Phosphate Sorption of Calcined Materials Used as Components of Soilless Root Media Characterized in Laboratory Studies

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Abstract. Calcined materials may contribute enhanced phosphate (PO4-P) retention to soilless root media used in container production. Properties of nutrient retention vary greatly depending on the parent clay and calcining treatment. This research characterized PO4-P sorption of various calcined clay products, including low and regular volatile material (LVM and RVM) 2:1 attapulgite, montmorillonite, and illite clays at various particle sizes; 1:1 kaolin clays in powder form; and diatomaceous earth. Extractable PO4-P, initial pH, PO4-P sorption isotherms, amount of P sorbed as a function of solution pH at a fixed total concentration, and degree of phosphorus saturation were determined. Initial pH of the clays ranged from 3.7 to 8.7. Sorption isotherms were conducted with initial adsorbate concentrations ranging from 0 to 200 mg L–1 PO4-P from KH2PO4. The calcined materials varied in their ability to sorb PO4-P and generally yielded L-type isotherms, indicating that the adsorbate had relatively high affinity for the calcined material sample surface at low surface coverage. Some 2:1 calcined clays exhibited substantial PO4-P retention, but 1:1 calcined clays and diatomaceous earth did not. Clays with less moisture (LVM) resulted in greater PO4-P sorption than those calcined at lower temperatures (RVM). Terra Green montmorillonites had higher PO4-P sorption than Terra Green attapulgites. Laboratory results indicated potential for substantive PO4-P retention by several of the calcined clay materials when used in container production. For most materials, PO4-P sorption did not show pronounced pH dependence, which suggests that PO4-P retention is not influenced by pH-dependent charge within the pH range of container production.

Small volumes (2% to 20%) of a variety of calcined clay-type products are being used as components of soilless root media because of their potential to increase nutrient retention, air space, water retention, and bulk density of mixes used for container production in the greenhouse and nursery industries. Properties imparted by these materials are inherited from the parent clay or source, particle size distribution, and calcining process. High calcining temperatures result in expansion of the crushed clay to form a porous structure that is physically and chemically stable. The resulting granules provide aeration to the root medium and hold water internally within their pore structure.

Traditionally, the soil component of root media used for crop production in containers imparted significant PO4-P retention to the root medium. Marconi and Nelson (1984) showed that over 33% of the total P applied was leached from a soilless root medium containing 1 peatmoss:1 vermiculite, but less than 5% was leached from a 1 sand:1 soil:1 peatmoss mix in a simulated plant-watering scheme. This difference, they concluded, was related to differences in P sorption by the various root medium components. Use of soil in container root media has fallen out of favor with commercial producers because it is relatively expensive compared with other components, variable from source to source, and must be pasteurized before use (Nelson, 2005).

Many types of calcined clay amendments may enhance PO4-P and water retention of soilless root media. Incorporation of 13% (by volume) of a calcined clay has been shown to reduce the amount of PO4-P leached from pine bark-based container media by 73% in production of L.oropelatum chinense var. rubrum R. Br. 'Blush' over a 16-week period (Ruter, 2003). Reduction in fertilizer and water use in poinsettia (Euphorbia pulcher-rima Willd. ex Klotzsch) with incorporation of calcined clays has been shown (Catananzaro and Bhatti, 2005; Catananzaro et al., 2004). Owen et al. (2003) found that amending a pine bark root medium with 8% (by volume) calcined clay led to increased nutrient retention and water-buffering capacity in production of container-grown Cotonaster dammeri C.K. Schneider ‘Skoghollm’. A root medium of 3 peat:5 compost:2 Turface (calcined arcilite clay; v/v/v) reduced PO4-P leaching by 70% compared with a control of 3 peat:5 compost:2 sand in production of black-eyed susan, Rudbeckia hirta L. (Bugbee and Eliot, 1998). Because use of calcined clays offers potential to reduce environmental impact from PO4-P leaching during container production, PO4-P retention and other properties of a variety of calcined materials should be characterized.

Clay surfaces bear an electrical charge that is a function of permanent charge, variable charge, and inner and outer surface charge. The resultant particle charge is either created through isomorphic substitution, protonation and deprotonation reactions or partial charge as expressed through the polarity of atoms at the clay surface (Essington, 2004). The silicate minerals present in clays develop a pH-dependent charge at the broken edges of the layer structure, which is a phenomenon that occurs in both 1:1 and 2:1 clay soils (Havlin et al., 2003). Sorption of PO4 by clay minerals has been attributed to a pH-dependent reaction of PO4 with calcium, iron (Fe), and aluminum (Al) in the clay (Havlin et al., 2003). Much of the P adsorption by soils can be attributed to chemisorptions involved in ligand exchange between PO4-P and hydroxyl ions at Fe and Al oxyhydroxides (Parfitt, 1978). pH-dependent PO4-P sorption by calcined clays has not been systematically investigated and it is not clear how the process of calcining changes the PO4-P sorption characteristics of clays.

The commercial calcining process results in low volatile material (LVM) or regular volatile material (RVM) moisture contents, depending on calcining temperatures. Calcining, generally, reduces the amount of water trapped between the clay’s silicate sheets and also produces a very hard granule that, even when fully saturated with water, does not break apart easily. The first stage of calcining, known as fluid bed drying, reduces the clay moisture level from 40% to 45% down to 6% to 9% using temperatures of 120 to 176 °C, resulting in RVM clays. The LVM clays have even lower moisture content of 0% to 3%, which is achieved by secondary calcining at temperatures in the range of 460 to 800 °C (Moll and Goss, 1997). Heating the clays

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causes aggregation of particles that optimizes sorbtivity by creating a stable porous internal structure. Calcining reduces the exchange capacity of the clays, but surface binding and internal pores maintain some nutrient retention capacity. X-ray diffraction studies on a 2:1 Ca-montmorillonite clay showed that heat treatment of 200 to 400 °C completely collapsed the interlayer, incorporating interlayer cations into the tetrahedral or unoccupied octahedral sheets (Bray et al., 1998). Noyan et al. (2006) evaluated the specific surface area, specific micropores volume, total surface acidity, and adsorption equilibrium constant of original and heated samples of a bentonite clay from Turkey. The specific area, micropores volume, and total surface acidity stayed constant as temperature increased to 450 °C and then decreased. Total surface acidity, in general, declined with increasing temperatures. The most acidic sites, however, increased with heating and especially at temperatures of dehydration (100 to 550 °C) and dehydroxylation (550 to 700 °C). Calcining temperatures for maximizing sorbtivity, generally, do not exceed the dehydration interval. Noyan et al. (2006) concluded that the decomposition of the 2:1 layers of the clay and collapsing of micro- and mesopores by intra- and interparticle sintering caused a rapid decrease in specific surface area and specific micropore volume as the temperature increased.

Diatomaceous earth (DE) is not derived from clay, but consists of granules mined from sedimentary rock deposits resulting from accumulation of amorphous silica comprising the cell walls of dead, single-celled organisms called diatoms (Handreck and Black, 2002). The usual commercial function of DE is as an absorbent. Although some commercial growers are using this material as a root medium component, it is not expected to sorb PO₄-P because it lacks charged sorption sites.

Phosphate retention properties of clays after calcining are generally unknown, and the role of pH-dependent edge charge in the PO₄-P retention of calcined materials is untested. In addition, the calcined materials themselves may provide PO₄-P and other nutrients as fertilizer if natural levels are high. Therefore, this research characterizes several calcined clay materials and diatomaceous earth as a basis to evaluate their potential to reduce PO₄-P leached during container production when used as components of soilless root media. Specifically, we 1) determined inherent PO₄-P by extraction and total P present in the mineral; 2) determined initial pH of unaltered samples; 3) characterized PO₄-P sorption at natural pH; 4) developed PO₄-P adsorption envelopes under variable pH conditions to establish the role of pH-dependent edge charge on PO₄-P retention; and 5) determined the initial degree of phosphorus saturation of calcined materials.

Materials and Methods

The tested calcined materials are commercially available (Table 1). The test materials included various particle sizes of 2:1 clays of attapulgite (Attasorb; Engelhard Corp., Quincy, FL) calcined at two temperatures, RVM and LVM; LVM montmorillonite mined in Mississippi and LVM attapulgite mined in Georgia (Terra Green; Oil-Dri Prod. Co., Ripley, MS) and montmorillonite + illite (Turface; Profile Products LLC, Buffalo Grove, IL); calcined 1:1 clays (Thiele Kaolin Co., Sandersville, GA) in powder form; and diatomaceous earth (Diatomite Eagle-Picher Minerals, Inc., Reno, NV). For ease of reference, the test materials were coded using trade name, temperature treatment, and particle size as mesh size designated by the manufacturer (Table 1). The materials were tested as received from the manufacturer.

Particle size distribution. Particle size distribution was determined by dry sieving. The sieving process was carried out using woven analytical precision sieves (USA standard testing sieves, ASTM specification; Fisher Scientific Co., Columbia, MD). Dry test materials were weighed to 1000 g and passed through a stack of eight sieves ranging from 5 mesh (400-µm nominal sieve opening) to 80 mesh (180-µm sieve opening) that were arranged in order of size with the smallest sieve at the bottom of the stack. Samples were uniformly shaken on a circular motion shaker set at 2.2 gₒ for 5 min. Sample recovered in each sieve was weighed and the proportions calculated as a percentage of the whole test sample (Table 2) averaged across three replications.

pH measurements. The pH was measured on a slurry consisting of 5 cm³ test material to 10 mL deionized water. Mixtures were thoroughly stirred and allowed to settle for 10 min before reading pH (Oyster pH meter; Extech Instr. Waltham, MA) at 27 °C. The data were analyzed using PROC GLM in SAS ver. 9.1 (SAS Institute, 2002) with three replicates per material.

Phosphorus extraction. Naturally occurring P present in the calcined materials was

Table 1. Calcined material trade names, sample codes, and descriptions of test materials provided by their sources.

| Trade name          | Volatile material characterization | Mesh size (standard US mesh) | Assigned code  | Test material description                                      |
|---------------------|-----------------------------------|------------------------------|----------------|---------------------------------------------------------------|
| Attasorbᵇ           | LVM                               | 8/16                         | A-LVM-8/16     | 1% to 10% quartz 90% to 99% Fuller’s earthᵇ; is a hydrous magnesium alumina silicate attapulgite; the deposits are on the Mississippi River between Memphis, TN, and Cincinnati, OH. |
| Attasorbᵇ           | RVM                               | 8/16                         | A-RVM-8/16     | Florida–Georgia border                                         |
| Attasorbᵇ           | LVM                               | 24/28                        | A-LVM-24/28    | Florida–Georgia border                                         |
| Attasorbᵇ           | RVM                               | 24/48                        | A-RVM-24/28    | Florida–Georgia border                                         |
| Terra Green attapulgiteᵇ | LVM                               | 24/48                        | T-A-24/28      | 10% to 20% quartz 80% to 90% Fuller’s earthᵇ; from Georgia mines |
| Terra Green attapulgiteᵇ | LVM                               | 16/30                        | T-A-16/30      | 10% to 20% quartz 80% to 90% Fuller’s earthᵇ; from Georgia mines |
| Terra Green attapulgiteᵇ | LVM                               | 5/20                         | T-A-5/20       | 10% to 20% quartz 80% to 90% Fuller’s earthᵇ; from Georgia mines |
| Terra Green montmorilloniteᵇ | LVM                               | 24/48                        | T-M-24/28      | 7% to 10% quartz 90% to 93% montmorillonite; from Mississippi mines |
| Terra Green montmorilloniteᵇ | LVM                               | 16/30                        | T-M-16/30      | 7% to 10% quartz 90% to 93% montmorillonite; from Mississippi mines |
| Terra Green montmorilloniteᵇ | LVM                               | 5/20                         | T-M-5/20       | 7% to 10% quartz 90% to 93% montmorillonite; from Mississippi mines |
| Turfaceᶜ            | Turface                          | Turface                      | Turface        | Product of calcining a smectite clay at temperatures ranging from 540 °C to 1100 °C. |
| Kaolin Hydrousᵇ      | Powder                            | K-Hyd-P                      |                | Hydrous kaolin.                                               |
| Kaorockᶜ            | Powder                            | K-LSA-P                      |                | Low surface area metakaolin.                                  |
| Kaocalᶜ             | Powder                            | K-P                          |                | Full calcined at 980 °C.                                     |
| Kaocal LAᶜ          | Powder                            | K-HSA-P                      |                | High surface area metakaolin calcined at less than 980 °C.    |
| Diatomiteᶜ          | Powder                            |                              |                | Diatomaceous earth consists of fossilized remains of diatoms, typical chemical composition of diatomaceous earth is 86% silica, 5% sodium, 3% magnesium, and 2% iron. |

ᵃLVM = low volatile material; clays calcined at ≈470 °C; RVM = regular volatile material; clays calcined at ≈180 °C.
ᵇTest material description was given in material safety data sheets (MSDS) from source unless stated otherwise.
ᶜEnglehard Corp., Quincy, FL.
ᵈFuller’s earth usually has a high magnesium oxide content. Two varieties of Fuller’s earth are mined, mainly in the southeastern states of the United States. These comprise the minerals montmorillonite or palygorskite (attapulgite) or a mixture of the two; some of the other minerals that may be present in fuller’s earth deposits are calcite, dolomite, and quartz.
ᵉOil-Dri Prod. Co., Ripley, MS.
ᶠProfile Products LLC, Buffalo Grove, IL.
ᵍThiele Kaolin Co., Sandersville, GA.
ʰEagle-Picher Minerals, Inc., Reno, NV.
Table 2. Particle size distribution of the 16 test materials.

| Code*         | Sieve no. | No. 5 | No. 8 | No. 10 | No. 18 | No. 20 | No. 35 | No. 60 | No. 80 |
|---------------|-----------|-------|-------|--------|--------|--------|--------|--------|--------|
| Mesh size     | 4.0 mm    | 2.38 mm | 2.00 mm | 1.00 mm | 0.85 μm | 0.5 μm | 0.25 μm | 0.18 μm |        |
|                | (standard US mesh) | | | | | | | |        |
| Percent by weight* | | | | | | | | |        |
| A-LVM-8/16    | 8/16      | 6     | 39    | 55     | 47     | 52     | 35     | 20     | 15     |
| A-RVM-8/16    | 8/16      | 3     | 40    | 57     | 47     | 52     | 35     | 20     | 15     |
| A-LVM-24/48   | 24/48     | 1     | 73    | 26     | 47     | 52     | 35     | 20     | 15     |
| A-RVM-24/48   | 24/48     | 2     | 71    | 25     | 47     | 52     | 35     | 20     | 15     |
| T-A-24/28     | 24/48     | 1     | 77    | 21     | 0      | 0      | 0      | 0      | 0      |
| T-M-24/28     | 24/48     | 1     | 74    | 18     | 0      | 0      | 0      | 0      | 0      |
| T-A-16/30     | 16/30     | 77    | 11    | 11     | 1      | 0      | 0      | 0      | 0      |
| T-M-16/30     | 16/30     | 44    | 20    | 35     | 1      | 0      | 0      | 0      | 0      |
| T-A-5/20      | 5/20      | 2     | 37    | 17     | 32     | 2      | 8      | 2      | 0      |
| T-M-5/20      | 5/20      | 3     | 52    | 14     | 29     | 1      | 1      | 1      | 0      |
| Turface       | 1         | 42    | 24    | 29     | 4      | 0      | 0      | 0      | 0      |
| K-Hyd-P       | Powder    | 100   | 0     | 0      | 0      | 0      | 0      | 0      | 0      |
| K-LSA-P       | Powder    | 100   | 0     | 0      | 0      | 0      | 0      | 0      | 0      |
| K-P           | Powder    | 100   | 0     | 0      | 0      | 0      | 0      | 0      | 0      |
| K-HSA-P       | Powder    | 100   | 0     | 0      | 0      | 0      | 0      | 0      | 0      |
| Diatomaceous earth | 3   | 84    | 8     | 5      | 0      | 0      | 0      | 0      | 0      |

*LVM = low volatile material; clays calcined at ≈470 °C. RVM = regular volatile material; clays calcined at ≈180 °C.

*Percent by weight of given particle size.

PO₄-P sorption isotherms. To characterize and compare P sorption of the calcined products, sorption isotherms were created for each test material. An amount equal in weight to 5 cm³ of each test material was determined and measured into 50-mL Erlenmeyer flasks. Thirty milliliters of acid extractant consisting of 0.5 N HCl and 0.2 N H₂SO₄ was added. The flasks were placed on a circular motion shaker at 2 g, for 10 h at 26.0 ± 2 °C, and after 10 h, the supernatant was transferred into 50-mL centrifuge tubes and centrifuged at 310 g for 5 min. Solution pH was adjusted by drop-wise addition of 5 M NaOH using p-nitrophenol as the indicator until the color of the sample just changed from colorless to yellow (Bender and Wood, 2000). Phosphate in the supernatant was then analyzed using the colorimetric method of Murphy and Riley (1962) on an ultraviolet/VIS spectrophotometer (Perkin-Elmer, Norwalk, CT). The experimental design was completely random (CRD) and each treatment was replicated three times. The data were analyzed using PROC GLM in SAS ver. 9.1 (SAS Institute, 2002).

Mehlich III (M3) extraction solution contained 0.2 N acetic acid, 0.25 N NH₄NO₃, 0.015 N NH₄F, 0.013 N HNO₃, and 0.001 N EDTA (Sen Tran and Simard, 1993). Mehlich III extractable P (1:5 test material:solution ratio) was analyzed with a Lachat-FIA system (Lachat FIA 800 series, Loveland, CO). The M3 procedure uses a strong acid extractant and estimates available P in acid soils. Two replications of each test material were run.

Finally, total P of the test materials was evaluated by colorimetric procedures following salicylic-sulfuric acid digestion (Bremner and Mulvaney, 1982; U.S. Environmental Protection Agency, 1984). The extract was analyzed by colorimetric procedures using the Technicon Auto Analyzer II (Technicon Industrial Systems, Tarrytown, NY). Two replications of each test material were run.

Regression analysis was performed to elucidate the amount adsorbed and buffer capacities, respectively, at the same point on the curve where C = 1 mg L⁻¹, and this point is the same for all the test materials. In our research, the parameters “a” and “b” were estimated by regression of the logarithmic form of the data obtained from sorption isotherms. Therefore, a plot of log P (y-axis variable) against log C (x-axis variable) yields a straight line with slope b/a and y-intercept of log a.

\[
\log P = \log a - \frac{b}{a} \log C \quad (3)
\]

From the Freundlich equation the parameter, “a” could be considered as a capacity factor and was referred to as P sorption capacity; this implies that a material having a larger “a” value has a larger sorption capacity than one with a smaller “a” value. Therefore, “a” value estimates were used to differentiate the P sorption capacities of calcined materials. The Freundlich equation does not predict or include a maximum adsorption capacity, but it is reliable with low solution P concentrations (Havlin et al., 2003). R values were determined for each Freundlich equation.

Adsorption envelopes. Adsorption envelopes were created to determine the amount of P adsorbed as a function of solution pH at the fixed total P concentration of 600 mg L⁻¹. An amount equal in weight to 5 cm³ volume of eight test materials, A-LVM-8/16, A-RVM-24/28, T-A-24/48, T-M-24/28, T-M-5/20, K-LSA-P, Turface, and Diatomite (Table 1), were equilibrated for 10 h at 25 °C with 25 mL KNO₃, A 2.5-mL aliquot of 600 mg P L⁻¹ from KH₂PO₄ was added and pH adjusted to ranges of 2 to 10 at intervals of one unit using additions of 0.1 M HNO₃ or 0.1 M KOH. Samples were centrifuged as described previously, decanted, filtered, and analyzed for PO₄-P concentration as described previously. The experimental design was CRD with three replications of each treatment. Eight test materials were subjected to nine pH levels.

Degree of phosphorus saturation. Degree of P saturation (DPS) estimates how close the test material is to being saturated with PO₄-P (Sharpley, 1995). The DPS of the calcined materials was determined to compare the level of initial saturation with PO₄-P of each material’s exchange sites. A DPS index (Pote et al., 1999) was created from soil test phosphorus (STP) determined by M3 extraction and a phosphorus sorption index (PSI) calculated from a single point isotherm (Bache and Williams, 1971; Sims et al., 2002). To establish the PSI, 30 mL of a 500
mg L⁻¹ PO₄-P sorbate solution from KH₂PO₄ was added to 5 cm³ of test material, equilibrated on a shaker for 18 h at 25 ± 2 °C, and centrifuged as described previously. Phosphorus was determined as described previously (Murphy and Riley, 1962). The PSI was calculated using the equation:

\[
\text{PSI} = q (\log C)^{-1}
\]

where \( q \) is the amount of P sorbed (mg kg⁻¹) and \( C \) is the equilibrium solution concentration (mg L⁻¹). The second step involved estimating DPS using the ratio of STP to (PSI + STP) and multiplying by 100: DPS = \( \frac{\text{STP}(\text{mg kg}^{-1})}{[\text{PSI} + \text{STP}(\text{mg kg}^{-1})]} \times 100 \).

### Results and Discussion

**Particle size distribution, pH, and bulk density.** Characterization of particle size distribution of the test materials is summarized in Table 2. Results follow U.S. standard mesh sizes.

Attasorb materials were alkaline with pH ranging from 8.2 to 8.7 (Table 3). Terra Green montmorillonites were acidic with pH ranging from 3.8 to 4.3, whereas Terra Green attapulgites were less acidic with pH ranging from 5.6 to 6.2. Turface and diatomite had pH values of 6.1 and 5.1, respectively (Table 3). The various calcined materials exhibited a wide range of pH. It is important for a grower to be aware of the pH levels that root medium components contribute to a mix because they may influence nutrient retention and management during production.

Calcinated materials have lower bulk density (less than 1 g cm⁻³) compared with most mineral soils, which have bulk densities between 1 and 2 g cm⁻³ (Hillel, 2004). Lower bulk densities after calcining indicate increased porosity of the test material. Compared with Attasorb and Terra Green materials, DE exhibited greater porosity (Table 3). Compared with clay soils, the granular test materials have the advantage of adding stable pore space to soilless root media, which contributes to beneficial physical properties in container production.

**Phosphorus content of calcined materials.** Total native P present in the materials was relatively high in the Attasorb and Terra Green attapulgites (700 to 2800 mg kg⁻¹; Table 3). This significant amount of PO₄-P may provide some P fertilizer during production and/or remain in the container after the production cycle concludes. Kaolin test materials contained between 580 and 670 mg kg⁻¹ P, whereas diatomite and Terra Green montmorillonite had the least native P at between 250 and 370 mg kg⁻¹ P (Table 3). High levels of native P in the calcined materials might be expected to reduce PO₄-P sorption capacity.

Phosphorus was extracted from the test materials using two procedures, an acid extraction and the M3 test, which was developed in North Carolina for routine analysis of P, potassium, calcium, magnesium, sodium, and micronutrients in acid soils. The two extraction methods yielded substantially different P contents (Table 3). Different chemical extractants are designed for soils depending on their chemical characteristics. Attapulgite test materials from two sources, which have pH ranging from 5.6 to 8.7, resulted in greater P extracted by 0.5 N HCl + 0.2 N H₂SO₄ than the M3 procedure, but the opposite was true for kaolinite test materials, which had pH of 4.5 to 5.3. The evolution of carbon dioxide during acid extraction of the Attasorb materials indicated a possible presence of free CaCO₃, which, in combination with the higher pH, suggested that the M3 test is not ideal for these calcareous clays. Results of the M3 test showed the influence of particle size on available PO₄-P with smaller sizes of the same material yielding more PO₄-P. Kaolinite materials KLSA-P and K-P yielded the most PO₄-P, 460 and 116 mg kg⁻¹ PO₄-P, respectively, from the M3 procedure. Attasorb RVM materials yielded more available PO₄-P compared with LVM materials (45 to 92 mg kg⁻¹ P and 6 to 14 mg kg⁻¹ P, respectively).

**PO₄-P isotherms.** The isotherms, which are L-type according to classification of sorption isotherms by shape, indicate molecular adsorption of PO₄-P (Figs. 1A, 2A, 3A).

### Table 3. Bulk density, pH, amount of P extracted from test materials from three different extraction procedures, degree of phosphorus saturation, P sorption index, and P sorption capacity, and buffer capacity calculated from the modified Freundlich equation.

| Test material code name | pH¹ | Bulk density (g cm⁻³) | Total P² (mg kg⁻¹) | P³ (mg kg⁻¹) | P⁴ (mg kg⁻¹) | Degree of phosphorus saturation (DPS; %)⁵ | P sorption index (PSI)⁶ (q² log C⁻¹) | Amount adsorbed (P sorption capacity) "a"⁷ (g m⁻³) | Buffer capacity "b" (L m⁻³)²⁸ |
|-------------------------|-----|----------------------|--------------------|-------------|-------------|-----------------------------------------|-------------------------------------|--------------------------------------|-------------------------------|
| A-LVM-24/48             | 8.4 | 0.75                 | 1.076 ± 198        | 306         | 14 ± 0.5    | 0.9                                      | 1.476                               | 495                                  | 241                           |
| A-RVM-24/28             | 8.5 | 0.76                 | 737 ± 156          | 534         | 92 ± 0.5    | 6.8                                      | 1.265                               | 230                                  | 106                           |
| A-LVM-8/16              | 8.2 | 0.76                 | 2.790 ± 147        | 231         | 6.5 ± 0.5   | 0.4                                      | 1.231                               | 320                                  | 150                           |
| A-RVM-8/16              | 8.7 | 0.80                 | 1.770 ± 14         | 146         | 45 ± 0.5    | 3.8                                      | 1.140                               | 220                                  | 102                           |
| A-LVM-5/25              | 8.4 | 0.76                 | 1.227 ± 150        | 245         | 20 ± 0.5    | 1.4                                      | 1.354                               | —                                    | —                             |
| T-A-24/28               | 5.7 | 0.58                 | 1.739 ± 212        | 166         | 70 ± 0.5    | 7.2                                      | 0.893                               | 210                                  | 97                            |
| T-A-16/30               | 5.6 | 0.52                 | 1.560 ± 97         | 250         | 34 ± 0.5    | 2.9                                      | 1.130                               | 240                                  | 103                           |
| T-A-5/20                | 6.2 | 0.67                 | 1.947 ± 88         | 60          | 39 ± 0.5    | 3.2                                      | 1.156                               | 250                                  | 114                           |
| T-M-24/28               | 4.3 | 0.72                 | 377 ± 11           | 37          | 107 ± 2.0   | 7.7                                      | 1.285                               | 425                                  | 202                           |
| T-M-16/30               | 4.0 | 0.71                 | 263 ± 31           | 19          | 65 ± 2.0    | 4.0                                      | 1.556                               | 590                                  | 295                           |
| T-M-5/20                | 3.8 | 0.77                 | 351 ± 21           | 78          | 35 ± 3.5    | 1.8                                      | 1.838                               | 700                                  | 357                           |
| Turface                 | 6.1 | 0.22                 | 345 ± 22           | 22          | 27 ± 3.0    | 4.1                                      | 0.637                               | 115                                  | 48                            |
| K-Hyd-P                 | 4.2 | 0.19                 | 264 ± 40           | 0.1         | 4 ± 0.0     | 0.5                                      | 0.736                               | 100                                  | 36                            |
| K-LSA-P                 | 4.6 | 0.15                 | 656 ± 17           | 47          | 460 ± 20    | 27.7                                     | 1.199                               | 120                                  | 48                            |
| K-P                     | 5.3 | 0.12                 | 652 ± 15           | 7           | 116 ± 0.5   | 13.9                                     | 0.725                               | 70                                   | 25                            |
| K-HSA-P                 | 4.5 | 0.26                 | 581 ± 21           | 23          | 93 ± 1.0    | 4.8                                      | 1.832                               | 130                                  | 53                            |
| Diatomite               | 5.1 | 0.37                 | 259 ± 52           | 34          | 24 ± 3.0    | 4.8                                      | 0.475                               | 28                                   | 10                            |
| Diatomite (calcined)    | 5.4 | 0.34                 | 179 ± 4            | 28          | 20 ± 1.5    | 4.7                                      | 0.398                               | —                                    | —                             |

¹PH measurements were taken on 1:2 (v/v) test material:deionized water.

²From salicylic-sulphuric acid digest.

³Mean ± SE (n = 2).

⁴From extract with 0.5 N HCl and 0.2 N H₂SO₄. Data are means of three replications; se = 12.7.

⁵From Mehlich III extraction procedure.

⁶Degree of phosphorus saturation (DPS) estimated from PSI and Mehlich III P.

⁷From calculated from a single-point isotherm based on 500 mg L⁻¹ PO₄-P concentration.

⁸From modified Freundlich model; "a" value estimates buffer power defined by the slope of the sorption curve at the point where quantity of sorbate (P)/equilibrium solution concentration (C) = 1 L⁻¹ mg⁻¹.

⁹LSD = least significant difference. Differences between means greater than the LSD indicate significant differences at \( P < 0.05 \). Different letters indicate statistically significant differences.
Green attapulgites had lower PO₄-P sorption, whereas the product mined in Georgia versus Mississippi. The materials indicated differences in the clays manufactured of the Terra Green calcined clay (Sud-chemie, Meigs, GA) on PO₄-P sorption with initial pH ranging from 5.6 to 6.2 (Table 3). The high PO₄-P sorption under lower pH could have involved the dissolution of Al in the clay lattice in the formation of AlPO₄ crystals. In acidic solutions, the mineral surface has a net (+) charge, although both (+) and (–) sites exist. The predominance of (+) charges readily attracts H₂PO₄⁻, which explained the lack of effect of particle size on PO₄-P sorption. The LVM materials had a tendency to disintegrate into smaller particles when in solution compared with the LVM materials; therefore, the difference between the eventual surface area of RVM clay particles was not as great, which explained the lack of effect of particle size on PO₄-P sorption. The LVM materials demonstrated better aggregate stability than RVM materials and would be preferred for use as soilless root medium components. Owen et al. (2007) compared the use of two temperature treatments (RVM and LVM) of a Georgian palygorskite–bentonite calcined clay at 8% by volume of a bark-based root medium; the mix with LVM clay leached 35% less PO₄-P than the mix containing RVM clay.

The Terra Green attapulgites that originated from Georgia, T-A-5/20, T-A-16/40, and T-A-24/48, resulted in PO₄-P sorption capacity, “a”, of 250, 240 and 210 g·m⁻³, respectively, showing no influence across these particle sizes on amount of PO₄-P sorbed (Table 3). Ruter (2003) investigated the influence of three particle sizes of calcined clay (Sud-chemie, Meigs, GA) on PO₄-P retention. He concluded that particle size had limited influence on amount of PO₄-P sorbed when particle sizes were greater than 3.36 mm and less than 1.00 mm (24/48 US mesh) and within the range of 1.00 to 3.36 mm (5/20 and 16/30 US mesh), 61%, 76%, and 74% reduction of PO₄ leached occurred, respectively.

The slopes of the isotherms are indicators of buffer capacity with steeper slopes indicating higher buffering capacity (Ozanne and Shaw, 1968). Such plots can be used to estimate the quantity of P to be applied to maintain the soil solution concentration at the desired level (Fox and Kamprath, 1970). Material with high PO₄-P sorption like Terra Green montmorillonites continued to sorb PO₄-P at even the highest levels of added PO₄-P (200 mg·L⁻¹; Fig. 1A). The higher PO₄-P buffer capacity of these materials would necessitate greater P addition to achieve 0.2 mg·L⁻¹ soluble PO₄-P, which is considered optimum for most plants (Beckwith, 1970). Material with high PO₄-P sorption like Terra Green montmorillonites continued to sorb PO₄-P at even the highest levels of added PO₄-P (200 mg·L⁻¹; Fig. 1A). The higher PO₄-P buffer capacity of these materials would necessitate greater P addition to achieve 0.2 mg·L⁻¹ soluble PO₄-P, which is considered optimum for most plants (Beckwith, 1970).
Fig. 5. Adsorption envelopes of PO₄-P in suspensions containing 50 PO₄-P mg L⁻¹ in 0.01 M KNO₃ solution for the various test materials (A–B). Sorption is expressed as the fraction of the average PO₄-P adsorbed (mg kg⁻¹) and maximum total PO₄-P concentration (mg kg⁻¹).

Adsorption envelopes. The Attasorb RVM material sorbed more PO₄-P with increasing pH with 0% sorbed at pH 2 to 3 and up to >90% sorbed at pH 10; ≈40% to 60% was sorbed at a pH range of 5 to 8 (Fig. 5B). The Attasorb LVM material, on the other hand, had 60% to 80% sorption over the pH range of 2 to 10, and the fraction generally increased as pH increased (Fig. 5B). The LVM materials (A-LVM-8/16, T-A-24/28) compared with an RVM material (A-RVM-24/28) showed yet another desirable characteristic of pH stability: sorption increased with increasing pH up to 6, and no significant change in PO₄-P sorption was observed from pH 6 to 9. Three possible mechanisms are proposed to explain the increasing PO₄-P sorption with increasing pH exhibited by Attasorb: precipitation of Ca phosphates, Ca-induced P sorption, or coadsorption of Ca and H₂PO₄⁻ as ion pairs or complexes (Essington, 2004).

Terra Green montmorillonite of 5/20 mesh had a stable, high PO₄-P sorption of 98% over the entire pH range, whereas the smaller particle size of this material, 24/28 mesh, had a higher sorption fraction of 85% to 90% between pH 2 and 8 with a sharp decrease in sorption after pH 8 to approximately only 20% PO₄-P sorption at pH 10 (Fig. 5B).

Surface area metakaolin (K-LSA-P) had a high PO₄-P sorption of 98% at pH 2 and 3, which decreased with increasing pH to 40% PO₄-P adsorbd at pH 10 (Fig. 5A).

The adsorption envelopes indicate that pH-dependent charge of the calcined materials is not a critical mechanism of PO₄-P sorption in greenhouse production. Laboratory results from various calcined clays demonstrate that the mechanism by which PO₄-P attaches to the surface of a calcined material is generally not pH-dependent within the pH range of 5.0 to 7.0 maintained during container production.

Degree of phosphorus saturation. The DPS was calculated using the ratio of M₃ PO₄-P to the experimentally determined PSI (Bache and Williams, 1971; Pote et al., 1999; Sims et al., 2002; Table 3). The DPS of the calcined materials generally suggested that they possess significant capacity to sorb PO₄-P with DPS less than 7.7% for all materials except two of the 1:1 kaolinites (Table 3). The low STP and high PSI values associated with several of the calcined materials, namely Attasorb LVM and Terra Green attapulgites and montmorillonites, suggest that a large quantity of vacant sites exist for PO₄-P sorption.

In summary, several of the calcined materials that we characterized could be used as a component of soilless media to decrease PO₄-P leaching. Results of isotherm and DPS calculations indicated that the most promising materials were Terra Green montmorillonites and attapulgites and Attasorb LVM attapulgites. The least promising materials were diatomaceous earth and kaolinites. The PO₄-P adsorption envelopes indicated that PO₄-P sorption was not strongly pH-dependent within the pH range of commercial production, indicating that pH-dependent charge is not a critical means of PO₄-P retention during greenhouse production. Calcining temperature affected optimal PO₄-P sorption: LVM attapulgites had better sorption than the RVM attapulgites that were calcined at lower temperatures, but Surfáce, which is also a 2:1 clay and calcined at a very high temperature, did not match the PO₄-P sorption of LVM attapulgites. Finally, the high level of native total P in some of the materials may provide some PO₄-P as fertilizer to crops.

Benefits of using calcined materials beyond PO₄-P retention may include increased water retention because the calcined products have significant moisture sorption properties, which are related to their primary commercial use as absorbents. The temperatures of calcining are crucial in determining the extent to which the hardened aggregates maintain internal porosity.

Limitations of using calcined products as soilless root medium components include the high cost of purchase and shipping, especially if used at high enough percentages in soilless root media to impart adequate benefit such as buffering against pH drift. Because the materials are mined, natural variability occurs at different mines and even mining depths within the same mine; this would contribute to lack of uniform and consistent quality attributes in the materials. Finally, if calcined materials with very high PO₄-P sorption capacity are used, the materials themselves may remove PO₄-P from root medium solution when used in tandem with very low rates of PO₄-P fertilization.

Future research should investigate optimal percentages of incorporation of calcined products into soilless media, especially under conditions of greenhouse production. The mechanism of PO₄-P sorption by the calcined materials is ambiguous and further research could elucidate these mechanisms. Phosphate desorption of the materials should be further evaluated. Finally, the economic benefits of reduced PO₄-P runoff in greenhouse effluent and reduced water use during production should be evaluated to help growers make decisions about using calcined materials.

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