

## Predicting the field performance of twelve commercial liming materials from southern Australia

M. K. Conyers, B.J. Scott, R. Fisher & W. Lill

*NSW Agriculture, Agricultural Research Institute, PMB, Pine Gully Road, Wagga Wagga, 2650 Australia*

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### Abstract

The relative performance of 12 commercial liming materials from southern Australia was evaluated in a field trial. The materials included 6 calcitic limestones, 3 coralline limestones, 1 earthy limestone and 2 dolomites. All 12 materials were chemically and physically analysed and assessed for their ability to change soil pH. Chemical efficiency% was taken to be the traditional  $\text{CaCO}_3$  - equivalent mass. The particle size analysis of each material was used to predict its physical efficiency% on the basis of our particle size model for calcitic limestones:

$$\Delta \text{pH} = a - b \log (\text{particle diameter})$$

where  $a = 2.875$  and  $b = 0.697$  for a  $5 \text{ t ha}^{-1}$  application rate at this trial site. The relationship is mathematically valid for particle diameters between 1 and  $13,000 \mu\text{m}$ . All commercial materials were applied at  $5 \text{ t ha}^{-1}$ . The particle size model was determined independently but concurrently at the same site. The model for physical efficiency % was expressed relative to a microfine grade of limestone ( $99\% < 75 \mu\text{m}$ ) which makes it transferable to other sites. The product of relative physical efficiency % and chemical efficiency ( $\text{CaCO}_3$  equivalent)% was used to predict the total efficiency % of each liming material in increasing soil pH. A comparison of the predicted total efficiency % was made with the actual total efficiency% of the 12 materials as measured in the field. During the first cropping season the model predicted the performance of the 6 calcitic limes:

$$\text{predicted} = 0.94 \text{ actual} + 3.95 \quad r = 0.97$$

The slope was not significantly different to unity nor the intercept to zero. The dolomites performed, on average, 15% poorer than predicted by the calcite-based model while the softer limes (coralline and earthy) performed 20% better than predicted. By 12 to 24 months these differences were attenuated and 10 of the 12 products were well predicted by the model. The performance of liming materials in increasing soil pH is considered to be the result of chemical composition (base content), particle size and the solubility of the dominant mineral. We propose the use of our predictive model to evaluate the relative total efficiency % of liming materials.

### Introduction

The cost of liming relative to the low value of produce from broad-acre agriculture in Australia necessitates that liming materials be used as efficiently as possible. Limestone is transported to our region over distances of 200–400 km from six different sources. We therefore need to be able to quantify the relative costs and

benefits of alternative products. The particle size of liming materials is known to be a major factor influencing both the rate of reaction of lime with soil and the potential extent of that reaction (Barber, 1984). Coarser particles may not effectively contribute to soil amelioration within the time-frame between lime applications. Accordingly, as limestone usage has increased in Australia, particle size has become a subject of inter-

est to researchers (Hodge and Lewis, 1994; Scott *et al.*, 1992). In a previous paper (Scott *et al.*, 1992) we addressed a number of ambiguities in the literature concerning the influence of particle size on lime effectiveness. Our study involved a factorial design with a broad set of 6 particle sizes, each size tightly ranged, at 3 application rates and for 4 sampling times over 3 years after liming. We measured soil pH,  $\text{Ca}_{\text{ex}}$  and grain yield on each plot. This enabled us to assess the relative value of particle size segregations of calcitic limestone with some accuracy.

We now attempt to validate the model, based on discrete sizings of calcite, on as wide a range of commercial liming materials as possible. The aim of the present study was to ascertain whether the field performance of 12 commercial liming materials from southern Australia could be accounted for by their chemical composition (base content) and by their particle size distribution. The value of particle size was modelled from the particle size segregations of Scott *et al.*, (1992).

## Materials and methods

The trial has been previously described by Scott *et al.* (1992).

### Experimental site

The trial was located 20 km east of Wagga Wagga in southern New South Wales. The soil type was an albic luvisol (FAO-UNESCO, 1974), aeris albaqualf (Soil Survey Staff, 1975), Dy 3.41/2 (Northcote, 1979) and a yellow podzolic/solodic intergrade (Stace *et al.*, 1968). The mineralogy was dominated by illite>kaolinite>quartz. The surface 10 cm soil had a mean pH ( $\text{CaCl}_2$ ) of 4.1, 0.7% organic C, 12% clay and an effective cation exchange capacity of 2.51 cmol (+)  $\text{kg}^{-1}$ .

### Experimental design

The experiment was a randomized block design with 31 treatments and four replicates. The treatments consisted of the control (unlimed), six particle size segregations at three application rates (2.5, 5 and 10 t  $\text{ha}^{-1}$ ) and 12 commercial liming materials at 5 t  $\text{ha}^{-1}$ . Control plots were distributed every sixth plot in a grid across the trial.

### Liming materials

Twelve commercial liming materials were collected from southern Australia (Tables 1 and 2). There were five products from New South Wales (NSW), two from Victoria (VIC), one from Tasmania (TAS), two from South Australia (SA) and two from Western Australia (WA). Two of the products were dolomites, three were coralline limestones, one was an earthy limestone and the remaining six were calcitic limestones. The coralline and earthy materials will be collectively referred to as soft limes. A microfine grade of calcitic limestone (Tables 1 and 2) was used as a reference material.

The Ca and Mg contents of the limes were determined by dissolution in 1.0 M HCl and by atomic absorption spectrophotometry. Samples were heated to 105 °C for moisture content and to 1100 °C for  $\text{CO}_2$  evolution (carbonate content).

The 12 commercial liming materials were dry sieved for 10 minutes, using a mechanical shaker, through British Standard Sieves of 2000, 1000, 710, 500, 250, 150 and 75  $\mu\text{m}$  aperture. Finer analyses, to 5  $\mu\text{m}$ , were provided on the microfine grade and commercial material NSW-1 by OMYA Southern Pty Ltd using laser diffraction.

The surface area of 9 of the 12 commercial liming materials was obtained by  $\text{N}_2$  adsorption and BET calculation (Brunauer *et al.*, 1938). Three of the products were too coarse to obtain reliable data (WA-2, VIC-2, SA-2).

Liming materials were weighed and hand-spread on the site in April 1986. The lime was incorporated by rotary hoe to about 10 cm depth.

### Field Measurements

The 152 plots were sampled to a 10 cm depth in April 1986 prior to the application of liming materials. The plot samples consisted of 10 cores per plot, each plot being 1.2 m wide by 10 m long. Sampling of all plots subsequently took place in November 1986 (6 months post liming) and in April of 1987 (12 months), 1988 (24 months) and 1989 (36 months). Soil sampling took place prior to harrowing and sowing in each year. Grain yield of wheat (*Triticum aestivum* cv. Millewa) was determined by mechanical harvesting of the whole plot.

Table 1. Chemical analysis of the 12 commercial liming materials and microfine limestone which were used in this study

Product	(Code)	Ca	Mg	H <sub>2</sub> O	CO <sub>3</sub>	Chemical efficiency %
—————%—————						
Calcites:						
NSW-1	(F)	38.3	0.4	0	58.5	97.2
NSW-2	(O)	35.2	1.7	0	57.7	94.6
NSW-3	(A)	38.1	0.1	0.1	57.7	95.9
NSW-4	(M)	38.5	0.3	0	59.2	98.0
VIC-1	(D)	31.9	3.8	0	57.4	93.1
TAS	(L)	34.3	0.5	0	52.8	87.6
Corals:						
SA-1	(G)	38.6	0.4	0.1	59.7	98.7
WA-1	(C)	35.2	0.3	1.8	54.8	90.3
WA-2 <sup>a</sup>	(W)	24.8	0.3	0.2	35.9	61.0
Earths:						
VIC-2 <sup>a</sup>	(P)	28.9	0.6	6.2	49.9	79.4
Dolomites:						
NSW-5	(U)	26.1	7.5	0	58.1	96.25
SA-2	(S)	23.1	10.2	0.1	61.8	100.00
Microfines:		37.8	0.4	0	58.0	96.2

<sup>a</sup> These products contained a small percentage of gypsum

### Soil analysis

Soil pH in 0.01 CaCl<sub>2</sub> (pH<sub>ca</sub>) was determined after a 1 hr end-over-end shake at 20 °C and in a 1:5 soil:solution extract. Exchangeable Mg (Mg<sub>ex</sub>) was determined by a BaCl<sub>2</sub> leach (Vimpany *et al.*, 1985).

### Predictive model

We have defined chemical efficiency % as

$$\sum (\text{chemical compounds \%} \times \text{Neutralizing Value})$$

where Neutralizing Value is, as traditionally, the molecular weight of CaCO<sub>3</sub> ÷ the molecular weight of the compound. In the cases of these naturally occurring materials,

$$\text{chemical efficiency \%} = (x\% \text{ CaCO}_3 \times 1.0) + (y\% \text{ MgCO}_3 \times 1.19)$$

where  $1.19 = 100.1 \div 84.3$

We have defined physical efficiency % as

$$\frac{(\Delta\text{pH due to particle size or product/} \Delta\text{pH due to microfines}) \times 100}{\Delta\text{pH due to microfines}}$$

Hence the particle size segregations and the commercial products are described relative to the microfines grade of limestone whose particle size analysis is described in Table 2. The physical efficiencies given in Table 3, based on Scott *et al.* (1992), are therefore relative values and independent of the pH buffering capacity at the site.

At a 5 t ha<sup>-1</sup> application rate the increase in soil pH at this site due to the particle size segregations was given by  $\Delta\text{pH} = 2.875 - 0.697 \log(\text{particle diameter})$  with particle diameter given in  $\mu\text{m}$  (Scott *et al.* 1992). Note that this equation is mathematically sensible only between 1 and 13,000  $\mu\text{m}$ . This equation has a limit of 2.875 as diameter approaches 1  $\mu\text{m}$ . The microfines

Table 2. Particle size distribution of the 12 commercial liming materials and microfine limestone which were used in this study

Product	% mass within each diameter range ( $\mu\text{m} \times 1000$ )							
	>2.0	2.0-1.0	1.0-0.71	0.71-0.5	0.5-0.25	0.25-0.15	0.15-0.075	<0.075
<b>Calcites</b>								
NSW-1	0	0	0	0	46	10.4	16.8	68.2
NSW-2	0	0	0	0	5.5	20.0	25.2	49.4
NSW-3	0	1.9	8.0	6.7	28.5	12.7	10.8	31.5
NSW-4	0.4	4.0	5.5	4.5	26.5	15.4	13.7	29.8
VIC-1	0	0.1	0.7	1.1	16.6	16.3	18.9	46.2
TAS	0.2	21.6	13.2	14.2	14.1	8.5	8.0	20.1
<b>Corals</b>								
SA-1	2.5	3.5	7.1	3.5	20.5	17.6	23.7	21.6
WA-1	0	0	0.1	0.1	7.4	32.7	31.5	28.2
WA-2	22.8	10.5	10.6	8.9	28.0	10.1	5.2	4.0
<b>Earths</b>								
VIC-2	16.3	22.0	10.3	6.2	22.3	9.9	7.4	5.7
<b>Dolomites</b>								
NSW-5	0	0.1	0.3	0.3	26.2	19.8	21.5	31.8
SA-2	4.8	5.7	2.2	1.4	10.7	36.5	25.6	13.2
Microfine	0	0	0	0	0	0.1	0.2	99.7

Table 3. The relative physical efficiencies (%) of particle size fractions of calcitic limestone at three application rates after 6 months<sup>a</sup>

Particle size range ( $\mu\text{m}$ )	Application Rate ( $\text{t ha}^{-1}$ )		
	2.5	5	10
2000-5000	9	13	29
500-1000	34	41	53
250-500	47	53	55
150-250	52	61	61
75-150	58	64	73
<75	100	100	100
(Absolute efficiency)	(82)	(83)	(85)

<sup>a</sup> Based on Scott *et al.* (1992)

limestone, our finest segregation, gave a  $\Delta\text{pH} = 2.39$ . That is, on an absolute scale, the finest particle size in this experiment is estimated to be only 83% efficient. As this segregation was three times the cost of the finest commercial product and as it was difficult to handle, we decided to adopt this finest segregation as the upper limit of practical significance. Hence all values in Table 3 are expressed relative to microfine lime not on an absolute scale as predicted by the equa-

tion. The bracketed values at the foot of Table 3 give the absolute efficiencies corresponding to the 100% relative efficiencies at each application rate.

**Statistical procedures.** The pH and yield data were analysed using spatial models (nearest neighbour) as given by Gleeson and Cullis (1987). All models were fitted using the computer program SAFE. Least significant differences are given for  $p \leq 0.05$ .

## Results

The mean pH achieved by each commercial liming material over the three years of the trial is shown for the calcites (Fig. 1A), coralline and earthy limestones (Fig. 1B) and the dolomites (Fig. 1C). The control and the microfine limestone (finest particle size) treatments are shown in each graph for comparison. The two dolomites performed similarly to each other (Fig. 1C) but poorly relative to most of the  $\text{CaCO}_3$  materials (Fig. 1A and B). The performance of these products, relative to microfine lime, is given in Table 4 as actual total efficiency % both at 6 months and averaged over 3 years. This latter value is based on the subjective

Table 4. Predicted Physical, Chemical and Total Efficiencies of 12 commercial liming materials and their Actual Total Efficiencies at 6 months and averaged over 3 years

Product	Predicted Efficiencies			Actual Total Efficiency	
	Physical %	Chemical %	Total % <sup>a</sup>	at 6 mo %	over 3 years%
Calcites					
NSW-1	86.0	97.2	83.6	85.6	77.7
NSW-2	77.7	94.6	73.5	71.2	64.0
NSW-3	63.6	95.9	61.0	65.5	61.8
NSW-4	63.2	98.0	62.0	57.2	53.6
VIC-1	74.6	93.1	69.4	69.4	58.2
TAS	52.1	87.6	45.6	46.3	45.8
Corals					
SA-1	59.9	98.7	59.1	79.9	69.0
WA-1	68.1	90.3	61.5	76.9	66.3
WA-2	39.6	61.0	24.1	44.1	36.1
Earths					
VIC-2	40.7	79.4	32.3	53.3	42.8
Dolomites					
NSW-5	67.5	96.2	65.0	52.8	54.7
SA-2	56.7	100.0	56.7	41.9	48.1

<sup>a</sup>Physical  $\times$  Chemical  $\div$  100 = Total

assessment that pH tended to plateau between 6 and 36 months (Fig. 1). The commercial products ranged in total efficiency from 42 to 86% at 6 months and from 36 to 78% averaged over 3 years. This means that there was a factor of 2  $\times$  covering the range of relative performance of the same mass of these commercial products.

The actual total efficiency % of these products (Table 4, columns 5 and 6) was compared with the predicted total efficiency % (Table 4, column 4) in Figure 2. The performance of the calcitic limestones at 6 months (Fig. 2A) was well predicted by the model:

$$\text{predicted} = 0.94 \text{ actual} + 3.95 \quad n = 6 \quad r = 0.97$$

The standard errors for the slope and intercept were 0.118 and 3.53 respectively. The slope was not significantly different to unity ( $t_4=0.51$ ) and the intercept was not significantly different to zero ( $t_4=1.118$ ). The predicted and actual total efficiencies of the calcitic limestones cannot be regarded as being different.

In contrast to the calcitic limestones, the two dolomites performed poorer than predicted while the coralline and earthy limes performed better than predicted. The overall regression equation for the 12 com-

mercial liming materials was:

$$\text{predicted} = 0.782 \text{ actual} + 9.32 \quad n = 12 \quad r = 0.691$$

After 12 months the performance of the 12 commercial liming materials was better predicted by the model:

$$\text{predicted} = 0.975 \text{ actual} + 7.32 \quad n = 12 \quad r = 0.800$$

Figure 2B shows that after 24 months the calcites and dolomites were nearly equally well predicted by the model and 2 of the 4 coralline and earthy limestones were close to the isoline:

$$\text{predicted} = 1.036 \text{ actual} - 4.03 \quad n = 12 \quad r = 0.812$$

After 1 to 2 years the dolomites and the softer limestones were performing more closely to the efficiency as predicted by the model based on calcitic limestones. Therefore the type of liming material influenced its initial performance (the first season) but ultimately, chemical composition and particle size dominated the total efficiency of the lime regardless of its source.

After 36 months however the soil pH under the finer products declined slightly while the coarser products continued to increase soil pH. Scott *et al.* (1992)

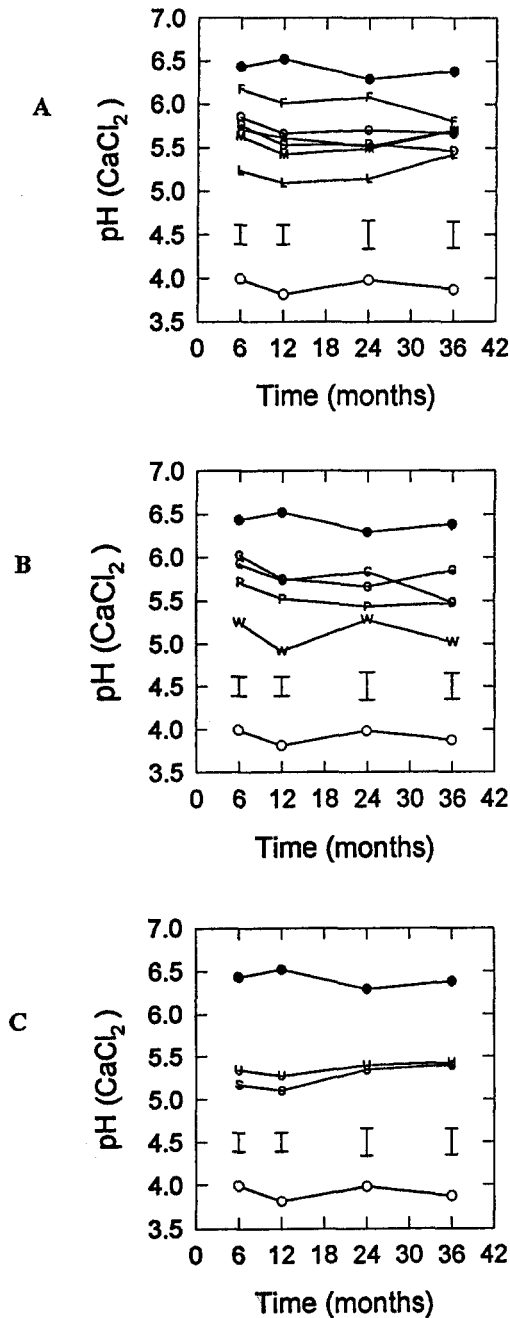


Figure 1. Effect of 12 commercial liming materials on soil pH over 3 years; A) calcitic limestones, B) corals and earthy lime, and C) dolomites. Alphabetic symbols represent the product codes of Table 1. Microfine (●) and control (○) treatments are shown on each graph plus LSD for  $p \leq 0.05$ .

demonstrated that there was small but significant convergence of pH with time. The net effect was a small rotation in the regression line through the data :

$$\text{predicted} = 1.199 \text{ actual} - 9.921 \quad n = 12 \quad r = 0.861$$

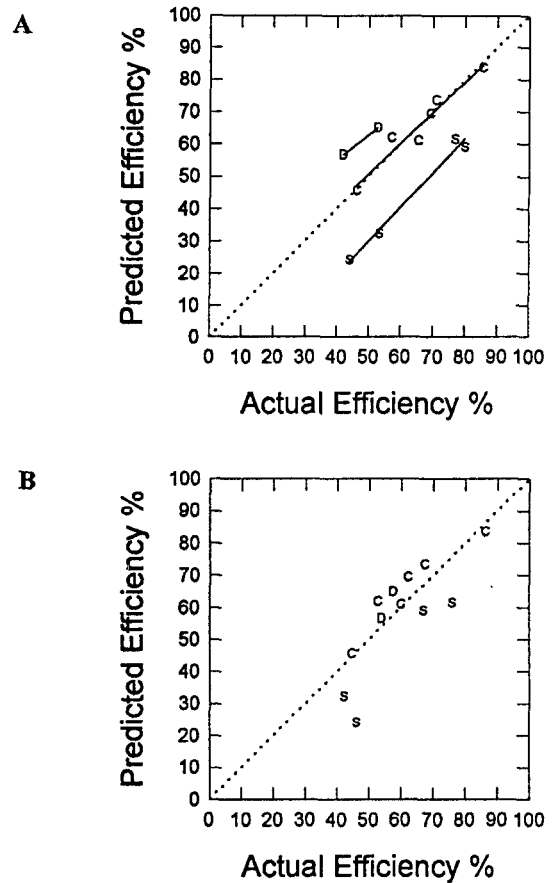


Figure 2. The relationship between predicted and actual total % efficiency of 12 commercial liming materials; A) at 6 months, B) at 24 months. Symbols on graphs: calcities (C), corals and earthy lime (S) and dolomites (D). The dotted line represents the isoline and the full lines on A) represent the regression lines for each product group (C, S and D).

Therefore the model to predict total efficiency is less useful 3 years after liming materials were applied.

The predicted physical efficiency % (Table 4, column 2), on the basis of particle size, correlated well with the independently measured surface area (or specific surface) of the products (Fig. 3A). There is a steep decline in efficiency below a surface area of approximately  $300 \text{ m}^2 \text{ kg}^{-1}$ . Conversely, above  $300 \text{ m}^2 \text{ kg}^{-1}$  there is a relatively slow increase in predicted physical efficiency as surface area increases. The fitted quadratic (Fig. 3A) has an  $r = 0.962$ , suggesting that there is little if any difference between calcites, dolomites and the soft limestones in shape factor (sphere to polyhedron) or exposure of internal surfaces of the particles. There is also a clear relation between actual total efficiency and surface area (Fig. 3B) which is similar to Fig. 3A. The dolomite has a relatively low total effi-

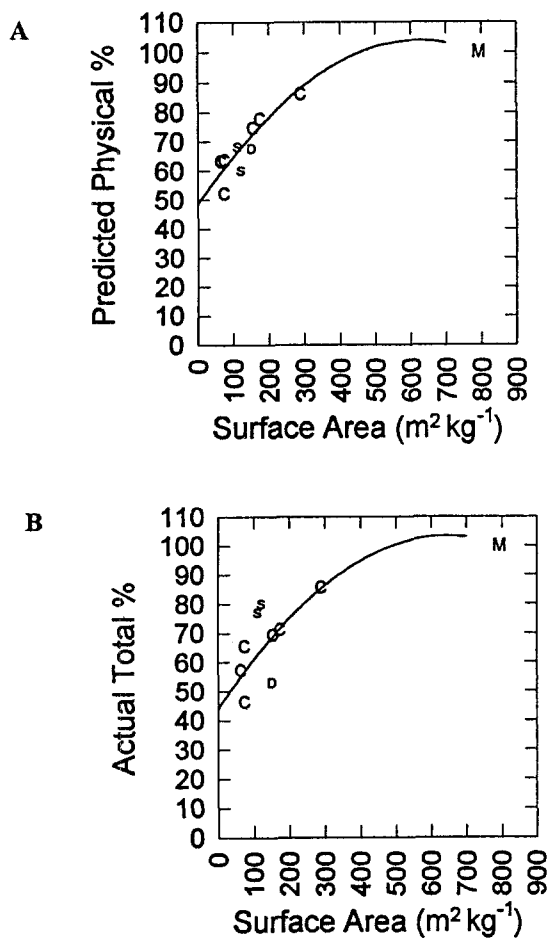


Figure 3. The relationship between surface area and A) the predicted physical efficiency, and B) the actual total efficiency of 9 commercial liming materials and microfine lime (M). Symbols represent calcites (C), corals and earthy lime (S) and dolomites (D).

ciency for its surface area. Its relatively poor performance must therefore be due to a lesser solubility. The coralline limes have a high total efficiency for their surface area, suggesting that they must be more soluble than calcites.

The increase in  $\text{Mg}_{\text{ex}}$  in the soil was directly proportional to the Mg content of the liming materials (Fig. 4) and was greatest for the 2 dolomites. The dolomites had no effect on yield other than through their effect on soil pH (Fig. 5) despite their addition of Mg to a surface soil initially low in  $\text{Mg}_{\text{ex}}$ .

We conclude that limestone performance can be described by physical fineness (surface area), chemical composition and presumably solubility. We can quantify physical fineness by routine procedures and then predict physical efficiency using our particle size model (Table 3). We can quantify chemical composi-

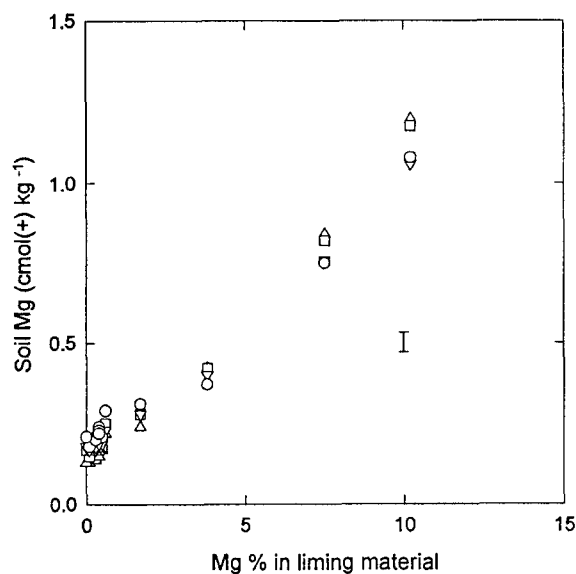


Figure 4. The increase in exchangeable soil Mg as caused by the Mg content of the liming material. November 1986 (O), April 1987 ( $\nabla$ ), April 1988 ( $\square$ ) and April ( $\Delta$ ). The average 5% LSD for the four years is also shown.

tion ( $\text{CO}_3$ , Ca, Mg) and calculate chemical efficiency. The remaining matter is to quantify the solubility of the liming materials. Such a task is complicated by the presence of Ca and Mg sulphates, as was the case for two of the softer limestones used in this study. As an approximation, the estimates made for each product on the basis of the calcitic limestone model can be modified by two generalisations. During the 6 to 12 months after applications;

1. dolomites performed as though 15% less efficient than predicted ( $\bar{x} \pm s = 13.55 \pm 1.84$ )
2. coralline and earthy limestones performed as though 20% more efficient than predicted ( $\bar{x} \pm s = 19.3 \pm 2.64\%$ )

Such a generalization may save the need for an additional test of the products, such as obtaining the solubility product.

## Discussion

The advance of this study is that chemical composition ( $\text{CaCO}_3$  equivalent) and our particle size model successfully described the field performance of six commercial calcitic limes from southern Australia, both in the short term (6 months) and the longer term (to 3 years). Further, the chemical and particle size model

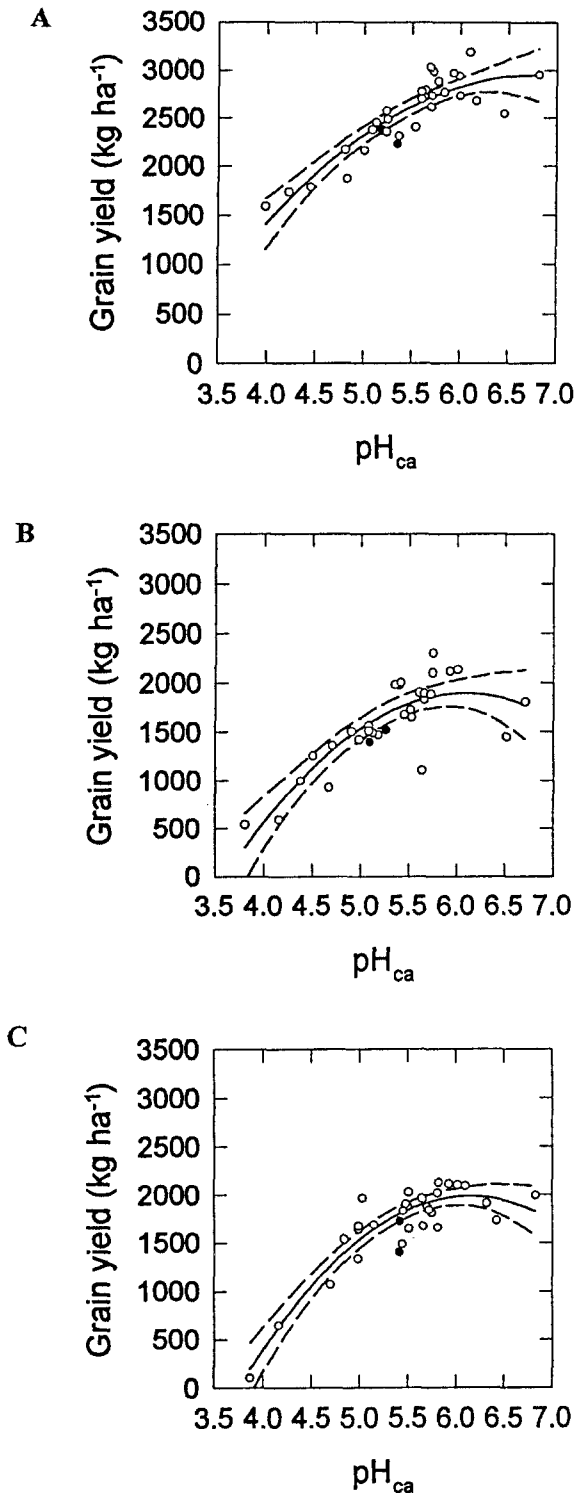


Figure 5. The dependence of yield upon soil pH in 1986 (A), 1987 (B) and 1989 (C). The regression line is shown as the solid line and the 95% C.I. as the dashed lines. Filled symbols represent dolomite data.

successfully described the field performance of the two dolomites and two of the four soft limes by 12 to 24 months after application. Particle size has been shown to have a major influence on the field performance of lime regardless of its source.

#### Effects of particle size

Scott *et al.* (1992) questioned the conventional wisdom that particles finer than 250  $\mu\text{m}$  are on the plateau of relative effectiveness *vs* particle size. This belief is reflected in New South Wales' legislation governing liming materials. The much quoted work of Meyer and Volk (1952) established the relative efficiency of liming materials in a pot trial at a single application rate (7.5 t ha<sup>-1</sup>), with a finest particle size segregation of <150  $\mu\text{m}$ . Scott *et al.* (1992) had two finer segregations than this. Further, the "average relative efficiency" of Meyer and Volk (1952) was based on an averaging of changes in pH,  $\text{Ca}_{\text{ex}}$ ,  $\text{H}_{\text{ex}}$  and lucerne yield as induced by the lime application. Our interest in lime is in its ability to change soil pH. Plant yields depend on several factors, only some of which are pH dependent, and the response of a plant to change in pH is not linear across the pH range of agricultural interest. The results of Scott *et al.* (1992) were more consistent with the results of Beacher *et al.* (1952). Our view is that if there is any plateau in relative efficiency *vs* particle size, it is at much finer particle size than 250  $\mu\text{m}$  and probably at <50  $\mu\text{m}$  based on the median particle diameters of the finest two calcitic limes in Fig. 3A. The major agreement of these studies is that particle size has a major impact on the value of liming materials. Our proposed refinement is that 100% physical efficiency, in a field situation, needs to be allocated to a particle size diameter no larger than 75  $\mu\text{m}$  (Table 3).

The effect of particle size on the surface area of coverage by lime particles is considered in Table 13 of Cregan *et al.* (1989). The finer the particles, the greater the surface area of ground which can be covered and the more particles which are likely to be found in each 1 cm<sup>3</sup> of soil after mixing. Assuming various distances of diffusion from the particles, the % volume of soil likely to be influenced by a lime application can be calculated (Table 14 of Cregan *et al.*, 1989). The distance of diffusion will be controlled by the physical properties of any given soil and by time. Therefore fineness influences not just the rate of dissolution but the proportion of the soil volume in contact with the particles.



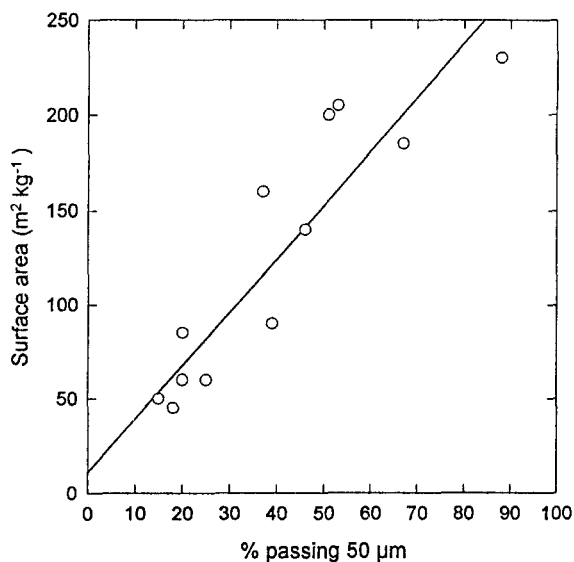


Figure 6. The relationship between the surface areas of 13 limestones and the percentage of each product finer than 50  $\mu\text{m}$ .

Barber (1984) concluded that particle size analysis and product surface area do not necessarily correlate. This was also our initial impression. We assumed that shape factors (eg. cube/sphere  $\approx 2 \times$ ) and possibly internal pores/cracks in particles contributed to the difference. For example, coralline limes probably had internal pores as well as irregular surfaces. Calcite lime particles may have more regular rhombohedral shapes. Ball milling may produce more spherical or at least more rounded particles than hammer milling. However we found that the measured, rather than calculated, surface area correlated well with the predicted physical efficiency % based on the particle size analysis. Data were made available to us by a major limestone company on a separate set of 13 commercial liming materials from New South Wales, Victoria and Queensland. The company also considered that there was a poor relationship between measured surface area and particle size distribution. However we have found this to be due to inappropriate calculations. Figure 6 shows that there is a strong correlation between the measured surface area and the % product finer than 50  $\mu\text{m}$ . That is, material coarser than 50  $\mu\text{m}$  diameter made a relatively small contribution to the total surface area of these 13 limestones. Most particle size analyses on limestones are undertaken using dry sieves which do not extend reliably to < 50  $\mu\text{m}$ . Sedimentation and laser diffraction are generally used to obtain particle sizings below 100  $\mu\text{m}$ . Laser diffraction has been found to give results more consistent with dry sieve analyses as sedimenta-

tion is sensitive to the shape of particles (South, 1985). Therefore consistency between measured surface area and particle size analysis can be obtained if the particle size analysis is able to describe the product to the fine end of its size distribution. This can be confirmed by simple calculations of surface area, whether assuming cubic or spherical particles.

#### *Calcitic, dolomitic and soft limes*

The poorer initial performance of dolomites is not a new finding. It is well known that dolomites need to be finer than calcites to achieve the same increase in pH (Barber, 1984). However it was possible that Mg would provide an additional benefit for plant growth as the initial soil  $\text{Mg}_{\text{ex}}$  was only 0.2  $\text{cmol}(+) \text{kg}^{-1}$ .

The 95% Confidence Interval is given for each regression line in Fig. 5 and shows that there was no yield benefit from the application of dolomite in any season other than through its effect on soil pH. Although the surface soil has little  $\text{Mg}_{\text{ex}}$ , visual assessments of plant response to Mg were limited to autumn (early growth). The subsoil at this site has in excess of 1  $\text{cmol}(+) \text{kg}^{-1}$  of Mg (> 20% of the effective cation exchange capacity).

The increase in  $\text{Mg}_{\text{ex}}$  was directly proportional to the Mg content of the liming material and little change in  $\text{Mg}_{\text{ex}}$  occurred between 6 months and 3 years after application (Fig. 4). However at the highest application the Mg recovered in the surface 10 cm represents only 1/3 of that applied. The 10.2% Mg of SA-2 dolomite was equivalent to 3.2  $\text{cmol}(+) \text{kg}^{-1}$  of Mg at a bulk density of 1.3  $\text{g cm}^{-3}$  of soil. However the initial effective cation exchange capacity of the soil was only 2.5  $\text{cmol}(+) \text{kg}^{-1}$  and after the 5 t  $\text{ha}^{-1}$  application of product increased to 4.4  $\text{cmol}(+) \text{kg}^{-1}$ . Therefore the poor recovery of Mg in the surface soil is likely to be due to leaching of dissolved Mg and also possibly to incomplete reaction of coarser particles.

Coralline and earthy limestones are likely to be composed of the aragonite form of  $\text{CaCO}_3$ . This crystal form is slightly more soluble ( $\log K=9.97$ , with  $\text{CO}_2$  in atm) than the calcite crystal form ( $\log K = 9.74$ ) of  $\text{CaCO}_3$  (Lindsay, 1979). Dolomite ( $\log K = 18.46$ ) is less soluble than calcite. For example, at a post-liming pH of 6, aragonite would require a  $[\text{Ca}] \approx 30 \text{ M}$  to maintain equilibrium with the soil solution, calcite would require  $[\text{Ca}] \approx 18 \text{ M}$  and dolomite would require  $[\text{Ca}+\text{Mg}] \approx 11 \text{ M}$ . Hence these minerals dissolve in acidic conditions as such high concentrations cannot be achieved. The observed departures from our

prediction of field performance at 6 months (Fig. 2A) are therefore consistent with the known solubilities of the pure mineral forms. The tendency of these differences to attenuate with time (Fig. 2A cf. 2B) indicates that these differences are less important in predicting the effectiveness of limes as the dissolution of the lime nears completion. There will be variations to the solubility product of aragonite, calcite and dolomite proportional to the composition of any given commercial product.

## Conclusions

There have been many attempts to find a single index for the "reactivity" of limestones (Barber, 1984). Limes have been reacted with solutions of oxalates and weak acids. However we wish to distinguish the three factors which control lime performance: *particle size*, *chemical composition* and *solubility*. Particle size determines the surface area of lime exposed and the distribution of particles throughout the soil volume. Chemical composition determines the quantity of base applied to the soil. Solubility determines the tendency of the material to dissolve and hence the rate of reaction of a given particle size. Any attempt to better predict the initial performance of a liming material should evaluate the solubility product of the material and not a vague notion of "reactivity". To complete our understanding of the field performance of commercial liming materials, we suggest two areas of work which could be addressed.

Firstly, the subject of limestone solubility could be clarified. The solubility product of liming materials could be established and then correlated with routine tests (such as acid dissolution in 1 hr) for that solubility. This subject is important only for predicting the performance of the liming materials within the first 6 to 24 months. In our circumstances we consider that we must use lime as efficiently as possible to ensure a rapid return on the investment in lime.

Secondly, we have used a segmented model to describe the physical efficiency of limestones. That is, each particle size range is multiplied by an efficiency factor (Table 3). In most commercial situations only one or two mesh divisions are legislatively required on the product label. Ideally we would like an analogue model whose position and slope could be set by the data on the label, enabling better comparison of the physical efficiency of alternative limestone sources available to a client.

## Agricultural Relevance

The field performance of commercial liming materials can be estimated using our chemical and physical model subject to two "rules of thumb". In the first 6 to 12 months after liming, soft limes perform 20% more efficiently than predicted, while dolomites perform 15% less efficiently than predicted. By 12 to 24 months after application these differences are attenuated. We believe that the "rules of thumb" are surrogates for the relative solubilities of these groups of liming materials.

The value of fineness has been underestimated by some previous studies. Particle sizes of 250  $\mu\text{m}$  do not represent a threshold of 100% relative efficiency. To obtain the maximum possible benefit from a liming material we recommend the use of the finest possible product which can be accessed and handled.

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