

## Original Paper

# Lime Fertilizer with Prolonged Balanced Effect Period

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### Abstract

*Soil acidification and decalcification are mostly continuous. From the aspect of soil quality maintenance and improvement, the soil requires stable calcium content. The more acidic is the soil and the finer are the lime fertilizer particles, the easier they dissolve, and the soil becomes poor in calcium. In order to modify the rate and duration of lime fertilizer dissolution, this work included investigation of solubility and dissolution rates of various fractions of limestone. Based on the dissolution rates of particles with different sizes, the content of different fractions can be calculated so as to make the solubility of lime fertilizer more stable and long-term. A long-term uniform solubility provides a more stable available calcium content in the soil, which facilitates the formation and development of beneficial soil characteristics. In the field trials, upon liming with a fertiliser with prolonged effect time, the content of available Ca in soil was more stable and remained at optimum level also in 4<sup>th</sup>-5<sup>th</sup> year.*

### Keywords

*soil decalcination, size of particles, limestone solubility, calcium*

## 1. Introduction

In practice, the need for liming is generally estimated according to soil acidity, but when the soil pH is 6.0, the hydrolytic acidity does not disappear, but in most of the soils the saturation rate is at least 80%, which is optimal for normal plant growth and development. The most important role in saturation belongs to calcium. Sufficient supply of calcium in the soil improves the soil structure, its air and water regime, nutrient intake, phosphorus intake, and the biological activity that leads to release of nutrients from the organic substance; reduces the accumulation of phytotoxic heavy metals in plants (Havlin<sup>2</sup> et al., 2005; McDowell et al., 2002; Molitor et al., 2012; Rogasik et al., 2005).

The leaching of carbonates is the main cause for decalcification of soils. The soils that are poor in carbonates need liming. The effectiveness of lime fertiliser depends on the size of lime fertiliser

particles—the finer they are, the more effective it is in neutralizing the acidity, but at the same time increases the leaching. Therefore, in conditions where evapotranspiration is lower than the amount of precipitation and this causes the leaching of carbonates from topsoil, the size of lime particles is a significant factor in their replacement. According to Finnish researchers (Kalkitusopas, 1999), the solubility of limestone calcium at the same temperature and CO<sub>2</sub> partial pressure depends primarily on its particle sizes and pH. For higher effect of lime fertilizer both during the initial and the end period of its influence, the lime fertiliser must contain the fractions of different particle size, which ensure the balanced solubility of lime fertiliser during the whole specified time period. The fine fractions of lime material (1-0.1 mm) dissolve and neutralize the soil quicker. The coarser fractions and lime fertiliser, which predominantly contains a coarse fraction 3-5 mm, dissolve significantly longer (Scott et al., 1992; Havlin et al., 2005; Viadé et al., 2011; Watling et al., 2010).

Therefore, for the continuous and stable development of soil quality, it is necessary that the available soil calcium content would be as stable as possible. In the study (Loide et al., 2014) on better provision of more stable calcium content in the soil, it was found that among the finely ground lime fertilizers used for liming, a lime fertilizer consisting of fractions with different size and different dissolution rate has a longer effect period. Compared to ground fine-grained lime fertilizer, a coarse-grained lime fertilizer with initially slower effect is intended for purposeful improvement of soil quality. In this work the authors clarify and supplement the information about the requirements, which should be met by a lime fertilizer of prolonged balanced effect.

## 2. Material and Methods

### 2.1 Laboratory Test

The granulometric composition necessary for providing of prolonged balanced effect of lime fertilizer may be calculated based on the results of the study of limestone narrow fractions dissolution kinetics in distilled water, the pH of which was brought to 4.0 for the 100-fold acceleration of the process (by adding to distilled water the potassium biphthalate C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub> 10.2 g l<sup>-1</sup>, which does not react with limestone).

For limestone solubility tests the authors used the Tamsalu formation Juuru stage Võhmuta deposit detritus limestone with stromatoporoids, the thickness of which is 0.1-2.4 m.

The chemical composition of the stone, in %, is: CaO-55; MgO-0.8; Fe<sub>2</sub>O<sub>3</sub>-0.05; SiO<sub>3</sub>-0.2; Al<sub>2</sub>O<sub>3</sub>-0.1; MnO-0.005; LOI-43.6.

### 2.2 Field Trials

The field trials were carried out on the acidic *Gleyic Podzoluvisol* (FAO-UNESCO, 1994) at Kuusiku (NW Estonia). The average rainfall per year is 750 mm, the average evapotranspiration is 290 mm less (Kask, 1996). The soil texture was:

**Table 1. Composition of Fraction 0-10 mm Separated at the Screens by the Permanent Natural Humidity of Rock**

Fraction, mm	Content, %
0-0.4	3.9
0.4-1.0	6.6
1.6-2.0	13.0
2.0-4.0	20.0
4.0-6.0	19.6
6.0-8.0	16.9
8.0-10.0	13.6
>10	6.4
Total	100.0

Sand 58.8, silt 32.9, clay 8.3%, humus content 2.7%. The agrochemical basic indicators of test soil were (0-20 cm):  $\text{pH}_{\text{KCl}}$  4.4-5.1, the content of available calcium 800-1010  $\text{mg kg}^{-1}$  in the Mehlich 3 extractant, respectively (Mehlich, 1984). Lime fertilisers: clinker kiln dust, neutralising capacity (Ca) 30%, and limestone: ground lime and equilibrated lime, neutralising capacity (Ca) 38.6%; reactivity correspondingly to 90, 53 and 26%. The proportion of different particulates: clinker kiln dust-100%<0.1 mm, ground lime-100%<2 mm and equilibrated lime-38%<1 mm, 19% 1-2 mm, 43%>2-4 mm (square mesh). Lime fertilisers were spread manually in springtime under the second cultivation or in the autumn before soil tillage. The doses of lime fertilisers: 5  $\text{t ha}^{-1}$ . The trials were carried out in 4 repeats; the size of trial lot was 60  $\text{m}^2$ . The field trials lasted 5 years. Field crops: barley-oats-barley-barley-peas (the work will not deal with the plant aspects). Lime assessment of the effects of available soil calcium content of the soil sample was taken every year after the harvest from 0-0.2 m soil. The soil analyses were run at the Laboratory of Agrochemistry at the Agricultural Research Centre.

### 3. Results

#### 3.1 Results of Laboratory Test

The limestone particles are irregularly shaped. Treating them conditionally as spheres, we may express the particle volume  $V$  as:

$$V = \frac{\pi d^3}{6} \quad (1)$$

Where  $d$  is the diameter of the particle.

A particle dissolves from the surface. When 10% is dissolved, the volume of the particle is:

$$V_{10} = \frac{\pi d_{10}^3}{6} \quad (2)$$

By dividing the corresponding parts of expressions (1) and (2) we receive:

$$\frac{V}{V_{10}} = \frac{d^3}{d_{10}^3}$$

Where  $d_{10} = d \sqrt[3]{\frac{V_{10}}{V}}$

Since  $V_{10} = 0.9V$ , then  $d_{10} = d \sqrt[3]{0.9}$

In a similar manner, by dissolution of 20% of limestone the  $d_{20} = d_{10} \sqrt[3]{0.8}$ , etc.

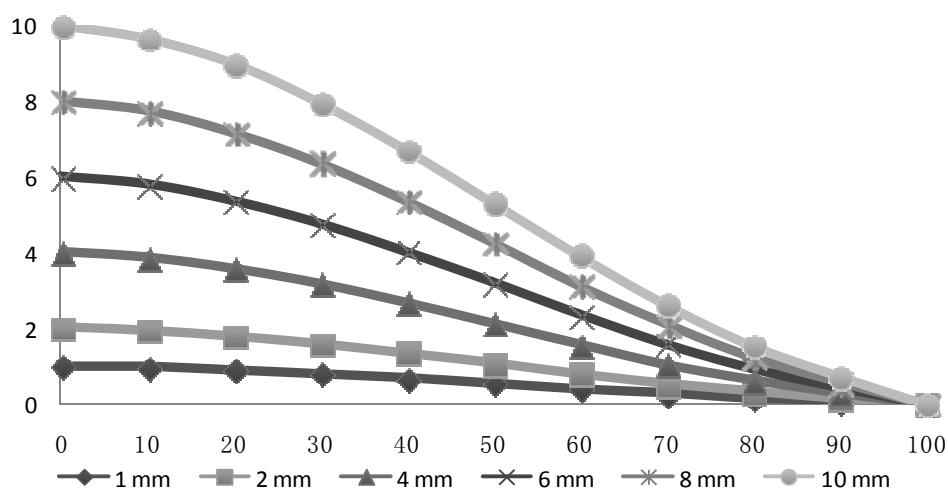
Thus we receive a relation between solubility of particle and decreasing of the particle size under its effect (Figure 1). In soil solution of topsoil and in distilled water with pH=4.0 the lime fertilizer dissolves differently. Therefore, the calculated result cannot be transferred to nature. The result obtained by comparing with the behaviour of the same limestone fraction in field experiments has an indicative meaning, which makes it possible to assess the stability of the limestone in topsoil (indirectly by the duration of the lime fertilizer effect).

From the solubility tests of narrow limestone fractions (Figure 2) it becomes clear that particles under 2 mm dissolve within 4 years completely. Particles with a size of 3-4 mm dissolve within 4 years by 70% and within 5 years by 75%, while the size of the particle decreases correspondingly to 0.9 and 0.7 millimetres.

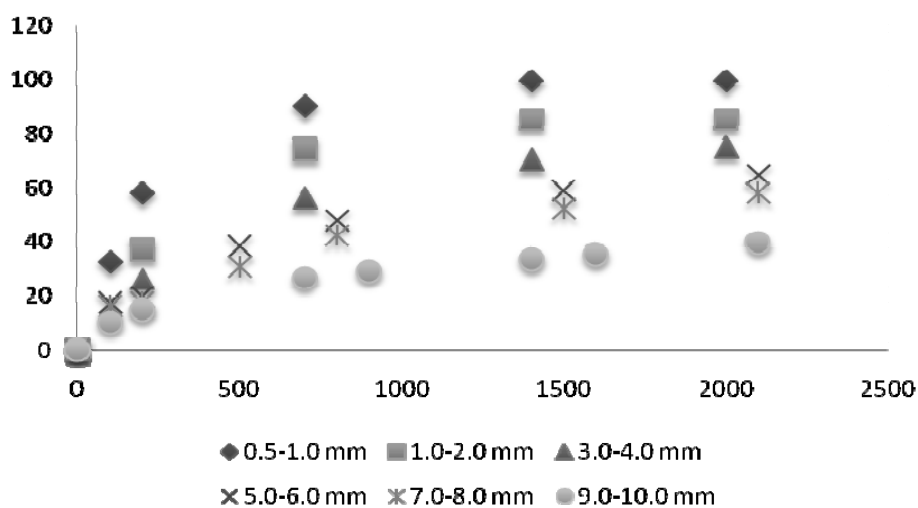
Taking into consideration the fact that during the first year the fraction 0.5-1.0 mm will dissolve by more than 60%, the lime fertilizer with a prolonged balanced effect should be primarily limited in the content of the dust fraction as it dissolves rapidly, especially in acidic media, and leaches through the soil to groundwater as gravitational water. It is reasonable to limit also the content of the fraction over 10 mm as these particles dissolve slowly (persist in soil for more than 10 years), destroying the soil structure. It is evident from the test results that even the presence of 6 mm and 8 mm particles in lime fertilizer does not significantly change the topsoil granulometry, as their contribution to liming fertilizer granulometry is below 20%. The sizes of limestone particles 4, 6, 8, and 10 mm reduced due to dissolution after 4 years correspondingly to 0.9, 2.5, 4.1 and 7.7 mm and after 5 years correspondingly to 0.7, 2.4, 3.7 and 7.4 mm. At the end of the test the insoluble part of different

limestone fractions was the following: 0.5-1.0 mm—0.6%; 1.0-2.0 mm—14.7%; 3.0-4.0—24.8%; 5.0-6.0 mm—35.0%; 7.0-8.0 mm—42.0%; 9.0-10.0 mm—60.2%.

Table 2 gives some picture about solubility of carbonate rock from Estonian quarries in distilled water with pH=4.0. As the test results show, the differences in solubility are small and remain within the limit of 10%.



**Figure 1. Relation between Solubility of Particle and Decreasing of the Particle Size under Its Effect**



**Figure 2. Solubility of Võhmata Limestone Narrow Fractions (mm) in Distilled (%/days) Water with pH=4.0**

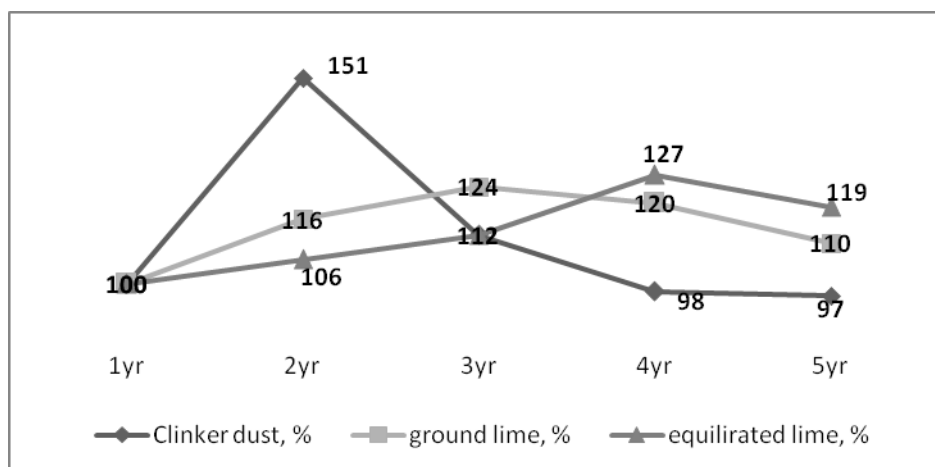
*Note.* +- Since we added to the distilled water 10.2 g/l<sup>-1</sup> potassium biphthalate  $C_8H_5KO_4$ , the actual duration of the test was 100 times shorter—21 days.

### 3.2 Results of Field Tests

By liming of acidic soil one must also take into consideration such property of lime fertilizer as its reactivity. The lime fertilizer with longer effect period consists of fractions with various dimensions, the reactivity of which depends on the size of the particles. While the average reactivity of equilibrated lime fertilizer is 26-29%, for specific particle sizes it makes up: 51% for particles <2 mm, 22% for particles 2-3 mm and 11% for particles >3 mm. Although, based on the solubility analyses, the lime fertilizer could also contain a coarser fraction of particles >6 mm, it is not expedient in practice due to the low spreading density of such large particles. Compared to 3 different levels of limestone (Figure 3), we can see that powdered clinker dust increased sharply the amount of calcium in the body (1010-1530 mg kg<sup>-1</sup>) but in the short term. The effect of lime fertilizer was lower and longer in the fractional composition of different materials (<0.15 mm 12%; 0.15-1.0 mm 32%; 1.0-2.0 mm 33% and 2.0-4.0 mm 23%). After five years, the soil of the lime fertilizer with a longer duration of action had the highest amount of calcium, and less lime fertilizer needed in the next milling.

**Table 2. Solubility of the Rock from Different Quarries (Fraction 0.5-1.0 mm) in Water with pH=4.0**

Name of the quarry, rock	Content in the rock, %		Specific weight of the rock, T/m <sup>3</sup>	Dissolution, % Days					Insoluble residue, %
	CaO	MgO		700	900	1400	1600	2100	
Karinu limestone	48.5	4.8	2.60	78.5	87.3	89.9	89.9	100	10.1
Röstla dolomite	22.1	14.9	2.85	78.5	83.1	92.2	96.9	100	14.3
Vasalemma crystalline limestone	47.1-55.2	0.3-5.0	2.62	87.2	91.0	94.7	96.2	100	3.4
Vasalemma amorphous and marly limestone	38.7-42.7	1.6-6.5	-	82.2	90.4	95.9	98.6	100	21.0
Anelema dolomite	Up to 31.0	14.2-21.7	2.62-2.74	78.2	79.5	97.4	100	100	18.5
Võhmuta limestone	-	-	2.59	91.7	93.4	100	100	100	5.2



**Figure 3. The Influence of Lime Fertilizers with Different Fineness Degree on the Dynamics of Available Soil Calcium Content**

#### 4. Discussion

Since the actual need for liming depends not only on the soil reaction, or pH, but rather on the level of soil saturation, where, in addition to potassium and magnesium, an important role belongs to calcium, then, for the purpose of simplicity, in practice the need for liming is estimated on the basis of the available calcium content providing the saturation degree of 80%. The critical available calcium content is in such case  $1500 \text{ mg kg}^{-1}$  (in the Mehlich 3 extractant).

Depending on the soil, this criterion enables to avoid excessive and insufficient liming and thereby to use the lime fertilizer more efficiently (Loide, 2006). It is also expedient to use lime fertilizer with a prolonged effect and longer resistance ability to leaching and runoff in the cases of minimized soil tillage and direct sowing. The study of the effect of the minimized tillage on the soil properties (PMK, 2018) revealed that when using these technologies, the superficial layer (0-0.05 m) of pseudopodzolic soils, which are deprived of carbonates (Stagnic Luvisol, WRB), intensively acidifies due to decomposition of accumulated organic matter and the use of physiologically acidic fertilizers. Consequently, the soil quality worsens, and it becomes more difficult for plants to uptake the nutrients, especially phosphorus.

When removing the soil acidity, it is important that the limed fertilizer would neutralize the acidity quickly and for a long period of time. The rate of acid neutralization depends on the proportion of lime fertilizer particles with specific sizes. Knowing the time it takes to dissipate each specific particle size, it is possible to adjust the proportion of specific fractions that depend on the dissolution intensity and duration. The study (Loide et al., 2014) identified the proportion of specific-sized fractions in lime fertilizer which provides a more stable calcium content in the soil: 7.4% 0-0.5 mm, 10.6% 0.5-1.0 mm, 15% 1.0-2.0 mm, 24% 2.0-3.0 mm, 43% 3.0-4.0 mm. By changing the proportion of the fractions, the speed and duration of the effect can be adjusted as needed. In order to achieve a faster effect, in practice the optimal fractional composition is: 38% <1 mm, 19% 1-2 mm, 43% >2-4 mm. In dry

conditions, it is advisable to use a higher proportion of fine fractions and in more humid climates a higher proportion of coarser fractions. The peculiarity of the described lime fertilizer is its balanced effect period (4-5 years) and the resulting benefits: its use will in the long run reduce the costs of transportation and spreading and the lime fertilizer is more resistant to leaching, which through the prolonged retention of calcium in the soil provides the stable conditions for formation of beneficial soil properties. The stability of calcium content helps to maintain and improve the soil quality. Calcium requirement is reduced in time if the process of liming with the long-lasting lime fertilizer is repeated.

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