Soil and Environmental Factors Influencing Ettringite Formation

Josh Liao[1], Ramesh S. Hegde, Ph.D.[1], Anand J. Puppala, Ph.D., P. E.[2] and

Rajan K. Vempati, Ph. D.[1]

[1]ChK Group, Inc., 2045 Belgium Drive, Plano, TX 75025

[2]Professor, Civil and Environmental Engineering Department, Box 19308, The University of Texas at Arlington, Arlington, TX, 76019, e Mail: anand@uta.edu

[4]President and Senior Research Scientist, ChK Group, Inc., 2045 Belgium Drive Plano, TX 75025, P. No. (214) 768-1278, Fax No. (214) 768-4089, e. Mail: chkgroup@worldnet.att.net

1   **Abstract**

2   Soil environmental conditions are complex and in dynamic states; hence, their role with respect
3   to the formation of ettringite, a soil heaving mineral, is poorly understood. Furthermore, the
4   protocol of ettringite synthesis in laboratory calls for the use of 10% sucrose solution, but its
5   purpose is not defined in the literature. Therefore, the objectives of this article are to: 1)
6   synthesize a single-phase ettringite using two Ca sources, $CaCl_2$ and CaO, and 2) study the
7   role/effect of following compounds, i.e., sucrose, citrate (plant exudate), selected chelates
8   including humic acid and alkalinity in the ettringite formation. In all syntheses, ettringite
9   forming candidate ions were present, i.e., calcium (Ca), aluminum (Al), sulfates (SO_4^{2-}), water
10 (H_2O) and optimum pH. Single-phased ettringite was formed in $CaCl_2$ in an open system
11 without the use of sucrose; however, in the case of quick lime (CaO) treatment of soil, this
12 mineral was formed only in a closed system which was free of CO_2. In the citrate system, very
13 small quantity of $CaCO_3$ was formed, no ettringite was formed, as Ca and/or Al was tightly
14 bound by the chelate. In the presence of selected chelates, i.e., ethylene-diaminetetraacetic acid
15 (EDTA) and diethyleneaminepentaacetic acid (DTPA), the use of $CaCl_2$ prevented ettringite
16 formation but not when CaO was the source. In the presence of humic acid system, ettringite
17 and $CaCO_3$ was formed irrespective of the Ca source. The presence of HCO_3^{2-} inhibited
18 ettringite formation and favored $CaCO_3$ formation. This study suggests that in addition to high
19 sulfate and reactive alumina containing soils, pH, alkalinity, citrate, and organic chelates
20 including organic matter may play a critical role in soil heaving phenomenon. The chemistry of
21 water, i.e., pH, alkalinity and sulfate content is also important. Most of these parameters can be
22 quantified to develop a predictive soil-heaving model which could save millions of dollars in
23 repairing heaved structures.

24 **Keywords**: alkalinity, chelates, citrate, liming, sucrose, soil heaving.

25

I. Introduction

1

2   Annually several millions of dollars are spent to repair concrete or flexible pavement
3 when pavements, foundations, and other concrete structures crack and shift. The annual cost of
4 damage done by expansive soils to roads, airports, and other buildings is more than the combined
5 estimate for floods, earthquakes, and tornadoes (Vitton et al. 2000). Frequent remediation of soil
6 heaving poses problems: 1) traffic congestion in areas of heavy road construction resulting in
7 increased fuel consumption, and 2) the air quality is affected when carbon monoxide and nitrous
8 oxide formed by car emissions react with free radicals to form ozone, a major air pollutant
9 responsible for asthma in children. Hence, soil heaving and their damage to pavement structures
10 should be addressed, both from maintenance cost reductions and potential environmental
11 damages.

12   Black clayey soils are primarily composed of montmorillonitic clays, which are
13 responsible for soil heaving. This is because water enters into their interlayers resulting in clay
14 swelling and upon drying causes shrinkage and soil cracking. To prevent soil heaving due to
15 montmorillonitic clays, the soils are mixed with lime before laying the concrete or pavement
16 structure. The purpose is for the Ca^{2+} dissolved from lime to enter the negatively charged
17 montmorillonite interlayers to decrease the diffuse double layer (DDL) thickness, resulting in
18 clay flocculation and stabilization. However, in some cases, lime-treated natural clayey soils
19 cause secondary soil heaving due to the formation of ettringite mineral, another swelling mineral.

20   Ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}, 26H_2O$, is a hydrated calcium alumino-sulfate mineral
21 which is formed at high pH in the presence of Ca^{2+}, SO_4^{2-}, and $Al(OH)_4^-$ (Puppala et al. 2005).
22 The addition of lime to soils results in high pH ($\geq$12) and release of Al from Al-containing
23 minerals, with the predominant species at that pH, being anionic ($Al(OH)_4^-$) (Lindsay 1979).
24 Lime is the source of Ca^{2+} for stabilization and that of sulfate to be either the native soil or water
25 used for either soil and/or curing concrete. Ettringite can form just months after construction
26 through a process called 'Delayed Ettringite Formation' (DEF), resulting in tremendous soil
27 heaving compared to the original native black soil.

28 **I.a. Ettringite Synthesis**

29   In the literature, there are several ettringite synthesis methods (Mylius 1933 as described
30 in Taylor 1990; Strubble and Brown 1984; Odler and Abdul-Maula 1984 and Jonathan et al.
31 1999) and the most commonly reported method has been the use of CaO and sucrose. However,
32 the exact role of the sucrose in synthesis has not been explained in the literature. Further, most
33 of the ettringite characterization work has been performed by X-ray diffraction (XRD), which is
34 not as sensitive in detecting the presence of additional $CaCO_3$ phase as Fourier Transform
35 Infrared Spectroscopy (FTIR). Second, the presence of excess organics, e.g., sucrose, in
36 ettringite matrix will modify the surface properties of the mineral; such as sorption, dissolution,
37 crystal morphology and growth properties, and chemical properties of the minerals. A single-
38 phased ettringite with pristine surfaces is critical in better understanding the following:

39 • Formation or prevention/inhibition of ettringite under natural environmental conditions, and

40 • Physical, chemical, mineralogical and surface properties.

41 **I.b. Influence of Chelates on Ettringite Formation**

42   Even though, extensive work on the role of organic chelates has been studied (Cody, et
43 al.) but little work on soils having natural organic matter consisting of fulvic acid and humic
44 acid and humin, which are good chelators of Al and Ca has been reported. Several plant roots
45 exude citrate (Hether et al. 1984; Marschner et al. 1987) in the soil environment, which is

1   another good chelator of Ca and Al cations. The role of organic matter and root exudates in
2   ettringite formation has not been previously reported or studied. Organic matter could play a
3   significant role during its decomposition in the ettringite formation as their byproducts are
4   excellent chelator of Al and generator of alkalinity resulting in the formation of $CaCO_3$. The
5   reservoir of cationic Al-complexed organic matter is likely to be displaced by Ca^{2+} released from
6   dissolution of soil-treated lime. Second, the role of alkalinity is critical in understanding the
7   ettringite formation. The sources of alkalinity in natural conditions are from plant and microbial
8   respiration in moist soils, plant and animal decomposition byproducts, natural waters and soils.
9   Most important, understanding the formation of ettringite in the presence and absence of
10   chelating agents may provide a clue for inhibition or prevention of soil heaving using these
11   natural resources.

12   In this study, two sources of Ca were used ($CaCl_2$ and CaO) for ettringite synthesis since
13   the former is more water soluble than the latter. Attempt was made to prepare a single-phased
14   ettringite in the absence of sucrose using two Ca^{2+} sources in the presence and absence of air as it
15   contains CO_2 (partial pressure (pp) ≥ 0.003) to initiate the $CaCO_3$ formation.

16   The objectives of this study are to:

17   • Synthesize and characterize a single-phased ettringite, and

18   • Determine various soil constituents affecting ettringite formation under
19   laboratory conditions, including the role of alkalinity.

20   **II. Materials and Methods**

21   **Formation of a-Single Phased Ettringite**

22   The various synthesis methods were formulated to make ettringrite in the absence of
23   sucrose. The following sections describe methods adopted to synthesize ettringite mineral.

24   **II.a. Ettringite Synthesis using CaO in Air**

25   In a beaker, 0.105 g of CaO was dissolved in 80 mL of distilled water (equilibrium pH =
26   12.1). In another beaker 0.731 g of sodium aluminate ($Na_2OAl_2O_3$) and 0.633 g of Na_2SO_4 were
27   dissolved in 120 mL of distilled water (equilibrium pH = 11.5). The two solutions were then
28   mixed in a separate container and stirred for 10 min, which resulted in the formation of a gel-like
29   suspension with the equilibrium pH of the suspension was 11.7. After 10 min, the gel was
30   allowed to settle, then filtered using Whatman filter paper 1.

31   **II.b. Ettringite Synthesis using CaO and Degassed Water**

32   The procedure in Experiment I was repeated using distilled water that was de-gassed by
33   boiling for 20 min then cooled and stored in a closed container to prevent exchange of
34   atmospheric CO_2 gas.

35   **II.c. Ettringite Synthesis using CaO in N_2 atmosphere**

36   In a similar experiment, the two solutions outlined in Experiment I were made and mixed
37   in a glove box under a nitrogen atmosphere. The solutions were also filtered and dried under a
38   constant stream of N_2. No attempt was made to degas the water used in solution preparation.

39   **II.d. Ettringite Synthesis using CaO in N_2 atmosphere in Degassed Water**

40   The procedure in above Experiment III was repeated using boiled, de-gassed H_2O in
41   accordance to the procedure explained in Experiment II.

42

1   **II.e. Ettringite Synthesis using CaCl₂ in Air**

2   The procedure in Experiment I was repeated using 0.207 g of $CaCl_2$ (molar equivalent to
3   0.105 g CaO) dissolved in 80 mL of distilled water to make up the Ca solution. The
4   concentration of Ca was maintained at that utilized in the CaO experiments. The rest of the
5   procedure was the same as described in Experiment I.

6   **II.f. Influence of Sucrose, Citrate, Chelates and Alkalinity in Ettringite Formation**

7   To the best of our knowledge, the role of natural soil chelates and alkalinity in the
8   formation of ettringite has not been investigated. This is important as soils contain several
9   chelating agents and alkalinity derived from root respiration, and residue of dead plants and
10   animals.

11   The purpose of this study is to understand the formation of ettringite in presence of
12   natural and synthetic chelating agents. The synthetic chelating agents used were
13   ethylenediaminetetraacetic acid (EDTA) and diethyleneaminepentaacetic acid (DTPA), which
14   are good chelators of Ca^{2+} and/or Al. However, EDTA is a better chelator of Ca^{2+} compared to
15   DTPA by an order of magnitude (Lindsay 1979). The natural chelating agents used are humic
16   acid and citrate.

17   **II.g. CaCl₂ Study**

18   In a beaker Ca solution was prepared by dissolving 0.5 g of $CaCl_2$ with a known amount
19   of chelate, e.g., DTPA = 0.157 g, EDTA = 0.16 g, Na-citrate = 0.263 g or humic acid = 0.16 g in
20   120 mL of distilled water. In another beaker 0.731 g of sodium aluminate ($Na_2OAl_2O_3$) and
21   0.633 g of Na_2SO_4 was dissolved in 120 mL of distilled water. The two solutions were then
22   mixed into a separate container and stirred for 10 min, which resulted in a gel-like material.
23   After 10 min, the mixed solutions were allowed to settle then filtered using a Whatman filter
24   paper 1.

25   For the sucrose study, same amounts of $CaCl_2$, $Na_2OAl_2O_3$ and Na_2SO_4 were weighed as
26   discussed in the above paragraph except that 10% sucrose solution was used to dissolve the
27   chemicals instead of water. In case of citrate study, 0.263 g of Na-citrate was added.

28   **II.h. CaO Study**

29   In a beaker, Ca solution was prepared by dissolving 0.252 g of CaO with a known
30   amount of chelate, e.g., 0.157 g DTPA, 0.16 g EDTA, Na-citrate = 0.263 g or 0.16 g humic acid
31   in 120 mL of distilled water. In another beaker 0.731 g $Na_2OAl_2O_3$ and 0.633 g Na_2SO_4 was
32   dissolved in 120 mL of distilled water. The two solutions were then mixed into a separate
33   container and stirred for 10 min, which resulted in a gel like material. After 10 min, the mixed
34   solutions were allowed to settle then filtered using a Whatman filter paper 1.

35   For the sucrose study, the same amounts of $CaCl_2$, $Na_2OAl_2O_3$ and Na_2SO_4 and similar
36   procedure were adopted as discussed in the above paragraph except that 10% sucrose solution
37   was used instead of water.

38   **II.i. Ettringite Formation in the Presence of Bicarbonates**

39   In a beaker, Ca solution was prepared by dissolving 0.105 g of CaO with a known
40   amount of chelate, e.g., 0.157 g DTPA, 0.16 g EDTA, Na-citrate = 0.263 g and 0.16 g humic
41   acid in 60 mL of distilled water, and the resulting equilibrium pH was 11.7. In a second beaker
42   0.731 g of $Na_2OAl_2O_3$ and 0.633 g of Na_2SO_4 were dissolved in 120 mL of distilled water, and
43   the resulting equilibrium pH was 11.5. The two solutions were then mixed into a separate
44   container containing 0.187 g of $NaHCO_3$ (4:1 Al:$NaHCO_3^-$ molar ratio) and stirred for 10 min

1 which resulted in formation of white precipitates. After 10 min, the mixed solutions were
2 allowed to settle then filtered using a using Whatman filter paper 1.

3 **II.f. Prevention of Ettringite Formation in the Presence of Modified Fly Ash**

4   The only ions that can be controlled to prevent secondary soil heaving minerals are the
5 anionic Al species. For this we believe that nanophase Fe oxide will be a good candidate as it
6 has ability to sorb anionic species, e.g., sulfate, arsenate, molybdate, etc. The nanophase Fe
7 oxide coated fly ash (NpFFA) was made by our patented process. A 10 g of fly ash was
8 transferred into a beaker and 15 ml of 35% $FeCl_3$ (1:1.5 ratio of solid to solution) was added.
9 The pH of the suspension was in the acid range of 2 to 3, so a strong base was added to bring it
10 to neutral pH. When pH of 7 was reached, the suspension was transferred to a roto-evaporator
11 and the suspension was swirled at a low speed for one hour at a speed of 90 rpm at 80° C. After
12 spinning for one hour, the contents were poured into a pan and bakes in an oven at 110° C till the
13 product was dry. The final product was reddish- brown color.

14 **Table 1: Ettringite syntheses in the presence of Nanophase Fe oxide coated fly ash**
15   **(NpFFA).**

Material	Control	Treatment 1	Treatment 2	Treatment 3	Treatment 4
NpFFA	0g	0.25g	0.50g	0.75g	1.00g

16   The ettringite was synthesized using 60 mg CaO, which was added to a 50-ml solution
17 containing 100 mg of Na_2SO_4 and 30 mg of $Na_2OAl_2O_3$ in a test tube. In the control no NpFFA
18 was added, but in another four test tubes NpFFA ranging from 0.25 g to 1 g were added (Table
19 1). The test tubes were then shaken for 24 hrs to get a good contact between the NpFFA and the
20 chemicals added.

21 **II.k. Mineralogical Analyses**

22   The following mineralogical analyses were performed:
23 <u>II.k.1. X-ray Diffraction (XRD):</u> The mineralogy of the samples was monitored by Phillips
24 X'Pert System diffractometer. The XRD patterns were recorded from 2 to 40 °2θ at a scan rate
25 of 3° min^{-1} using Ni-filtered CuKα (1.584Å) radiation.
26 <u>II.k.2. Fourier Transformation Infrared Spectroscopy (FTIR):</u> The FTIR spectra were collected
27 in the diffuse reflectance mode using Perkin Elmer 2000. Three hundred mg of KBr was mixed
28 with 6 mg of the sample and 128 scans were collected and averaged.
29 <u>II.k.3. Thermogravimetry:</u> Thermogravimetric analysis of all synthesized samples was made
30 using a TA Instruments TGA. The analysis was made by heating the sample from ambient
31 temperature to 950^oC at a rate of 20^oC per minute while under a nitrogen atmosphere. The total
32 weight loss over the temperature range was then calculated using the TA Instruments Universal
33 Analysis software.

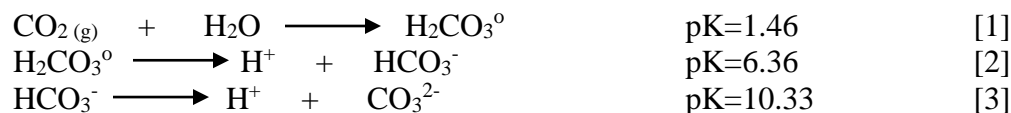34   **III. Results and Discussion**

35   The use of CaO as a source of Ca^{2+} for ettringite synthesis in air resulted in formation of
36 additional $CaCO_3$ phase; however, under N_2 atmosphere only a single-phased ettringite was
37 observed (Table 2). The presence of $CaCO_3$ was confirmed by a XRD peak at 303 Å, and FTIR
38 bands at 873 and 710 cm^{-1} (Fig. 1 and 2). When $CaCl_2$ was used as a source of Ca^{2+} only
39 ettringite phase (Fig. 3) was observed both in presence and absence of air. Interestingly, the
40 XRD peak intensities of different ettringite Miller indices in N_2 system was different compared

1 to that made in air. This may be due to differences in particle morphology and/or crystal growth
2 habits. Similar behavior was observed for goethite (Fe oxide mineral) synthesized under
3 different environmental conditions by one of the authors (Vempati unpublished). The
4 differences in peak heights or intensities of Miller indices could affect semi-quantification of
5 ettringite using XRD in case this observation is neglected.
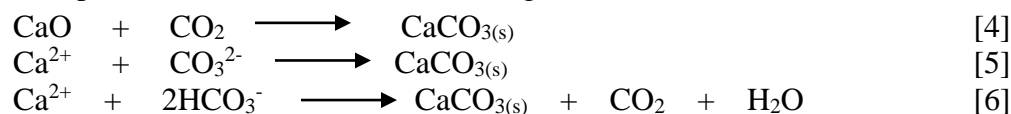
6 **Table 2. Ettringite synthesis in air and N_2 atmosphere.**

Ca-Source	Atmosphere	H_2O	CaCO$_3$ presence
CaO	Air	distilled	Yes
CaO	Air	distilled, degassed	Yes
CaCl$_2$	Air	distilled	No
CaO	N_2	distilled	No
CaO	N_2	distilled, de-gassed	No

15　　　　Using degassed water did not prevent $CaCO_3$ formation in CaO-air system in an open
16 system. The equilibrium pHs of dissolved CaO and $CaCl_2$ in open systems in water were 11.7
17 and 6.6, respectively. Since, the experiments were performed in air, the CO_2 present in
18 atmosphere was sufficient to initiate carbonate reactions. The dominant carbonate species in the
19 CaO-air system are CO_3^{2-} and HCO_3^- (the former being the dominant species) and in the $CaCl_2$-
20 air system are $H_2CO_3^o$ and HCO_3^- (both being in equal proportion) (See Fig. 4). The various
21 carbonate species in water are given in Eq. 1 to Eq. 3:

$$CO_{2\,(g)} + H_2O \longrightarrow H_2CO_3^o \qquad pK=1.46 \qquad [1]$$
$$H_2CO_3^o \longrightarrow H^+ + HCO_3^- \qquad pK=6.36 \qquad [2]$$
$$HCO_3^- \longrightarrow H^+ + CO_3^{2-} \qquad pK=10.33 \qquad [3]$$

25 **g=gas phase**

26　　　　The various processes of $CaCO_3$ formation are given below:

$$CaO + CO_2 \longrightarrow CaCO_{3(s)} \qquad [4]$$
$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_{3(s)} \qquad [5]$$
$$Ca^{2+} + 2HCO_3^- \longrightarrow CaCO_{3(s)} + CO_2 + H_2O \qquad [6]$$

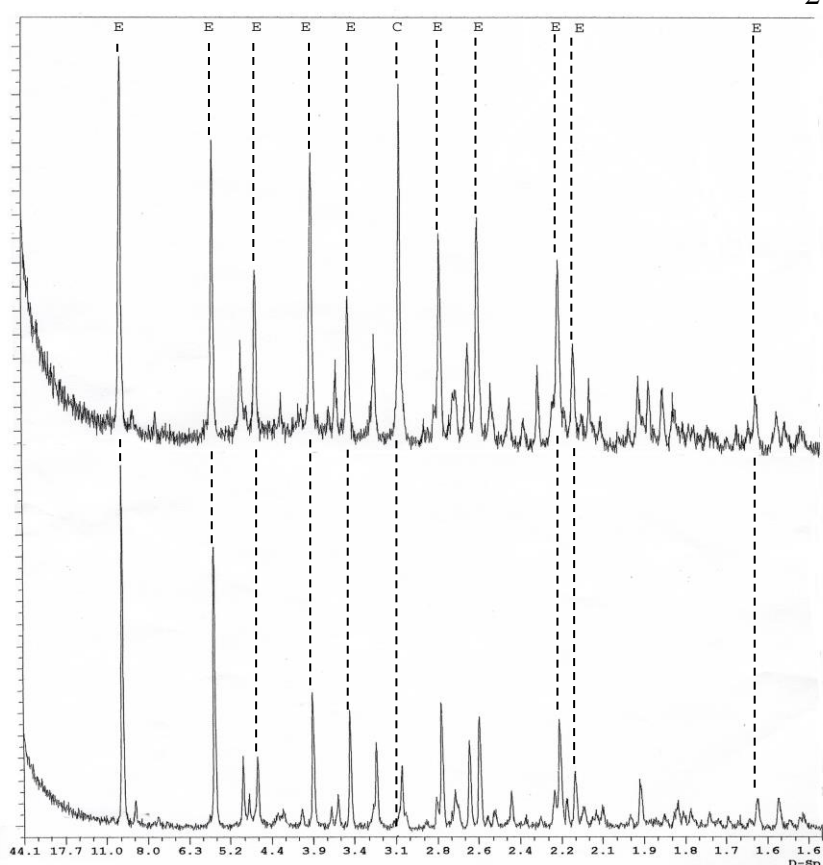30 **s=solid phase CaCO$_{3(s)}$**

31　　　　The $CaCO_3$ in either Ca-Cl or Ca-O system may form by any of the methods listed in Eq.
32 4 to Eq. 6. The absence of $CaCO_3$ formation in Ca-Cl aqueous system may be due to stable ion-
33 pairing of $CaCl^+$ and $CaCl_2^o$ species (Lindsay 1979).

34 These experiments suggest that alkalinity and pH in soil and water systems does influence the
35 formation of a single-phased ettringite formation. Thus, organic matter and the partial pressure
36 of CO_2 could influence the formation $CaCO_3$ thus preventing ettringite formation. In the N_2
37 system, pure ettringite is formed in the CaO because of absence of atmospheric CO_2 to initiate
38 alkalinity reactions thus preventing $CaCO_3$ formation.

39 **III.a. Stability of Synthesized Ettringite**

40　　　　The thermo-gravimetric analysis indicated that pure ettringite is stable up to 293 K, and
41 the weight loss was 70% at 313 K (Fig. 5). Interestingly, drying of ettringite resulted in losing
42

1   its gel-like properties irreversibly after sample rehydration. This is due to irreversible loss of water from the ettringite structure. Further, in laboratory synthesis ettringite formation occurs only at temperature <313 K.

2   water from the ettringite structure. Further, in laboratory synthesis ettringite formation occurs only at temperature <313 K.

III.b. Role of Chelates, Sucrose and Ettringite in Ettringite Formation

When $CaCl_2$ was the Ca source, there was no ettringite or $CaCO_3$ formation in the presence of either DTPA or EDTA chelates but in the presence of sucrose a single-phased ettringite was formed (Table 3). The absence of ettringite formation in $CaCl_2$-chelate system, shows that either Ca-Cl species are very stable and thus unable to interact with either dissolved

27 **Fig. 1. X-ray diffraction (XRD) patterns of ettringite synthesized using two Ca sources in**
28 **air:(A) CaO, and (B) $CaCl_2$ (E and C refer to ettringite and calcium carbonate,**
29 **respectively.**

30 **Table 3. Formation of ettringite in the presence of chelates and two Ca sources.**

S. No.	Ca Source	Chelate	Ettringite	$CaCO_3$
1)	$CaCl_2$	DTPA	N	N
2)	$CaCl_2$	EDTA	N	N
3)	$CaCl_2$	Humic	Y	Y
4)	$CaCl_2$	Succrose	Y	N
5)	$CaCl_2$	Citrate	N	N
6)	CaO	DTPA	Y	N
7)	CaO	EDTA	Y	N
8)	CaO	Humic Acid	Y	Y
9)	CaO	Succrose	Y	N
10)	CaO	Citrate	N	N

1 **Table 4. The FTIR band positions for ettringite and crystalline $CaCO_3$.**

Band Position (cm^{-1})	Band Assignment
3638	OH-Stretching Al-OH and/or $\equiv$Ca-OH and $\equiv$Ca-OH$_2$
3440	OH-Stretching water
1658	OH-Bending of water
1405	CO_3^{2-} ν_3 asymmetric stretching
1110	SO_4^{2-} ν_3 asymmetric stretching
986	SO_4^{2-} ν_1 symmetric stretching
869†	Al-OH bending vibration; CO_3^{2-} ν_2 symmetric stretching
874	CO_3^{2-} ν_2 symmetrical stretching from $CaCO_3$
796	CO_3^{2-} ν_2 symmetrical stretching
710	CO_3^{2-} ν_4 symmetrical stretching from $CaCO_3$
621	ν_4 S-O bending vibration
528	Al-OH bending vibration

17 CO_2 in water or alumina preventing the formation of $CaCO_3$ and ettringite phases. Second, it is
18 likely that Al is complexed with DTPA and EDTA and thus unable for ettringite formation.
19   The final pH, after adding $Na_2OAl_2O_3$ and Na_2SO_4 in both the systems was 11 ($\pm$ 0.2).
20 The absence of $CaCO_3$ in the sucrose solution indicates that it may be preventing atmospheric
21 CO_2 contact with water, thus preventing alkalinity species being formed.
22   When CaO was the Ca source, single-phased ettringite was formed in the presence of
23 DTPA, EDTA and sucrose. Interestingly, both ettringite and $CaCO_3$ were formed in the
24 presence of humic acid; irrespective, of Ca source. The presence of ettringite in a humic acid
25 system is disturbing because the study shows that in soils containing high organic matter, Al
26 could be released during liming to induce soil heaving. The role of humic acid in ettringite
27 formation needs to be further investigated.
28   The absence of ettringite formation and the low yield of $CaCO_3$ in the citrate system
29 indicates that it is an excellent chelator of Ca and Al; thus, preventing the formation of $CaCO_3$
30 and ettringite.

31 **III.c. Determination of Al-Complexed with Humic Acid**

32   This study shows that Al-complexed by humic acid could lead to formation of ettringite.
This form of Al can be quantified by treating the soil with 30% H_2O_2 (Jackson 1969). However,
this procedure will not differentiate other chelating agents, i.e., humic acid, citrate, fulvic acid,
humin, etc., present in the given soil environment.
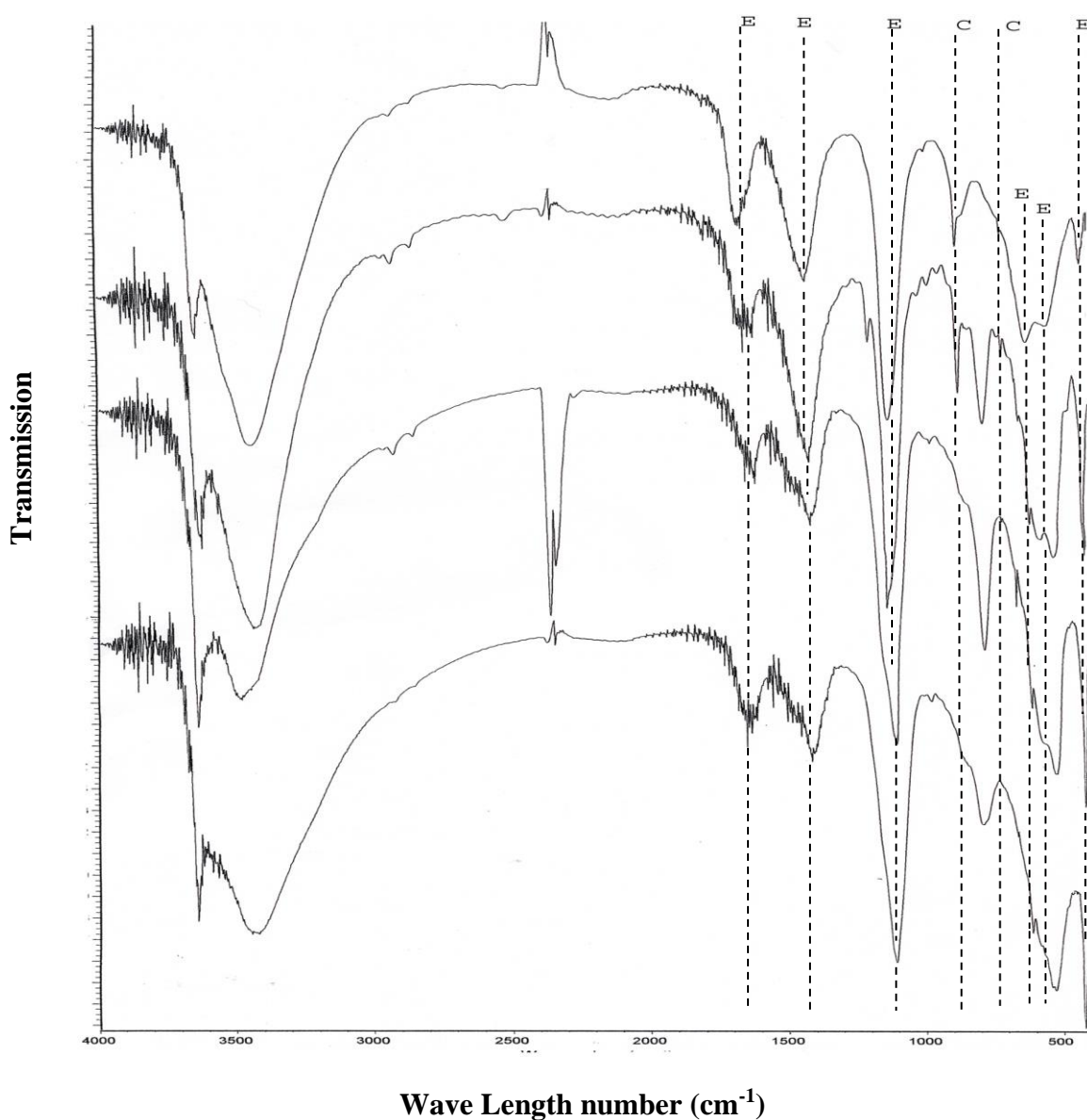
Fig. 2. FTIR spectra of ettringite formed using various Ca-sources: (A) CaO in air, (B) CaO in air using de-gassed H_2O, (C) CaO in a N_2 atmosphere, and (D) CaO in N_2 atmosphere using de-gassed H_2O (E and C labeled to ettringite and carbonate, respectively). The FTIR band positions are given in Tables 4.

(a)   (b)
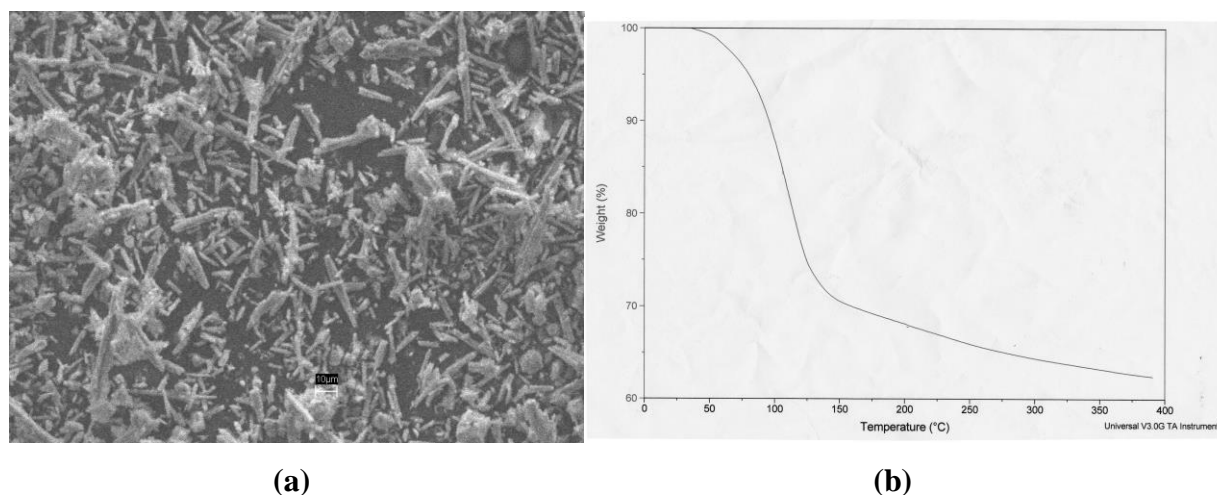
Fig. 3. a) Scanning Electron Microscope (SEM) image of ettringite mineral (the scale
**indicates 1 μm distance) and, b) Thermogravimetric analysis of synthesized**
ettringite.

(a)   (b)

d-Spacing (nm)   **Wavenumber (cm^{-1})**
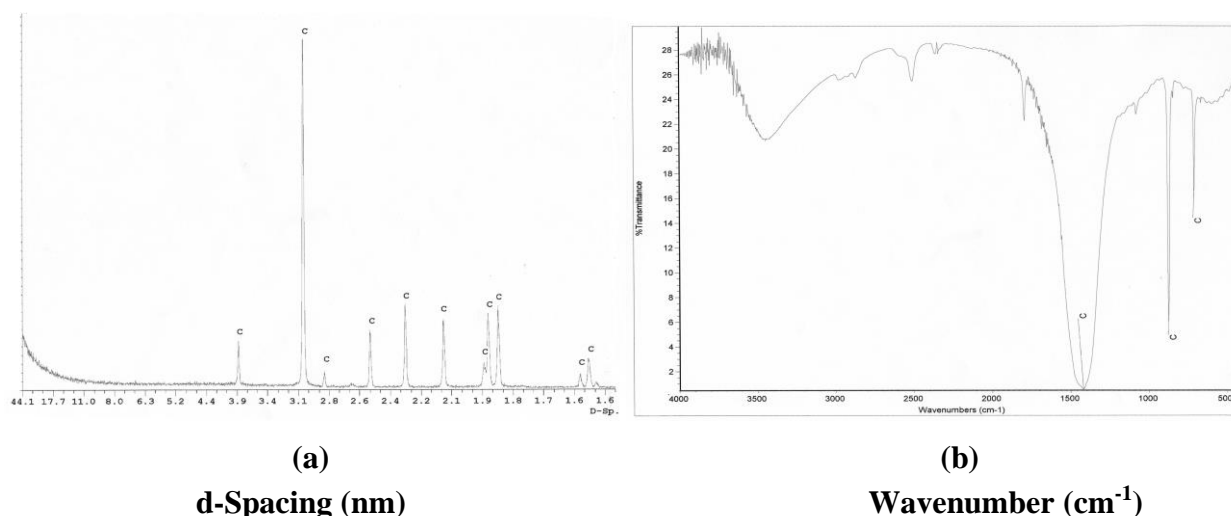
Fig. 4. a) X-ray diffraction and b) Fourier Transformed Infra-Red of crystalline CaCO3.

III.d. Role of Bicarbonate in Ettringite Formation

No ettringite was formed when bicarbonate in the form of $NaHCO_3$ was added in both the CaO and $CaCl_2$ systems. Bicarbonate inhibits ettringite growth and stimulates carbonate formation at high pH through the following reactions (Eqs. 4 to 6):

To recapitulate, Equation 4 shows the reaction between Ca^{2+}, derived from CaO, and atmospheric CO_2 to form $CaCO_3$. This is because CaO is a hygroscopic compound which initiates the above reaction. Equation 6 reveals adding HCO_3^- to the system can also produce $CaCO_3$. The CO_3^{2-} becomes the dominant carbonate species at pH $\geq$ 10.5 to form $CaCO_3$. Experiment 1 suggests that atmospheric CO_2 is sufficient to form CO_3^{2-} over a 10-minute ettringite synthesis in the CaO system. Adding $NaHCO_3$ or high alkaline water gives the system additional HCO_3^- and/or CO_3^{2-} to form $CaCO_3$; thus, inhibiting the formation of ettringite.

III.e. Ettringite Retardation by Nanophase Fe oxide Treated Fly Ash
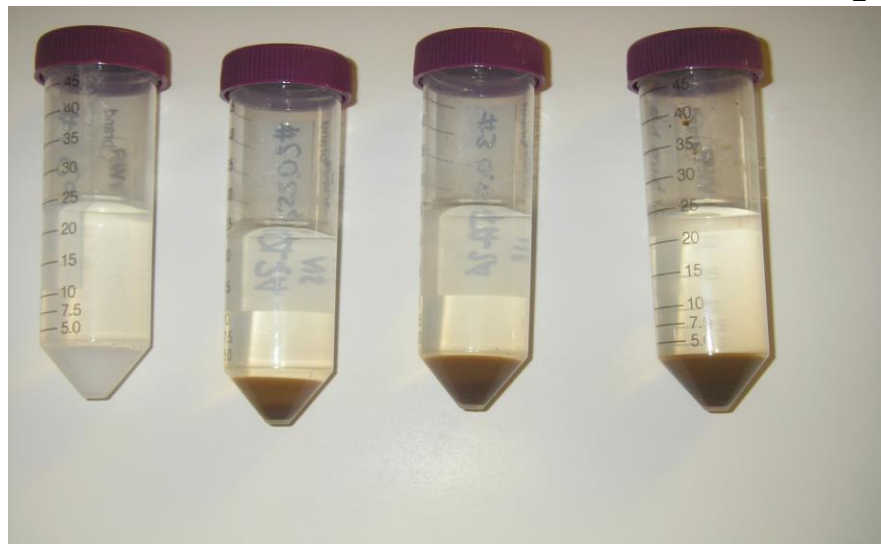
The treatment of nanophase Fe oxide coated Fly Ash (NpFF) resulted in prevention of ettringite. The Fig. 5 shows that the control contains a white gel like material which was confirmed as ettringite by XRD and FTIR. Whereas, addition of 0.25 g of Fe oxide resulted in prevention of ettringite.

Fig 5. The test tubes from left to right contains following amounts of NpFF 0, 0.25g, 0.5 g and 0.75 g. The white gel like material in the bottom of the 0 g of NpFF test tube is ettringitef; whereas, no ettringite was formed in the treated tubes.

IV. Conclusions and Further Research

The study shows that a single-phased ettringite can be synthesized using $CaCl_2$ without the use of sucrose; however, if CaO is used a freshly opened or tightly closed bottle, and CO_2 free environment and degassed water are recommended. This is important for understanding the physical, chemical and mineralogical, and crystal growth properties of the pristine ettringite surfaces. The presence of $CaCO_3$ can be detected either by X-ray diffraction (XRD) and/or Fourier transform infrared spectroscopy (FTIR).

In the presence of chelates, EDTA and DTPA, the use of $CaCl_2$ prevented ettringite formation but not when CaO was the source. In the presence of humic acid system, ettringite and $CaCO_3$ was formed irrespective of the Ca source. This suggests that soil organic matter may play a major role in the ettringite formation. This needs to be further investigated.

Thus, the roles of pH, temperature, chelating agents including root exudates, and atmospheric CO_2 on ettringite formation were identified through this study. In a solution containing Ca^{2+}, SO_4^{2-} anionic Al species and high pH, the absence or presence of CO_2 plays a critical role in the formation of a single-phased ettringite or ettringite-$CaCO_3$ mix. Also, temperature >40°C retards the formation of ettringite (not shown in the experiment). The addition of bicarbonate to the ettringite forming environment favors the formation of $CaCO_3$.

In summary, the formation of ettringite in soils (applicable to concrete) depend on several environmental factors, i.e., Ca source, pH, water soluble sulfate content, reactive alumina and humic acid content, alkalinity levels of soil and water, and temperature. This is discussed below:

1. **Ca Source:** Lime applied to prevent swelling of montmorillonitic or black soils.
2. **High pH:** A pH >10 induced by lime addition.
3. **Reactive Al and Humic Acid Content**: from amorphous and poorly-crystalline aluminosilicates (clays), natural Al polymers, the hydroxyaluminum phases existing in

the smectite/montmorillonite interlayers in clays, Al oxides and hydroxides, aluminum and silicate minerals (aluminosilicate) and organic matter (decay plant/animal materials). We have shown that Al present in humic acid (organic matter), could play a significant role in formation of ettringite at high pH. Besides, recycled cement pavements, cement, and fly ash are sources of amorphous aluminosilicates. Whereas, the crystalline clays (montmorillonite) are very stable and do not dissolve at the liming pH, the amorphous and poorly-crystalline materials have high surface areas, and dissolve much faster than crystalline clays. The Al released from the above phases can be quantified by reactive alumina (Wattanasanticharoen, et al., 2005).

4. **<u>Water Soluble Sulfate Content</u>:** These are present in the native soil or local water or derived from adding fly ash containing sulfate.

5. **<u>Moisture and Temperature</u>:** Optimum moisture and temperature (<60ºC) are essential. It is instructive to state that ettringite is formed several days after soil liming, where the temperature is <40ºC; hence, is referred to as delayed ettringite formation (DEF) in literature. Wetting and drying conditions could also lead to its formation.

This research has demonstreated that even though soil is a complex and dynamic system, secondary soil heaving predictive models can be developed by monitoring following parameters, e. g., pH, reactive Al and humic acid bound Al, water soluble Ca^{2+} and SO_4^- concentrations in soils and alkalinity.

V. Acknowledgement

VI. References

Heather, N. H., Olsen, R. A., and Jackson, L. L. (1984). "Chemical identification of iron reductants exudated by plant roots." *J. Plant Nutr.*, 7, 667-676.

Intharasombat, N. (2003). "Ettringite Formation in Lime Treated Sulfate Soils: Verification by Mineralogical and Swell Testing," MS Thesis, The University of Texas at Arlington, Arlington, Texas.

Jackson, M. L. (1969). Soil chemical analysis. Advance course. 2nd Edition. Published by M. L. Jackson, Dept. Soil Science, Univ. of Wisconsin, Madison, Wis. 53706.

Jonathan, L. W., Griffin, P. V. C., Andrew, W., and Roger, D. (1999). "Design and synthesis of macrocyclic ligands for specific interaction with crystalline ettringite and demonstration of a variable mechanisms for the setting of Cement." *J. Chem. Soc., Perkin Tans.*, 2 (10), 1973-1981.

Lindsay, Willard L. (1979). *Chemical Equilibria in Soils*. John Wiley & Sons, New York, NY.

Marschner, H., Romheld, V. and Kissel, M. (1987). "Differential strategies in higher plants in mobilization and uptake of iron." *J. Plant Nutr.* 9, 695-713.

1   Odler, I. and Abdul-Maula, M. (1984). "Possibilities of quantitative determination of the Aft-
2   (ettringite) and AFm-(monosulfate) phases in hydrated cement paste." *Cem. Concr. Res.* 1,
3   133-141.

4   Puppala, A.J., Wattanasanticharoen, E., Inthrasombat, N., Hoyos, L. R. (2003). "Studies to
5   Understand Soil Compositional and Environmental Variables on Sulfate Heave Problems."
6   *Proceedings, Soil Rock America, 12th Pan American Conference on Soil Mechanics and*
7   *Geotechnical Engineering*, Boston, Massachusetts, June 22 - 25.

8   Puppala, A.J., Intharasombat, N., and Vempati, R. K. (2005). Experimental Studies on
9   Ettringite Induced Heaving in Soils." *ASCE Journal of Geotechnical and Geoenvironmental*
10   *Engineering*, 131(3), 325-337.

11   Strubble, L. J. and Brown, J. P. (1984). An evaluation of ettringite and related compounds for
12   use in solar energy storage. *Progress Report, NBSIR 84-2942*, Nation Bureau of Standards,
13   Gaitherburg, Maryland.

14   Taylor, H. F. W. (1990). *Cement Chemistry*: New York, Academic Press Ltd 475 p.

15   Vitton, S. J., and Harris, W. W. (2000). The Engineering Significance of Shrinkage and
16   Swelling Soils in Blast Damage Investigations [Online]. Available at
17   <http://www.isee.org/tis/Proceed/Research/96Resrch/9607r.pdf>

18   Wattanasanticharoen, E., Puppala, A. J., Hoyos, L. R. and Vempati, R. K. (2005) "Soluble
19   Sulfate and Reactive Alumina Measurements in Cement and Lime Treated Sulfate Rich
20   Clays." *Proceedings, 16th International Conference on Soil Mechanics and Geotechnical*
21   *Engineering*, Osaka, Japan, September 12 – 16.

22   Wattanasanticharoen, E. (2004). "Experimental Studies to Evaluate Volume Change Movements
23   in Chemically Treated Sulfate Rich Soils." PhD Thesis, The University of Texas at Arlington,
24   Arlington, Texas, August, 2004, 295 pages.