# SOME THOUGHTS ON SOIL ACIDITY AND LIMING

(Met opsomming in Afrikaans)

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## Abstract

Lime requirement is most appropriately defined in terms of the minimum soil-pH value above which no significant crop response can be expected from additional liming. Besides affecting pH, liming is inevitably bound up with such questions as CEC, the degree of base saturation, buffer capacity, Al and Mn toxicities and P availability. Recent advances in soil chemistry and improvements in analytical techniques have led to a clearer understanding of the manner in which these factors interact to affect soil conditions and plant growth.

In a wide range of acid Natal soils, exchangeable $Al^{3+}$ rather than adsorbed H+ has been shown to be the main source of acidity. Maximum response to lime is obtained at the point where active Al is effectively suppressed. The readily-determined exchangeable aluminium index (EAI) has proved to be an excellent criterion on which to base liming recommendations for routine advisory purposes. When applied to certain South African soils, the widely-accepted American criterion of liming to pH 6,5 leads to unrealistically high values for lime requirement. The explanation lies in the large pH-dependent negative charge developed with rising pH in many of our subtropical soils.

Crop response to liming is ascribed to elimination of Al toxicity as a growth-limiting factor rather than to improved P availability. In the soils investigated, P-fixing capacity is not markedly reduced by liming but overliming reduces P availability to plants. Because root development is severely restricted in the presence of even very small amounts of active Al, moisture reserves remain untapped in times of stress unless $Al^{3+}$ in the subsoil is eliminated.

## Introduction

Soil acidity has attracted great interest ever since it was first recognised by applying the litmus-paper test. Ideas on the nature of soil acidity and the need for liming have undergone constant evolutionary change as outlined by Jenny (1961) in his masterly review, *Reflections on the soil acidity merry-go-round.* He recalls how Veitch in 1904 was the first to draw attention to the presence of active Al in acid soils, how this was lost sight of in the heyday of pH and the hydrogen electrode and how it has once again come under the searchlight. Recent advances have shed more light on how the jigsaw of pH, variable CEC, degree of saturation, buffer capacity, exchangeable $Al^{3+}$, lime requirement and crop response to liming, and also P availability in acid soils may be fitted together. An attempt is made here to review some of the more important practical aspects of the inter-relationships which exist between these factors.

## Measurement of soil pH

Soil pH has become accepted as the simplest criterion of the need for lime but if different investigators are to speak in comparable terms, there is need for standardising the technique for pH measurement. Now that there is greater clarity on the influence of the soil:solution ratio, salt effects, time of equilibration and suspension effects, the following procedure based on the method of Schofield & Taylor (1955) which provides a more stable basis for expressing pH value, is perhaps least open to criticism.
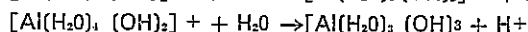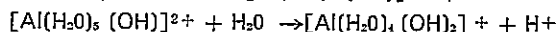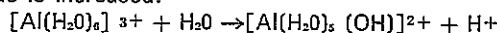
To the equivalent of 20 g dry soil in a 100 ml beaker add

50 ml 0,1M $CaCl_2$; stir for 15 seconds and then intermittently over a period of two hours; allow to settle and measure with the bulb of the glass electrode positioned in the sediment and the porous plug of the calomel electrode in the supernatant.

This seems preferable to the use of N KCl which creates a rather severe and unnatural environment. As a guide, a pH value of 4,8 in 0,01M $CaCl_2$ is in most cases approximately equivalent to pH 5,3 ($H_2O$) and values below these warrant investigation of the need for liming.

## The nature of soil acidity

Besides mineral and weak organic acids, exchangeable H+ in equilibrium with the soil solution has long been regarded as the main source of acidity. The validity of this concept has been seriously questioned by le Roux & de Villiers (1965) and also numerous others. They showed that at or near the field pH value, very little titratable acidity was present in the soils they studied. They support Russell (1954) in regarding exchangeable $Al^{3+}$ in six-co-ordination as the principal source of H+ (or hydronium) in accordance with the following well-known hydrolysis sequence as pH value is increased:

$$[Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(H_2O)_5 (OH)]^{2+} + H+$$

$$[Al(H_2O)_5 (OH)]^{2+} + H_2O \rightarrow [Al(H_2O)_4 (OH)_2] + + H+$$

$$[Al(H_2O)_4 (OH)_2] + + H_2O \rightarrow [Al(H_2O)_3 (OH)_3 + H+$$

Accordingly, 1 me% of exchangeable $Al^{3+}$ per ha (30 cm) would generate sufficient acidity to require well over two metric tons of 100% $CaCO_3$ for its neutralization.

To complete the destruction of the long-cherished model of an acid soil, these workers and also Reeve & Sumner (1971) showed that the various soils (mainly oxisols) they studied are in fact virtually saturated with metal cations at their field-pH values, leaving little if any room for exchangeable H+:

The data in Table 1 shows that when the AEC is subtracted from CEC at 'field' pH the result corresponds very closely with net CEC and with the sum of the exchangeable metal cations.

It remains to be seen in what measure these findings are also applicable to other soils. Similar evidence pre-

TABLE 1 *Exchange properties of some Natal soils, me% (Mean of eight Oxisols) (After Reeve & Sumner (1971))*

| Depth cm | Exch Al | Exch bases | Exch metal cations | CEC | | | AEC** |
|---|---|---|---|---|---|---|---|
| | | | | 'field' pH | Nett* | pH 7,0 | |
| 0-15 | 1,4 | 3,8 | 5,2 | 6,4 | 5,2 | 27 | 0,8 |
| 15-30 | 1,4 | 2,3 | 3,7 | 5,9 | 4,1 | 24 | 1,3 |
| 30-40 | 1,3 | 1,5 | 2,8 | 4,8 | 2,9 | 21 | 1,8 |
| 45-60 | 1,3 | 1,2 | 2,5 | 4,4 | 2,3 | 20 | 1,8 |
| 60-75 | 1,4 | 0,9 | 2,4 | 4,6 | 2,3 | 19 | 2,2 |
| 75-90 | 1,3 | 0,9 | 2,2 | 4,5 | 2,1 | 18 | 2,2 |

*Nett CEC determined by washing with water after equilibration with $NH_4Cl$ solution

**AEC = anion exchange capacity

sented by le Roux & de Villiers (1965) included data for moderately-leached soils.

## The definition of CEC

Many soils, particularly those that are highly weathered and acid, develop a large pH-dependent negative charge CEC) which, if measured by he widely usedt N NH₄ OAC method at pH 7, may be 3-5 times greater than the CEC at field pH. Values for the degree of saturation based on data for CEC derived from methods using buffered solutions at high pH (ammonium acetate and Mehlich's $BaCl_2$-TEA) are thus largely meaningless as they may bear no relation to the condition with which crops in the field are confronted. (le Roux & de Villiers, 1966; Fieldes & Schofield, 1960).
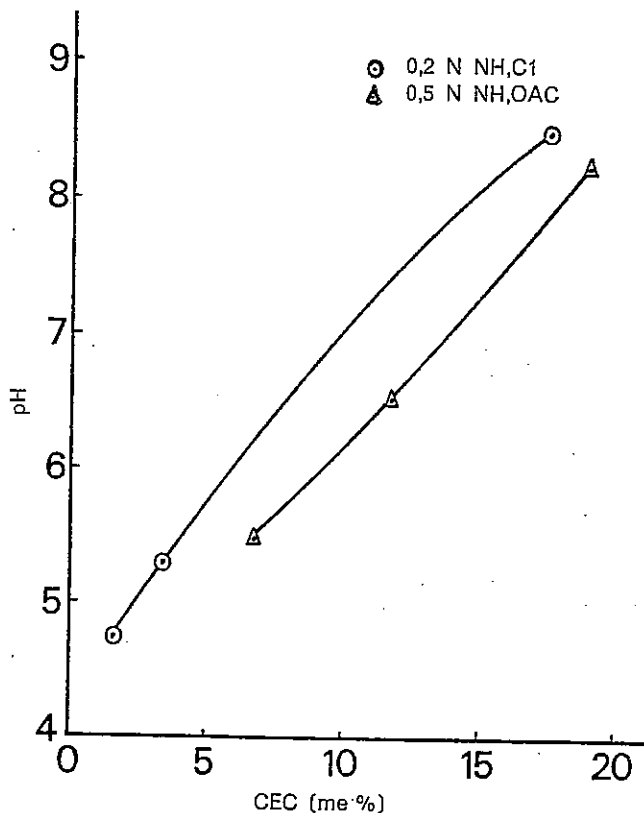


Fig 1 Variation in CEC with pH value and equilibrating salt (After le Roux & de Villiers, 1966).

Reeve & Sumner (1971) point out that at low electrolyte concentrations the positive charges (AEC) in acid soils reduce the CEC. They suggest that this is due to the interaction of the double layers and that the net CEC found after washing the soil free of the exchanging salt with water, is in fact the effective CEC under field conditions — Table 1.

In the light of these findings it becomes clear why such unrealistically high values for lime requirement are obtained on many of our soils by the buffer method to pH 6,5 of Shoemaker, McClean & Pratt (1961) so widely used in the USA. On average, eight Natal soils showed a lime requirement of 9,4 metric tons $CaCO_3$ per ha by the SMP method (pH 6,0) whereas a test crop (Trudan) gave its maximum yield at an average application of only 2,4 metric tons per ha.

The pH-dependent negative charge finds its expression as an increase in CEC as pH rises and this is what appears to have generated the excessive apparent lime requirement. The increase charge was thought to be due to dissociation of H+ from OH groups (Schofield, 1949) but more recent

work suggests that deprotonation of the functional Al-OH₂ groups in allophane and aluminous chlorite is the more likely source (de Villiers & Jackson, 1967, a, b). These minerals are commonly present in substantial amounts in acid soils.

## Definition of lime requirements

If the current American recommendation of liming to pH 6,5 (7,0 for lucerne) is unacceptable in the case of many South African soils, the question arises what pH objectives or other criterion should be used for estimating lime requirement. The most rational answer would be to define lime requirement as that amount above which there is no significant crop response to further applications of lime.

Reeve & Sumner (1970) suggest that the first consideration in attempting to improve yields must be removal or suppression of exchangeable $Al^{3+}$ in order to eliminate its known toxic effect. They further postulate that if exchangeable $Al^{3+}$ is the main source of soil acidity, the amount present will be directly related to lime requirement. To test this hypothesis they added increasing amounts of lime to eight Natal Oxisols in 5 kg pots which also received standard additions of N, P, K and trace elements. Trudan (Sorghum sudanense) was used as test crop under greenhouse conditions. The yield data are shown in Figure 2.
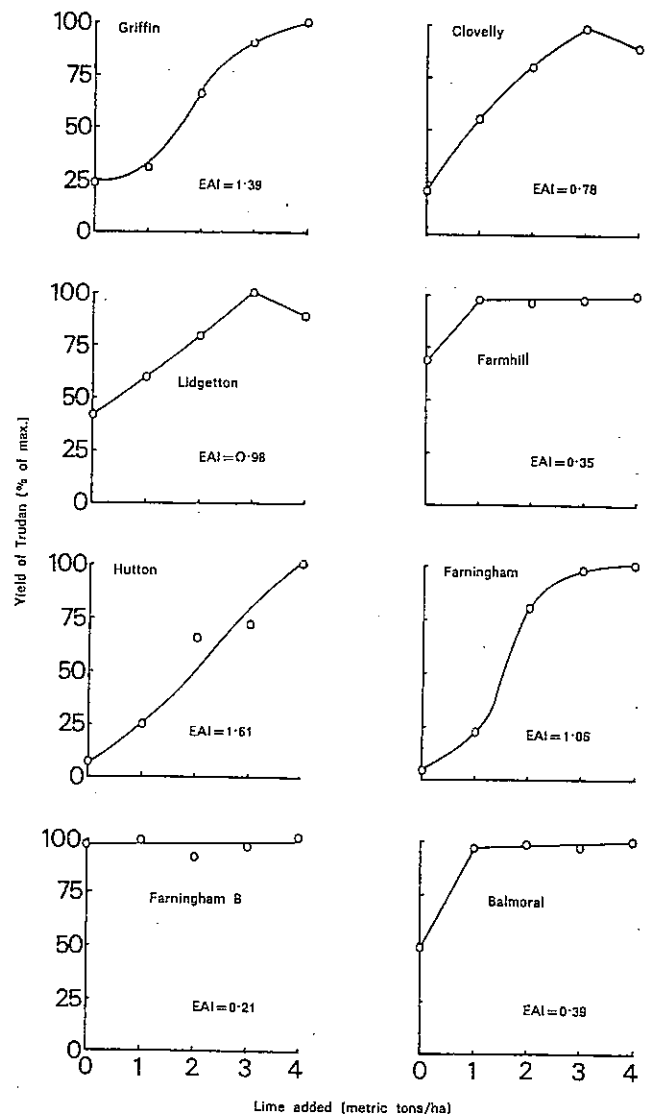


Fig 2 Effect of lime on yield of Trudan on eight Natal Oxisols [EAI values (me/100 g) refer to unlimed soil; LSD (0,05) shown as vertical lines]. (After Reeve & sumner, 1970, b)

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TABLE 2 *Lime requirements of eight Natal Oxisols according to different criteria (metric tons $CaCO_3$/ha) (After Reeve & Sumner, 1970)*

| Soil series | Criterion | | | |
|---|---|---|---|---|
| | Max yield (Trudan) | Exch Al to 0,2 me% | pH 6,0 SMP | pH 6,5 SMP |
| Griffin | 4,0 | 4,0 | 13,0 | 19,5 |
| Clovelly | 3,0 | 2,8 | 10,0 | 15,0 |
| Lidgetton | 3,0 | 3,0 | 10,0 | 15,0 |
| Farmhill | 1,0 | 0,8 | 9,0 | 13,5 |
| Hutton | 4,0 | 4,6 | 10,0 | 15,0 |
| Farningham A | 3,0 | 2,8 | 8,0 | 12,0 |
| Farningham B | 0,0 | 0,0 | 9,0 | 13,5 |
| Balmoral | 1,0 | 1,0 | 6,0 | 9,0 |
| Means | 2,4 | 2,4 | 9,4 | 14,1 |

Table 2 shows the close agreement between lime required for maximum yield and that needed to reduce exchangeable $Al^{3+}$ to 0,2 me% which was regarded as the critical level in these fairly well buffered soils.

Figure 3 illustrates the progressive reduction of the exchangeable aluminium index (EAI) (which closely reflects exchangeable $Al^{3+}$ but is more easily determined), with increasing increments of lime. These data are replotted in Figure 4 to show the relationship between EAI and the amount of lime required to reduce the EAI to 0,2 me%. Sumner has found this relationship to hold for a wide selection of mainly sandy soils from many parts of South Africa and neighbouring territories.
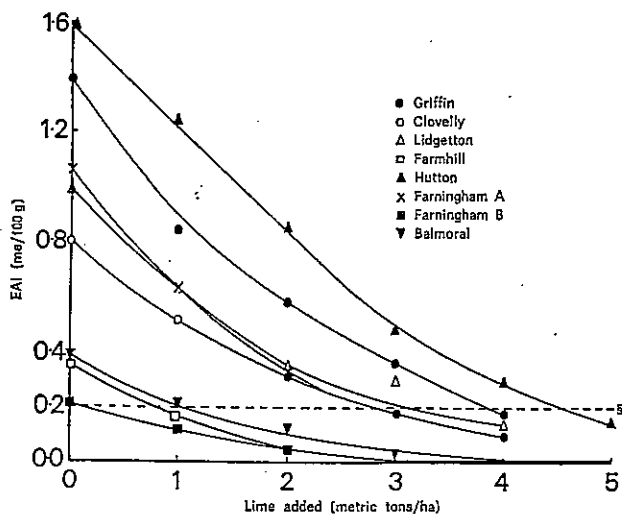


Fig 3 Effect of $CaCO_3$ on EAI values of eight Natal Oxisols. § determined separately. (After Reeve & Sumner, 1970 b.)
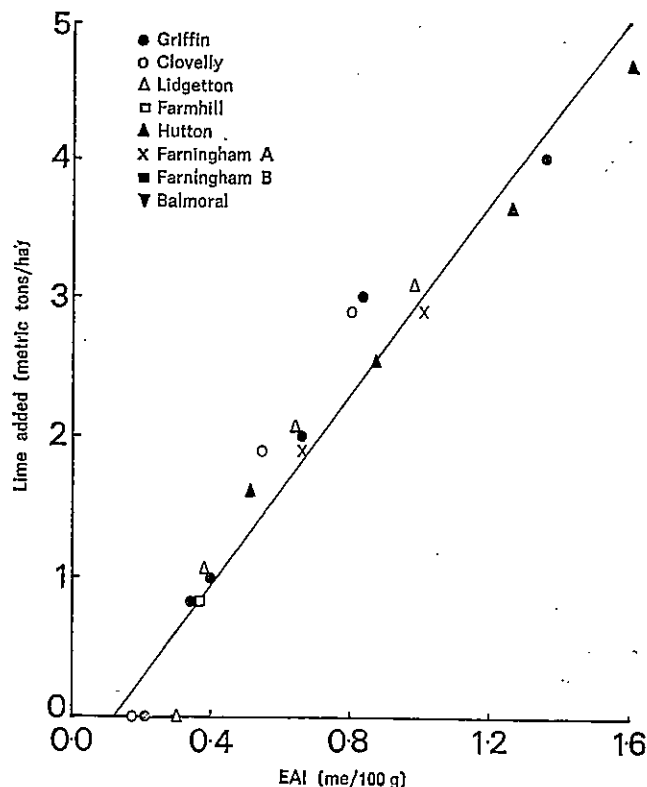


Fig 4 Relationship between EAI and lime required to reduce EAI to 0,2 me/100 g in eight Natal Oxisols. (Lime req. = 3,353 EAI — 0,393; r = 0,973). (After Reeve & Sumner, 1970 b).

In general, it is found that soils above pH 4,8 ($CaCl_2$) do not require liming although those below this value do not always contain exchangeable $Al^{3+}$.

It is of interest to note the conclusion of Fisher (1969) who reviewed the results of many field experiments, involving the use of lime, conducted over a long period in Missouri. His object was to identify with greater precision the pH value above which the probability of response from a variety of crops to further liming is small. With some exceptions he found on average that soybeans, lucerne, maize, cotton and wheat failed to respond significantly to lime above pH (1:1; soil:0,01M $CaCl_2$) values of 5,4, 5,7, 5,4, 5,2 and 4,8 respectively. He draws the overall conclusion that "there is a low probability of obtaining appreciable increase in crop yields by liming soils having a pH of 5,5 or above". Recent reviews of experimental evidence from other parts of America confirm Fisher's findings. There is thus ample support for the view that the higher pH values previously held to be desirable cannot be justified in practice.

Reeve & Sumner (1970) working with a range of reasonably well buffered soils with appreciable clay content regarded 0,2 me% exchangeable $Al^{3+}$ as the maximum consistent with good crop growth. Subsequently Sumner & Meyer (1971) examined a wide range of sandy soils and found that the majority showed EAI values in excess of 0,05 me%. It appears that sensitive crops are already adversely affected at this level in poorly-buffered soils and that in such cases it is desirable to reduce the value to zero. Very little extra lime would achieve this.

With few exceptions, EAI values show an irregular but definite increase with depth and this raises the troublesome problem of the need for subsoil liming. All except the most tolerant crops suffer root damage at concentrations of 2-3

ppm $Al^{3+}$ in the equilibrium soil solution. Sufficient exchangeable $Al^{3+}$ to subtend even this low concentration in the subsoil will preclude healthy root development. The implication for yield reduction during periods of moisture stress, when subsoil reserves must remain largely inaccessible to crops because of poor root penetration, is obvious. Unpublished work by Sumner conducted both in the field and in large drums in the greenhouse where soil was limed to different depths illustrate the need for eliminating $Al^{3+}$ in the subsoil. Even when only small amounts of exchangeable $Al^{3+}$ were present in sandy soils, plants wilted irreversibly while adequate moisture was still available 15 cm below the horizon to which lime had been applied.

Reeve used samples from a long-term field experiment on a soil of the Farningham series on Tabamhlope Experiment Station to investigate to what extent lime incorporated in an acid topsoil would also affect the subsoil. Certain plots had received up to three dressings of 4,24 metric tons per ha of dolomotic lime at 5-yearly intervals. Depth of cultivation had not exceeded 20 cm and he found (personal communication) that even 14 years after the initial application, the effect of the lime had barely penetrated 25 cm below plough depth. On the same experiment Orchard (unpublished) found that maize that had received a total of 12,8 metric tons of lime per ha was markedly superior for eight consecutive years to where 6,4 metric tons had been applied. On this soil only 8,1 metric tons was required to eliminate exchangeable $Al^{3+}$ to a depth of 75 cm. The superiority of treatments where the topsoil had been slightly overlimed, could be accounted for if it is assumed that the subsoil had in such cases been ameliorated to a greater extent than where the lighter dressing had been applied.

This example serves to illustrate the care with which yield-response data from liming experiments should be interpreted. Failure to appreciate fully the various factors involved has no doubt contributed to the conflicting views of different workers on the question of desirable pH value and other criteria for estimating lime requirement.

## Influence of liming on P availability

The high P-fixing capacity of many acid soils is commonly ascribed to the presence of active Fe and Al which form very insoluble precipitates with phosphate. If this view is valid, it follows that once active Fe and Al have been suppressed by liming there should be a marked reduction in P-fixing capacity and hence an improvement in availability of applied P.

Reeve & Sumner (1970) investigated this possibilty by standard pot technique in the greenhouse using a range of acid soils of varying exchangeable $Al^{3+}$ content. They first constructed desorption isotherms by plotting the amounts of P recoverable with Bray's extractant No 2 (0,03 N $NH_4F$ in 0,1 N HCl) from the various soils after they had been equilibrated with increasing concentrations of added phosphate. The resulting curves were linear and their slopes indicated large differences in P-fixing capacity. These differences were closely reflected by response of the test crop to P additions.

The strong correlation (r = 0.83××) between the desorption index and crop response to added P left little doubt that fixation of added P was largely responsible for the observed yield differences. In the same factorial experiment, four different levels of lime had also been used, the two highest levels being in excess of the amount required to eliminate all active Fe and Al. On average, yields at the two higher liming rates were depressed, which was interpreted as evidence that liming in excess of the quantity required for suppressing $Al^{3+}$ could interfere

with P availability. By using ameliorants other than lime (gypsum and Silene, a calcium silicate), it was possible to separate Al toxicity from other nutritional effects, particularly the availability of P to the crop. They showed that although lime eliminated exchangeable $Al^{3+}$, it failed to reduce P fixation significantly. They thus support the ideas of Hsu (1965) who regards P as being fixed on sesquioxic-adsorbing surfaces by a chemisorption mechanism. The ease of desorption is governed by the degree of saturation of such surfaces with phosphate.

In order to test the response of maize in the field under conditions of increasing saturation of the P-adsorbing complex, Orchard & Sumner (unpublished) used just sufficient lime to eliminate all active Al in a soil of the Farningham series. In addition to a standard dressing of N, K and trace elements, they applied single superphosphate at four widely spaced levels, viz, 1½, 3, 6 and 12 metric tons per ha. Grain yield was found to rise steadily over this range from 10 147 kg to 12 367 kg which illustrates how difficult it can be to quench the P-fixing capacity of the adsorbing surfaces under field conditions even in the absence of exchangeable $Al^{3+}$.

## Opsomming

### GEDAGTES OOR GRONDSUURHEID EN BEKALKING

Kalkbehoefte kan gepas gedefinieer word in terme van die minimum pH waarbo geen betekenisvolle oesverbetering as gevolg van verdere bekalking verwag kan word nie. Benewens die invloed van bekalking op pH hou dit ook verband met sake soos katioonuitruilvermoë, die graad van baseversadiging, bufferkapasiteit, aluminium- en mangaantoksisiteit en fosfor-toeganklikheid. Onlangse vordering op die gebied van grondskeikunde en analitiese tegnieke het tot 'n beter begrip gelei van die wyse waarop interaksie tussen hierdie faktore grondkondisies en plantegroei beïnvloed.

In 'n wye reeks van suur Natalse gronde is dit aangetoon dat uitruilbare $Al^{3+}$ eerder as geadsorbeerde $H^+$ die grootste bron van suurheid is. Die maksimum reaksie op kalk word verkry wanneer die aktiewe Al effektief onderdruk is. Die maklikbepaalbare uitruilbare aluminium-indeks het 'n uitstekende basis vir bekalkingsaanbevelings geblyk te wees. Wanneer die algemeen aanvaarde Amerikaanse norm van bekalking tot by pH 6,5 op Suid-Afrikaanse gronde toegepas word, word onrealistiese hoë waardes vir die kalkbehoefte verkry. Die rede hiervoor is geleë in die hoë pH-bepaalde negatiewe lading wat met stygende pH in baie van ons subtropiese gronde ontwikkel.

Opbrengsverhoging deur bekalking kan daaraan toegeskryf word dat Al-toksisiteit as 'n groeibeperkende faktor uitgeskakel word eerder as dat P-toeganklikheid verbeter word. In die gronde wat ondersoek is, is die P-vasleggingsvermoë nie noemenswaardig verlaag deur bekalking nie, maar oorbekalking het P-toeganklikheid vir plante verlaag. Omdat wortelontwikkeling ernstig benadeel word deur selfs 'n geringe hoeveelheid aktiewe Al, sal vogreserwes in tye van stremming nie benut kan word nie tensy $Al^{3+}$ in die ondergrond uitgeskakel word.

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