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

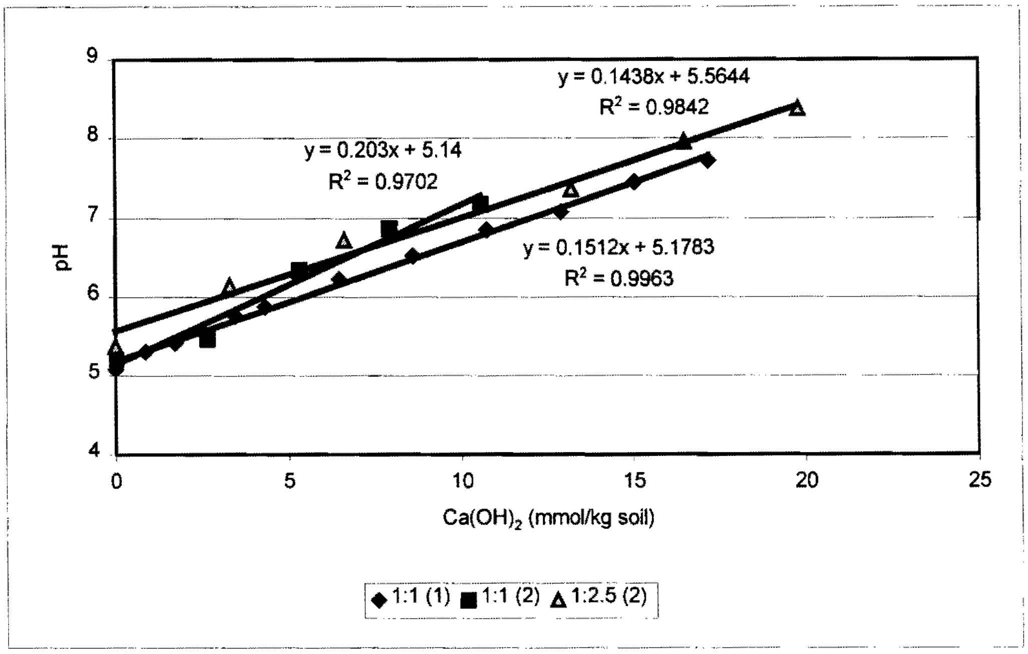

Figure 4.1. $Ca(OH)_2$ buffer curves for three determinations.

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.

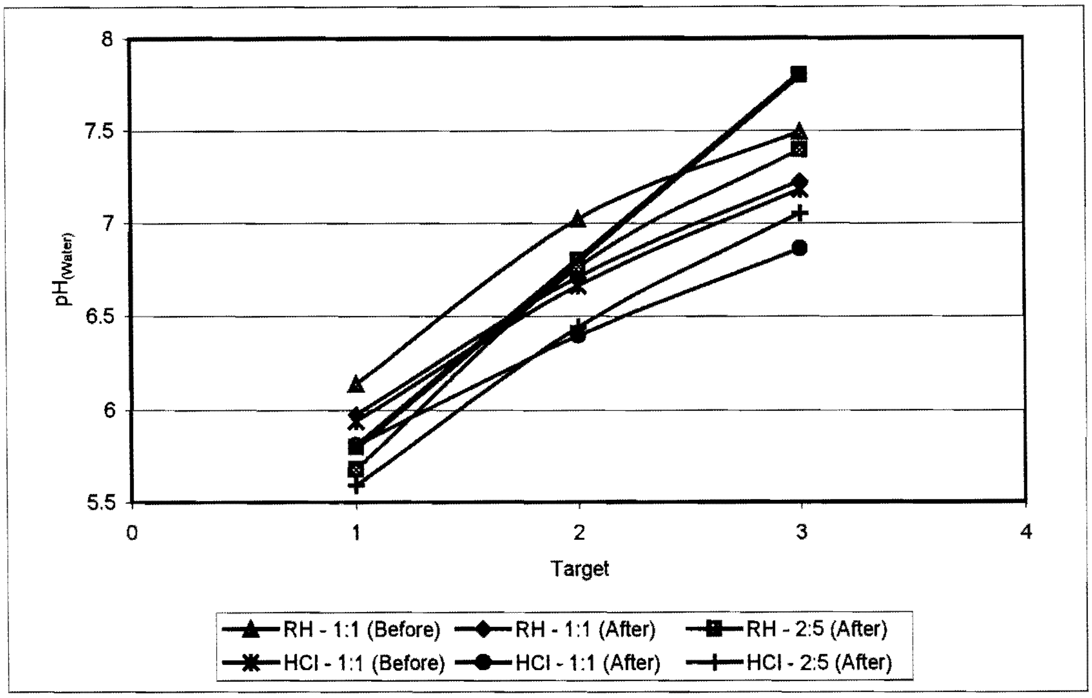

Figure 4.2. Average $pH_{(Water)}$ values for six methods used compared with the target values.

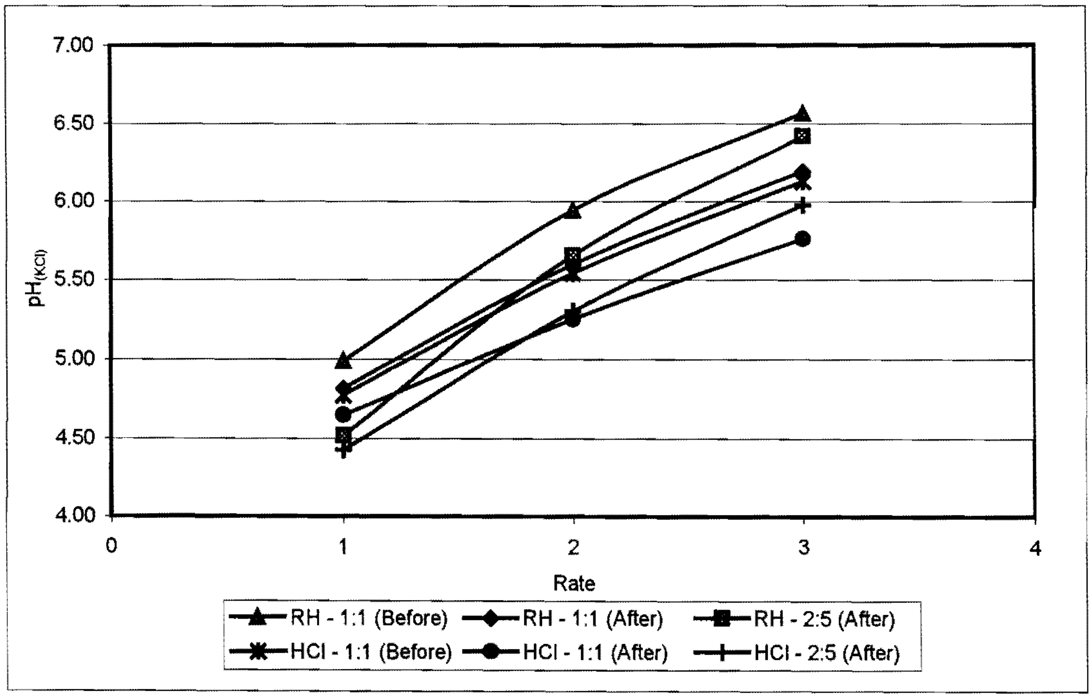

Figure 4.3. Average $pH_{(KCl)}$ values for the six methods used.

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.

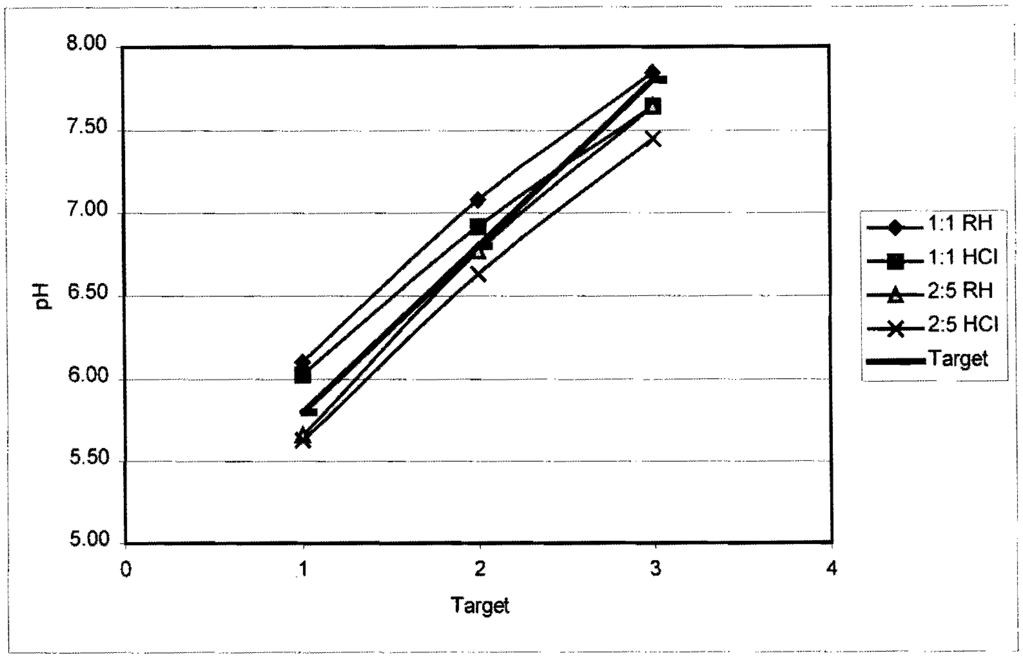

Figure 4.4. Predicted pH values for Lime 7 from calculated lime recommendations.

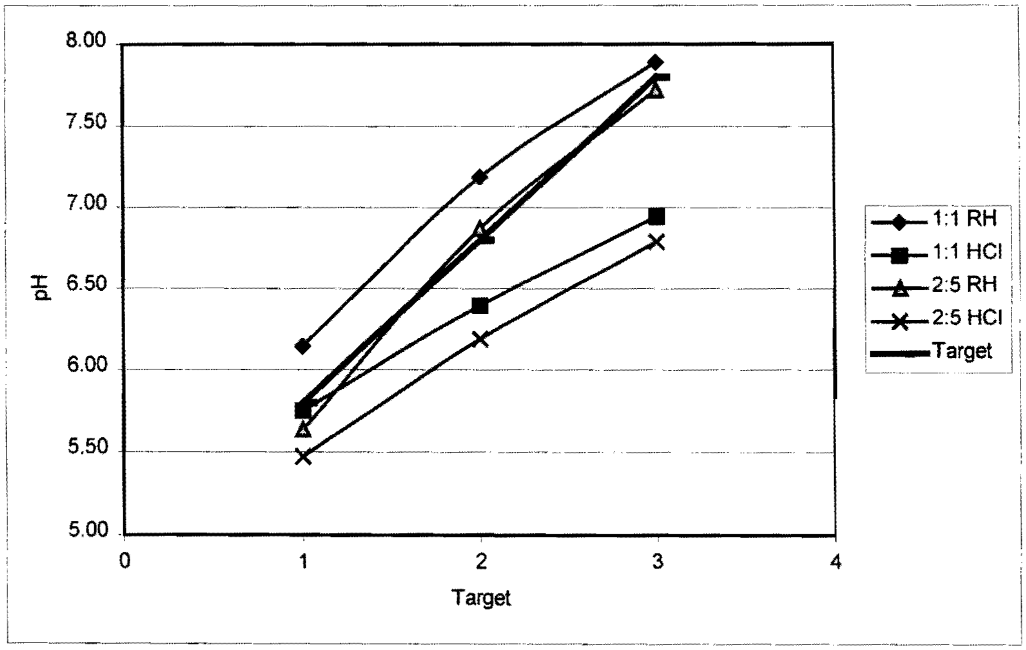

Figure 4.5. Predicted pH values for Lime 2 from calculated lime recommendations.

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.