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	1:1 (50g soil)	1:1 (50g soil)
Test	Trial 1	Trial 2
$Ca(OH)_2$ added (mmol/kg soil)	pH	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

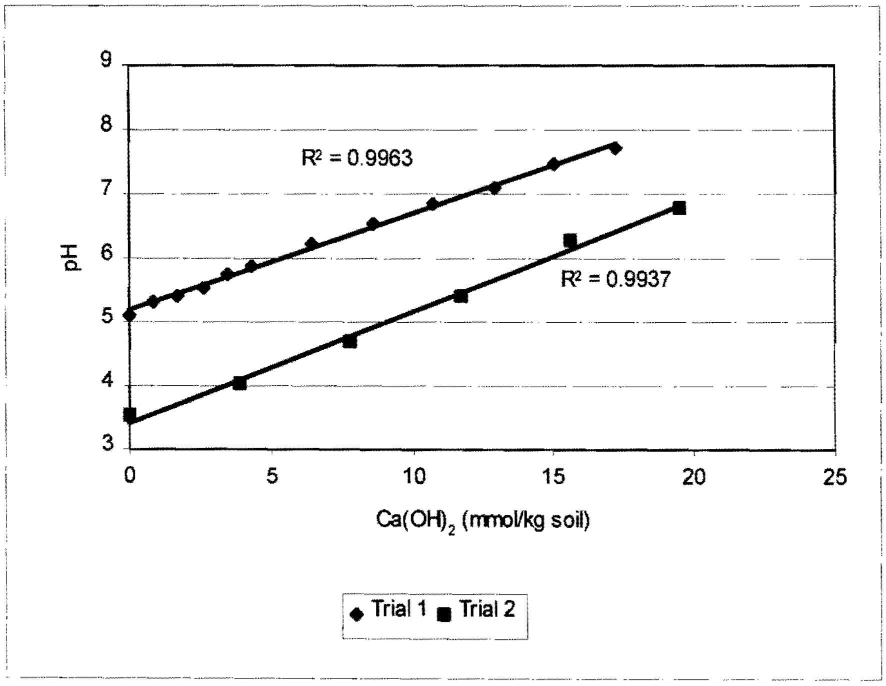

Figure 3.1. $Ca(OH)_2$ incubation curve for Trial 1 and 2.

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 HCl %	RH-Value %	PH 5.8 lime g.pot^{-1} (ton.ha^{-1})	pH 6.8 lime g.pot^{-1} (ton.ha^{-1})	pH 7.8 lime g.pot^{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 lime ton.ha^{-1}	pH 6.8 lime ton.ha^{-1}	pH 7.8 lime 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.

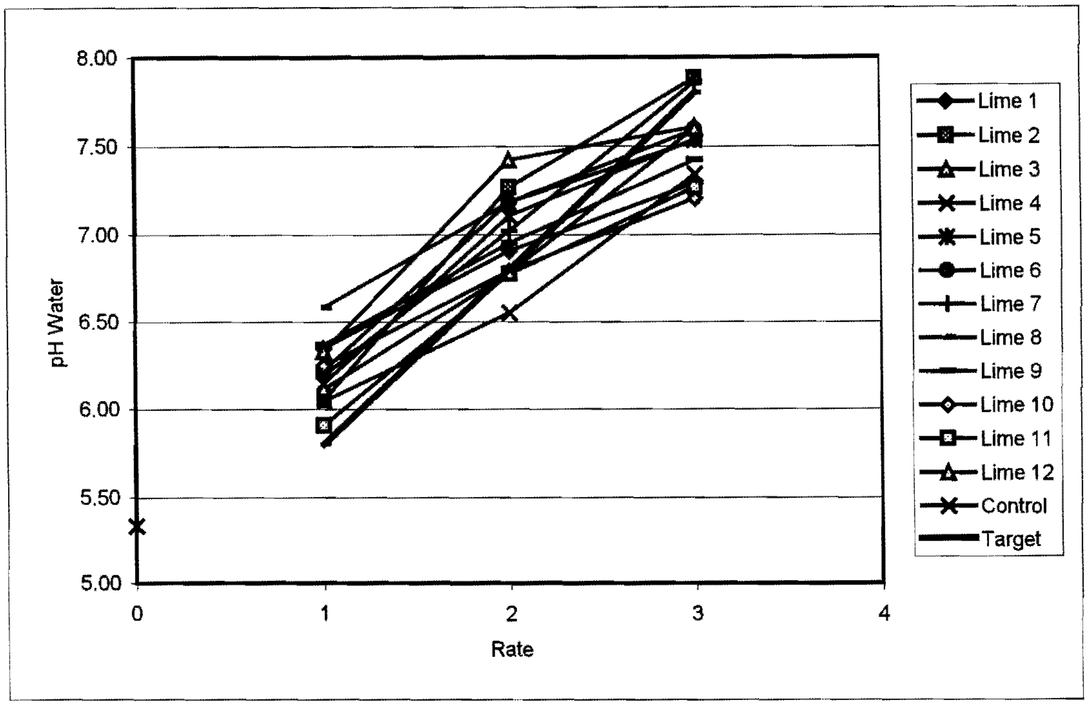

Figure 3.2: pH($_{\text{Water}}$) results for three target applications after three months (Trial 1). Note: The thick black line represents the target pH values.

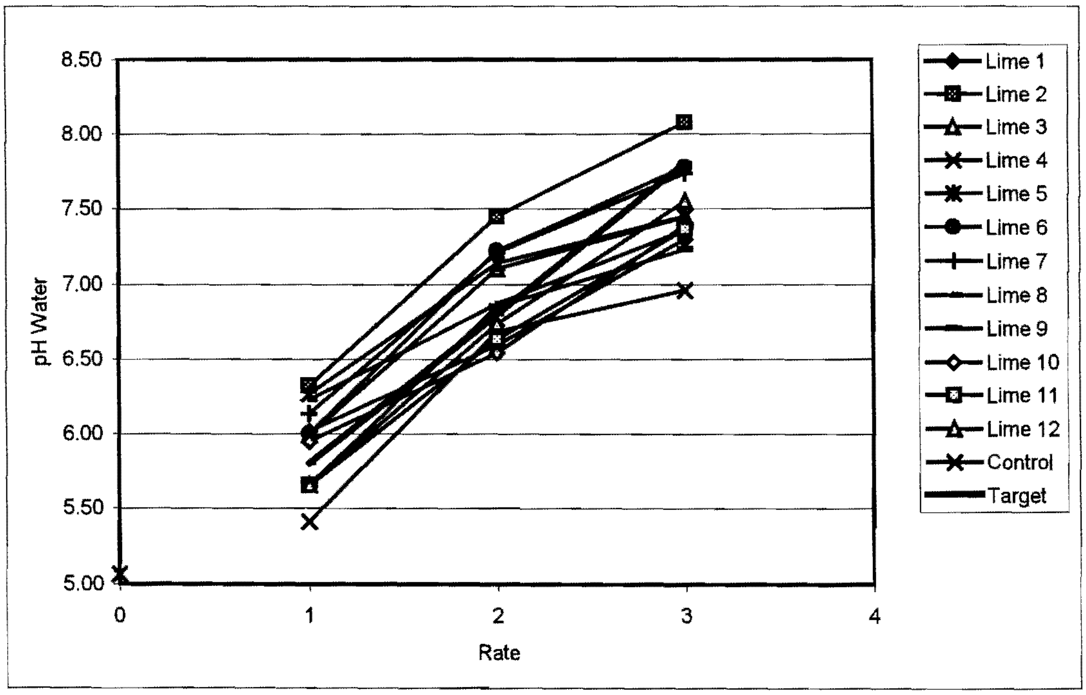

Figure 3.3: pH($_{\text{Water}}$) results for three target applications after seven months (Trial 1). Note: The thick black line represents the target pH values.

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.