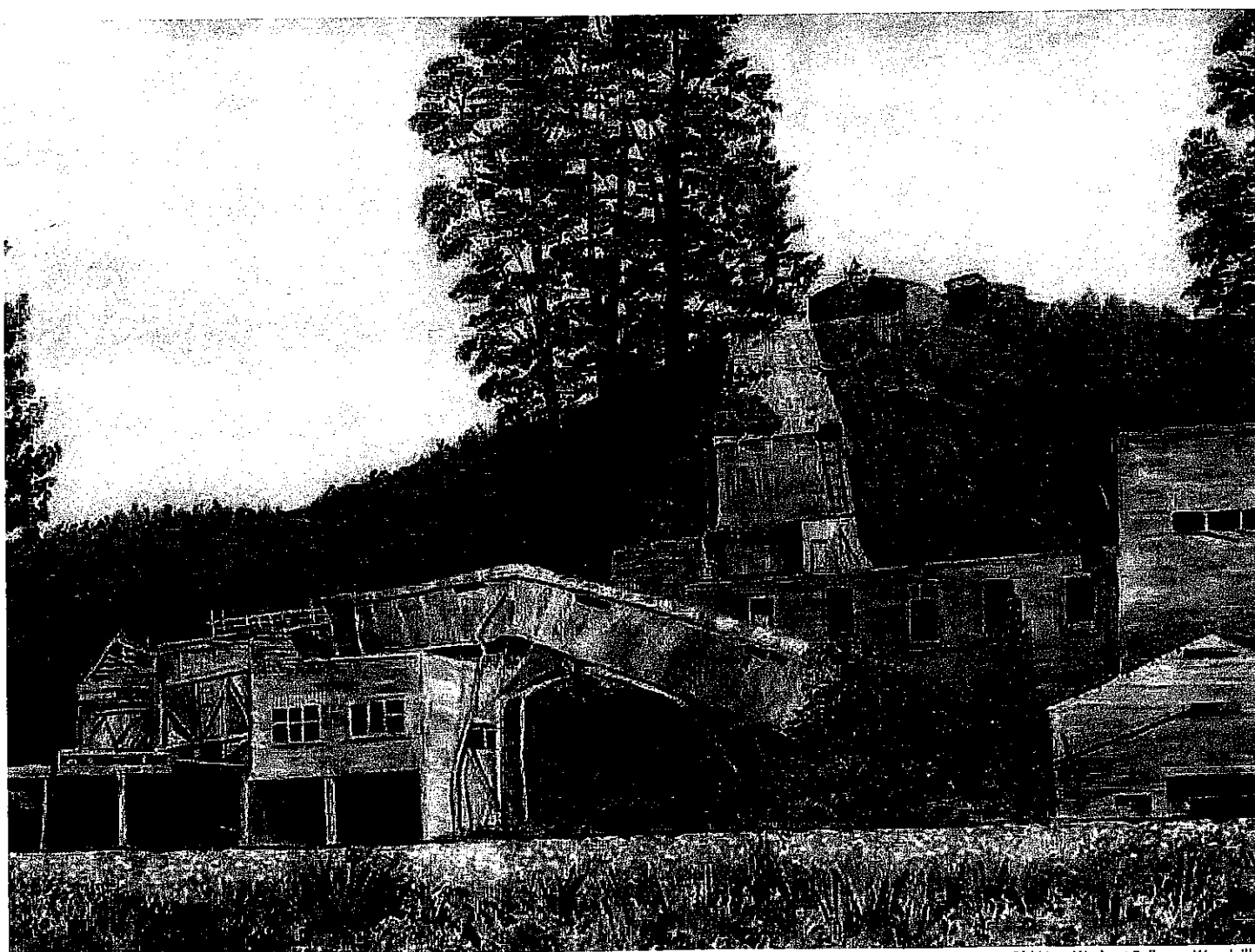


Review of lime dissolution rates and agronomic effectiveness as a function of particle size.

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Fertilizer and Lime Research Centre
Massey University



Old Lime Works at Ballance, Woodville.



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Summary:

A review of the existing literature describing the rate of dissolution of agricultural lime as a function of particle size is presented.

Lime dissolution models based on a constant rate of dissolution of lime mass per unit surface area adequately explained crop and pasture yield responses to agricultural lime.

Lime dissolution models predict that the removal of fines (<0.325 mm) from a typical Ag-lime will reduce the short-term (first 20-50 days) liming potential by approximately half (from 38 to 21% of product dissolved after 50 days). Over a longer term (1 year) the dissolution of both Ag-lime and Ag-lime with fines removed will be similar, with the total dissolution of each product converging at approximately one year.

If liming equivalence was required within 6 months, then to achieve the same agronomic response, 1.5 to 1.65 times of the coarser lime would be required compared to common agricultural lime with fines included.

Introduction:

The effectiveness of Ag-lime in neutralizing soil acidity and mitigating the effects of acid-induced metal phyto-toxicity has been studied by numerous authors. This has led to the development of lime quality criteria such as calcium carbonate equivalence to define the potential neutralizing power, and particle size to define the time dependent reactivity of the Ag-lime.

Milling lime to meet the particle size criteria described by Fertmark (Fertmark 2010), as “not less than 95% by weight shall be able to pass through a 2.00 mm sieve, and not less than 50% by weight shall be able to pass through a 0.5 mm sieve”, results in a high quantity of very reactive fine limestone less than 0.25 mm. Grafton (2000) identified powder flow problems due to increased cohesion of mixtures with this fine fraction. This problem affects ground spreading (Alley et al. 1980) in which bridging occurs when more than 60% passes through 0.15 mm and in aircraft (Grafton 2010) when the lime contained particles less than 0.425 mm. Grafton (2011) proposed a recommendation for fixed-wing aerial-spread lime to have the less than 0.325 mm particles removed. In terms of agronomic effectiveness this

increased coarseness is of concern and the aim of this review to determine the potential effect of fines removal on the rate of dissolution of limestone and soil acid neutralisation.

Limestone reactivity and dissolution

The reactivity of agricultural limestone was initially assessed in the 1930's and 50's by Bear and Allen (1932) using field incubations in a silt loam textured soil of pH 4.65_(in CaCl₂). They considered the rate of dissolution to be proportional to surface area, resulting in a model (Equation 1) in which the fraction (P) of limestone remaining was equal to the cube of the particle diameter ($d-a_t$) at time (t) over the initial particle diameter (d). This assumes the rate of change in diameter (a) is constant, per unit time (t). n is the number of particle size classes.

$$P = \sum_n^1 \left(\frac{d_n - a_t}{d_n} \right)^3 \quad \text{Eq 1.}$$

This principle was used by Schollenberger and Salter (1945) to develop a chart for evaluating agricultural limestones, based on the neutralising power equivalent to calcium carbonate, % Mg (which reduces dissolution rate) and particle size distribution. The rate of particle size reduction was assumed to be constant as described by Bear and Allen (1932). The total amount dissolved was calculated as the sum of the amount dissolved in each size class over time. This chart allows estimation of lime dissolution at time intervals of 3 months, 1 year, 4 years and 16 years based on initial size class profile of the limestone.

In New Zealand, Elphick (1955) further developed the model by using the geometric mean diameter of each size class to calculate the dissolution rate. Elphick (1955) found this to be an adequate method for determining limestone dissolution of particles down to a mass mean size of 0.150mm, at which point the model underestimated the dissolution rate most likely due to the spherical geometric approximation used.

This model of dissolution based on constant reduction in diameter can be rewritten as:

$$\frac{dm}{dt} = k S \quad \text{Eq 2.}$$

The rate of dissolution with time (dm/dt) is equal to the rate constant k (kg/m²/day) multiplied by the surface area (S). Using a numerical solution for spherical geometries and $k = 0.0013$ kg/m²/day, the data of Elphick (1955) was effectively modelled (Figure 1.) by the constant rate model.

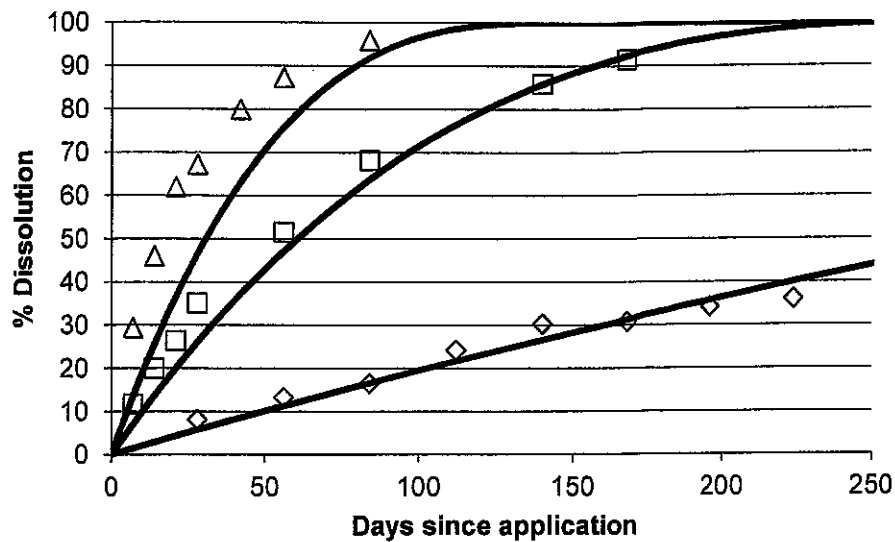


Figure 1. Constant rate model of limestone dissolution for size fractions:
 2-0.84 mm \diamond , 0.4-0.177 mm \square , 0.177-0.104 mm Δ .
 Using data from Elphick (1955) and $k = 0.0013 \text{ kg/m}^2/\text{day}$ and a density of limestone of 2940 kg/m^3 .

Elphick (1955) conducted these experiments under near field moisture capacity conditions with the lime mixed in the soil. These conditions optimize the dissolution of the lime and would require additional terms for variations in soil volumetric water capacity and variations in soil temperature to be taken into account for modelling surface application in the field.

Motto and Melsted (1960) further developed a semi-empirical model to estimate the final soil pH (pH_f) at time (t) based on an initial pH (pH_0), base saturation (B), application rate (R) and particle surface area (S):

$$pH_f = pH_0 + b \log(1 - t)$$

where

$$b = a + D \log\left(\frac{RS}{B}\right)$$

and a and D are constants .

In 1986-87 a more fundamental diffusion model was developed by Nye and Ameloko (1986, 1987). The fundamental model of Nye and Ameloko (1987) has not been used by research scientists to assess lime dissolution. The reason is that detailed soil chemical measurements are required to run the model.

Effect of removal of fines on modelled lime dissolution rate

The constant dissolution rate model (Equation 2) is the simplest and most robust means to illustrate the change in liming value when fines are removed from aerial Ag-lime.

Based on typical size analysis (Table 1) the removal of < 0.325 mm particle would reduce the initial dissolution from 20% to 9% in 20 days and 38% to 21% in 50 days (Figure 2), however after one year of optimal soil moisture and temperature conditions it would be expected that the extent of dissolution of the two limes would be approaching being equal values (approximately 80%, Figure 2).

Table 1. Typical particle size analysis of Ag-lime from data Grafton (2010), % mass basis.

Particle Diameter	>2.0 mm	1-2.0 mm	0.5-1.0 mm	0.25-0.5 mm	0.25-0.15 mm	<0.15 mm
% mass	5%	20%	25%	20%	10%	20%

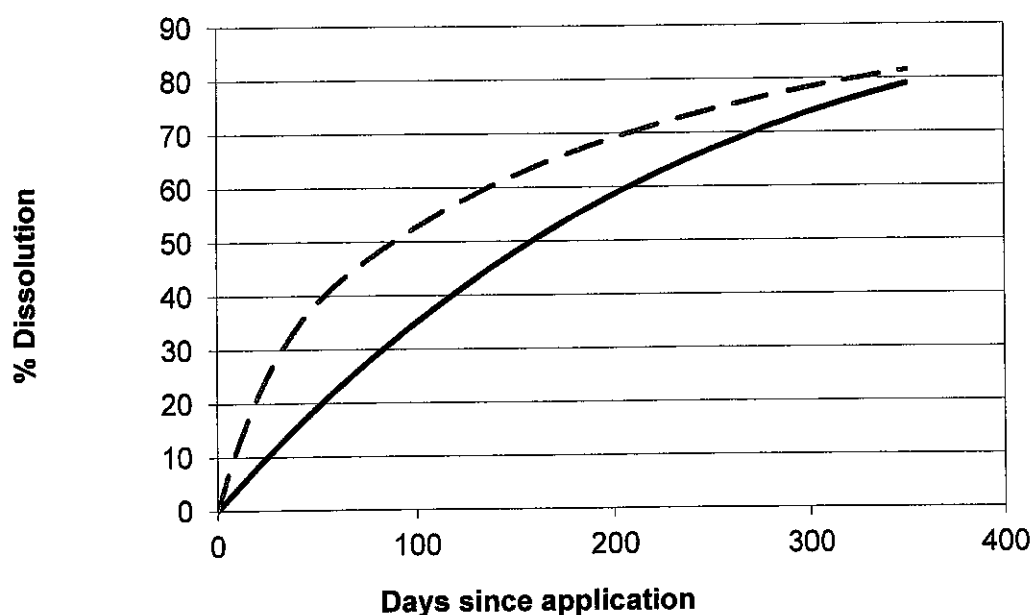


Figure 2. Modelled dissolution of Ag-lime under ideal conditions using constant dissolution rate model (Elphick 1955). Grey dashed line is for typical Ag-lime, the black line is for Ag-lime with <0.325 mm particles removed.

In reality it may be expected due to drier soil moisture conditions in the field that dissolution may be 2 to 3 times longer in the field than predicted in Figure 2.

Assessment of the effect of lime particle size on crop yield

The effect of lime particle size on crop yields was discussed by Barber (1984), who reviewed trial data from 9 field trials on a wide range of crops from cereals to clover. Barber (1984) summarized the trial results in terms of % yield relative to the finest fraction (<0.177mm).

Table 2. Agronomic relative yield from different lime size classes from nine crop trials. (Barber 1984)

Particle size	Average % relative yield (all results n=9)	Average % relative yield (negative lime responses removed n=5)	Range % relative yield
4.76 - 2.00 mm	33	0	0-50
2.00 - 0.841 mm	54	11	11-96
0.841 - 0.400 mm	84	50.6	34-100
0.400 – 0.177 mm	99	76.4	61-100
<0.177 mm	100	100	78-100

N = 5 crops, Mangolds, Carrots, Alfalfa, Sudan grass and Crimson clover

Barber found that out of nine trials, four trials showed negative yield responses to lime resulting in the wide range of results. The negative yield responses are associated with soils that have initial pH's close to optimum values for crop production (pH 5.7 – 6.2), or the test crop was not a recognised acid-sensitive species.

In pasture response trials on an acid soil (pH 4.85) in Spain Alvarez et al. (2010) showed that dolomitic lime applied at 3 t ha⁻¹ in particle size ranges 2-4 mm, 0.5-2 mm, 0.25-0.5 mm and <0.25 mm) had different levels of effectiveness over the 2 following years. The coarsest fraction had no significant effect on soil pH, or alleviation of aluminium toxicity in both years. In year 2, only the finest fraction caused significant changes in soil chemistry and increases in the establishment and yield of new species.

Conyers et al. (1996) and Scott et al. (1992) showed that the relative effectiveness of lime in terms of soil pH change (ΔpH) increased with reducing particle size according to the following equation, on an acidic podsol soil in NSW with surface soil pH of 4.1 and solodic subsoil of pH 5.4:

$$\Delta pH = 2.875 - 0.697 \log(d) \text{ at 6 months following application of } 5 \text{ t ha}^{-1}.$$

Their work showed that the effectiveness of lime did not plateau at particle diameters of 0.250 mm but continued to increase with reduced particle diameter and increased surface area (Conyers et al. 1996). Wheat yield responses to lime rate and particle size in these trials resulted from soil acid neutralisation and soil pH change. Yields on unlimed plots ranged from 0-1500 kg ha⁻¹ at pHs close to 4. On limed plots with pH raised to pH 6, yields ranged from 2000-3000 kg ha⁻¹, dependent on climate variation between years. Conyers et al.

(1996) proposed total effectiveness indices of limestone based on both particle size efficiency factor (EF) and calcium carbonate equivalence (CCE); this was further developed for pastoral systems by Haby and Leonard (2002) to give an effective liming material (ELM). Haby and Leonard however used a wide range of size classes and assumed classes < 0.250 mm in diameter to be 1 EF (100% effectiveness) while Conyers et al. (1996) use twice the number of size classes.

Table 3. Effectiveness factors (EF) of lime size classes, ^a Haby and Leonard (2002), ^bConyers et al. (1996).

Particle Size class (mm)	EF ^a	Particle Size class (mm)	EF ^b at 2.5t ha ⁻¹	EF ^b at 5.0 t ha ⁻¹
> 2.36	0	2-5	0.09	0.13
2.36-0.85	0.2	0.5-1	0.34	0.41
0.25- 0.85	0.6	0.25-0.5	0.47	0.53
< 0.25	1.0	0.15-0.25	0.52	0.61
		0.075-0.150	0.58	0.64
		<0.075	1.00	1.00

EF values (Table 3) are derived from crop and pasture growth responses to each size class. The pattern of change in EF value with particle size (Figure 3) is predicted by the dissolution model results of Barber (1984). The % dissolution estimated at 90 and 180 days (Figure 3, based on Equation 2) encompasses the range of agronomic responses. The EF values are dominated by short term crop responses (Barber 1984; Conyers et. al., 1996). However, in pastoral systems (Haby and Leonard, 2002), longer response times are accepted and less frequent applications of lime are common.

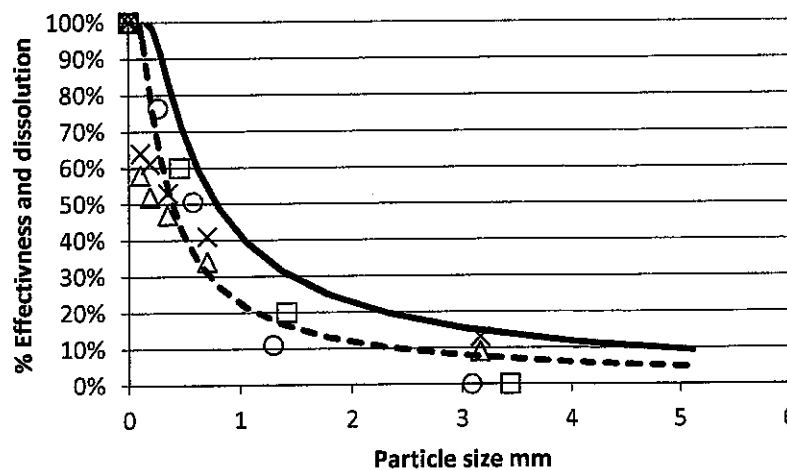


Figure 3. Comparison of % agronomic effectiveness (EF value) and dissolution of limestone as a function of particle size. Agronomic effectiveness data from Barber (1984) O, Haby and Leonard (2002) □, Conyers et al. (1996) Δ at 2.5 t/ha and X 5t/ha. Modelled lines based on Elphick (1955) with $k = 0.0013 \text{ kg/m}^2/\text{day}$ and a density of 2940 kg/m^3 at 90 days (dashed line) and 180 days (solid line).

Effect of fine fraction removal

Based on the EF factors (Table 3) and the particle size profile of Ag-lime (Table 1), the effect of fines removal on ELM can be estimated (Conyers et al. 1996). EF values for typical Ag-lime have a weighted mean average EF of 0.43 to 0.48. The removal of fines (< 0.325) reduces the EF factor to between 0.26 to 0.31. This implies that for the same effect, 1.53-1.65 times the quantity of lime is required to achieve the same pH change in 6 months. The same reduction in agronomic effectiveness can be calculated from the results from Barber (1984), where approximately 1.3 times more lime is required to obtain the same acid neutralising effect within 1 year and 1.55 times more for the same neutralisation effect within 6 months.

Conclusions

The review of dissolution rates and agronomic effectiveness of Ag-lime has revealed that a simple model for the estimation of lime dissolution can provide a prediction of agronomic effectiveness, which is consistent with field based assessments. These models have been used for the assessment of lime reactivity and development of regulatory specifications for agricultural particle size profiles.

The application of a dissolution model to assess the effect of fines removal (<0.325 mm) from a typical Ag-lime predicted that without fines the initial dissolution of lime will reduce liming potential by approximately half during the first 20-50 days. Over a longer term the dissolution of both Ag-lime with and without fines converge at approximately one year under ideal soil moisture and temperature conditions.

The particle dissolution and agronomic models based on short term crop responses within 6 months have indicated that for the same agronomic response 1.5 to 1.65 times more lime would be required due to the removal of fines. However for hill country pastures with infrequent lime applications, the same liming value will be realised by the coarse lime and current "Ag-Lime" within 1-2 years.

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