

Effectiveness of Lime Particle Size in the Neutralisation of Sulfidic Acid Sulfate Soil Materials

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Abstract

The effectiveness of the acid neutralising capacity of a range of lime particle sizes in alkaline and acidic sulfidic acid sulfate soils has been determined by an incubation method. The criterion for acceptable acid neutralising capacity was the ability of the neutralising material (e.g. lime) to maintain the soil materials' pH at greater than or equal to 6.5. In incubated alkaline sulfidic soil materials this criterion was satisfied by lime particle sizes below 1 mm; while in incubated acidic sulfidic soil materials, a particle size of below 0.5 mm was required. This experiment has demonstrated, for the first time, the lime particle sizes required for the optimum treatment and remediation of sulfidic acid sulfate soil materials.

Key Words

Lime, acid sulfate soil, particle size, neutralisation, remediation

Introduction

Prior to this study, the appropriate particle size range of carbonate liming materials that can effectively neutralise existing and/or potential acidity within acid sulfate soils had not been determined directly. The effectiveness of agricultural lime (i.e. ground geological limestone) has been accepted on the basis of particle size to be: 100% effective for particles <0.300 mm; 60% effective between 0.300 mm to 0.850 mm and; 0.10% effective for particles >0.850 mm (Stone *et al.* 1998). These values have apparently been derived from liming studies of agricultural soils, which are usually very different in behaviour from acid sulfate soils and, accordingly, managers use these assumptions with less-than-total confidence. A demonstration of uncertainty regarding particle size effectiveness in acid sulfate soil management is the recent liming of acid sulfate soils in South Australia at Currency Creek on the Lower Lakes of the River Murray with ultra-fine lime to ensure effective treatment (SA DEH 2009). Superfine (<0.45 μm) lime is generally supplied for enrichment of calcium-depleted alkaline or circumneutral soils and has a considerably higher cost due to the requirement for further processing by ball mill after the initial crushing stage (Whear 2009). Here we use direct incubation/remediation trials using representative acid sulfate soil materials and a range of particle size fractions of agricultural lime to provide the first data on liming efficacy in acid sulfate soil materials in relation to the particle size of agricultural lime. Further studies are currently being undertaken in order to develop a comprehensive assessment of lime particle size efficiency in a wider range of acid sulfate soil materials.

Method

Mined geological limestone (calcite, CaCO_3), representative of the liming material generally used for remediation and treatment of acid sulfate soil materials was characterised by a variety of techniques and used to determine the effect, over time, of the various particle sizes on the pH of incubated acid sulfate soil samples. The mineralogy and crystal structure of the lime was determined by X-ray Diffraction (XRD) and the morphology of the lime before and after incubation was characterised by Analytical Scanning Electron Microscopy (ASEM). Chemical composition of the lime was confirmed by Energy Dispersive X-ray analysis (EDX) and X-ray Photoelectron Spectroscopy (XPS) before and after incubation.

Experimental

Lime was sourced from South Queensland Lime Pty Ltd in various grades and sieved to make fractions of 1 - 2 mm, 0.5 - 1 mm, 250 - 500 μm , 180 - 250 μm , 125 - 180 μm , 90 - 125 μm , 63 - 90 μm . Particles below 63 μm were gravity separated to 20 - 63 μm and < 20 μm fractions. The alkaline sulfidic acid sulfate materials used for this study were collected from the Tuckean Nature Reserve, NSW; with acidic sulfidic materials collected from Yamba, NSW. The extracted soils were transported and stored under thermally isolated conditions and with zero headspace in order to minimise air ingress. Sulfide content was determined

by the Chromium Reducible Sulfur (S_{CR}) method 22B; and Titratable Actual Acidity (TAA) by method 23F of the Acid Sulfate Soils Laboratory Methods Guidelines (Ahern *et al.* 2004). The liming rate was calculated using the liming conventions of the Acid Sulfate Soils Laboratory Methods Guidelines (Ahern *et al.* 2004), using the net acidity (assuming negligible existing ANC based on past experience with these soils), a safety factor of 1.5 and a lime purity of 96% of pure $CaCO_3$ as per supplier specifications. The entire range of lime particle sizes was examined in the alkaline sulfidic soil, while the fractions examined in the acidic sulfidic soils ranged from 1 - 2 mm to 125 - 180 μm . A lower limit of 125 - 180 μm was used in the acidic sulfidic study as preliminary assessment had determined the effectiveness of lime of this particle size for sulfidic soil. The acid sulfate soil materials were mixed with agricultural lime fractions at the required liming rate for each soil and incubated as 10 cm x 12 cm blocks of 2 mm in height (Sullivan *et al.* 2009). Incubations were kept moist by covering with sponge moistened by spraying with ultrapure water. Sampling was initially undertaken at weekly intervals, and with decreasing frequency after the first four weeks. Determination of pH was undertaken on strips of soil cut from the incubation slabs and mixed 1:1 by weight with ultrapure water. The pH was measured using an Orion 420A+ pH meter and Thermo 910600 temperature-compensated combination pH probe. The instrument was calibrated daily with fresh pH 4 & 9 buffers and referenced to a check buffer at pH 7.

XPS studies of the lime particles before and after incubation were undertaken on a Kratos AXIS Ultra HSA X-ray Photoelectron Spectrometer using monochromated 1486.6 eV Al K_{α} irradiation generated by a voltage of 15 kV and with a current of 10 mA. A hybrid (magnetic/electrostatic) lens was used to collect the ejected electrons. A pass energy of 160 eV, 1 eV step and 100 ms dwell time was applied for survey scans, with detail scans run at pass energy of 20 eV, 0.05 eV step and 250 ms dwell time. Charge was neutralized using an electron flood gun and binding energies were referenced to adventitious carbon at 285 eV. Particles were removed from incubated samples at 16 weeks for XPS study and were rinsed repeatedly with ultrapure water with gentle agitation prior to drying under desiccation for XPS analysis. SEM images and elemental analyses were obtained using a Leica 440 ASEM, using carbon coated particles of agricultural lime including untreated, incubated and incubated particles Na_2CO_3 treated. XRD studies were performed on a Bruker Endeavour D4 X-ray diffractometer using a particle size of <20 μm .

Results

Figure 1 shows the pH incubation data for the unoxidised, initially alkaline sulfidic Tuckean soil. With the exception the 1 - 2 mm grade of agricultural lime, the pH of all limed incubating soil materials showed adequate neutralisation resulting in maintenance of pH >6.5 over the duration of the experiment.

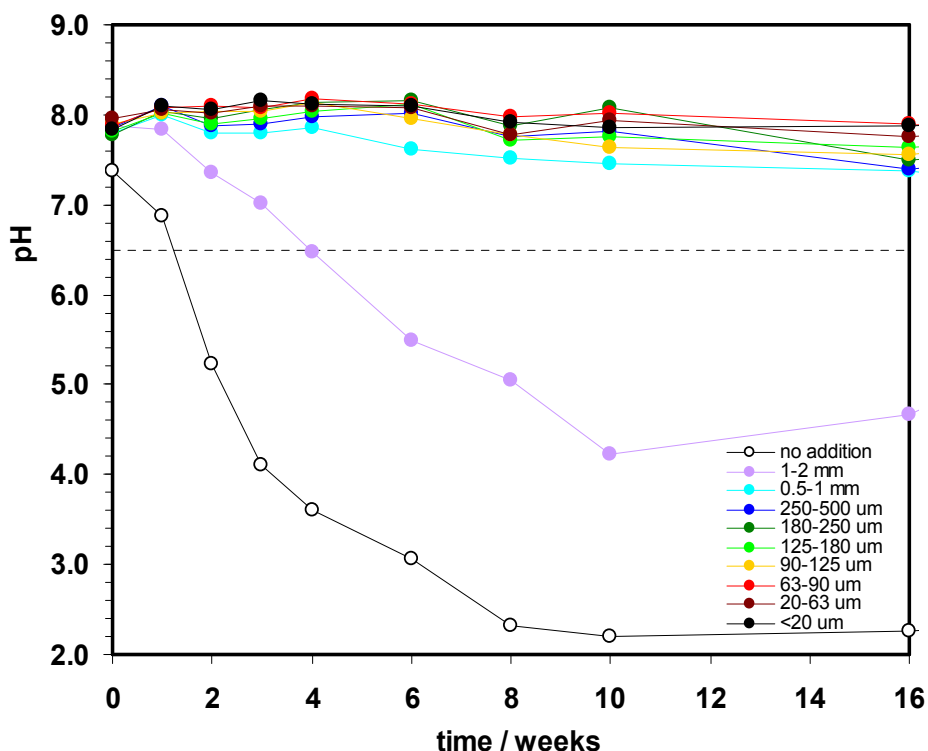


Figure 1. Incubating alkaline sulfidic soil pH data when treated with a range of agricultural lime particle sizes. Each data point represents a duplicate mean.

It can be inferred from these data that, for neutral or alkaline sulfidic material that is subject to oxidation, liming materials need to be <1.0 mm in size in order to effect remediation upon exposure of the soil to oxygen. Of course, this inference needs to be verified for other neutral or alkaline sulfidic materials.

Figure 2 shows the pH incubation data for the partially-oxidised acidic sulfidic Yamba soil. The pH of all limed incubating soil materials with the exception of those where lime in the 1 - 2 mm and 0.5 - 1 mm grades show adequate neutralisation resulting in maintenance of pH >6.5 within 1 week of lime addition. It can be inferred from these data that, for oxidised acidic material with some remaining sulfidic component, liming materials need to be <0.5 mm in size in order to effect remediation. Again, this inference needs to be verified for other acidic sulfidic materials

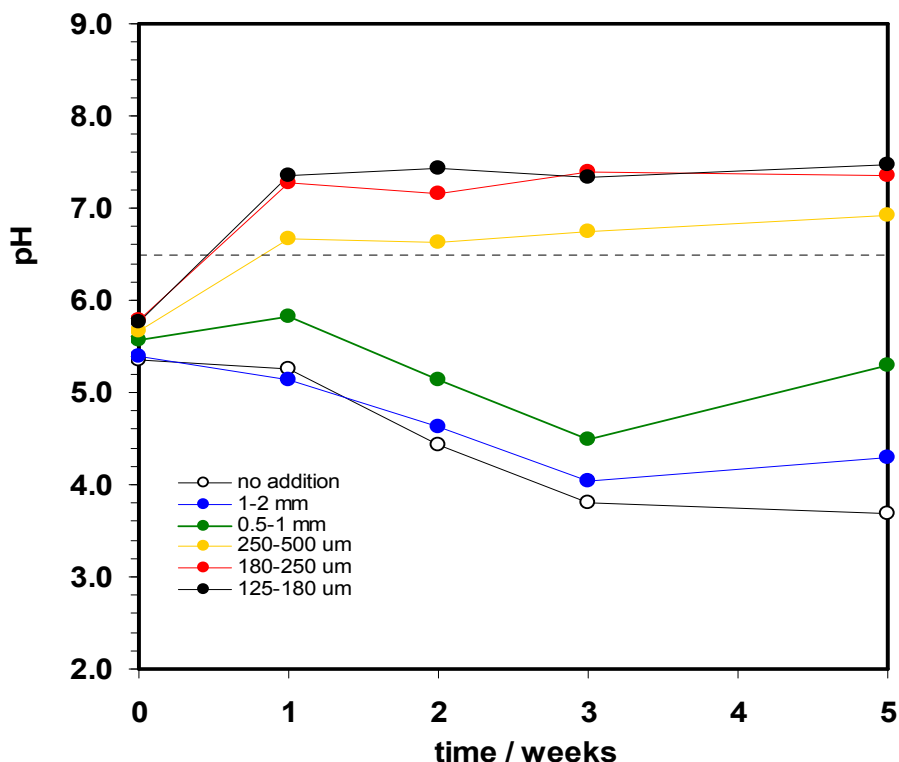


Figure 2. Incubating acidic sulfidic soil pH data when treated with a range of agricultural lime particle sizes. Each data point represents a duplicate mean.

XRD studies of lime powdered to <20 μm showed the mineralogy of the lime to be calcite. Figure 3 presents SEM images of a ball-milled agricultural lime particle and a particle after incubation in an acidic sulfidic soil for 16 weeks. Fine lime particles can be seen adhering to the 1 - 2 mm particle after grinding, but these are removed, presumably by dissolution, after prolonged incubation.

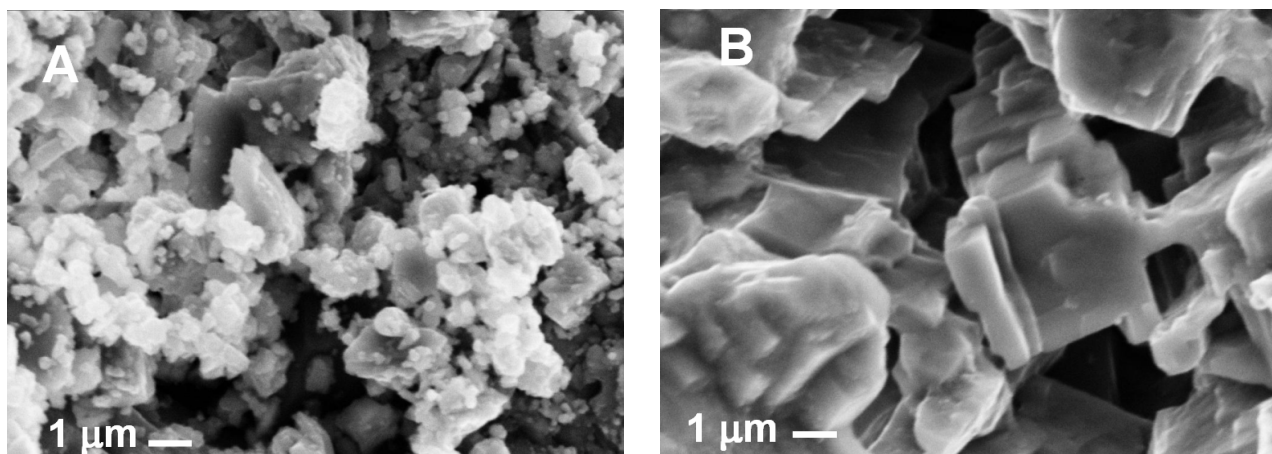


Figure 3. A) SEM image of surface of a sieved 2 mm lime particle showing adherent microparticles; B) surface of effective lime particle after incubation in acid sulfate soil for 16 weeks.

Etching of the calcite is clearly observed as a consequence of incubation in Figure 3B, exposing an internal structure with an apparent rhombohedral habit. The formation of channels within the structure can also be observed.

Lime particles were examined by XPS in order to determine if a passivating surficial layer, e.g. ferric or gypsic precipitate (Soler *et al.* 2008) had formed, which may have prevented further dissolution from the lime particles. A lime particle was selected as a standard from particles subjected to ball mill grinding and sieved to 1 - 2 mm. The sample showed predominantly Ca, C and O with an impurity from Si and Al below the instrumental limit of detection of 1 atom %. Carbonate samples incubated in the sulfidic Tuckean soil were removed after 16 weeks, by which time samples limed with 1 - 2 mm particles had reached a pH of 4.7. This lime grade was considered ineffective as it was unable to neutralise the acidity of the surrounding soil material by raising the pH above 6.5. The soil material limed with 0.5 - 1 mm particles had a pH of 7.4 by 16 weeks and these lime particles were considered effective. Both the effective and ineffective lime particles show similar surface characteristics when observed by XPS. Peaks due to Si, Al and Fe were observed, with a trace of Mg below the quantifiable limit. The presence of surface contamination by nanoparticulate clays was observed during ASEM analysis of the incubated particles. Interference by adherent clay particles would obscure any differences due to the surface coating of the effective and ineffective lime particles as determinable by XPS. In an attempt to overcome clay contamination, incubated samples of effective and ineffective incubated lime particles were further treated with 0.01 M Na₂CO₃ in an attempt to disperse and remove clay particles from the surface. XPS of these samples showed a relative decrease of Si, Al and Fe, while SEM imaging showed an apparent restructuring of the surface. The combination of clay contamination in untreated samples; significant risk of surface layer disruption during restructuring and carbonate precipitation in samples treated with dispersant; and the roughness of the surfaces of the incubated lime particles prevented the unambiguous determination of the presence of a passivation layer on incubated lime materials using XPS. Studies using transmission electron microscopy (TEM) may be of greater benefit.

Conclusion

The data indicates *inter alia* that if acidic sulfidic soil materials require liming, then agricultural lime with particles sized below 0.5 mm can be relied upon to neutralise the acidity that exists and may develop over time scales appropriate to management (i.e. ~1 week). In the case of the treatment of neutral/alkaline sulfidic materials to prevent acidification, the data indicates that agricultural lime below 1.0 mm in particle size would be effective. Verification of this liming behaviour for other sulfidic materials is currently in progress.

Acknowledgements

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