



# Natural organic matter and the formation of calcium-silicate-hydrates in lime-stabilized smectites: A thermal analysis study

Omar R. Harvey<sup>a,\*</sup>, John P. Harris<sup>b</sup>, Bruce E. Herbert<sup>c</sup>, Eric A. Stiffler<sup>c</sup>, Stephen P. Haney<sup>c</sup>

<sup>a</sup> Water Management and Hydrological Sciences, Texas A & M University, 3408 TAMU, College Station, TX 77843-3408, United States

<sup>b</sup> Texas Transportation Institute, Texas A & M University, 3135 TAMU, College Station, TX 77843-3135, United States

<sup>c</sup> Department of Geology and Geophysics, Texas A & M University, 3115 TAMU, College Station, TX 77843-3115, United States

## ARTICLE INFO

### Article history:

Received 8 February 2010

Received in revised form 30 March 2010

Accepted 2 April 2010

Available online 10 April 2010

### Keywords:

Calcium-silicate-hydrates

Differential scanning calorimetry

Soil stabilization

Pozzolanic reactions

Organic matter

Smectites

## ABSTRACT

Processes accounting for the negative effects of soil organic matter on strength development in lime-stabilized soils are not clearly understood. We used heat-flow differential scanning calorimetry and thermogravimetry to elucidate how natural organic matter (NOM) content and source influences the formation of calcium-silicate-hydrates (CSHs) in lime-stabilized smectites. The formation of CSH was strongly correlated with strength ( $r \geq 0.95$ ) and decreased with increasing NOM content indicating that organic matter influenced strength development in lime-stabilized soils largely by inhibiting the formation of pozzolanic reaction products such as the CSHs. The degree of inhibition was also dependent on the type of pozzolanic reaction product and the NOM source. For example, the formation of CSH2 was less inhibited by NOM, than was the formation of CSH1. Inhibitory effects of NOM sources followed the order fulvic acid > humic acid > lignite and could be explained by considering their acid–base properties.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Long-term strength development in lime- or cement-stabilized soils is attributed to the formation of pozzolanic reaction products. One major class of pozzolanic product formed in stabilized soils is the calcium-silicate-hydrates (CSHs) which are typically designated as CSH gel, CSH1 or CSH2. CSH gel is amorphous, while CSH1 and CSH2 are poorly crystalline with Ca:Si ratio close to 1 and 2, respectively [1]. Formation of CSH compounds in lime–soil systems occurs via a dissolution–precipitation mechanism [2]. In the dissolution phase the high (>12) pH environment, created by the addition of the lime to the soil, results in incongruent dissolution of silica from silicate bearing soil minerals (e.g. clays and quartz) and congruent dissolution of more soluble Si-bearing minerals such as microcrystalline opal. In the precipitation phase the dissolved silica reacts with free calcium (from soil solution or dissolved lime) to form the CSH precipitate; which increases soil strength through cementation of soil particles.

Perturbation in either the dissolution or precipitation phase of CSH formation is likely to have significant impacts on the stabilization of soils with lime or cement. Although the effects of lime/cement addition on soil properties have been widely studied, very little direct information is available on the influence of soil

properties on the formation/activity of pozzolanic reaction products such as CSH. For example, addition of lime or cement to soils containing organic matter is known to result in much lower relative strength gains than a soil with little or no organic matter [3–6]. However, it is unclear whether the negative impact of organic matter on lime/cement stabilization is due to inhibition of pozzolanic reaction product formation or inhibition of its cementation activity. Addressing such fundamental questions are paramount to the elucidation of mechanisms influencing pozzolanic product formation/activity in lime or cement-stabilized soil systems and potential implications for project design and mitigation efforts in both engineering and environmental applications (e.g. highway construction and waste solidification). Recent studies [6,7] have also highlighted the need for more research on understanding the fundamental mechanisms contributing to changes in the geotechnical properties of stabilized organic soils.

Investigation of the influence of soil characteristics on CSH formation in lime/cement-stabilized soils can be operationally constrained by both the nature and quantity of CSH in the system. For example, the poorly crystalline nature of CSH phases formed in soils make them difficult to study by crystallographic techniques such as X-ray diffraction. Characterizing CSH formation using XRD requires hydrothermal incubation conditions and/or sample incubation periods on the order of several months to years [1,2,8]. Considering that assessments of stabilization are typically conducted within days or weeks of treatment and environmental temperatures are typically <40 °C, such an approach would be

\* Corresponding author. Tel.: +1 979 739 2220; fax: +1 979 845 1272.  
E-mail address: [orharvey@tamu.edu](mailto:orharvey@tamu.edu) (O.R. Harvey).

impractical. Thermal analysis is widely used in the identification of new phases formed in lime- or cement-stabilized soils and has been used to identify CSH in lime/cement-stabilized systems [1,8–10]. To our knowledge, no previous study has applied thermal analysis to the investigation of the influence that perturbants may have on pozzolanic activity in either lime- or cement-stabilized soils.

In this study, heat-flow differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis were used to investigate CSH formation/activity in lime-stabilized smectitic soils containing natural organic matter. Objectives were (i) to determine how organic matter influenced CSH formation/activity and subsequently lime stabilization of soils and (ii) to evaluate the influence of different types of organic matter on CSH formation/activity in lime-stabilized soils. The study was part of a larger research effort to elucidate the mechanisms of interaction of soil organic matter in lime-stabilized soils and to develop effective strategies to mitigate the negative impact of organic matter on soil stabilization. We postulated that if organic matter influenced lime stabilization via inhibition of pozzolanic product formation, then formation of CSH should decrease with increasing organic matter content. On the other hand, if organic matter influenced lime stabilization via inhibition of soil cementation then CSH formation should be similar, irrespective of organic matter source or content.

## 2. Materials and methods

### 2.1. Soils, lime and natural organic matter

We used model soils comprising 60.0% quartz sand and 40.0% smectitic clay, by weight. Two model soils were used: one containing a Gonzales clay (Southern Clay Products, Gonzales, TX) and the other a Panther Creek clay (Ward Natural Science, Rochester, NY). X-ray diffraction confirmed both clays to be smectites (to be discussed later). The clays were described by the suppliers as a Ca-bentonite and Na-montmorillonite, respectively and were selected to represent smectitic soil with different mineralogies. For simplicity, the model soils were referred to as GB and PCM for Gonzalez bentonite and Panther Creek montmorillonite, respectively. Clays were obtained as fine powders and were used as received. Cation exchange capacity of the GB clay was  $81 \text{ cmol kg}^{-1}$  and that of the PCM clay was  $93 \text{ cmol kg}^{-1}$ . The quartz sand used was a silica sand (AGSCO Corp., Wheeling, IL). The lime used was a hydrated lime ( $\text{CaOH}_2$ ; Fisher Scientific, Pittsburg, PA). Organic matter from four sources was used: (i) a commercial humic acid (cHA; MP Biomedical, Solon, OH); soil humic acid (sHA); soil fulvic acid (sFA) and lignite. The cHA was used as received while the sHA and sFA were extracted from a local surface soil (Gladewater series; very-fine, smectitic, thermic Chromic Epiaquerts) and purified according to techniques described in Tan [11]. The lignite was received as large clods from a local mine site (Rockdale, TX) and prior to using, was grounded to pass through a  $63 \mu\text{m}$  sieve.

### 2.2. Paste experiments

Two sets of paste experiments were conducted. The first set of paste experiments was conducted primarily to elucidate qualitative changes in lime–soil reaction products as a function of lime content in the absence of organic matter. In these experiments, 1:1 solid:solution pastes were incubated (100% humidity;  $23^\circ\text{C}$  for 10 days) in a walk-in environmental chamber (SureTemp, Raleigh, NC). Besides being kept in storage containers, to prevent samples getting wet, no attempt was made to actively prevent carbonation of samples during incubation. Pastes contained: 10 g model soil; 0–20% hydrated lime; and an equivalent mass of de-ionized water. The second set of the paste experiments was conducted to eval-

uate the effect of different sources of natural organic matter on lime–clay reactions. The composition of the pastes in these experiments were 10.0 g model soil; 8.0% or 12.0% hydrated lime for the GB and PCM, respectively; 0–5.0% natural organic matter; and an equivalent mass of de-ionized water. Incubation temperature and humidity conditions were the same as in the first set of paste experiments, but incubation times were 28 days rather than 10 days.

Following incubation the pastes were flash frozen using liquid nitrogen (to inhibit further reaction), freeze dried, lightly crushed and sieved through a  $63 \mu\text{m}$  sieve. Mineralogical composition of the  $<63 \mu\text{m}$  fraction was assessed using X-ray diffraction (XRD), DSC and TG/DTG. For XRD analysis (Bruker D8 X-ray diffractometer; Bruker, Madison, WI), samples were mounted as dry powders and scanned over the  $4\text{--}70 2\theta$  range. For DSC and TG/DTG analysis (SDT Q600, TA instruments, New Castle, DE), approximately 20 mg of  $<63 \mu\text{m}$  fraction of each paste were placed in a ceramic sample crucible and analyzed between 50 and  $1000^\circ\text{C}$  at a ramping rate  $10^\circ\text{C min}^{-1}$ .

### 2.3. Core experiments

Cylindrical samples, 5 cm high and 3.3 cm in diameter, of model soil–lime–organic matter mixtures were molded using the Harvard miniature apparatus (Humboldt, Norridge, IL). Each molded sample contained 60% sand, 40% clay, 6% lime, 0–5% cHA and 22.5% moisture content by weight and was packed to a dry bulk density of  $1.63 \text{ g cm}^{-3}$ . Molded samples were incubated at 100% humidity and  $23^\circ\text{C}$  for 3, 7, 10, 14 and 28 days. For a given incubation period, samples were molded in triplicates for each of the 4 cHA contents resulting in a total of 24 (4 cHA content  $\times$  2 clay types  $\times$  3 replicates) samples per incubation period.

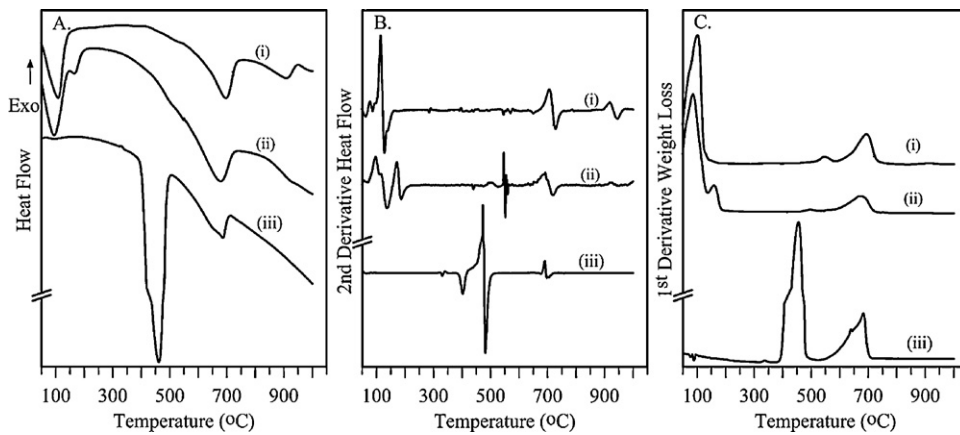
Following incubation, the unconfined compressive strengths (UCS) of the molded samples were measured (Instron Universal Testing System, model 5583, Norwood, MA), dried at  $70^\circ\text{C}$  for 24 h, lightly crushed and sieved through a  $63 \mu\text{m}$  sieve. About 40 mg of the  $\leq 63 \mu\text{m}$  fraction was then analyzed by DSC and TG/DTG as described earlier.

## 3. Results and discussion

### 3.1. Lime–soil reactions in organic matter-free conditions

Thermograms for GB, PCM and hydrated lime starting materials are shown in Fig. 1 and those for the 10 days incubated lime–soil pastes are shown in Fig. 2. Comparison of the thermograms in the two figures showed several common, as well as distinct, features. Endothermic heat flow and associated weight loss observed at  $50\text{--}200$  and  $>300^\circ\text{C}$  in both the clays (Fig. 1) and incubated pastes (Fig. 2) are attributable to dehydration and dehydroxylation of clay [12], respectively. Additional endothermic heat flow and associated weight loss in the lime starting material and pastes were attributable to dehydration/dehydroxylation of the  $\text{CaOH}_2$  ( $350\text{--}500^\circ\text{C}$ ) and degradation of  $\text{CaCO}_3$  ( $500\text{--}700^\circ\text{C}$ ). The presence of  $\text{CaCO}_3$  in the starting material and incubated pastes is indicative of carbonation. The weight loss associated with  $\text{CaCO}_3$  impurity in the starting material was 4.2%. Detectable carbonation in incubated lime–soil paste was only apparent in samples containing  $>8\%$  lime (for PCM) and  $>12\%$  lime for the GB samples. This coincided with the occurrence of unconsumed lime (as evidenced by the  $350\text{--}500^\circ\text{C}$  endotherm in these samples) and was consistent with previous work which found that  $\text{CaCO}_3$  often form as a result of the reaction of  $\text{CO}_2$  with lime in lime-stabilized soils [8,13,14].

In addition to carbonation reactions, difference in the hydration characteristics of the clays (Fig. 1), changes in hydration character-

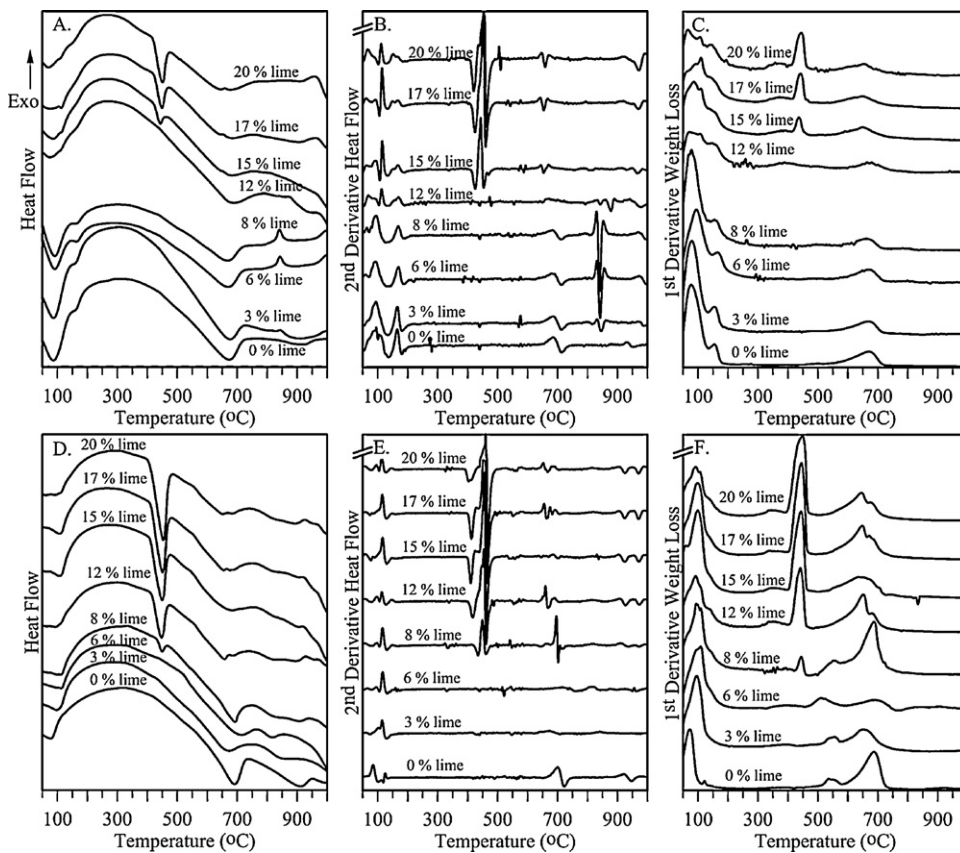


**Fig. 1.** (A and B) Differential scanning calorimetry and (C) derivative thermogravimetry thermograms of (i) Panther Creek montmorillonite, (ii) Gonzalez bentonite, and (iii) hydrated lime starting materials.

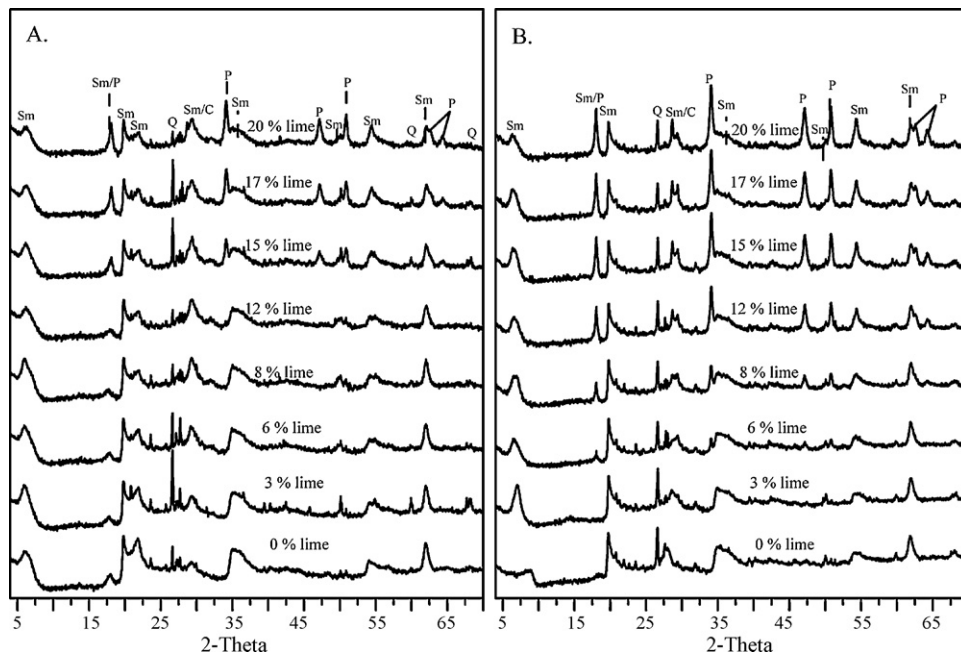
istics with lime content and formation of new reaction products in the lime–soil paste were also apparent (Fig. 2). Differences in the thermal behavior of the clays are attributable to differences in the dominant exchangeable cations and their respective hydration characteristics. For example, the endothermic peak at approximately 170 °C in the GB starting material (not observed in the PCM starting material) is consistent with the loss of water from the hydration sphere of  $\text{Ca}^{2+}$  [15]. Increasing lime content in the lime–soil paste also resulted in the broadening of the dehydration region to higher temperatures (Fig. 2).

For GB pastes containing  $\geq 12\%$  lime, and PCM pastes containing  $\geq 6\%$  an additional weight loss (dehydration) peak around 150 °C were also apparent. These peaks were not observed in the starting

materials and were more clearly revealed upon second derivative analysis (Fig. 2B and E). Coincident with the occurrence of the 150 °C dehydration peak was a doublet of exothermic peaks, occurring in the 800–900 °C range for the 12% lime GB paste and the 900–1000 °C range for GB and PCM pastes containing  $>12\%$  and  $\geq 6\%$  lime, respectively (Fig. 2B and E). The presence of these peaks in the lime paste (and absence from the starting materials) was indicative of the formation of new reaction products. Earlier studies [8–10,16] of lime–clay systems have attributed the occurrence of water loss peaks around 120–160 °C to the dehydration of CSH and exothermic peaks in the 900–1000 °C range to the recrystallization of CSH<sub>2</sub>. In our study, the exothermic nature and the absence of any weight loss associated with the 900–1000 °C peaks



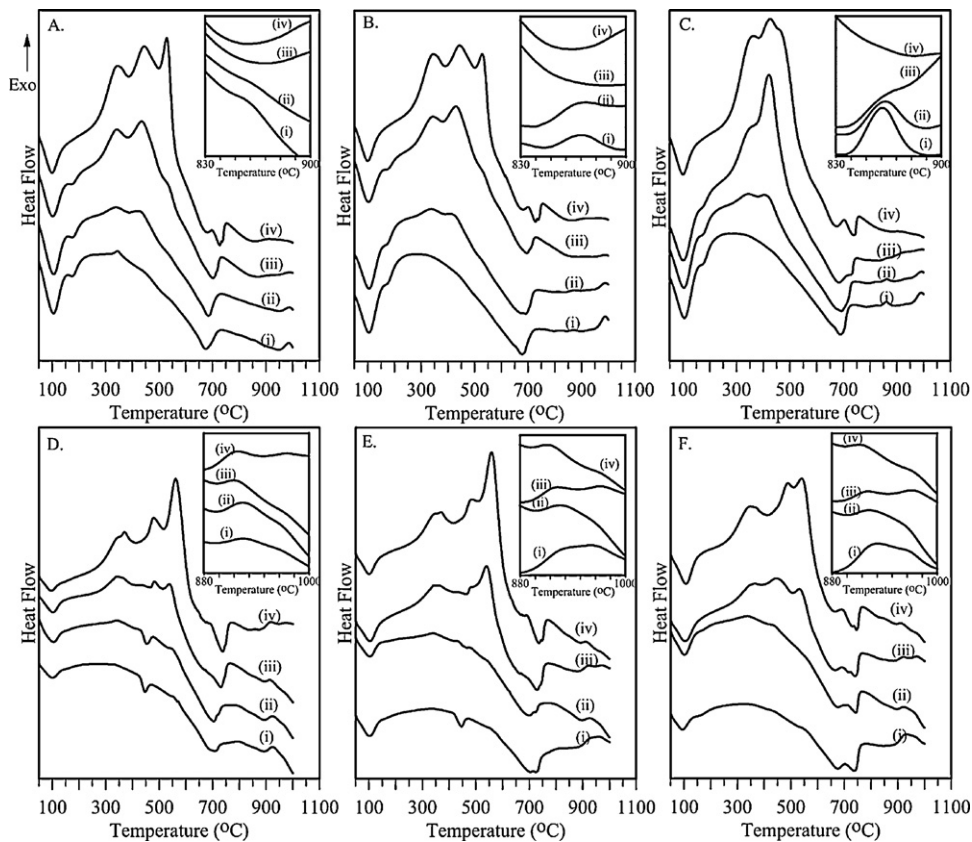
**Fig. 2.** (A, B, D and E) Differential scanning calorimetry and (C and F) derivative thermogravimetry thermograms of 10-day incubated (A–C) Panther Creek montmorillonite and (D–F) Gonzales bentonite pastes containing different amounts of hydrated lime.



**Fig. 3.** X-ray diffractograms of 10-day incubated 1:1 soil:water (A) Gonzales bentonite, and (B) Panther Creek montmorillonite pastes containing 0–20% hydrated lime. Peaks indicate the presence of smectite (Sm),  $\text{CaOH}_2$ -portlandite (P), quartz (Q) and possibly calcite (C).

observed in our study were consistent with such recrystallization reactions [12]. Additional weight loss in the 300–350 °C range for these GB and PCM samples (Fig. 2C and F) provided further evidence for CSH<sub>2</sub> formation [8]. Glenn [8] suggested that the occurrence of the additional weight loss in the 300–350 °C range was useful in dis-

tinguishing CSH<sub>2</sub> from CSH<sub>1</sub> (which showed no such weight loss). However, we found that designation of the 150 °C peak to the sole dehydration of CSH<sub>1</sub> was difficult since dehydration of interlayer and associated hydrated cations (such as  $\text{Ca}^{2+}$ ) occurs in the same region.



**Fig. 4.** Thermograms of molded (A–C) Gonzalez bentonite and (D–F) Panther Creek montmorillonite samples containing six percent hydrated lime plus (i) 0%, (ii) 0.5%, (iii) 2% or (iv) 5% commercial humic acid. Samples were incubated at 100% humidity and 23 °C for (A and D) 3 days, (B and E) 7 days or (C and F) 28 days.

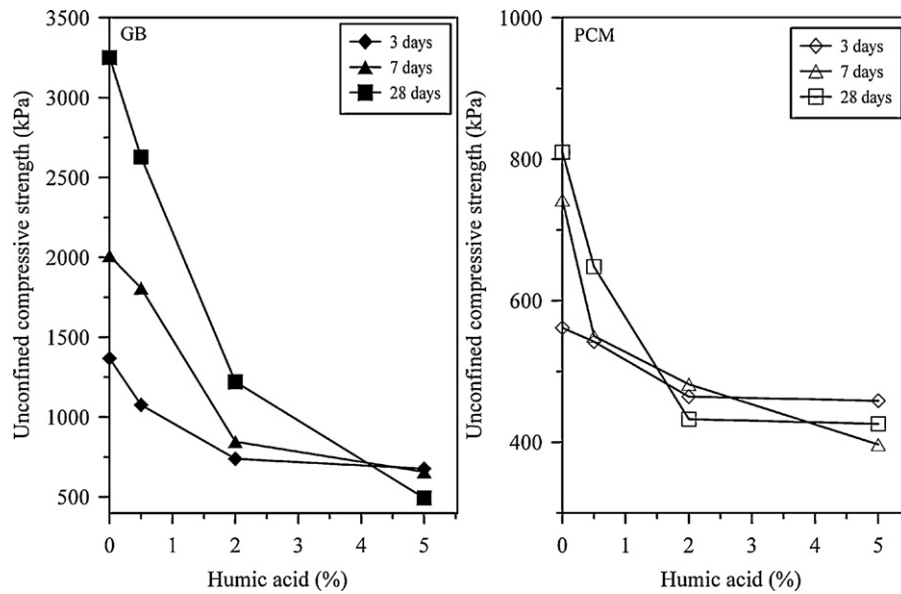


Fig. 5. Unconfined compressive strength of molded lime-stabilized samples as a function of commercial humic acid added. Samples were incubated at 100% humidity and 23 °C for 3 days, 7 days or 28 days.

Formation of new reaction products was also evident in the 3–8% lime GB pastes. In contrast to that observed at higher lime contents and for PCM pastes, the new reaction product in GB pastes containing 3–8% lime was evident as a single exothermic peak between 800 and 900 °C (Fig. 2A and B). No weight loss was associated with the exothermic peak, also consistent with a re-crystallization reaction (Fig. 2C). Earlier studies [8,10] have attributed the occurrence of an exothermic peak around 850 °C to the presence of CSH1. The increase in intensity of the 850 °C peak with lime content up to 8% lime is indicative of increase CSH1 production with lime content. At 12% lime there appeared to be a transition from CSH1 to CSH2 formation. For the PCM pastes only CSH2 formation was observed, with its production increasing up to 12% lime and then leveling off. The formation of CSH2 appears to be favored under excess lime conditions.

No new reaction products were observed in the 3% lime PCM paste, however, some transitions were apparent when compared to the 0% lime sample. Most notably were changes in hydration and the disappearance of the dehydroxylation peak at around 950 °C. X-ray diffraction analysis (Fig. 3) also showed an increase in inter-layer *d*-spacing (from 1.0 to 1.4 nm) consistent with the increase in hydration and Ca<sup>2+</sup> exchange for Na<sup>+</sup> [8,13]. Only diffraction peaks attributable to starting materials and possibly calcite were observed in lime-soil paste of Fig. 3, indicating that the new reaction products formed were either present in small quantities (<5%) or amorphous to poorly crystalline.

### 3.2. Lime-soil reactions in the presence of natural organic matter

Differential scanning calorimetry thermograms for molded cylindrical samples containing varying quantities of organic matter are shown in Fig. 4. As in the organic matter-free paste experiments, exothermic peaks attributable to the formation of CSH phases were also observed in molded samples containing organic matter. New exothermic peaks in the 200–600 °C range, which increased in intensity with increasing organic matter content were attributable to the oxidation of the added humic acid (cHA). Other peaks such as those observed between 300 and 350 °C in the 3-day GB sample as well as the 3- and 7-day PCM samples appear to be transitional phases, likely associated with the hydrated lime starting material (Fig. 1).

For a given incubation period, the concomitant decrease in the intensity (and in some cases the absence) of the CSH peaks observed with increasing cHA content indicated that the presence of humic acid had an inhibitory effect on the formation of CSH (Fig. 4 insets). Unconfined compressive strengths (UCS) of the lime-stabilized cores also decreased with increasing humic acid content (Fig. 5).

A strong linear correlation between the UCS of the cores and the amount of energy evolved (given by peak area) during CSH re-crystallization point to a direct link between CSH formation and strength development (Fig. 6). Calculated coefficient of variation for both UCS and CSH peak areas (based on triplicate samples of selected cores) was <20%. The strong correlation between CSH peak area and UCS was a very significant observation as it points to the inhibition of CSH formation as the primary mode of action of natural organic matter as a perturbant in lime-stabilized soils. The

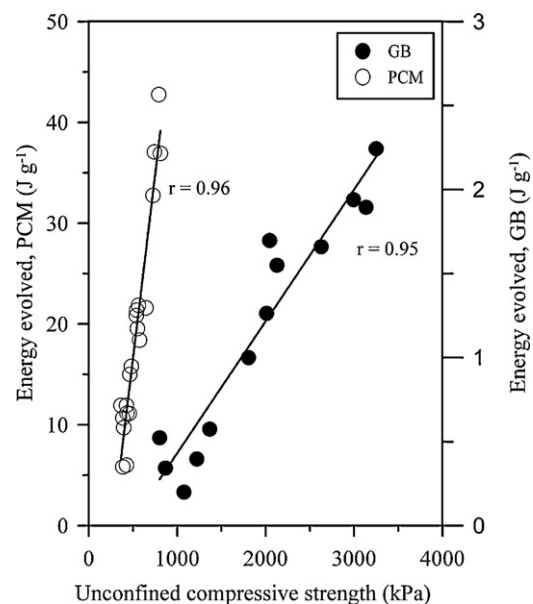
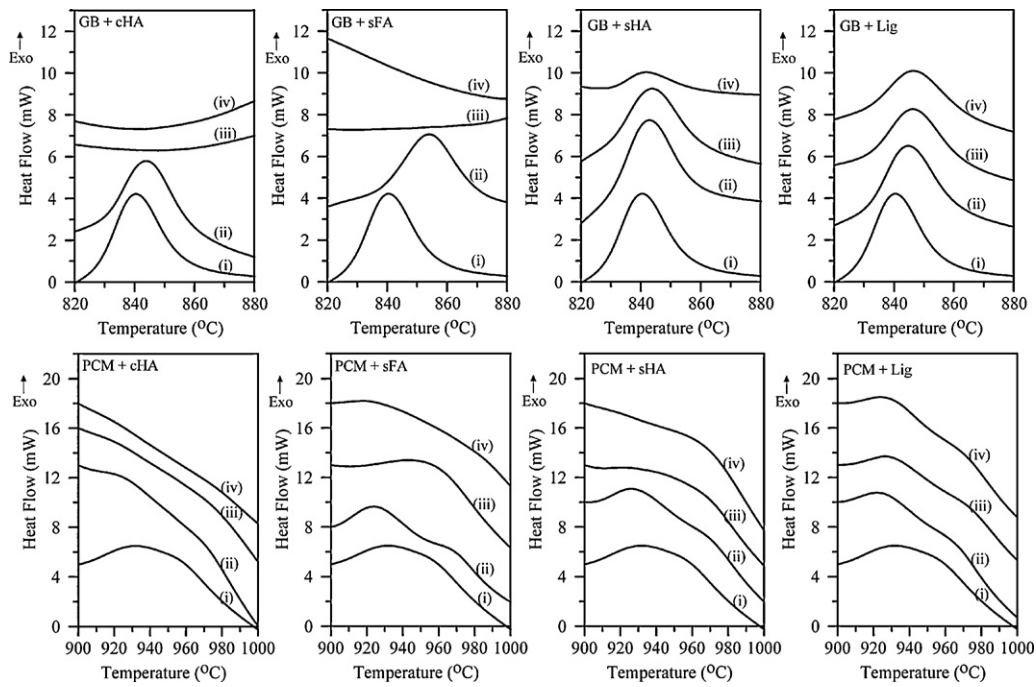


Fig. 6. Relationship between unconfined compressive strength of molded lime-stabilized samples and integral heat of CSH re-crystallization.



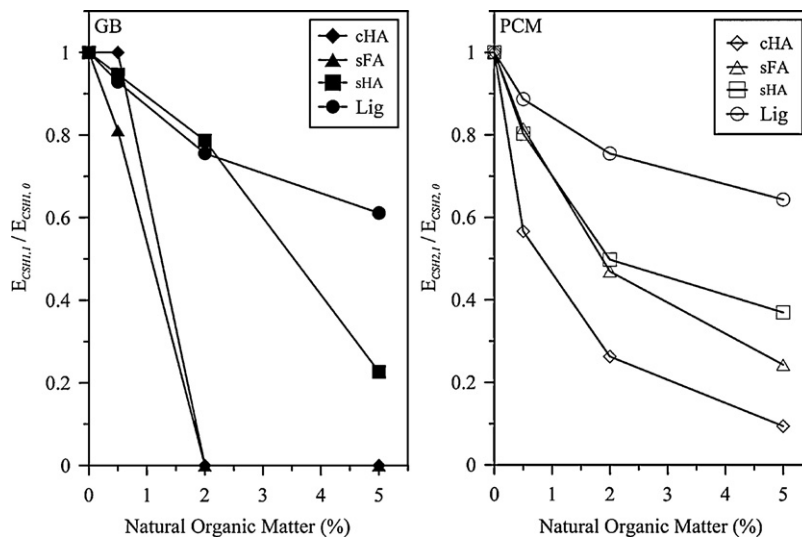
**Fig. 7.** Intensity of DSC peaks attributable to CSH formation in GB (8% lime) and PCM (12% lime) pastes containing (i) 0%, (ii) 0.5%, (iii) 2% or (iv) 5% natural organic matter as commercial humic acid (cHA), soil fulvic acid (sFA), soil humic acid (sHA) and lignite (Lig). Samples were incubated at 100% humidity and 23 °C for 28 days.

decrease in intensity of the CSH peaks with increasing cHA content also provided a valid explanation for the observed decrease in strength gains in lime/cement-stabilized soils as soil organic matter content increase.

In the presence of organic matter, changes in CSH formation (peak intensity) varied with both the type of clay and the CSH phase formed. For example, although the formation of CSH1 was completely inhibited in GB samples containing 5% cHA (and in some cases 2% cHA), the formation of CSH2 in the PCM samples was only retarded. This suggested that in addition to organic matter content, soil mineralogy will have a considerable influence on the degree to which CSH formation in lime/cement-stabilized soils is inhibited by organic matter. The influence of soil mineralogy on organic matter inhibition of CSH formation in lime/cement-stabilized soils also

presents one plausible explanation for the variability in successful stabilization of organic soils reported in the literature [4,17,18].

Both the formation of CSH and its inhibition by cHA showed evidence consistent with kinetically controlled processes. For example, the insets in Fig. 4 showed that, with the exception of the 5% cHA GB sample (which showed no evidence of CSH formation) the intensity of the CSH peaks for a given cHA content generally increased with time. Increase in CSH peak intensity with time was indicative of a temporal increase in CSH formation, and was consistent with studies of strength development in lime/cement-stabilized soils [13]. Further evidence of the kinetically controlled inhibition of CSH formation by organic matter was apparent in molded GB samples containing 2% cHA (Fig. 4 insets). No CSH was formed in these samples until after 10 days of incubation (com-



**Fig. 8.** Change in calcium-silicate-hydrate formation with natural organic matter content in GB and PCM pastes. Values are based on the integral heats of CSH re-crystallization in organic matter-containing samples ( $E_{\text{CSH}, i=0.5, 2 \text{ or } 5\%}$ ) compared to organic-free samples ( $E_{\text{CSH}, 0}$ ). Natural organic matter was present as commercial humic acid (cHA), soil fulvic acid (sFA), soil humic acid (sHA) and lignite (Lig).

pared to 3 days for 0 and 0.5% cHA samples). The additional lag of 7 days for the molded GB sample containing 2% cHA suggested an initial inhibition of CSH formation which was overcome with time. Such inhibition was attributable to cHA exhibiting kinetic controls on the dissolution and/or precipitation stage of CSH formation.

Based on the known acid–base properties of humic acid and other component of soil organic matter [11,19], several mechanisms (likely acting simultaneously) could potentially explain the inhibitory effects of cHA on CSH formation. The first and most commonly cited mechanism is the complexation of dissolved  $\text{Ca}^{2+}$  ions by organic matter in order to satisfy its cation exchange capacity. Eades and Grim [2] suggested that replacement of adsorbed cations on clays by  $\text{Ca}^{2+}$  preceded the formation of new reaction products with CSH forming only after exchange sites become fully occupied by  $\text{Ca}^{2+}$ . The presence of natural organic matter sources, such as humic and fulvic acids in a soil will increase its cation exchange capacity [11]. Consequently, more  $\text{Ca}^{2+}$  would be required to satisfy the cation exchange capacity of a soil as organic matter content increase and thereby reduce the amount of  $\text{Ca}^{2+}$  available for CSH formation. Complexation of  $\text{Ca}^{2+}$  would therefore be expected to affect the precipitation phase of CSH formation and have been used to explain lower strengths gain in lime-stabilized soils [4,7,17,18]. Based on equilibrium principles, increased complexation of  $\text{Ca}^{2+}$  by organic matter would enhance the dissolution of lime. This was consistent with the increased level of carbonation (as indicated by the double endotherm around 700–800 °C) observed in molded samples, as cHA content increased (Fig. 4).

A second possible mechanism is the buffering of the pH by the organic matter. Acidic functional groups from the organic matter may buffer the pH, reducing the dissolution of silicate minerals and limiting the amount of silica available for CSH formation. This may explain why precipitation of CSH2, with its higher Ca:Si, was less affected by increasing organic matter content. Other possible mechanisms include: (i) the direct interaction of dissolved organic components with clays thereby reducing the surface area available for dissolution and (ii) interaction of dissolved or undissolved organic matter with dissolved silica species thereby inhibiting nucleation and precipitation of CSH phases.

In addition to inhibitory effects on CSH formation and increased carbonation, there was some evidence to suggest that organic matter may also influence the hydration characteristics of the clay. For example, the absence of the endotherm attributable to interlayer water associated with hydration sphere of  $\text{Ca}^{2+}$  (approximately 150 °C), particularly in the 5% cHA GB samples, suggests that organic matter may influence lime–smectite reaction through alteration of the clay's interlayer (Fig. 4). This was supported by X-ray diffraction which showed a decrease in the interlayer spacing of the 5% cHA GB sample compared to the 0, 0.5 and 2% cHA samples (Supporting Information 1).

### 3.3. Effect of natural organic matter source on calcium-silicate-hydrate formation

Increasing soil fulvic acid (sFA), soil humic acid (sHA), commercial humic acid (cHA) or lignite content all had an inhibitory effect on the formation of CSH in the lime-stabilized paste (Fig. 7). In addition to varying with the amount of organic matter, the degree of inhibition was also a function of the type of natural organic matter, the nature of the clay and subsequently the CSH phase formed. By assuming that (i) maximum formation of CSH was achieved in the 0% organic matter samples and (ii) the energy evolved during re-crystallization is directly proportional to the CSH formation, the change in CSH formation for a given source was calculated as:  $\Delta\text{CSH}_x = 1 - (E_{\text{CSH}_x,i}/E_{\text{CSH}_x,0})$ , where,  $\Delta\text{CSH}_x$  represents the change in the formation of CSH phase  $x$  (1 or 2); and  $E_{\text{CSH}_x,i}/E_{\text{CSH}_x,0}$  is the ratio of the energy ( $\text{J g}^{-1}$ ) evolved during

re-crystallization of CSH1 or CSH2 in the presence of  $i$  amount of a given organic source to that evolved in the absence of that organic matter source ( $E_{\text{CSH}_x,0}$ ). Here values for  $i$  were 0.5, 2, or 5% representing the amount of cHA, sFA, sHA or lignite present in the lime-stabilized paste. Energy of re-crystallization of CSH was determined by integration of heat-flow thermograms shown in Fig. 7. Limits for integration were determined from corresponding second derivative thermograms (not shown).

With the exception of lignite, which had similar effects on CSH1 and CSH2 formation, the effect of natural organic matter was greater on CSH1 formation than on CSH2 formation. For example, an addition of 2% sFA resulted in a 53% decrease in CSH2 formation compared to 100% loss in CSH1 formation (Fig. 8). For a given CSH phase the general order of influence of natural organic matter on its formation was  $\text{cHA} \geq \text{sFA} > \text{sHA} > \text{Lig}$ . That lignite had the least negative impact on CSH formation could be attributed to its lower solubility, lower CEC and lower buffering capacity compared to cHA, sFA or sHA. In contrast to the humic and fulvic acids which would be soluble under the high pH conditions created by the addition of lime to a soil, lignite is insoluble due largely in part to its non-polar nature. Interactions involving soluble species from lignite are therefore unlikely. Similarly the absence of any significant cation exchange capacity or acidic characteristics makes complexation of  $\text{Ca}^{2+}$  or buffering unlikely mechanisms accounting for the changes in CSH formation due to increasing lignite content (Fig. 8). It is unclear what mechanisms are operational in the lignite samples. The larger effect of sFA on CSH formation compared to sHA is attributable to the greater acidic/CEC character of fulvic acids compared to humic acids.

## 4. Summary and conclusions

Thermal analysis was used to investigate the influence of natural organic matter on calcium-silicate-hydrate formation in two model soils containing clays of different mineralogies (a Gonzales bentonite and a Panther Creek montmorillonite) in an effort to understand the mechanism of organic matter control on CSH formation in lime-stabilized soils. In the absence of organic matter, the quantity and type of CSH phase formed in a given soil was found to depend on the nature of the clay and the amount of lime added. Formation of CSH1 was favored in the Gonzales bentonite at 3–8% lime, while CSH2 was favored at higher lime contents and in the Panther Creek montmorillonite. The organic matter used in this research was found to inhibit both CSH1 and CSH2 formation in lime-stabilized soils. The degree of inhibition was a function of the amount and type of organic matter, as well as the CSH phase. Increasing organic matter content increased the inhibition of CSH formation. For the organic matter sources studied a general order of  $\text{cHA} \geq \text{sFA} > \text{sHA} > \text{Lig}$  can be described. Humic and fulvic acids had a greater inhibitory effect on CSH1 than CSH2 while lignite had the similar effects on both CSH phase.

In addition to pointing to the inhibition of CSH formation as a primary mode of action of organic matter influence on pozzolanic activity in the lime-stabilized soils, the results of this research have significant implications for lime stabilization of soils. Paramount to any discussion on the topic is the recognition that mitigation of organic soils using lime as stabilizer is a multi-variate problem. Significant consideration must be given to soil and environmental characteristics including (but not limited to) the nature of the soil minerals, amount and characteristics of the organic matter present and the type of pozzolanic product likely to be formed.

## Acknowledgement

Financial support for this research was provided by the Texas Department of Transportation (Project No. 45540).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tca.2010.04.007](https://doi.org/10.1016/j.tca.2010.04.007).

## References

- [1] S. Diamond, J.L. White, W.L. Dolch, *Clays Clay Miner.* 12 (1963) 359.
- [2] J.L. Eades, R.E. Grim, High Res. Board, Bull. 262, Washington, DC (1960) 51.
- [3] H. Chen, Q. Wang, *Bull. Eng. Geol. Environ.* 65 (2006) 445.
- [4] K.E. Clare, P.T. Sherwood, *J. Appl. Chem.* 4 (1954) 625.
- [5] H. Tremblay, J. Duchesne, J. Locat, S. Leroueil, *Can. Geotech. J.* 39 (2002) 535.
- [6] M.B. Hampton, T.B. Edil, in: A. Maher, D.S. Yang (Eds.), *Soil Improvement for Big Digs: Geotechnical Special Publication*, ACSE, Reston, Virginia, 1998.
- [7] D.H. Chen, Z.M. Si, M. Saribudak, *J. Perform. Constr. Facil.* 23 (2009) 100.
- [8] G.R. Glenn, *High. Res. Rec.* (1970) 122.
- [9] A. Bakolas, E. Aggelakopoulou, A. Moropoulou, *J. Therm. Anal. Calorim.* 92 (2008) 345.
- [10] P. Ubbriaco, F. Tasselli, *J. Therm. Anal. Calorim.* 52 (1998) 1047.
- [11] K.H. Tan, *Humic Matter in Soil and the Environment: Principles and Controversies*, Marcel Dekker, New York, 2003.
- [12] A.D. Karathanasis, in: A.L. Ulery, R.L. Drees (Eds.), *Methods of Soil Analysis. Part 5. Mineralogical Methods*, Soil Science Society of America, Madison, WI, 2008, p. p117.
- [13] F.G. Bell, *Eng. Geol.* 42 (1996) 223.
- [14] J.L. Eades, F.P. Nichols, R.E. Grim, High Res. Board, Bull. 335, Washington, DC (1962) 31.
- [15] B. Caglar, B. Afsin, A. Tabak, E. Eren, *Chem. Eng. J.* 149 (2009) 242.
- [16] A. Bakolas, E. Aggelakopoulou, A. Moropoulou, S. Anagnostopoulou, *J. Therm. Anal. Calorim.* 84 (2006) 157.
- [17] S. Hebib, E.R. Farrell, *Can. Geotech. J.* 40 (2003) 107.
- [18] B.B.K. Huat, S. Maail, T.A. Mohammed, *Am. J. Appl. Sci.* 2 (2005) 1113.
- [19] F.J. Stevenson, *Humus Chemistry: Genesis, Composition, Reactions*, 2nd ed., John Wiley & Sons, New York, 1994.