

A Protocol to Quantify the Reactivity of Carbonate Limestone for Horticultural Substrates

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Abstract

The current method for comparing the reactivity of different limestones used to correct pH in horticultural substrates is based on batch trials, where the limestones are incorporated into the substrate and the pH is measured over time (typically up to 28 d.). Our objective was to test a laboratory approach to provide a rapid analytical test on reactivity of various limestone sources. 4M HCl was added to a lime sample, and the volume of CO₂ released into a burette was measured over time. Reagent grade CaCO₃ and two commercially available pulverized dolomitic limestones were tested.. In addition, six particle size fractions derived from each of the limestone samples were also evaluated for reaction rate and the corresponding pH responses. 100% of CaCO₃ reacted in less than a minute after acid addition, whereas it took 3.9 and 11.5 minutes, respectively, for 50% of the limestone samples to react, and 14 and 52 minutes, respectively, for 90% neutralization. Reaction rate increased as the particle size decreased, however, similar reaction rate was observed for the particle sizes larger than 150 μm (>100 U.S. mesh). Time to 90% reaction was negatively correlated with pH response when 6 g of each lime was incorporated per L of peat substrate. It may be possible to establish a lime reactivity index, for example based on the time required for 50% or 90% reaction, and thereby provide a rapid screening of different limestone sources.

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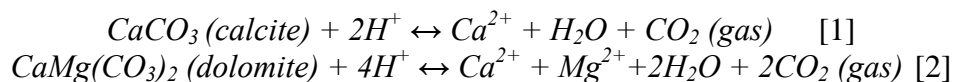
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Introduction

Liming materials are added to container substrates to increase the pH to a level that is acceptable for plant growth (Nelson, 2003; Peterson, 1981; Warncke and Krauskopf, 1983). The quantity of lime required (incorporation rate), as well as the time needed to reach a stable pH depends not only on the materials used to produce the substrate, but also on the lime's chemical composition (Argo and Fisher, 2002), particle size (Argo and Biernbaum, 1996; Chapin, 1980; Gibaly and Axley, 1955; Sheldrake, 1980; Williams et al., 1988), surface area (Barber, 1984; Haby and Leonard, 2002; Love and Whittaker, 1954, Parfitt and Ellis, 1966), crystal structure (Rippy, 2005), and chemical contaminants (B. Ellis, personal communications).

While much is known in general terms about different factors that affect the reactivity of different liming materials, little specific information exists about individual lime sources because of the cost and time required to make the laboratory measurements. Instead, the standard commercial practice for evaluating the incorporation rates and/or reaction times of liming material is based on the trial-and-error method of using a "wet-out test" (Argo and Fisher, 2002) where the lime is incorporated into media and pH change is measured over time (up to 28 d.). In our opinion, a simple laboratory test measuring lime reactivity has potential to rapidly evaluate alternative multiple sources and may provide an indicator of field performance. Quantifying a liming material's reactivity is particularly important because most of the buffering (resistance) to pH change in container media comes from unreacted "residual" lime in the substrate (Argo and Biernbaum, 1997).

The most commonly-used liming materials for greenhouse media are carbonate-based, either calcium carbonate (calcite) or calcium magnesium carbonate (dolomite) (Nelson, 2003). When carbonate-based limestone is reacted with acid, calcium (Ca^{2+}) and/or magnesium (Mg^{2+}), water (H_2O), and carbon dioxide (CO_2) gas result:



The CO_2 gas evolved upon application of strong acid to lime can be measured, and the unreacted lime concentration (on the left side of Equations 1 and 2) can be determined by subtraction.

There are at least four quantitative techniques to determine the amount of CO_2 gas evolved, (1) measurement of the volume of CO_2 upon application of strong acid by displacement of liquid in a burette (Dreimanis, 1962); (2) measurement of the mass of CO_2 evolved upon application of strong acid by adsorption and gravimetric determination (Allison and Moodie, 1965; Anderson 1982; Raad, 1978); (3) measurement of the mass of CO_2 evolved upon application of strong acid using gas chromatography (Barker and Chatten 1982); (4) measurement of the mass of CO_2 evolved upon application of strong acid by absorption and coulometric titration (Engleman et al., 1985). Gravimetric methods are slow and not accurate at low levels of CO_2 (Grogan, 1998), and gas chromatography requires expensive equipment and is also time consuming (Chan, 1986). Coulometric titration offers relatively rapid analysis and excellent precision, but the equipment is expensive. Measurement of CO_2 by volume displacement is rapid, inexpensive and the most widely-used method.

The volume displacement of CO₂ can be determined with a Chittick apparatus (or variants thereof), which is easily constructed from basic laboratory glassware and tubing (Dreimanis, 1962). Once the device is calibrated by use of prepared standards, media samples are introduced and reacted with HCl, and the volume of CO₂ released is measured, and the amount of carbonate lime can be then calculated with the Ideal Gas Law with the known air temperature and air pressure.

The goal of this research was to develop and test a protocol for quantifying reactivity rate in lime based on a gasometric system. Specific objectives of this study were to: (1) calibrate a gasometric system for CO₂ measurement using standard reagent grade CaCO₃; (2) determine the reaction time of liming materials that differed in source and particle size; and (3) compare results from the gasometric system with the pH response when the tested liming materials were incorporated into a peat medium.

Materials and Methods

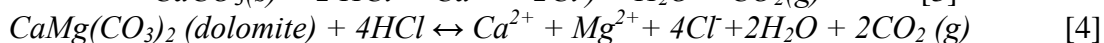
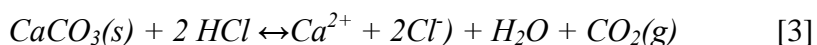
Objective (1): To calibrate a gasometric system for CO₂ measurement

A Chittick apparatus (AOAC Official Method 923.02) was adapted for gasometric determination of carbon dioxide. The apparatus consisted of a gas measuring burette, acid dispensing burette, level burette and 250 ml decomposition flask (Fig. 1). The displacement solution in the measuring burette (*D* in Fig. 1) was composed of 100 g NaCl, 1g NaHCO₃ plus 2 mL Methyl Orange (0.5% aqueous solution) in 350 mL of water. Sufficient 4M HCl was then added to turn the solution pink (pH 2.0), and the solution was stirred until all CO₂ gas was removed as described by AOAC Official Method 923.02.

The general procedure involved dissolving a carbonate limestone sample material and liberating CO₂ gas using an acid solution (4M HCl). A small weighed limestone sample material (0.2g) was placed in the bottom of the decomposition flask (*A* in Fig. 1) which was connected with apparatus. Stopcock *C* was opened, and burette *E* was used to bring the displacement solution to the zero mark. The acid dispensing burette *F* was added to the reaction flask, *A*. The apparatus was left to stand for two min. for temperature and pressure within the apparatus to come to room conditions.

The stopcock *C* was then closed, and the leveling burette *E* was lowered below the surface level of the gas-measuring burette *D* to reduce the pressure within the apparatus. 5 ml of 4M HCl was slowly added to the reaction flask from burette *F*. To prevent escape of liberated CO₂ through the acid burette into the air, at all times during reaction the surface of the displacement solution in the leveling burette *E* was kept lower than that in gas measuring burette *D*. The decomposition flask *A* was shaken to mix the contents, and the apparatus was left to stand for 5 min. (or longer depending on reaction time of the lime, as discussed later), to reach equilibrium. The pressure was equalized in the measuring burette *D*, using the leveling burette *E*, and the volume of gas was read in the measuring burette *D*. The temperature and barometric pressure of air surrounding apparatus was measured. The air temperature was maintained stable at 22°C and the air pressure was approximately 0.998 atm. Measured temperature and pressure for each experimental run were used in calculations for reported results.

After reaction of the lime with acid, CO₂ is liberated with the equation



Because the evolved gas was captured in the burette D , the measured gas volume change could be related to the mass of CO_2 . The CO_2 was saturated with water vapor in equilibrium with the liquid water in the flask and maintained a saturated vapor pressure, P_w , corresponding to room temperature. Therefore, the pressure of carbon dioxide, P_{CO_2} , in the system equaled the barometric pressure, P_{bar} minus P_w . Assuming that all of the carbonate reacted, the amount of carbon dioxide liberated could be determined using the Ideal Gas Law in the form

$$N_{\text{CO}_2} = P_{\text{CO}_2} V_{\text{CO}_2} / RT. \quad [5]$$

Where N_{CO_2} represents the moles of CO_2 liberated, P_{CO_2} represents CO_2 partial pressure (atm), V_{CO_2} represents the volume of CO_2 (L) liberated, R is the universal gas constant (0.0821 L atm/mol K), and T is temperature (K) ($^{\circ}\text{C} + 273.2$). N_{CO_2} equals the moles of carbonate material decomposed according to the stoichiometry of equations [3] and [4].

Because the solubility of CO_2 is very low in a strong acid solution (Stumm and Morgan, 1996), the amount of CO_2 dissolved in the acid digestion solution was ignored. The displacement solution was saturated with CO_2 gas by adding NaHCO_3 with all the excess CO_2 removed. The amount of CO_2 dissolved in the displacement solution during the measurement period was therefore ignored.

In order to develop calibration curves between measured weight of CaCO_3 and moles of CO_2 captured, 0, 0.025, 0.05, 0.1, 0.2, 0.4, 0.6, and 0.8 gram samples (three replicates per mass) of reagent grade CaCO_3 were reacted with 5 mL 4M HCl in the gasometric system. Measured and calculated CaCO_3 (and CO_2) were compared using linear regression (PROC GLM, SAS Institute, 1999) to check for accuracy and precision.

Objective (2): To determine the reaction time of liming materials that differed in source and particle size

We evaluated reagent-grade CaCO_3 (termed “ CaCO_3 ” in results), and two pulverized-dolomitic limestones used in commercial container substrates [termed “NLS” (National Lime and Stone Co., P.O. Box 120, Findlay, Ohio 45839-0120) and “Oldcastle” (Yardright Select, Oldcastle Stone Products[®], 2200 Sullivan Trail, Easton, PA 18040)]. We also evaluated six particle size fractions derived from each of the two commercial limestones (NLS and Oldcastle). Accurate definition of the six particle size segregations was obtained by screening each through standard U.S. meshes. The particle distribution as shown in Table 1 was then measured using the dry sieving method and the fraction of each particle size range was saved for later lime reactivity measurement and pH response evaluation. In addition to the particle size distribution, chemical composition, purity and the reaction of the three tested lime materials were tested and are listed in Table 1. The neutralizing value in calcium carbonate equivalents (CCE) of the tested liming materials was determined based on the AOAC Official Method 955.01. The liming materials were digested using AOAC 962.01 procedure and their chemical composition was analyzed using inductively-coupled plasma (ICP) atomic emission spectrophotometry.

To determine an appropriate acid strength for the lime reactivity protocol, we added three 5 mL replicate samples of either 4M or 6M HCl to 0.2 g NLS lime samples. The average volume of CO_2 was measured over time and a quadratic curve was fit to the percent lime reacted over time. No difference was found (F-test $p > 0.05$) between acid concentrations, so

the 4M acid was used for all lime analysis because it was safe to handle compared with 6M HCl, although 6M HCl was used by Dreimanis (1962).

To determine differences in reactivity between lime sources and particle size segregations, the volume of CO₂ liberated over time was quantified for each lime by reacting three replicate 0.2 g lime samples with 5 mL of 4M HCl. The percentage of CO₂ recovered was plotted over time and a monomolecular curve was fitted for each lime and each particle size fraction within lime. The equation of the monomolecular function was as

$$\text{CO}_2 \text{ Recovered (\%)} = \textit{start} + (\textit{asymptote} - \textit{start}) * (1 - e^{-k*\textit{time}}) \quad [6]$$

Where k represented the rate at which the reaction reached the asymptote; \textit{start} represented the instant percent CO₂ recovered when the reaction started; $\textit{asymptote}$ represented the maximum CO₂ recovered; \textit{time} represented reaction time (min).

The model fittings to the data were done using SAS's nonlinear regression procedure (PROC NLIN) (SAS Institute, 1999). An F-test was used to compare whether there was a difference in the reaction curve functions between lime types, and particle size ranges.

We used the reaction curves for each lime to estimate (a) the time until 50% or 90% of the calcium carbonate equivalents was digested for the sample, and (b) the percentage of calcium carbonate equivalents digested after 5 minutes. These two measurements were made because we hypothesized they would be easier to quantify and interpret than the repeated measurements required to quantify a reaction curve over time, and may therefore be more useful for rapid screening of lime sources. 90% reaction was selected because impurity of commercial grade liming materials may mean that 100% recovery may not occur. At 5 minutes, we observed in a pilot study that there was considerable separation of reaction curves between lime types and particle size fractions, indicating it was an appropriate point in time to compare differences between lime types.

Objective (3): To compare results from the gasometric system with the pH response when the tested liming materials were incorporated into a peat medium

A Canadian sphagnum peat medium (Professional Black Bale Peat, SunGro Horticulture Inc., Bellevue, Wash.) with long fibers and little dust (Von Post scale 2-3; Puustjarvi and Robertson, 1975) was used for pH response evaluation. The lime incorporation rate was 6 g of lime per L of peat medium, based on recommended amending rate for general greenhouse crops (Nelson, 2003). Two pH response experiments were conducted. For the experiment 1, the three lime sources of reagent CaCO₃, NLS and Oldcastle were mixed at 6 g of lime per liter of peat medium. Substrate moisture was brought to a wetness of 0.3 (v/v) using deionized water after the lime materials were incorporated. The media were stored at room temperature in a plastic bag that was opened for one minute 2-3 times per day to allow for lime reaction and gas exchange. Substrate-pH and EC were measured using the saturated-medium extract (SME) method with distilled water as the extractant (Warncke, 1986). Substrate-pH was measured at day 0, 1, 7, 14, 40 using a Corning 250 ion analyzer (Corning Incorporated, New York). Three replicates were measured for all pH tests.

For experiment 2, six particle size fractions (as shown in Table 1) of each of the two commercial limes were mixed at 6 g L⁻¹ of peat substrate for pH response evaluation as described previously. Substrate moisture was brought to container capacity (around saturated point) in an open plastic bag and was incubated at room temperature (22°C). Substrate-pH was measured at day 0, 1, 2, 3, 4, 5, 6, 7, 14, 21 and 28 with three replicates. At each time of

pH measurement, solutions were squeezed out of the substrate and pH was measured directly in the solution. Data were analyzed using PROC GLM (SAS Inst.) by date and means were separated by Tukey's HSD ($P \leq 0.05$).

The relationship between the lime reactivity (time required for 90% reaction, and percent reaction after 5 min) and the resultant substrate-pH responses at day 1, day 7, day 14, day 21, and day 28 were plotted and analyzed using SAS PROC REG with stepwise elimination option by date and lime type. The "best fit curves" were then selected, and F-test ($p \leq 0.05$) was conducted to evaluate the differences between curves at each date.

Results and Discussion

The adapted Chittick apparatus precisely and accurately determined the amount of CO_2 gas evolved by the reaction of reagent CaCO_3 at amounts from 0 to 8 mMol (0 to 0.8 grams) with 4M HCl (Fig. 2). In calibrating the system, the only technical challenge was to ensure there were no leaks and to maintain stable temperature. The reaction time was very rapid and time to complete digestion depended on the amount of CaCO_3 reacted. The average reaction time for 0.025, 0.05, 0.1, 0.2, 0.4, 0.6 and 0.8 g CaCO_3 was 7, 15, 20, 27, 48, 102 and 160 sec, respectively.

Characteristics of the three lime materials are presented in Table 1. CaCO_3 had the finest particle size, followed by NLS and Oldcastle, and increasing particle size is known to decrease lime reactivity (Argo and Biernbaum, 1996; Barber, 1984; Haby and Leonard, 2002; Love and Whittaker, 1954). NLS and Oldcastle had similar percentages of calcium and magnesium, and CaCO_3 tends to be more chemically reactive than dolomite (Argo and Biernbaum, 1996). Because of the lower molecular weight of Mg compared with Ca, the neutralizing value of NLS and Oldcastle was greater than CaCO_3 for a given mass.

The reaction curve over time for the three lime types is plotted in Figure 3. Reaction rate decreased in the order of $\text{CaCO}_3 > \text{NLS} > \text{Oldcastle}$. After 5 minutes, the observed percentage of each 0.2g sample reacted differed between lime types, with 100% of CaCO_3 reacted, compared with 58.5% for NLS and 29.4% for Oldcastle (Fig. 3, Table 1).

The reaction curve over time was plotted in Figure 4 for each particle size fraction of the two commercial limestones. The parameter estimates of the monomolecular function for each particle size fraction and the two unscreened commercial limestones were shown in Table 2. Using the monomolecular function to estimate the time required to react 90% of the neutralizing value (CCE) of each unscreened sample, the required duration was 17 sec, 15.2 min, and 49.5 min, for CaCO_3 , NLS, and Oldcastle, respectively (Table 1). For screened samples, the duration to 50% and 90% reaction for different particle size fractions increased in order of (a) finer than 45 μm > (b) 45-75 μm > (c) 75-150 μm > (d) 150-250 μm > (e) 250-850 μm > (f) coarser than 850 μm for both commercial limestone types.

The lime reaction rate was consistently slow in the particle size range of 20-100 U. S. mesh (150-850 μm), and also for the lime fraction greater than 20 U.S. mesh (850 μm) fractions (which was only present in Oldcastle). The slow reaction rate for large particles compared with smaller particles was quantified in the estimated value of parameter k , the estimated time required for 50% and 90% reaction, and the reaction at 5 min (Table 2).

When limes were incorporated into peat (Experiment 1), the substrate-pH response over time differed between lime types (Fig. 5). The pH of peat containing CaCO_3 increased rapidly and reached a stable pH 7.2 by day 7 (Fig. 5A). The pH of peat containing unscreened

NLS increased slower than that containing CaCO_3 and reached a stable pH of 6.4 by day 14. The pH of peat containing the unscreened Oldcastle increased at the slowest rate, and had not reached a stable pH after 40 days.

The greatest differences in pH response between particle sizes (Experiment 2) occurred one day after measurement (Fig. 6), and differences became less pronounced as the experiment progressed. The time required to reach at least pH 6.5 for the particle size fraction of $<45 \mu\text{m}$, $45\text{-}75 \mu\text{m}$, $75\text{-}150 \mu\text{m}$ and $150\text{-}250 \mu\text{m}$ for both NLS and Oldcastle was 7, 7, 14, and 28 days, respectively. The lime sample in the particle size fraction $>850 \mu\text{m}$ (Oldcastle only) and $250\text{-}850 \mu\text{m}$ had not reached the pH 6.5 level after 28 days.

Thus, the difference in the reaction rate between the two unscreened limestones was due to (a) the greater proportion of large particles (25% $>250 \mu\text{m}$) contained in the Oldcastle (Table 1), and (b) the lower overall reactivity of the Oldcastle lime at each size fraction (Fig. 6) when compared with that of NLS using both the gasometric method (Fig. 3) and pH response in peat substrate (Fig. 5).

Regression analysis indicated that lime reaction rate (both time to 90% reaction and amount reacted after 5 min) using the gasometric system was correlated with the initial substrate-pH response at day 1 and day 14 in peat substrate (Table 3, Fig. 7). The stepwise regression method found that quadratic curves best fitted the data with the highest r^2 and p-value. The correlation curves of reaction rate versus substrate pH at day 1 were statistically different between NLS and Oldcastle. However, the differences between the two lime types at day 14 were no longer significant. The pooled data were therefore analyzed and fitted into one curve for the pH data at day 14 (Table 3). At day 28, there was no significant relationship ($p=0.1205$) between the percent reaction after 5 min versus the resulting substrate-pH (data not shown), whereas a significant correlation relationship ($r^2 = 0.54$, $p=0.0063$) held for the time to 90% neutralization.

Fine particles (which passed through a 100 U.S. mesh, $< 150 \mu\text{m}$, symbols N1-3 and O1-3 in Fig. 7) had a straight-line correlation between time to 90% reaction or the percent reaction after 5 min and the substrate pH. There was a negative correlation between the time to 90% reaction and the corresponding substrate-pH at day 1 and day 14 (Fig. 7A and 7C). In contrast, a positive correlation was found between the percentage of lime reacted at 5 min and the substrate-pH at day 1 and 14 (Fig. 7B and 7D).

There was nonlinear and greater variation between limestones for particles coarser than $150 \mu\text{m}$ (symbols N4-5 and O4-6 in Fig. 7). For example, the O4-O6 particle size fraction for Oldcastle had similar time to 90% reaction, but a wide range (4.44 to 6.25) in substrate pH (Fig. 7C). In other words, the reactivity measured by the gasometric system correlated well to the substrate-pH for fine particle size fractions only.

The poor relationship between the gasometric reactivity and substrate pH for the coarse particles may be caused by physical properties such as porosity. Rippey (2005) suggested that coarse limestone particles had a greater percent surface area from internal pores than fine particles. When incorporated into a substrate, internal limestone pores can be filled with a highly basic solution where high $[\text{OH}^-]$ slows lime reaction rate within the pores compared with reaction of external surfaces (Sparks, 2003). Some other factors can also inhibit limestone dissolution reactions when the liming materials were incorporated into the substrate. The Fe and organic C in soil solutions can be coated to the surface of fresh limestone particles by precipitates (Warfvinge and Sverdrup, 1989). These coatings, formed from the oxidation of amorphous iron carbonate readily precipitating on the mineral surfaces,

inhibit limestone dissolution reaction. Since coarse particles have low exposed exterior surface area in general, and higher possible internal surfaces (or internal pores) than fine particles, reaction rate of coarse particles with the weak acids in the peat substrate would be slowed significantly.

In contrast, in the CO₂ gasometric system, the strong acid may react at almost the same rate with both the external and internal surfaces. The measured reaction indices in the gasometric system could therefore overestimate the corresponding pH responses in the substrate for coarse limestones. The gasometric system would be therefore more appropriate to evaluate the reactivity of fine limestone samples (particles less than 150 μm). Liming materials used for horticultural substrates normally have a very fine particle size. In an unpublished survey of 30 samples from horticultural industry, we found that 75% lime samples had over 90% of total mass passed through 100 U. S. mesh (<150 μm) (from unpublished data). The gasometric system could therefore be an effective method to help evaluate liming materials in horticultural substrates.

Conclusions

The gasometric test accurately quantified total lime mass for CaCO₃. Lime reactivity, as measured by both the gasometric method and substrate-pH response, consistently decreased in the order of CaCO₃ > NLS > Oldcastle. For the particle size fractions tested, the lime reactivity measured by the CO₂ release system correlated well with the initial substrate-pH responses, especially for fine particles (< 150 μm).

Multiple factors affect the reactivity of a particular lime, some of which are costly and time-consuming to measure (for example particle surface area). It may be possible to establish a lime reactivity index based on the time required to reach the 90% reaction measurements, and thereby provide a rapid screening of limes. Further gasometric analysis of lime types used in horticultural substrates is therefore needed.

Our pilot studies indicate that the gasometric method may also be modified to quantify unreacted “residual” lime (Argo and Biernbaum, 1996, 1997) in peat-based substrates during production. If accurate, this type of soil test would provide important information for substrate buffering as well as pH management. However, because hydrated lime (Ca(OH)₂) is sometimes used in conjunction with carbonate limestones in container media, a different approach may be needed to quantify reactivity of blended liming materials containing hydrated lime, or residual hydrated lime in a growing medium, because Ca(OH)₂ does not release CO₂ following acid digestion.

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Table 1. Characteristics of the three tested lime materials

Values		CaCO ₃	NLS	Oldcastle
Screen Size (U.S. mesh)	Diameter (μm)	Percent passing mesh		
20	850	100	100	99.5
60	250	100	99.4	74.0
100	150	100	94.1	52.7
200	75	100	70.1	27.6
325	45	100	51.5	16.9
Screen Size (U.S. mesh)	Diameter (μm)	Percent retained		
20	850	0	0	0.5
60	250	0	0.6	25.6
100	150	0	5.2	21.3
200	75	0	24.0	25.1
325	45	0	18.6	10.8
<325	<45	100	51.5	16.9
Chemical analysis				
	Ca (%)	40	19.8	20.7
	Mg (%)	0	11.7	11.9
	CaO (%)	56	27.8	28.9
	MgO (%)	0	19.3	19.7
	CaCO ₃ (%)	100	49.6	51.7
	MgCO ₃ (%)	0	40.6	41.5
Neutralizing value (Calcium carbonate equivalents) ^z		99.9b	106.9a	106.8a
Percent reacted with 4M HCl after 5 minutes ^z		100a	58.5b	29.4c
Time required for 90% of 0.2 g sample to react with 4 M HCl (min) ^z		<1c	15.2b	49.5a
Substrate-pH after 14d at 6 g lime/L peat ^z		7.16a	6.47b	5.66c

^z Mean separation using Tukey's HSD_{0.05}

Table 2. Parameter estimates \pm standard error, calculated correlation coefficient (Pseudo- R^2) for the nonlinear monomolecular fit, the time to 50% lime neutralization, the time to 90% lime neutralization and the percent reaction at 5 min for acid reaction of the two unscreened lime samples and the different particle size fractions within each lime.

Lime Type	Particle size range (U.S. mesh)	Diameter (μm)	Rate K	Start	Asymptote	R^2	Time to 50% reaction (min)	Time to 90% reaction (min)	Reaction at 5 min (%)
NLS	20-60	250-850	0.087 ± 0.002	0.0095 ± 0.0084	0.976 ± 0.007	0.994	8.17	29.39	34.9
	60-100	150-250	0.100 ± 0.002	0.0108 ± 0.0053	0.978 ± 0.004	0.998	7.08	25.32	38.9
	100-200	75-150	0.107 ± 0.002	0.0091 ± 0.0054	0.979 ± 0.004	0.998	6.59	23.43	41.1
	200-325	45-75	0.129 ± 0.003	0.0243 ± 0.0084	0.990 ± 0.007	0.995	5.27	18.46	48.3
	<325	<45	0.269 ± 0.006	0.0355 ± 0.0086	0.973 ± 0.005	0.995	2.54	9.47	72.9
	Overall		0.169 ± 0.004	0.0586 ± 0.0096	0.982 ± 0.006	0.993	3.85	14.32	58.5
Oldcastle	>20	>850	0.033 ± 0.001	0.0599 ± 0.0074	0.973 ± 0.011	0.994	19.93	76.48	19.9
	20-60	250-850	0.033 ± 0.001	0.0624 ± 0.0045	0.991 ± 0.007	0.997	19.31	70.72	20.4
	60-100	150-250	0.035 ± 0.001	0.0616 ± 0.0078	0.974 ± 0.011	0.991	19.00	72.99	20.6
	100-200	75-150	0.050 ± 0.001	0.0485 ± 0.0047	0.996 ± 0.007	0.997	12.93	45.79	25.8
	200-325	45-75	0.067 ± 0.001	0.0236 ± 0.0059	0.995 ± 0.006	0.997	10.14	34.97	29.8
	<325	<45	0.241 ± 0.009	0.0291 ± 0.0147	0.957 ± 0.008	0.987	2.94	11.55	67.9
	Overall		0.059 ± 0.002	0.0714 ± 0.0062	0.940 ± 0.007	0.995	11.49	51.99	29.4

Table 3. Parameter estimates, r^2 and p value for the stepwise regression analysis curve fit between lime reaction rate (both time to 90% reaction and amount reacted after 5 min) using the CO₂ gasometric system and the substrate-pH response at day 1 and day 14 in peat substrate. At day 1, the fitted curves were significantly different between NLS and Oldcastle. At day 14, since the two curves were not statistically different using F-test, the pooled curve was presented.

Lime type	Percent reaction after 5 min			Min to 90% reaction		
	pH (Y) relationship with reaction rate (X)	r^2	p value	pH (Y) relationship with reaction rate (X)	r^2	p value
	pH at day 1					
NLS	$Y = -4.38 + 0.337 X - 0.00269 X^2$	0.960	0.0404	$Y = 6.36 - 0.00249 X^2$	0.9315	0.0078
Oldcastle	$Y = -0.39 + 0.273 X - 0.00268 X^2$	0.906	0.0288	$Y = 5.73 - 0.00032 X^2$	0.8968	0.0041
	pH at day 14					
Pooled data	$Y = 4.61 + 0.059 X - 0.00036 X^2$	0.507	0.0413	$Y = 6.78 - 0.00026 X^2$	0.6245	0.0022

Figure 1. A gasometric system for CO₂ measurement adapted from Chittick apparatus (AOAC Official Method 923.02). The decomposition flask, A, was connected through the side hose connection by rubber tube, B, provided with a stopcock, C, to a graduated gas-measuring burette, D, which was connected in turn with level burette, E, using a rubber tube. For the decomposition flask, A, a 250 ml wide mouth filter flask was fitted with a one hole rubber stopper, with a extended tip of 10 mL acid dispensing burette F passed through the hole.

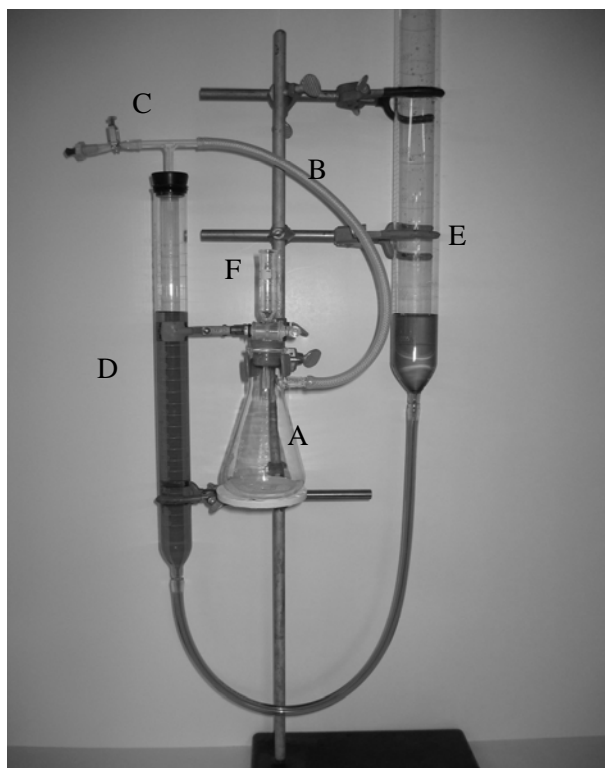


Figure 2. The relationship of between the mmol of CO₂ gas measured in the displacement burette, and the mmol of CaCO₃ measured gravimetrically. Symbols represent individual replicate measurements.

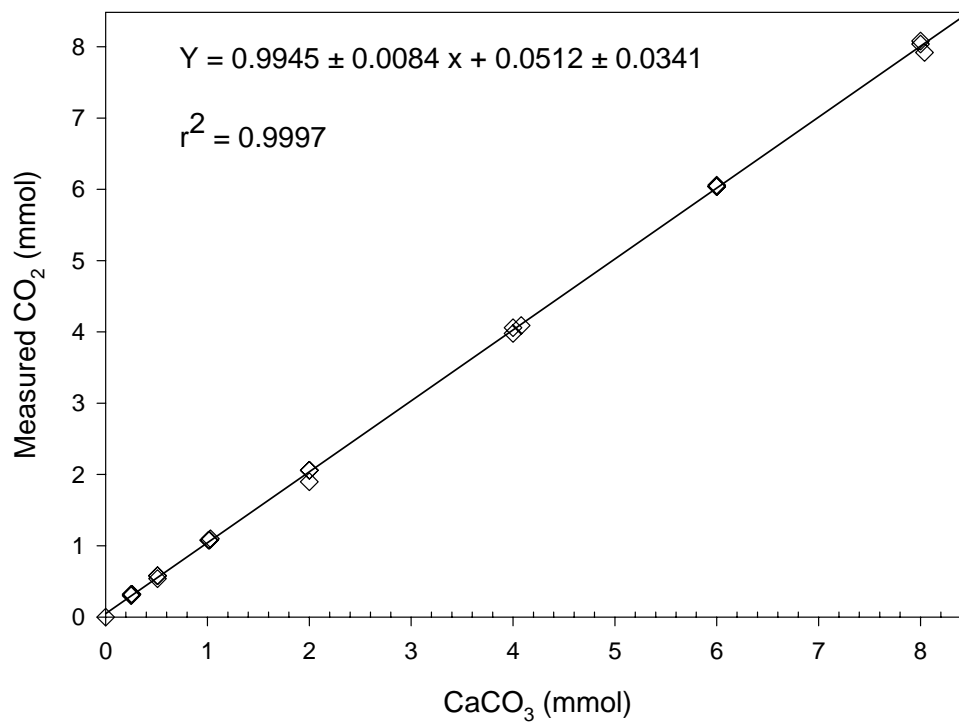


Figure 3. Figure 3. The reaction time of three lime types based on CO₂ measurement. 0.2 g samples were reacted with a strong acid (5 ml of 4M HCl). The mmol of CO₂ measured by displacement was converted into the percentage vertical scale based on the neutralizing value (Calcium carbonate equivalents) for each lime type, from Table 1. The horizontal axis represents time after acid was mixed with the lime sample. Symbols represent an average of three measurements \pm one standard error.

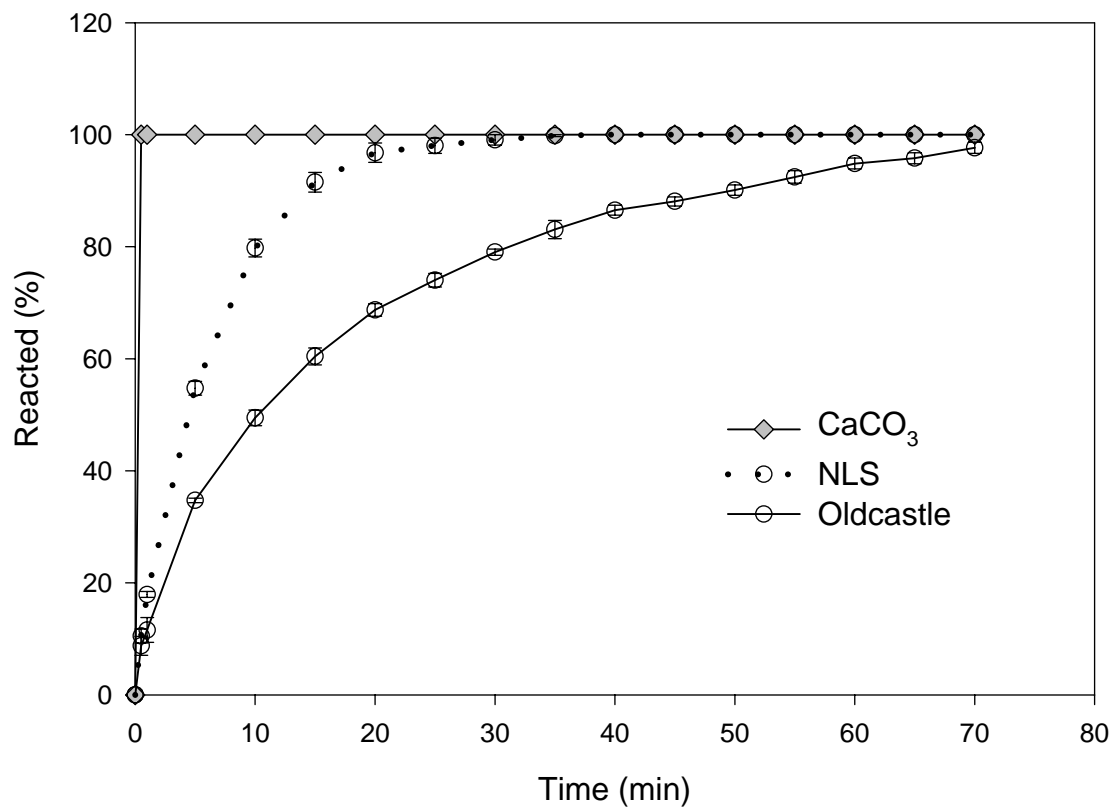


Figure 4. The reaction time for CaCO_3 and different particle sizes of NLS (A) and Oldcastle (B) based on CO_2 measurement. 0.2 g samples were reacted with a strong acid (5 ml of 4M HCl). The mmol of CO_2 measured by displacement was converted into the percentage vertical scale based on the neutralizing value (Calcium carbonate equivalents) for each lime type, from Table 1. The horizontal axis represents time after acid was mixed with the lime sample. Symbols represent an average of three measurements \pm one standard error. Solid lines represent the fit of the monomolecular function. The corresponding parameter estimates were shown in Table 2.

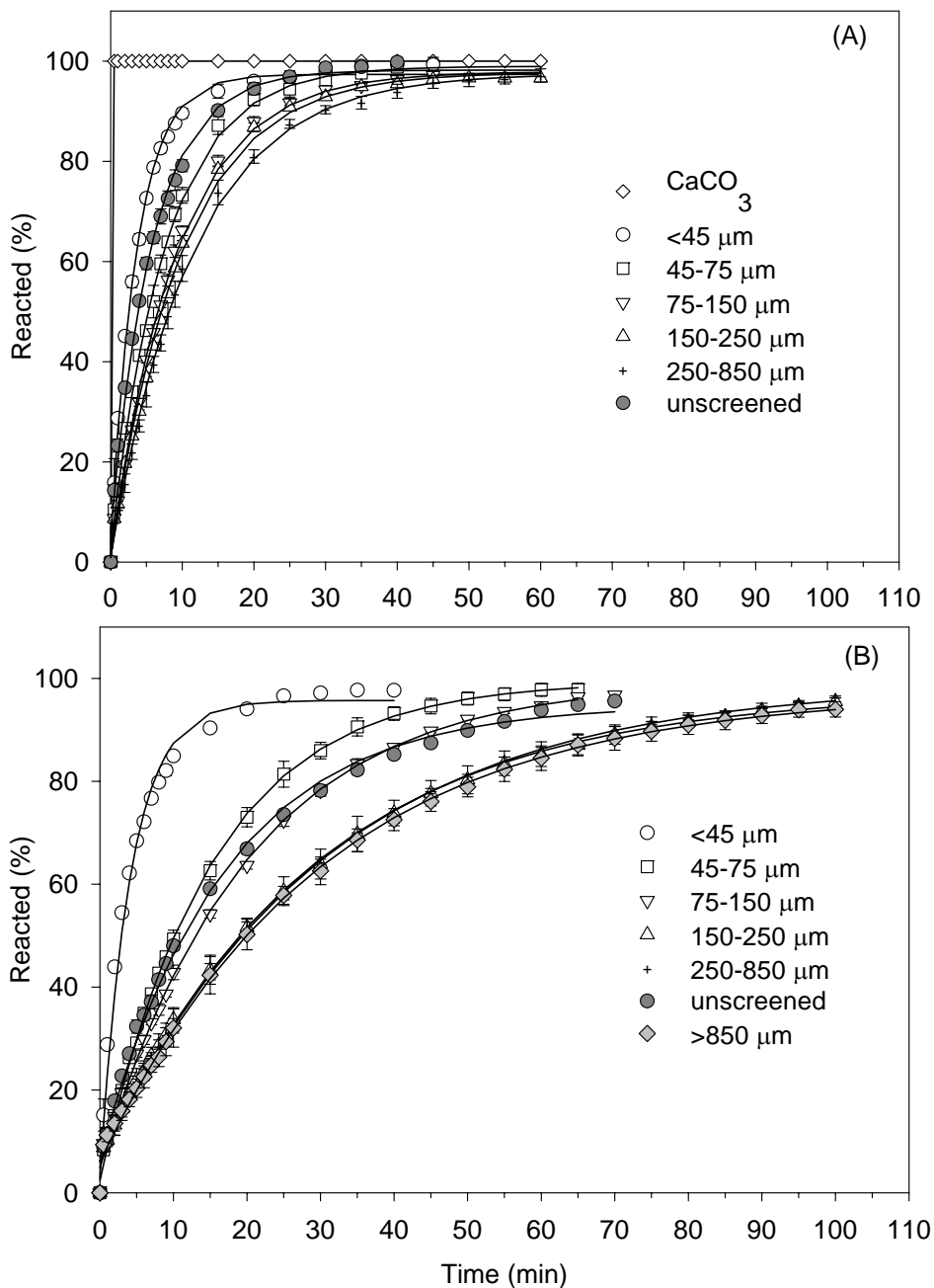


Figure 5. Changes in the substrate-pH of a peat substrate over time for peat amended with $6 \text{ g} \cdot \text{L}^{-1}$ of three different lime sources (reagent CaCO_3 , unscreened NLS and Oldcastle). Symbols represent an average of three measurements \pm one standard error.

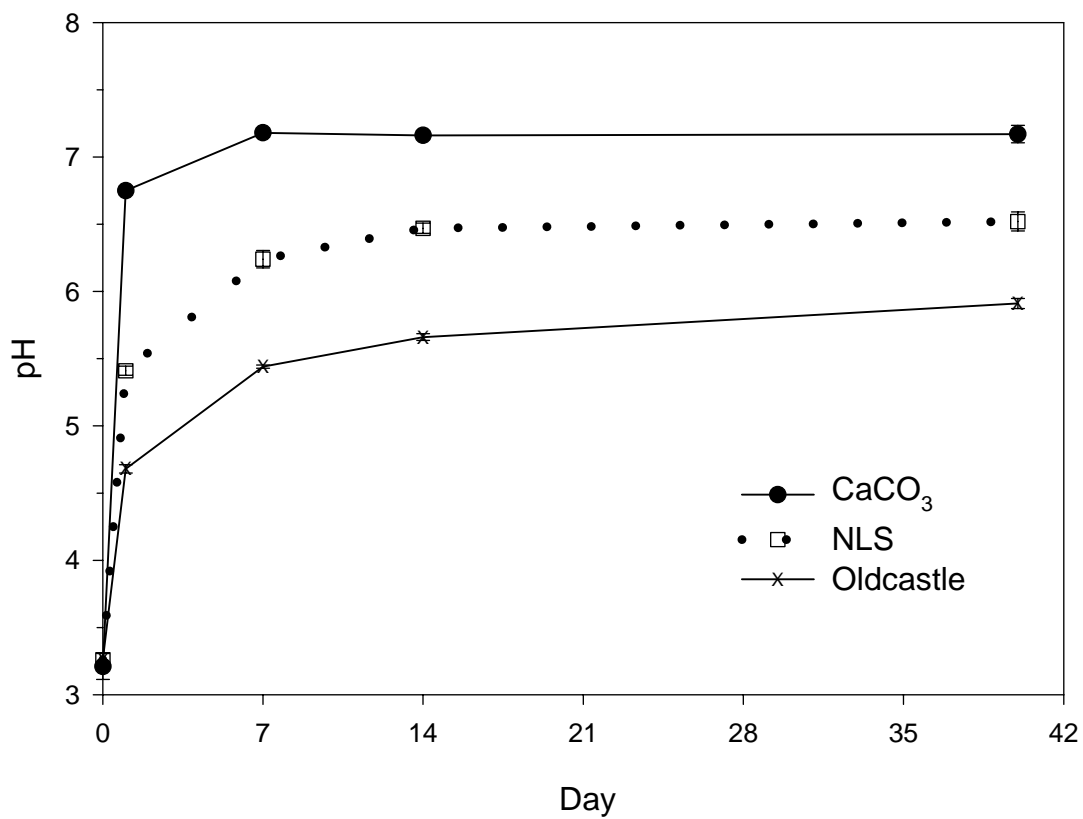


Figure 6. The substrate-pH of a peat substrate amended with various particle size fractions of NLS and Oldcastle incorporated at 6 g L⁻¹ in experiment 2, measured at either day 1 (A), day 7 (B) day 14 (C) or day 28 (C), respectively. Letters represent mean separation using Tukey's HSD_{0.05}.

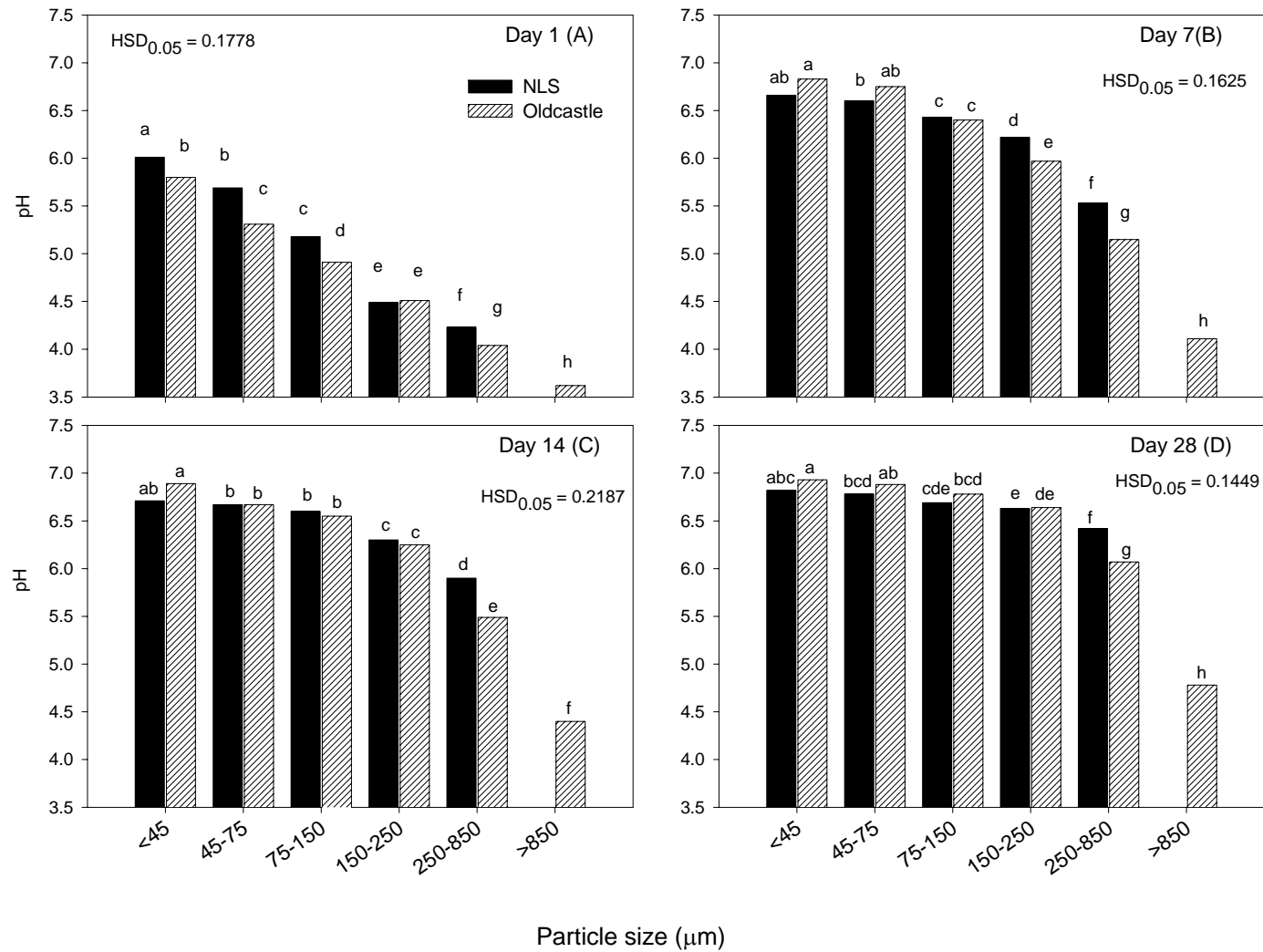


Figure 7. The relationship between lime reaction rate and substrate-pH response for the tested different particle size fractions. 90% reaction time was compared with substrate-pH at day 1 (A) and day 14 (C). Percent of lime reacted after 5 min was also compared with substrate-pH at day 1 (B) and day 14 (D). The symbols of R, N and O represent reagent CaCO_3 , NLS and Oldcastle, respectively. The subscript number of 1, 2, 3, 4, 5, and 6 represent particle size fractions $<45 \mu\text{m}$, $45\text{-}75 \mu\text{m}$, $75\text{-}150 \mu\text{m}$, $150\text{-}250 \mu\text{m}$, $250\text{-}850 \mu\text{m}$ and $>850 \mu\text{m}$, respectively. Symbols represent an average of three measurements. The corresponding regression analyses were shown in Table 3.

