low P-concentration the P-uptake was very low leading to the conclusion that the P was not available from the slags. This could also be because the P-levels in the slags were lower than reported by the producers and that the P desorbtion rate of the soil is very low. Due to the difficulty in differentiating between P reserves in the soil and P applied through the slags a different approach should be considered when testing P-availability from slags.

OPSOMMING (AFRIKAANS)

Staalverwerkingsnewe-produkte word gereëld gebruik as landboukalke op die Suid Afrikaanse Hoëveld waar gronde onderhewig is aan natuurlike en antropogeniese versuring. Hierdie materiale is die produkte van 'n suiweringsproses wat ten doel het om fosfor en silika van yster (of verwante) erts te ontrek. In die proses word verskeie onsuiwerhede soos swaar metale in die slak geïnkorporeer en het hierdie situasie gelei tot vrae oor die impak van dié metale op die omgewing en gesondheid.

Twee pot eksperimente is gedoen om die swaar metale en fosfor se bio-beskikbaareid vanaf die slakke te toets. Pot eksperimente verskil van veld eksperimente deurdat verhoogde opname van metale vanuit grond in potte gewoonlik plaasvind. Grond pH beïnvloed die mobiliteit van die swaar metale. Die slakke is dus tot soortgelyke pH teikens toegedien om die kalke met hoë en lae swaar metal konsentrasies te vergelyk.

Die Harssuspensiemetode (RH-waarde) is gebruik as 'n aanduiding van die kalke se reaktiwiteit en 'n $Ca(OH)_2$ ekwilibrasie metode is gebruik om die grond se kalkbehoefte te bepaal. Twaalf kalke is versamel met die hulp van personeel van die Registrateur van Misstowwe en is in die swaar metaal eksperiment toegedien om drie teiken pH waardes van 5.8, 6.8, en 7.8 te verkry. 'n Verdere eksperiment om fosfaat beskikbaarheid te bepaal is gedoen deurdat vier slakke toegedien is aan 'n verskillende grond tot pH teiken waardes van 5.5, 6.0, en 6.5.

Die swaarmetaal opname is bepaal deur die gebruik van spinasie as toetsgewas. Die vlakke was baie hoog in die plante. Daar was egter geen noemenswaardige verskil tussen die hoë metaal inhoud kalke en dié met laer vlakke nie. Spinasie akkumuleer hoë vlakke spoor elemente en vererger dus swaar metaal opname in vergeleke met ander gewasse. Die gevolgtrekking is dat die slakke min gevaar inhou in die korttermyn. Na aanleiding van die aard van die eksperimente is dit nie moontlik om kommentaar te lewer op die wenslikheid van die langtermyn gebruik van slakke nie. Verdere navorsing is nodig om die impak te bepaal wanneer swaar metaal konsentrasies verhoog word en bestuurspraktyke lei tot versuring van die grond.

Die RH-waarde is bewys as die mees akkurate aanduiding van reaktiwiteit indien vergelyk met die Kalsium Karbonaat Ekwivalent (KKE) in HCl. Twee verskillende grond-tot-oplossing verhoudings (1:1 and 1:2.5) in die $Ca(OH)_2$ bepalings was gebruik en is vergeyk met die pH waardes aan die einde van die eksperiment. Die 1:2.5 verhouding gekombineer met die RH-waarde het pH voorspelling gelewer wat die naaste aan die teiken waardes was. Alhoewel al die metodes waardes gelewer het wat redelik naby aan die werklike waardes was het die KKE in HCl parameter tot wyer variasie gelei. In kalke waar daar 'n klein verskil was tussen die KKE in HCl en RH waardes was daar 'n klein verskil in die pH waardes verkry. In kalke met 'n groot verskil tussen die KKE in HCl en die RH waardes was daar 'n ooreenstemmende groot verskil tussen die voorspelde pH waardes verkry.

In die bepaling van die P-beskikbaarheid van die slakke wil dit voorkom asof die Si in die slakke die P-konsentrasies in die plante (spinasie) beïnvloed het. In 'n grond met 'n lae P-konsentrasie was die P-opname laag wat lei tot die gevolgtrekking dat die P nie beskikbaar was vanuit die slakke nie. Dit kan toegeskryf word daaraan dat die P-vlakke in die slakke laer is as wat weergegee is deur die produseerders van die slakke en dat die P desorpsie tempo van die grond baie laag is. Na aanleiding van die onvermoë om te onderskei tussen P reserwes in die grond en die P toegedien deur die slakke sal 'n ander benadering oorweeg moet word wanneer P-beskikbaarheid van slakke bepaal word.

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CHAPTER 1

GENERAL INTRODUCTION

INTRODUCTION

Soil acidity is becoming a grave cause of concern in many parts of South Africa where many soils are very sensitive to acidification and where generally not enough lime is used. Liming materials vary considerably in type and reactivity and this contributes to the "confusion" of which lime and what quantity to use. Slags (metal industry by-products) are regularly used as a liming material on the South African Highveld due to its high acid neutralizing capacity, the proximity of the source and the nature of the soils in the area. Being a waste product, it does not cost the same amount as regular limestones and is therefore an attractive option in an industry where profit margins are low. It is furthermore beneficial to the industry to be able to use the waste product constructively as well as to remove it from the premises.

Agricultural Soil Acidification

Man induced acidification of soils is one of the major concerns in the agricultural and environmental fields today. The soil pH has a major influence on the availability of different nutrient elements (Fölscher, 1975; Sumner, 1975; Sumner, Fey & Noble, 1991) in losses through leaching of the basic cations, P fixation and N uptake by plants. It furthermore influences the pollution hazard of several heavy metals (Løbersli, Gjengedal & Steinnes, 1991). Not only does it impact on crop production on the high potential soils with high rainfall in southern Africa (Manson, 1995), but it also influences environmental aspects such as pollution of rivers and wetlands as well as increased uptake of hazardous elements by plants, animals and ultimately man.

It is estimated that in the summer rainfall area in South Africa west of the Drakensberg, a minimum of 2.7 million ha is acidified to some extent. This figure excludes the extent of acidified soils in areas of Kwa-Zulu Natal. It is furthermore estimated that a total of 2 million ha of land in the summer rainfall area is also affected by subsoil acidity (Beukes, 1995). Soil acidification occurs mainly in areas that are classified as sub-tropical with well drained soils, and in which the nitrification rate of applied N fertiliser is very rapid (Claassens, *et al.*, 2000). One such area in the summer rainfall region is the Highveld of the Mpumalanga Province where many soils are very sensitive to acidification (Fey & Dodds, 1998).

Many industrial activities influence the acidifying process through atmospheric pollution (Tyson, Kruger & Louw, 1988; Held, *et al.*, 1996), as well as agricultural and forestry activities (Fey & Dodds, 1998). One of the major causes of acid soils in agriculture is the oxidation of applied reduced N-fertilizers, as well as organic material, in the dryland production of crops (Theron & Haylett, 1953; Theron, 1961). This is a global problem, especially in tropical and sub-tropical regions – when reduced N-fertiliser is applied excessively (Wallace, 1994). Without an accompanying liming program, the large-scale application of acidifying fertiliser in summer rainfall production of crops leads to highly acidified soils, especially when well drained and poorly buffered (Adams & Pearson, 1969). Wallace (1994) states that ammonium sources of nitrogen produce the equivalent of 3.5kg sulphuric acid per kilogram nitrogen and that 3.57kg pure $CaCO_3$ per kilogram of applied nitrogen fertiliser is required to neutralise its effect. This translates into the necessity of applying the equivalent of a ton of pure calcite to neutralise the acidity generated by the applied N-fertiliser (Bornman, 1993).

For the effective uptake of nutrients by plants and therefore the effective utilisation of fertilisers, the soil pH must be at an optimum (generally between pH 5.5 and 6.5 in water for most commercial crops). The excessive use of acidifying fertilisers therefore has a negative effect on the uptake and utilisation of other nutrients, thereby increasing the cost of fertilisation. South African figures quoted by Bornman (1985) indicate that the use of N fertilisers increased drastically without an increase in the use of lime – a recipe for the large-scale acidification of soils. As mentioned earlier, this is a global problem, one that has also caused much comment in countries like the USA, Australia, and countries in South America.

Lime Reactivity and Lime Requirement

A factor compounding the problem of inadequate lime use is the fact that in some cases the reactivity of the lime is far from desired levels (Fölscher & Bornman, 1985; Claassens *et al.*, 2000). This would not be such a big problem if the users of the lime were correctly informed with respect to the reactivity of the lime they use. Lime from different sources and fineness react differently, therefore creating a further problem for the user. Bornman (1985) developed the Resin Suspension Method (RSM) to predict the reactivity of liming materials. This method, having gained wide acceptance in South Africa, still lacks the international exposure it deserves – an aspect addressed by Claassens *et al.*, (2000).

Slags as Liming Materials

Slags are regularly used as liming materials in agriculture due to its high acid neutralising capacity. They originate from a purification step in the manufacturing of steel and different alloys. Lime is added to the molten ore to precipitate different phosphorus and silica compounds that are naturally found in the ore. The precipitate forms foam that is separated from the melt and is discarded in heaps. From here the solidified slag is crushed and then used as and agricultural lime.

Slags contain impurities derived from ore processing, including many heavy metals that hold a potential threat to the environment. The type of impurity depends on the source of the ore and can reach levels of several parts per thousand. Many studies have been done on the effect of heavy metals in the environment and its bioavailability, but most of these have focused on sewage sludges. The "lack of interest" could possibly be ascribed to the fact that the application of slags increases the pH of the acid soils. The solubility or availability of many heavy metals is reduced and therefore poses a very decreased threat compared to metals applied in other materials such as sewage sludges.

In the past slags have also regularly been used as a phosphorus fertiliser mainly due to the high P content. Presently this is not the case due to lower P contents, although there is still the possibility of a beneficial effect on the mobilization of soil P through the application of silica in the slags (Hingston, *et al.*, 1967; Ivanov, 1992)

The guidelines in terms of recommended maximum levels of heavy metal application to soils accepted for South Africa are based on the use of sewage sludge and not slags. Maximum heavy metal concentration guidelines are sometimes difficult to use due to the naturally high concentrations of certain elements in South African soils. The Guidelines need to be refined and updated for the use of slags but this cannot be done without a proper understanding of how slags and the heavy metals therein behave after application. With ever increasing emphasis on and awareness of sound environmental practices, the use of slags has lead to questions with respect to its effect on the environment.

Testing of Slags

When the testing of slags in terms of heavy metal availability is considered there are several possible approaches. The ideal would be to test the identity and quantity of a metal that is released from the slag in the soil through different soil extraction procedures as well as uptake by different crops in the field. The time and cost implications for such tests are immense, especially if a whole range of liming materials have to be tested. A cost-effective alternative usually is the use of pot trials. Pot trials have the restriction that metal uptake by plants is normally exaggerated due to a combination of factors. This in turn leads to the lack of adequate reference materials due to the exaggerated metal levels in the plant. These levels could, if not evaluated in the proper context, lead to the making of erroneous conclusions. This study was therefore planned in the specific way as discussed in the following chapters, keeping in mind the restrictions imposed by the chosen method.

AIM OF THE STUDY

Considering the questions that arise during the use of slags as liming materials, it was decided to set up different trials to determine the plant-availability of heavy metals and phosphorus from these slags. The aim of the study comprises four objectives namely:

- Determine the identity and concentration of heavy metals, added to the soil through the application of slags, and its availability to plants. Furthermore, to determine whether these metals pose a threat to man or the environment and draw a conclusion concerning the desirability of using slags as liming materials.
- Determine the reactivity of the liming materials in the soil and make a deduction as to the desirability of the RH-value as a reactivity index in the determination of lime requirement.
- Compare the two reactivity determination methods used in South Africa today (the Resin Suspension Method and the Calcium Carbonate Equivalent in hydrochloric acid) in terms of accuracy through modelling.
- Determine the amount of P available to the plant from the applied slags and make deductions concerning the influence Si has on soil P and P applied.

CHAPTER 2

HEAVY METAL AVAILABILITY FROM SLAGS

INTRODUCTION

Slags are often used as agricultural limes due to its high CCE when finely ground. The area around Middelburg and Witbank on the Eastern Highveld of South Africa has soils that are prone to natural and man induced acidification and also has two steel producers that produce a large amount of slags. Due to the proximity of the source and the acidity problem this is also the area with the highest probable use of slags.

These slags contain impurities in the form of heavy metals and in some cases these impurities can reach levels of several parts per thousand. Although this is a cause of concern in the environmental field today due to possible pollution of whole ecosystems and subsequently the food chain, very little has been published in South Africa concerning the hazard posed by the heavy metals contained in the slags.

Testing heavy metals for bioavailability is problematic due to a variety of reasons. These include differences in test crops, extraction methods, test conditions, and lack of adequate reference crops or values. A proper understanding of all the factors is a prerequisite to assessing materials for the bioavailability of the metals that it contains.

The Use of Slags as Liming Materials

Lime can be applied in different forms of which calcitic and/or dolomitic lime is known best. Other liming materials include different slags derived from the processing of steel. Lime has a rather uniform composition and the neutralising reaction is thus quite simple. In water $CaCO_3$ dissolves and hydrolyses to form OH^- as follows:

$$CaCO_3 + H_2O \Leftrightarrow Ca^{2+} + HCO_3^- + OH^- \qquad (2.1)$$

The solubility of lime in water is very low and the neutralising effect is due mainly to a contact exchange reaction on the soil particle surface (Jenny and Overstreet, 1938; Warfvinge and Sverdrup, 1989). The produced OH^- ions react with H_3O^+ ions that are formed by the oxidation of reduced N and with exchangeable Al^{3+}. The equation for the complete reaction is:

$$2\ \text{Al-clay} + 3CaCO_3 + 3H_2O \Leftrightarrow 3\ \text{Ca-clay} + 2Al(OH)_3 + 3CO_2 \qquad (2.2)$$

The slag's composition differs due to different processes used in the processing of steel, therefore the neutralising reaction is not precisely known. It is not a pure carbonate but also contains Ca-silicate and could react (together with other constituents) in the following manner:

$$SiO_5Ca_3 + 6H^+ \Leftrightarrow 3Ca^{2+} + SiO_2 + 3H_2O \qquad (2.3)$$
$$SiO_4Ca_2 + 4H^+ \Leftrightarrow 2Ca^{2+} + SiO_2 + 2H_2O \qquad (2.4)$$
$$2CaO.Fe_2O_3 + 16H^+ \Leftrightarrow 2Ca^{2+} + 4Fe^{3+} + 8H_2O \qquad (2.5)$$
$$FeO.MnO + 4H^+ \Leftrightarrow Fe^{2+} + Mn^{2+} + 2H_2O \qquad (2.6)$$
$$CaO + H_2O \Leftrightarrow Ca(OH)_2 \qquad (2.7)$$
$$Ca(OH)_2 + 2H^+ \Leftrightarrow Ca^{2+} + 2H_2O \qquad (2.8)$$
$$MgO + 2H^+ \Leftrightarrow Mg^{2+} + H_2O \qquad (2.9)$$

(After Balcázar, 1998, as quoted in Vanacker, 1999).

Several types of slags are used as agricultural liming materials, such as blast furnace slag, open-hearth slag, and basic slag. These are all the by-products of steel processing plants and their composition depend on the raw material (ore), the specific process, and the product of the plant. Due to this, Ca and Mg aluminosilicates, Fe, Mn, phosphates, and other elements such as Cr, Ni, Co, Cd, Cu, Zn, Mo, and Ba may occur in differing quantities. Some of the elements can reach concentrations of several parts per thousand, which are then added to the soil.

Two main forms of slags are produced in and distributed from the heart of the Loskop Dam catchment area near Witbank and Middelburg. This is also the area in which soil acidification is reaching critical proportions in parts, and in which many soils are very sensitive to acidification (Fey & Dodds, 1998). The waste product, if finely ground, has a high Calcium Carbonate Equivalent (CCE) and is relatively cheap in comparison to other mined liming materials. Due to high transport costs and the proximity of the slags, large quantities are used in the area. As mentioned earlier, a source of concern is the fact that slags contain varying amounts of trace elements and heavy metals and that although most of the elements are not plant available at the pH levels in the soil after liming, the build-up of these elements could be detrimental in the long-term. Table 2.1 gives an indication of the average composition of the slags.

TABLE 2.1. Average composition of slags before refining into agricultural lime (Source: Columbus Steel and Highveld Steel).

Chemical Compound	Columbus Steel %	Highveld Steel %
Al_2O_3	2.3	1.3
CaO	49.5	55.4
Cr_2O_3	3.0	-
FeO	0.6	16.7
MgO	11.4	6.5
MnO	0.9	1.1
P	-	0.4
S	-	0.4
SiO_2	30.6	17.9
TiO_2	0.7	-
V_2O_5	-	1.6

Heavy Metals in Soils

In order to better appreciate the effect of added heavy metals to the soil through the application of slags, it is necessary to have an idea how these metals act in soils. It is furthermore necessary to understand how different soils, originating from different parent materials and soil processes, will react to the addition of these slags in terms of the presence and bio-availability of these metals. Although "heavy metals" are by definition those elements having a density greater than five, here it will refer to the metals generally used and discharged by industry (Jones & Jarvis, 1981). The metals discussed in this study all occupy positions in the first transition series of the periodic table.

In recent years many comprehensive works (Kabata-Pendias & Pendias, 1992; Alloway, 1995) as well as research publications on the bio-availability and contamination of heavy metals in soils have been published, the scope of which is too wide to cover in this study. Many of these concern pollution with heavy metals through the application of sewage sludge (Steyn, 1994; Tsadilas, *et al.*, 1995; Brallier, *et al.*, 1996; Hooda, *et al.*, 1997) but very few touch on pollution through the use of slags (Amaral Sobrinho, *et al.*, 1992; Amaral Sobrinho, *et al.*, 1993). Different researchers and institutions developed many techniques and guidelines to evaluate the data, but due to variation in all the aspects of research, there is still a long way to go in standardising testing procedures and reference levels of these elements in soils (McLaughlin, *et al.*, 2000). The fact remains that the use of materials that contain heavy metals in quantities to pose a threat to the environment leads to the necessity of proper research and guidelines to minimise the material's impact on the environment.

McLaughlin, *et al.*, (2000) discuss several influences on concentration, activity and speciation of metals in soil solutions that affect the phyto- or bioavailability of metals in the soil. It is stated that the above mentioned, as well as plant genotypic variation in metal uptake or tolerance, and the complexity involved with the plant-rhizosphere-soil interaction all contribute to making soil testing for heavy metal phyto-availability inherently difficult. They do a review on literature on the correlation of extraction techniques with the bioavailability of heavy metals and their conclusion is that "no single soil test will outperform others in all situations…" A five points set of quality screening criteria is outlined and the option of the partitioning of calibration data in regions, or according to an environmental endpoint (plant toxicity, microbial toxicity, crop metal uptake) is urged. Furthermore, pathways and test methodologies are suggested to focus and improve research efforts in the soil testing for metals and metalloids.

Several factors may influence the bioavailability of heavy metals in the soil. According to Løbersli, *et al.*, (1991), one of these – soil acidity – is a major factor. Although heavy metals occur in soils as rare elements, the human mediated addition of these to soils could increase their uptake by plants, thereby increasing the toxic effect it has on plants and plant consumers. The capacity of the soil to adsorb or precipitate metals generally increases with increasing pH and a maximum is reached at neutral or slightly alkaline conditions, with As, Mo, and Se being exceptions. Cr^{6+} is also an exception, being more mobile under alkaline conditions (Adriano, 1986; McLaughlin, *et al.*, 2000). As the pH decreases there is a strong increase in the solubility of heavy metal complexes, which leads to higher bioavailability and consequently a possible higher uptake by plants (Mayer, 1991).

Soil pH

The effect pH has on the heavy metal bio-availability has been confirmed in many different studies that range from metal availability after sewage application (Hooda, *et al.*, 1997) to the adsorption of metals on clay fraction minerals (Jinadasa, Dissanayake, & Weerasooriya, 1995; Kaupenjohann and Wilcke, 1995; Schwarz, *et al.*, 1999). The reasons vary from its influence on the dominant species in solution at different pH levels (McLaughlin, *et al.*, 2000) to the altered stability (or solubility) of minerals containing the metals during the addition or removal of H^+ (Schwarz, *et al.*, 1999). For most metals plant content is positively correlated with soil solution concentration, which, in turn, is directly related to soil pH (Kabata-Pendias & Pendias, 1992).

Cr^{3+} is considered very stable in soils and at a pH of 5.5 and higher is almost completely precipitated (Kabata-Pendias & Pendias, 1992) whereas Cr^{6+} is more stable at low pH than in neutral to alkaline (pH 7.5) soils (Grove and Ellis, 1980). Jinadasa, *et al.*, (1995) found that Cr was more strongly adsorbed on synthetically prepared goethite than Cd and Pb, and sorption strength was strongly pH-dependent.

Both the Co (Steyn, 1994) and Ni (Gupta and Gupta, 1998) availabilities are also strongly influenced by pH with increased availability at low pH.

In soils the available Mn fraction is very low (traces) but increases with decreasing pH and reduced conditions. It is less available in alkaline soils and there are not many reports of toxicity in plants (Kabata-Pendias & Kabata, 1992).

Many remedies for toxic levels of metals in soils have been proposed and tested but in most cases metal toxicities are alleviated through the addition of lime (Hooda, *et al.*, 1997; Kabata-Pendias & Pendias, 1992), thereby increasing the soil pH and lowering the activities of the metals in solution.

Speciation and Valency

Chrome's valency ranges from +2 to +6, but its natural occurrence is restricted to +3 (chromic) and +6 (chromate), with Cr^{6+} being more soluble than Cr^{3+}. Cr can form different complex ionic species e.g. $Cr(OH)^{2+}$, CrO_4^{2-}, CrO_3^{3-}. Chromite (the mineral) is the most common due to its resistance to weathering, but with continued oxidation Cr forms the more mobile chromate ion (CrO_4^{2-}) (Grove and Ellis, 1980; Kabata-Pendias & Pendias, 1992). Biological reduction of Cr^{6+} to Cr^{3+} is common in soils but biological oxidation of Cr^{3+} to Cr^{6+} has not been reported (Bartlett and Kimble, 1976; Cifuentes, Lindemann, & Barton, 1996).

Ni^{+}, Ni^{2+} and Ni^{3+} are the possible valencies of Nickel (Stoeppler & Ostapczuk, 1992) but in soils it is mainly found as Ni^{2+} and very rarely as Ni^{+} (Pais & Benton-Jones, 1997). Ni is most mobile in sewage sludge where it forms organic chelates.

Co^{2+} and Co^{3+} are the oxidation states in which Co can occur in nature. Although organic chelates of Co are relatively mobile, Co is generally unavailable to plants in high organic content soils even though the Co content may be high. (Kabata-Pendias & Kabata, 1992).

Mn is found in soils in three oxidation states with the Mn^{2+} state being soluble, mobile and easily available to plants. Mn^{4+} is practically insoluble, non-mobile and unavailable, while Mn^{3+} is relatively scarce (Aubert and Pinta, 1977).

Adsorption of Heavy Metals on Different Soil Surfaces and Soil Structural Aspects

The clay particles in the soil can adsorb heavy metals when added; thereafter the risk of contamination depends on the stability of the sorbed phase. For this reason it is necessary to have an accurate and thorough knowledge of the factors that influence the stability of the sorbed species (Fendorf & Gunter, 1996).

The clay content and clay type of a soil can often positively be correlated with the amount of metals taken up by plants (Kabata-Pendias & Kabata, 1992; Hooda, *et al.*, 1997) In many cases the horizon in which an increased content of metals is found, the metal is associated with certain clay minerals (illuvial horizon) or organic material in the A-horizon (Aubert and Pinta, 1977). Structural aspects of soils also play a role in that lithogenic metals such as Al, Fe, or Cr show lower total concentrations on aggregate surfaces than in aggregate cores, whereas ubiquitously deposited metals such as Cd, Pb, or Zn show higher total concentrations on aggregate surfaces (Wilcke and Amelung, 1996).

Different clay minerals in the soil have different affinities for metals. This effect is mainly attributed to the effects of pH on variable-charged sorption sites, which also leads to the instability of Cr^{6+} at higher pH, mainly due to the form of the oxyanions (CrO_4^{2-}) in solution (McLaughlin, *et al.*, 2000). Jinadasa, *et al.*, (1995) found that the metal ion adsorption on synthetically prepared goethite was strongly pH-dependent and that Cr was more strongly adsorbed than Cd and Pb on it. Fendorf and Gunter (1996) found that Cr^{3+} was more stable when precipitated on goethite than on silica. When a soil system buffers the addition of acid, heavy metals (e.g. Cr) bound in silicates are released into the soil solution due to the silicate's destruction during the buffering process (Kaupenjohann and Wilcke, 1995).

The time elapsed after application of heavy metals to the soils also plays a role. Grove and Ellis (1980) found that all extractable Cr fractions, except amorphous and crystalline forms, decreased considerably after a few days to weeks after application. This was especially so for Cr^{3+} in moderately acid to neutral soils and Cr^{6+} in acid soils. Water extractable Cr^{6+} decreased only over several weeks in moderately acidic to alkaline (pH 7.5) soils.

Co is relatively mobile in oxidising acid environments but does not migrate in a soluble phase due to highly selective adsorption by Fe and Mn oxides (especially if the pH increases) (Kabata-Pendias & Kabata, 1992).

Due to the different minerals and conditions in soils, the metals exhibit different stabilities according to the results of different authors. Paz-Gonzáles, Taboada-Castro, & Taboada-Castro (2000) found, confirming the results of other studies, that the mobility of certain metals decreased in the order Zn > Cu > Ni > Co > Cr. Jinadasa, *et al.*, (1995) found that the metal ion adsorption capacity order on goethite was $Cr^{3+} > Pb^{2+} > Cd^{2+}$. In a study on sewage amended soil the sequence of metal concentration was found to be Zn > Cu > Ni > Cd > Pb (Hooda, *et al.*, 1997). In another study in Australia (Phillips and Chapple, 1995) the mobility decrease was Zn > Cr ≈ Cu ≈ Pb. Schwarz, *et al.*, (1999) found that, in a trial on the heavy metal release from soils during acidification, Cd was the most and Cr the least mobile.

From the above it is clear that different soil conditions and minerals lead to different metal availabilities – an aspect discussed in detail by McBride (1989).

Natural Occurrence

The natural Cr content in soil varies due to texture (high in clay, low in sand), organic C content, iron oxide content and parent material (Aubert and Pinta, 1977). Ultramafic and mafic rocks contain levels of a few parts per thousand and acid igneous and sedimentary rocks ranges between 5 to 120 $mg.kg^{-1}$ (Kabata-Pendias & Pendias, 1992).

Total Cr levels in SA soils are generally higher than the maximum values stipulated by law (Steyn, personal communication). Paz-Gonzáles, *et al.*, (2000) also indicated that soils formed on ultramafic rocks had total Cr and Ni levels higher than acceptable, but this was due to its lithogenic origin. A site in Brisbane, Australia, was concluded to pose no environmental and health risk although the total concentration of some metals was up to 40 times the acceptable values adopted for Australia. This was due to the metals (including Cr) being only slightly leachable and very immobile (Phillips and Chapple, 1995).

Total Ni content in soils varies from traces to more than 5000 mg.kg^{-1} in ultrabasic rocks. Generally older soils, peaty and sandy soils contain the lowest levels, and clayey and high organic content soils contain higher levels. Total Co levels vary from 0.05 to 300 mg.kg^{-1}. (Aubert and Pinta, 1977). Ni and Co is closely associated with Fe and Mn oxides and organic material (chelates) and Ni is similar to Co but is less strongly fixed to soil components (Kabata Pendias & Pendias, 1992), therefore more mobile.

Total Mn levels in soils vary from traces to 10 000 mg.kg^{-1} (Aubert and Pinta, 1977) but pose no threat due to the prevalent pH levels and redox conditions in most soils.

Extraction and Metal Interaction

Ethylenediaminetetraaceticacid (EDTA) extraction was found or proposed by many researchers to give a very good indication of the pollution hazard of heavy metals. Paz-Gonzáles, *et al.*, (2000) found, in a study in Northwest Spain, that the EDTA-extractable heavy metal levels were generally low (no indication was given as to the type of EDTA salt used). EDTA was also found to be a reliable test for predicting plant available metals (Hooda, *et al.*, 1997) and Brummer and van der Merwe (1989) indicated that the NH_4-EDTA-extractable heavy metals concentration gives a better estimate of those potentially available, and therefore suggested it to be used in the establishing of preliminary threshold values for heavy metals for South African soils. Canet, *et al.*, (1998) found that only small amounts of Cr could be extracted with Na_2EDTA after sludge application increased soil heavy metals contents.

Steyn (1994) emphasises the influence pH has on the extractant used. In many cases the buffer capacity of NH_4-EDTA had been exceeded by the application of lime to the test soil. Some of the other extractants (Ammonium Bicarbonate-Diethylenetriamine-pentaacetic Acid - AB-DTPA) did not have the same problem due to it having been developed to prevent competition with Ca^{2+}. The extracting agents used generally gave a good indication of the bio-available metals and indicated a decrease with increased $CaCO_3$ applications. The EPA method 3050, though, did not predict the bioavailability of metals well at all. De Abreu, *et al.*, (1995) however, state that several extractants were ineffective in evaluating metal availability in wheat and beans.

Many strong extracting agents exist and can be used to extract metals like Cr after it has been strongly sorbed by the solid phase of the soil. Grove and Ellis (1980) found that extractable Cr fractions were low in all but the strongest extracting agents and that water extractable Cr was insignificant compared to the stronger extracting agents.

Crop used and Total Soil Metal Content

Hooda, *et al.*, (1997) conducted a trial to determine the heavy metal availability from soils treated previously with sewage sludge and in which the sludge had time to equilibrate with the soil. The results indicated that the crop used and type of metal analysed influenced the amount that was taken up. A further factor was the total metal content in the soil. Cd, Ni, and Zn levels showed the greatest increases over background levels and Cu and Pb less so, with spinach (known for its hyper-accumulating tendencies) accumulating the most, carrot intermediate levels and wheat the least. Bhattacharjee, *et al.*, (1998) found relatively wide variation in the metal contents of spinach in a study on natural soils.

The variation described above is caused by many differences that exist in plants with respect to plant genetic variation in metal uptake or tolerance, variation within cultivars, the soils on which these plants evolved, and the complexity involved with the plant-rhizosphere-soil interaction (McLaughlin, *et al.*, 2000). Steyn (1994) stresses the point that simplified assumptions concerning which plants absorb the most trace elements cannot be made and that it depends on the species of plant and the metal concerned.

Sampling and Testing

Cr occurs ubiquitously in nature; therefore care must be taken to avoid sample contamination during collection, preparation and analysis. It is very valuable to use standard reference materials to aid in the accurate determination thereof (Miller-Ihli, 1992). Miller-Ihli (1992) goes on to extensively describe sample collection, handling, and preparation strategies to avoid sample contamination.

Sampling and testing for Ni and Co levels above 0.2 $mg.kg^{-1}$ poses no problem. For lower levels there are many pollutants in a laboratory i.e. stainless steel instruments and dust, and care should be taken in sample preparation and handling (Stoeppler & Ostapczuk, 1992).

The preferred method of testing for most heavy metals is with inductively coupled plasma-mass spectrometry (ICP-MS) although it is still a relatively new technique (Steyn, 1994). It is a relatively simple technique but it is very sensitive and can detect elements at levels below $\mu g.dm^{-3}$. Steyn (1994) stipulates the capabilities of ICP-MS and discusses the requirements for sample preparation when determining heavy metals by ICP-MS.

Testing for Cr speciation can be problematic and several researchers have developed or attempted to develop ways to do this (Fodor and Fischer, 1995). Prokisch, *et al.*, (1995) describes a simple and inexpensive method for determining the speciation of Cr in soil extracts by using acidic-activated aluminium oxide to separate Cr^{3+} and Cr^{6+} during testing.

Essentiality, Toxicity and Plant Uptake

Many of the heavy metals added to the soil are also essential elements for plants and or man. The levels needed by either differ but excessive amounts can lead to health complications and even death in man. An example is Cr^{3+} that is essential to animals and man at low levels to maintain normal glucose metabolism (Recommended Daily Allowance (RDA) levels of 50 to 200 $\mu g.day^{-1}$), but at high levels as Cr^{6+} it is toxic to plants and carcinogenic in animals and man (Miller-Ihli, 1992). Table 2.2 summarises the main aspects concerning the elements of interest in this study.

TABLE 2.2. Heavy metal content, essentiality and toxicity in plants, animals, and man (After Pais and Benton Jones, 1997).

Element	Content in plants (mg.kg^{-1})	Reference plant (mg.kg^{-1})	Phyto-toxicity (mg.kg^{-1})	Essential for plants	Essential in animals/ man	RDA in man mg.day^{-1}
Cobalt (Co)	Legumes 0.10-0.57 Grass 0.03-0.27	0.2	-	No (Suggested for legumes)	Yes	-
Chromium (Cr)	0.02-0.2	1.5	>10	No	Yes	0.05–0.2
Manganese (Mn)	10-500	200	Varies largely	Yes	Yes	0.4-10
Nickel (Ni)	0.3-3.5 (pasture plants)	1.5	Varies largely	Suggested	Yes	0.3-0.5

* Recommended Daily Allowance

Although available Cr^{6+} is toxic to plants and animals (Miller-Ihli, 1992), the uptake of Cr from soils by crops is generally insignificant (Gupta & Gupta, 1998) due to the strong adsorption thereof on the clay fraction in soils, therefore posing a minimal hazard to plants and soil organisms (McLaughlin, *et al.*, 2000).

Some plants act as hyperaccumulators of certain elements. An example is Ni where concentrations of more than 6000 mg.kg^{-1} were found in plants grown on soils with elevated Ni levels. The Co content of foodstuffs (e.g. cabbage) may be as high as 100 mg.kg^{-1} (Kabata-Pendias & Kabata, 1992).

Mn is readily taken up by plants, therefore the plant Mn concentration should be a direct function of the soluble Mn pool in soils (Kabata-Pendias & Kabata, 1992) with deficiencies generally experienced on alkaline soils and toxicities in acid soils with pH levels much below 5 (Aubert and Pinta, 1977).

Acceptable Levels – Legislation and Suggested Levels

Existing guidelines (Table 2.3) set the maximum permissible levels of contaminants that can be added to the soil in South Africa. These guidelines are for sewage sludge but could also be used for liming materials. When the levels of these elements are considered in the soil, the practice in the past was to use total concentration values. McLaughlin, *et al.*, (2000) indicates that during recent years the trend has shifted more to "mobile" concentration. Brummer and van der Merwe (1989) indicated that the NH_4-EDTA-extractable heavy metals concentration gives a better estimate of its potential availability and therefore suggested the levels in Table 2.3 as the preliminary threshold values. Threshold values for application of metals at certain soil pH levels were also given but these are not necessarily applicable in the case of slags due to the rise in pH it brings about.

TABLE 2.3. Maximum permissible contaminant concentration ($mg.kg^{-1}$, dry basis) in ameliorants (Department of National Health and Population Development, 1991) and suggested preliminary threshold value for NH_4-EDTA (pH 4.5) extractable heavy metals for the soils of South Africa. (Brummer and van der Merwe, 1989)

Element	Maximum permissible concentration ($mg.kg^{-1}$)	Suggested threshold values (NH_4-EDTA extractable) ($mg.kg^{-1}$) soil
Cd	20	1
Co	100	10
Cr	1750	50
Cu	750	60
Hg	10	1
Mo	25	-
Ni	200	20
Pb	400	100
Zn	2750	100
As	15	-
Se	15	-
B	80	-
F	400	-

MATERIALS AND METHODS

Introduction

Considering all the variables involved in the testing for heavy metal availability it was decided to test the liming materials on a "worst case scenario" with spinach as a test crop. The trial had to discriminate between the limes in terms of metal availability, therefore a suitable control treatment was needed that could equal the neutralising capability of the slags but without the metal content. A normal blank treatment would not suffice due to the major pH difference between the blank and the slag treatments. The ideal control treatment would be pure lime, which could be tested at similar pH levels in the soil, therefore removing the influence of the background metal concentration in the soil. In this trial lime that contains no metals or very low concentrations of heavy metals was used as a control.

Liming Materials

Twenty-four different lime samples were collected from different sources with the aid and under the supervision of representatives from the Registrar of Fertilisers. The lime samples were put through a splitter to ensure homogeneity and sealed on site in tins. From the 24 limes only 12 were selected due to their origin and heavy metal content. Of the 12 selected samples five were slags, two from paper mills and five were natural limes.

Soil

The soil was chosen from the Eastern Highveld – an area where there is an increased probability of farmers using slags as agricultural limes due to the proximity of the source. Some chemical and physical properties of the soils are listed in Table 2.4.

TABLE 2.4: Selected chemical and physical properties of the soil used in the study.

Parameter	
Texture	Sandy Clay Loam
$pH_{(Water)}$	5.1
$pH_{(KCl)}$	3.9
Ammonium acetate extractable: ($mg.kg^{-1}$)	
Ca	622
Mg	151
K	217
Na	0
P – Bray 1 ($mg.kg^{-1}$)	21.93

Heavy Metal Content of Limes

To determine the identity and approximate concentration of the heavy metals that could pose a danger after the application of slags, a semi-quantitative scan (ICP-MS) was done on the twenty-four liming materials by the Institute for Soil, Climate and Water (ISCW). From the scan certain limes were selected that contain high levels of: Co, Cr, Mn, and Ni. On the grounds of the scan results, eight of the liming materials were further digested with $HClO_4/HNO_3$. The procedure followed was the same as a wet digestion for plant materials as prescribed by ALASA (1998) with the exception that a lime sample of 10g was digested in $100cm^3$ of the acid. The resultant solution was tested quantitatively Cr, Co, and Ni with ICP-MS, and Mn by Atomic Adsorption Spectrophotometry.

The liming materials that contained no heavy metals were used as reference materials (controls). No known reference values or plant materials were available and this was exacerbated by the fact that plants in pots do not perform like plants in the field (Steyn, 1994), therefore leading to the generation of results that will not correlate well with values from reference plants from the field. The main motivation therefore was to minimise the variability by subjecting each plant to the same set of variables except for the type of lime and therefore also the respective heavy metals.

Crops

Two crops were used namely wheat (*Triticum aestivum* ssp. *vulgare* McKey) and spinach (*Spinacia oleracea* L*)* Spinach was chosen due to its hyper-accumulating properties (Hooda, *et al.*, 1997), and wheat to verify heavy metal levels if excessive levels were found in the spinach. The crops were grown in the soil for a period of eight weeks, after which it was harvested. A follow-up trial with eight weeks of growth (wheat) was also done although the data is not presented here.

Treatments

The twelve liming materials were added to the soil at three different rates to attain pH target values of 5.8, 6.8, and 7.8. Each treatment was replicated four times. For a detail exposition of the reaction of the liming materials in terms of pH see Chapters 3 and 4. The follow up trial made use of the same soil and pots with a new growth of spinach and wheat.

Fertilisers

The plants in the pots were top dressed through the growing season with NH_4NO_3 and KCl to ensure adequate growth.

Harvest, Sample Preparation and Plant Analysis

After the specified growth period the plants were harvested, washed, and dried in an oven at 65°C overnight. The dried plant material was weighed and the spinach and wheat ground in a mill with tungsten blades to avoid Cr contamination.

An H_2SO_4 digestion (ALASA, 1998) was used to determine the P and N content and an $HClO_4$:$2HNO_3$ digestion (ALASA, 1998) to determine the heavy metal and trace element content of the spinach. Co, Cr, and Ni were determined by ICP-MS, and Mn by Atomic Adsorption Spectrophotometry.

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Due to cost constraints only the spinach of the first harvest was analysed for heavy metals. Only the limes with high heavy metal contents and ones with low contents were used during analysis of plant material. This served a two-fold purpose namely to amplify the differences between the limes without cluttering the graphs with additional data, and to be able to do more of the relevant determinations without wasting funds.

Variation in the Cr values prompted a further Cr analysis as described above.

Statistical Analysis

Due to the cost involved the replicates of the plant samples were pooled before chemical analysis. No statistical evaluation could therefore be done on the results of the heavy metal analysis results due the fact that there was only one determination per sample. The R-squared value (coefficient of determination) in the figures indicates the variation of the values on the Y-axis that is “accounted for” by linear (or other) regression of the Y values on the X values (Samuels, 1991). A value of 1 indicates a very good correlation between the data sets. Note that if the regression line nears horizontal the R-squared value nears 0.

Soil Sampling and Sample Preparation

Soil samples were taken after the first harvest of the spinach and wheat from each pot. After the second harvest of wheat the soil was removed from the pots and a representative sample was taken from each pot. The samples were dried in an oven at 65°C overnight and stored until further determinations had to be done.

EDTA Extractions

Due to cost implications only some of the soils treated with slags were selected to test for NH_4-EDTA extractable metals (two to three soils per metal). This was done to compare metal levels in the soils with those found in the plants (after Brummer and van der Merwe (1989)) and was done after the completion of the follow up trial. The method as described by The Non-affiliated Soil Analysis Work Committee (1990) was used.

NH_4-EDTA was chosen as general extracting agent due to its regular use in other studies and the fact that Brummer and van der Merwe (1989) proposed it as the standard for heavy metal testing in terms of potentially plant available metals in SA. Furthermore, the data produced could be compared with data from numerous other studies.

RESULTS AND DISCUSSION

Chromium

Table 2.5 indicates the amounts of lime added to the pots to attain the desired pH, the Cr content of the limes as well as the increase in Cr concentration per pot. In Table 2.6 the concentration of Cr in the leaves of the spinach and the increased uptake compared to the control are indicated.

Figures 2.1 and 2.2 indicate the Cr concentration of the spinach leaves for each lime and as a trend against the resultant pH values respectively. There is no clear pH trend in the Cr uptake discernable from Fig. 2.2.

An aspect that influenced the results is the interference of chlorine compounds with Cr in ICP-MS determination when perchloric acid is used. Cr is known for its difficulty in determination due to its ubiquitous nature. Wet digestion in nitric acid alone did not prove satisfactory in a study by Blincoe, *et al.*, (1987). Due to the digestion procedures used in this trial ($HClO_4/HNO_3$) the data was most probably influenced by interferences caused by $^{35}ClOH^+$ and $^{40}Ar^{12}C^+$ during the determination of ^{52}Cr (Steyn, personal communication). Perchloric acid is not normally used when determining Cr by ICP-MS. Therefore the values presented in the two tables and figures are not reliable and the data of very little value.

TABLE 2.5. Chromium content of limes and amounts of lime and Cr added per pot.

Lime no	Rate	Cr Content of Lime (mg.kg^{-1})	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg^{-1})
2	1	514.82* (1263.90)**	6.89	4.10	1.16
	2		17.59	10.60	2.96
	3		28.30	17.00	4.77
3	1	510.18 (1077.80)	5.41	3.20	0.78
	2		13.81	8.30	1.98
	3		22.22	13.30	3.19
4	1	192.81	3.60	2.20	0.09
	2		9.20	5.50	0.24
	3		14.80	8.90	0.38
6	1	518.26 (1180.10)	5.91	3.50	0.93
	2		15.09	9.10	2.37
	3		24.26	14.60	3.82
7 (Control)	1	8.64	3.79	2.30	0.00
	2		9.68	5.80	0.01
	3		15.56	9.30	0.02
9	1	10.09 (20.81)	5.47	3.30	0.02
	2		13.97	8.40	0.04
	3		22.47	13.50	0.06
10	1	4.74 (15.04)	7.30	4.40	0.01
	2		18.65	11.20	0.04
	3		30.00	18.00	0.06
11	1	264.28 (257.07)	3.70	2.20	0.13
	2		9.45	5.70	0.32
	3		15.21	9.10	0.52
12	1	336.45	8.70	5.20	0.39
	2		22.21	13.30	1.00
	3		35.73	21.50	1.60

*** Semi-quantitative determination by ICP MS-scan**

**** Quantitative determination by ICP MS**

TABLE 2.6. Chromium content (mg.kg^{-1}) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	First Cr Analysis (mg.kg^{-1})	Second Cr Analysis (mg.kg^{-1})	pH
2	1	5.2	21.8	10.7	6.05
	2	8.86	21.9	10.4	7.27
	3	10.67	23.6	9.5	7.88
3	1	5.93	26.0	10.5	6.33
	2	6.42	24.7	11.4	7.42
	3	9.26	21.8	10.8	7.61
4	1	5.68	23.2	-	6.05
	2	9.16	20.9	-	6.55
	3	9.38	19.6	-	7.34
6	1	5.19	19.9	8.9	6.22
	2	7.35	20.3	8.3	7.18
	3	7.2	21.9	10.4	7.60
7 (Control)	1	8.33	21.8	7.2	6.19
	2	12.84	19.5	7.4	7.02
	3	14.66	21.8	7.5	7.86
9	1	5.98	20.8	6.9	6.37
	2	9.32	20.7	9.2	6.95
	3	9.94	20.0	7.3	7.43
10	1	5.5	22.5	-	6.25
	2	7.44	21.6	-	6.79
	3	11.04	21.8	-	7.21
11	1	5.51	19.9	-	5.91
	2	8.03	24.3	-	6.78
	3	9.79	18.4	-	7.27
12	1	3.19	18.8	-	6.12
	2	8.75	20.5	-	6.78
	3	9.66	21.5	-	7.60

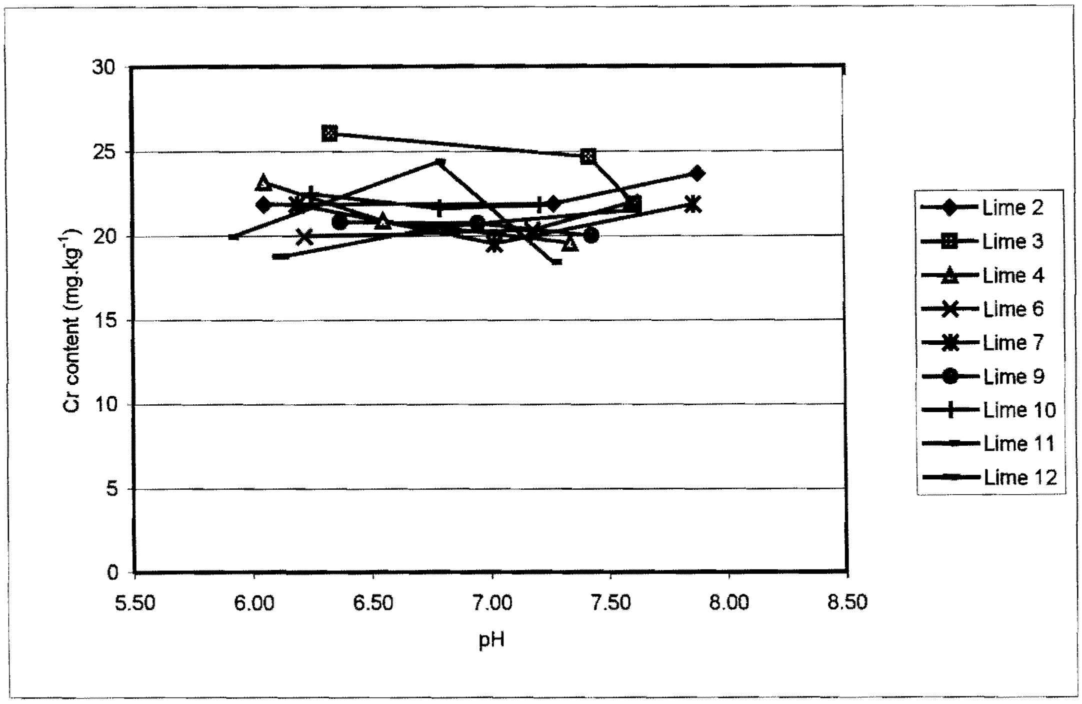

Figure 2.1. Cr content of spinach leaves for each lime at the average pH value.

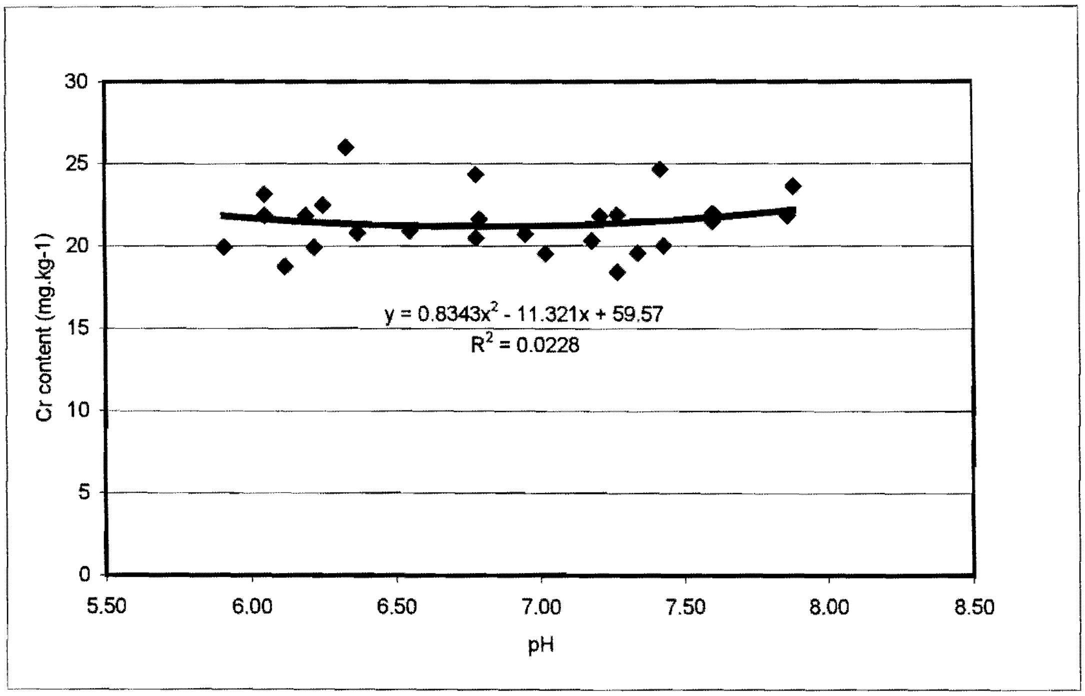

Figure 2.2. Trend in Cr uptake across nine limes at the average pH value.

The NH_4-EDTA extraction results on some of the soils (Table 2.7) indicate very low levels. These levels are far below the level suggested in Table 2.3 and therefore pose very little risk.

TABLE 2.7. NH_4-EDTA extraction (Cr) on soils ameliorated with Limes 2, 3, and 6, seven months after lime application.

Rate	NH_4-EDTA extractable Cr (mg.kg^{-1})		
Control	0.1754		
	Lime 2	Lime 3	Lime 6
1	0.1609	0.0771	0.0376
2	0.1832	0.0801	0.0793
3	0.3117	0.1243	0.1125

Nickel

Table 2.8 indicates the amounts of lime added to the pots to attain the desired pH, the Ni content of the limes as well as the increase in Ni concentration per pot. The values from the ICP-MS semi-quantitative scan were in some cases very close to the values of the subsequent determination (in brackets). Widely differing amounts of Ni (as calculated) was added to the soil with lime 2 the highest and lime 8 the lowest. Lime 8 therefore served as the control.

In Table 2.9 the concentration of Ni in the leaves of the spinach and deviation from the control are indicated. Figures 2.3 and 2.4 indicate the Ni concentration of the spinach leaves for each lime and as a trend against the resultant pH values respectively. Again the values are very high compared to levels of 0.3-3.5 mg.kg^{-1} in unpolluted plants and the "reference plant" levels from Table 2.2 of 1.5 mg.kg^{-1}. Phytotoxic levels for Ni vary greatly with plant species. The levels from this study fall into the range of the values for Ni found in spinach grown on soils in India (Bhattacharjee, *et al.*, 1998) which ranged from 1 to 21 mg.kg^{-1}, but are generally above the levels found in spinach grown on sludge contaminated soil (mean of 9.46 mg.kg^{-1}) as reported by Hooda, *et al.*, (1997).

TABLE 2.8. Nickel content of limes and amounts of lime and Ni added per pot.

Lime no	Rate	Ni Content of Lime (mg.kg^{-1})	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg^{-1})
2	1	555.28* (565.63)**	6.89	4.10	0.51
	2		17.59	10.60	1.30
	3		28.30	17.00	2.10
3	1	69.37 (63.97)	5.41	3.20	0.05
	2		13.81	8.30	0.13
	3		22.22	13.30	0.21
5	1	15.05 (6.98)	6.95	4.20	0.01
	2		17.74	10.70	0.04
	3		28.54	17.10	0.06
6	1	72.19 (70.83)	5.91	3.50	0.06
	2		15.09	9.10	0.15
	3		24.26	14.60	0.23
8 (Control)	1	13.81 (1.62)	7.43	4.50	0.01
	2		18.98	11.40	0.03
	3		30.52	18.30	0.06
11	1	47.79	3.70	2.20	0.02
	2		9.45	5.70	0.06
	3		15.21	9.10	0.10
12	1	69.34	8.70	5.20	0.08
	2		22.21	13.30	0.21
	3		35.73	21.50	0.33

*** Semi-quantitative determination by ICP MS-scan**

**** Quantitative determination by ICP MS**

TABLE 2.9. Nickel content ($mg.kg^{-1}$) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Ni ($mg.kg^{-1}$)	Minus control ($mg.kg^{-1}$)	pH
2	1	5.2	10.95	-2.18	6.05
	2	8.86	10.23	-1.13	7.27
	3	10.67	10.61	0.41	7.88
3	1	5.93	14.24	1.11	6.33
	2	6.42	12.81	1.45	7.42
	3	9.26	10.97	0.77	7.61
5	1	6.16	12.23	-0.90	6.15
	2	6.89	12.47	1.11	7.11
	3	8.49	10.10	-0.10	7.54
6	1	5.19	13.05	-0.08	6.22
	2	7.35	11.65	0.29	7.18
	3	7.2	11.72	1.52	7.60
8 (Control)	1	3.26	13.13	0	6.58
	2	6.85	11.36	0	7.18
	3	7.94	10.20	0	7.53
11	1	5.51	13.00	-0.13	5.91
	2	8.03	13.33	1.97	6.78
	3	9.79	8.21	-1.99	7.27
12	1	3.19	12.18	-0.95	6.12
	2	8.75	13.09	1.73	6.78
	3	9.66	9.76	-0.44	7.60

The relatively high levels could be ascribed to the fact that the spinach did not perform well in the pots (unlike the wheat) (Appendix 6). This could have contributed to elevated levels in the plants and could confirm the statement by Jones and Jarvis (1981) siting many studies that uptake of heavy metals in pots is often exaggerated.

The variation in the values for the Ni-content of spinach indicates that all the values are rather close and that there is no discernable trend with respect to a specific lime leading to a higher uptake. Rather, all the limes seemed to perform similarly with the Ni uptake being a function of the pH.

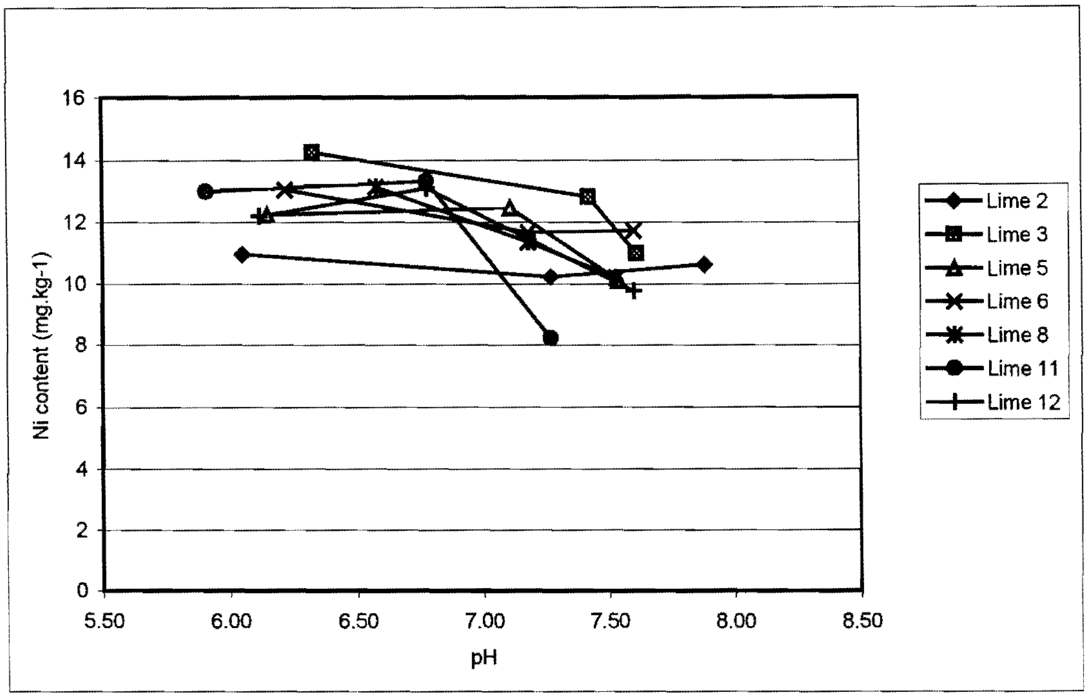

Figure 2.3. Ni content of spinach leaves for each lime at the average pH value.

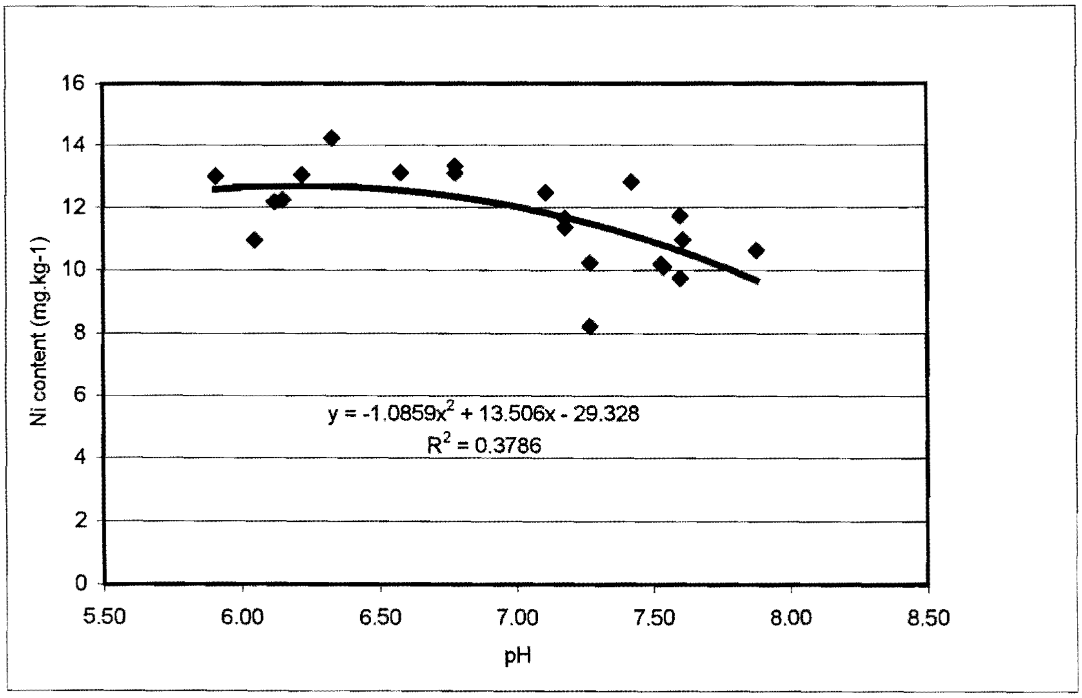

Figure 2.4. Trend in Ni uptake across nine limes at the average pH value.

No Ni was detected in the NH_4-EDTA extraction. According to Steyn (personal communication) this is uncommon and factors other than those discussed here could have contributed to the inability to detect Ni.

Cobalt

Table 2.10 indicates the amounts of lime added to the pots to attain the desired pH, the Co content of the limes as well as the increase in Co concentration per pot. Widely differing amounts of Co was added to the soil with lime 3 the highest and lime 8 the lowest. Lime 8 therefore served as the control treatment.

TABLE 2.10. Cobalt content of limes and amounts of lime and Co added per pot.

Lime no	Rate	Co Content of Lime ($mg.kg^{-1}$)	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil ($mg.kg^{-1}$)
1	1	9.56*	5.94	3.60	0.008
	2		15.16	9.10	0.019
	3		24.38	14.60	0.031
2	1	8.56 (7.12)**	6.89	4.10	0.008
	2		17.59	10.60	0.020
	3		28.30	17.00	0.032
3	1	20.95 (18.64)	5.41	3.20	0.015
	2		13.81	8.30	0.039
	3		22.22	13.30	0.062
5	1	3.38 (3.80)	6.95	4.20	0.003
	2		17.74	10.70	0.008
	3		28.54	17.10	0.013
6	1	19.11 (19.87)	5.91	3.50	0.015
	2		15.09	9.10	0.038
	3		24.26	14.60	0.062
8 (Control)	1	3.10 (3.16)	7.43	4.50	0.003
	2		18.98	11.40	0.008
	3		30.52	18.30	0.013

*** Semi-quantitative determination by ICP MS-scan**

**** Quantitative determination by ICP MS**

The calculated concentration increase in the soil is very low, indicating a very insignificant hazard. In Table 2.11 the concentration of Co in the leaves of the spinach and deviation from the control are indicated. The levels in the leaves are very high when compared to the concentration increase due to the addition of the limes (or slags), but moderately high when compared to natural levels of 0.1-0.57 mg.kg^{-1} and the "reference plant" levels from Table 2.2 of 0.2 mg.kg^{-1}. Values for Co compare favourably with those found in spinach grown on soils in India (Bhattacharjee, *et al.*, 1998), which ranged from 1 to 7 mg.kg^{-1}.

Figures 2.5 and 2.6 indicate the Co concentration of the spinach leaves for each lime and as a trend against the resultant pH values respectively.

TABLE 2.11. Cobalt content (mg.kg^{-1}) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Co (mg.kg^{-1})	Minus control (mg.kg^{-1})	pH
1	1	4.33	2.60	0.17	6.35
	2	4.71	1.63	0.11	6.91
	3	8.96	1.40	-0.01	7.29
2	1	5.2	2.36	-0.07	6.05
	2	8.86	1.81	0.29	7.27
	3	10.67	1.14	-0.27	7.88
3	1	5.93	2.74	0.31	6.33
	2	6.42	2.31	0.79	7.42
	3	9.26	2.34	0.93	7.61
5	1	6.16	2.60	0.17	6.15
	2	6.89	1.56	0.04	7.11
	3	8.49	1.52	0.11	7.54
6	1	5.19	2.14	-0.29	6.22
	2	7.35	1.34	-0.18	7.18
	3	7.2	1.74	0.33	7.60
8 (Control)	1	3.26	2.43	0	6.58
	2	6.85	1.52	0	7.18
	3	7.94	1.41	0	7.53

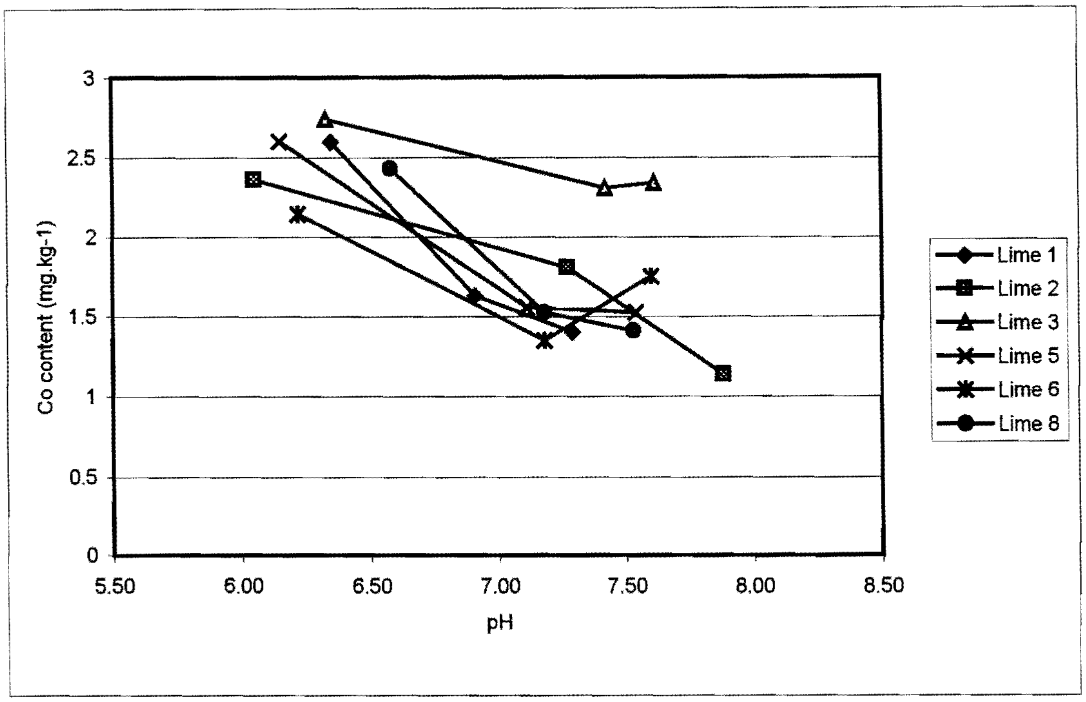

Figure 2.5. Co content of spinach leaves for each lime at the average pH value.

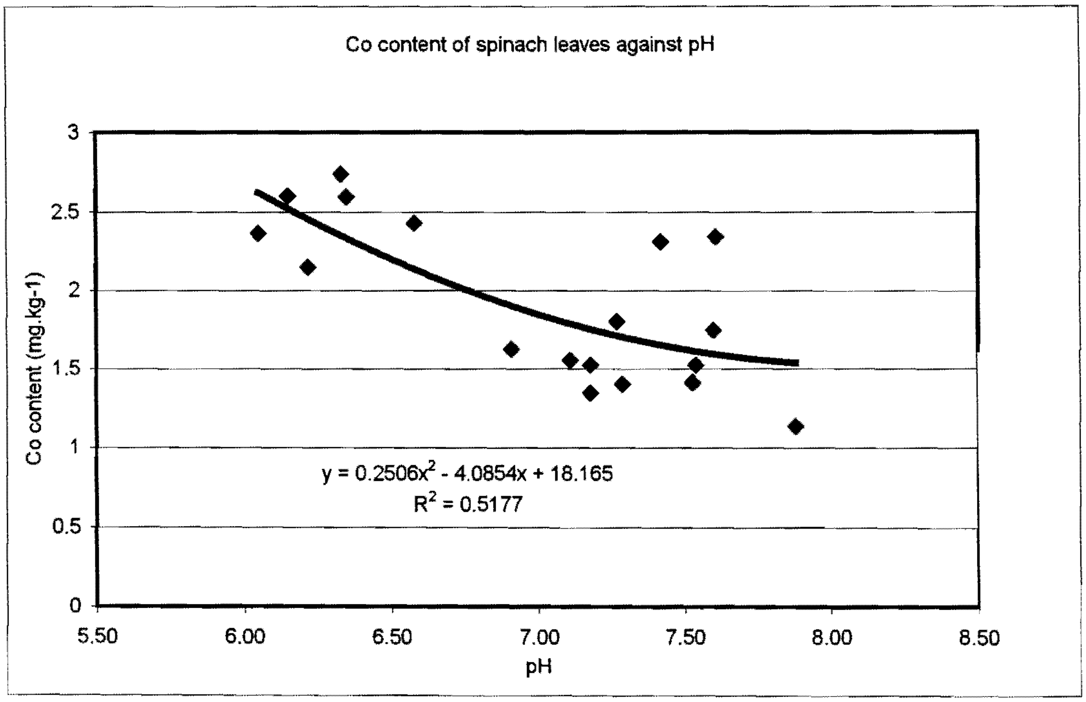

Figure 2.6. Trend in Co uptake across nine limes at the average pH value.

From Fig. 2.6 a very clear pH dependant Co uptake is discernable. The NH_4-EDTA extraction of Co (Table 2.12) of some of the soils yielded values generally two to three-fold higher than the levels in the plant. In this case it would seem that NH_4-EDTA was a relatively good indication of the amount of Co potentially available to the plant. Furthermore, these values seem to indicate a high background level in the soil, which would explain the levels in the plants when compared to the levels in the limes.

TABLE 2.12. NH_4-EDTA extraction (Co) on soil ameliorated with Limes 3 and 6, seven months after lime application.

Rate	NH_4-EDTA exstractable Co (mg.kg^{-1})	
Control	3.885	
	Lime 3	Lime 6
1	3.899	4.068
2	4.203	4.333
3	4.206	4.390

The small variation in the values for the Co-content of spinach indicates that all the values are rather close and that there is no discernable trend with respect to a specific lime leading to a higher uptake.

Manganese

Table 2.13 indicates the amounts of lime added to the pots to attain the desired pH, the Mn content of some of the limes as well as the increase in Mn concentration per pot. The values from the ICP-MS semi-quantitative scan differed very substantially from the values of the subsequent determination due to the scan's inability to accurately depict levels as high as those in the limes. The scan results are not indicated. From the subsequent determinations (only four) it is clear that the limes contained very high levels of Mn.

In Table 2.14 the concentration of Mn in the leaves of the spinach is indicated. Figures 2.7 and 2.8 indicate the Mn concentration of the spinach leaves for each lime and as a trend against the resultant pH values respectively.

TABLE 2.13. Manganese content of limes and amounts of lime and Mn added per pot.

Lime no	Rate	Mn Content of Lime (mg.kg^{-1})	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg^{-1})
1	1		5.94	3.60	
	2		15.16	9.10	
	3		24.38	14.60	
2	1	8050.00	6.89	4.10	7.40
	2		17.59	10.60	18.88
	3		28.30	17.00	30.38
3	1	10450.00	5.41	3.20	7.54
	2		13.81	8.30	19.24
	3		22.22	13.30	30.96
4	1		3.60	2.20	
	2		9.20	5.50	
	3		14.80	8.90	
5	1		6.95	4.20	
	2		17.74	10.70	
	3		28.54	17.10	
6	1	6550.00	5.91	3.50	5.16
	2		15.09	9.10	13.18
	3		24.26	14.60	21.19
7	1		3.79	2.30	
	2		9.68	5.80	
	3		15.56	9.30	
8	1		7.43	4.50	
	2		18.98	11.40	
	3		30.52	18.30	
9	1		5.47	3.30	
	2		13.97	8.40	
	3		22.47	13.50	
10	1		7.30	4.40	
	2		18.65	11.20	
	3		30.00	18.00	
11	1	12800.00	3.70	2.20	6.31
	2		9.45	5.70	16.13
	3		15.21	9.10	25.96
12	1		8.70	5.20	
	2		22.21	13.30	
	3		35.73	21.50	

The values are high when compared to natural levels of 10-500 mg.kg^{-1} and the "reference plant" levels from Table 2.2 of 200 mg.kg^{-1}. The levels fall into the top end of the range of Mn levels found in spinach grown on soils in India (Bhattacharjee, *et al.*, 1998), which ranged from 31 to 979 mg.kg^{-1}.

TABLE 2.14. Manganese content (mg.kg^{-1}) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Mn (mg.kg^{-1})	pH
1	1	4.33	915.0	6.35
	2	4.71	603.0	6.91
	3	8.96	576.0	7.29
2	1	5.2	796.5	6.05
	2	8.86	652.5	7.27
	3	10.67	535.5	7.88
3	1	5.93	990.0	6.33
	2	6.42	702.0	7.42
	3	9.26	688.5	7.61
4	1	5.68	945.0	6.05
	2	9.16	652.5	6.55
	3	9.38	454.5	7.34
5	1	6.16	900.0	6.15
	2	6.89	490.5	7.11
	3	8.49	504.0	7.54
6	1	5.19	895.5	6.22
	2	7.35	418.5	7.18
	3	7.2	535.5	7.60
7	1	8.33	1050.0	6.19
	2	12.84	733.5	7.02
	3	14.66	612.0	7.86
8	1	3.26	1110.0	6.58
	2	6.85	558.0	7.18
	3	7.94	540.0	7.53
9	1	5.98	931.5	6.37
	2	9.32	571.5	6.95
	3	9.94	702.0	7.43
10	1	5.5	886.5	6.25
	2	7.44	616.5	6.79
	3	11.04	549.0	7.21
11	1	5.51	930.0	5.91
	2	8.03	706.5	6.78
	3	9.79	630.0	7.27
12	1	3.19	886.5	6.12
	2	8.75	625.5	6.78
	3	9.66	679.5	7.60

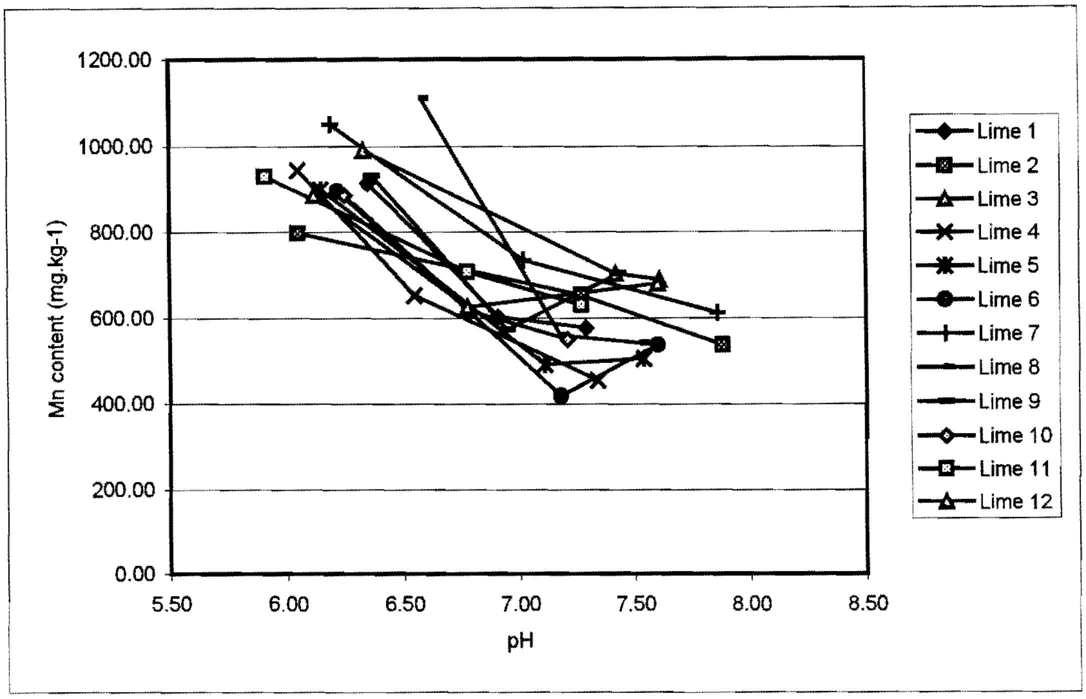

Figure 2.7. Mn content of spinach leaves for each lime at the average pH value.

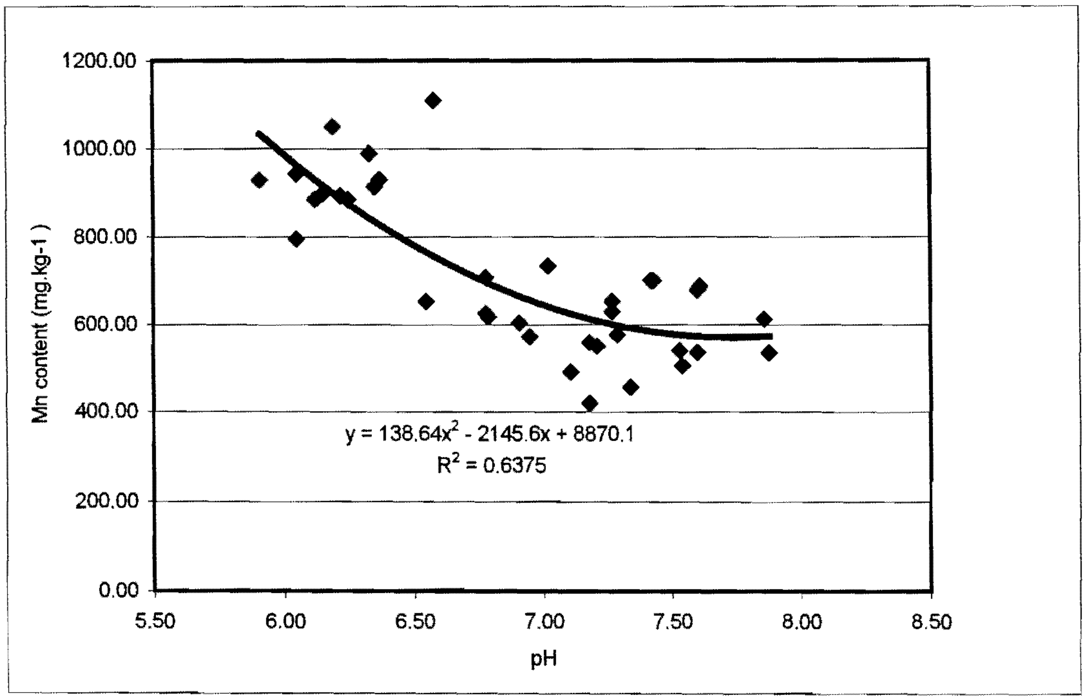

Figure 2.8. Trend in Mn uptake across nine limes at the average pH value.

The uptake of Mn was a function of pH as is seen in the clear pH trend in Fig. 2.8. As in the case of the previously discussed metals, the high concentration in the plants could be ascribed to the fact that conditions in pots exaggerate metal uptake. Again there is very little difference between the Mn concentrations of any of the plants grown on the different limes, which indicate that the Mn taken up must be from a background source and not the limes.

Other Heavy Metals

The spinach was also tested for other metals but these were not included in the study. These metals are Zn, Cu, Mo, and Ba, and their results are listed in Appendix 2.

CONCLUSION

Although the heavy metal levels in the spinach were relatively high in absolute terms, these high levels are ascribed to other factors than the metal content of the limes. The main factor being the effect of plants grown in pots and the possible exaggerated uptake of the metals.

In relative terms the values indicate small variation between high and low metal content limes, which would seem to indicate that there is no greater risk in using slags than using ordinary limes. The immediate risk concerning metal uptake from applied slags is therefore deemed to be low.

Differences between limes in terms of heavy metal uptake were also amplified in the same manner as the absolute heavy metal values were amplified by pot conditions, It is very probable that what seems to be large differences in some cases could in effect be very small differences in field conditions. This aspect would best be studied in more detail.

In most of the cases the metal concentration in the spinach decreased with increasing pH, as was expected from the literature.

Although the speciation of Cr has not been addressed in this study, it is of critical importance that the slags be tested with respect to the dominant species in soils after slag application. The toxicities of the two Cr species differ quite substantially, therefore speciation is important when referring to absolute concentrations.

Levels of the metals in the limes, although not posing an immediate threat, could become hazardous when large amounts of a specific slag is applied over a long period of time. As long as the soil's pH remains within relatively neutral boundaries, the metals will pose no threat. This situation could change when the soil is left to acidify or when it is acidified artificially through cultivation without further adequate lime inputs. Safe levels of metals in slags or liming materials should be determined by taking into account the natural acidity of the soils they are applied to, to prevent excessive application to soils that could acidify naturally to pH levels that could pose a hazard in metal bioavailability. This aspect definitely deserves further study.

The effect of growing plants in pots and the exaggerated uptake of metals could have contributed to the high levels found in the plants. The making of conclusions concerning heavy metal levels in plants grown in pots should therefore be done with the utmost care. A proper control treatment is an absolute necessity to assist in the making of sound deductions. The results gained from this study, however, could be compared meaningfully due to the difference between the limes in terms of their heavy metal composition as well as similarity in terms of their effect on pH of the soil.

Although EDTA has been suggested as an extractant that gives a good indication of the metals that are potentially plant available in soils, it would not seem to be the case in soils in pots for the elements tested.

CHAPTER 3

REACTIVITY OF LIMING MATERIALS

INTRODUCTION

The application of lime has become to many farmers an issue of choice rather than necessity. In an industry where profit margins are low due to increasing input costs, one of the first ameliorants to be excluded is lime. This is due to the cost of transporting the lime and incorporating it into the soil. In many cases the liming materials do not perform as well as the user had expected and it contributes to the farmers reluctance to apply adequate amounts of lime.

Many different lime requirement methods and reactivity parameters exist and the use of these different methods by consultants adds to the confusion of the farmer. Some of the methods lead to amounts of lime required that are in excess of what the farmer would be willing to apply, even though they may be realistic, and this leads to the gradual acidification of the top and subsoil. This is a critical factor and one that is less readily rectified by surface application of lime unless the lime is incorporated physically into the lower soil horizons.

A drawback of many lime reactivity indicators is the fact that they are either cumbersome to determine or that they do not give a realistic indication of the lime's reactivity in a specific soil.

Reserve Acidity

The soil's ability to buffer a change in pH is dependent on the reserve acidity or buffer capacity, which in turn is a function of the types of clay minerals and their amounts present in the soil (Van Breemen, 1991). Furthermore, the buffer capacity is influenced largely by the amount of H^+ and Al^{3+} adsorbed on the exchange complex, with Al^{3+} being dominant at very low pH. High concentrations of H^+ lead to Al^{3+} release from clay mineral structures and its subsequent adsorption on the clay particles (McBride, 1994).

When lime is added to an acid soil, the change in pH is buffered by the following reaction:

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^- \qquad (3.1)$$

where the OH^- neutralises any excess H^+ in solution. The calcium exchanges Al^{3+} on the clay particles in the following reaction:

$$2Al^{3+}\text{-clay} + 3Ca^{2+} \rightarrow 2Al^{3+} + 3Ca^{2+}\text{-clay} \qquad (3.2)$$

The Al^{3+}that is exchanged from the clay particles, then hydrolyses and precipitates as an aluminium hydroxide mineral and has no further influence on the pH of the soil until the soil acidifies again with and acid input of some sort (McBride, 1994).

Lime Requirement

The soil's lime requirement (LR) is the amount of lime needed to change the pH of the soil to a desired level. It could also refer to the amount of lime needed to attain a specific chemical state, such as the amount of lime needed to neutralise all exchangeable acidity to a pH of 7 (or arguably a base saturation of 100%). Presently LR more regularly refers to the amount of lime needed to reduce Al^{3+} toxicity or acid saturation to acceptable levels (McBride, 1994).

In terms of lime requirement determinations there are several methods used in the world today with some gaining wide acceptance. Ernani and Almeida (1986) found that all methods tested in Brazilian soils gave a good indication of lime requirement, except a method based on base saturation of the soil, which underestimated it greatly. In Cuba, on sandy soils, tobacco responded best to rates of lime calculated by the saturation method, which (with others) gave the best estimation of lime requirement (Morejon, *et al.*, 1991).

Although some of the above authors had good results with saturation methods McBride (1994) states that base saturation and acid saturation are concepts that are difficult to define, misleading and "even irrelevant, therefore not very useful".

Edmeades, Wheeler, & Waller (1984) found that several other lime requirement methods (Shoemaker-McLean-Pratt (SMP) single and double buffer, and $Ca(OH)_2$ titration) gave good correlations with one another. Similar results were reported by Warman, Walsh, & Rodd (2000), who found that the SMP method most closely estimated the amount of lime needed to bring the soil pH to 6.5. They found, however, that all the lime requirement methods (three) underestimated the amount of lime needed to bring the soil to the specified target pH. These results confirm findings by Doerge and Gardner (1988) that found that all the lime requirement methods tested under-predicted soil pH values when not calibrated under field conditions. This shows the importance of including field conditions and soils from similar geographic regions when calibrating lime requirement tests when using the SMP method.

From all the above-mentioned studies very little could be deduced with regards to the inclusion of a reactivity parameter of the limes used and may partly be the reason for the underestimation of the lime requirement.

Lime Reactivity

The amount of lime required to neutralise acidity in a soil is not only a function of the pH buffering capacity of the soil but also the reactivity of the liming material. Sources and types of limes differ in composition and therefore react differently in soil. A lot has been written concerning the reactivity of liming materials and the scope of research varies from chemical to physical properties such as the particle sizes of the lime.

Bornman (1985) developed the Resin Suspension Method (RSM), which rests on the principle that lime's reaction in the soil is a contact exchange reaction (Jenny and Overstreet, 1938; Warfvinge and Sverdrup, 1989). The RH-value ("Relatiewe Harswaarde" – as the resultant value is known) that is determined after a 24-hour laboratory analysis shows a high degree of correlation with 3-month incubation values. Several inter-laboratory trials have been done to determine the accuracy of the method both between and within laboratories (Claassens, *et al.,* 2000). The RH-value indicated a high degree of correlation with incubation studies (Fölscher & Bornman, 1985) and also in its determination by different laboratories (Bornman, Coetzee, & van Vuuren, 1988), and therefore gives a good indication of the reactivity of a liming material.

Differing views exist on the applicability of the RH-value. Van der Watt and Croft (1993) stated that the RH-value is very useful in that it correlates well with both particle size and an incubation parameter calculated in a trial on liming materials, and Beukes (1995) states that the RH-value is superior to other methods used to determine lime reactivity. On the other hand, Venter (1997) says that, although a distinction can be made between different liming materials on the grounds of the Resin Suspension method, this method is in its present form not suited to calculate equivalent amounts of lime from different sources.

Several other studies have been done on the effective neutralizing capacity or reactivity of liming materials. Most of these focused on HCl dissolution, particle size and crystallinity (Sajwan, Evangelou, & Lumbanraja, 1991), Ca and Mg content correlated with an HCl titration (Duarte, *et al.*, 1993), and base saturation, exchangeable Al and Ca + Mg in heavy clay dystrophic latosols (Borges, *et al.*, 1987). In the study by Duarte, *et al.*, (1993), the HCl-titration gave higher values in some cases than the Ca and Mg content. The Calcium Carbonate Equivalent (CCE) in HCl (0.5N) method overrated lime reactivity and lead to the inability of two lime requirement methods (slightly modified SMP and "Natal" method) to accurately predict lime requirement in a study by Haumann (1986).

The finding by Haumann (1986) was to be expected due to the fact that the soil consists mainly of numerous forms of weak acids that buffer a change in pH (McBride, 1994). Therefore lime in soil will not react as it would in a strong acid solution like HCl.

Study Aims

The aim of this study is to determine the reactivity of the liming materials (used in a trial for testing the bioavailability of heavy metals and phosphorus) in the soil and make a deduction as to the desirability of the RH-value as a reactivity index in the determination of lime requirement. Furthermore, the aim is to compare the RH-value to the CCE HCl and draw conclusions concerning its effectiveness in the making of a lime recommendation.

MATERIALS AND METHODS

Two trials were conducted to test the contribution of slags to heavy metal pollution (bioavailability) and available P in soil. The trials were planned in such a way that the resultant soil analysis (pH) would be able to give an indication of the efficiency of the RH-value.

Trial 1 consisted of a pot trial in a glasshouse where twelve liming materials were tested. The liming materials were added to the soil at four different rates (no lime added and three target pH values of 5.8, 6.8, and 7.8). Each treatment was replicated four times. Trial 2 consisted of five liming materials, added to the soil at four different rates (no lime added and three target pH values of 5.5, 6.0, and 6.5) with four replicates of each treatment.

Soil

The soil in Trial 1 was chosen from the Eastern Highveld – an area where there is an increased probability of farmers using slags as agricultural limes. The soil in Trial 2 was collected from the experimental farm of the University of Pretoria and was chosen for its low pH and low P content. Some chemical and physical properties of the soils are listed in Table 3.1.

TABLE 3.1. Selected chemical and physical properties of the soils used in the study.

Parameter	Trial 1	Trial 2
Texture	Sandy Clay Loam	Sandy Clay
$pH_{(Water)}$	5.1	4.1
$pH_{(KCl)}$	3.9	3.6
Ammonium acetate extractable: ($mgkg^{-1}$)		
Ca	622	49
Mg	151	8
K	217	50
Na	0	20
P (Bray 1)	21.93	2.58

Lime Requirement

Each soil's lime requirement was determined by the incremental addition of a saturated $Ca(OH)_2$ solution to 50g of soil in a soil to solution ratio of 1:1. The solution was stirred immediately after mixing and left to equilibrate for 24 hours, after which the pH was determined. The concentration of the saturated $Ca(OH)_2$ solution was determined by titration with a 0.01M HCl solution.

The $Ca(OH)_2$ values were transformed into values consistent with an equivalent amount of pure $CaCO_3$ to take into account the difference in molecular weight between the hydroxyl and carbonate groups. The limes used contained varying amounts of total Ca and Mg, differing from those of a pure $CaCO_3$, and also different basic anions in the form of carbonates, silicates or even hydroxyls.

Liming Materials

Twenty-four different lime samples were collected from different sources with the aid and under the supervision of representatives from the Registrar of Fertilisers. The lime samples were put through a splitter to ensure homogeneity and sealed on site in tins. The limes were analysed by an independent laboratory for total Ca and Mg content (AA method as prescribed by ALASA, 1998), CCE in HCl (ALASA, 1998), RH-value (according to Bornman (1985)) and different sieve fractions. From the 24 limes 12 were selected for Trial 1 due to being slags (5), paper mill wastes (2) or natural limes (5). For trial 2 four slags were chosen on the basis of its P content to determine the amount of available P to the plant.

Lime Application

The amount of pure $CaCO_3$ required for each target pH value was calculated as described above. These values were adapted to ton per hectare and the data used to calculate the amount needed to neutralise the soil in pots of 7.5kg (Trial 1) and 4kg (Trial 2). Neutralisation to a depth of 30cm and a soil bulk density of 1.5 $Mg.m^{-3}$ was assumed.

The amount determined above was multiplied by two factors. The first factor, by which the amount of $CaCO_3$ was multiplied, was calculated from CCE of the lime that was corrected to 100%. For example: Lime 1 has a CCE of 71.08%. This value corrected to 100% yields a factor of 1.41 and it was assumed that incorporating this factor meant applying all limes to the same equivalent amount of pure $CaCO_3$. The incorporation of this factor into the lime recommendation somewhat distorted the results (for a detailed discussion see section “Conclusions and Recommendations”).

A second factor, the correction of the RH-value to 100%, was multiplied with the amounts of lime determined above. For example: Lime 1 has an RH-value of 75.83%. This value corrected to 100% yields a factor of 1.32.

The procedure as above was followed for every lime in Trial 1 and Trial 2. Due to the acid nature of the soil in Trial 2 (Table 3.1) and the amount of lime required, lower targets were chosen. A laboratory reagent $CaCO_3$ was chosen as the control treatment and its reactivity assumed to be 100%.

In both the trials the pre-determined amount of lime was applied to the soil for each pot. Care was taken to ensure that the lime was mixed well with all the soil in the pot. The pots were regularly watered but no leaching was allowed.

Measurement of pH, Statistical Analysis

Soil samples from the pots in Trial 1 were taken three months after lime application (small sample through profile of pot) and again seven months (representative sample of whole pot) after lime application. In Trial 2 the sampling (representative sample of whole pot) was done three months after lime application. Of each soil sample in Trial 1 and 2 a $pH_{(Water)}$ and $pH_{(KCl)}$ was determined by the standard method described by The Non-affiliated Soil Analysis Work Committee (1990) with a Cyberscan pH meter and Hanna Instruments electrode (nr. HI 1230). The results were statistically analysed using the SAS® System statistical program to obtain the Analysis of Variance (ANOVA) and the LSD – Tukey to determine significant differences.

RESULTS AND DISCUSSION

Lime Requirement Determination

In Table 3.2 the results of the $Ca(OH)_2$ treatments are given and Figure 3.1 indicates the resultant incubation curves for Trial 1 and 2. From the incubation values it is clear that the soil used in Trial 2 was substantially more acidic than the soil in Trial 1 (Table 3.1). Both the determinations indicated a very pronounced linear trend as indicated by the R^2 values.

TABLE 3.2. Resultant pH values after incubation with $Ca(OH)_2$ (Trial 1 and 2).

Soil – Solution ratio Test $Ca(OH)_2$ added (mmol/kg soil)	1:1 (50g soil) Trial 1 pH	1:1 (50g soil) Trial 2 pH
0	5.08	3.53
0.86	5.30	-
1.72	5.42	-
2.58	5.53	-
3.44	5.76	-
3.90	-	4.02
4.30	5.88	-
6.45	6.22	-
7.80	-	4.69
8.60	6.52	-
10.75	6.85	-
11.70	-	5.42
12.90	7.08	-
15.05	7.46	-
15.60	-	6.29
17.20	7.72	-
19.50	-	6.79

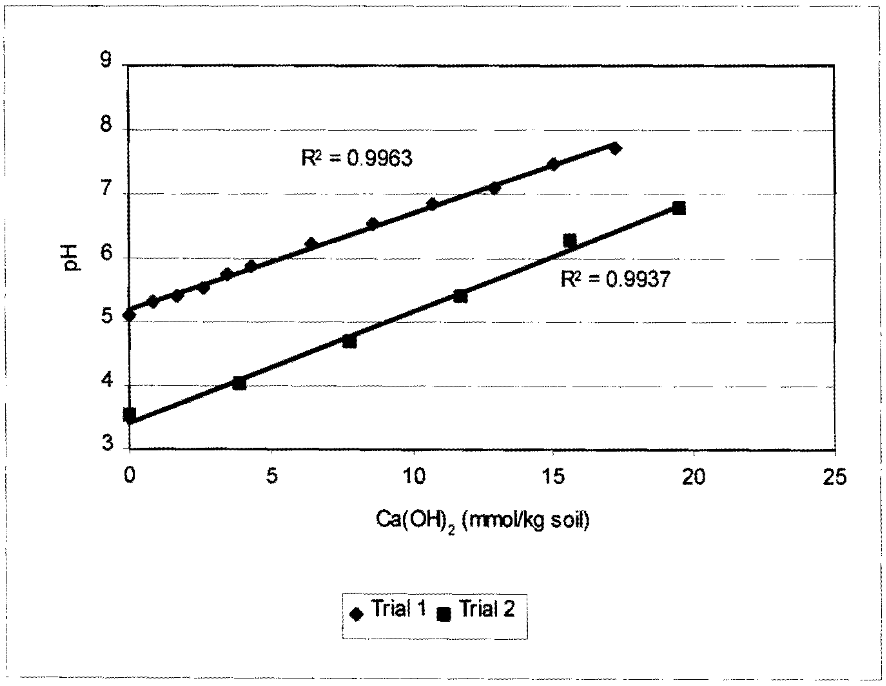

Figure 3.1. $Ca(OH)_2$ incubation curve for Trial 1 and 2.

Table 3.3 gives the amount of $CaCO_3$ that was required for each pot (in both trials) to ameliorate the pH to the desired level.

TABLE 3.3. Amount of $CaCO_3$ required per pot to attain the target pH.

Trial 1		Trial 2	
Target pH	$CaCO_3$ (g) required per 7.5kg pot	Target pH	$CaCO_3$ (g) required per 4kg pot
5.8	3.20	5.5	4.77
6.8	8.17	6.0	5.92
7.8	13.14	6.5	7.07

Characteristics of the Liming Materials

The details of the chemical and physical properties of all the limes sampled are given in Appendix 1. The limes indicated by an asterisk were selected for the study and were chosen according to the criteria listed in Chapter 1 and not on any of the characteristics listed below. Table 3.4 gives some of the physical and chemical characteristics of the twelve liming materials selected from all the samples. The CCE HCl values differ from the RH-values and in some cases the differences are substantial (Lime 2 compared to Lime 1). In all the cases the RH-values are lower than the CCE HCl values which would indicate a lower reactivity in a weaker acid solution. This difference could be ascribed to the different chemical and physical composition of the limes. Lime 11 is a slag that is a product of an iron recycling plant with a high CaO content and this accounts for the high CCE HCl value.

TABLE 3.4. Results of laboratory analysis of twelve liming materials.

Lime No	Ca Total %	Mg Total %	CCE HCl %	RH-Value %	% Passing sieve size:			
					< 1.7 mm	< 1.0 mm	< 0.25 mm	< 0.106 mm
1	17.20	11.23	83.00	75.83	98.52	96.89	91.66	84.13
2	30.02	7.37	95.48	49.67	95.53	87.93	67.45	39.90
3	31.06	5.57	84.98	64.57	99.36	92.01	64.98	42.48
4	37.76	0.95	98.04	91.72	99.90	99.80	98.90	98.13
5	16.27	14.63	85.75	59.60	97.70	88.35	66.20	59.80
6	27.02	9.32	95.88	59.60	99.59	91.21	59.58	37.25
7	37.30	1.18	98.54	87.75	99.96	99.86	98.48	94.88
8	16.64	14.68	88.38	54.97	87.04	72.46	50.73	43.75
9	18.20	11.99	87.98	77.48	99.71	89.46	57.13	29.00
10	19.95	12.11	91.40	54.64	99.68	99.30	73.58	67.56
11	40.43	4.95	104.28	76.16	99.53	99.13	89.73	61.53
12	26.02	5.55	74.90	46.59	97.67	80.77	43.57	22.87

Lime Application

Table 3.5 indicates the amount of lime needed per pot for Trial 1 with the RH-values taken into account to attain the target pH. These values were derived from those in Table 3.3 and calculated as discussed earlier. Values in brackets indicate the equivalent amount of lime required in ton ha^{-1}. As mentioned earlier two factors were built into the lime recommendation of which the one distorted the pH results somewhat. This factor varied from 0.9 to 1.4 and the amounts indicated in Table 3.5 were the actual amounts added to the pots.

TABLE 3.5. Analysis results of twelve liming materials and amounts added per pot (Trial 1).

Lime no	CCE*	CCE	RH-Value	PH 5.8	pH 6.8	pH 7.8
		HCl		lime g.pot^{-1}	lime g.pot^{-1}	lime g.pot^{1-}
	%	%	%	(ton.ha^{-1})	(ton.ha^{-1})	(ton.ha^{-1})
1	71.08	83.00	75.83	5.94 (3.6)	15.16 (9.1)	24.38 (14.6)
2	93.48	95.48	49.67	6.89 (4.1)	17.59 (10.6)	28.30 (17.0)
3	91.58	84.98	64.57	5.41 (3.2)	13.81 (8.3)	22.22 (13.3)
4	96.78	98.04	91.72	3.60 (2.2)	9.20 (5.5)	14.80 (8.9)
5	77.25	85.75	59.60	6.95 (4.2)	17.74 (10.7)	28.54 (17.1)
6	90.85	95.88	59.60	5.91 (3.5)	15.09 (9.1)	24.26 (14.6)
7	96.20	98.54	87.75	3.79 (2.3)	9.68 (5.8)	15.56 (9.3)
8	78.30	88.38	54.97	7.43 (4.5)	18.98 (11.4)	30.52 (18.3)
9	75.48	87.98	77.48	5.47 (3.3)	13.97 (8.4)	22.47 (13.5)
10	80.15	91.40	54.64	7.30 (4.4)	18.65 (11.2)	30.00 (18.0)
11	113.45	104.28	76.16	3.70 (2.2)	9.45 (5.7)	15.21 (9.1)
12	78.93	74.90	46.59	8.70 (5.2)	22.21 (13.3)	35.73 (21.5)

* Calculated from the Ca and Mg content of the limes

When the factor mentioned above was omitted the values were corrected to those indicated in Table 3.6. These values only include a correction based on the RH-value.

TABLE 3.6. Corrected amounts of lime needed per pot expressed in the equivalent of ton.ha^{-1} (Trial 1).

Lime no	pH 5.8	pH 6.8	pH 7.8
	lime	lime	lime
	ton.ha^{-1}	ton.ha^{-1}	ton.ha^{-1}
1	2.5	6.5	10.4
2	3.9	9.9	15.9
3	3.0	7.6	12.2
4	2.1	5.3	8.6
5	3.2	8.2	13.2
6	3.2	8.2	13.2
7	2.2	5.6	9.0
8	3.5	8.9	14.3
9	2.5	6.3	10.2
10	3.5	9.0	14.4
11	2.5	6.4	10.4
12	4.1	10.5	16.9

From the tables it is clear that the reactivity of the liming materials varied considerably with the amount of lime required per hectare ranging from 2.2 (corrected to 2.1) tons (Lime 4) to 5.2 (corrected to 4.1) tons (Lime 12) for the first target. (Refer to Chapter 4 for calculations involving the corrected amounts of lime). The differences are amplified by the higher application rates in targets 2 and 3.

The values calculated for the three targets in Trial 2 are indicated in Table 3.7. Again the variability in the liming materials is clear when the amounts of lime per hectare are taken into account. In this case the control treatment was a laboratory reagent $CaCO_3$ and its reactivity was assumed to be 100%. The same factors as in Trial 1 were used in the calculation of the Trial 2 lime requirement values. Corrected values are given in Table 3.8.

TABLE 3.7. Analysis results of four liming materials (and $CaCO_3$ Lab Reagent) and amounts added per pot (Trial 2).

Lime no	CCE HCl %	CCE Resin %	pH 5.5 lime g.pot^{-1} (ton.ha^{-1})	PH 6.0 lime g.pot^{-1} (ton.ha^{-1})	PH 6.5 lime g.pot^{1-} (ton.ha^{-1})
2	95.48	49.67	10.28 (11.6)	12.76 (14.4)	15.24 (17.1)
3	84.98	64.57	8.08 (9.1)	10.02 (11.3)	11.97 (13.5)
6	95.88	59.60	8.82 (9.9)	10.94 (12.3)	13.07 (14.7)
11	104.28	76.16	5.53 (6.2)	6.86 (7.7)	8.19 (9.2)
13*	100+	100+	4.78 (5.4)	5.93 (6.7)	7.08 (8.0)

* Laboratory Reagent (analytical)

\+ Assumed

TABLE 3.8. Corrected amounts of lime needed per pot expressed in the equivalent of ton.ha^{-1} (Trial 2).

Lime no	CCE Resin %	pH 5.5 lime ton.ha^{-1}	PH 6.0 lime ton.ha^{-1}	PH 6.5 lime ton.ha^{-1}
2	49.67	10.8	13.4	16.0
3	64.57	8.3	10.3	12.3
6	59.60	9.0	11.2	13.3
11	76.16	7.1	8.7	10.4
13*	100+	5.4	6.7	8.0

* Laboratory Reagent (analytical)

\+ Assumed

Results of pH Determination

Trial 1

The pH results of the two samplings (after three and seven months) in Trial 1 are given in Appendix 3 with a graphic representation of the average of four repetitions in Figure 3.2 for the sampling after three months and Figure 3.3 for the sampling after seven months respectively. In Table 3.9 the deviation of the results of both samplings from the target values are given for the different targets. Values in the each column with the same letter do not differ significantly.

The limes that performed better than anticipated during the first sampling also performed better during the second and vice versa. Generally most of the limes showed a decrease in pH from the first sampling to the second. This was to be expected due to the acidification processes that were active during the three and seven month periods. Some limes however, and specifically Lime 2, showed an increase throughout. This can be explained by the fact that Lime 2 has a very low RH-value and therefore a large amount was added to the pots as well as the fact that the RH-value predicts the amount of lime that will react over a three months period. The large inactive component (over three months) of the lime keeps on reacting after three months whereas the limes with smaller amounts added has no reserve left to react.

The variability in the pH results (and therefore reactivity) of the liming materials increased with increased application rates. At a target pH of 5.8 and 6.8 the average $pH_{(Water)}$ values showed only a slight variation, indicating that the RH-value performed well in the prediction of the reactivity of the liming materials. The increased variation at target pH 7.8 is ascribed to the underestimation of lime requirement at such high pH values coupled to the altered chemical conditions (equilibrium of different limes) governing lime dissolution at pH levels above neutral.

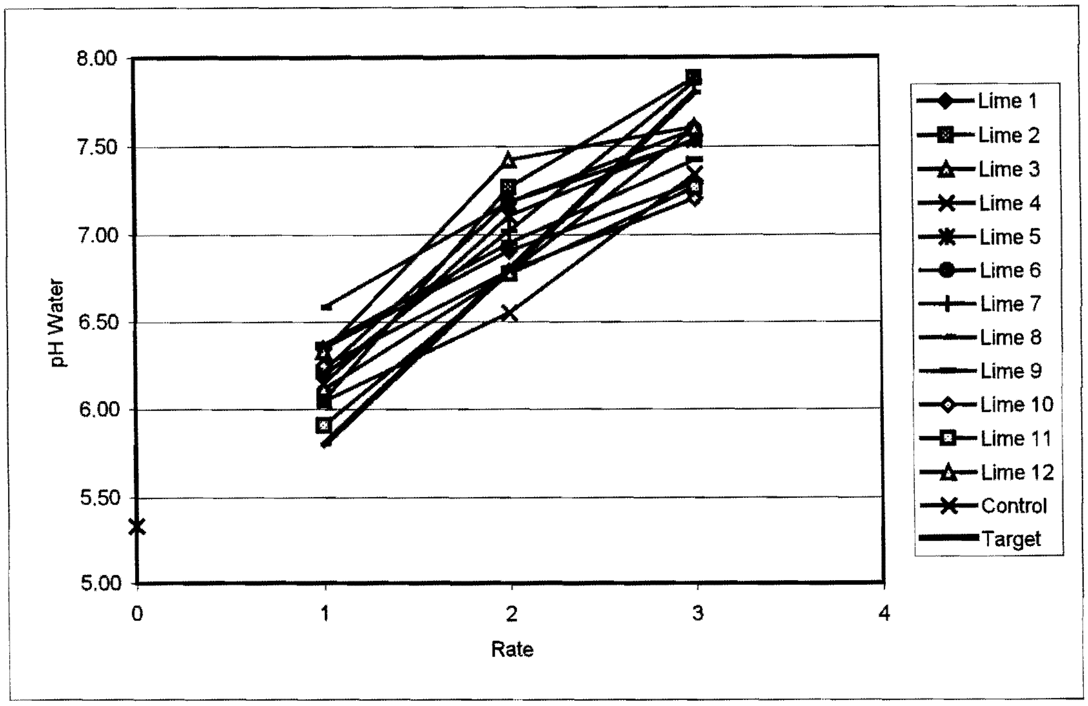

Figure 3.2: pH($_{\text{Water}}$) results for three target applications after three months (Trial 1). Note: The thick black line represents the target pH values.

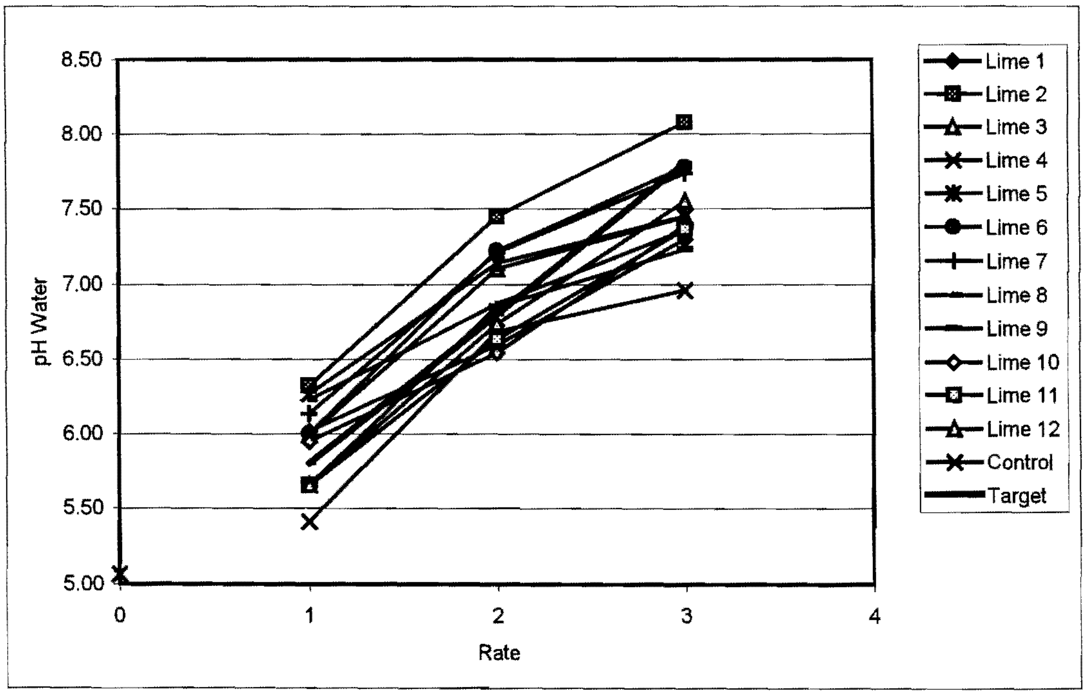

Figure 3.3: pH($_{\text{Water}}$) results for three target applications after seven months (Trial 1). Note: The thick black line represents the target pH values.

TABLE 3.9. The deviation of the pH$_{(Water)}$ values from target pH for three rates at three and seven months after lime application for Trial 1*.

Target pH: 5.8			Target pH: 6.8			Target pH: 7.8		
Months	Lime	Deviation	Months	Lime	Deviation	Months	Lime	Deviation
3	8	0.78^{a}	7	2	0.65^{d}	7	2	0.28^{g}
3	9	0.57^{a}	3	3	0.62^{de}	3	2	0.08^{gh}
3	1	0.55^{a}	3	2	0.47^{def}	3	7	0.06^{gh}
3	3	0.53^{ab}	7	6	0.42^{def}	7	6	-0.03^{ghi}
7	2	0.52^{ab}	7	7	0.41^{def}	7	7	-0.07^{ghij}
7	5	0.47^{ab}	3	8	0.38^{def}	3	3	-0.19^{hijk}
3	10	0.45^{ab}	3	6	0.38^{def}	3	12	-0.20^{hijk}
7	8	0.43^{ab}	7	5	0.34^{def}	3	6	-0.21^{hijk}
3	6	0.42^{ab}	3	5	0.31^{def}	7	12	-0.25^{hijk}
3	7	0.39^{ab}	7	3	0.30^{def}	3	5	-0.26^{hijk}
3	5	0.35^{ab}	3	7	0.22^{def}	3	8	-0.27^{hijk}
7	7	0.33^{ab}	3	9	0.15^{def}	7	5	-0.35^{ijk}
3	12	0.32^{ab}	3	1	0.11^{def}	7	3	-0.36^{ijk}
3	2	0.25^{abc}	7	8	0.07^{def}	3	9	-0.38^{ijk}
3	4	0.25^{abc}	7	9	0.05^{def}	7	10	-0.41^{ijk}
7	1	0.22^{abc}	3	10	-0.01^{def}	7	11	-0.44^{jkl}
7	6	0.20^{abc}	3	12	-0.02^{def}	7	8	-0.44^{jkl}
7	3	0.19^{abc}	3	11	-0.03^{def}	3	4	-0.46^{jkl}
7	10	0.15^{abc}	7	12	-0.06^{def}	7	1	-0.50^{kl}
3	11	0.11^{abc}	7	4	-0.11^{def}	3	1	-0.51^{kl}
7	12	-0.14^{bc}	7	11	-0.17^{ef}	3	11	-0.53^{kl}
7	9	-0.14^{bc}	7	1	-0.20^{f}	7	9	-0.57^{kl}
7	11	-0.15^{bc}	3	4	-0.25^{f}	3	10	-0.60^{kl}
7	4	-0.39^{c}	7	10	-0.26^{f}	7	4	-0.84^{l}

*Values with the same letters in every column indicate no significant difference

Tables 3.10 and 3.11 indicate the average pH$_{(KCl)}$ values of four repetitions after three and seven months respectively. Although there was no pH$_{(KCl)}$ target values set, the statistical significance of the values were deemed important enough to report. From the values and its close correlation, especially at the first target rate of application, it is clear that the RH-value gives a very good indication of the reactivity of the liming materials, albeit at pH values lower than the values measured in water.

TABLE 3.10. Trial 1 $pH_{(KCl)}$ results after 3 months*.

Lime no.	Target 1 ($pH_{(Water)}$ 5.8)	Target 2 ($pH_{(Water)}$ 6.8)	Target 3 ($pH_{(Water)}$ 7.8)
1	5.30^{a}	5.95^{bc}	6.40^{efg}
2	4.92^{a}	6.63^{b}	7.03^{d}
3	5.13^{a}	6.24^{bc}	6.71^{def}
4	4.66^{a}	5.50^{c}	6.01^{g}
5	4.82^{a}	6.28^{bc}	6.80^{de}
6	4.87^{a}	6.20^{bc}	6.67^{def}
7	4.85^{a}	5.95^{bc}	6.67^{def}
8	4.92^{a}	6.14^{bc}	6.58^{def}
9	5.15^{a}	5.61^{c}	6.59^{def}
10	4.94^{a}	5.79^{c}	6.22^{fg}
11	4.63^{a}	5.65^{c}	6.24^{efg}
12	4.97^{a}	5.97^{bc}	6.66^{def}
Average	4.9	5.9	6.5

*Values with the same letters in every column indicate no significant difference

TABLE 3.11. Trial 1 $pH_{(KCl)}$ results after 7 months*.

Lime no.	Target 1 ($pH_{(Water)}$ 5.8)	Target 2 ($pH_{(Water)}$ 6.8)	Target 3 ($pH_{(Water)}$ 7.8)
1	4.93^{a}	6.01^{bcd}	6.42^{gh}
2	5.28^{a}	6.39^{b}	7.10^{e}
3	5.05^{a}	6.28^{bc}	7.03^{ef}
4	4.75^{a}	5.71^{cd}	5.97^{h}
5	5.10^{a}	6.29^{bc}	6.70^{efg}
6	4.95^{a}	6.37^{b}	6.82^{efg}
7	4.96^{a}	6.32^{b}	6.79^{efg}
8	5.20^{a}	6.18^{bcd}	6.56^{fg}
9	4.78^{a}	6.00^{bcd}	6.49^{g}
10	4.90^{a}	5.66^{d}	6.33^{gh}
11	4.70^{a}	5.65^{d}	6.47^{gh}
12	4.84^{a}	6.28^{bc}	6.78^{efg}
Average	5.0	6.1	6.6

*Values with the same letters in every column indicate no significant difference

Values for the first application rate (Table 3.9) generally surpassed the target (pH 5.8) and values for the last mostly under-performed. The values for the target of 6.8 were generally closest to the target. Reasons for this could be that $Ca(OH)_2$ is much more soluble in water than $CaCO_3$, leading to the more effective exchange of acidity on the exchange complex during the lime requirement determination. All the $Ca(OH)_2$ is in solution during the determination whereas all the $CaCO_3$ is not when applied to the soil. This leads to a much higher frequency of contact between the $Ca(OH)_2$ and the clay particles, which in turn leads to more effective neutralization. The lime's solubility in the soil solution is mainly determined by the acid buffering capacity of the solution, which in turn is determined by the rate of release of protons or acid cations from the exchange complex of the soil. With the soil having a relatively high buffer capacity in terms of reserve acidity it lead to an increased solubility of lime therefore leading to a higher reactivity at low application rates than the RH-value would indicate. At pH values higher than 7 (target 3), the solubility of the lime was influenced by an excess of OH^- ions that effectively decreased the release of CO_2 from the carbonates, therefore leading to a lower reactivity of the liming materials than the RH-value would indicate.

A further factor is the mixing of the lime with the soil. Even with an intense effort the degree of mixing cannot be very high, with parts of the soil having received more lime than other parts. This leads to a higher pH in these parts that has an effect on lime dissolution. When sampling a soil where the above is the case a certain variation in the values is expected.

Trial 2

The pH-values obtained and its deviation from the target values for Trial 2 are indicated in Table 3.12. There was a large variation from the target values with Lime 2 – with the rest performing fairly closely to the target. The same trend was found as in Trial 1 concerning the limes that performed well and those that did not. One factor influencing the variation between the liming materials in Trial 1 was the amount applied. Increased variation occurred with larger applications to higher pH target values. In Trial 2 the required lime applications (Table 3.7) were much higher than those in Trial 1 (Table 3.5) due to a much lower soil pH of a different soil. For the lower target pH-value with the larger amounts of lime required there was therefore a higher probability for increased variation. A further observation is the fact that the laboratory reagent $CaCO_3$ under performed. The reason for this is not clear considering that the reagent is usually used as a standard and that it was considered fine enough to secure the assumed reactivity. The RH-value, however, was developed for commercial limes, which seldom have a reactivity of 100%. It can therefore be expected that a factor was built into the RH-value to ensure adequate reactivity for commercial limes and that this factor was not taken into account when using the laboratory reagent.

TABLE 3.12. Trial 2 $pH_{(Water)}$ value deviation from target pH for three rates*.

Lime	Target pH: 5.5	Target pH: 6.0	Target pH: 6.5
		Deviation	
2	**1.01^{a}**	**0.87^{d}**	**0.67^{h}**
3	**0.36^{b}**	**0.09^{e}**	**0.17^{i}**
6	**0.10^{b}**	-0.05^{ef}	**0.09^{i}**
Lab R	-0.46^{c}	-0.6^{fg}	-0.73^{j}
11	-0.56^{c}	-0.97^{g}	-0.97^{j}

*Values with the same letters in every column indicate no significant difference

CONCLUSIONS AND RECOMMENDATIONS

The amounts of lime required for the target pH-values (Trial 1) were very high and amounts of lime required for the target of 6.8 are in most cases already far in excess of the amount that any farmer would consider applying to his lands. This illustrates a few points namely:

- Agricultural fields should not be left to acidify through the inadequate application of lime. This could lead to a situation where it becomes uneconomical or close to impossible to rectify the pH of the soil with consequent inevitable losses in yields. A further consequence is subsoil acidity, which is even more difficult to rectify.

- Each farmer should draw up a response curve for his lands – comparing yield, pH and economy. By doing this he would know which pH is the ideal for the specific soil and can therefore make more informed lime recommendations. Over-liming, but more specifically under-liming, could thus be minimized.

- The method used predicted high amounts of lime needed to neutralize the acid soil. From the results it is clear that these values were not excessive but rather very realistic. It is therefore very important to ensure the realistic evaluation of the soil and lime with the consequent application of the correct amount of lime needed for the specific soil.

From the values it is clear that the RH-value gave a very good indication of the reactivity of the lime over both a three and seven months period. It is furthermore clear that the $Ca(OH)_2$ lime requirement determination method is relatively accurate in that it predicted the amounts required relatively well. It is suggested that the RH-value and a suitable soil pH buffer determination (such as the one in this study) be done when making a lime recommendation. The ease of performing the tests discussed above and the simplicity of calculation removes many sources of possible error.

A shortcoming of the method used for these soils is the facts that it slightly over-predicted the amount required for the pH target of 5.8 and under-predicted the amount required for pH 7.8. This could be due to a different soil to solution ratio that is used when determining the pH of the soil after sampling. The correction of the amounts of lime required as well as different soil to solution ratios in the lime requirement determination will be modelled in Chapter 4.

Very little data is available concerning the performance of the RH-value in predicting lime requirement in field conditions. It is therefore suggested that studies be conducted in the field to confirm the effectiveness of this value.

CHAPTER 4

MODELING OF pH RESULTS

INTRODUCTION

The results discussed in Chapter 3 reflect on the effectiveness of using a $Ca(OH)_2$ incubation to determine the lime requirement and by using the RH-value to obtain a factor that is an indication of the reactivity of the liming materials. Although the use of the RH-value to adapt the theoretical lime requirement according to the incubation curve indicated a high degree of accuracy it must be noted that the lime requirement determination was done in a soil to solution ratio of 1:1. This would not have presented a problem in this study had the pH-values been determined in a similar ratio. The ratio used in this study, however, was 1:2.5. It is therefore expected that the results would reflect a slight difference due to a difference in the solution salt concentration and junction potential.

The above served as the motivation to do additional buffer determinations in a 1:2.5 ratio to ascertain whether there would be a difference in the amount of lime required for a specific target pH. If the values differed, the aim was then to model these results to determine a regression equation that could be used to give the best indication of lime requirement and the lime's reactivity.

MATERIALS AND METHODS

Two additional but different buffer curves were done to determine lime requirement at the end of the trial (Trial 1) on the control soil. This soil had only received fertiliser additions during the trial and no lime. One determination was done in a soil to solution ratio of 1:1 (50g soil) and another was done in a ratio of 1:2.5 (20g soil). The method used is as described in Chapter 3. The 1:2.5 ratio was also used by Bornman (1985) in the determination of the RH-value. These two sets of results were compared with each other and with the original buffer curve at the start of the trial. Using the regression equations of each determination, the amount of $Ca(OH)_2$ required for the pH targets 5.8, 6.8, and 7.8, was calculated and recalculated for pure $CaCO_3$.

To model the pH results, three steps were followed. Firstly, the average pH-value obtained for each of the target application rates for every lime (Chapter 3 and Appendix 3) was used to obtain a regression equation describing the relationship between lime application and pH for every lime. Secondly, using both the RH- and CCE HCl-values, different lime recommendations were made for each lime using the results of the different buffer curves determined above. Thirdly, using the regression equations of the limes' incubation curves, the resultant pH value was calculated for every "lime application" as calculated from the different lime recommendations. The results were statistically analysed using the SAS® System to obtain the Analysis of Variance (ANOVA) and the LSD – Tukey to determine significant differences.

RESULTS AND DISCUSSION

The results of the two lime requirement determinations compared to the original one are given in Table 4.1 and the values are presented graphically in Figure 4.1. From the results it seems that the soil was less buffered, at the end of the trial, in the low pH range compared to the start of the trial. Although the values differed slightly the slopes of the regression lines are the same, indicating a very similar buffer capacity throughout the seven months. There was also a slight difference between the values for the different ratios. The difference between the 1:1 ratio and 1:2.5 ratio values is ascribed to a "dilution" effect due to the smaller volume of soil to solution and a subsequent lower salt and proton concentration in the solution. The lower salt concentration in turn lead to a junction potential that differed from the one in the 1:1 soil to solution ratios. In all three cases the incubation values had a linear trend with a very good correlation. From the small difference it was concluded that the values from the second determination (specifically the 1:2.5 ratio values) could be used in the modelling of the different methods.

TABLE 4.1. Resultant pH values after incubation with $Ca(OH)_2$ at different stages of Trial 1.

Soil – Solution ratio	1:1 (50g soil)	1:1 (50g soil)	1:2.5 (20g soil)
Stage	Before trial	After trial	After trial
$Ca(OH)_2$ added (mmol/kg soil)	pH	pH	pH
0	5.08	5.20	5.37
0.86	5.30	-	-
1.72	5.42	-	-
2.15	-	-	-
2.58	5.53	-	-
2.64	-	5.47	-
3.30	-	-	6.14
3.44	5.76	-	-
4.30	5.88	-	-
5.28	-	6.34	-
6.45	6.22	-	-
6.60	-	-	6.72
7.92	-	6.87	-
8.60	6.52	-	-
10.56	-	7.18	-
10.75	6.85	-	-
12.90	7.08	-	-
13.20	-	-	7.37
15.05	7.46	-	-
16.50	-	-	7.96
17.20	7.72	-	-
19.80	-	-	8.37

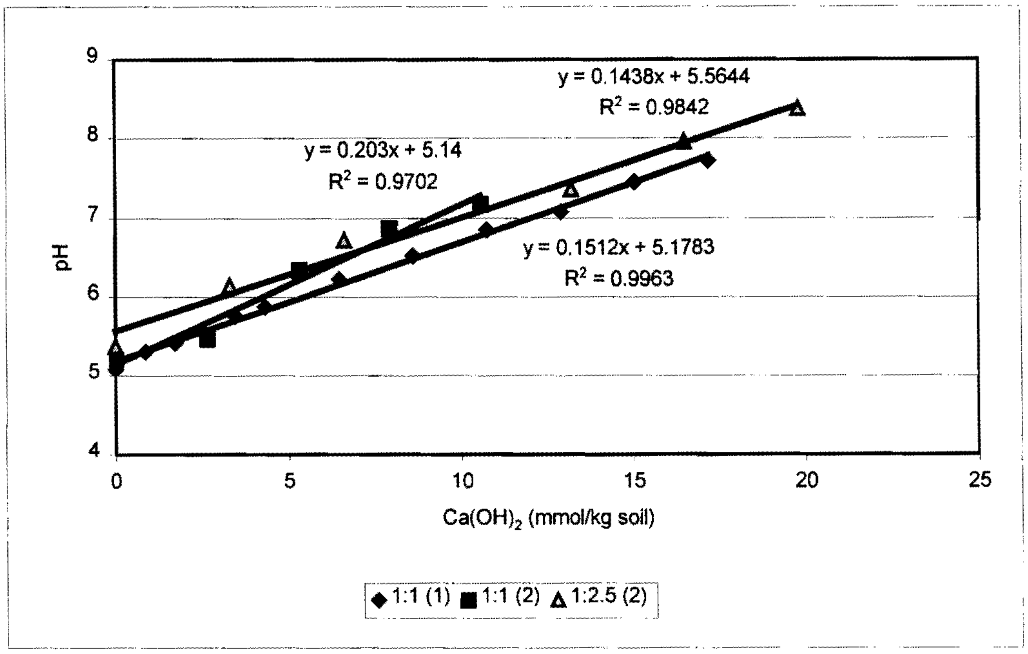

Figure 4.1. $Ca(OH)_2$ buffer curves for three determinations.

The incubation curves and derived equations drawn up for every lime ($pH_{(Water)}$ and $pH_{(KCl)}$ values) are given in Appendix 4 and the calculations on which the modelling is based are given in Appendix 5.

An aspect that is not covered by this study but which is none the less worthy of note is the fact that the lime incubation pH values in KCl remain at least one pH unit below the values in water throughout (Figures 1 through 12 in Appendix 4). Theoretically the $pH_{(KCl)}$ values should approach the $pH_{(Water)}$ values as the acid saturation decreases somewhat below a pH of 7. The fact that this is not the case sheds some doubt on the use of a solution with a strong electrolyte concentration such as 1M for KCl instead of 0.01M in the case of $CaCl_2$.

Figures 4.2 and 4.3 give the predicted averages over the twelve limes with each method used for both pH determination methods. Table 4.2 indicates the average of the "performance" of 12 limes for every method used in the modelling.

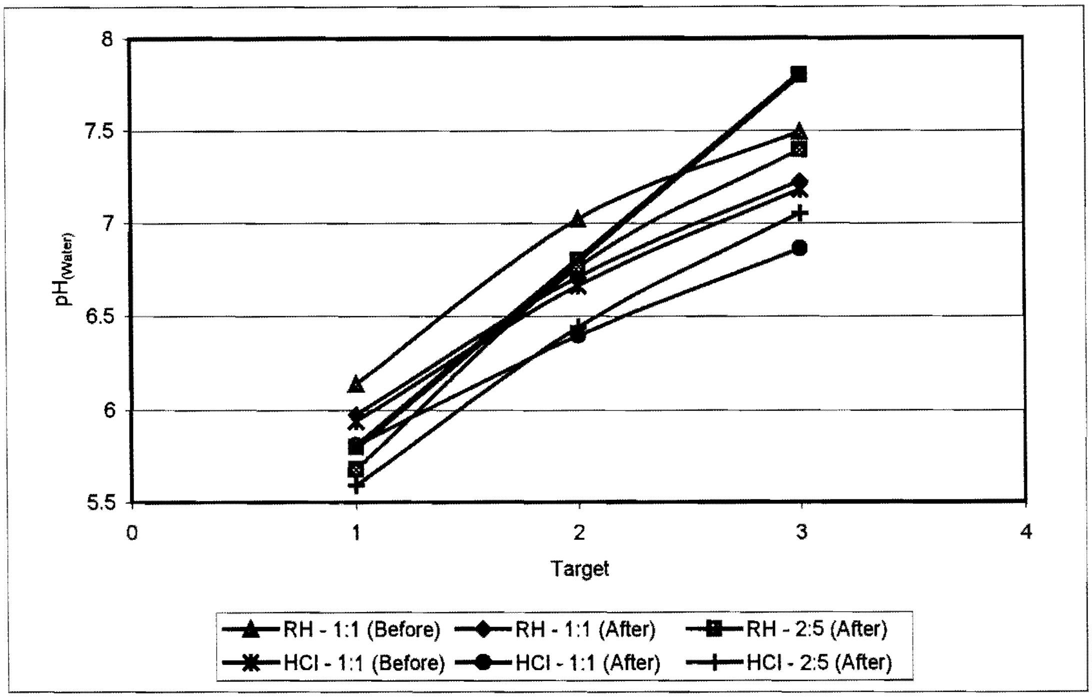

Figure 4.2. Average $pH_{(Water)}$ values for six methods used compared with the target values.

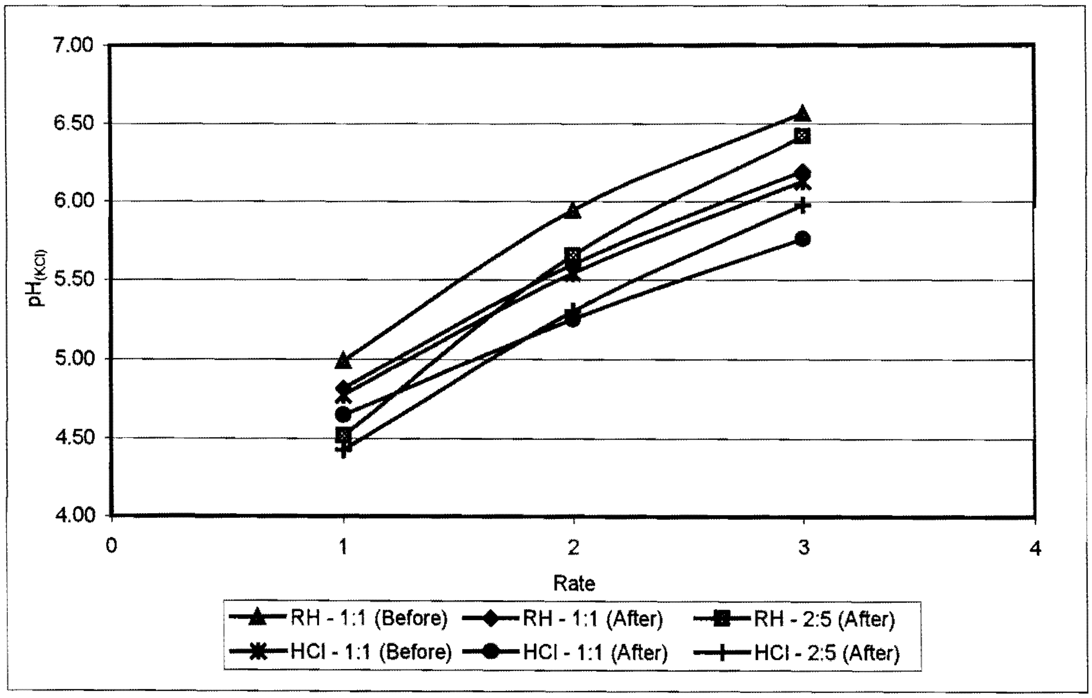

Figure 4.3. Average $pH_{(KCl)}$ values for the six methods used.

Several of the methods predicted an average value close to the target for each target but the one method that predicted close values consistently was the RH 1:2.5 (A). Most of the HCl methods under-predicted lime requirement and the RH 1:1 methods tended to over-predict lime requirement at low targets and, like all the other methods, under-predict it at high targets. The two 1:2.5 methods (RH and HCl) exhibited regression curve slopes closer to that of the targets whereas the 1:1 methods all had flatter slopes. The RH 1:2.5 (A) though was much closer to the targets than the HCl 1:2.5 (A).

TABLE 4.2. Deviation of mean values from targets for 12 liming materials as predicted by three different lime requirement determinations and two different reactivity determinations (RH = Resin Suspension Method, HCl = CCE HCl method, A = After trial, B = Before trial).[*]

Target pH 5.8		Target pH 6.8		Target pH 7.8	
Method	Deviation	Method	Deviation	Method	Deviation
RH 1:1 (B)	0.34^{a}	RH 1:1 (B)	0.22^{f}	RH 1:1 (B)	-0.31^{j}
RH 1:1 (A)	0.17^{b}	RH 1:2.5 (A)	-0.04^{fg}	RH 1:2.5 (A)	-0.40^{jk}
HCl 1:1 (B)	0.14^{bc}	RH 1:1 (A)	-0.09^{g}	RH 1:1 (A)	-0.58^{jkl}
HCl 1:1 (A)	0.01^{cd}	HCl 1:1 (B)	-0.14^{gh}	HCl 1:1 (B)	-0.62^{kl}
RH 1:2.5 (A)	-0.12^{de}	HCl 1:2.5 (A)	-0.36^{hi}	HCl 1:2.5 (A)	-0.75^{lm}
HCl 1:2.5 (A)	-0.20^{e}	HCl 1:1 (A)	-0.41^{i}	HCl 1:1 (A)	-0.94^{m}

[*] Values with the same letters indicate no significant difference

The variation between the methods was generally small with a very similar spread in pH values although the difference between the HCl and RH methods was relatively large for some limes as can be seen from Tables 6 – 11 in Appendix 5. The difference between the results of the HCl- and RH-methods was small for the limes that had a high RH-value (and therefore close to the CCE HCl-value) but was large for those that had low RH values compared to the CCE HCl. Two examples at the extremes are Limes 2 and 7, which are indicated in Figures 4.4 and 4.5. Specifically in the case of these limes the CCE HCl value under-predicted the reactivity quite substantially. In the case of both these limes the RH 1:2.5 (A) method gave the closest fit to the targets.

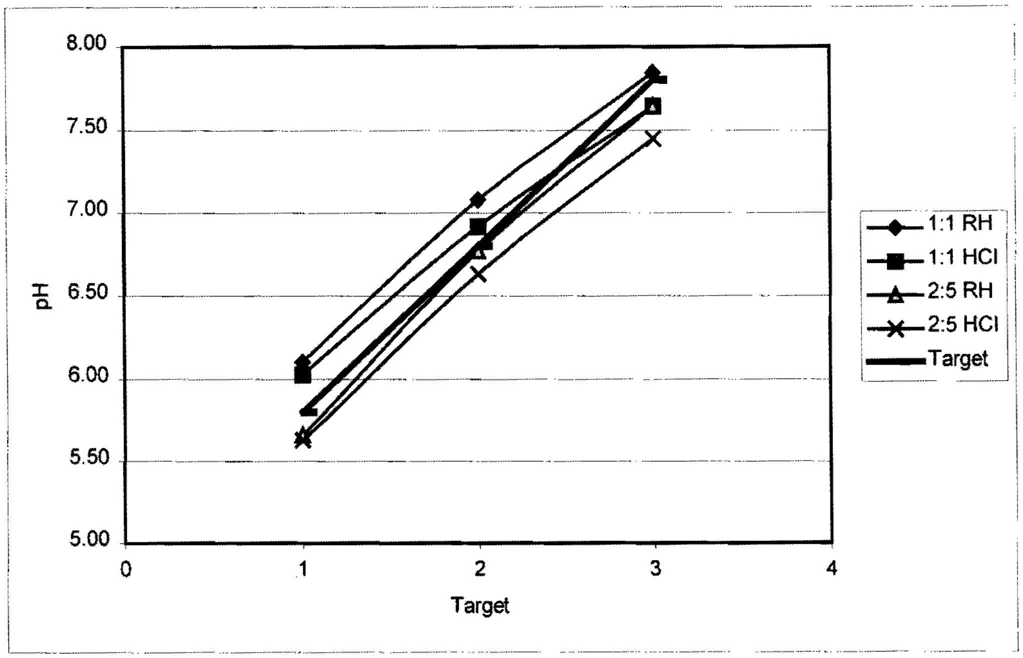

Figure 4.4. Predicted pH values for Lime 7 from calculated lime recommendations.

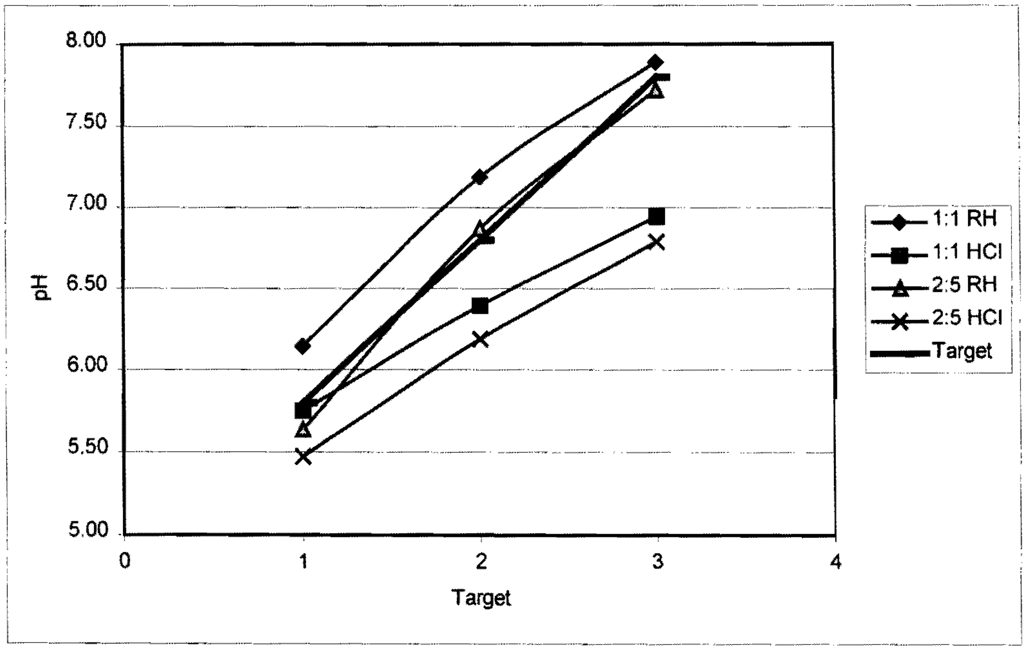

Figure 4.5. Predicted pH values for Lime 2 from calculated lime recommendations.

CONCLUSIONS

The RH 1:1 (B) values are, by virtue of the fact that they were the values used to base the modelling on, very close to the values obtained in the trial. Taking this fact into account, it is quite clear that the CCE HCl method highly overrated the reactivity of limes 2, 6, 8, 9, 10 and 12. In the case specifically of the mentioned limes the, RH-value gave a much more realistic indication of their reactivity.

The Resin Suspension Method is superior to the CCE HCl method in giving an indication of the reactivity of liming materials. The difference between the two methods is not very pronounced when limes that have a RH-value close to that of the CCE HCl are taken into account but becomes very pronounced when limes with RH-values lower than that of the CCE HCl are considered. In any further evaluation of liming materials in terms of reactivity this aspect should be noted. The RH-value though does not make provision for the altered solubilities of liming materials at pH levels far above and below 6.3 (Bornman, 1985).

Soil is a dynamic open system and has, depending on its composition in terms of dominant minerals and chemistry, a certain buffering capacity concerning changes in pH. Most acid soils that are still under crops have $pH_{(Water)}$ values between 4 and 5.5. The predominant acids in soils are relatively weak and do not compare with strong acid solutions like HCl. The dissolution of lime in a concentrated HCl solution would therefore lead to erroneous deductions with regard to its reactivity. Hence it is recommended that the RH-value be the only reactivity parameter used when making a lime recommendation.

When considering the lime requirement determination it is clear that the 1:2.5 method yielded more realistic values. This is most probably due to the fact that the pH measurement afterwards in the soil is done in a similar solution to soil ratio, and that the consequent dilution or concentration effect is minimised. It appears that the most realistic values to use when making a lime recommendation are those around a neutral pH and this should be kept in mind when making such a recommendation.

Although the use of a 1M KCl solution is accepted as standard by many local researchers, the pH data in this trial leads to questions concerning its applicability as an indication of pH. This aspect definitely needs further clarification.

CHAPTER 5

PHOSPHORUS AVAILABILITY FROM SLAGS

INTRODUCTION

Phosphorus is found in soils under normal pH conditions mainly in the $H_2PO_4^-$ form and is subject to reactions with sesquioxide mineral surfaces at acidic pH (Mengel & Kirkby, 1987). This is one of the main reasons for the widespread deficiency of P in South African soils. From a plant nutrition perspective three main soil P fractions are important namely:

- P in the soil solution
- P in the labile pool
- P in the non-labile pool

The reaction of P with sesquioxide mineral surfaces leads to the situation where the P concentration in the soil solution is very low yet in equilibrium with the P held on particle surfaces. The non-labile pool is the largest and contains the insoluble P that can only be released very slowly into the labile pool. In soils with an above neutral pH the P reacts mainly with Ca to form insoluble minerals such as apetite (Mengel & Kirkby, 1987).

In the case where soils with a low pH and a high P-fixing capacity undergo a change in pH (increase) as in the case of lime addition the P becomes more available due to a change in the charge properties of the soil (Hingston. *et al.*, 1967).

Silica in the form of H_4SiO_4 is also found in the soil solution and its concentration is determined by the soil solution pH and through equilibrium with several Si minerals present in the soil (Elgawhary & Lindsay, 1972). Both P and Si are found in the soil solution in the form of anions and tend to undergo similar reactions with soil minerals (Hingston, *et al.*, 1967). Although P is more strongly bonded to sesquioxides than Si both of these compete for the same adsorption sites on minerals. The soil minerals and their affinity for P and also the P and Si anion concentration in solution, therefore, determine equilibrium. The adsorption of P is much stronger than Si at acidic pH but this situation changes at neutral and alkaline pH when Si is more strongly adsorbed (Hingston, *et al.*, 1967).

A further factor influencing the P equilibrium in the soil solution is the Si concentration and changes therein. If the Si concentration increases and the pH of the soil rises to neutral or alkaline the Si begins to replace P on the soil particles. The result of this effect is an increase in the labile P-pool and a subsequent increased uptake by plants grown on this soil (Reifenberg & Buckwold, 1954; Raupach & Piper, 1959; Datta, Shinde, & Kamath, 1962; Scheffer & Henze, 1962). In pure nutrient solutions there is an antagonistic effect between P and Si in terms of plant uptake but in soils on the other hand the "antagonism" leads to higher P levels in plants (Gaussmann, 1962).

Slags in many cases contain appreciable amounts of either P or Si or both (Table 5.1). In the USA basic slag was used until 1975 as a source of P, but the P-content has since decreased from 50-100g P kg^{-1} to around 10g P kg^{-1} (Barber, 1984). Most of the phosphates in the slag are complex and not soluble in water, but it is released in soil and is therefore more available to the plant, especially when the slags are very fine (Cooke, 1982).

The effect of Si in slags has already been thoroughly documented (Neergaard, 1962; Scheffer & Henze, 1962; Hunter, 1965; Roy, Ali, & Fox, 1971) and is regularly used to motivate the use of slags as agricultural limes. The amount of P applied to the soil during the use of slags could, if available to the plant, reduce the farmer's need for fertiliser P from other sources

TABLE 5.1. Average P and Si content of two slags before refining into agricultural lime (Source: Columbus Steel and Highveld Steel).

Chemical Compound	Columbus Steel %	Highveld Steel %
P	-	0.4
SiO_2	30.6	17.9

The Si seems to have a pronounced effect on the mobilisation of soil-P in soils with a high P fixing capacity as well as the plant uptake of fertiliser-P in soils with lower P fixing capacities (Datta, *et al.*, 1962).

The pH where the above-mentioned competition between Si and P becomes significant is above 6.5, which would imply that the user would have to lime to levels higher than these to benefit from it. This would be impractical and could cause other nutritional problems.

Very little work has been done on the interaction of Si and P from slags in recent years except for a few recent studies in Eastern Europe (Ivanov, 1992) as well as studies on the ability of slags to immobilise excessive P in solution in Western Europe (Vanacker, 1999). Most of the work done on P availability from slags took place in the 1950s and '60s.

The aim of this study was to determine the amount of P available to the plant from the applied slags and make deductions concerning the influence Si has on soil P and P applied.

MATERIALS AND METHODS

The testing of P availability from slags was carried out in two trials. Trial 1 has already been discussed in detail in Chapter 2. Amongst others the spinach was tested for P by H_2SO_4/H_2O_2 digestion solution (ALASA, 1998) and the P determined by Auto Analyser (AA).

For Trial 2 a soil with a low pH and P content (Table 3.1) was chosen to minimise the effect of Si on soil-P. Four slags and a laboratory reagent $CaCO_3$ were added to this soil in 4 kg pots at three pH targets (5.5, 6.0, and 6.5) and the amounts of lime were calculated as described in Chapter 3. The slags were selected from the original liming materials in Trial 1. Each slag was digested with $HClO_4$:$2HNO_3$ (ALASA, 1998) and the amount of P determined by Auto Analyser. This digestion procedure was chosen due to the influence of Sulphur on the AA, even though the above reagent was prescribed for plant material and an H_2SO_4 digestion prescribed for limes.

The citric acid soluble P of each slag was determined in a 2% aqueous citric acid solution by adding 5g of the liming material to 500ml of the solution (ALASA, 1998). The solution was stirred for 30 minutes and the P determined by AA again.

Wheat was simultaneously grown in the same pots for three months, harvested, weighed and P determined on the plant material as for the spinach in Trial 1.

RESULTS AND DISCUSSION

The total and citric acid soluble P content of the slags are given in Table 5.2. The levels for Limes 3 and 6 are lower than expected when the values of Table 5.1 are taken into account. A factor that could play a role here is the addition of other liming materials (dolomitic limes) to the slags in its preparation to comply with the regulations for dolomitic lime, therefore diluting the slag in terms of P content. Furthermore, the values given in Table 5.1 are long-term average values obtained from the industry and the possibility exists that the P-content varied and was lower than average at the time of sampling. The citric acid soluble P seems in most cases to be two thirds of the total value.

TABLE 5.2. Total and citric acid soluble P in four slags.

Lime	Source	Total P (%)	Citric Acid Soluble P (%)
2	Columbus	0.006	0.004
3	Highveld	0.126	0.095
6	Highveld	0.126	0.089
11	ISCOR Vereniging	0.019	0.015

The P levels in the plants for Trial 1 are tabulated in Table 5.3 and presented graphically in Figures 5.1 and 5.2. In most cases the P-uptake increased moderately with increasing pH. All the limes performed more or less the same with regard to P uptake by the spinach except for Lime 2 (and to a lesser extent Lime 11 at neutral pH values), which had a higher P-uptake above pH 6.5. Lime 2 has a very low P-content (Table 5.2) but high Si content (Table 5.1) and the soil had a relatively high P-content (Table 3.1). It is difficult to conclude whether the increase in P-content can be attributed to the higher availability soil P at higher pH, or due to the presence of Si from the slag. Limes 3 and 6 contain higher amounts of P than Lime 2 and both indicated a slight increase in P-uptake at pH values above 7.5. The P-content of the slags is probably too low to make any significant contribution to the plant available P.

TABLE 5.3. P-content of spinach leaves for twelve liming materials (Trial 1).

Lime	Application rate	Spinach P content (%)	pH of soil
1	1	0.19	6.35
	2	0.21	6.91
	3	0.21	7.29
2	1	0.25	6.05
	2	0.35	7.27
	3	0.42	7.88
3	1	0.26	6.33
	2	0.27	7.42
	3	0.32	7.61
4	1	0.26	6.05
	2	0.21	6.55
	3	0.25	7.34
5	1	0.20	6.15
	2	0.29	7.11
	3	0.30	7.54
6	1	0.23	6.22
	2	0.26	7.18
	3	0.32	7.60
7	1	0.20	6.19
	2	0.26	7.02
	3	0.30	7.86
8	1	0.18	6.58
	2	0.22	7.18
	3	0.24	7.53
9	1	0.23	6.37
	2	0.24	6.95
	3	0.24	7.43
10	1	0.18	6.25
	2	0.23	6.79
	3	0.20	7.21
11	1	0.19	5.91
	2	0.28	6.78
	3	0.28	7.27
12	1	0.18	6.12
	2	0.21	6.78
	3	0.28	7.60

The soil chosen for Trial 2 had a much lower P-content to reduce the effect of Si on soil P and to limit the plant P-content mainly to the P available from the slag. The P content of the wheat grown in this trial is indicated in Table 5.4 and Figure 5.3.

Contrary to the spinach, the P content of the wheat decreased with an increasing pH. The values though are influenced by the increase in growth of the plants with the higher application rates of the lime. Figure 5.4 indicates the wheat growth per pot. With the low amount of available P the concentration in the plant decreased as the plant mass increased. This is to a very large extent confirmed by the amounts of P taken from the soil (Table 5.4) although it appears that some of the slags performed marginally better than others. From the P contents of the plants it would seem that the slags contributed very little P. When the amount of P that was added to the soil in the different slags (Table 5.5) is calculated, it is clear that these values are very low and it would therefore be difficult to distinguish between P from the slags or the soil. If all the lime reacted in the soil and most of the P was in the available form these values would still be low but there might have been a difference between the limes with low levels and those with high levels in terms of P-uptake.

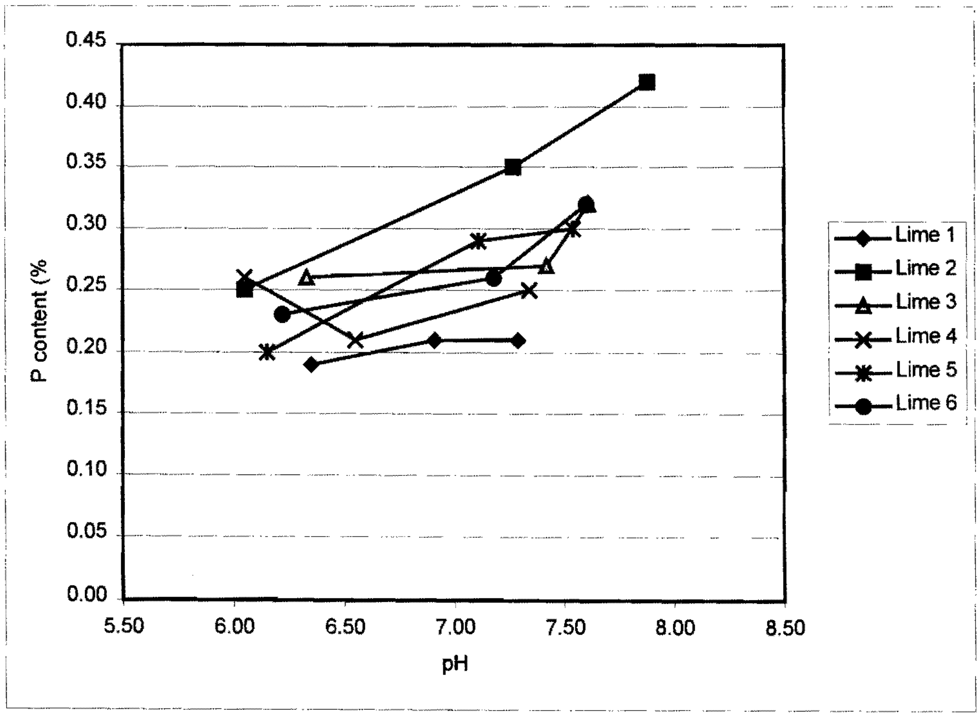

Figure 5.1. P content of spinach grown on soil ameliorated with Limes 1 to 6.

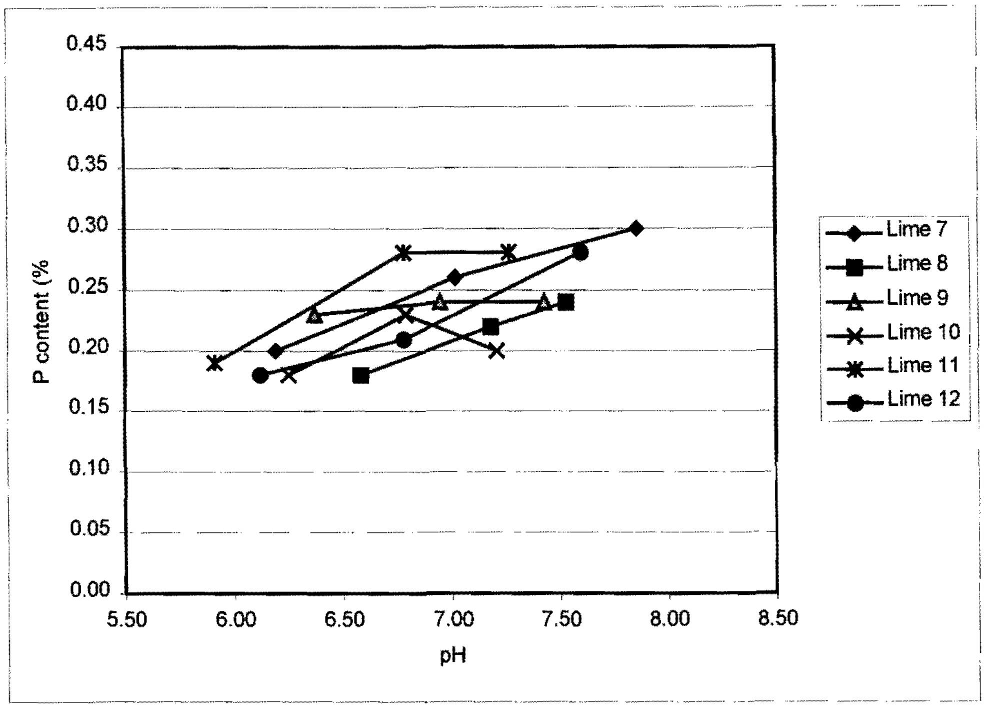

Figure 5.2. P content of spinach grown on soil ameliorated with Limes 7 to 12.

TABLE 5.4. Wheat yield and P content for four slags and a control treatment at three different application rates.

Lime	Application rate	Yield per pot (g)	Wheat P content (mg.kg^{-1})	P taken up (mg)	pH of soil
2	1	27.81	353.94	9.8	6.51
	2	32.25	232.03	7.5	6.87
	3	38.84	212.32	8.2	7.17
3	1	27.62	394.32	10.9	5.86
	2	30.93	352.89	10.9	6.09
	3	28.04	383.24	10.7	6.67
6	1	26.93	418.88	11.3	5.6
	2	25.09	372.77	9.4	5.95
	3	26.93	343.49	9.3	6.59
11	1	25.27	427.28	10.8	4.95
	2	27.48	497.77	13.7	5.04
	3	28.73	413.64	11.9	5.53
Lab	1	17.74	578.06	10.3	5.04
	2	17.72	622.59	11.0	5.43
	3	20.18	552.67	11.2	5.77

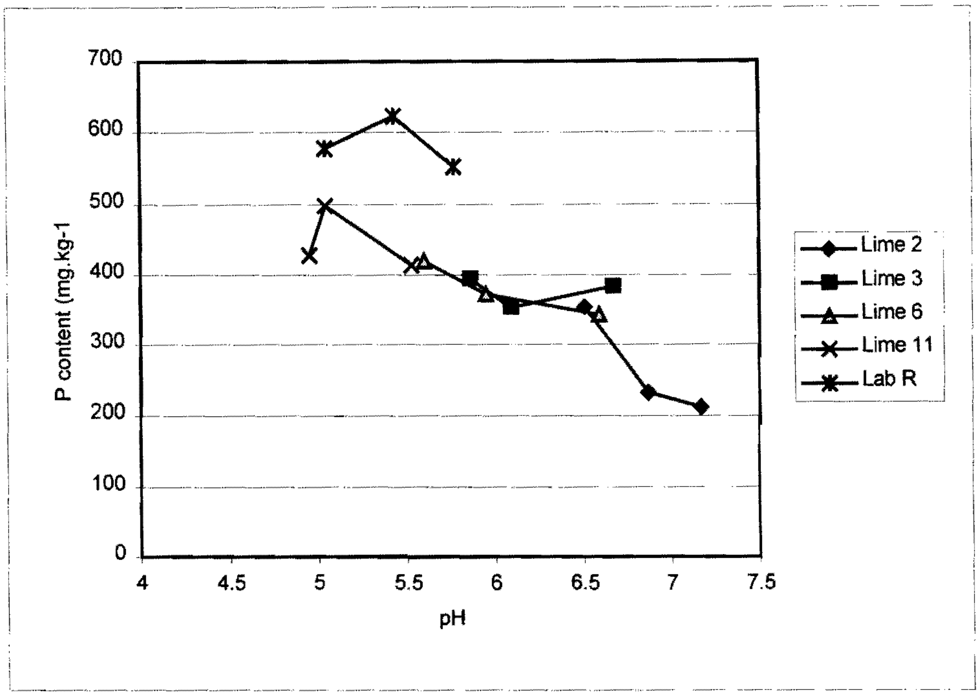

Figure 5.3. P content of wheat plants grown on soil ameliorated with four slags and a lime laboratory reagent at three application rates.

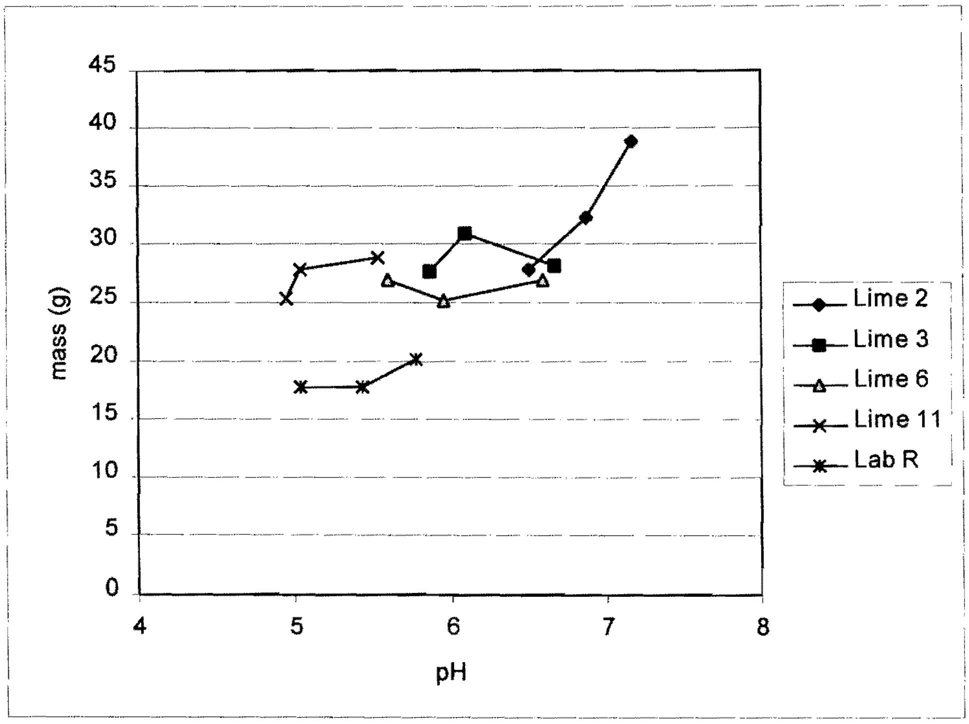

Figure 5.4. Average yield of wheat plants grown on soil ameliorated with five different liming materials at three application rates.

TABLE 5.5. Amounts of P applied to the soil in the different limes and application rates.

Lime	Rate	P-content (%)	Lime added (g pot^{-1})	P added (mg pot^{-1})	P added (kg ha^{-1})
2	1	0.006	10.28	0.62	0.70
	2		12.76	0.77	0.87
	3		15.24	0.91	1.02
3	1	0.126	8.08	10.18	11.45
	2		10.02	12.63	14.21
	3		11.97	15.08	16.97
6	1	0.126	8.82	11.11	12.50
	2		10.94	13.78	15.50
	3		13.07	16.47	18.53
11	1	0.019	5.53	1.05	1.18
	2		6.86	1.30	1.46
	3		8.19	1.56	1.76
Lab R	1	0	4.78	0	0
	2		5.93	0	0
	3		7.08	0	0

CONCLUSIONS

No clear indication exists concerning the amount of available P contributed by the slags and distinguishing it from the P supplied by the soil in the trials discussed above. Several problems exist namely:

- Low P-content of the slags,
- Small amounts of P in the slags that are immediately plant available due to the slow reaction of the liming materials in soil,
- The trials did not allow sufficient time for the P to be released,
- The trials did not allow for sufficient P to build up in the soil.

Although low, the contribution of P from the soil is relatively much higher than from the slags, therefore masking the slags' contribution. The trials therefore are very limited in their ability to predict P availability from the slags. The only indication concerning increased P uptake was in Trial 1 involving a lime with a very low P content but a high Si content.

In order to quantify the amount of P available from the slags, future trials would have to take into account the long-term application of slags and the simultaneous reacidification of the soil. In such a case the P applied in the slags would have had time to be released and consequently be adsorbed or fixed by the soil. It could be possible then to quantify the added P through P fractionations and/or long-term plant-uptake trials.

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APPENDIX 1
CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE LIMES COLLECTED

Ref no	Trial no	Ca	Mg	CCE HCl	RH-value	Sieve Fraction Analysis (% passing)				Lime type
		%	%	%	%	SF<1.7mm	SF<1.0mm	SF<0.25mm	SF<0.106mm	
K001*	1	17.20	11.23	83.00	75.83	98.52	96.89	91.66	84.13	Dolomitic
K002*+	2	30.02	7.37	95.48	49.67	95.53	87.93	67.45	39.90	Slag
K003*+	3	31.06	5.57	84.98	64.57	99.36	92.01	64.98	42.48	Dolomitic
K004*	4	37.76	0.95	98.04	91.72	99.90	99.80	98.90	98.13	Paper mill waste
K005		28.36	8.59	97.30	55.63	99.28	91.32	63.90	44.80	Slag
K006		18.74	12.49	87.31	47.02	94.06	80.83	47.78	34.00	Dolomitic
K007		18.86	11.62	84.84	72.19	99.80	99.56	99.44	94.58	Dolomitic
K008		32.08	4.61	93.75	53.31	99.43	92.10	61.67	39.90	Slag
K009		40.43	4.95	104.28	76.16	99.53	99.13	89.73	61.53	Slag
K010		17.54	10.56	79.35	72.19	99.55	99.00	87.30	73.60	Dolomitic
K011*	5	16.27	14.63	85.75	59.60	97.70	88.35	66.20	59.80	Dolomitic
K012		29.51	7.24	95.53	45.36	88.11	82.56	61.10	31.40	Slag
K013*+	6	27.02	9.32	95.88	59.60	99.59	91.21	59.58	37.25	Slag
K014		1.43	14.68	50.83	10.93	88.19	75.24	48.61	37.68	Magnesite mine by-product
K015*	7	37.30	1.18	98.54	87.75	99.96	99.86	98.48	94.88	Paper mill waste
K016		26.51	4.85	89.79	33.77	76.88	61.18	35.43	24.15	Slag
K017*	8	16.64	14.68	88.38	54.97	87.04	72.46	50.73	43.75	Dolomitic
K018		35.08	0.94	85.38	75.17	99.15	98.65	96.90	96.25	Sugar industry by-product
K019		19.04	14.32	95.31	67.55	99.18	96.83	77.53	57.60	Dolomitic
K020		32.81	1.69	86.65	50.99	99.94	99.84	52.46	37.18	Calcitic
K021*	9	18.20	11.99	87.98	77.48	99.71	98.46	57.13	29.00	Dolomitic
K022*	10	19.95	12.11	91.40	54.64	99.68	99.30	73.58	67.56	Dolomitic
K023*+	11	40.43	4.95	104.28	76.16	99.53	99.13	89.73	61.53	Slag
K024*	12	26.02	5.55	74.90	46.59	97.67	80.77	43.57	22.87	Slag

* Limes selected for Trial 1
\+ Limes selected for Trial 2

APPENDIX 2

TEST RESULTS OF METALS NOT INCLUDED IN STUDY

1. Copper

TABLE 1. Copper content of limes and amounts of lime and Co added per pot.

Lime no	Rate	Cu Content of Lime (mg.kg^{-1})	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg^{-1})
1	1	23.03*	5.94	3.60	0.02
	2		15.16	9.10	0.05
	3		24.38	14.60	0.07
2	1	32.30 (14.00)**	6.89	4.10	0.03
	2		17.59	10.60	0.08
	3		28.30	17.00	0.12
3	1	43.73 (40.00)	5.41	3.20	0.03
	2		13.81	8.30	0.08
	3		22.22	13.30	0.13
4	1	7.34	3.60	2.20	0.00
	2		9.20	5.50	0.01
	3		14.80	8.90	0.01
5	1	5.77	6.95	4.20	0.01
	2		17.74	10.70	0.01
	3		28.54	17.10	0.02
6	1	35.98 (36.00)	5.91	3.50	0.03
	2		15.09	9.10	0.07
	3		24.26	14.60	0.12
7	1	5.40	3.79	2.30	0.00
	2		9.68	5.80	0.01
	3		15.56	9.30	0.01
8	1	4.06	7.43	4.50	0.00
	2		18.98	11.40	0.01
	3		30.52	18.30	0.02
9	1	11.76	5.47	3.30	0.01
	2		13.97	8.40	0.02
	3		22.47	13.50	0.04
10	1	10.37	7.30	4.40	0.01
	2		18.65	11.20	0.03
	3		30.00	18.00	0.04
11	1	47.50 (109.00)	3.70	2.20	0.02
	2		9.45	5.70	0.06
	3		15.21	9.10	0.10
12	1	140.95	8.70	5.20	0.16
	2		22.21	13.30	0.42
	3		35.73	21.50	0.67

*** Semi-quantitative determination by ICP MS-scan**

**** Quantitative determination by ICP MS**

TABLE 2. Copper content ($mg.kg^{-1}$) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Cu ($mg.kg^{-1}$)	pH
1	1	4.33	12	6.35
	2	4.71	6	6.91
	3	8.96	4.5	7.29
2	1	5.2	7.5	6.05
	2	8.86	7.5	7.27
	3	10.67	10.5	7.88
3	1	5.93	6	6.33
	2	6.42	4.5	7.42
	3	9.26	10.5	7.61
4	1	5.68	13.5	6.05
	2	9.16	7.5	6.55
	3	9.38	7.5	7.34
5	1	6.16	6	6.15
	2	6.89	3	7.11
	3	8.49	4.5	7.54
6	1	5.19	9	6.22
	2	7.35	6	7.18
	3	7.2	10.5	7.60
7	1	8.33	6	6.19
	2	12.84	13.5	7.02
	3	14.66	12	7.86
8	1	3.26	6	6.58
	2	6.85	3	7.18
	3	7.94	4.5	7.53
9	1	5.98	4.5	6.37
	2	9.32	7.5	6.95
	3	9.94	12	7.43
10	1	5.5	6	6.25
	2	7.44	6	6.79
	3	11.04	10.5	7.21
11	1	5.51	6	5.91
	2	8.03	4.5	6.78
	3	9.79	9	7.27
12	1	3.19	3	6.12
	2	8.75	7.5	6.78
	3	9.66	7.5	7.60

2. Zinc

TABLE 3. Zinc content of limes and amounts of lime and Zn added per pot.

Lime no	Rate	Zn Content of Lime (mg.kg^{-1})	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg^{-1})
1	1	27.48*	5.94	3.60	0.0218
	2		15.16	9.10	0.0555
	3		24.38	14.60	0.0893
2	1	42.94 (31.00)**	6.89	4.10	0.0285
	2		17.59	10.60	0.0727
	3		28.30	17.00	0.1170
3	1	30.49 (49.00)	5.41	3.20	0.0353
	2		13.81	8.30	0.0902
	3		22.22	13.30	0.1452
4	1	8.68	3.60	2.20	0.0042
	2		9.20	5.50	0.0106
	3		14.80	8.90	0.0171
5	1	5.68	6.95	4.20	0.0053
	2		17.74	10.70	0.0134
	3		28.54	17.10	0.0216
6	1	25.74 (54.00)	5.91	3.50	0.0426
	2		15.09	9.10	0.1086
	3		24.26	14.60	0.1747
7	1	6.12	3.79	2.30	0.0031
	2		9.68	5.80	0.0079
	3		15.56	9.30	0.0127
8	1	4.19	7.43	4.50	0.0042
	2		18.98	11.40	0.0106
	3		30.52	18.30	0.0171
9	1	11.91	5.47	3.30	0.0087
	2		13.97	8.40	0.0222
	3		22.47	13.50	0.0357
10	1	4.33	7.30	4.40	0.0042
	2		18.65	11.20	0.0108
	3		30.00	18.00	0.0173
11	1	64.22 (202)	3.70	2.20	0.0997
	2		9.45	5.70	0.2545
	3		15.21	9.10	0.4097
12	1	281.41	8.70	5.20	0.3264
	2		22.21	13.30	0.8333
	3		35.73	21.50	1.3406

* **Semi-quantitative determination by ICP MS-scan**

** **Quantitative determination by ICP MS**

TABLE 4. Zinc content ($mg.kg^{-1}$) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Zn ($mg.kg^{-1}$)	pH
1	1	4.33	228	6.35
	2	4.71	136	6.91
	3	8.96	123	7.29
2	1	5.2	162	6.05
	2	8.86	123	7.27
	3	10.67	88	7.88
3	1	5.93	194	6.33
	2	6.42	124	7.42
	3	9.26	146	7.61
4	1	5.68	201	6.05
	2	9.16	148	6.55
	3	9.38	112	7.34
5	1	6.16	200	6.15
	2	6.89	120	7.11
	3	8.49	136	7.54
6	1	5.19	172	6.22
	2	7.35	92	7.18
	3	7.2	96	7.60
7	1	8.33	194	6.19
	2	12.84	164	7.02
	3	14.66	132	7.86
8	1	3.26	184	6.58
	2	6.85	128	7.18
	3	7.94	117	7.53
9	1	5.98	189	6.37
	2	9.32	158	6.95
	3	9.94	132	7.43
10	1	5.5	186	6.25
	2	7.44	144	6.79
	3	11.04	150	7.21
11	1	5.51	178	5.91
	2	8.03	141	6.78
	3	9.79	129	7.27
12	1	3.19	147	6.12
	2	8.75	124	6.78
	3	9.66	111	7.60

3. Barium

TABLE 5. Barium content of limes and amounts of lime and Ba added per pot.

Lime no	Rate	Ba Content of Lime (mg.kg^{-1})	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil (mg.kg^{-1})
2	1	114.20* (106.14)**	6.89	4.10	0.10
	2		17.59	10.60	0.27
	3		28.30	17.00	0.43
3	2	65.57	13.81	8.30	0.12
	3		22.22	13.30	0.19
4	1	143.42	3.60	2.20	0.07
	2		9.20	5.50	0.18
	3		14.80	8.90	0.28
10	1	15.80 (14.20)	7.30	4.40	0.02
	2		18.65	11.20	0.04
	3		30.00	18.00	0.06
11	1	185.87 (147.27)	3.70	2.20	0.09
	2		9.45	5.70	0.23
	3		15.21	9.10	0.38
12	1	481.21	8.70	5.20	0.56
	2		22.21	13.30	1.43
	3		35.73	21.50	2.29

*** Semi-quantitative determination by ICP MS-scan**

**** Quantitative determination by ICP MS**

TABLE 6. Barium content (mg.kg^{-1}) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Ba (mg.kg^{-1})	pH
2	1	5.2	28.06	6.05
	2	8.86	7.20	7.27
	3	10.67	0.06	7.88
3	2	6.42	14.55	7.42
	3	9.26	6.99	7.61
4	1	5.68	58.76	6.05
	2	9.16	25.75	6.55
	3	9.38	25.22	7.34
10	1	5.5	45.52	6.25
	2	7.44	30.29	6.79
	3	11.04	20.73	7.21
11	1	5.51	40.52	5.91
	2	8.03	17.37	6.78
	3	9.79	4.56	7.27
12	1	3.19	44.18	6.12
	2	8.75	10.44	6.78
	3	9.66	8.08	7.60

TABLE 7. NH_4-EDTA extraction (Ba) on soil from lime 11.

Rate	NH_4-EDTA extractable Ba ($mg.kg^{-1}$)
Control	4.416
1	5.026
2	4.779
3	4.840

4. Molybdenum

TABLE 8. Molybdenum content of limes and amounts of lime and Mo added per pot.

Lime no	Rate	Mo Content of Lime ($mg.kg^{-1}$)	Lime added per pot (g)	Equivalence in Ton/ha	Concentration increase in the soil ($mg.kg^{-1}$)
2	1	40.11* (28.85)**	6.89	4.10	0.0368
	2		17.59	10.60	0.0941
	3		28.30	17.00	0.1513
3	1	2.44 (0.82)	5.41	3.20	0.0018
	2		13.81	8.30	0.0045
	3		22.22	13.30	0.0072
5	1	0 (0)	6.95	4.20	0.0000
	2		17.74	10.70	0.0000
	3		28.54	17.10	0.0000
8	1	0 (0)	7.43	4.50	0.0000
	2		18.98	11.40	0.0000
	3		30.52	18.30	0.0000
11	1	14.84	3.70	2.20	0.0073
	2		9.45	5.70	0.0187
	3		15.21	9.10	0.0301

* Semi-quantitative determination by ICP MS-scan

** Quantitative determination by ICP MS

TABLE 9. Molybdenum content ($mg.kg^{-1}$) of spinach leaves and pH of the growth medium.

Lime no	Rate	Spinach dry mass (g)	Mo ($mg.kg^{-1}$)	pH
2	1	5.2	0.00	6.05
	2	8.86	0.34	7.27
	3	10.67	0.50	7.88
3	1	5.93	-	6.33
	2	6.42	0.50	7.42
	3	9.26	0.70	7.61
5	1	6.16	0.00	6.15
	2	6.89	0.29	7.11
	3	8.49	0.24	7.54
8	1	3.26	0.07	6.58
	2	6.85	0.26	7.18
	3	7.94	0.28	7.53
11	1	5.51	0.08	5.91
	2	8.03	0.37	6.78
	3	9.79	0.16	7.27

APPENDIX 3

pH RESULTS FOR TRIAL 1 AND TRIAL 2

Table 1 to 4 present the $pH_{(Water)}$ and $pH_{(KCl)}$ results for Trial 1. Table 5 and 6 present the values for Trial 2.

TABLE 1. Trial 1 $pH_{(Water)}$ values (first sampling) for twelve liming materials at three application rates.

Rate	Lime no.	pH (Replications)				Average
		1	2	3	4	
Control	Control	5.24	5.31	5.32	5.46	5.33
1	1	6.27	6.30	6.37	6.46	6.35
2	1	6.80	6.88	6.96	6.99	6.91
3	1	7.16	7.28	7.30	7.42	7.29
1	2	5.78	5.87	6.06	6.50	6.05
2	2	7.09	7.25	7.32	7.41	7.27
3	2	7.76	7.81	7.93	8.03	7.88
1	3	6.21	6.29	6.32	6.50	6.33
2	3	7.29	7.41	7.42	7.57	7.42
3	3	7.52	7.57	7.60	7.74	7.61
1	4	5.74	5.95	6.08	6.41	6.05
2	4	6.10	6.60	6.64	6.86	6.55
3	4	7.15	7.23	7.30	7.69	7.34
1	5	5.87	6.08	6.09	6.55	6.15
2	5	6.67	7.13	7.27	7.35	7.11
3	5	7.37	7.55	7.59	7.65	7.54
1	6	6.10	6.20	6.23	6.36	6.22
2	6	7.09	7.18	7.19	7.27	7.18
3	6	7.26	7.65	7.73	7.74	7.60
1	7	6.01	6.14	6.22	6.40	6.19
2	7	6.30	6.96	7.10	7.73	7.02
3	7	7.77	7.84	7.90	7.93	7.86
1	8	6.48	6.58	6.6	6.67	6.58
2	8	6.71	7.20	7.35	7.47	7.18
3	8	7.31	7.53	7.55	7.74	7.53
1	9	6.09	6.21	6.41	6.76	6.37
2	9	6.82	6.96	6.98	7.05	6.95
3	9	7.19	7.43	7.48	7.60	7.43
1	10	6.08	6.18	6.35	6.38	6.25
2	10	6.49	6.80	6.89	6.99	6.79
3	10	7.10	7.11	7.29	7.32	7.21
1	11	5.67	5.95	6.00	6.01	5.91
2	11	6.52	6.74	6.91	6.93	6.78
3	11	7.04	7.20	7.36	7.47	7.27
1	12	5.77	5.93	6.22	6.54	6.12
2	12	6.56	6.63	6.92	7.02	6.78
3	12	7.49	7.60	7.60	7.72	7.60

TABLE 2. Trial 1 $pH_{(Water)}$ values (second sampling) for twelve liming materials at three application rates.

Rate	Lime no.	pH (Replications)				Average
		1	2	3	4	
Control	Control	4.90	5.16	5.05	5.14	5.06
1	1	6.08	6.05	6.24	5.70	6.02
2	1	6.56	6.13	6.89	6.81	6.60
3	1	7.20	7.28	7.30	7.41	7.30
1	2	6.36	6.75	6.40	5.77	6.32
2	2	7.58	7.75	7.14	7.33	7.45
3	2	8.22	7.97	8.16	7.95	8.08
1	3	6.13	6.08	5.64	6.12	5.99
2	3	6.82	7.23	7.15	7.20	7.10
3	3	7.56	7.46	7.47	7.29	7.45
1	4	5.35	5.37	5.02	5.90	5.41
2	4	6.23	6.73	7.02	6.77	6.69
3	4	6.68	7.24	6.86	7.06	6.96
1	5	6.66	6.24	5.88	6.28	6.27
2	5	6.88	7.10	7.28	7.30	7.14
3	5	7.32	7.38	7.57	7.52	7.45
1	6	6.02	6.10	6.25	5.62	6.00
2	6	7.02	6.96	7.58	7.33	7.22
3	6	7.75	7.52	8.06	7.77	7.78
1	7	6.32	6.39	6.05	5.77	6.13
2	7	6.69	7.58	7.24	7.32	7.21
3	7	7.54	7.75	7.66	7.98	7.73
1	8	5.90	6.28	6.39	6.34	6.23
2	8	6.54	7.10	6.94	6.90	6.87
3	8	7.32	7.44	7.35	7.33	7.36
1	9	4.97	5.86	6.03	5.77	5.66
2	9	6.81	6.77	7.03	6.80	6.85
3	9	7.34	7.22	7.04	7.32	7.23
1	10	6.01	5.92	5.76	6.11	5.95
2	10	6.71	6.75	7.16	5.56	6.55
3	10	7.25	7.37	7.57	7.36	7.39
1	11	5.87	5.65	5.48	5.60	5.65
2	11	6.32	6.60	6.69	6.93	6.64
3	11	7.33	7.23	7.37	7.53	7.37
1	12	5.40	5.75	5.76	5.72	5.66
2	12	6.47	6.61	6.88	6.99	6.74
3	12	7.50	7.69	7.35	7.65	7.55

TABLE 3. Trial 1 $pH_{(KCl)}$ values (first sampling) for twelve liming materials at three application rates.

Rate	Lime no.	pH (Replications)				Average
		1	2	3	4	
Control	Control	4.17	4.21	4.24	4.26	4.22
1	1	5.08	5.01	5.71	5.38	5.30
2	1	6.07	6.11	6.03	5.58	5.95
3	1	6.40	6.46	6.33	6.40	6.40
1	2	4.69	4.85	5.17	4.95	4.92
2	2	6.80	6.61	6.63	6.46	6.63
3	2	6.63	7.12	7.32	7.03	7.03
1	3	5.63	5.04	4.77	5.06	5.13
2	3	6.77	6.22	5.97	5.99	6.24
3	3	6.72	6.77	6.75	6.58	6.71
1	4	4.40	4.68	5.00	4.54	4.66
2	4	5.47	5.04	5.76	5.73	5.50
3	4	5.56	6.08	5.94	6.45	6.01
1	5	4.65	4.72	4.89	5.01	4.82
2	5	5.94	6.14	6.47	6.57	6.28
3	5	6.58	6.86	6.84	6.91	6.80
1	6	4.71	4.77	4.86	5.12	4.87
2	6	6.23	6.18	6.27	6.12	6.20
3	6	6.21	6.81	6.77	6.89	6.67
1	7	4.87	4.96	4.63	4.92	4.85
2	7	6.34	5.90	6.40	5.16	5.95
3	7	6.47	6.46	6.86	6.89	6.67
1	8	4.64	4.99	5.17	4.88	4.92
2	8	6.20	6.38	5.72	6.27	6.14
3	8	6.47	6.61	6.47	6.76	6.58
1	9	5.09	5.90	4.78	4.81	5.15
2	9	5.70	5.51	5.59	5.63	5.61
3	9	6.27	6.77	6.75	6.58	6.59
1	10	4.90	5.01	5.06	4.77	4.94
2	10	5.39	5.82	6.14	5.79	5.79
3	10	6.18	6.19	6.18	6.32	6.22
1	11	4.64	4.83	4.56	4.50	4.63
2	11	6.22	5.45	5.77	5.15	5.65
3	11	5.96	6.40	6.01	6.60	6.24
1	12	5.06	4.71	4.56	5.53	4.97
2	12	5.86	5.66	6.13	6.24	5.97
3	12	6.52	6.79	6.42	6.90	6.66

TABLE 4. Trial 1 $pH_{(KCl)}$ values (second sampling) for twelve liming materials at three application rates.

Rate	Lime no.	pH (Replications)				Average
		1	2	3	4	
Control	Control	4.17	4.28	4.17	4.28	4.23
1	1	4.67	4.91	4.99	5.13	4.93
2	1	6.00	6.03	6.09	5.90	6.01
3	1	6.33	6.39	6.48	6.47	6.42
1	2	5.01	5.13	5.84	5.14	5.28
2	2	6.51	6.63	6.01	6.40	6.39
3	2	7.10	7.06	7.18	7.07	7.10
1	3	5.25	4.83	4.81	5.30	5.05
2	3	6.32	6.37	6.33	6.11	6.28
3	3	7.08	6.86	6.91	7.25	7.03
1	4	5.02	4.62	4.50	4.84	4.75
2	4	5.38	5.88	5.86	5.71	5.71
3	4	5.55	6.25	5.85	6.21	5.97
1	5	5.01	5.28	4.89	5.20	5.10
2	5	6.20	6.21	6.24	6.51	6.29
3	5	6.70	6.55	6.65	6.90	6.70
1	6	4.93	5.32	5.01	4.55	4.95
2	6	6.11	6.16	6.62	6.58	6.37
3	6	6.74	6.71	7.03	6.80	6.82
1	7	4.93	5.21	4.78	4.92	4.96
2	7	5.78	6.81	6.14	6.55	6.32
3	7	6.54	6.95	6.72	6.94	6.79
1	8	4.98	5.18	5.33	5.29	5.20
2	8	5.94	6.33	6.28	6.15	6.18
3	8	6.42	6.63	6.55	6.64	6.56
1	9	4.65	4.64	4.85	4.99	4.78
2	9	6.16	5.76	6.13	5.95	6.00
3	9	6.53	6.33	6.48	6.60	6.49
1	10	4.97	4.84	5.17	4.61	4.90
2	10	5.35	6.13	5.71	5.45	5.66
3	10	6.68	5.61	6.58	6.45	6.33
1	11	4.71	4.53	4.95	4.61	4.70
2	11	5.30	5.76	5.59	5.94	5.65
3	11	6.35	6.36	6.46	6.69	6.47
1	12	4.39	5.18	4.96	4.82	4.84
2	12	6.20	6.20	6.33	6.37	6.28
3	12	6.64	6.90	6.75	6.83	6.78

TABLE 5. Trial 2 pH$_{(Water)}$ values for four slags and one laboratory reagent at three application rates.

Rate	Lime no.	pH (Replications)				Average
		1	2	3	4	
Control	Control	4.08	3.97	4.02	4.03	4.03
1	2	6.65	6.53	6.51	6.35	6.51
2	2	7.18	6.82	6.80	6.67	6.87
3	2	6.98	7.21	7.19	7.30	7.17
1	3	6.13	5.77	5.98	5.55	5.86
2	3	5.75	6.25	6.33	6.01	6.09
3	3	6.84	6.71	6.54	6.60	6.67
1	6	5.35	5.86	5.66	5.51	5.60
2	6	5.90	5.48	6.21	6.20	5.95
3	6	6.51	6.49	6.67	6.69	6.59
1	11	4.91	4.98	4.95	4.94	4.95
2	11	5.23	4.73	5.20	4.98	5.04
3	11	5.68	5.14	5.40	5.89	5.53
1	Lab R	4.66	5.09	5.14	5.27	5.04
2	Lab R	5.40	5.11	5.58	5.62	5.43
3	Lab R	5.65	5.65	5.78	5.99	5.77

TABLE 6. Trial 2 pH$_{(KCl)}$ values for four slags and one laboratory reagent at three application rates.

Rate	Lime no.	pH (Replications)				Average
		1	2	3	4	
Control	Control	3.63	3.61	3.60	3.63	3.62
1	2	5.88	5.85	5.98	5.70	5.85
2	2	6.42	6.03	6.08	5.84	6.09
3	2	6.40	6.43	6.44	6.45	6.43
1	3	4.50	5.09	4.66	5.12	4.84
2	3	4.91	5.22	5.42	5.54	5.27
3	3	5.62	5.58	5.68	5.67	5.64
1	6	4.80	5.12	5.09	4.87	4.97
2	6	5.46	5.88	4.87	5.58	5.45
3	6	5.77	5.80	6.04	6.07	5.92
1	11	4.34	4.35	4.33	4.37	4.35
2	11	4.58	4.18	4.59	4.45	4.45
3	11	4.76	4.51	4.71	5.14	4.78
1	Lab R	4.03	4.39	4.25	4.32	4.25
2	Lab R	4.80	4.89	4.85	4.35	4.72
3	Lab R	4.83	5.29	5.16	5.11	5.10

APPENDIX 4

LIME INCUBATION CURVES

1. Incubation Curves

Figures 1 to 12 indicate the average value of four $pH_{(Water)}$ and $pH_{(KCl)}$ replicates for each lime. The figure number corresponds with the lime number. The results of each lime were used to calculate the correlation coefficient between the pH and lime requirement as well as regression equation.

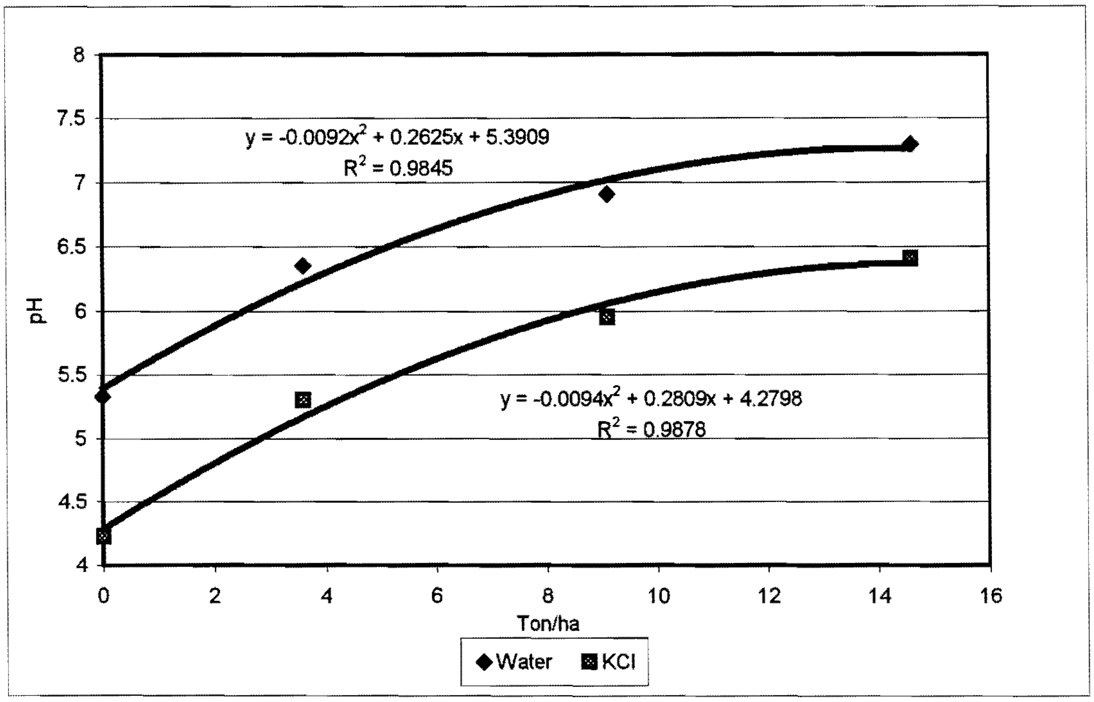

Figure 1. The relationship of the $\mathrm{pH}_{(\text{Water and KCl})}$ after a three month incubation period for Lime 1 with corresponding regression equation and coefficient of determination.

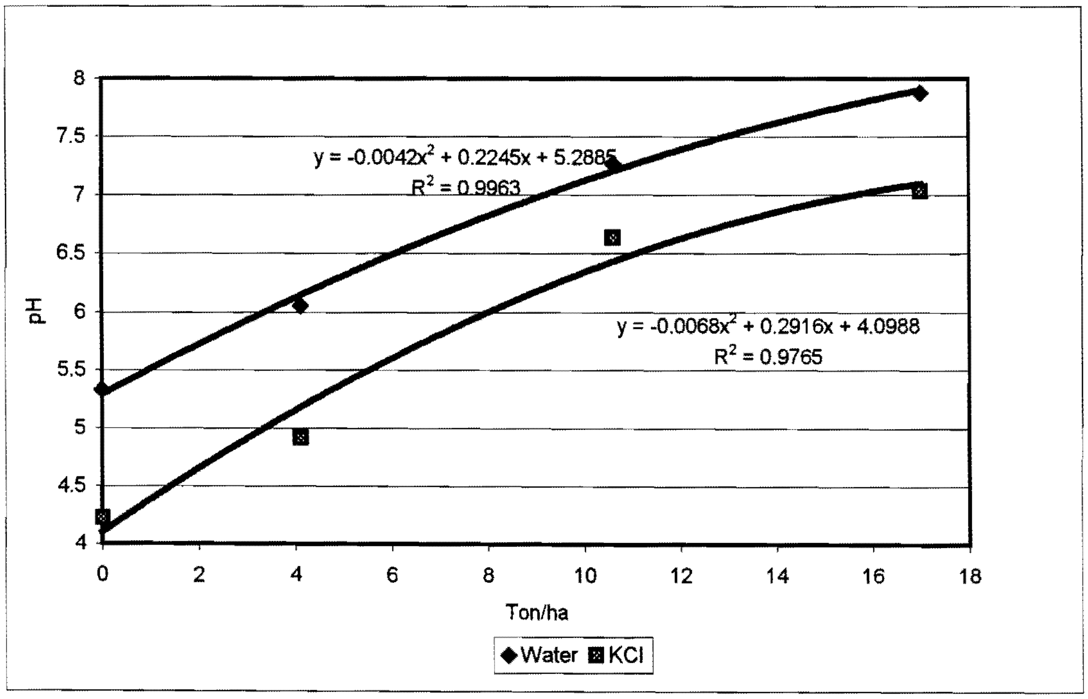

Figure 2. The relationship of the $\mathrm{pH}_{(\text{Water and KCl})}$ after a three month incubation period for Lime 2 with corresponding regression equation and coefficient of determination.

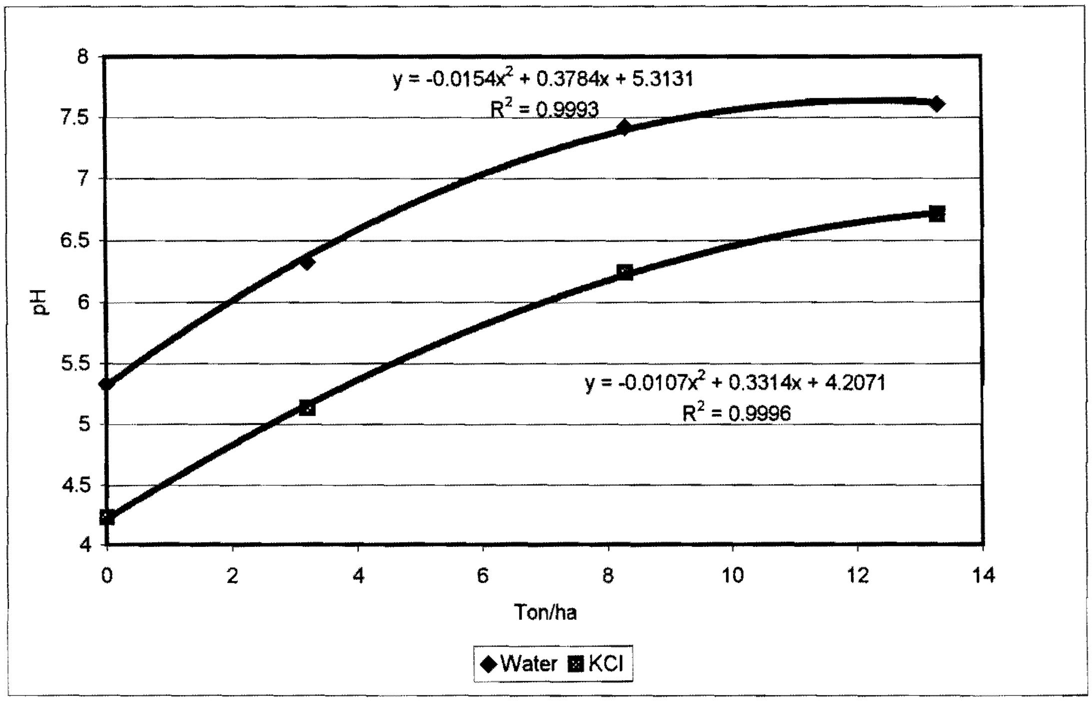

Figure 3. The relationship of the pH$_{(\text{Water and KCl})}$ after a three month incubation period for Lime 3 with corresponding regression equation and coefficient of determination.

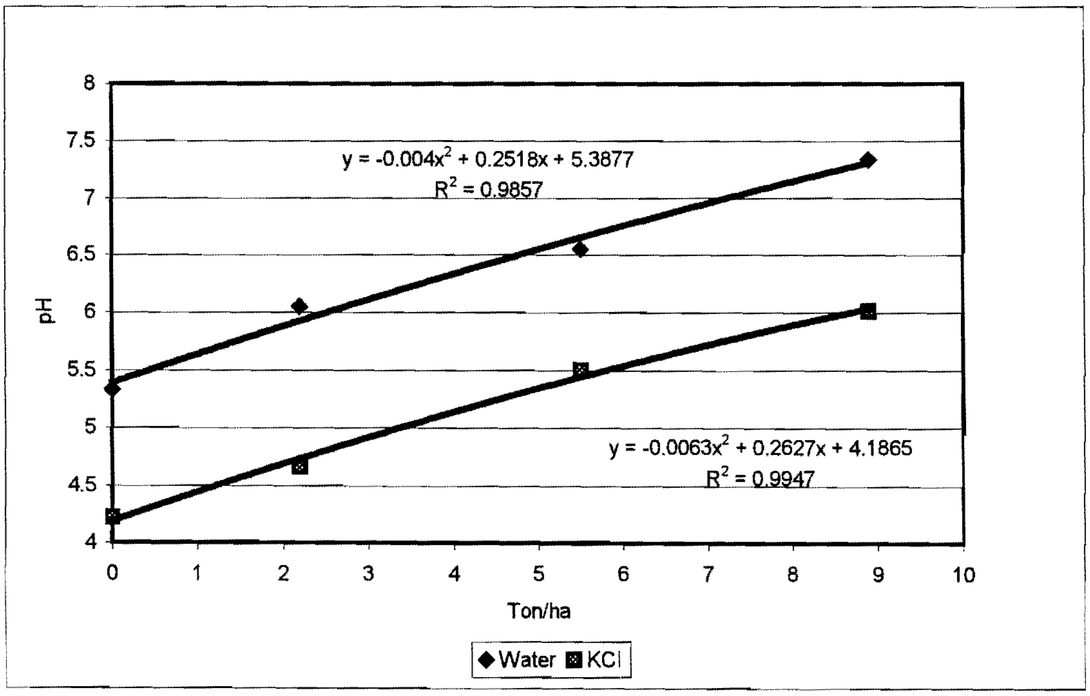

Figure 4. The relationship of the pH$_{(\text{Water and KCl})}$ after a three month incubation period for Lime 4 with corresponding regression equation and coefficient of determination.

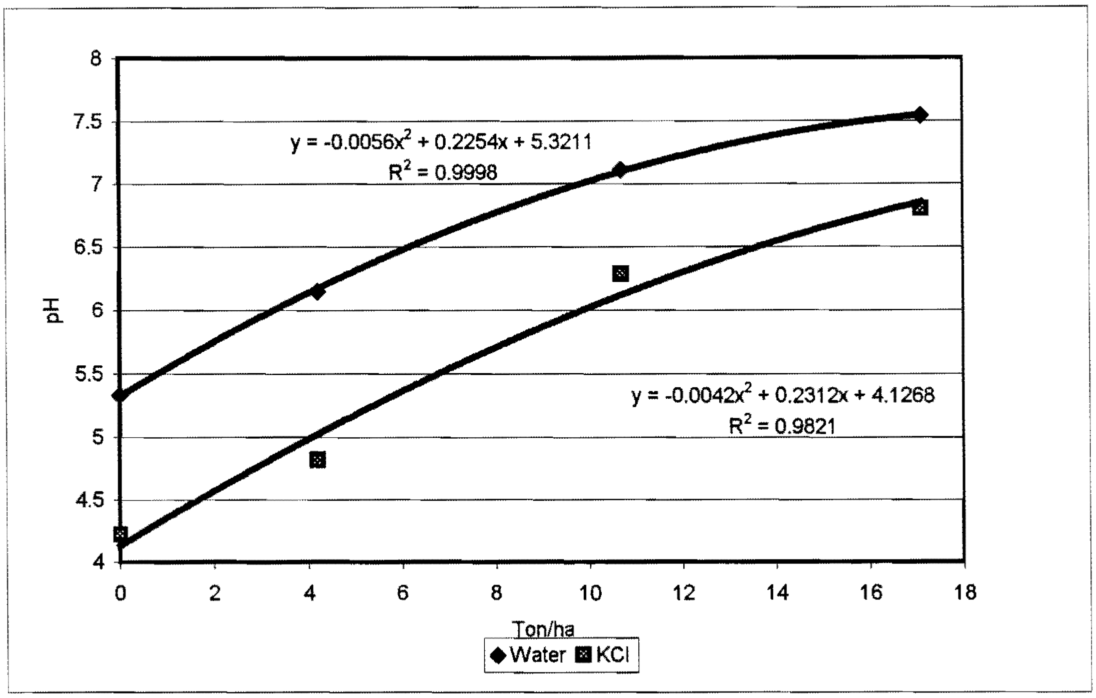

Figure 5. The relationship of the $pH_{(Water\ and\ KCl)}$ after a three month incubation period for Lime 5 with corresponding regression equation and coefficient of determination.

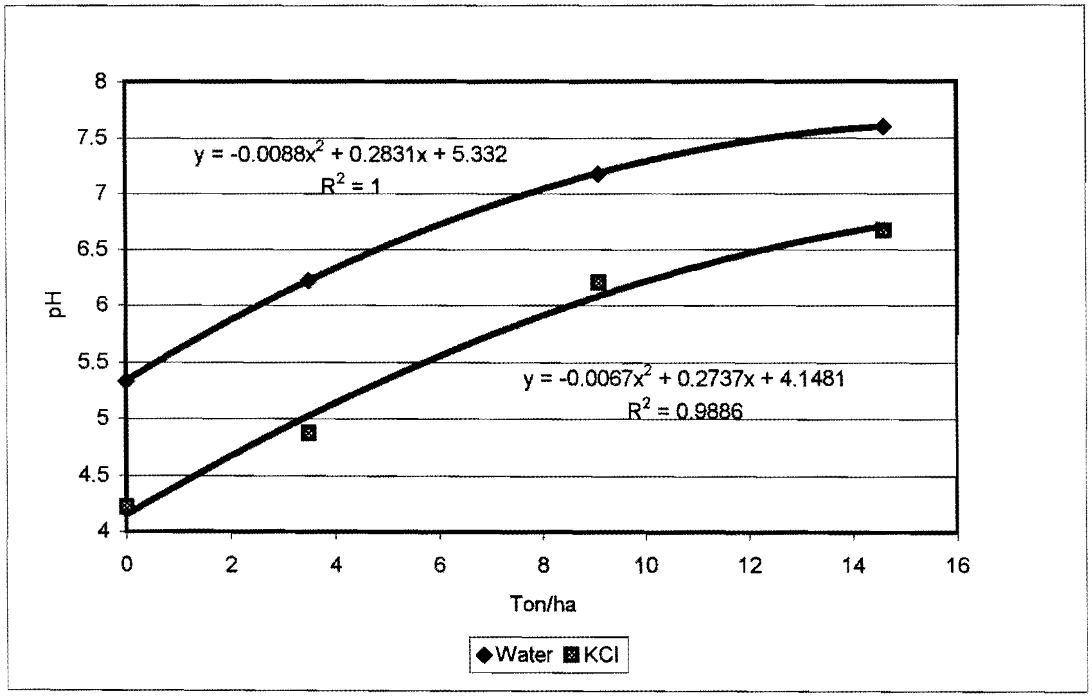

Figure 6. The relationship of the $pH_{(Water\ and\ KCl)}$ after a three month incubation period for Lime 6 with corresponding regression equation and coefficient of determination.

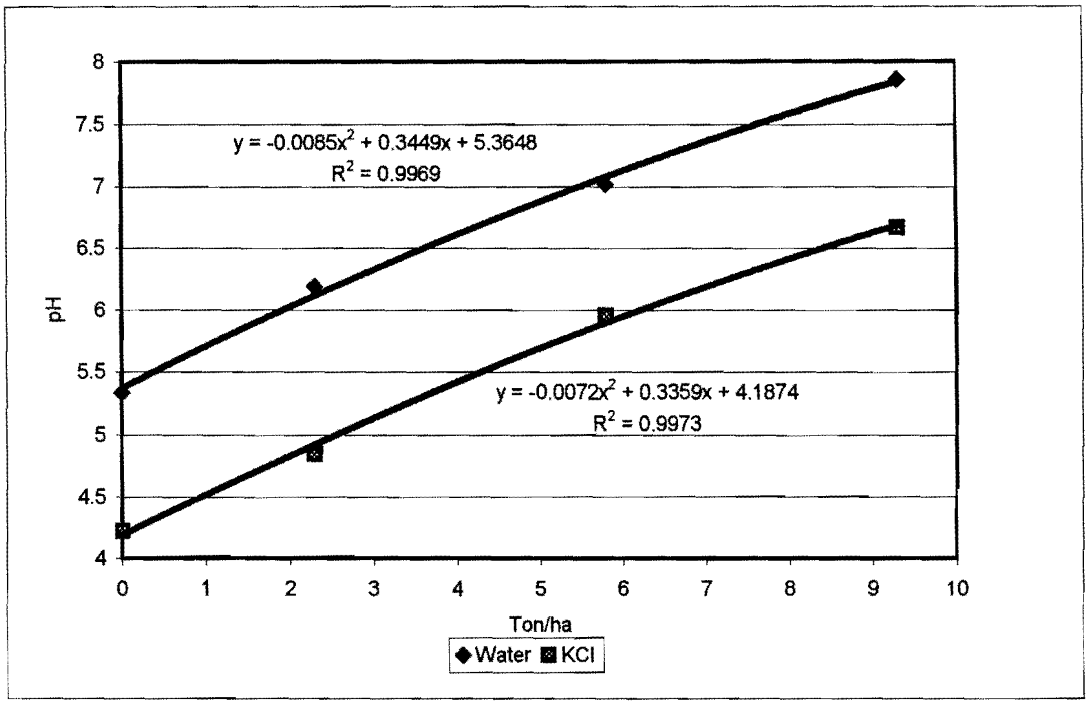

Figure 7. The relationship of the $pH_{(Water\ and\ KCl)}$ after a three month incubation period for Lime 7 with corresponding regression equation and coefficient of determination.

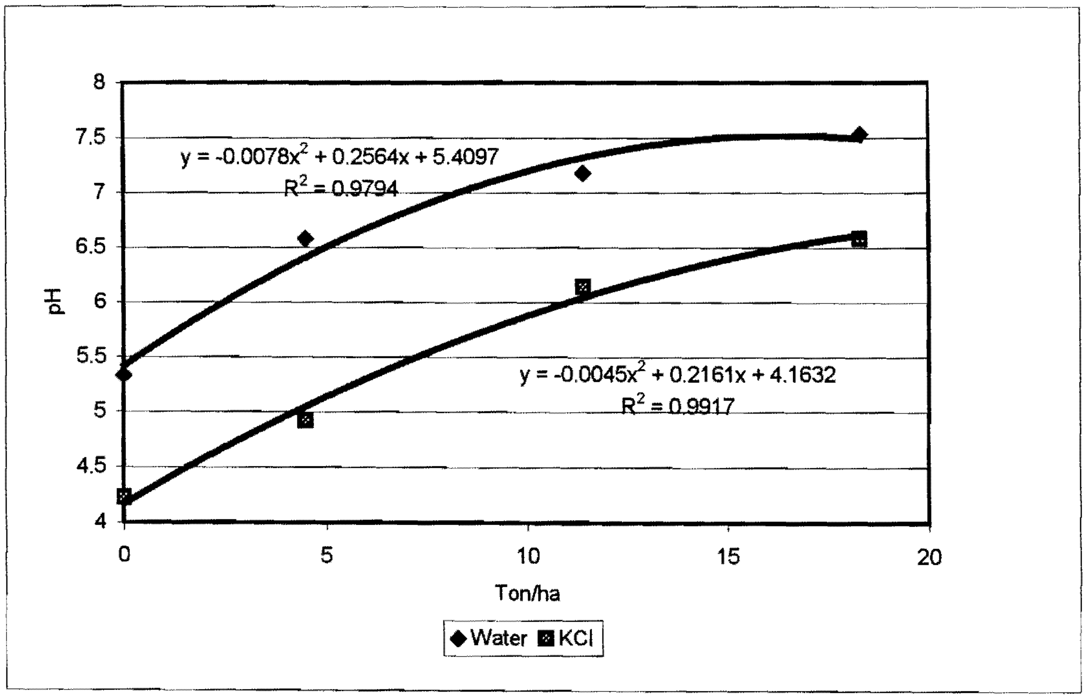

Figure 8. The relationship of the $pH_{(Water\ and\ KCl)}$ after a three month incubation period for Lime 8 with corresponding regression equation and coefficient of determination.

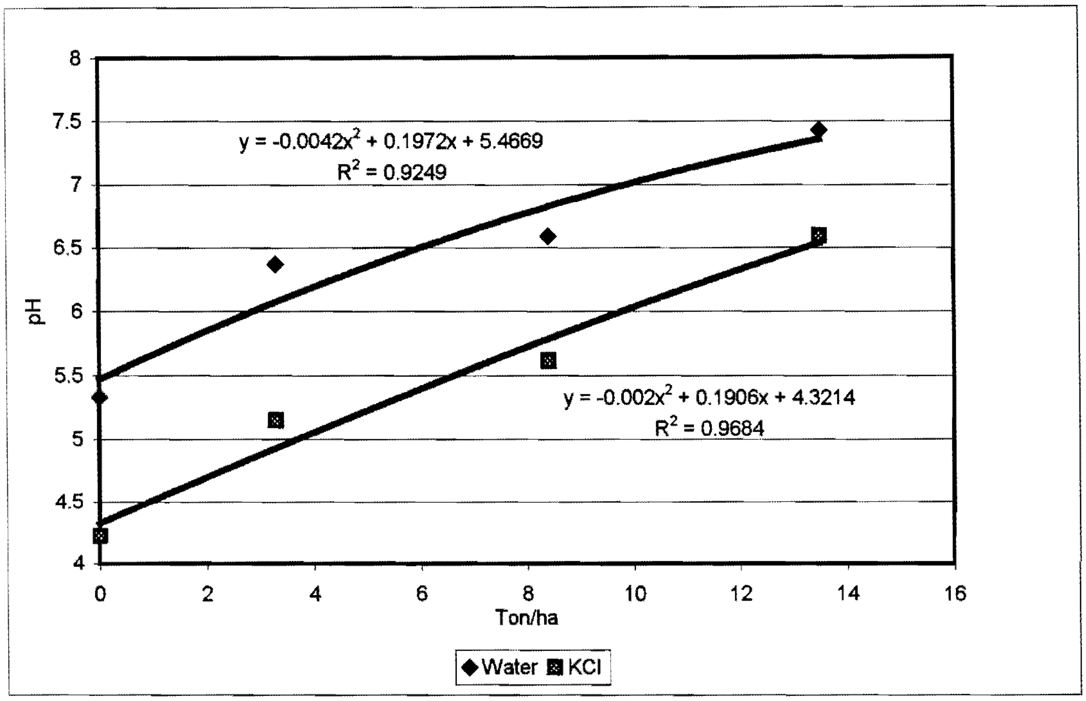

Figure 9. The relationship of the pH$_{\text{(Water and KCl)}}$ after a three month incubation period for Lime 9 with corresponding regression equation and coefficient of determination.

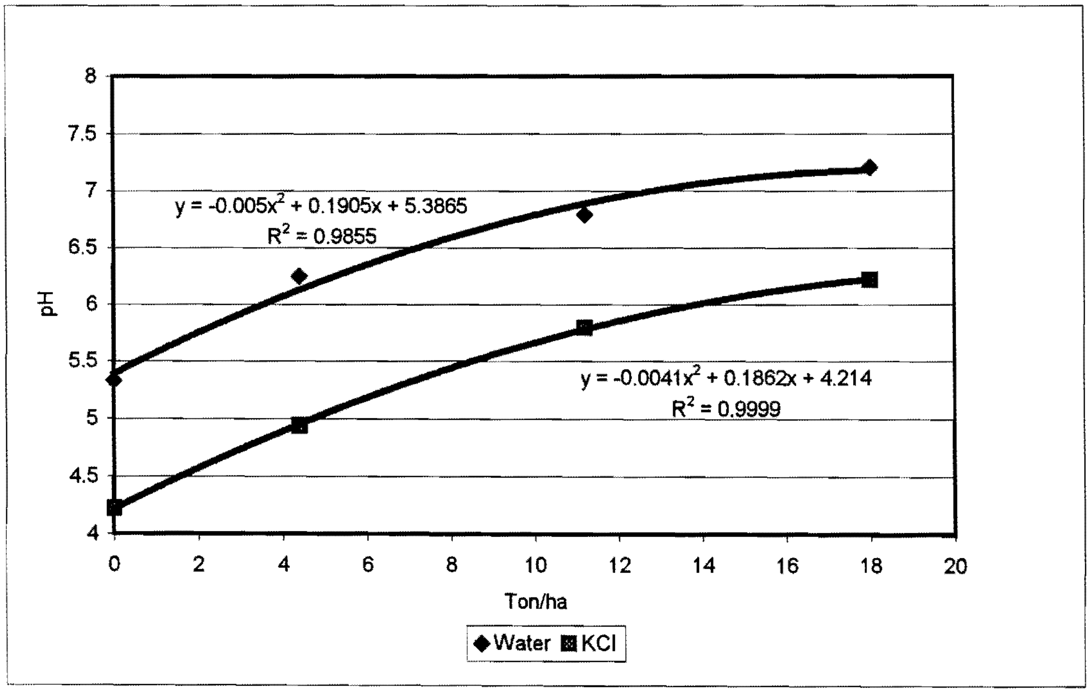

Figure 10. The relationship of the pH$_{\text{(Water and KCl)}}$ after a three month incubation period for Lime 10 with corresponding regression equation and coefficient of determination.

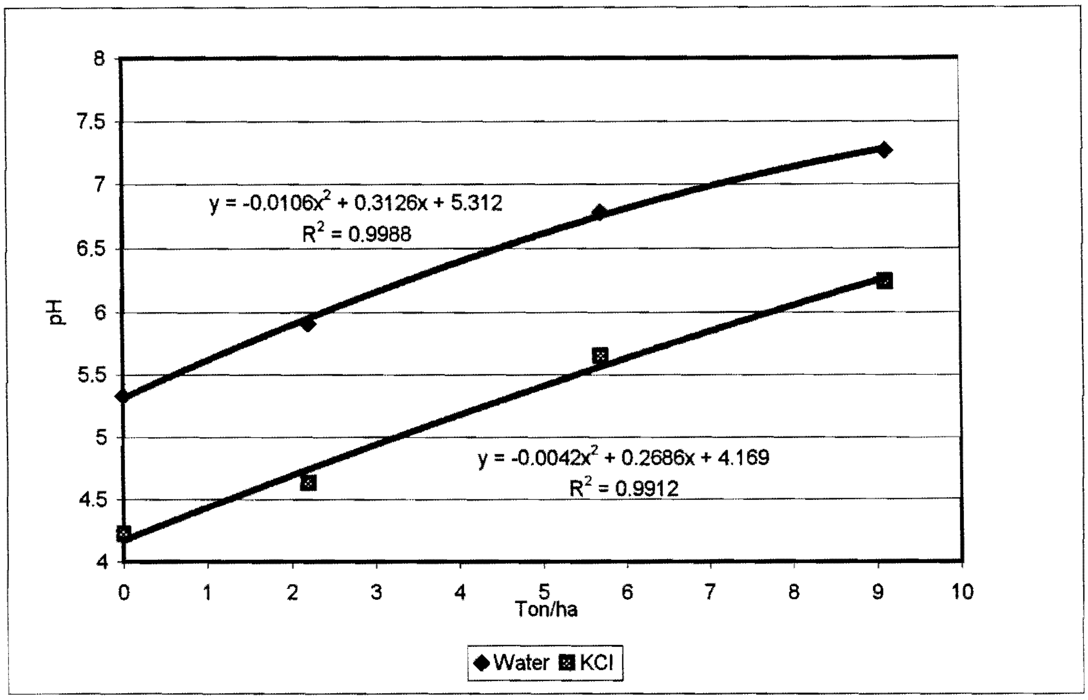

Figure 11. The relationship of the pH$_{(\text{Water and KCl})}$ after a three month incubation period for Lime 11 with corresponding regression equation and coefficient of determination.

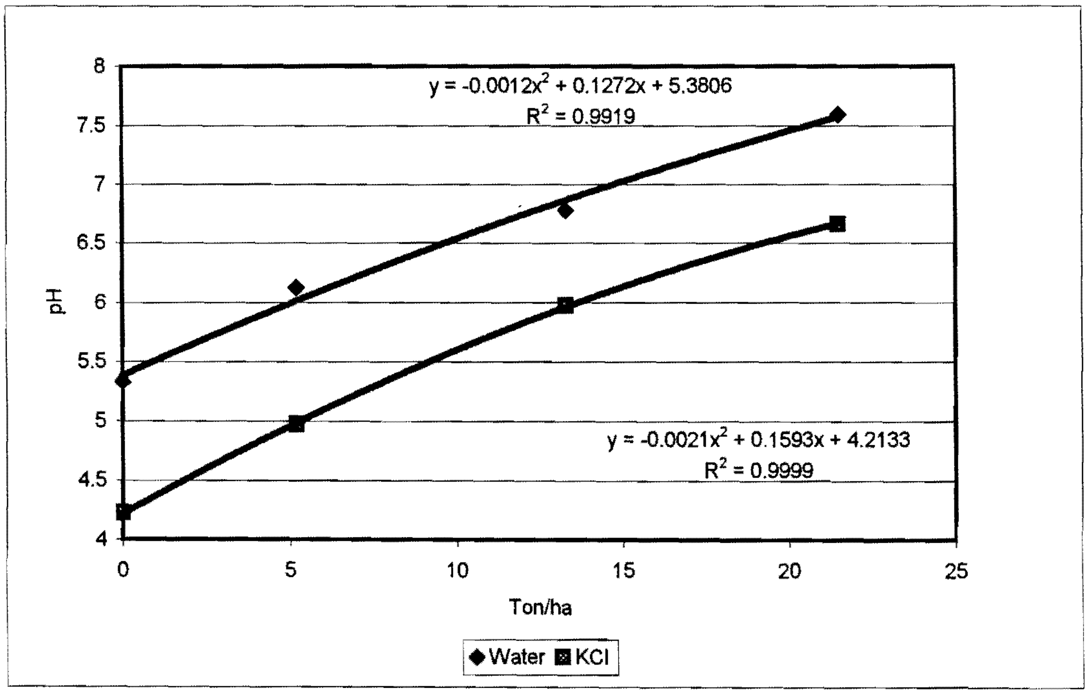

Figure 12. The relationship of the pH$_{(\text{Water and KCl})}$ after a three month incubation period for Lime 12 with corresponding regression equation and coefficient of determination.

APPENDIX 5

MODELING OF pH RESULTS

1. Correction Factors

Correction factors according to the CCE HCl as well as RH-values were calculated for each lime to correct the lime required to 100% reactivity. The value multiplied by the factor yields 100.

TABLE 1. Calculated factors to obtain 100% reactivity for different limes.

Lime no.	CCE HCl %	Factor 1	RH-value %	Factor 2
1	83.00	1.20	75.83	1.32
2	95.48	1.05	49.67	2.01
3	84.98	1.18	64.57	1.55
4	98.04	1.02	91.72	1.09
5	85.75	1.17	59.60	1.68
6	95.88	1.04	59.60	1.68
7	98.54	1.01	87.75	1.14
8	88.38	1.13	54.97	1.82
9	87.98	1.14	77.48	1.29
10	91.40	1.09	54.64	1.83
11	104.28	0.96	76.16	1.31
12	74.90	1.34	46.59	2.15

2. Lime Requirement

In Table 2 the amounts of pure $CaCO_3$ needed to attain the specific target pH values as calculated from the different buffer solution ratios are listed.

TABLE 2. Amount of pure $CaCO_3$ needed (ton.ha^{-1}) to change the soil pH to the desired target, as calculated from the regression equation in Fig. 4.1.

Target pH	Soil to Solution Ratio (Time of Determination)		
	Ratio 1:1 (Before)	Ratio 1:1 (After)	Ratio 1:2.5 (After)
5.8	1.91 ton.ha^{-1}	1.47 ton.ha^{-1}	0.74 ton.ha^{-1}
6.8	4.90 ton.ha^{-1}	3.69 ton.ha^{-1}	3.87 ton.ha^{-1}
7.8	7.88 ton.ha^{-1}	5.91 ton.ha^{-1}	7.01 ton.ha^{-1}

3. Lime Recommendation

In Tables 3 to 5 the lime recommendation values as calculated by the different methods, using the data from Tables 1 and 2, are presented for each target pH-value respectively.

TABLE 3. Lime recommendation values (ton.ha^{-1}) as calculated from different methods for target pH 5.8.

Lime no.	Ratio 1:1 (Before)		Ratio 1:1 (After)		Ratio 1:2.5 (After)	
	RH-Value	CCE HCl	RH-Value	CCE HCl	RH-Value	CCE HCl
1	2.52	2.31	1.93	1.77	0.97	0.89
2	3.85	2.00	2.95	1.54	1.49	0.77
3	2.96	2.25	2.27	1.72	1.14	0.87
4	2.09	1.95	1.60	1.49	0.81	0.75
5	3.21	2.23	2.46	1.71	1.24	0.86
6	3.21	2.00	2.46	1.53	1.24	0.77
7	2.18	1.94	1.67	1.49	0.84	0.75
8	3.48	2.17	2.67	1.66	1.34	0.84
9	2.47	2.18	1.89	1.67	0.95	0.84
10	3.50	2.09	2.68	1.60	1.35	0.81
11	2.51	1.84	1.92	1.41	0.97	0.71
12	4.11	2.56	3.15	1.96	1.59	0.99

TABLE 4. Lime recommendation values (ton.ha^{-1}) as calculated from different methods for target pH 6.8.

Lime no.	Ratio 1:1 (Before)		Ratio 1:1 (After)		Ratio 1:2.5 (After)	
	RH-Value	CCE HCl	RH-Value	CCE HCl	RH-Value	CCE HCl
1	6.46	5.90	4.86	4.44	5.11	4.67
2	9.89	5.13	7.42	3.86	7.80	4.06
3	7.58	5.76	5.71	4.34	6.00	4.56
4	5.34	4.99	4.02	3.76	4.22	3.95
5	8.22	5.71	6.19	4.30	6.50	4.52
6	8.22	5.11	6.19	3.84	6.50	4.04
7	5.58	4.97	4.20	3.74	4.42	3.93
8	8.91	5.54	6.71	4.17	7.05	4.38
9	6.32	5.57	4.76	4.19	5.00	4.40
10	8.96	5.36	6.75	4.03	7.09	4.24
11	6.43	4.70	4.84	3.54	5.09	3.72
12	10.51	6.54	7.91	4.92	8.32	5.17

TABLE 5. Lime recommendation values (ton.ha^{-1}) as calculated from different methods for target pH 7.8.

Lime no.	Ratio 1:1 (Before)		Ratio 1:1 (After)		Ratio 1:2.5 (After)	
	RH-Value	CCE HCl	RH-Value	CCE HCl	RH-Value	CCE HCl
1	10.39	9.49	7.79	7.12	9.24	8.45
2	15.86	8.25	11.89	6.19	14.11	7.34
3	12.20	9.27	9.15	6.95	10.86	8.25
4	8.59	8.04	6.44	6.03	7.64	7.15
5	13.22	9.19	9.91	6.89	11.76	8.18
6	13.22	8.22	9.91	6.16	11.76	7.31
7	8.98	8.00	6.73	5.99	7.99	7.11
8	14.33	8.92	10.75	6.68	12.75	7.93
9	10.17	8.96	7.62	6.71	9.05	7.97
10	14.42	8.62	10.81	6.46	12.83	7.67
11	10.35	7.56	7.76	5.66	9.20	6.72
12	16.91	10.52	12.68	7.89	15.05	9.36

4. Resultant pH-values

The resultant $pH_{(Water)}$-values as calculated from the incubation curves (Appendix 2) and the different methods are presented in Tables 6 to 8 for each target value respectively, and in Tables 9 to 11 for $pH_{(KCl)}$-values for each target value respectively.

TABLE 6. Resultant $pH_{(Water)}$ values calculated from lime incubation curves for the different methods (target pH 5.8).

Lime no.	Ratio 1:1 (Before)		Ratio 1:1 (After)		Ratio 1:2.5 (After)	
	RH-Value	CCE HCl	RH-Value	CCE HCl	RH-Value	CCE HCl
1	5.99	5.95	5.86	5.83	5.64	5.62
2	6.09	5.72	5.91	5.62	5.61	5.46
3	6.30	6.09	6.09	5.92	5.73	5.63
4	5.90	5.86	5.78	5.76	5.59	5.58
5	5.99	5.80	5.84	5.69	5.59	5.51
6	6.15	5.86	5.97	5.74	5.67	5.54
7	6.08	6.00	5.92	5.86	5.65	5.62
8	6.21	5.93	6.04	5.81	5.74	5.62
9	5.93	5.88	5.82	5.78	5.65	5.63
10	5.99	5.76	5.86	5.68	5.63	5.54
11	6.03	5.85	5.87	5.73	5.61	5.53
12	5.88	5.70	5.77	5.62	5.58	5.50
Average	6.04	5.87	5.90	5.75	5.64	5.56

TABLE 7. Resultant pH$_{(Water)}$ values calculated from lime incubation curves for the different methods (target pH 6.8).

Lime no.	Ratio 1:1 (Before)		Ratio 1:1 (After)		Ratio 1:2.5 (After)	
	RH-Value	CCE HCl	RH-Value	CCE HCl	RH-Value	CCE HCl
1	6.70	6.62	6.45	6.38	6.49	6.42
2	7.09	6.33	6.72	6.09	6.78	6.13
3	7.30	6.98	6.97	6.66	7.03	6.72
4	6.62	6.55	6.34	6.28	6.38	6.32
5	6.79	6.43	6.50	6.19	6.55	6.23
6	7.06	6.55	6.75	6.29	6.80	6.33
7	7.02	6.87	6.66	6.54	6.72	6.59
8	7.07	6.59	6.78	6.34	6.83	6.38
9	6.55	6.43	6.31	6.22	6.35	6.25
10	6.69	6.26	6.44	6.07	6.49	6.10
11	6.88	6.55	6.58	6.28	6.63	6.33
12	6.58	6.16	6.31	5.98	6.36	6.01
Average	6.86	6.53	6.57	6.28	6.62	6.32

TABLE 8. Resultant pH$_{(Water)}$ values calculated from lime incubation curves for the different methods (target pH 7.8).

Lime no.	Ratio 1:1 (Before)		Ratio 1:1 (After)		Ratio 1:2.5 (After)	
	RH-Value	CCE HCl	RH-Value	CCE HCl	RH-Value	CCE HCl
1	7.13	7.05	6.88	6.79	7.03	6.95
2	7.79	6.86	7.36	6.52	7.62	6.71
3	7.64	7.50	7.49	7.20	7.61	7.39
4	7.26	7.15	6.84	6.76	7.08	6.98
5	7.32	6.92	7.01	6.61	7.20	6.79
6	7.54	7.06	7.27	6.74	7.44	6.93
7	7.78	7.58	7.30	7.13	7.58	7.39
8	7.48	7.08	7.26	6.77	7.41	6.95
9	6.90	7.22	6.60	6.89	6.77	7.08
10	7.09	6.66	6.86	6.41	7.01	6.55
11	7.41	7.07	7.10	6.74	7.29	6.93
12	7.19	6.59	6.80	6.31	7.02	6.47
Average	7.39	7.03	7.08	6.72	7.27	6.90

TABLE 9. Resultant pH$_{(KCl)}$ values calculated from lime incubation curves for the different methods (target pH$_{(Water)}$ 5.8).

Lime no.	Ratio 1:1 (Before)		Ratio 1:1 (After)		Ratio 1:2.5 (After)	
	RH-Value	CCE HCl	RH-Value	CCE HCl	RH-Value	CCE HCl
1	5.16	5.09	4.97	4.92	4.65	4.62
2	5.19	4.69	4.95	4.56	4.55	4.34
3	5.17	4.96	4.96	4.79	4.60	4.51
4	4.72	4.69	4.60	4.58	4.40	4.39
5	5.02	4.76	4.82	4.62	4.49	4.38
6	5.03	4.72	4.84	4.59	4.51	4.38
7	4.91	4.84	4.75	4.69	4.48	4.44
8	5.04	4.73	4.85	4.60	4.52	4.39
9	4.92	4.85	4.79	4.73	4.56	4.53
10	4.95	4.67	4.79	4.57	4.52	4.40
11	4.74	4.59	4.61	4.50	4.40	4.34
12	4.99	4.71	4.81	4.60	4.52	4.41

TABLE 10. Resultant pH$_{(KCl)}$ values calculated from lime incubation curves for the different methods (target pH$_{(Water)}$ 6.8).

Lime no.	Ratio 1:1 (Before)		Ratio 1:1 (After)		Ratio 1:2.5 (After)	
	RH-Value	CCE HCl	RH-Value	CCE HCl	RH-Value	CCE HCl
1	6.06	5.96	5.76	5.67	5.81	5.72
2	6.42	5.49	5.99	5.19	6.06	5.24
3	6.22	5.87	5.86	5.54	5.92	5.59
4	5.44	5.37	5.17	5.11	5.21	5.15
5	6.11	5.61	5.71	5.28	5.77	5.34
6	6.08	5.47	5.70	5.19	5.76	5.23
7	5.89	5.73	5.52	5.38	5.58	5.44
8	6.04	5.47	5.68	5.19	5.74	5.23
9	5.78	5.62	5.44	5.32	5.50	5.37
10	5.78	5.28	5.49	5.05	5.54	5.08
11	5.56	5.21	5.24	4.97	5.29	5.00
12	5.96	5.39	5.60	5.13	5.66	5.17

TABLE 11. Resultant $pH_{(KCl)}$ values calculated from lime incubation curves for the different methods (target $pH_{(Water)}$ 7.8).

Lime no.	Ratio 1:1 (Before)		Ratio 1:1 (After)		Ratio 1:2.5 (After)	
	RH-Value	CCE HCl	RH-Value	CCE HCl	RH-Value	CCE HCl
1	6.38	6.35	6.23	6.15	6.34	6.29
2	7.09	6.14	6.71	5.73	6.95	5.97
3	6.72	6.47	6.45	6.11	6.63	6.32
4	6.02	5.93	5.66	5.58	5.87	5.78
5	6.85	6.28	6.40	5.85	6.67	6.10
6	6.71	6.08	6.34	5.70	6.57	5.92
7	6.70	6.48	6.19	6.00	6.48	6.28
8	6.61	6.04	6.28	5.68	6.49	5.89
9	6.53	6.30	6.04	5.86	6.32	6.11
10	6.24	5.74	5.98	5.45	6.14	5.62
11	6.27	5.77	5.81	5.41	6.07	5.61
12	6.66	5.96	6.23	5.60	6.49	5.81

Figures 1 through 12 indicate the predicted pH values for each lime as calculated above.

Note: The second lime requirement in the 1:1 soil to solution ratio (RH and HCl) is not indicated in the figures.

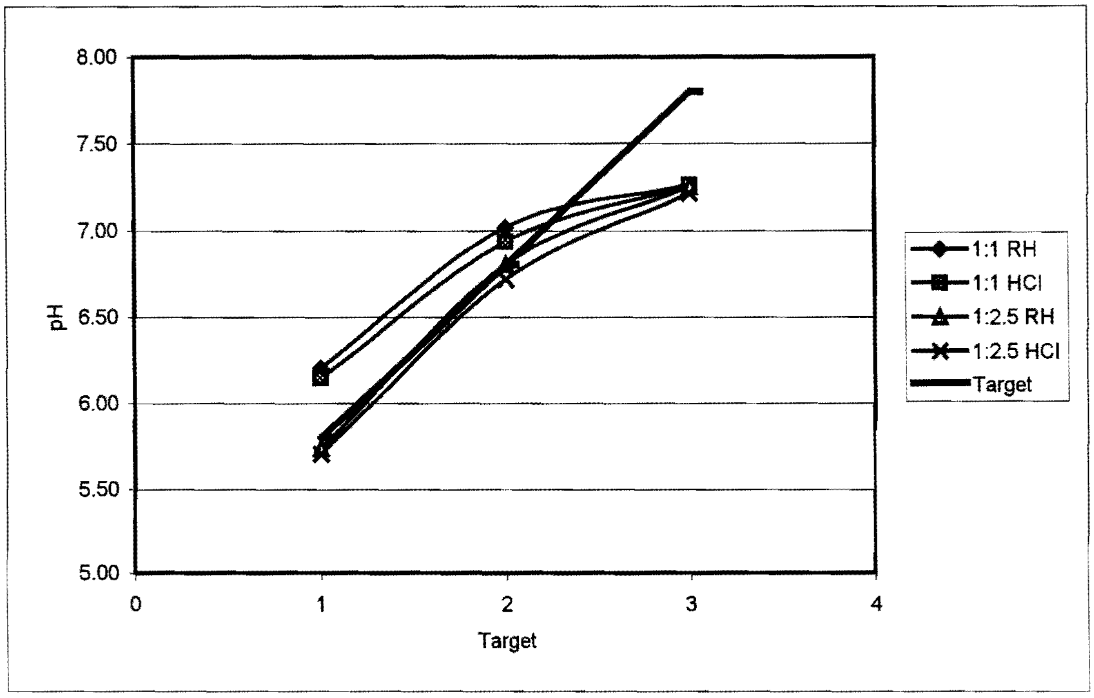

Figure 1. Predicted pH values for Lime 1 from calculated lime recommendations.

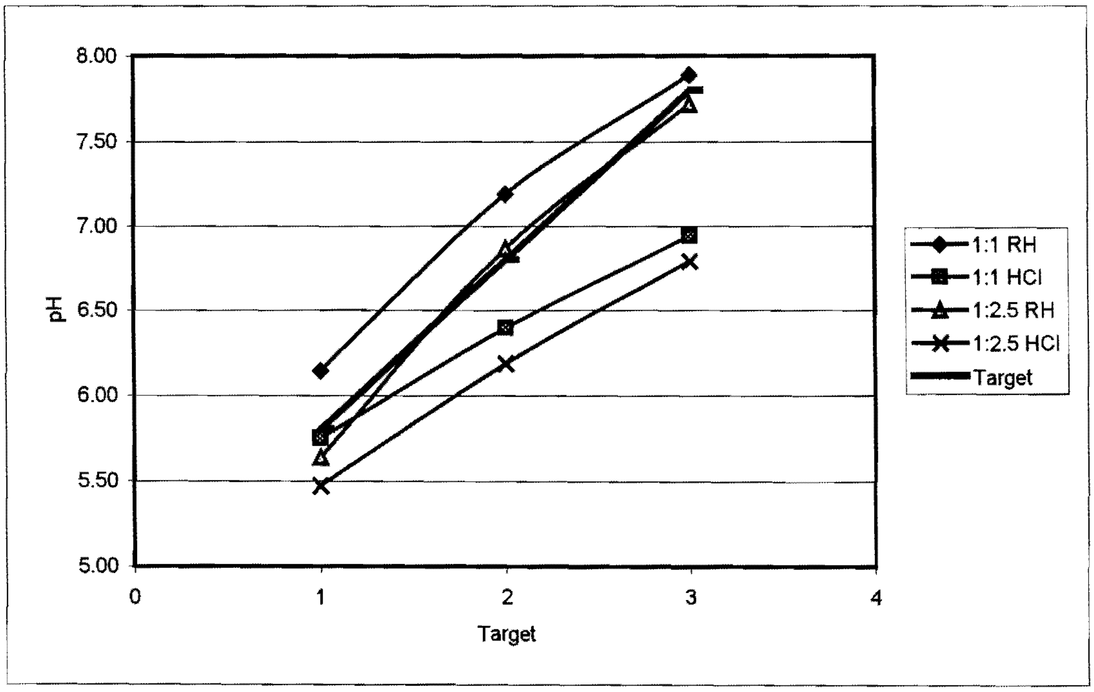

Figure 2. Predicted pH values for Lime 2 from calculated lime recommendations.

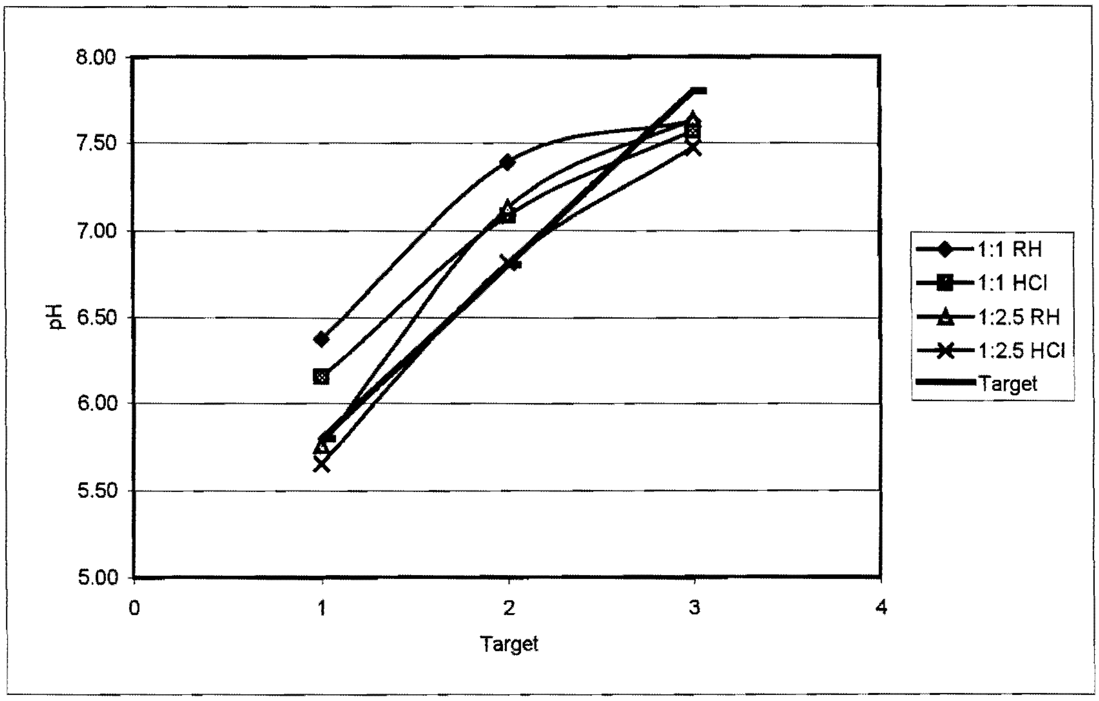

Figure 3. Predicted pH values for Lime 3 from calculated lime recommendations.

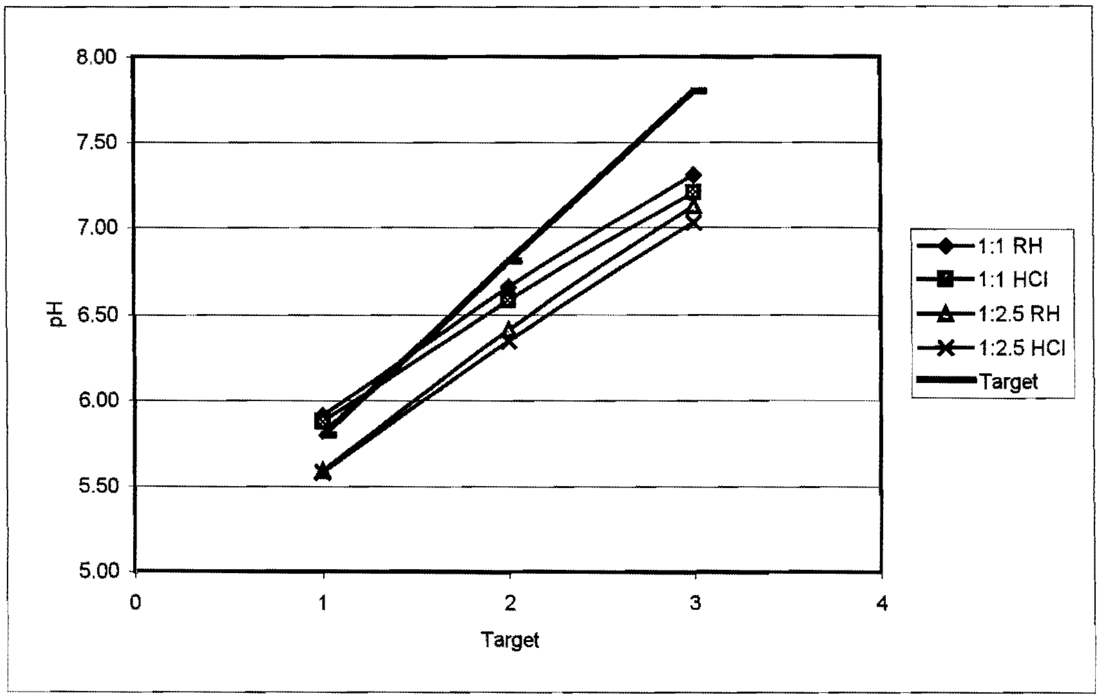

Figure 4. Predicted pH values for Lime 4 from calculated lime recommendations.

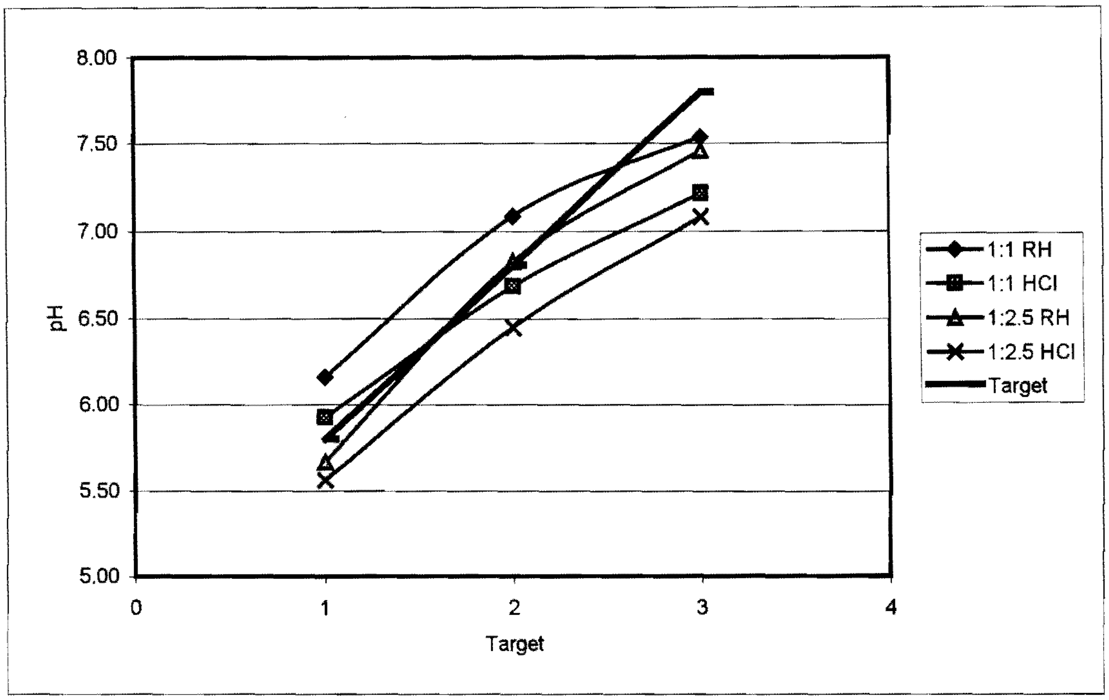

Figure 5. Predicted pH values for Lime 5 from calculated lime recommendations.

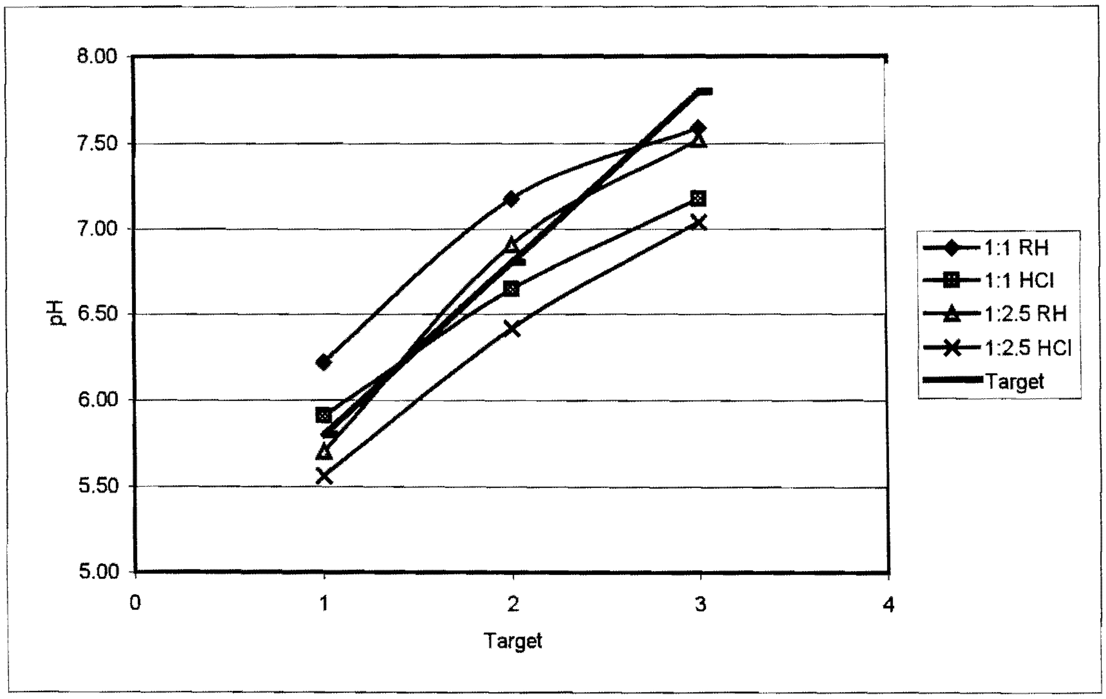

Figure 6. Predicted pH values for Lime 6 from calculated lime recommendations.

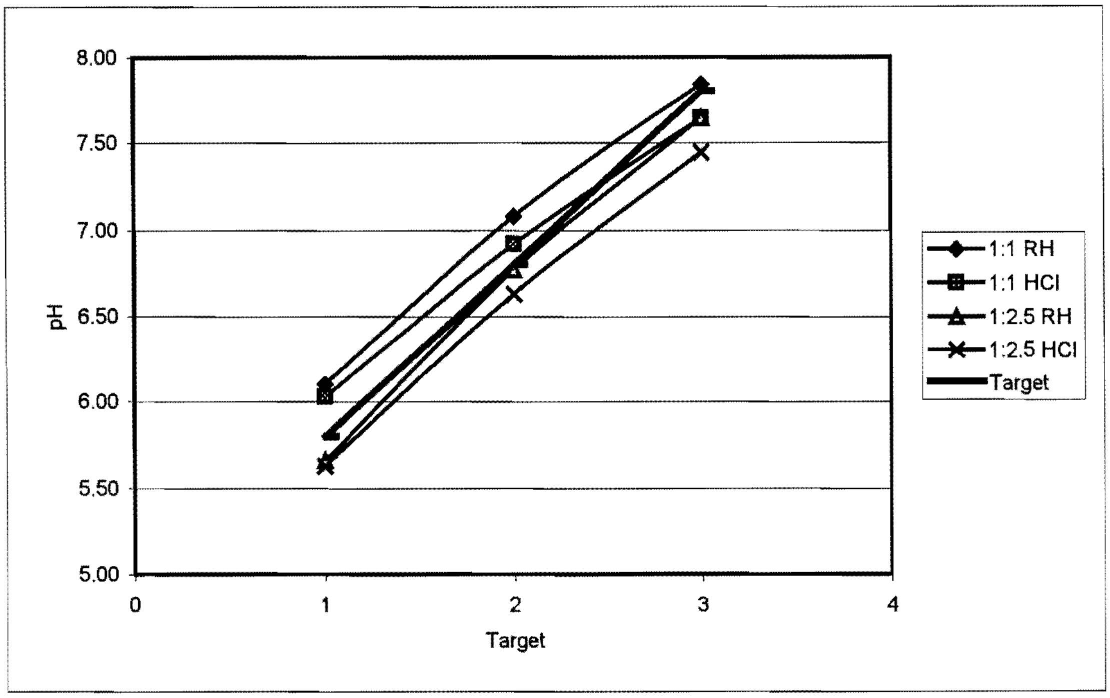

Figure 7. Predicted pH values for Lime 7 from calculated lime recommendations.

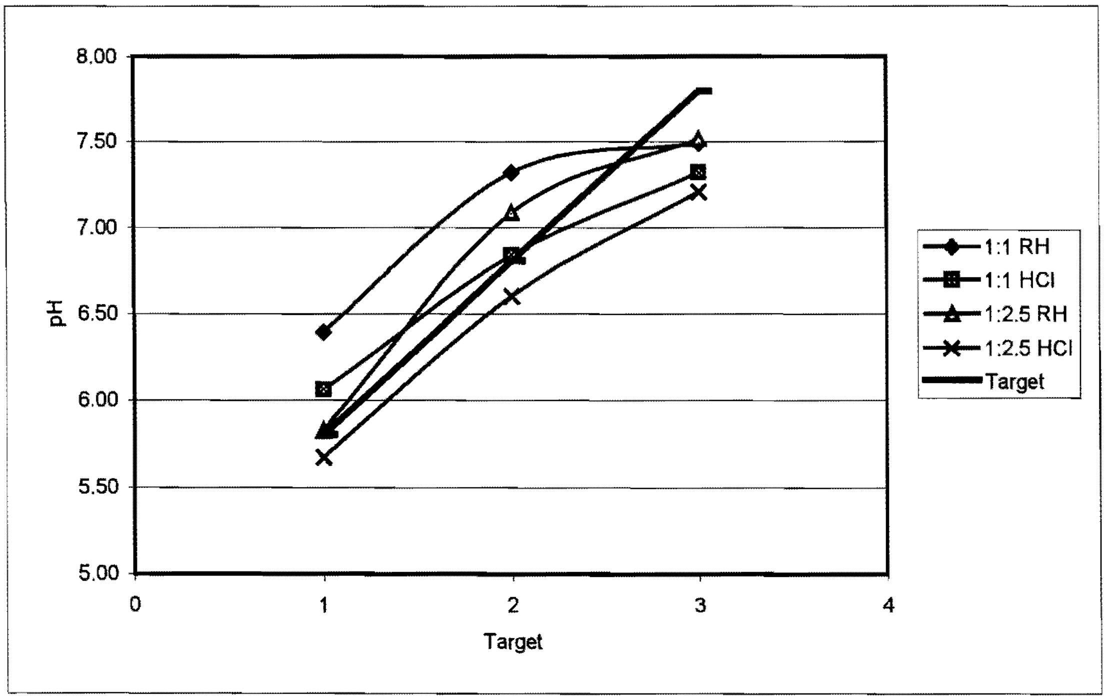

Figure 8. Predicted pH values for Lime 8 from calculated lime recommendations.

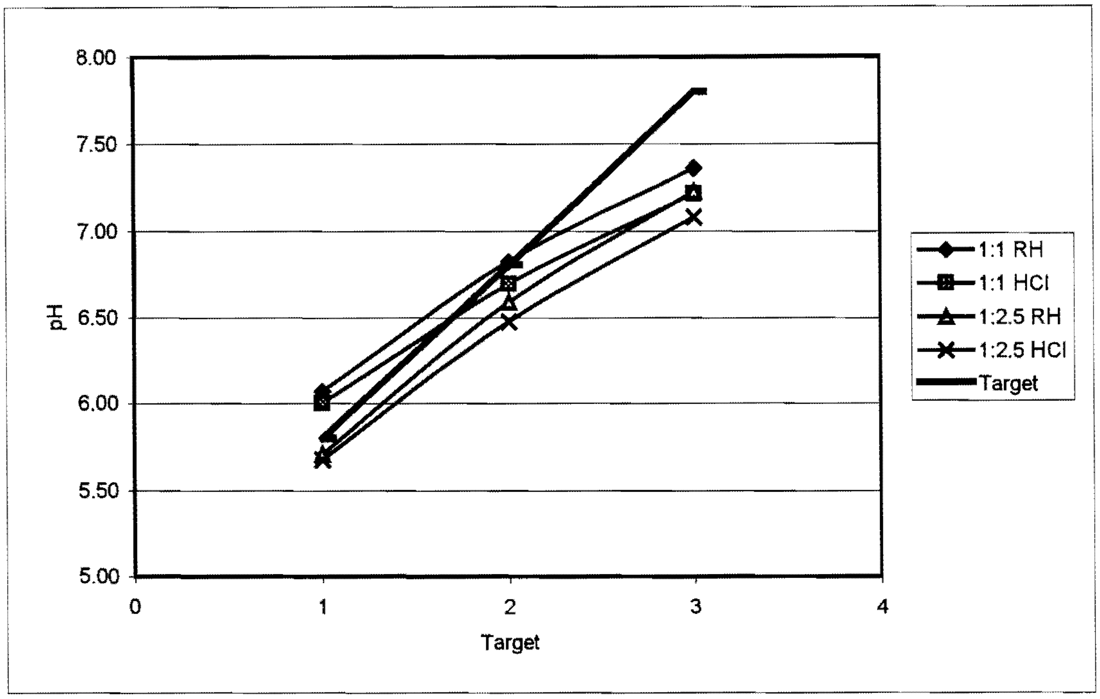

Figure 9. Predicted pH values for Lime 9 from calculated lime recommendations.

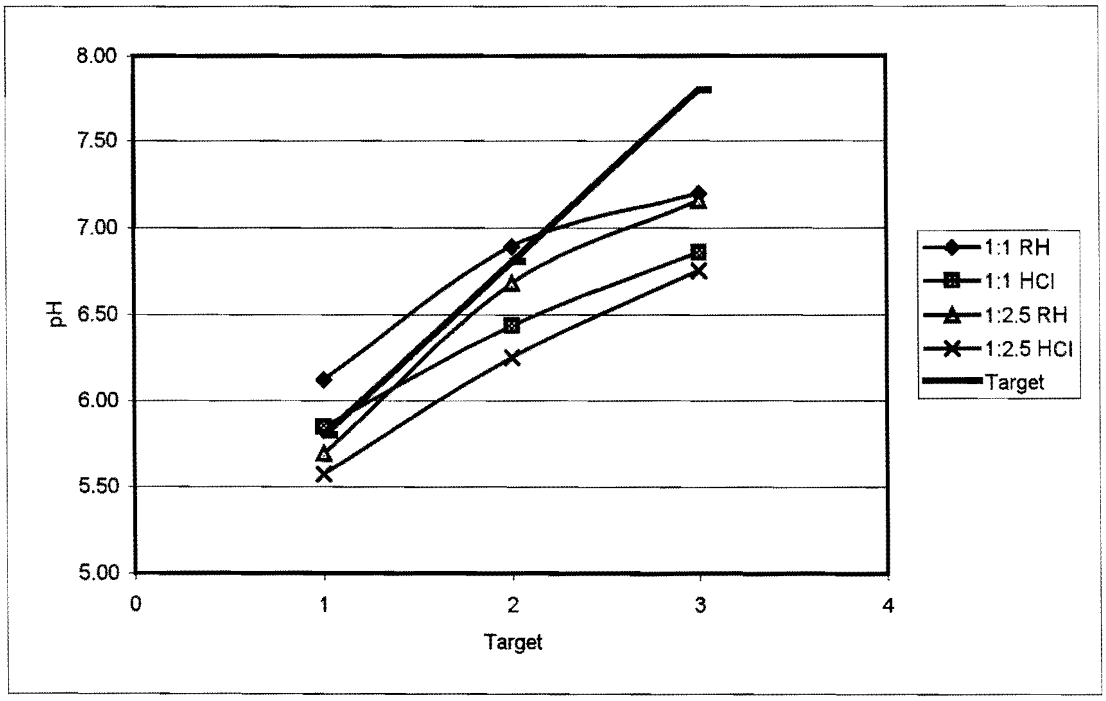

Figure 10. Predicted pH values for Lime 10 from calculated lime recommendations.

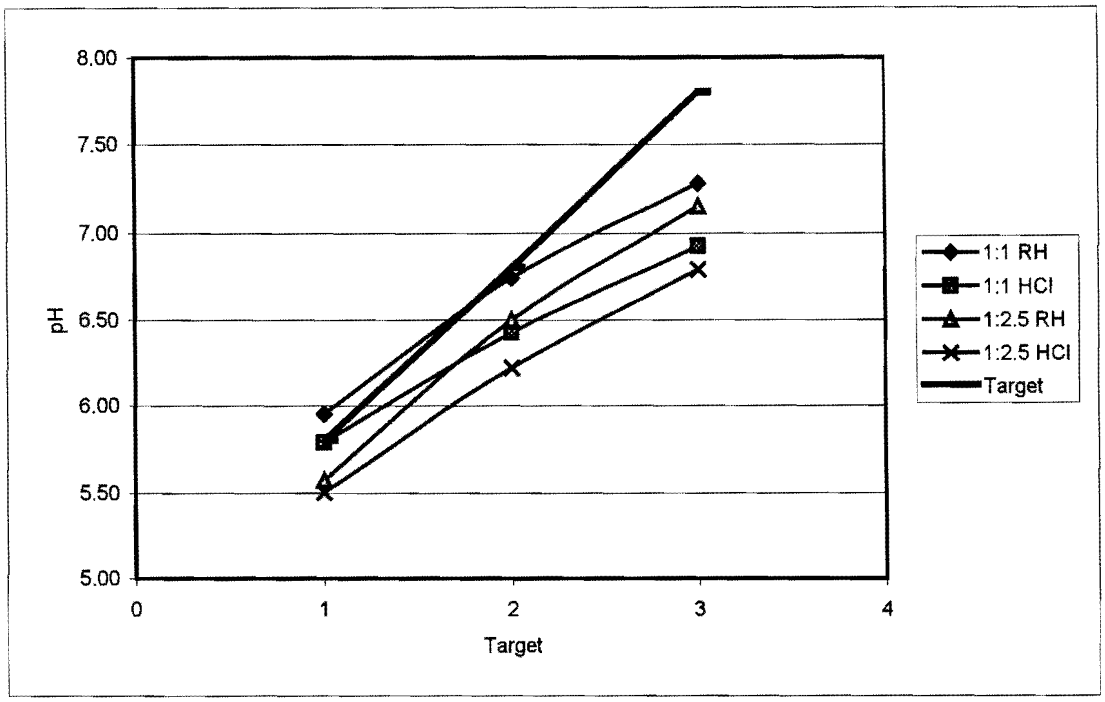

Figure 11. Predicted pH values for Lime 11 from calculated lime recommendations.

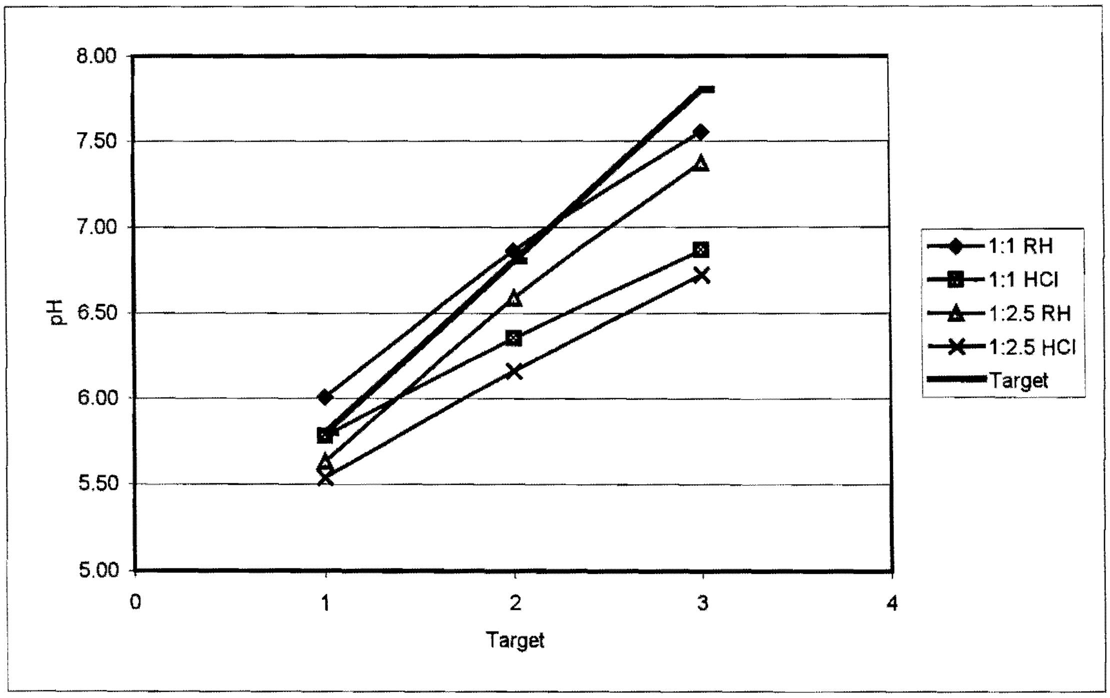

Figure 12. Predicted pH values for Lime 12 from calculated lime recommendations.

APPENDIX 6

YIELD OF WHEAT AND SPINACH

TABLE 1. Total wheat yield per rate of lime application.

Lime no.	Rate	Yield per four pots (g) First harvest	pH	Yield per four pots (g) Second harvest	pH
	Control	35.65	5.33	26.65	5.06
1	1	30.48	6.35	32.02	6.02
	2	26.70	6.91	46.03	6.60
	3	37.04	7.29	47.99	7.30
2	1	33.83	6.05	40.54	6.32
	2	41.14	7.27	43.67	7.45
	3	50.27	7.88	50.14	8.08
3	1	30.37	6.33	46.32	5.99
	2	33.30	7.42	45.07	7.10
	3	37.00	7.61	44.48	7.45
4	1	31.37	6.05	37.72	5.41
	2	32.68	6.55	30.21	6.69
	3	32.97	7.34	36.51	6.96
5	1	30.05	6.15	39.02	6.27
	2	35.55	7.11	42.62	7.14
	3	35.04	7.54	37.88	7.45
6	1	29.72	6.22	41.46	6.00
	2	40.10	7.18	46.52	7.22
	3	44.93	7.60	45.35	7.78
7	1	30.09	6.19	38.71	6.13
	2	34.01	7.02	53.54	7.21
	3	34.87	7.86	52.65	7.73
8	1	36.12	6.58	33.81	6.23
	2	38.51	7.18	44.77	6.87
	3	34.65	7.53	43.52	7.36
9	1	30.80	6.37	32.19	5.66
	2	31.75	6.95	44.19	6.85
	3	31.55	7.43	48.22	7.23
10	1	32.88	6.25	29.05	5.95
	2	30.46	6.79	51.84	6.55
	3	31.78	7.21	46.05	7.39
11	1	29.55	5.91	34.51	5.65
	2	34.27	6.78	39.07	6.64
	3	39.08	7.27	41.66	7.37
12	1	30.01	6.12	34.24	5.66
	2	26.85	6.78	44.63	6.74
	3	36.95	7.60	38.56	7.55

Table 2. Total spinach yield per rate of lime application.

Lime no.	Rate	Yield per four pots (g) First harvest	pH
	Control	0.29	5.33
1	1	4.33	6.35
	2	4.71	6.91
	3	8.96	7.29
2	1	5.2	6.05
	2	8.86	7.27
	3	10.67	7.88
3	1	5.93	6.33
	2	6.42	7.42
	3	9.26	7.61
4	1	5.68	6.05
	2	9.16	6.55
	3	9.38	7.34
5	1	6.16	6.15
	2	6.89	7.11
	3	8.49	7.54
6	1	5.19	6.22
	2	7.35	7.18
	3	7.2	7.60
7	1	8.33	6.19
	2	12.84	7.02
	3	14.66	7.86
8	1	3.26	6.58
	2	6.85	7.18
	3	7.94	7.53
9	1	5.98	6.37
	2	9.32	6.95
	3	9.94	7.43
10	1	5.5	6.25
	2	7.44	6.79
	3	11.04	7.21
11	1	5.51	5.91
	2	8.03	6.78
	3	9.79	7.27
12	1	3.19	6.12
	2	8.75	6.78
	3	9.66	7.60

Note: Due to poor growth no data exists for second spinach harvest