SULFATE INDUCED HEAVE: ADDRESSING ETTRINGITE BEHAVIOR IN LIME TREATED SOILS AND IN CEMENTITIOUS MATERIALS

A Dissertation

by

SYAM KUMAR KOCHYIL SASIDHARAN NAIR

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2010

Major Subject: Civil Engineering

Sulfate Induced Heave: Addressing Ettringite Behavior in Lime Treated Soils and in Cementitious Materials

SULFATE INDUCED HEAVE: ADDRESSING ETTRINGITE BEHAVIOR IN LIME TREATED SOILS AND IN CEMENTITIOUS MATERIALS

A Dissertation

by

SYAM KUMAR KOCHYIL SASIDHARAN NAIR

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Approved by:

Chair of Committee,	Dallas Little
Committee Members,	Bruce Herbert
	Robert Lytton
	Richard Loeppert
Head of Department,	John Niedzwecki

December 2010

Major Subject: Civil Engineering

ABSTRACT

Sulfate Induced Heave: Addressing Ettringite Behavior in Lime Treated Soils and in Cementitious Materials. (December 2010)

Syam Kumar Kochyil Sasidharan Nair, B. Tech., College of Engineering, Trivandrum, India; M. Eng., Texas A&M University

Chair of Advisory Committee: Dr. Dallas Little

Civil engineers are at times required to stabilize sulfate bearing clay soils with calcium based stabilizers. Deleterious heaving in these stabilized soils may result over time. This dissertation addresses critical questions regarding the consequences of treating sulfate laden soils with calcium-based stabilizers. The use of a differential scanning calorimeter was introduced in this research as a tool to quantify the amount of ettringite formed in stabilized soils.

The first part of this dissertation provides a case history analysis of the expansion history compared to the ettringite growth history of three controlled low strength mixtures containing fly ash with relatively high sulfate contents. Ettringite growth and measurable volume changes were monitored simultaneously for mixtures subjected to different environmental conditions. The observations verified the role of water in causing expansion when ettringite mineral is present. Sorption of water by the ettringite molecule was found to be a part of the reason for expansion.

The second part of this dissertation evaluates the existence of threshold sulfate levels in soils as well as the role of soil mineralogy in defining the sensitivity of soils to sulfate-induced damage. A differential scanning calorimeter and thermodynamics based phase diagram approach are used to evaluate the role of soil minerals. The observations substantiated the difference in sensitivity of soils to ettringite formation, and also verified the existence of a threshold level of soluble sulfates in soils that can trigger substantial ettringite growth.

The third part of this dissertation identifies alternative, probable mechanisms of swelling when sulfate laden soils are stabilized with lime. The swelling distress observed in stabilized soils is found to be due to one or a combination of three separate mechanisms: (1) volumetric expansion during ettringite formation, (2) water movement triggered by a high osmotic suction caused by sulfate salts, and (3) the ability of the ettringite mineral to absorb water and contribute to the swelling process.

DEDICATION

To all those who pursue knowledge for the betterment of society

ACKNOWLEDGEMENTS

I would like to extend my sincere gratitude to Dr. Dallas Little, my committee chair, for providing me with the opportunity and invaluable support to conduct this research. What I have learned working with him far exceeds the research that is documented in this dissertation. I would also like to thank Dr. Bruce Herbert, my graduate committee member, for his support and valuable insights that has helped me get thorough many rough patches in my research. I also wish to thank my graduate committee members, Dr. Robert Lytton and Dr. Richard Loeppert, for their support and encouragement in pursuing this research. I also acknowledge the technical staff at Texas Transportation Institute (TTI) for their help in executing this research.

I appreciate the support of my colleagues Dr. Amit Bhasin, Srikant Bondugula, Hakan Sahin who were directly involved in various stages of my research. I also wish to thank Ms. Barbara Hein for extending the necessary administrative support for executing this research, and Sean Kohl, manager TA Instruments, for extending the necessary technical support for the differential scanning calorimeter.

I acknowledge the support and encouragement of my family members, Mr. Gopalakrishnan Nair, Mrs. Radhamony Amma, Mr. Sasidharan Nair, Mrs. Sobhana Kumari, Mrs. Shanthamma and Mr. Suresh for their support and encouragement. I also wish to extend my sincere gratitude to Mrs. Girija Suresh for her time, help and support to my family during the final years of my degree program. Finally, I wish to

acknowledge the support and encouragement of my wife, Lekshmi Girija, who inspired me to pursue this path and stood by me through all its ebbs and flows.

TABLE OF CONTENTS

Page

LIST OF FIGURES

FIGURE Page

LIST OF TABLES

1. INTRODUCTION

1.1. Overview

Long term performance of pavement structures often depends on the stability of the underlying soils. Engineering design of these constructed facilities relies on the assumption that each layer in the pavement has the minimum specified structural quality to support and distribute the super imposed loads. These layers must resist excessive permanent deformation, resist shear and avoid excessive deflection that may result in fatigue cracking in overlying layers. Available earth materials do not always meet these requirements and may require improvements to their engineering properties in order to transform these inexpensive earth materials into effective construction materials. This is often accomplished by physical or chemical stabilization of these natural soils. Selection of techniques to be used in stabilization is site specific and is based on the required engineering properties and on the physio-chemical characteristics of natural soils.

Over the years engineers have tried different methods, including thermal, electrical, mechanical or chemical means, to stabilize soils that are subject to fluctuations in strength and stiffness properties as a function of fluctuation in moisture content. Among these techniques, the first two options are rarely used. Mechanical stabilization, or compaction, is the densification of soil by application of mechanical energy. Densification occurs as air is expelled from soil voids without significant change

---

This dissertation follows the style of *Journal of Geotechnical and Geoenvironmental Engineering*, ASCE.

in water content. This method is particularly effective for cohesion less soils where compaction energy can cause particle rearrangement and particle interlocking. But, the technique may not be effective if these soils are subjected to significant moisture fluctuations. The efficacy of compaction may also diminish with an increase of the fine content, fraction smaller than about 75 μm, of the soil. This is because cohesion and inter particle bonding interferes with particle rearrangement during compaction. Altering the physio-chemical properties of fine-grained soils by means of chemical stabilizers/modifiers is a more effective form of durable stabilization than densification in these fine-grained soils. Chemical stabilization of non-cohesive, coarse grained soils, soils with greater than 50 percent by weight coarser than 75 μm is also beneficial if a substantial stabilization reaction can be achieved in these soils. The strength improvement in these cases can be much higher, often greater than ten fold, when compared to the strength of the untreated material.

In place soil treatment using calcium-based stabilizers is an economically feasible solution alternative to address strength deficiencies and problematic shrink/swell behavior in unstable subgrade soils. Soil instability, in most cases, originates from the presence of clay or silt whose instability is normally triggered by a change in moisture content. Even though stabilization improves engineering properties, problems can arise when calcium-based stabilizers are used in soils rich in sulfate-bearing minerals. Stabilization of sulfate rich soils in the presence of excess moisture may lead to the formation of minerals such as ettringite and/or thaumasite and can cause distress in or even destruction of pavement structures due to heaving (Mitchell 1986; Hunter 1990).

These distresses typically occur when cementitious materials containing calcium oxide are used to stabilize soils and/or aggregates containing sulfates or when these stabilized layers are exposed to solutions high in soluble sulfates. These distresses are often initiated deep within the stabilized layers and therefore any remediation may require the removal and reconstruction of the entire pavement section. Since the cost incurred in maintenance and/or reconstruction often outweighs the economic feasibility of stabilization, it is critical to the success of the stabilization alternative to be able to predict or evaluate the potential for sulfate induced structural distress prior to application of calcium based stabilizers.

Even though sulfate-induced heave in stabilized soils was first reported by Sherwood in 1962, the problem received national attention only in the mid-1980s when Mitchell reported a case study based on his experience at an arterial street in Las Vegas, Nevada (Sherwood 1962; Mitchell 1986). Many cases were reported after that where clay soils with high sulfate content were found to expand and destroy the pavement structures when treated with calcium based stabilizers (Hunter 1988, Petry and Little 1992). To date, the focus of research in addressing these deleterious reactions has largely concentrated on the role of sulfates in causing these expansive reactions. A general belief among most practitioners is that ettringite formation in soils is fast and occurs when sulfate sources are available in soil. Hence, to identify the potential for sulfate induced expansion (ettringite formation) in soils stabilized with calcium-based stabilizers, practitioners rely on empirically derived threshold sulfate levels, a measure of water soluble sulfate in soil, beyond which significant ettringite and/or thaumasite growth and, therefore, significant structural distress occurs. Although these threshold-based predictions hold reasonably well in most cases, the literature documents cases where sulfate-induced distress has occurred at sulfate levels below 1,000 ppm and where it has not occurred at sulfate levels as high as 10,000 ppm or even higher (Hunter 1988; Mitchell and Dermatas 1992; Puppala et al. 2002; Little et al. 2005). These observations suggest the existence of factors other than sulfate content, possibly the availability of aluminum from clays, in defining the extent of formation of ettringite in stabilized soils. Therefore, experience alone and "rules-of-thumb" based on experience are not often sufficient to deal with this complex issue.

Apart from the discrepancies in sulfate levels causing these distresses, the time window between stabilization and manifestation of distress also vary among reported field observations. Documented reports indicate these distresses to occur either immediately after placement and compaction of stabilized layers or in some cases months or even years after lime treatment (Mitchell 1986; Hunter 1988; Petry 1994; Perrin 1992; Burkart 1999; Kota 1996). These expansion mechanisms are complex and often confusing with considerable variation in the amount of distress associated with a specific sulfate concentration. No rules or guidelines can therefore be established regarding the proportionality between the amount of ettringite formed and the extent of expansion in the stabilized media. Currently, laboratory based physical tests, like the swell test, are also used along with sulfate quantification techniques to determine the potential for expansive swell after stabilization. Qualitative techniques like x-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy are then used to verify the presence of ettringite in soil. Even though the results of swell testing are valuable, using these for techniques to identify ettringite potential in stabilized soils may sometimes be misleading or at least incomplete. The results of swell testing, in most cases, are found to be dependent on sulfate levels in soil and seldom seen to be influenced by differences in soil mineralogy. Volume changes associated with these swell tests are often attributed to ettringite formation in stabilized soils. The known capabilities of calcium based stabilizers to reduce shrink swell potential of expansive soils, when combined with the understanding of deleterious expansion potential of the ettringite mineral, have led to the conclusion that the expansion during swell testing in sulfate rich soils is due to ettringite formation. However, swell testing alone does not provide a convincing basis for judging the potential for sulfate-induce damage. First of all such testing does not identify factors that influence whether or not ettringite has the thermodynamic potential to form nor the kinetics of its formation. Furthermore the presence of salts in the soil matrix may also influence the soil-water suction characteristics of the soil matrix, and the impact of these on swell apart from or in concert with expansive mineral formation must be considered in a complete analysis of the cause(s) of damage. Therefore new techniques need to be developed to evaluate ettringite growth in stabilized soils and link these to already established threshold risk levels to define the deleterious expansion potential of sulfate bearing soils during stabilization.

1.2. Problem Statement and Research Objectives

Even though significant research has been done on ettringite formation during stabilization of sulfate bearing soils, uncertainties do exist among engineers when dealing with these deleterious sulfate reactions. A general belief among many practicing engineers is that ettringite formation in soils is fast and sulfate content in soil is the sole factor in deciding the extent of mineral formation. Controlled experimental studies, on the other hand, support a time dependent ettringite growth when conditions are appropriate (Mitchell and Dermatas 1992; Dermatas 1995; Ohaydi and Young 2008; Little et al. 2005). This time dependency is possibly due to the role of soil minerals in providing aluminum needed for ettringite formation which is often ignored in the current risk assessment techniques for stabilized soils. This research focuses on the development of a new technique, using a differential scanning calorimeter, to quantify ettringite growth in lime stabilized soils which will be used to identify the role of soil mineralogy in defining the extent of ettringite growth in these soils. Questions still remain regarding swelling associated with ettringite formation concerning how much the matrix can expand if the soil cannot accommodate these newly formed ettringite crystals. Even though molar volume calculations, based on volume changes in reactants and products during mineral formation, can be used to determine volume changes, the extent of measurable expansion may vary with the physio-chemical properties of the stabilized media, availability of water and timing and rate of crystal growth etc. (Odler and Glasser 1988; Mitchell and Dermatas 1992; Dermatas 1995; Little and Graves 1995; Older and Subauste 1999; Little et al. 2005; Dermatas et al. 2006). This research aimed toward the development of a better understanding of the role of some of these factors on expansion associated with ettringite formation:

This research addressed the following objectives

1. Develop a methodology to quantify ettringite formation in lime treated soils.
2. Identify the role of water in the mechanism of expansion associated with ettringite formation.
3. Identify the impact of soluble sulfate salts on swell behavior apart from or in concert with the formation of the expansive mineral ettringite.
4. Investigate alternate reasons for swelling when sulfate sources are present.

1.3. Dissertation Outline

The dissertation is a synthesis of three different research tasks directed towards a better understanding of the impact of the formation of mineral ettringite and the associated expansive behavior of the matrix during the stabilization process. The body of this dissertation consists of four papers, presented according to style and format of the Journal of Geotechnical and Geoenvironmental Engineering, as well as the guidelines provided in the Texas A&M University Thesis Manual. Three of these papers have been published in refereed journals and the fourth paper has been submitted to the Journal of the Transportation Research Board for consideration for publications, as is described in more detail in the following paragraph. The dissertation is organized in six sections as described below.

Section 1 is an introduction that consists of an overview, problem statement and research objectives and the dissertation outline.

Section 2 presents a literature review that gathers the existing information pertinent to achieving the research objectives. The section includes excerpts from the paper “Addressing sulfate induced heaving in lime treated soils” published in the Journal of Geotechnical and Geoenvironmental Engineering© [2010]. Authors of this paper are: Dallas Little, Syam Nair and Bruce Herbert.

Section 3 is a reprint of the paper “Water: The key to Expansion of Ettringite in Cementitious Materials” whose final form has been published in the Journal of Transportation Research Board© [2009]. The paper addresses the role of water in causing expansion when ettringite mineral is present in cementitious materials. The authors of this paper are Syam Nair and Dallas Little.

Section 4 is a reprint of paper “Validation of Sensitivity of Sulfate-Bearing Soils to Ettringite Growth Based on Differential Scanning Calorimetry” whose final form has been published in the Journal of Transportation Research Board© [2009]. The paper addresses the role of soil mineralogy on the formation of ettringite mineral in lime treated soils. The authors of this paper are Dallas Little and Syam Nair.

Section 5 is a paper that addresses the mechanisms of heaving associated with ettringite formation in lime treated soils. The paper has been submitted for publication in the Journal of Transportation Research Board and is currently in review. The paper also addresses alternate mechanisms that can cause heaving in lime treated soils when sulfate salts are present. The authors of this paper are Syam Nair and Dallas Little.

Section 6 represents the conclusions and recommendations of the dissertation. The section also include a topic for future research along with some preliminary results showing a technique that can be used in conjunction with pre-existing techniques to reduce the extent of swelling in lime stabilized sulfate bearing soils.

Appendix A has the detailed procedure used for the synthesis of mineral ettringite in the laboratory. The process is a modified version of a technique used by Perkins and Parmer. Professor Bruce Herbert and his research group in Geology and Geophysics Department, Texas A&M University, were instrumental in developing and standardizing this procedure.

Appendix B has the detailed procedure used for quantifying ettringite in lime treated soils. Sample preparation techniques, curing and testing conditions and analysis techniques are detailed in this section.

Appendix C presents details of a simple technique, without the use of strong chemical reagents, which can be used to separate sand fraction in soil from silt and clay. The silt and clay fraction can then be used for ettringite quantification testing by following techniques discussed in Appendix B.

2. LITERATURE REVIEW*

2.1. Introduction

Sulfate induced heaving, due to the formation of expansive minerals like ettringite and thaumasite, has been recognized as a problem in Portland cement concrete, stabilized soils, weathered cements, alkaline fly ashes, FGD wastes, chromite ore processing residues and cement based waste solidification products (Sherwood 1962; Mitchell 1986; Hunter 1988; Petry and Little 1992; Dermatas 1995; Myneni et al. 1998; Wild et al. 1999; Taylor et al. 2001; Mindess et al. 2002; Harris 2004; Dermatas et al. 2005; Lee et al. 2005). The ettringite group can be described by the general formula $[Ca_6[X(OH)_6]_2(Y)_3.26H_2O$, where X represents a site occupied by trivalent metals like Al^{3+}, Fe^{3+}, or Cr^{3+} and Y represents site occupied by oxanions like SO_4^{2-}, CO_3^{2-}, SeO_4^{2-} or CrO_4^{2-}. Alternate substitution can involve ions like $B(OH)^{4-}$ and AsO_4^{3-}, which requires stoichiometric adjustments within the structure (Myneni et al. 1997). The presence of ettringite in fly ash and concrete and its exchange capacity with environmental contaminants like arsenic, chromium and selenium makes it effective in preventing environmental contamination and useful in waste stabilization. Ettringite typically precipitates in environments where the pH remains high with high activities of Ca^{2+}, Al(aq), and SO_4^{2-} (Perkins and Palmer 1999; Mitchell and Dermatas 1992; Warren

---

[*] Part of the data reported in this section is reprinted from "Addressing sulfate induced heaving in lime treated soils" by Dallas Little, Syam Nair and Bruce Herbert. J*ournal of Geotechnical and Geoenvironmental Engineering*, 136(1), © American Society of Civil Engineers [2010].

and Reardon 1994). Geochemical factors such as pH, temperature, activities (i.e. effective concentration) of participating ions in solution, dissolved CO2 and H2O etc. can all influence the precipitation and stability of ettringite in soil water systems (Ogawa and Roy 1981; Damidot and Glasser 1993; Myneni et al. 1998; Little et al. 2005).

Even though previous studies have identified the primary environmental and geochemical factors that influence ettringite formation, misconceptions still remain among engineers regarding the kinetics of mineral precipitation and the role of soil minerals in providing reagents needed for ettringite growth. Furthermore, there are uncertainties on the extent of expansion associated with the mineral precipitation and on the mechanisms causing these expansions. The literature review addresses some of these issues and includes 1) the current practices used for risk assessment in stabilized soils 2) the chemistry and structure of ettringite mineral and the link between the structure of ettringite and the mechanism of expansion and damage 3) the mechanism of heaving or disruption during ettringite formation 4) the mechanism of ettringite growth in cementitious materials and in stabilized soils 5) explanations on the fundamental differences between ettringite formation in soils versus ettringite formation in cementitious materials and hypothesizes a two-phase mechanism for ettringite mineral growth in soils treated with calcium-based stabilizers 6) volume changes that can occur during ettringite formation and explains how the swell behavior can vary with changes in environmental conditions leading to mineral precipitation 7) sulfate availability in lime stabilized soils and 8) explains some of the misconception on ettringite formation in stabilized soils.

2.2. Current Practices on Risk Assessment in Stabilized Soils

Sulfate ions are a key ingredient in the formation of ettringite and therefore an accurate assessment of the amount of soluble sulfates is critical in identifying the risk of deleterious sulfate reactions during the stabilization process. The current methodology to identify risk of sulfate-induced damage is based on quantifying the concentration of available (usually water soluble) sulfates in the soil. Sulfate contents are generally expressed either in ppm (parts per million) or mg/kg (which is equal to ppm) or in a percent dry weight of soil (10,000 ppm or 10,000 mg/kg is equal to 1 percent by mass). These water soluble sulfate levels in soils, measured using gravimetric or colorimetric techniques like AASHTO T 290, CL-2105, TEX-145-E etc., are correlated to observed field behavior in these soils to identify the risk associated with a given sulfate concentration (Table 2-1). Based on these empirical evidences, engineers have identified the threshold sulfate levels beyond which significant ettringite and/or thaumasite growth and, therefore, significant structural distress occurs (Little and Graves 1995; Harris et al. 2003).

Table 2-1. Level of risk associated with lime stabilization in sulfate-bearing clays (Little and Graves 1995)

Risk Involved	Soluble Sulfate Concentrations	
	Parts Per Million	Percent dry weight
Low Risk	Below 3,000 ppm.	Below 0.3%
Moderate Risk	Between 3,000 and 5,000 ppm	Between 0.3% and 0.5%
Moderate to High Risk	Between 5,000 and 8,000 ppm	Between 0.5% and 0.8%
High to Unacceptable Risk	Greater than 8,000 ppm	Greater than 0.8%
Unacceptable Risk	Greater than 10,000 ppm	Greater than 1.0%

The Texas Department of Transportation (TxDOT) recommends a safety limit of 0.2 percent by mass for soluble sulfate as a threshold separating a safe acceptable risk from low to moderate risk. This limiting value agrees with studies of Petry and Little (1992). But Mitchell and Dermatas (1992) defined 0.3 percent soluble sulfates by mass as the safe limit for sulfates in soils, whereas Puppala et al. (2002) observed sulfate concentrations from as low as 0.1 to 0.2 percent to be capable of causing expansive reactions. Although these "rules of thump" may stand accurate in most cases, cases were reported in literature where soils with varying levels of sulfates, from above 1,000 ppm to 10,000 ppm, precipitate ettringite when treated with calcium-based stabilizers (Hunter 1988; Little et al. 2005; Mitchell and Dermatas 1992; Mitchell 1986; Puppala et al. 2002). These observed variations are possibly due to the difference in the mineralogy of the soils as the type and percentage of minerals, primarily clay minerals, in the soil determines the release of aluminum required to form ettringite (Petry and Little 1992; Mitchell and Dermatas 1992).

2.3. Chemistry of Ettringite and Thaumasite Formation

Ettringite is a calcium alumino-sulfate mineral that precipitates under alkaline (high pH) conditions in soil and concrete systems with high sulfate activity (Petry and Little 1992; Warren and Reardon 1994; Kota et al. 1996; Perkins and Palmer 1999; Jallad et al. 2003). Although researchers have reported ettringite to be stable at pH levels close to 9.0, it is generally agreed that ettringite precipitates at pH conditions above 10.7 (Myneni et al.1998). Among the several calcium-aluminum-sulfate hydrates can form in these high pH conditions, only mono-sulfate hydrate and tri-sulfate hydrate forms are stable in solution (Lerch et al. 1929). Formation or hydration of the mono-sulfate phase does not result in expansion, whereas the formation and/or hydration of the tri-sulfate phase can cause significant volume changes in stabilized layers. A categorical explanation of the mechanism of formation of these tri-sulfate phases in stabilized soils was first provided by Hunter (1988) and was based on the geological, geochemical, and mineralogical reasons for their precipitation. Chemistry of ettringite formation is given in equation [2-1].

$$6Ca^{2+} + 2Al(OH)_4^- + 4OH^- + 3(SO_4)^{2-} + 26H_2O \rightarrow Ca_6[Al(OH)_6]_2.(SO_4)_3.26H_2O \qquad (2\text{-}1)$$

Resources needed to form ettringite are made available partly by the stabilizers and partly by minerals present in soil. For 1 mole of ettringite to form 6 moles of Ca2+, 2 moles of Al^{3+}, 3 moles of SO_{42-}, and 32 moles of water are required. Calcium ions are provided by lime, Portland cement, or fly ash; alumina is supplied by dissolution of oxyhydroxides and phyllosilicates; and sulfates are supplied by dissolution of sulfate salts present in soil or by migration of sulfate ions as water diffuses through the matrix (Hunter 1988; Little 2005; Petry and Little 1992; Mitchell and Dermatas 1992; Ouhadi and Young 2008; Dermatas 1995). Even though these components may be available, thermodynamic favorability and concentration of limiting reagents control the precipitation of ettringite in these stabilized soils (Little 2005).

Thaumasite, a silica-bearing analog of ettringite represented by the structural formula $[Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2 \bullet 24H_2O]$, is believed to form in lime treated soils and Portland cement concrete structures as a result of low temperature sulfate reaction and intensive carbonation (Bensted 2003). Although a clear consensus does not exist on how thaumasite forms, it is believed that thaumasite uses ettringite as the template for initial formation after which it is forms directly from solution (Kohler et al. 2006). Chemistry of thaumasite formation is given in equation [2-2].

$$\begin{aligned} &Ca_6[Al(OH)_6]_2 \bullet (SO_4)_3 \bullet 26H_2O + 2(H_2SiO_4)^{2-} + 2CO_3{}^{2-} + O_2 \rightarrow \\ &Ca_6[Si(OH)_6]_2 \bullet (SO_4)_2 \bullet (CO_3)_2 \bullet 24H_2O + 2Al(OH)_4^- + SO_4{}^{2-} + 4OH^- + 2H_2O \end{aligned} \tag{2-2}$$

A low temperature, generally considered to be 15 °C, and intensive carbonation are required to form and maintain thaumasite as a stable phase in the matrix (Hunter 1988; Bensted 2000). Along with carbonates and sulfate ions, thaumasite consists of silicon, which is derived from the decomposition of C-S-H formed during cementing reactions in stabilized soils (Crammond 1985; Kohler et al. 2006). A lesser concentration of reactive alumina combined with a higher calcium and sulfate content favor the decomposition of cementitious materials. Silicon needed for thaumasite growth may also be provided from the remnants of unreacted calcium silicates in cement or from soluble silica in clays or microcrystalline silt fractions in soil.

2.4. Structure of Ettringite and Thaumasite

The ettringite mineral has a needle like structure with lengths varying from a few microns to as high as 200 μm (Moore and Taylor 1970; Dermatas 1995; Dermatas et al. 2005; Moon et al. 2007). The tubular structure consists of columns and channels running parallel to the c-axis (Moore and Taylor 1970). The columns primarily consist of aluminum octahedrons and calcium polyhedrons. Calcium polyhedrons are shaped as triagonal prisms where water and hydroxyl ions occupy four apices each. The tubular structure is formed by a chain of one alumina and three calcium polyhedrons that repeats uniformly to form a $\{Ca_6[Al(OH)_6]_2.24H_2O\}^{6+}$ structure. Two aluminum octahedrons ($[Al(OH)_6]^{3-}$) are connected by a group of three calcium polyhedrons. Shared hydroxyl ions (OH^-) bridge the calcium and aluminum polyhedra and form a continuous chain extending along the c-axis of the mineral (Moore and Taylor 1970; Myneni et al. 1997). The coordination polyhedra are completed by water molecules. A single $\{Ca_6[Al(OH)_6]_2 \bullet 24H_2O\}^{6+}$ column showing aluminum polyhedra and part of the calcium polyhedra is shown in Fig. 2-1(b).

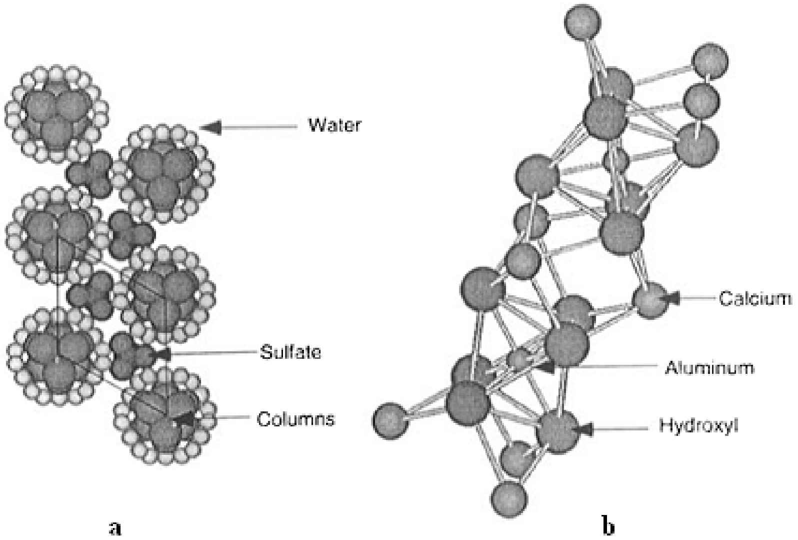


Fig. 2-1. Schematic of Ettringite molecule (Myneni et al. 1997)

The channel between the columns consists of $[(SO_4)_3 \bullet 2H_2O]^{6-}$ ions (Fig. 2-1a). Sulfate ions occupy the channel and bind the columns into a crystal and also form H-bonds with Ca-coordinated water molecules (Moore and Taylor 1970; Skoblinskaya and Krasilinkov 1975). Water molecules in ettringite structure are positioned at four distinct locations: in the inter column channel, at the two main apices, at two additional apices of calcium polyhedra and as hydroxyl ions linking calcium and aluminum ions. Due to a high weight percent of water in ettringite, water is important to the stability of the mineral structure. Both calcium and sulfate ions can accommodate exchangeable water molecules in their structure which is important to the stability of the mineral (Shimada and Young 2001). The channel structure can also hold additional water which corroborates experimental observations of ettringite crystal swelling when water is available (Mehta 1973). The tubular structure of ettringite is different from the structure of clays and soil minerals and hence the anisotropic growth of these crystals can exert expansive pressure on stabilized layers.

The structure of thaumasite is similar to that of ettringite with Si substituting for Al within the columns and interstitial replacement of CO_3^{2-} and $(SO)_4^{2-}$ groups for $(SO)_4^{2-}$ and water. The thaumasite framework consists of columns with $[Ca_6[Si(OH)_6]_2 \bullet 24H_2O]^{8+}$ oriented along the c axis and $[(CO_3)_2(SO_4)_2]^{8-}$ groups are distributed through inter columnar channels (Crammond 1985). Even though the two minerals have similar structural arrangement, the expansive capability of thaumasite is less when compared to ettringite as the mineral occupies only 45 percent of the volume of ettringite from which it is derived (Bensted 2000; Crammond 2003). Hence thaumasite formation results in “crumbling” of the matrix and also a loss of bonding and reduction in compressive strength of the matrix (Bensted 2000; Crammond 2003).

2.5. Mechanism of Ettringite Growth

2.5.1 Cementitious Materials

The kinetics of ettringite precipitation is fast when the components needed for formation are readily available in solution and the precipitation achieves steady state in approximately 150 hours (Damidot and Glasser 1993; Myneni et al. 1997). Mineral precipitation, in this case, will depend on the availability of reactants and the existence of thermodynamically favorable conditions in the matrix. Portland cement hydration is designed so that most ettringite forms relatively quickly as gypsum is utilized to prevent the rapid hydration of tri-calcium aluminate. The components, in dry form, are uniformly blended and by nature of their particle size distribution have a very large surface area. Hence when mixed with water to form cement paste, this high surface area translates to a higher reactivity as the reactants rapidly become available in solution as soluble ions.

Two mechanisms of ettringite formation in cement have been proposed: topochemical reaction and through solution reaction (Skalny et al. 2002). Many consider ettringite formation to be a topochemical reaction mechanism and the crystal growth to occur at the solid solution interface (Ogawa and Roy 1982; Odler and Glasser 1988; Taylor et al. 2001). Topochemical reaction is favored when the capability of the products to crystallize is greater than the rate of dissolution of the reactants. Therefore, when a sufficiently high concentration of lime is present and sulfate ions are available in solution, aluminum ions dissolving out cannot migrate far from the aluminum source due to the super saturation of liquid phase with respect to ettringite. Hence crystals precipitate preferentially on the surface of the alumina bearing phase in a topochemical reaction (Deng and Tang 1994). Other than topochemical reaction, ettringite can also form through a solution mechanism where the products precipitate randomly from the liquid phase after attaining a state of super saturation. When the concentration of lime is low the aluminum ions can migrate more freely in solution and ettringite can precipitate from solution under favorable conditions (Deng and Tang 1994).

2.5.2 Stabilized Soils

Soils differ from cements in three important characteristics: particle size, dissolution properties of minerals at high pH levels and interactions with the environment. Even though clay colloids are much smaller than Portland cement particles, when soil systems are treated with calcium based stabilizers such as lime or Portland cement, the particles flocculate and agglomerate into larger composite particles, which normally have a substantially smaller surface area than Portland cement particles. In addition, the soil minerals have a well defined crystal structure. Hence, the kinetics of mineral solubility at high pH conditions is generally slower than the rate of dissolution of ions from cement components. Moreover, the effect of weathering and varying environmental conditions creates heterogeneity in the distribution of reactive soil minerals. Hence the availability of components needed for ettringite formation may depend on factors other than just the concentration of reactive minerals in soil. Therefore, there is no reason to assume that because ettringite occurs rapidly, say within the first day or so of cement hydration, it should also occur rapidly in stabilized soils.

Finally, due to a lower rigidity of the stabilized soil matrix when compared to Portland cement, soils are more open systems where ettringite reactants can diffuse more easily into the matrix, resulting in additional ettringite precipitation (Hunter 1988). Water can also move more easily into the stabilized layers after pozzolanic hardening has become substantially complete and solubilize the available sulfates resulting in additional heaving. Literature suggests that ettringite formation in stabilized soils can either be due to a topochemical or through-solution mechanism (Dermatas 1995; Dermatas 2006a). But for stabilized soils, pH conditions or rather the concentration of free lime can vary with location and time. Hence, as detailed in section 2.5.1, the conditions which influence the mobility of dissolved aluminum will be different in each case. Hence a combination of the two mechanisms may cause ettringite precipitation in stabilized soils.

2.5.3 Hypothesis on Ettringite Formation and Growth in Stabilized Soils

Due to limited availability of aluminum and sulfate ions during initial stabilization reactions, it is possible that the ettringite precipitating during this time acts as nucleation sites for future growth when both sulfate and alumina become available. Water moving into the system can solubilize unreacted lime and also act as a medium for ion migration and therefore become a continuous source of reagents at these nucleation sites (Hunter 1988; Burkart et al. 1999). As such, the formation is analogous to the growth of other crystals in which the process begins with nucleation followed by a time dependent crystal growth as shown in Fig. 2-2.

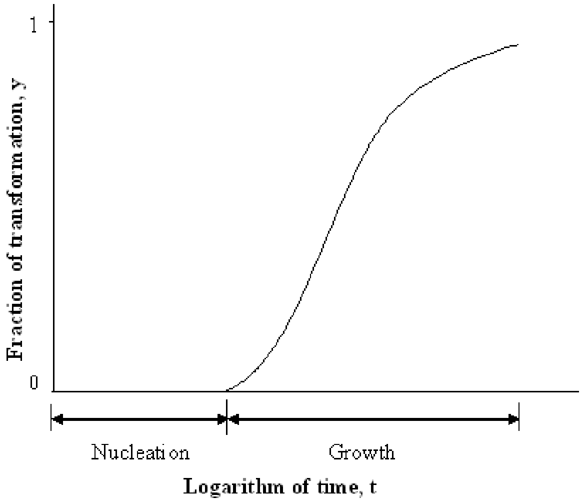


Fig. 2-2. Schematic of nucleation and rate of crystal growth (Callister 2001)

Both nucleation and subsequent crystal growth are controlled by the degree of saturation. Saturation occurs when the crystal is in equilibrium with the solution, i.e., the rate of dissolution equals the rate of crystallization. Before saturation, the free energy of the system increases as the reaction among ions progresses into solution. Precipitates formed during the reaction re-dissolve and stay in solution until a critical energy level is attained (Callister 2001). This energy barrier corresponds to activation free energy beyond which the crystals remains stable in solution. Under constant conditions of temperature and pressure the reactions occur spontaneously moving the system towards equilibrium and a state of minimum free energy. Once crystals are formed the rate of growth depends on the diffusion of ions to the nucleation sites. A general form of the crystal growth is given in Eq. (2-3):

$$y = 1 - \exp\left(-kt^{n}\right) \tag{2-3}$$

where y is the amount of crystal growth, t is time, and k and n are time-independent constants. The degree of nucleation also affects the rate of crystal growth. A small number of or random nucleation sites means fewer sites are available for crystal growth whereas a higher or a more evenly dispersed nucleation sites can cause more rapid and evenly dispersed crystal growth. The rate, r, of crystal growth is also affected by temperature, T, as generally determined by the Arrhenius relationship and is given in Eq. (2-4):

$$r = Ae^{\left(-\frac{Q}{RT}\right)} \tag{2-4}$$

where, Q is activation energy; A is a temperature independent constant and T the absolute temperature.

Mineral precipitation in soil-water system can be explained based on Guy-Lussac-Ostwald (GLO) step rule. In an aqueous phase where the reagents are already in solution, the sequence of minerals precipitating out depends on the initial composition of the system. Initially, the formation of phases with the fastest precipitation rate is favored (Langmuir 1997). The kinetics of ettringite formation is fast and hence the extent of nucleation and crystal growth depends on availability of the limiting reagent in solution. Thereafter, the system will form phases that require lower activation free energy. Nucleation of soluble phases is kinetically favored as the soluble phases have a lower mineral-solution interfacial energy and thus lower nucleation energy when compared to less soluble analogues. Finally, other competing phases forming in solution may also affect the kinetics of the reaction.

2.6. Mechanism of Heaving or Disruption

At least two theories exist regarding the cause of expansion during ettringite formation: (1) topochemical formation of ettringite and the anisotropic growth of the crystals (Ogawa and Roy 1982; Odler and Glasser 1988), and (2) expansion caused by absorption of water by ettringite crystals (Mehta 1973a). Since ettringite crystals are formed in a basic environment, they carry a negative surface charge which is capable of lowering the chemical potential of adsorbed water (Mehta and Wang 1982). A combination of this negative charge and a high surface area is responsible for attraction of large amounts of water. Since there is no inter crystalline chemical bonding among ettringite crystals, the absorbed water molecules can cause inter-particle repulsion resulting in overall expansion of the matrix (Mehta 1973a). This mechanism is similar to electrostatic attraction of bi-polar water molecules by some clays causing swelling of clay layers. Again, water absorption has been proven to be one of the factors that intensify the expansion when these minerals are present in the system (Odler and Glasser 1988, Older and Subauste 1999; Ouhadi and Yong 2008). Hence it is reasonable to believe that either one of the above theories or a combination of both may result in expansive behavior when ettringite is present (Deng and Tang 1994). Either way, the presence of external water is a decisive factor in causing deleterious expansion in stabilized soils.

2.7. Volume Changes Due to Ettringite Formation

To relate the sulfate levels in soil to expansion associated with ettringite formation, stoichiometric calculations, using a factor-label or unit conversion method, are first used to determine the maximum possible amount of ettringite that can form in any system. As an example, let us consider a soil with one percent soluble sulfate content, i.e. one percent soluble sulfate by mass or weight of soil. If sulfates are the limiting reagent in ettringite formation, the relationship between soluble sulfate and ettringite formed is linear. The stochiometric transformation of one percent sulfate (equivalent to 10,000 ppm sulfates in solution) to mass of ettringite is given in Eq. (2-5):

$$\frac{1g\,SO_4}{100g\,Soil}\times\frac{1mol\,SO_4}{96g\,SO_4}\times\frac{1mol\,E}{3mol\,SO_4}\times\frac{1254g\,E}{1mol\,E}=\frac{4.36g\,E}{100g\,Soil}=4.36\%E\,(E=ettringite) \qquad (2\text{-}5)$$

Again, the mass of the product can be no greater than the mass of the reactants, but expansion occurs because the molar volume of ettringite is greater than the molar volume of the reagents. This can be shown from molar volume calculations based on a simple chemical equation, Equation 3, showing the chemistry of ettringite precipitation.

$$C_3A+3C\overline{S}H_2+26H_2O\rightarrow C_3A\cdot 3C\overline{S}H_2\cdot H_{26} \qquad (2\text{-}6)$$

In equation 2-6, C_3A is tricalicum aluminate, $C\overline{S}H_2$ is gypsum, and H is water. The stochiometric proportions in Eq. (2-6) indicate that, for one mole of ettringite to form 1 mole of C3A, 3 moles of $C\overline{S}H_2$ and 26 moles of water are required. From the literature, we know that the molecular volume of C_3A = 89.1 cm3/mol, $C\overline{S}H_2$ = 74.2 cm3/mol and ettringite = 737.6 cm3/mol. Normally a Portland cement concrete mixture requires a water cement ratio of between 0.4 to and 0.55. Since no additional water is added during the early hours of cement hydration, the water consumed in ettringite formation is removed from within the system which is considered to be partially responsible for the high slump loss in PCC (Mehta 1973b). The volume change within the matrix when one mole of C_3A combines with three moles of CaSO4 to form ettringite by consuming water from within the matrix is given by Eq. (2-7):

$$Volume\ \ Change = \left[\frac{MolarVolume_{\mathrm{Pr}oducts} - MolarVolume_{\mathrm{Re}agents}}{MolarVolume_{\mathrm{Re}agents}} \right] \tag{2-7}$$

$$Volume\,Change_{(Matrix\,Water\,Source)} = \left[\frac{737.6 - 311.7 - 468.52}{780.22} \right] = -\,0.05\,or\,5\ percent\ shrinkage$$

However, stabilized soils are open systems where the mobility of water is not restricted. Since the volume changes are dependent on molar volume of components removed from the system, the source of water contributing to ettringite formation, whether internal or external to the system has a profound effect in deciding whether a significant expansion or contraction occurs during the process. Based on Eq. (2-7), the volume changes associated with ettringite formation when water consumed in ettringite formation is considered to be from outside the matrix is given by:

$$Volume\,Change_{(External\,Water\,Source)} = \left[\frac{737.6 - 311.7}{311.7} \right] = 1.37\,or\,137\ percent\ \exp ansion$$

Again, during the precipitation process mass is conserved, but the volume that the mass of the product displaces, when normalized on the molecular scale, is greater than the volume displaced by the components, when normalized in the same manner. Therefore, the resulting volume change is very large and is the root cause of expansion. The amount of ettringite formed (shown as a percentage of the mass) for a given concentration of sulfates and the associated volumetric changes is given in Table (2-2).

Table 2-2. Volumetric changes due to ettringite formation considering sulfate content as the limiting reagent

Sulfate content (ppm)	% Ettringite formed	Using water from the matrix		Using water from external source	
		Unit volume change (%)	Total shrinkage (%)	Unit volume change (%)	Total expansion (%)
1,000	0.44	-0.05	-0.02	1.37	0.60
3,000	1.31	-0.05	-0.07	1.37	1.79
5,000	2.18	-0.05	-0.12	1.37	2.98
10,000	4.36	-0.05	-0.23	1.37	5.96
30,000	13.07	-0.05	-0.70	1.37	17.87
50,000	21.78	-0.05	-1.17	1.37	29.79
70,000	30.49	-0.05	-1.64	1.37	41.70
100,000	43.55	-0.05	-2.34	1.37	59.57

Field observations also support the role of external water in expansion of the matrix. In many reported cases of expansion in stabilized soils, the stabilized layers were found to expand and heave over extended periods and water was documented to be a part of the process (Hunter 1988; Perrin 1992; Kota et al. 1996). Areas of observed distress in these cases were found near water sources and the disturbed sections showed higher, often considerably higher, water content than the water used in the stabilization process. Hence the water that triggers expansion probably came from outside the matrix. This supports the molar volume calculations where ettringite formation using water external to the matrix has been shown to cause expansion or swelling in the matrix.

During the treatment of soils with calcium-based stabilizers, the water added during the construction process, 20 to 25 percent by weight, is not likely to develop expansion. The lack of rigidity in the stabilized matrix is one possible reason for the absence of immediate expansion as the higher void content in the matrix can accommodate the newly formed ettringite crystals (Little and Graves 1995; Dermatas 1995; Little et al. 2005). In addition, as discussed earlier, it is also probable that the kinetics of mineral dissolution is slower in soils compared to cement (Ouhadi and Yong. 2008). Although the pozzolanic reactions in soil are slow, the hydrated phases start forming almost immediately after mixing and result in a steady increase in matrix strength. Therefore, it is likely that the cementitious reactions consume some of the water available during lime stabilization and hence only a portion of water added may be available for initial ettringite formation. Due to this limited availability of water, the solubility properties of sulfate bearing minerals present in soil can influence the amount of soluble sulfates made available for ettringite formation.

2.8. Sulfate Availability in Stabilized Soils

Sulfate occurrence in soil is not normally uniform but rather exists in seams and stratified pockets. These hot spots can vary in shape and size from as little as 10-25 m in diameter to extended sulfate seams (Herbert and Little 2006). Typically, sulfate ions are made available from dissolution of these sulfate salts depending on their type and solubility properties and environmental conditions in the stabilized layers. Surface bedrocks are also a major source of sulfur for soils all around the world. Among the sulfur-bearing minerals identified in sedimentary rocks, iron sulfide polymorphs, pyrite and marcasite, are the more common forms, of which pyrite is the most common (Berry et al. 1983). Oxidation of these sulfide groups in an acidic environment can release sulfate ions into soils. These sulfate ions can migrate with water movement during precipitation and ground water flow providing a continuing source of sulfate needed for ettringite formation.

2.8.1 Solubility of Sulfates in Stabilized Soil

Although different sulfur bearing phases such as pyrites, marcasite, and greigite and sulfate forms like gypsum, anhydrite, barite, and jarosite, exist in natural soil; their presence alone does not make the soil problematic. The dissolution properties of these phases and existing environmental conditions contribute to the release of sulfates into stabilized layers (Cripps et al. 2003). The solubility of gypsum, the predominant sulfate-bearing mineral in soil, is 2.58g per liter of water (Burkart et al. 1999). Solubility is also dependent on particle size and surface area of crystals (Harris et al. 2003). Size distribution of gypsum crystals can vary from visible crystals to microscopic crystalline phases in soil. Smaller particle size provides higher surface area which translates to faster dissolution of minerals when in contact with water. Therefore, fine-grained gypsum, if present, can dissolve faster and release ions faster when compared to coarse-grained fractions in soil. The solubility is also pH dependent and is low at high pH conditions (Petry 1994). But even without considering pH dependency, the water content used in mixing and compaction of stabilized soils is much too low to solubilize all of the sulfates available in the soil. As an example, one mole of gypsum has a mass of 172g and contains 96g of SO4. Therefore, if one mixes 25 g of water (25 percent) with 100g of dry soil that contains only 0.3 percent or 0.3g of gypsum (0.167 percent sulfate) and 5 percent lime (Ca0), only about 1/5th of the available sulfates can be solubilized with this quantity of mixing and/or compaction water.

$$\frac{2.58\,g\,Gypsum}{100\,g\,Soil}\times\frac{1\,mol\,Gypsum}{172\,g\,Gypsum}\times\frac{96\,g\,SO_4}{1\,mol\,Gypsum}\times\frac{25\,g\,H_2O}{100\,g\,H_2O}=\frac{0.036\,g\,SO_4}{100\,g\,Soil}=0.036\%\,SO_4 \qquad (2\text{-}8)$$

Equation (2-8) emphasizes the fact that, in the soil-calcium-based stabilizer system it is unlikely that the initial mixing water will be able to solubilize the entire quantity of available sulfates into solution to be consumed in ettringite formation. It is more likely that the available mixing water will support the formation of nucleation sites that can facilitate further crystal growth and expansion under favorable thermodynamic and pH conditions. Presence of these isolated nucleation sites may facilitate localized expansion in the matrix during additional ettringite growth causing distresses in stabilized layers. Hence the strategy of using excess water during mixing and providing extended mellowing time prior to compaction may facilitate a more uniform distribution of these nucleation sites and can help prevent localized expansions in stabilized layers as observed by many researchers (Little 1995; Harris et al. 2003; TxDOT 2005). It is also noteworthy that the presence of more soluble sulfate salts, like sodium sulfate, in soils may lead to more available sulfate ions in the mixing water and may lead to a higher sulfate availabilty, when compared to dissolution of gypsum.

2.8.2 Spatial Variability of Sulfates

Among all the chemical constituents that comprise ettringite, SO42- ions are likely to have the highest spatial variation due to variation in source rocks and as a result of their hydrologic mobility. The relative amount of sulfate in a soil's parent material can vary considerably among soil formations. In addition, hydrologic processes can influence redistribution of sulfate ions and localized accumulation in natural soils: surface/subsurface runoff and the upward migration of water from a shallow water-table aquifer through capillary action. In both cases, sulfate accumulates as the water evaporates and dissolved salts precipitate. Sulfate concentrations are generally higher in subsurface layers where the processes of moisture infiltration and evaporation and transpiration reach a state of general equilibrium and deposit a higher concentration of sulfates at a specific depth within the pedological profile of the soil.

2.8.3 Mobility of Sulfate Ions

Sulfate ions can be transported with water over significant distances due to its relatively weak adsorption to soil minerals (Fig. 2-3).

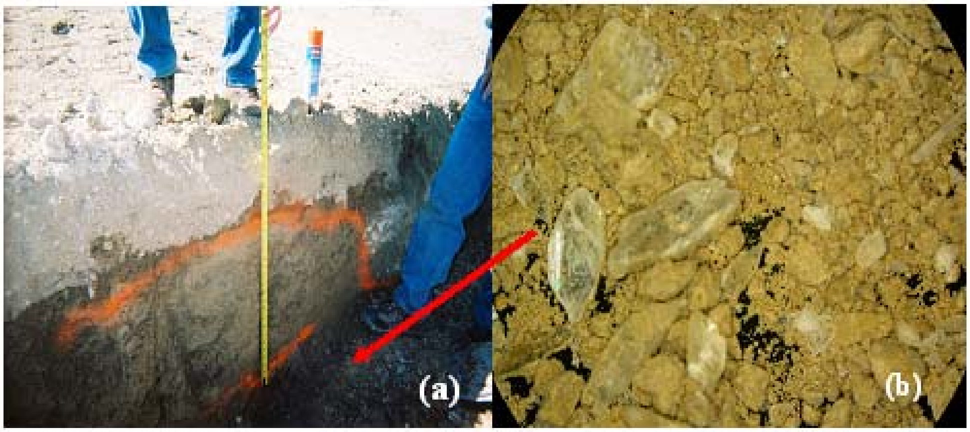


Fig. 2-3. (a) Gypsum crystals observed below heaved lime treated layers at U.S 287 Berthoud Pass, Colorado (b) Optical microscopy image of soil collected from the location showing visible gypsum crystals in soil (JGGE)

These sulfate movement can occur under various potentials: water moving through a gravity head, water moving via capillary rise, water moving in the vapor form due to temperature, humidity, or salt concentration differentials (Hunter 1988; Burkart et al. 1999; Little 2005).

2.8.3.1. Influence of Soil Type on Mobility

Suction potential of soils can provide the potential to draw water from the underlying water table which can transfer the dissolved sulfate ions in to the stabilized layers or in to the natural soil. Soil properties can therefore have a strong impact on soil conductivity, and by implication, on sulfate concentration. For soils with low hydraulic conductivity, the flow of water can be interrupted and the dissolved sulfate ions are not easily transported through these sections. Therefore, soils with low hydraulic conductivity, high capillarity, and high suction properties can create sulfate reservoirs in subgrade sections. Even though, these properties are typically associated with clays and shales, it is important to note that soil texture is not the only factor controlling soil conductivities. High sulfate pockets can also exist in gravely, sandy, and silty soils.

2.8.3.2. Influence of Climatic Characteristics on Mobility

Climatic conditions can influence movement of sulfate ions in soils. In dry arid areas, sulfate deposits are likely to be found in near-surface environments due to evaporation processes, which leave previously dissolved sulfate ions in the top soil. In wet and humid areas, water infiltration can carry sulfate ions into deeper strata which can be transferred back to the surface due to capillary action. Climatic changes can also influence the mobility of sulfate ions. In drier months, evaporation/transpiration processes are likely to favor the accumulation of sulfates in low-lying areas and near dry stream channels due to the proximity of the groundwater table to the land surface in these areas (Herbert and Little 2006; Burkhart et al. 1999). During rainfall events, the sulfate crystals in soils, precipitated during dry seasons, can be washed along the slopes or through desiccation cracks in clays into stabilized layers in low lying areas. Surface water can also gain access to sulfate minerals in soil through seepage, through surface cracks and openings, or through permeable layers in the pavement section. Surface runoff and rainfall can also be the source of water needed for ettringite formation.

2.8.3.3 Influence of Topography and Drainage on Mobility

Topographic slope influences hydrologic processes, including overland flow and subsurface flow and therefore has a strong influence on residual sulfate concentrations in soils. As detailed earlier, sulfate salts, sulfates from oxidation of surface bedrocks and dissolved sulfate ions form the major source of sulfates for ettringite growth (Cripps et al 2003). Topography influences the transport of these relatively nonreactive solute sulfates along a gravity gradient (downhill). In rolling terrains, significant sulfate concentrations may accumulate in low-lying areas due to surface runoff creating sulfate hot spots in the soil (Herbert and Little 2006; Burkhart et al. 1999). Slopes shaped by erosion can transport sulfate ions to locations far from parent source and into pavement sections that might intercept these flow channels. A rolling topography favors the process and the risk due to sulfate heave is increased when these soils occur in areas that are dissected by stream erosion. Therefore, topography, through its influence on hydrology, is likely to have a strong influence on the redistribution of sulfates along the landscape (Herbert and Little 2006).

Drainage features can influence surface run off/infiltration which in turn can provide water and define the availability of sulfate ions in the stabilized layers (Burkart et al 1999; Little and Petry 1992; Herbert and Little 2006). Low-lying areas with poor drainage features can accumulate excess water which increases the risk for sulfate heave in the location.

2.9. Misconceptions Regarding Ettringite Formation in Stabilized Soils

The most common misconception in dealing with stabilization of sulfate rich soils is that lime is the only stabilizer that causes sulfate heave. This is not true, as any of the calcium-based stabilizers can cause sulfate heave in soils. In fact, free lime formed during hydration of calcium silicate can induce the formation of these expansive minerals. Cases have been reported where soils stabilized with Portland cement and/or fly ash has heaved (Rollings et al. 1999). The effect of different cement types and the influence of various compositions of fly ash on ettringite/thaumasite formation are not completely understood and further investigation in this area is needed. The literature does demonstrate rather convincingly that an abundance of readily soluble silica, such as that that might be present in some fly ash, ground granulated blast furnace slag, or in cement, can favor the formation of a type of calcium-silicate-hydrate mineral that is thermodynamically favored over the formation of ettringite. To this end sources of soluble silica have been used to avert the formation of ettringite (Wild et al 1999).

Another assertion of some credibility is that the use of low calcium stabilizers, like class F fly ash, can minimize ettringite induced heaving soils. Even though this may be right to a certain extent, the pozzolanic capability of the stabilizer is impeded by the lack of available calcium and a high pH which makes these low calcium stabilizers ineffective as a stabilizing agent for soils (Berger et al. 2001).

Another common belief is that sulfate-resistant cement can be effective in reducing ettringite formation in soils. Sulfate-resistant cement has a limited concentration of alumina in the form of tri-calcium aluminate and can therefore resist the formation of delayed ettringite in cement concrete structures where the source of alumina is solely from the cement. However, the use of a low aluminum cement to treat or stabilize a clayey soil, where the sources for aluminum are essentially unlimited, may not be effective in preventing ettringite formation over time (Berger et al. 2001).

Although the kinetics of the dissolution of alumina from the clay may be very slow, it may occur over time if the pH remains high enough to solubilize the clay minerals.

3. WATER: THE KEY TO EXPANSION OF ETTRINGITE IN CEMENTITIOUS MATERIALS*

3.1. Introduction

Volume changes associated with ettringite formation are known to cause internal stresses strong enough to damage pavement sections (Mitchell 1986; Hunter 1990; Petry and Little 1992; Perrin 1992). These distresses typically occur when cementitious materials containing calcium oxide are used to stabilize soils and/or aggregates containing sulfates or when the system is exposed to solutions high in sulfates (Harris et al 2004). To date, the focus of research has largely concentrated on the role of sulfates in causing these expansive reactions with much less attention given to the importance of water in the process. While previous studies have identified most environmental and geochemical factors that influence ettringite formation, questions still remain regarding the mechanisms that cause these minerals to expand. These expansion mechanisms are complex and often confusing with considerable variation in the amount of distress associated with a specific sulfate concentration. But a subtle similarity among many observed cases is that locations of distress are often associated with a clearly defined water source (Hunter 1990; Perrin 1992; Kota et al. 1996). Even though the composition of ettringite shows copious amount is needed for ettringite to form, it may be the timing

---

[*] From Nair, S., and D. Little. Water as the Key to Expansion of Ettringite in Cementitious Materials. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2104,* pp. 55-62. Copyright, National Academy of Sciences, Washington, D.C., 2009. Reproduced with permission of the Transportation Research Board.

of the introduction of water that defines whether on not deleterious expansion results.

3.2. Background

From a chemical standpoint, the mechanism of ettringite formation is well understood. Ettringite [$Ca_6[Al(OH)_6]_2.(SO_4)_3.26H_2O$] precipitates in environments with high pH, and sufficiently high activities of Ca2+, Al(aq), and SO42- (Perkins and Parmer 1999; Mitchell and Dermatas 1992; Warren and Reardon 1994). Even though many sulfate bearing phases are formed during these reactions, only mono and tri sulfate phases are stable in aqueous environments (Lerch et al. 1929). Precipitation and stability of ettringite in the system is controlled by pH, temperature, ion activities and concentrations of dissolved CO2 and H2O (Little et al. 2005; Myneni et al 1998; Damidot and Glasser 1993; Ogawa and Roy 1981). Although ettringite is known to form as micron size crystals with a tubular structure the mechanism and the scale of expansion associated with the mineral precipitation are still not well defined, at least with respect to stabilized pavement sub-layers (Moore and Taylor 1970).

A definitive relationship is yet to be established between the amount of ettringite precipitated and the associated volume changes in the matrix. Expansion may vary among pavement layers due to differences in construction methods; availability of water; ion migration; and the void structure within the pavement material (Harris et al 2004; Little et al 2005). Again, it is also possible for cementitious materials to contain significant amounts of ettringite with minimal volume changes (Lea and Desch 1940; Mehta 1973a). This is possibly due to ettringite precipitation during early stages of cement hydration where internal stresses are accommodated by plastic deformation in the material, or it may be due to the ability of the void structure to accommodate post-compaction mineral growth. Furthermore, to complicate the issue, two theories exist regarding the cause of expansion in the matrix. Both theories (explanations) are based on critical underlying assumptions. The topochemical mechanism of precipitation supports an increase in crystallization pressures, crystal interlocking and an orientated crystal growth that results in expansion in the matrix (Ogawa and Roy 1982). On the other hand, researchers who support a solution mechanism of ettringite formation suggest that water absorption by the ettringite molecule is the reason for expansion. The colloidal ettringite precipitating in the matrix has a high surface area and a negative surface charge that is capable of absorbing water and causing expansion (Mehta 1973 b; Deng and Tang 1994). A combination of the two mechanisms is also considered as the reason for expansion (Deng and Tang 1994). Regardless of the preferred explanation, water is a key to the cause of expansion in the matrix (Odler and Subauste 1999; Odler and Glasser 1988).

The objective of this study is to help identify the role of water (pure water as well as sulfate-laden water) in the mechanism of expansion associated with ettringite formation in a system stabilized with calcium-based, cementitious materials. The findings from this study are supported by a case study in which a controlled low strength material (CLSM) was produced using a fly ash containing approximately nine percent sulfite.

3.3. Hypothesis of Role of Water in Sulfate-Induced Expansion

The authors believe that evidence revealed within this paper substantiates a general hypothesis regarding the effect of ettringite formation on expansion. In general, for a "closed system" where the stoichiometric proportions of the constituents required to form ettringite are contained within the system, the molar volume of the product (ettringite) is smaller than the molar volume of the constituents (aluminum, calcium oxide, sulfate, and water) that produce the reaction. This can be shown by using stoichiometric calculations based on the chemistry of ettringite formation during cement hydration [Equation 3-1].

$$C_3A + 3C\overline{S}H_2 + 26H_2O \rightarrow C_3A.3C\overline{S}H_2.H_{26} \tag{3-1}$$

Based on stoichiometric proportions, for one mole of ettringite to form, one mole of tricalcium aluminate (abbreviated C_3A, where C - CaO and A - Al_2O_3), three moles of gypsum (abbreviated as $C\overline{S}H_2$, where $\overline{S}$ - SO_4^{2-} and H - H_2O), and 26 moles of water are required. From the literature, we know that the molecular volume of C_3A = 89.1 cm3/mol, $C\overline{S}H_2$ = 74.2 cm3/mol, H_2O = 18.02 cm3/mol and ettringite = 737.6 cm3/mol. Volume change associated with a product formation can be determined using Equation [3-2].

$$VolumeChange = \left[\frac{MolarVolume_{\mathrm{Pr}\,oducts} - MolarVolume_{\mathrm{Re}\,agents}}{MolarVolume_{\mathrm{Re}\,agents}}\right] \tag{3-2}$$

Therefore, based on equation [3-1], the volume change that occurs when one mole of C_3A combines with three moles of gypsum ($C\bar{S}H_2$) to form ettringite by consuming 26 moles of water from the matrix is given as:

Volume change (Closed system) = $\left[\frac{737.6 - 311.7 - 468.52}{780.22}\right]$ = -0.05 or 5 percent shrinkage

where 311.7 is the molar volume of one mole of C_3A and three moles of $C\bar{S}H_2$; and 468.52 is the molar volume of 26 moles of water.

For an "open system", where water associated with ettringite formation enters the matrix from outside, the formation of ettringite from the appropriate stoichiometric proportions of the reactants, results in an expansion of the matrix. In this case the molar volume of 26 moles of water is not subtracted in the numerator because the water is introduced from outside the system.

Volume change (System open to water) = $\left[\frac{737.6 - 311.7}{311.7}\right]$=1.37 or 137 percent expansion.

In an "open system" the introduction of the large amount of water required in the formation of ettringite from outside the system, results in considerable expansion. In addition to expansion due to crystal growth of ettringite from external water, our research shows evidence of an additional mechanism of expansion. This may be due to sorption of water on or within the ettringite crystal matrix. The literature supports these findings (Mehta and Fu 1978). Finally, if sulfate-bearing water in lieu of water is introduced from an external source, additional sulfate, if sulfate is the limiting reagent, will stoichiometrically support additional ettringite growth.

In summary then, ettringite-induced expansion can occur because of: (1) external water entering the system to form the mineral ettringite, (2) external water and additional sulfate ions (when sulfate is the limiting reagent) entering the system to form ettringite, and/or (3) additional water entering the system that is sorbed onto or within the ettringite crystal matrix.

3.4. Materials and Methods

The CLSMs at the focus of this study consisted of a composite of fly ash and bottom ash, Portland cement, fine aggregates, water and an air entraining admixture. The ash used to prepare flowable fill mixtures was provided by an electrical power plant. The size fraction of ash particles varied from close to 1.0 mm to less than 75µm with more than 30 percent smaller than 150µm. A typical ash composition based on oxide analysis includes 39.08 % SiO_2, 23.95 % CaO, 16.22 % Al_2O_3, 9.20 % SO_3, 6.54 % Fe_2O_3, 1.19 % MgO, 1.09 % K_2O and 1.33 % Na_2O. Except for the ash, locally available materials were used in mix preparation. Type 1 Portland cement corresponding to ASTM C 150, siliceous sand typical of blow sand or river sand found locally in Texas and tap water were used to prepare CLSM mixes. A commercially available air entraining admixture was also used to provide stable air contents in the mixtures. Although the chemicals contained in the water added to each mixture may have some impact, the authors consider the relative impact among mixtures to be similar as the same water was added to each mixture.

3.4.1 Mix Design

CLSM mixtures were proportioned by trial and error to achieve the required material properties. Mixtures were designed to limit target strength to below 200 psi (1.4 MPa), to produce a target unit weight close to 100 lb/ft3 (59 kg/m3), and to produce target flowability (slump) of close to 10 inches (0.254 m). Components were loaded manually and mixed to a uniform consistency in a 1.5 cu. ft paddle concrete mixer. Cement and ash contents were varied from 30 to 240 lb/yd3 (18 to 142 kg/m3) and from 0 to 725 lb/yd3 (0 to 430 kg/m3), respectively, to establish the combinations required to attain the desired material properties. Concentrations of the air entraining admixture and water were also varied to achieve the required unit weight and flow properties. Unit weights of the mixes were determined following ASTM D 6023 and flowability was measured using ASTM method D 6103. Twenty-one (21) trial combinations were evaluated to determine two mix proportions that met target requirements. The selected mixtures are identified in Table (3-1) as mixtures A and B.

Table 3-1. Details of mix design of samples used in the study

Mix	Mix proportions in lbs (Kg)				Unit wt in cf (kg/m3)	Flowability in inch. (m)
	Cement	Fly Ash	Water	Sand		
A	43 (20)	426 (193)	444 (201)	1569 (712)	92 (1474)	9.44 (0.24)
B	82 (37)	412 (187)	441 (200)	1451 (658)	88.3 (1414)	10.13 (0.26)
C	135 (61)	452 (205)	540 (245)	1513 (686)	97.9 (1568)	8.50 (0.22)

Ettringite growth was quantified in the selected mixtures (A and B) and associated expansion was measured in the prepared samples. The control sample (Mix C) with three times the lowest cement content was also evaluated in order to determine the influence of matrix strength on expansion.

3.4.2 Sample Preparation

3.4.2.1. Ettringite Synthesis and Testing

Pure ettringite was synthesized in the laboratory using a modified method (Perkins and Palmer 1999; Cody et al 2004). Ettringite was then quantified using a differential scanning calorimeter (DSC), Q-2000 manufactured by TA Instruments, to determine the properties and behavior of pure ettringite. Samples were heated at rate of 20C/minute and tested over temperatures ranging of 25^{o}C to 175^{o}C. Heat flow from the sample was integrated over time to determine the normalized heat released by pure ettringite over the selected temperature range. A Rigaku x-ray diffractometer was also used to verify properties of synthesized ettringite. Copper, Cu kα radiation was used at a scan speed of 3^{o}/min with a scanning angle ranging from 3 to 70 degrees.

3.4.2.2. Compressive Strength of CLSM Mixtures

Samples of freshly mixed CLSM were collected following ASTM D 5971. Fresh mixtures were used to prepare samples for compressive strength testing, to measure the quantity of ettringite, and to determine volume change in each mixture. The unconfined compressive strength of the CLSM mixtures was measured on samples with unbounded caps in accordance with ASTM D 4832. Duplicate cylindrical samples (4-inch x 8-inch) were prepared for the three mixtures for compressive strength testing.

Mixtures were cured under two different curing regimes: “moist cure” samples were cured under 100 percent relative humidity at 25^{o}C; “dry cure” samples were also cured at 25^{o}C, and at ambient humidity. The only moisture available in the “dry cured” samples was the initial mixing water. All samples were initially cured, under the respective environments, in the compaction molds for 48 hours due to the fragile nature of the specimens. Following this 48 hours of initial cure, the samples were extruded from their molds and subjected to their respective environments for 14, 28 and 56 days prior to compressive strength testing.

3.4.3 Volume Changes in CLSM Mixtures

Duplicate cylindrical samples (6-inch x 12-inch) were prepared for each of the three mixtures to determine volume changes in the mixtures. Samples of mixtures A and B were subjected to the same curing condition prescribed for compression testing. However, for “moist cure” samples, in addition to being placed in a 100 percent relative humidity environment, these samples were also placed on porous stones with water level at the top of the stone. Therefore, the “moist cure” samples were allowed to take on water from the 100 percent relative humidity environment and by capillary suction. These mixtures were cured for 7, 14, 28 and 56 days as were the “dry cure” samples. The control mixture (mixture C) was subjected to a third curing condition, represented as “sulfate cure” in addition to the “dry” and “moist cure” previously described. In “sulfate cure", a sulfate solution was prepared by mixing 50 g of reagent grade sodium sulfate in one liter of water. Cylindrical samples were exposed to the sodium sulfate solution through the same capillary suction as the "moist cure" samples and for the same time periods as the other two samples. This approach was used to determine the effect of external sulfate movement into the samples. Axial and circumferential expansions were measured over time for all the three mixtures under respective curing conditions. Measurements were taken to the nearest 0.5 mm using a clear plastic tape. Circumferential measurements were taken near the top, center and bottom of the sample. Height was measured at three locations 120° apart. Respective measurements were averaged to determine volume changes in the sample.

3.4.4 Ettringite Quantification in CLSM Mixtures

Cube samples (2-inch x 2-inch x 2-inch) were prepared for quantification of ettringite formed in the mixes during curing periods. A differential scanning calorimeter (DSC) was used for quantification. These samples were removed from molds after 48 hours and cured in exactly the same manner and for the same time period as the volume change samples. Mixtures A and B were subjected to the "dry" and "moist curing" regimes described earlier whereas the control mixture (Mixture C) was subjected to "sulfate cure" in addition to the "dry" and "moist curing".

Samples were removed from the curing chamber at the end of curing period and air dried for DSC analysis. Acetone was then used to remove water of hydration. The dried samples were gently pulverized with a mortar and pestle to break down the aggregation of cementitious materials without reducing the size of sand grains. Pulverized mixes were then sieved through a No. 50 sieve to remove non-reactive sand fractions in the mix. Ten (10) mg of each sample was randomly selected from each mix for evaluation. The normalized heat energy exotherm for synthesized ettringite was compared with energy released by the CLSM mixture to quantify the ettringite content in the sample. The concentrations were then translated back to the ettringite content in the CLSM mixes based on the law of proportions. A standard addition technique using purely synthesized ettringite in the x-ray diffractometer was used to verify DSC results.

3.5. Results

3.5.1 Compressive Strength of CLSM Mixtures

Preliminary assessment of pozzolanic reactivity and ettringite formation potential of CLSM mixes was made by measuring pH values of pure fly ash and of prepared mixtures. A paste, with one part ash and five parts water, was used to measure pH of the pure ash. An average of three pH measurements for ash paste was found to be 11.91. For CLSM mixes, irrespective of differences in cement content, the pH remained fairly constant and above 12.00. Pozzolanic reactivity of the mixes was determined based on long term strength gain for moist cure CLSM mixes (Fig. 3-1).

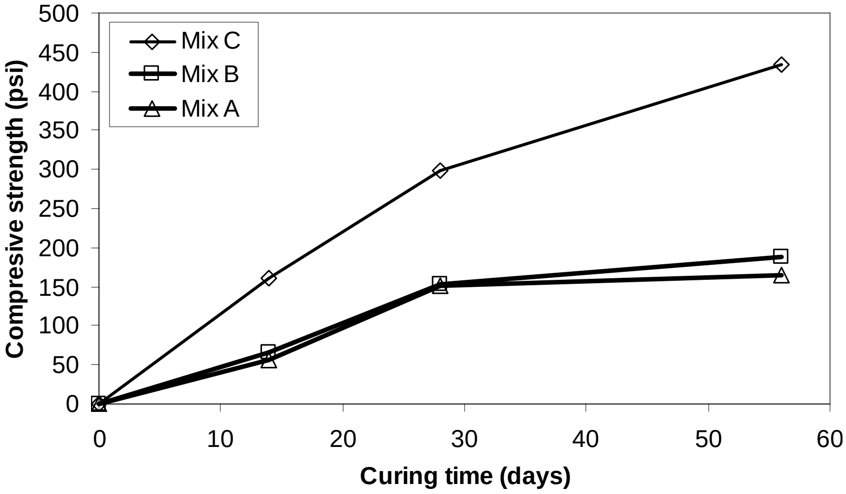


Fig. 3-1. Long term strength gain in CLSM mixtures with varying cement contents

CLSM mixtures showed a progressive increase in compressive strength with curing time. Fifty-six (56) day strengths attained by mixtures A and B were below the strength limit of 200 psi (1.4 MPa) selected as target threshold strength for their use as a low strength material. Compressive strength was also found to increase with cement content. Strength gain in the control mixture (mixture C) was significantly greater when compared to mixture A and B. The pH measurements and compressive strength observations are consistent with oxide analysis of ash particles. Oxides of aluminum and sulfur in ash particles when combined with available calcium at high pH conditions can provide favorable conditions for ettringite formation in these mixes.

3.5.2 Ettringite Quantification in CLSM Mixtures

Synthesized ettringite was tested using a differential scanning calorimeter (DSC) to determine the properties and behavior of the mineral. Ettringite was found to progressively lose water of crystallization with increasing temperature. The behavior of synthesized ettringite agreed well with observations of other researchers (Ogawa and Roy 1981; Odler and Abdul-Maula 1984; Shimada and Young 2001). An endotherm was found to be located close to 110^{o}C and was selected as the characteristic peak for ettringite quantification and was also used for quantitative analysis. Normalized heat energy for synthesized ettringite taken from an average of three samples was found to be 42.5 J/g. This value was compared with the endotherm created by the CLSM sample to quantify ettringite concentrations in the CLSM mixtures. A typical DSC analysis of a CLSM sub-sample randomly selected from a 7 day "moist cured" control sample (mixture C), is shown in Fig. 3-2.

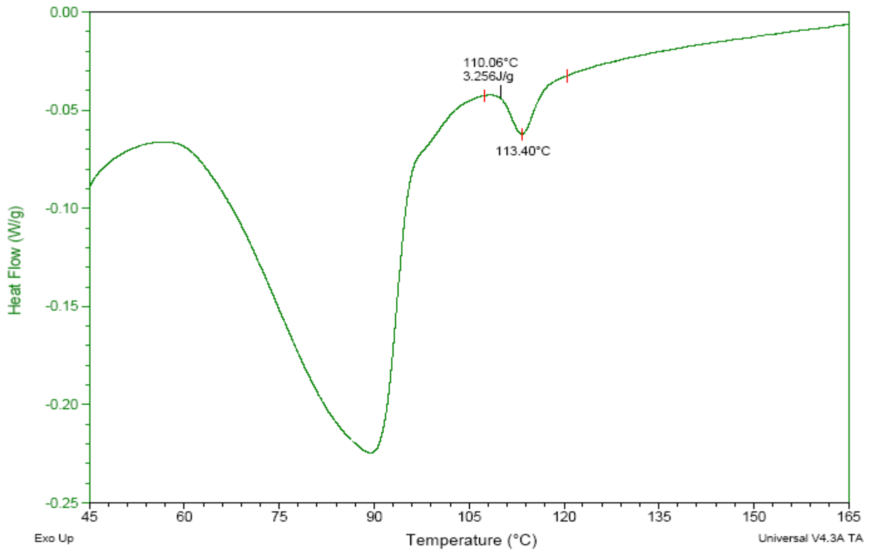


Fig. 3-2. DSC analysis of 7 day moist cured control sample (mixture C)

The endotherm starting above 650C was not used to identify ettringite concentration as this endotherm may overlap with the dehydration peaks of physical and chemically bound water in the sample. Normalized heat released from the sample was related to a concentration of 5.28 percent ettringite in the CLSM sample based on the law of proportions (Fig. 3-2). The measured quantity of ettringite was found to be less than the stoichiometric proportions that are calculated based on available sulfate in the ash and cement used in mix design. Concentrations of ettringite were measured for all samples using the DSC.

3.5.3 Ettringite Contents and Volume Changes in CLSM Mixtures

Fig. 3-3 presents a comparison of the quantities of ettringite detected in the control mixture (mixture C) and the measured volume changes in samples cured under various environmental conditions. Ettringite concentration in mixture C was determined from 2-inch x 2-inch x 2-inch samples subjected to three curing conditions. The related volumetric expansions were measured on 6-inch x 12-inch cylindrical samples cured under the same conditions. Ettringite concentrations shown in Fig. 3-3 are an average of five individual measurements taken on randomly selected samples for each method of cure.

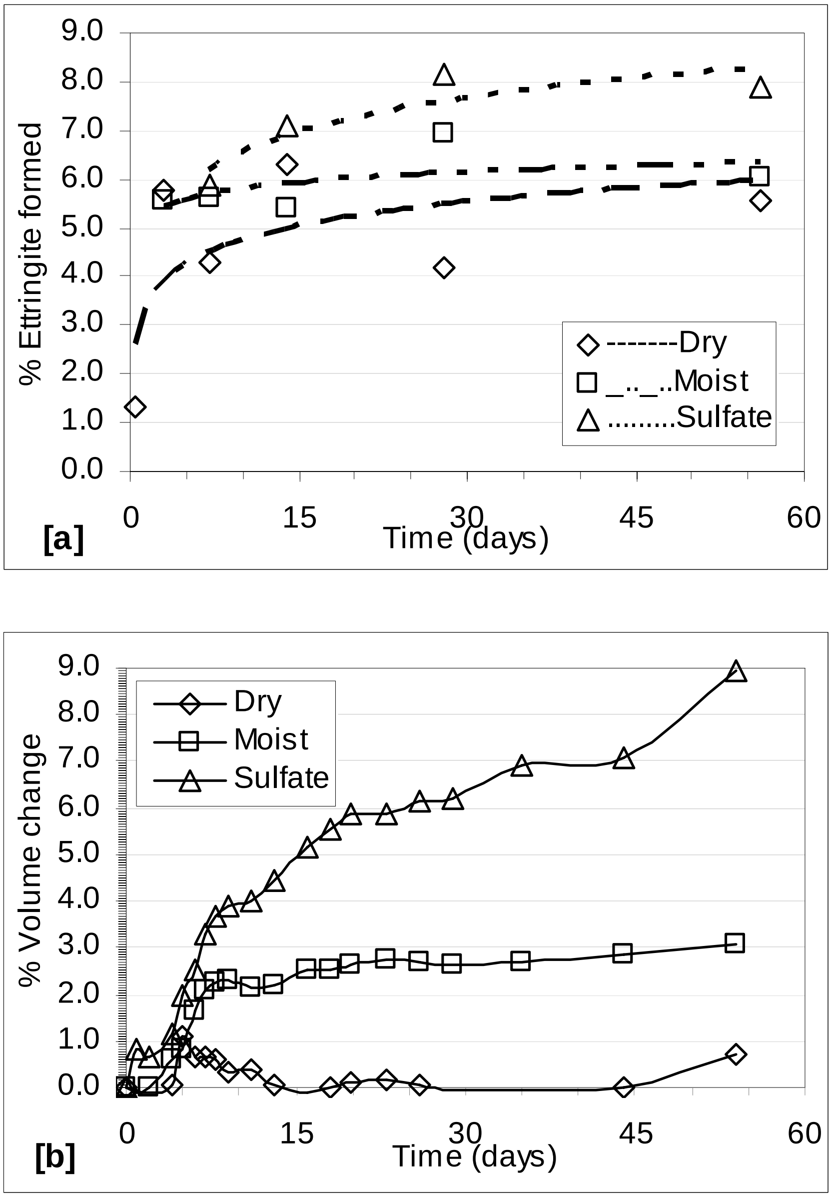


Fig. 3-3. Comparison of the concentration of ettringite formed in mixture C and the related volume changes against curing time

A higher concentration of ettringite was found to form in mixture C when the CLSM samples were exposed to sulfate laden water than under other conditions of cure. This is consistent with the oxide analysis of the ash sample, which showed a stoichiometrically higher concentration of alumina and lime to be present than needed for ettringite formation. Therefore, the available sulfate concentration becomes the limiting reagent for ettringite formation in these mixtures. Sulfate cured samples also showed a progressive increase in ettringite concentration with curing time. Observed volume changes in “sulfate cured” samples were also consistent with the increase in ettringite quantities. The concentration of ettringite under “dry” and “moist cure” conditions was similar. However, only the “moist cure” samples showed a volume increase with curing time. Although the DSC measurements showed ettringite to be present in “dry cure” samples, volume measurement showed no indications of swelling. The samples were also tested in an x-ray diffractometer to confirm the presence of ettringite in the samples. Ettringite quantities and the resulting volume change in mixture A is given in Fig. 3-4 (a) and in Fig. 3-4 (b) for mixture B.

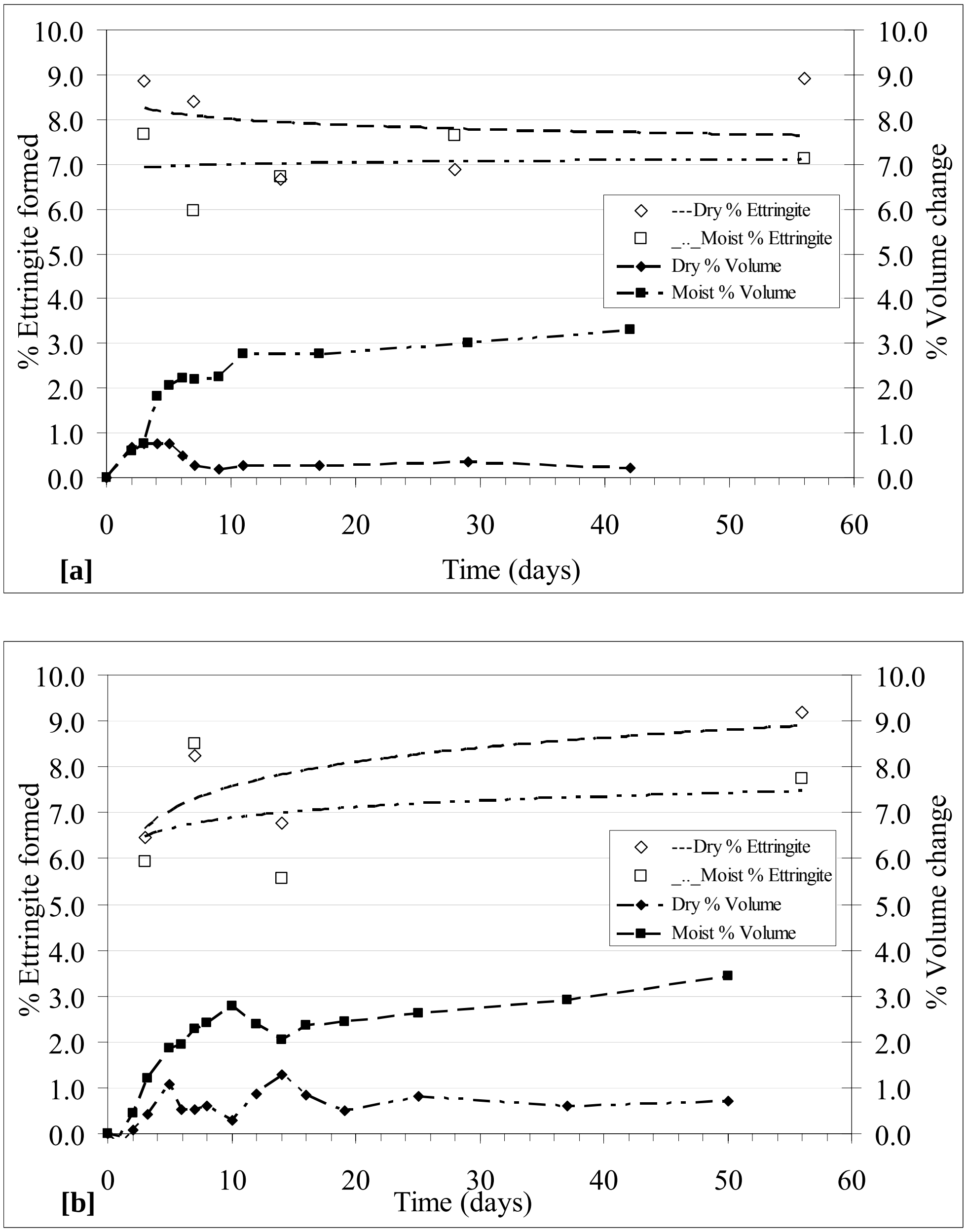


Fig. 3-4. Comparison of ettringite concentration and associated volume changes measured against curing time for (a) mixture A and (b) mixture B

As for mixture C, the quantity of ettringite formed under “dry” and “wet cure” regimes was similar for mixtures A and B. Although the majority of ettringite was observed to form within the first few days, the quantity of ettringite continued to increase with curing time. Typically around six to nine percent ettringite was found to form in the samples. The measured quantities in mixtures A and B were slightly higher than quantities measured in the control mixtures samples. Similar to observations made in the control sample (Fig. 3-3), the “dry cure” samples prepared from mixtures A and B did not show any significant volumetric expansion. On the other hand, “moist cure” samples showed a progressive increase in volume with curing time. Again, this is similar to observations in the control sample (Fig. 3-3). A maximum expansion of approximately three percent was observed in both mixtures. A difference in the compressive strength among the three samples appeared not to have any influence on the extent of swelling in these mixtures (Fig. 3-1). However, the rate of expansion upon exposure to moisture was observed to be slightly faster for mixtures with lower cement content (mixtures A and B) when compared to the control sample.

Table 3-2. Comparison of ettringite quantities measured using DSC with standard addition technique using XRD

Sample Name	Ettringite Concentrations (Percent)	
	DSC Method	XRD Standard Addition Method
Mixture-C-14 day Dry cure	6.3	7.1
Mixture-B-3 day Dry cure	6.5	5.4
Mixture-A-14 day Dry cure	6.7	6.3

Standard addition using synthesized ettringite was performed in an x-ray diffractometer to verify ettringite concentrations measured using DSC. A comparison of results obtained for randomly selected samples are given in Table [3-2]. A reasonable correlation was found between quantities of ettringite measured using DSC and XRD techniques. Furthermore, these techniques demonstrated that most of the ettringite formed early in the curing period and that approximately 60 to 80 percent of sulfates in the mix are being used up for ettringite formation.

3.6. Discussion

The quantities of ettringite measured in all three mixtures (A, B, and C) cured under both "dry" and "moist" conditions were similar. DSC measurements indicate that somewhere between about six and nine percent ettringite formed in the prepared mixtures (Fig. 3-3 and 3-4). Measured quantities of ettringite are in agreement with quantities calculated based on stoichiometric proportions of constituents including available SO3, Al2O3, and CaO in the ash. Based on the weight percent of fly ash used in the mixtures, a 9.2 percent SO3 content of the ash can contribute to form a maximum of 10.3 percent ettringite in the CLSM mixture. Considering the concentration of sulfates available in the cement used in preparing the mixtures, the amount of ettringite that actually formed was below maximum stoichiometric proportions.

A major portion of the total ettringite formation was found to precipitate within the first three days of the hydration process in both "dry" and "moist cure" regimes (Fig. 3-3 and 3-4). The plastic nature of the mixtures required the samples in both cases to be left inside the cylindrical molds for the first 48 hours. Due to limited loss of mixing water and restricted access of external water, it is reasonable to consider that similar conditions may have existed in “dry” and “moist cure” samples during initial (first 48 hours) hydration periods. Also, water used for cementitious reactions and ettringite formation in both curing conditions can be safely considered to be taken from within the matrix. The ratio of weight of water to cementitious products was about 0.90 (Table 3-1). Hence a similar concentration of ettringite precipitating in “dry” and “moist cure” samples during initial hydration periods is justifiable.

The observed behavior during the first three days of “dry” and “moist cure” showed slight shrinkage. This shrinkage may be partially due to loss of water due to drying, due to restructuring of the mixture water during the hydration process and partially due to ettringite formation in the mix (Lea and Desch 1940; Mehta 1973a). As previously shown, ettringite formation can in some cases cause a reduction in volume due to the difference in molar volume between “reactants or components” and the “product”, ettringite, when all the components needed to form the product is available from inside the system (Mehta 1973a; Hansen et al. 1988). This probably is the reason for the lack of apparent volume increase during initial curing periods. However, a supply of water from outside was observed to cause volumetric expansions in the mix (Fig. 3-4). This is consistent with observations made by Mehta (Mehta and Wang 1982; Mehta and Fu 1978).

Although the amount of ettringite formed in “dry” and “moist cure” samples was similar, only “moist cure” samples demonstrated volumetric expansion with extended periods of curing (greater than three days) (Fig. 3-3 and 3-4). This may either be due to additional growth of ettringite crystals or due to expansion of ettringite crystals already formed in the system (Ogawa and Roy 1982; Mehta and Wang 1982). However, since the quantities of ettringite in both dry and moist cure samples were similar, based on DSC and XRD analysis, it is logical to eliminate additional ettringite growth in "moist cured" samples as the cause of expansion. Since the majority of ettringite formed during the first three days of hydration, water absorption of already precipitated ettringite may be the major source of volume change in moist cure samples.

When the control sample was exposed to sulfate laden water introduced from outside the matrix, there is a considerable increase in expansion as well as a concomitant increase in the mass of ettringite formed (Fig. 3-3). Measured concentrations indicate a time dependent increase of ettringite content in the sample and not an immediate or sudden crystal growth. The growth of crystals over time is therefore dependent on the diffusion of water and sulfate ions to the nucleation sites. Hence ettringite precipitation from a micro-structural standpoint is probably due to a two step process: a rapid nucleation step followed by crystal growth which is time dependent (Callister 2001). Also, the possibility of ettringite precipitated initially acting as nucleation sites for future crystal growth should be considered.

Expansion in the control samples (mixture C) upon exposure to a sulfate-bearing solution was significantly greater than expansion observed during "moist curing". As previously mentioned, the quantity of ettringite measured in sulfate-cured samples increased with curing time. The only variable that is different between "moist" and “sulfate cure” for the mixture C samples is the presence of additional sulfate ions, which can therefore be considered as the source for additional ettringite growth in these samples. Hence for the control samples, both the additional sulfate ions and the external water probably contributed to ettringite formation. Molar volume calculations, similar to those discussed by Hansen and Offutt (1988), show a substantial increase in the final volume of the system when water from outside the matrix is consumed in ettringite formation (Eq. 3-2). The observations under “sulfate cure” conditions support the molar volume calculations and the hypothesis of expansion. Therefore, a combination of crystal growth and water adsorption by ettringite crystals can be considered as the reason for the observed expansion in these samples. This agrees well with observations of Deng and Tang (1994).

3.7. Conclusions

The following conclusions can be drawn from this study:

1. Although the presence of water is critical in ettringite formation, it is the timing of the introduction of water that determines, to a large degree, the extent of expansion in the matrix. This finding substantiates the importance of employing good drainage engineering practices from design through construction.
2. The formation of ettringite due to water available in the mixture and based on the water soluble sulfate carried by the mixing water, may not and probably does not contribute to expansion. Instead, molar volume calculations indicate that the formation of ettringite under these conditions actually results in shrinkage.

3. Virtually all ettringite formed within the first 72 hours of cure in the samples evaluated in the empirical phase of this research; and expansion occurred in samples where external water was available during curing but without a significant increase in the quantity of ettringite. Observations of long term cure for the mixtures evaluated in this study, demonstrate that expansion was due to sorption of water within the ettringite matrix and not due to additional ettringite crystal growth.
4. When the mixture system is open to an "external" source of water, molar volume calculations support a substantial increase in volume due to the formation of ettringite. This is due to the addition of the 26 moles of water from an external source that is not initially part of the system [See Eq. 3-2].
5. Empirical observations demonstrated a significantly greater level of expansion when samples are exposed to a source of sulfate-bearing water as opposed to extended curing in non-sulfate bearing water or in ambient humidity curing conditions. This volume increase is partially due to ettringite precipitation using an external source of water and the additional crystal growth due to availability of more of the limiting reagent, sulfate, in the system. This additional crystal growth may occur at previously established ettringite nucleation sites. Based on these observations, it can be concluded that expansion associated with ettringite growth due to influx of sulfate laden water may induce a higher level of distress when compared to sulfates already present in the system.

4. VALIDATION OF SENSITIVITY OF SULFATE-BEARING SOILS TO ETTRINGITE GROWTH BASED ON DIFFERENTIAL SCANNING CALORIMETRY*

4.1. Introduction

Practicing engineers often evaluate sulfate induced expansion (ettringite formation) in soil stabilized with lime, Portland cement, or other calcium-based stabilizers based on empirically derived threshold sulfate levels (Little and Graves 1995; Harris et al 2004). Although these threshold-based predictions hold reasonably well in most cases, the literature documents cases where sulfate-induced distress has occurred at sulfate levels below 1,000 ppm and where it has not occurred at sulfate levels as high as 10,000 ppm or even higher (Hunter 1990; Little et al. 2005; Mitchell and Dermatas 1992; Puppala et al 2005). Therefore, experience alone and “rules-of-thumb” based on experience are not often sufficient to deal with this complex issue. Thermodynamic models are effective means by which to predict mineral precipitation in complex systems (Hunter 1990; Mohamed et al 1995; Damidot and Glasser 1993). Little et al. demonstrated the use of thermodynamic stability diagrams/phase diagrams in predicting ettringite growth in sulfate-bearing soils treated with lime (Little et al. 2005). For phase diagrams, decision making often requires familiarity with complex geochemical properties of soil minerals.

---

* From Little, D., and S. Nair. Validation of Sensitivity of Sulfate-Bearing Soils to Ettringite Growth by Differential Scanning Calorimetry. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2104,* pp. 63-70. Copyright, National Academy of Sciences, Washington, D.C., 2009. Reproduced with permission of the Transportation Research Board.

Since a reasonable level of geochemical expertise is required to use these geochemical models effectively, this method is not amenable for use by most practicing engineers. This paper focuses on the use of a differential scanning calorimeter (DSC) to assess the sensitivity of sulfate-bearing soils when treated with calcium-based stabilizers to deleterious reactions, especially the formation of ettringite.

4.2. Background

Ettringite precipitation in soils is complex and is dependent on factors including soil composition, construction methods, availability of water, ion migration and the void structure in pavement layers (Harris et al. 2004; Little et al. 2005; Petry and Little 1992; Perrin 1992). Geochemical factors such as pH, temperature, ion activity and dissolved ion concentrations also influence the precipitation and stability of ettringite in soil water systems (Little et al. 2005; Damidot and Glasser 1993; Myneni et al. 1998). The geochemical mechanism of ettringite precipitation was first explained by Hunter (1990). The chemical basis for ettringite formation as explained by Hunter is given in Equation [4-1].

$$6Ca^{2+} + 2Al(OH)_4^{-} + 4OH^{-} + 3(SO_4)^{2-} + 26H_2O \rightarrow Ca_6[Al(OH)_6]_2.(SO_4)_3.26H_2O \qquad (4\text{-}1)$$

Ettringite precipitates in environments where the pH remains high with high activities of Ca2+, Al(aq), and SO42- (Perkins and Palmer 1999). The calcium ions needed for ettringite formation are provided partly by lime or lime contained in other calcium-based stabilizers such as Portland cement; aluminum is supplied by dissolution of oxy-hydroxides and phyllo-silicates; and sulfates are supplied by dissolution of sulfate bearing phases in soil (Little et al. 2005; Mitchell and Dermatas 1992; Petry and Little 1992; Burkart et al. 1999). Even when all of the above reactants are available, precipitation of ettringite may depend on the thermodynamic favorability and the quantity of limiting reactants in the system (Little et al. 2005). Often during lime treatment of sulfate bearing soils, aluminum ions form the limiting reagent that determines the extent of ettringite precipitation (Dermatas 1995). For most soils, clay-size particles are the major source for aluminum. Many clay particles are susceptible to some level of dissolution at high pH conditions due to their high surface area and the nature of their crystalline structure. Therefore, a higher clay concentration in soils often translates to higher quantities of available aluminum in soils (Dermatas 1995). Aluminum availability further depends on the type of clay and its solubility properties (Dermatas 1995; Sherwood 1962). Under favorable conditions as discussed earlier, the reactants combine to form a complex mineral structure, ettringite, which often tends to form micron size fibrous crystals upon precipitation (Moore and Taylor 1970).

The ettringite mineral has a tubular structure with columns and channels running parallel to the c-axis (Moore and Taylor 1970). The columns primarily consist of aluminum octahedrons and calcium polyhedrons. Calcium polyhedrons are shaped as triagonal prisms where water and hydroxyl ions occupy four apices each. The tubular structure is formed by a chain of one alumina and three calcium polyhedrons that repeats uniformly to form a $\{Ca_6[Al(OH)_6]_2.24H_2O\}^{6+}$ structure. Two aluminum octahedrons ($[Al(OH)_6]^{3-}$) are connected by a group of three calcium polyhedrons. Shared hydroxyl ions (OH^-) bridge the calcium and aluminum polyhedra and form a continuous chain extending along the c-axis of the mineral (Moore and Taylor 1970; Myneni et al. 1997). The coordination polyhedra are completed by water molecules. The channels between columns are occupied by $[(SO_4)_3.2H_2O]^{6-}$ ions. These sulfate ions essentially bind the channels together forming the crystal and also form hydrogen bonds with exchangeable water in the calcium polyhedron (Moore and Taylor 1970; Skoblinskaya and krasilnikov 1975). Both sulfate ions and calcium polyhedra can accommodate exchangeable water within the tubular structure (Shimada and Young 2001).

Water molecules in ettringite structure are positioned at four distinct locations: in the inter column channel, at the two main apices, at two additional apices of calcium polyhedra and as hydroxyl ions linking calcium and aluminum ions. Due to a high weight percent of water in ettringite, water is important to the stability of the mineral structure. The mineral is thermally unstable at elevated temperatures (Shimada and Young 2001; Zhou and Glasser 2001). The ettringite loses water from the column and channels during heating causing a disintegration of the mineral structure (Shimada and Young 2001). When heated, the mineral show a progressive loss of water which is possibly due to a difference in bonding energy for water positioned at different locations. Therefore the conditions and the structural changes associated with dehydration will be different for each type of water molecules (Shimada and Young 2001). A differential scanning calorimeter can be used to measure the heat release associated with water loss in the mineral and can be used to quantify the concentration of ettringite present in the matrix (Shimada and Young 2001; Ogawa and Roy 1981; Odler and Abdul maula 1984).

The objective of this research was two-fold: (1) to evaluate the sensitivity of five different soils to ettringite formation, and (2) to assess the efficacy of the differential scanning calorimetry (DSC) as a tool to evaluate such sensitivity for the five sulfate bearing soils. A second objective was to compare quantities of ettringite measured using the DSC to quantities calculated based on mass-balance calculations and the thermodynamic phase diagram approach.

4.3. Materials and Methods

Five soils used in the study were selected by the Colorado Department of Transportation based on differences in mineralogical characteristics and sulfate concentrations. Each soil belongs to a different soil series. All chemicals used in the study were reagent grade materials.

4.3.1 Soil Classification and Sulfate Testing

The soils were pretreated before mineralogical analysis and subjected to fractionation and dispersion to separate sand, silt and clay fractions (Jackson 1969). Mineralogical characterization of soils was based on x-ray diffraction analysis using a Rigaku x-ray diffractometer. Sand, silt and clay fractions were analyzed separately to obtain a semi-quantitative estimate of soil mineralogy. Clay fractions were subjected to magnesium saturation, glycerol solvation and heat treatments to distinguish among clay minerals. Sulfate concentrations in soils were determined in accordance with the standard test method Tex-145E (2005).

4.3.2 Phase Diagram Approach

Thermodynamic stability of minerals precipitating in lime treated soils was determined by the predominance approach using the React program in Geochemist's Workbench software. Assumptions and steps established by Little et al. were followed in developing the Phase diagrams (Little et al. 2005). Since the approach does not consider the kinetic aspects of mineral dissolution, additional assumptions were made based on established mineral properties. Generally, sand fractions in soils were considered non-reactive and only ten percent of the silt fractions were considered to be reactive. The models were developed by allowing soils to react with lime in an aqueous environment under constant temperature and pressure conditions. Input parameters used in defining the lime-soil-water system for the five soils are given in Table (4-1). The soil matrices were characterized in terms of their chemical composition to define the available reactants (Little et al. 2005). The aqueous media was characterized by measured concentrations of ions released by soils into solution.

Table 4-1. React input parameters for five soils

Variable	Units	React Input				
		Halaquepts	Ildefonso	Berthoud	Bloom clay	Dwyer sand
[1]Water	Free kg	0.3	0.3	0.3	0.3	0.3
pH	-	12	12	12	12	12
Temperature	^{o}C	25	25	25	25	25
Pressure	bar	1.013	1.013	1.013	1.013	1.013
K+	mg / kg	44	52	45	93	41
Ca2+	mg / kg	165	612	1030	1980	43
Fe3+	mg / kg	5	2	2	2	13
Al3+	mg / kg	7	4	2	2	23
Cl-	mg / kg	44	770	32	381	61
[2]SO42-	mg / kg	1680	2400	2760	11840	100
SiO2(aq)	mg / kg	19	18	32	30	91
[3]Calcite	g	35	85	20	35	10
[3]Quartz	g	480	430	350	370	510
Kaolinite	g	25	70	50	55	15
[3]Muscovite	g	20	5	5	10	10
Smectite (low Fe, Mg)	g	15	10	105	65	15
[3]Illite	g	30	20	75	70	10
[3]Dolomite	g	-	10	15	20	10
[3]Potassium Feldspar	g	60	35	45	40	85
Lime	g	35	35	35	35	35

---

[1] Activity held constant at 1.0

[2] Input varied for sensitivity analysis

[3] Silt and sand or silt and clay combined

Ion concentrations in Table 4-1 were determined by chemical analysis at a soil to water dilution ratio of 1:10. The soil systems containing dissolved ions and minerals were subjected to speciation at a pH of 12 in the presence of five percent lime by weight. The ion activities were determined after speciation and used to identify stability fields of minerals.

4.3.3 DSC Approach

4.3.3.1 Sample Preparation

A representative soil fraction smaller that 75 μm was used in sample preparation. Soil samples were prepared by mixing 2.5 grams of soil with five percent lime by weight at optimum moisture content. Varying concentrations of sodium sulfate were also added to soil to provide increasing concentrations of sulfates in the mixtures. Lime, water and sodium sulfate were initially mixed inside a 50 ml centrifuge tube using a vortex mixer. Soils were then added to the suspension and mixed using the vortex mixer. The soil samples were then subjected to accelerated cure at 40^{o}C for different time periods. The samples were kept moist throughout the curing time. At the end of curing periods, soil samples were removed from the centrifuge tubes, filtered using a frit sand filter and dried using acetone. The residue was then dried in an oven at temperature below 45^{o}C for four hours and stored inside a desiccator. A control sample was also prepared for each soil after removing available sulfates using a sulfate extraction technique detailed in Tex-145E (2005). Residual soil was air dried and ground to pass a 75 μm sieve. The same procedure described earlier, but without adding sodium sulfate, was used to prepare control samples for the five soils. Pure ettringite was synthesized in the lab using a modified method and was used to define the control exotherm for the comparative baseline.

4.3.3.2 DSC Data Analysis

A Q-2000 differential scanning calorimeter manufactured by TA instruments was used in this study to detect and quantify ettringite. 10 mg sub-samples were randomly selected from the prepared soil samples and used for ettringite quantification using the DSC. Samples were heated at the rate of 2^{o}C per minute and tested over temperatures ranging from 25^{o}C to 175^{o}C. The system was purged with nitrogen gas at the rate of 10 ml/min during testing. Heat flow from the test sample was integrated over time to determine the heat released from the sample. Synthesized ettringite was also tested under similar conditions in the DSC to determine the properties and behavior of the pure mineral. The quantity of ettringite in each soil sub samples was determined based on comparison with a standard curve prepared using the control sample with known concentrations of synthesized ettringite.

4.3.3.3 Uncertainties and Limitations

Differentiating ettringite signals becomes difficult when other hydration phases interfere, especially at low ettringite concentrations. The heterogeneity of ettringite formation within the sample can create significant variability in measurements. In addition, changes in ettringite crystallinity cannot be accounted for in this method. Therefore, a comparison of heat signals at different curing periods cannot differentiate whether the increase is due to a purer crystalline structure of existing ettringite or due to additional ettringite formation. Since differences in heat signals due to difference in crystalline structure are not expected to be significant compared to differences in quantity of the target material, ettringite, the increase was attributed to new mineral precipitation. Uncertainties associated with geochemical modeling are discussed in detail by Little et al. (Little et al. 2005).

4.4. Results and Discussion

4.4.1 Soil Classification and Sulfate Testing

The reactive silt and clay contents of the five soils vary considerably. Soil classification for the soils based on the USDA textural classification chart and measured sulfate concentrations, determined in accordance with Tex 145 E (2005), for the five soils are given in Table (4-2).

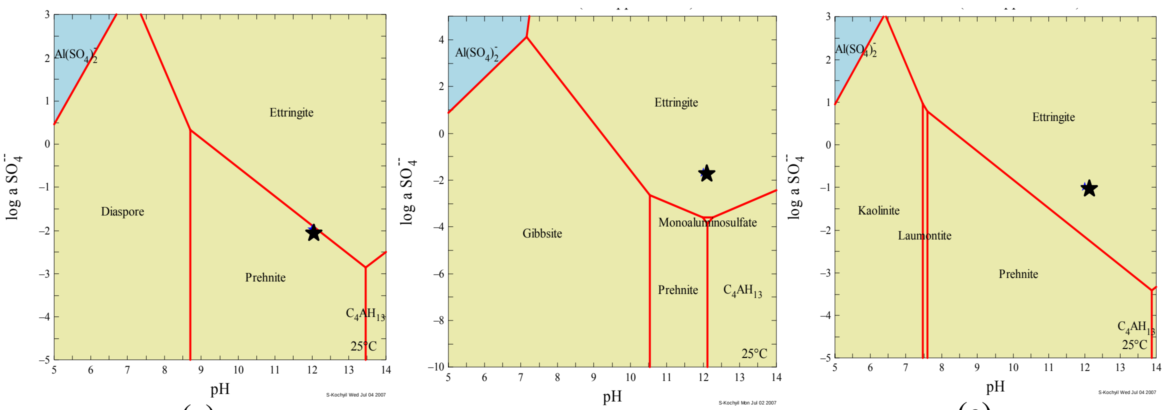
Table 4-2. Particle size distribution and water soluble sulfate contents in five soils

Soil Type	Sands (%)	Silts (%)	Clays (%)	Typical	Sulfate Content
Halaquepts	70	20	10	Sandy loam	1,680
Ildefonso	58	27	15	Sandy loam	2,400
Berthoud	37	28	35	Clay loam	2,760
Bloom Clay	19	51	30	Silty clay	11,840
Dwyer Sand	76	17	7	Fine sand	100

Halaquepts and Dwyer sand were found to have lower concentrations of silt and clay when compared to the other three soils. Berthoud and Bloom clay soils had the highest concentration of reactive clay fraction among the five soils. Considering clays to be the major source of alumina in soils, Halaquepts and Dwyer sand would be expected to have the lowest reactivity in terms of ettringite formation (Mitchell and Dermatas 1992; Puppala et al. 2005). The sulfate concentrations given in Table (4-2) are based on an average of three different samples selected from each soil. Sulfate levels in all but the Bloom clay were found to be below 3,000 ppm. These four soils may therefore be considered to carry a low level of risk for ettringite formation based on available sulfate contents (TXDOT 2005).

4.4.2 Soil Sensitivity Based on Thermodynamic Phase Diagrams

The mineralogical details and sulfate concentrations were used to prepare thermodynamic phase diagrams to predict the behavior of five soils when treated with lime (Table 4-1). The minerals present in soils were subjected to speciation in the presence of lime and water so that equilibrium based on mass and charge balance conditions was achieved. A predominance approach was used in the study to identify the secondary mineral phases precipitated in the system. The predominance approach considers the aqueous chemistry of the system under the given conditions and determines the dominant species present at equilibrium condition (Little et al. 2005).



(a) (b) (c)

Fig. 4-1. Comparison of stability fields in soils with naturally available sulfate concentrations (a) Halaquepts soil (b) Ildefonso soil (c) Bloom clay soil

Phase diagrams predictions on the behavior of Halaquepts, Ildefonso and bloom clay soils are given in Fig. 4-1. The influence of mineralogy on soil behavior is evident in the predicted behaviors of Halaquepts and Ildefonso soil (Fig. 4-1 a and b). Although the two soils have similar sulfate concentrations, the soils differ significantly in mineralogical characteristics (Table 4-2). Accordingly, the stability fields of secondary minerals precipitated are different for the two soils. The locus of pH 12 and the sulfate activity for the Ildefonso soil is in the polygon representing ettringite whereas for the Halaquepts soil the locus falls in the prehnite polygon (Fig. 4-1). The Ildefonso soil has higher clay content than the Halaquepts soil and is dominated by kaolinites. The kaolinite content in the Ildefonso soil is approximately three times the concentration in the Halaquepts soil (Table 4-1) which contributes to more readily available aluminum needed for ettringite formation (Mitchell and Dermatas 1992). Therefore, ettringite becomes a stable phase in the Ildefonso soil even at low sulfate concentrations.

For the Bloom clay soil, both clay content and available sulfate concentrations are significantly higher than the other two soils (Table 4-2). Therefore, based on established sulfate threshold levels, this soil can be considered to be at higher risk to form ettringite (Little and Graves 1995; Harris et al. 2004). Phase diagrams for the Bloom clay soil substantiate this and show ettringite to be the stable phase when the soil is treated with lime (Figure 4-1c). High sulfate content and plentiful aluminum sources make Bloom clay soil problematic at naturally occurring sulfate concentrations.

The behavior of the Berthoud soil was similar to the Ildefonso soil. For the Berthoud soil the locus of pH equal to 12 and the sulfate activity, consistent with a sulfate concentration of 2,760 ppm, falls within the ettringite polygon. Since the measured clay content of this soil was higher than all the other soils used in the study, higher aluminum availability from clay dissolution may again contribute to the higher reactivity of this soil (Table 4-2). For the Dwyer sand, both the measured sulfate content and available clay concentrations were lower than for other soils used in the study (Table 4-2). A sulfate content of 2,000 ppm, well above the natural sulfate content in this soil, was selected for developing the phase diagrams to compare the reactivity of the Dwyer sand with other soils used in the study. The phase diagrams indicate the locus to fall well within the prehnite polygon. Although the sulfate content used in developing phase diagrams was similar to sulfate levels in the Ildefonso soil, the results indicate that ettringite is not a thermodynamically stable phase in the Dwyer sand at this sulfate level. This is possibly due to a lack of readily available aluminum to form ettringite.

Although the phase diagrams are consistent with observed soil chemical and mineralogical data, it is important to note that the phase diagrams only indicate the stable phase of the soil system at the given sulfate concentration. These diagrams do not define the extent of ettringite formation. Stoichiometric calculations can be used to predict the quantity of ettringite that will form for selected conditions. An example calculation for the amount of ettringite (E) formed from a specific mass of sulfate, SO4, is given in equation [4-2].

$$\frac{0.2gSO_4}{100gSoil} \times \frac{1molSO_4}{96gSO_4} \times \frac{1molE}{3molSO_4} \times \frac{1254gE}{1molE} = \frac{0.871gE}{100gSoil} = 0.87\%E \qquad (4\text{-}2)$$

This stoichiometric calculation determines the mass of ettringite formed in soils with 2,000 ppm (0.2 percent) sulfates. Concentrations are determined based on mass-balance calculations using sulfate as the limiting reagent during ettringite formation. These stoichiometric calculations define a reasonable boundary for maximum ettringite quantities in the system. Nevertheless, the amount of available water and the type of sulfate source in the soil are critical in deciding the concentration of sulfates that are made available for ettringite formation. Let us consider the case where gypsum is the major sulfate source in the soil. One mole of gypsum has a mass of 172 g out of which 96 g are comprised of sulfate ions. The solubility of gypsum in water is 2.58 g/L which can contribute 1.44 g (1440 ppm) of SO4 ions dissolved in one liter of water (Burkart et al. 1999). Now, if we consider adding 30 g of water for mixing and compaction purposes to 100 g of soil (30 percent), the quantity of sulfates that can be solubilized by the mixing water is:

$$\frac{30g\ H_2O}{1000g\ H_2O} \times 2.58g\ Gypsum \times \frac{96\,g}{172\,g} = 0.043g\ SO_4 = 0.043\,\%\ SO_4$$

Now assume that 100g of soil contains 0.358g or 0.358 percent gypsum (equivalent to 2,000 ppm sulfates). The same amount of available water can only dissolve a maximum of 1/5th of the available sulfates in the soil. Therefore, it is important to note that the rate and extent of ettringite growth is dependent upon conditions created by a number of factors associated with soils. These include, but are not limited to, factors like sulfate concentrations, water availability, ion availability, environmental conditions etc (Harris et al. 2004; Little et al. 2005; Perrin 1992; Dermatas 1995).

4.4.3 Soil Sensitivity to Ettringite Formation based on DSC Approach

To verify the observations based on the phase diagram approach, soil samples prepared using Ildefonso and Halaquepts soils were tested using a DSC. A comparison of ettringite growth in the two soils with increasing sulfate concentrations at different curing times is given in Fig. 4-2. In order to evaluate the effect of increasing sulfate content, it was necessary to spike the soils with additional sulfate since the in situ concentrations of sulfate were relatively low for all but one soil (Bloom clay). Several options were available for doing this. The best option would have been to find soil with no sulfates and to add sulfates to that soil. That option was not available. The second option was to extract sulfates form the soil at hand, but that option risked depleting the sample of some of the highly reactive fine clays and possible reactive silts. Therefore, sodium sulfate was added to the baseline soil (containing a certain level of natural sulfate – primarily gypsum) in each case.

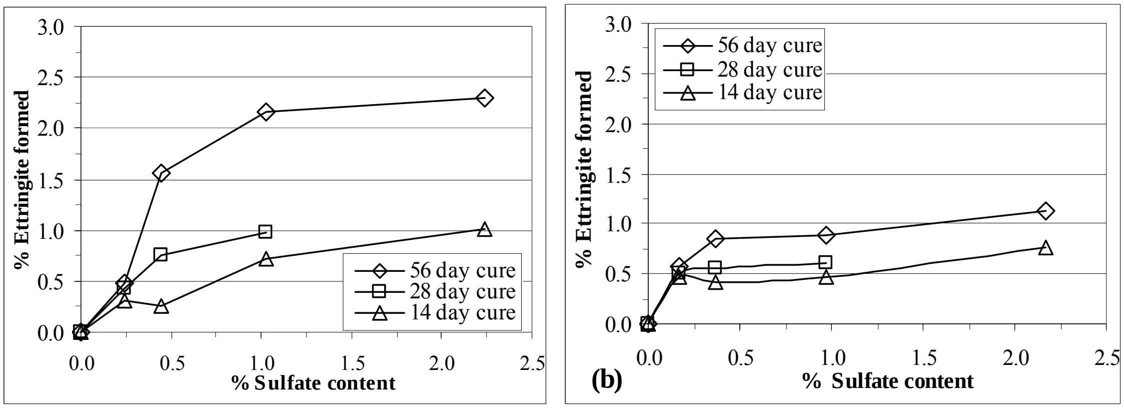


Fig. 4-2. Comparison of ettringite growth at known sulfate concentrations for different curing times (a) Ildefonso soil and (b) Halaquepts soil

Both Ildefonso and Halaquepts appear to form significantly smaller but similar concentrations of ettringite at sulfate concentrations below 0.3 percent. But the soil behavior changes significantly with an increase in available sulfate concentrations. The Ildefonso soil was found to form higher ettringite concentrations with an increase in sulfate concentrations. A comparison of ettringite content in the two soils, after 56 days of curing with more than two percent soluble sulfates, shows that the Ildefonso soil forms approximately twice as much ettringite as the Halaquepts soil. Ettringite concentrations in both soils were also found to increase with curing time. The rate of ettringite growth at a given sulfate content with curing time was also higher in the

Ildefonso soil when compared to the Halaquepts soils. These observations signify the influence of factors other than sulfate content on the extent of ettringite forming in the soils (Little et al. 2005; Dermatas 1995).

Since the curing conditions and the concentration of lime, sulfates and water are similar for both soils, it is reasonable to assume that the mineralogical differences in these soils is causing the observed differences in behavior. A higher concentration of reactive fines in the Ildefonso soil may have caused the increased reactivity of this soil (Puppala et al. 2005). A progressive dissolution of aluminum bearing phases, both in the silt and clay fractions, may have caused this gradual increase in ettringite content with curing time (Mitchell and Dermatas 1992). The concentration of soluble silica in soils, possibly from dissolution of the microcrystalline silt fraction, can also influence ettringite precipitation (Wild et al. 2003). Although this was not established in the study, a difference in silt to clay ratio among soils can contribute to different silica content in these soils. It is possible for silica bearing phases such as feldspars and opal, when contained in the fine silt or even clay sized fraction, to provide soluble silica under high pH conditions just as clay can. Ion concentrations in solution, surface area, surface defects and solubility properties of minerals can all impact the extent of mineral dissolution (Little et al. 2005). The behavior of Berthoud soils was also found to be similar to the Ildefonso soil under similar treatment conditions (Fig. 4-3).

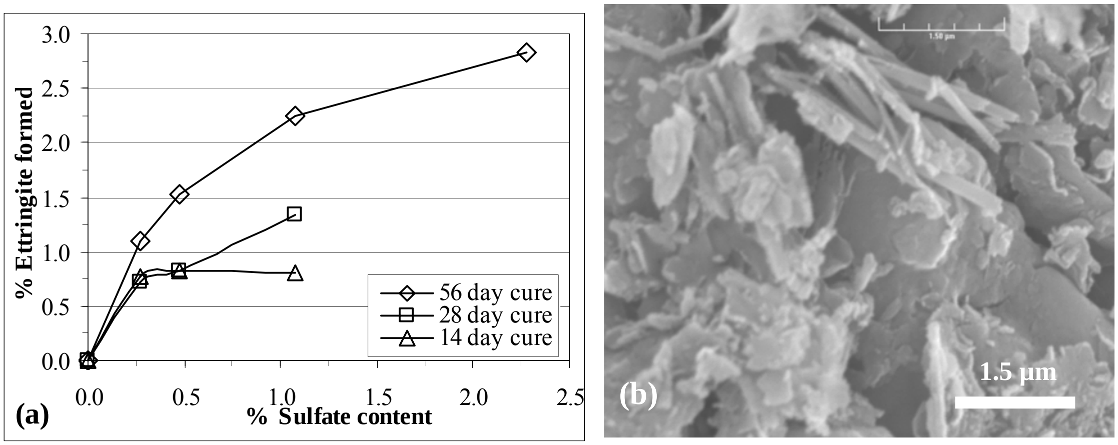


Fig. 4-3. (a) Observed ettringite concentrations in Berthoud soil measured using DSC and (b) SEM images of ettringite in the sample after 28 day cure (Mag. x5450)

Based on the DSC analysis, for the Berthoud soil, a gradual increase in ettringite content is noted with increasing sulfate concentration. Again, as for the other soils, for the Berthoud soil, there was no significant ettringite formation at sulfate contents of less than about 0.3 percent (3,000 ppm). The ettringite content determined by the DSC analysis after 56 days of cure and for a sulfate content of approximately 3,000 ppm, was about 1.25 percent. Comparing this with the maximum quantity of ettringite stoichiometrically possible (1.30 percent) indicates that most of the natural sulfates had been used to form ettringite at this point.

Measured quantities of ettringite after 56 days of cure were slightly higher for Berthoud soils compared with the Ildefonso soil treated and cured under similar conditions. This higher quantity of ettringite in the Berthoud soil is probably due to a combination of a higher sulfate content and lower silt to clay ratio in the Berthoud soil. The Berthoud soil also has a higher clay concentration when compared to Ildefonso soil with both kaolinite and smectites present in significant amounts (Table 4-1). Considering the faster dissolution and easier aluminum release from kaolinite, ettringite formation during initial curing periods may be due to the partial dissolution of kaolinites in these soils (Mitchell and Dermatas 1992). The gradual increase in ettringite content in Berthoud soil with increasing curing time may be due to a slower but progressive dissolution of smectites in these soils (Dermatas 1995). This further substantiates the role of clay minerals in impacting soil behavior. The presence of ettringite in the Berthoud soil was confirmed using scanning electron microscopy (SEM). SEM micrographs for 28-day cured samples show well formed ettringite crystals but restricted and distributed randomly on the surfaces of clay particles (Fig. 4-3).

4.4.4 Ettringite Growth in Soil: Comparison of Phase Diagram Approach and DSC

A comparison of ettringite concentrations predicted to form in soils based on the phase diagram approach (mass-balance calculations) and the actual quantities of ettringite measured using the DSC is given in Fig.4-4. A sensitivity study was done by varying the concentration of available sulfates in the phase diagram approach. Soil samples for DSC testing were prepared by adding known sulfate concentrations to soils prior to lime treatment and curing. The maximum possible ettringite formation for the given sulfate content is determined using stoichiometric calculations and presented as the line “stoichiometry” in Figure 4-4.

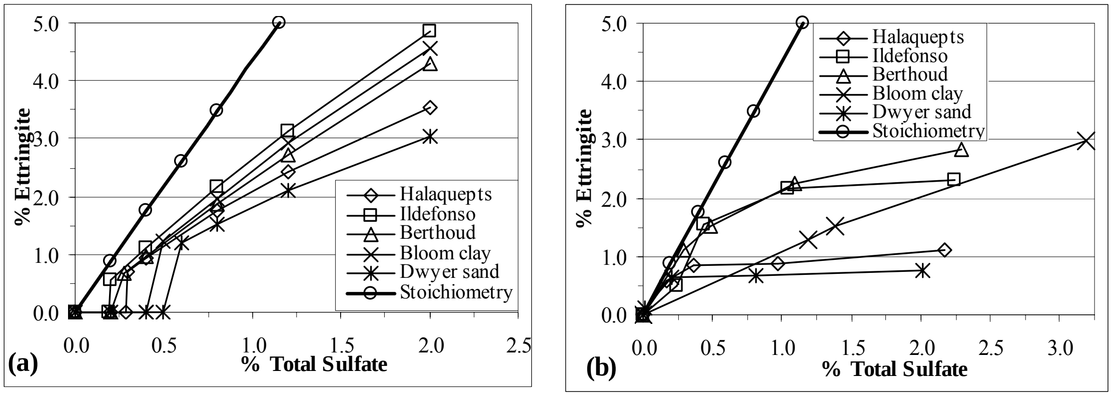


Fig. 4-4. Comparison ettringite concentrations in soils at varying sulfate contents based on (a) predictions using Phase diagram approach and (b) concentrations measured using DSC after 56 day curing

The predictions using the phase diagram approach agree relatively well with experimental observations based on the DSC. Both techniques show a progressive increase in ettringite content with increase in sulfate concentrations and the observed concentrations are below stoichiometric limits. The trend related to reactivities of the soils is also relatively similar for both approaches. Both approaches show Ildefonso, Bloom clay and Berthoud soils to form more ettringite at a given sulfate contents in comparison to Halaquepts and Dwyer sand. It should be noted that the natural sulfate content of the Bloom clay is about 12,000 ppm (1.2 percent) and the sensitivity to additional sulfates above the 1.2 percent was investigated in the study (Table 4-2). In both approaches, the only difference among the soils used in the sensitivity study is their mineralogy, more specifically, the concentration of reactive clay fractions. The observations verify the influence of soil mineralogy and suggest that soil reactivity closely parallels the available clay content in these soils (Puppala et al. 2005). Although this is true, the observed weight percentages of ettringite are not proportional to the clay concentrations. The difference is probably due to the difference in solubility properties of individual clay minerals and/or due to the interference of other competing chemical processes occurring in soil system (Mitchell and Dermatas 1992; Puppala et al. 2005; Wild et al. 2003).

The rank order of ettringite formation sensitivity was the same for all but one of the five soils whether based on the mass-balance calculation (phase diagram) approach or measured directly using the DSC. The “outlier”, Bloom clay soil, is ranked different in the phase diagram approach when compared with DSC measurements. DSC measurements show the soil to form approximately 1.5 percent ettringite at a sulfate concentration of approximately 14,000 ppm (1.4 percent). However, out of the 14,000 ppm sulfates available in this soil, approximately 12,000 ppm (1.2 percent) is from the gypsum source in the natural soil with the remainder added to the soil as sodium sulfate (Table 4-2). Considering the low solubility of gypsum with respect to sodium sulfate, a limited dissolution of gypsum induces a kinetics inhibition to ettringite precipitation which detected by the DSC as a lower quantity of ettringite in the sample. But since the phase diagram assumes that all reactions move to equilibrium or completion, the differences in dissolution of gypsum and sodium sulfate are not considered in the mass-balance calculations (Burkart et al. 1999). Since the kinetic inhibitions are not accounted for by the phase diagrams, ettringite concentrations in soils are higher for phase diagram approach when compared to measurements with the DSC.

For all the five soils, the general trend for ettringite growth at sulfate concentrations below 0.3 percent (3,000 ppm) appears to be similar. The fact that very low concentrations of ettringite are measured for all five soils when sulfate concentrations are below about 3,000 ppm continues to validate or reaffirm the empirical evidence from the field where a soluble sulfate level of 2000 to 3,000 ppm might differentiate soils with little or no risk from those of notable risk (Little and Graves 1995; Petry and Little 1992). Of course, this assumes that sulfates external to the system are not allowed to enter the system. The observed data also seems to support the idea proposed by Little et al. that an extended mellowing before compaction allows the formation of ettringite during which sulfate is consumed (Little and Graves 1995). This reduces post compaction ettringite formation and the resultant heaving associated with ettringite formation. However, based on the example presented previously in this paper, massive amounts of water would be required to solubilize all gypsum available in the soil, even if it is only in the range of 3,000 ppm. The authors believe, however, that more nucleation sites for ettringite crystal growth are created by adding the maximum amount of water practicable and extending the mellowing periods as much as possible. These nucleation sites, especially when well dispersed throughout the soil mass provide a source of more rapid and uniform crystal growth and consumption of sulfates. Harris et al. also validated the concept of the existence of sulfate threshold level in soil and the role of extended mellowing in soils to reduce post compaction ettringite formation (Harris et al. 2004).

4.5. Conclusions

The following conclusions can be derived from the study:

1 The basis for the empirical threshold of between about 2,000 ppm and 3,000 ppm soluble sulfate as the point at which deleterious expansion damage might begin to occur in soils treated with calcium-bases stabilizers is supported by this research.

2 The DSC is a useful tool based on its ability to define the sensitivity of soils to ettringite formation as a function of sulfate content upon the addition of calcium-based stabilizers.

3 Observations using the DSC are in reasonable agreement with predictions made using phase diagram approach. The major differences appear to be based on the fact that the phase diagram approach assumes that all reactions proceed to equilibrium while kinetics impacts the direct DSC measurements.

4 Based on our observations, the extent of ettringite formation in the soils evaluated can be considered to be dependent on reactive clay content in the soil. But no definitive relationship was observed between clay content and weight percent of ettringite formed in soils.

5. MECHANISMS OF DISTRESS ASSOCIATED WITH SULFATE INDUCED HEAVING IN LIME TREATED SOILS*

5.1. Introduction

Since the late 1980's, numerous cases related to sulfate induced heave have been reported in the United States where sulfate laden soils subjected to lime treatment were found to expand and heave after or during stabilization (Mitchell 1986; Hunter 1990; Petry and Little 1992; Petry 1994; Little 2005). Further investigations revealed the presence of the mineral ettringite within distressed sections and attributed observed distress to the expansive properties of ettringite. Even though this may be true in most cases, the time window between the observation of distress and the subsequent forensic evaluations left room for doubt as to whether the ettringite caused the observed distress or was formed between the observed distress and the time of the forensic investigation. In fact, geochemical conditions in the stabilized layers after distress are often ideal for ettringite formation as there is readily available calcium from lime dissolution, aluminum from dissolution of clays, soluble sulfates and copious amounts of water. Prior research on ettringite formation in stabilized soils also supports a time dependent ettringite growth in soils when conditions are appropriate (Mitchell and Dermatas 1992; Dermatas 1995; Ouhadi and Young 2008; Little et al. 2010). Hence it is possible that the

---

[*] From Nair, S., and D. Little. Mechanisms of Distress Associated with Sulfate Induced Heaving in Lime Treated Soils. Submitted for presentation at the 90th Annual Meeting of the Transportation Research Board, January 2011, Washington, D.C. Copyright, National Academy of Sciences, Washington, D.C., 2010. Reproduced with permission of the Transportation Research Board.

ettringite identified during these forensic investigations might have formed after heaving in the stabilized layers. The question of practical significance is then, what caused the observed swell in these stabilized sections? The focus of this study was to investigate whether alternative mechanisms contribute to distress, primarily swelling related, in lime stabilized soils.

5.2. Background

While previous studies have identified the primary environmental and geochemical factors that influence ettringite formation, less attention has been given to understanding the mechanisms that cause these stabilized layers to heave. Formation of the expansive mineral, ettringite, during stabilization, is an obvious potential cause of distress. Ettringite is a hydrated calcium alumino-sulfate mineral and is typically comprised of needle-like crystals of lengths varying from a few microns to as much as 200 μm (Dermatas 1995; Moore and Taylor 1970; Moon et al. 2007). Ettringite precipitates under alkaline (high pH) conditions in lime treated soils or soils treated with other calcium-based stabilizers and in the presence of high sulfate activity (Petry and Little 1992; Warren and Reardon 1994; Perkins and Parmer 1999; Jallad et al. 2003; Myneni et al. 1998). Anisotropic growth of ettringite crystals can exert expansive pressure on stabilized layers due to particle interlocking causing the matrix to swell (Ogawa and Roy 1981; Odler and Glasser 1988). A second reason for swell is the highly active surface properties of ettringite which makes it capable of holding additional water after precipitation (Mehta 1973; Mehta and Wang 1982). This translates into swelling in the matrix when water becomes available (Mehta 1973; Mehta and Wang 1982).

A third possible reason for swell, which has not been clearly identified in the literature, at least to the best knowledge of the authors, is the role of sulfate salts in inducing sufficient water influx into the stabilized sections to cause volumetric expansion. Salt content can influence soil-water suction characteristics and can induce swell behavior when water becomes available. Soil suction is a potential energy quantity and is also the energy responsible for soil water retention. Total suction in soils is the sum of the matric and osmotic components (Krahn and Fredlund 1972). Matric suction, the negative pressure developed in soil water due to capillary and absorption forces, can fundamentally be related to soil structure, clay mineralogy and clay chemistry (Krahn and Fredlund 1972; Petry and Jiang 2007; Fredlund and Rahardjo 1993). Osmotic suction, the suction potential resulting from salts present in the soil pore water, is caused by a differential concentration of salts and the development of an osmotic gradient that can attract additional water into the matrix.

In many if not most cases, field observations related to ettringite induced distress may be divided into two distress types: (1) expansion that occurs immediately after placement and compaction of stabilized layers (2) expansion that manifests months or even years after lime treatment (Mitchell 1986; Hunter 1990; Petry 1994; Perrin 1992; Burkhart et al. 1999; Kota et al. 1996). Investigations of most sections that have experienced rapid heaving, have revealed the presence of an external sulfate source close to the distressed section, either at very shallow depths in the underlying native soil or along cut sections abutting the stabilized sections (Little 2005; Perrin 1992; Burkhart et al. 1999; Kota et al. 1996). In many cases heaving was associated with major rainfall events that occurred shortly after construction. The damage occurring in these cases was severe along areas of poor drainage where surface water or the ground water table, possibly carrying sulfate ions, was able to migrate into these stabilized layers. Although investigations have revealed the presence of ettringite in these distressed sections, immediate formation of ettringite may not be the reason for this expansion as the aluminum availability in these soils is defined by the kinetics of dissolution of silt and clay fractions in the soil (Petry and Little 1992; Mitchell and Dermatas 1992; Dermatas 1995; Little et al. 2005). The second distress type, where expansion manifests long after lime treatment, is consistent with time dependent ettringite growth reported in controlled experimental studies (Mitchell and Dermatas 1992; Dermatas 1995; Little and Nair 2007; Little et al. 2003). Irrespective of whether the swell occurred early on or over time, a subtle similarity among these cases is a sufficient supply of water (Hunter 1990; Little 2005; Little et al. 2005; Perrin 1992; Kota et al. 1996).

5.3. Research Objectives

The objective of this research is to identify the impact of soluble sulfate salts on swell behavior apart from or in concert with the formation of the expansive mineral ettringite. The research focuses on addressing the following questions:

Whether the sole reason for heaving observed in stabilized layers is the molar volume increase due to the formation of ettringite, and the capacity of the ettringite mineral to absorb additional water and cause post ettringite formation expansion.

Whether the impact of a high sulfate salt content on osmotic suction in these soils is significant enough to cause water sorption into the matrix that can impart swell behavior apart from the formation of ettringite.

This research addresses the hypothesis that swelling in sulfate-bearing fine-grained soils is due to one or a combination of three separate mechanisms:

1. Volumetric expansion due to mineral formation
2. The ability of the sulfate salts in the soil mass to cause an osmotic suction sufficiently high to trigger water movement into the system, and
3. The ability of the ettringite mineral to absorb water and swell after formation.

5.4. Materials and Methods

A mix proportion of 40 percent commercially available kaolinite clay and 60 percent ASTM 20-30 (Ottawa) sand was used in this study to replicate typical clay soils encountered during stabilization and also to ensure that availability of aluminum bearing phases (supplied by the kaolinite) did not limit ettringite growth. Commercially available lime ($Ca(OH)_2$) and deionized water (DI) were used to prepare the lime-soil mixtures. Three reagent grade sulfate sources: aluminum sulfate octadecahydrate, sodium sulfate and calcium sulfate were carefully selected to create different conditions of elemental availability in the mixtures. The aluminum sulfate octadecahydrate provided stochiometric proportions of aluminum and sulfate required for ettringite precipitation and ensured a readily available source of alumina without depending on dissolution from clay minerals. On the contrary, when gypsum and sodium sulfate reagents are the source of sulfate, aluminum needed for ettringite formation must come from dissolution of clay minerals (in this case kaolinite). Due to its high solubility, sodium sulfate will rapidly release sulfate ions into solution and can act as a readily available sulfate source even at lower moisture contents such as those used in construction. On the other hand, sulfate dissolution from gypsum is limited and is therefore dependent on the amount of water available in the mixture (Burkart et al. 1999). Growth of ettringite crystals in soils containing gypsum can continue over long periods as more sulfates is released from the gypsum into the mixture.

Irrespective of the method of sulfate introduction, either as a solid or as a solution, mixes are identified in this paper based on the type of reagent providing soluble sulfate for ettringite formation ("RA" for aluminum sulfate octadecahydrate , "RS" for sodium sulfate and "RC" for calcium sulfate). A third alpha designator "M" or "S" represents whether the sulfate source was added during mixing (present inside the matrix) or was in solution and introduced by soaking. Hence lime soil mixes where aluminum sulfate octadecahydrate was present inside the matrix are referred to as "RAM" and mixes where aluminum sulfate octadecahydrate was introduced through soaking (solution) are referred to as "RAS". Similarly when sodium and calcium sulfates were present inside the matrix the mixes are referred to as "RSM" and "RCM", respectively, and when introduced through soaking (solution) the mixes are referred to as "RSS" and "RCS", respectively. Lime treated mixtures without any sulfate source are referred to as "control" mixtures or samples.

5.4.1 Swell Testing

Samples used for swell measurement (4-inch x 4.5-inch) were prepared by mixing the soil and sulfate salts with five percent lime ($Ca(OH)2$) by weight. Lime-soil-salt mixtures were compacted in one lift using a Superpave Gyratory compactor at densities that corresponded to those achieved using the standard proctor test. All samples were sealed in air tight plastic bags immediately after compaction and left undisturbed for three days (conditioning period) to complete initial cation exchange, particle size modification and pozzolanic mechanisms and to achieve sufficient strength to stand up to soaking. Samples used to monitor the effect of strength on swelling were subjected to accelerated cure for 7 days at 104^{o}F (40^{o}C) after the conditioning period. Control samples were prepared following a similar protocol but without adding sulfate reagents. All samples, both cured and uncured, were air dried for three days prior to soak to initiate capillary suction. Duplicate samples were subjected to a three dimensional swell test modeled after Petry's work to determine volume changes in the sample (Harris et al. 2004). Axial and circumferential expansions were measured over time for all the mixtures under the respective conditions. Measurements were taken to the nearest 0.002 in (0.5 mm) using a clear plastic tape. Circumferential measurements were taken near the top, center and bottom of the sample. Specimen height was measured at three locations, 120^{o} apart. Respective measurements were averaged to determine volume changes in the sample.

Two sulfate exposure conditions were investigated: (1) sulfate source introduced as dissolved sulfate ions in soaking water to replicate external sulfate movement and (2) sulfate source directly present in the stabilized soil matrix. For the first exposure condition, to represent external sulfate movement, sulfate salts were dissolved in deionized water (DI) and this solution was then used as soaking water during the initial phase of swell testing. Upon completion of a two day soaking period, the samples were removed and placed in sealed plastic bags and left to equilibrate for five days. After this equilibration period, the samples were exposed to soaking with DI water (without sulfates) over time to investigate volume change behavior due to the presence of ettringite in these mixes. For the second condition, when sulfate sources were present in the stabilized soil, DI water (without sulfates) was used for capillary soak for the entire duration of swell testing. Sulfate concentrations used in each case are detailed in the appropriate sections.

5.4.2 Matric Suction and Total Suction

Two different approaches were used to measure the suction of lime-soil mixtures. Total suction in the samples was measured using a filter paper method in accordance to ASTM D 5298. Schleicher & Schuell No. 589-WH filter paper was used in testing and a calibration curve developed by Bulut et al. (2001) was used to determine suction values for soil samples. The filter paper method was not used to determine matric suction as it was difficult to cut the sample and make a smooth, flat surface in order to establish intimate contact between the lime treated sample and the filter paper. Hence the matric suction was determined using a pressure plate apparatus in accordance with ASTM D 6836. Due to the height constraint on water equilibration time in the pressure plate apparatus a 1.3-inch x 0.6-inch cylindrical sample was used in all suction measurements.

A smaller diameter sample was used to avoid the risk of soaked samples falling apart during the test procedure. Samples with required dimensions were prepared using a Harvard miniature compaction apparatus. The same techniques, mix proportioning and sample conditioning, used to prepare swell test samples were followed in preparing suction measurement samples. Triplicate samples were tested for every condition presented in the study.

The objective of the suction testing was to simultaneously determine both matric suction and total suction in the sample at given moisture content. Since two different test methods were used, all test samples after a respective conditioning and soaking protocol were left inside the pressure plate until the moisture content was equilibrated at the applied air pressure. Samples for total suction measurements were then removed from the pressure plate to perform the filter paper test. Upon completion of filter paper test, the samples were oven dried to determine the percent moisture content in the mix.

5.4.3 X-Ray Diffraction

A Rigaku x-ray diffractometer was used to verify the presence of ettringite in the stabilized mixes. Copper, Cu kα radiation was used at a scan speed of 3^{o}/min with a scanning angle ranging from 3 to 60 degrees. Cylindrical samples 1.3-inch x 0.6-inch were prepared for x-ray diffraction testing for all test conditions investigated in the study. The same techniques, mix proportioning and sample conditioning used to prepare samples for swell tests and suction measurements, were followed in preparing these samples. Upon completion of the test, the samples were air dried, pulverized and sieved through a No. 50 sieve to remove non-reactive sand fractions. Sub samples for XRD analysis were then randomly selected from each mix for evaluation.

5.5. Results and Discussion

Preliminary assessment of pozzolanic reactivity of the mixes and their potential to form ettringite was made by measuring pH values of lime treated mixtures in accordance with ASTM D 6276. According to the literature (Myneni et al. 1998), a pH of greater than about 10.7 is generally required for continued ettringite growth. Three pH measurements were made for each lime-soil mixture to assess this potential. The average pH values for the control samples and samples containing 5,000 ppm of RA, RS, and RC, respectively were: 12.31, 11.95, 12.36 and 12.26. Irrespective of method of sulfate addition, either as sulfate salt or as a solution, the pH remained above 11.75 and was high enough to create conditions favorable for ettringite formation in these mixes (Warren and Reardon 1994; Perkins and Palmer 1999; Myneni et al. 1998). The behavior of lime treated soils when exposed to sulfate laden water is shown in Fig. 5-1.

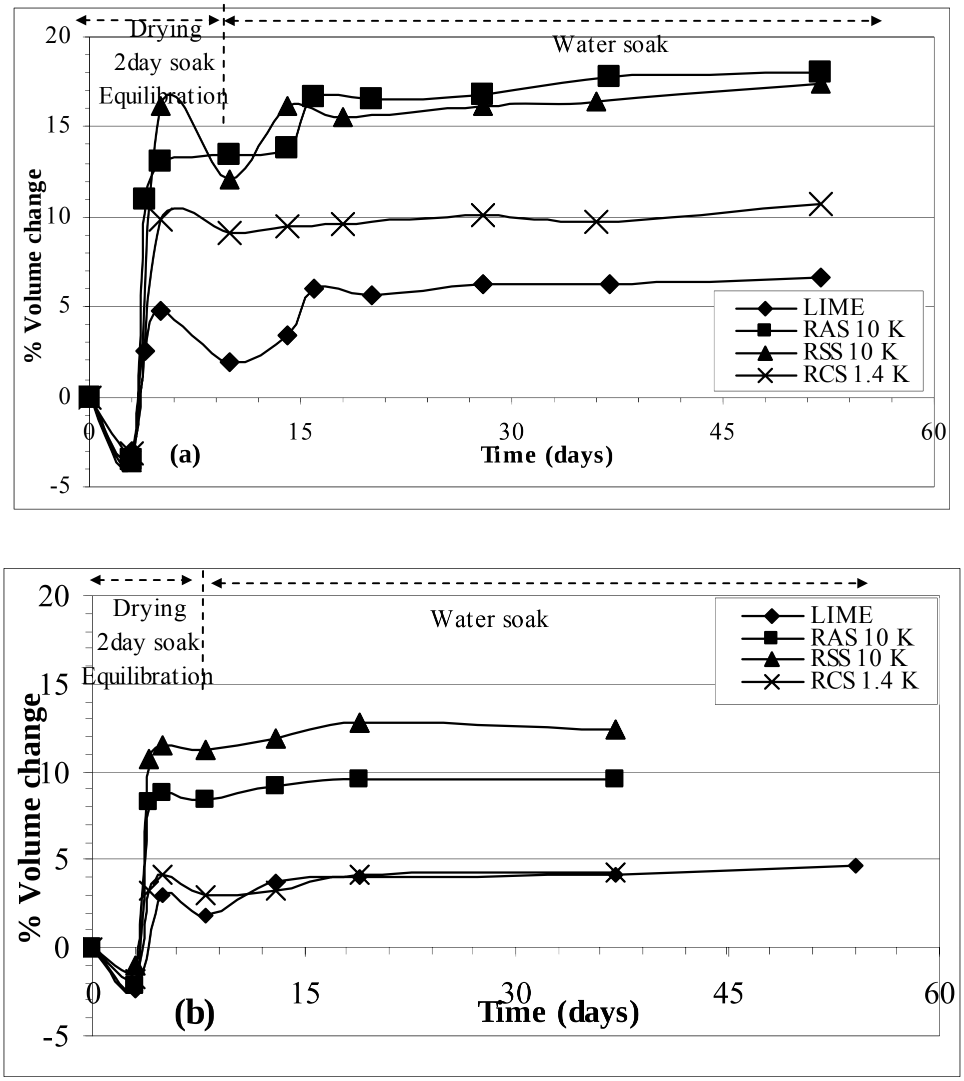


Fig. 5-1. Swell behavior in lime treated soils when subjected to external sulfate movement: (a) mixes without cure, and (b) mixes subjected to accelerated cure for 7-days

Volumetric swell behavior of mixes exposed to sulfate concentrations of 10,000 ppm provided by RA and RS and 1,400 ppm provided by RC solution are presented in Fig. 5-1. A lower concentration was used in the case of RC due to the limited solubility of gypsum (2.58 gm/l) in water (Burkart et al. 1999). As shown on the figure, one set of samples was exposed without cure and the other was exposed following 7-day cure at 104°F (40°C). For un-cured samples, an exposure to sulfate solutions resulted in significant and sudden expansion, within two days of capillary soak. The mix behavior presented in Fig. 5-1a is representative of field conditions where external sulfate movement occurs immediately after mixing and compaction. Uncured RAS and RSS mixes (dissolved sulfate content of 10,000 ppm) experienced the greatest amount of heaving, approximately three times the swell measured in the control sample exposed to DI water, whereas mix RCS (dissolved sulfate content of 1,400 ppm) experienced double the swell with respect to the control sample which is approximately two-thirds of the swell of the RAS and RSS mixes. The observations in Fig. 5-1a are consistent with reported cases of sudden swelling in stabilized layers immediately after compaction and placement (Petry 1994; Perrin 1992; Kota et al. 1996). During extended DI water soaking after an equilibration period, neither the control mix nor the RCS mix showed significant volume increase. Mixes RAS and RSS showed approximately five percent volume increase during this time period, which may either be due to additional ettringite growth, due to water absorption by ettringite formed during the equilibrium period, or due to salt induced water movement into the mixes (Little et al. 2010; Mehta 1973; Mehta and Wang 1982). But prior research has shown that molar volume changes are minimal when all the components needed for ettringite formation are provided from inside the matrix (Little et al. 2010; Nair and Little 2009). Hence, additional ettringite growth may not be the reason for the volume increase during DI water soaking.

The effect of matrix strength on swelling is suggested in Fig. 5-1b. Accelerated curing for 7-days at 104^{o}F (40^{o}C) significantly reduced the swell in all the mixes, even for mix RAS, during exposure to external sulfate movement as compared to uncured samples (Fig. 5-1a,b). Since the expansive stresses exerted by ettringite are orders of magnitude higher than the tensile strengths of the stabilized soil, the soil matrix should not be able to resist these swell pressures (Hoglund 1992; Subauste and Odler 2002). Therefore, the cause of swell observed during the two days of exposure to the sulfate solution is not likely to be solely due to ettringite formation, but also to swell mechanisms that induce lesser stresses such that the relatively modest tensile strengths derived from pozzolanic reactions would have some effect. Hence the presence of dissolved salts in the water may also have contributed to this higher swell observed in these mixes. Mix RCS (dissolved sulfate content of 1,400 ppm) cured for 7 days at 104^{o} F did not demonstrate additional swelling when subjected to soaking in sulfate laden water when compared to the control samples. If the presence of dissolved salts is causing the swell, then the dissolved sulfate content in this case corresponds to maximum gypsum solubility (2.58 g/l). Therefore, a sudden (within two days) swelling is not likely to occur when a stabilized layer with sufficient strength is subjected to sulfate laden water influx where gypsum is the source of sulfates.

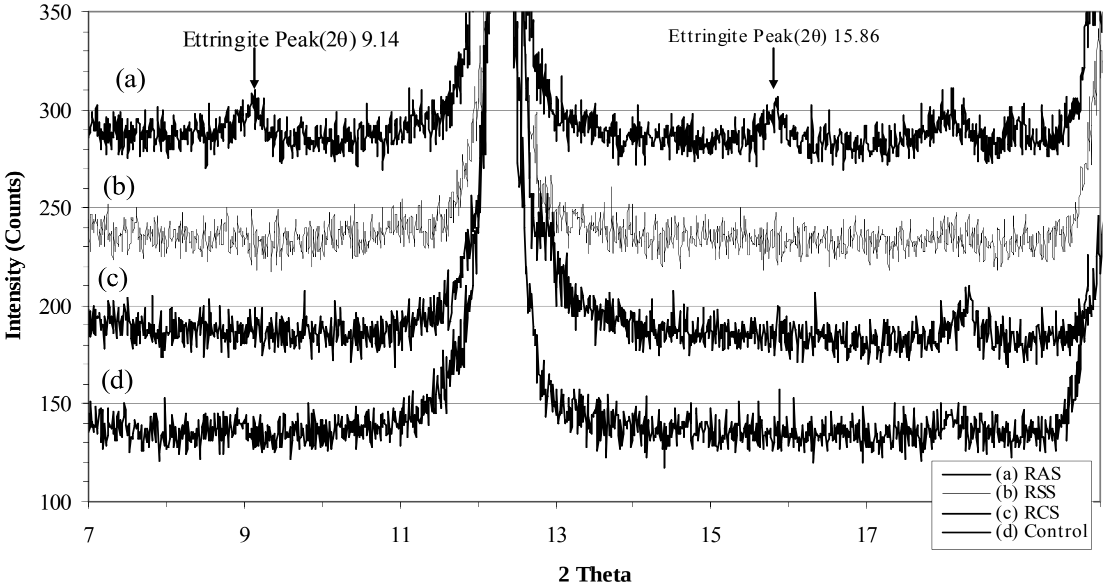


Fig. 5-2. XRD data of lime treated soils after 2 day capillary soak in sulfate solution

X-ray diffraction (XRD) testing was performed in order to evaluate the presence of ettringite in all mixes. Figure 5-2 shows partial XRD patterns from 7° to 20° 2-theta for lime soil mixtures subjected to capillary soak with three different sulfate solutions and with DI water. Two XRD peaks at 2θ 9.14 (d-spacing 9.67 $\overset{0}{A}$) and 2θ-15.86 (d-spacing 5.58 $\overset{0}{A}$) are indicative of the presence of ettringite. The broad peak at or near 2θ 12° (d-spacing 7.16 $\overset{0}{A}$) corresponds to kaolinite which is the major clay source in all samples. X-ray diffraction results indicate the presence of detectable amounts of ettringite only in mix RAS.

Even though no ettringite was detected in mixes RSS and RCS, these samples demonstrated significantly higher swelling when compared to samples soaked with DI water. This supports the earlier observations that additional mechanisms, possibly the presence of dissolved salts in the soaking water, cause greater swell in these mixes. The increases in water content during RA, RS, RC and DI water soaking were 11.8, 11.1, 8.7 and 4.7 percent respectively. Hence it is reasonable to consider that the sorption of water resulting in an increase in water contents, when dissolved salts are present in the soaking water, was a strong contributor to if not the primary reason for expansion when the matrix has low strength.

Since the swell behavior was found to be dependent on the soluble sulfate concentration in the soaking water, suction measurements were conducted to verify the role of salts in inducing water movement in to the matrix. The results of suction measurements on mix RSS and the control mix are given in Fig. 5-3.

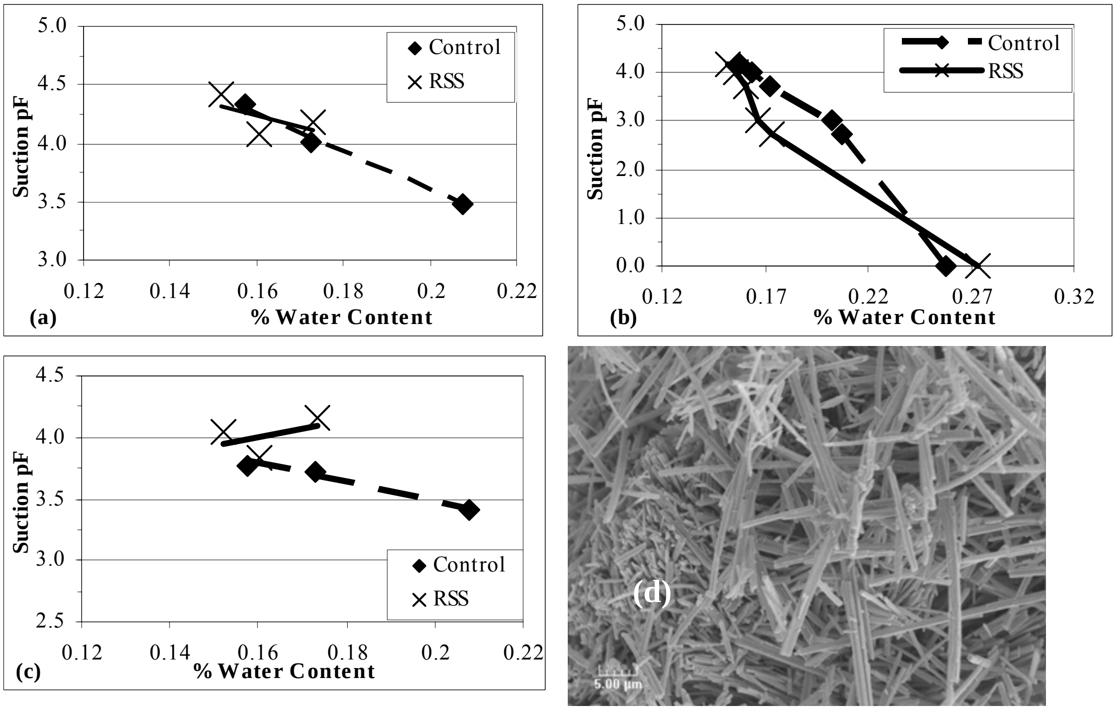


Fig. 5-3. Comparison of soil suction measurements in mix RSS and Control sample (a) Total suction (b) Matric suction (c) Osmotic suction (d) SEM image of ettringite in mix RAS after 2 day exposure to aluminum sulfate solution

The goal of suction testing was to confirm the impact of suction due to salt concentration on swell. Mix RSS was selected for suction testing. Mix RSS demonstrated the greatest volume change during swell testing (Fig. 5-1), and the very early swell in RSS is not likely to be due to ettringite formation as such formation is dependent on the kinetics of dissolution of aluminum from the kaolinite (Mitchell and Dermatas 1992; Dermatas 1995; Little et al. 2010). Mix RAS, on the other hand, provides the stoichiometric quantity of sulfate and readily available aluminum required to form a sufficient quantity of ettringite during the early stages of the swell test. The presence of appreciable quantities of ettringite could confound the suction testing on

RAS. Even though both total and osmotic suctions for mix RSS were found to increase with water content (Fig. 5-3a,c), the effect was more prominent on osmotic suction. This is in agreement with the movement of higher amounts of dissolved sulfate salts in to the stabilized layers. Both total and osmotic suction decreased with increase in water content for the control samples. This is possibly due to dilution of dissolved lime in the matrix. An assay of the components contributing to total suction show two completely different mechanisms behind water absorption in the two mixes (Fig. 5-3b,c). Water absorption in the control mix was dominated by matric suction, which is known to be inversely related to water content in the mix (Krahn and Fredlund 1972; Fredlund and Rahardjo 1993). Water absorption in mix RSS was dominated by the osmotic suction which is a function of salt content in the mix (Krahn and Fredlund 1972; Fredlund and Rahardjo 1993). The suction potential of mix RSS will therefore increase with external sulfate movement resulting in higher water absorption causing increased swell. Hence it is reasonable to say that a higher osmotic suction, created by the soluble salts in the soaking water (probably) caused additional water movement and therefore contributed to early swelling in mixes RAS, RSS and RCS. Furthermore, the swelling observed in mixes RAS and RSS during extended DI water soak after the five day equilibration period may have resulted from additional water movement caused in part by ettringite mineral growth and in part by unreacted salts in the matrix.

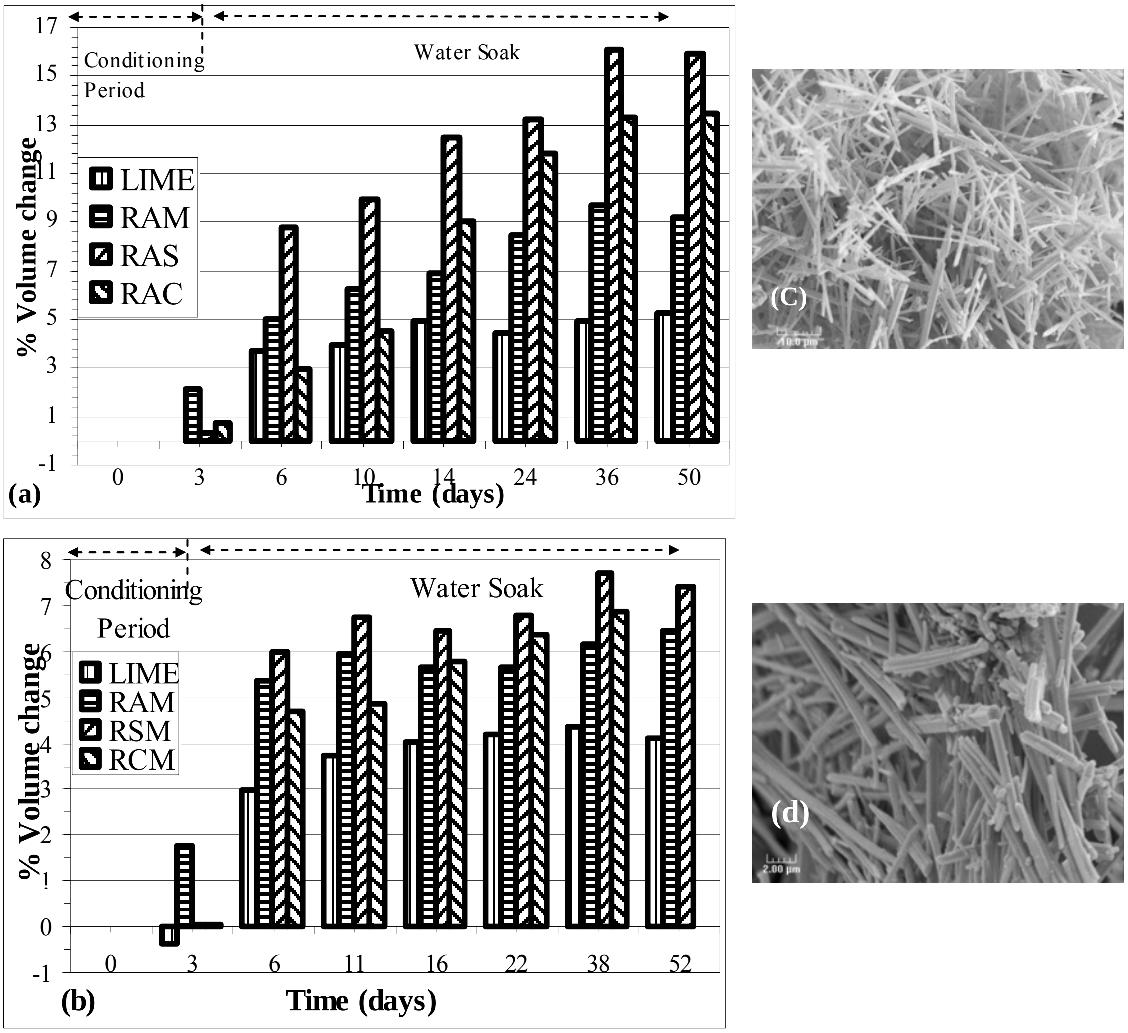


Fig. 5-4. Behavior of soils when a sulfate source is present inside the matrix (a) volume change without cure (b) volume change after accelerated cure (c) SEM image of mix RAM after 10 days (d) SEM image of RCM after 18 days

Fig. 5-4a,b shows volumetric swell in stabilized soils when sulfate sources are present inside the matrix (shrinkage in the mixes during air drying is not shown in the figure). All mixes except the control mix contain 5,000 ppm of soluble sulfates from three different sulfate sources. All samples were subjected to capillary soak with DI water for an extended time period to monitor volume change behavior. Mix RAM demonstrated approximately two percent swell during the three day conditioning period, prior to water soak, possibly due to formation of ettringite. The observation closely matches molar volume calculations which suggest a volume increase of 2.47 percent if all of reagent RA was transformed to mineral ettringite (Little et al. 2010; Nair and Little 2009). Although no external water was introduced into these mixes during conditioning period, due to the high solubility of reagent RA, the mixing water was sufficient to dissolve RA and provide stoichiometric proportions of water needed for ettringite formation. Hence the observed swell can, with reasonable probability, be attributed to precipitation of ettringite. X-ray diffraction verified the presence of ettringite in these mixes. No other samples showed significant volume change during the conditioning period.

During DI water soak, uncured and cured RAM mixes experienced notable swell, 3.98 percent and 2.34 percent respectively, when compared to the control samples subjected to similar conditions. Volume increases for mixes RSM and RCM without cure were 10.7 percent and 8.2 percent, respectively. However, when subjected to accelerated cure, the observed volume increases were 3.3 percent and 2.8 percent, respectively, which was comparable to behavior of mix RAM. The XRD analysis of mixes RSM and RCM showed no evidence of ettringite during the first 21 days of water soaking. But SEM imaging of mix RCM mix after 18 day soak showed evidence of tubular ettringite crystals in one location indicating the formation of smaller quantities of ettringite, possibly below the detection limit of XRD (Fig. 5-4d). In comparison, SEM images of mix RAM after 10 days showed well formed ettringite crystals (Fig. 5-4c). XRD spectra indicating the presence of ettringite during DI water soak is presented in Fig 5-5.

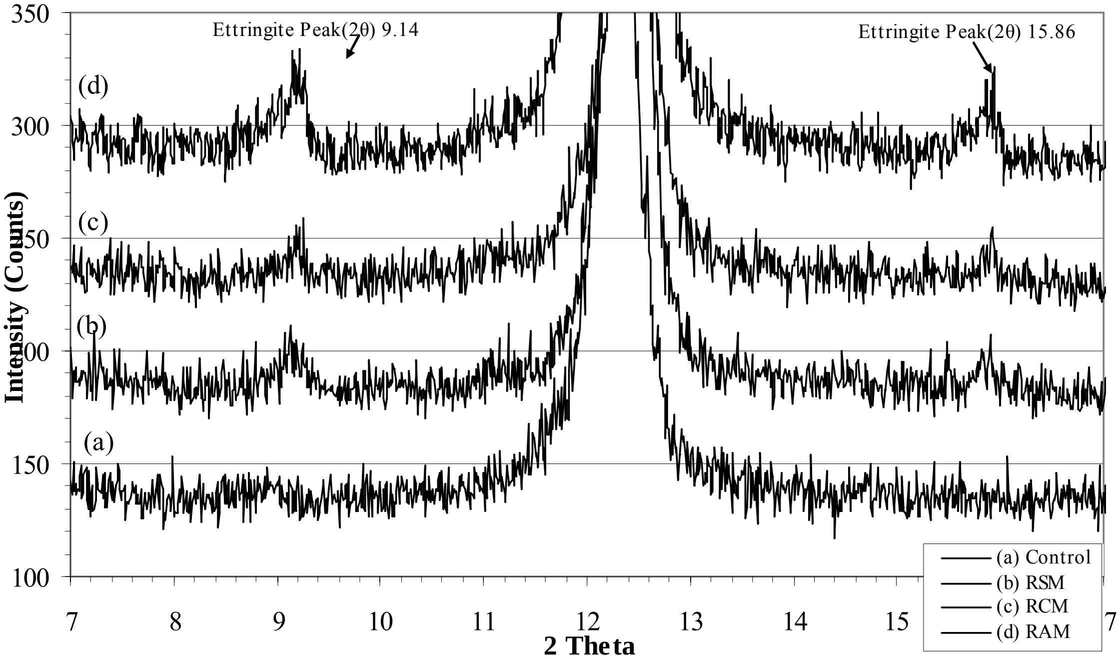


Fig. 5-5. XRD data of sulfate bearing soils after DI water soak (a) Control sample (b) Mix RS (c) Mix RC (d) Mix RA

Observations in Figure 5-5 clearly indicate the presence of mineral ettringite in all samples except for the control sample (Fig. 5-5a). Mix RAM showed well defined ettringite peaks after 10 days of mixing (Fig. 5-5d). Peak intensities were also high for mix RAM compared to mixes RSM and RCM after 28 days, suggesting a relatively higher ettringite concentration in that mix. Since the soluble sulfate content for all mixes was the same, lower ettringite content in mixes RSM and RCM suggests aluminum as the limiting reagent in these mixtures which further validates the role of soil mineralogy and mineral dissolution on the extent of ettringite formation in lime treated soils (Mitchell and Dermatas 1992; Dermatas 1995; Ouhadi and Young 2008; Little et al. 2010).

For a sulfate concentration of 5,000 ppm, the presence of ettringite was detected only in mix RAM during the conditioning period (Fig. 5-4a) and the concentrations were found to increase after the first few days of soaking (Fig. 5-5d). Hence the major part of swell observed in this mix is probably due to the formation and water absorption of ettringite and partly due to unreacted RA present in the mix (Mehta 1973; Mehta and Wang 1982; Nair and little 2009). A comparison of swell behavior during the conditioning period (Fig. 5-4) to the predicted volume change based on molar volume calculation support this observation (Little et al. 2010; Nair and Little 2009). For mixes RSM and RCM, the presence of relatively lower concentrations of ettringite, if any at all, during the time period where the mixes experienced significant heaving, suggests water movement into the matrix as the major source for swelling in these mixes (Fig. 5-4 and 5-5). To verify this, the suction behavior of these mixes was evaluated and presented in Fig. 5-6.

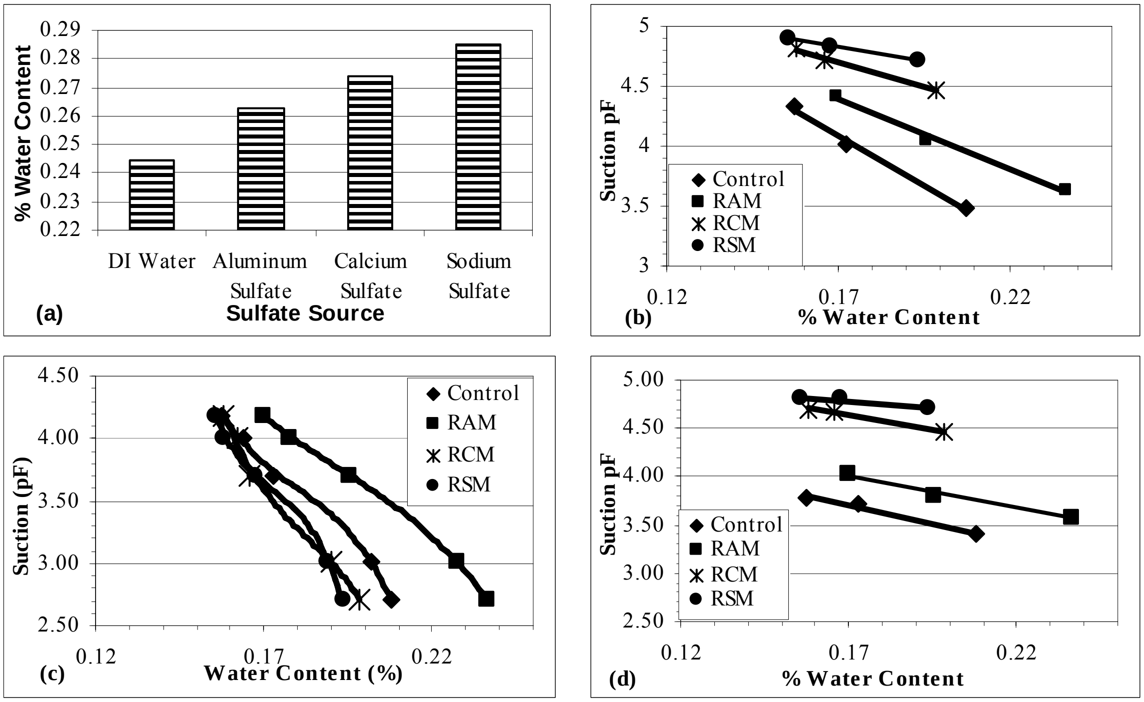


Fig. 5-6. Comparison of soil suction measurements in lime treated sulfate bearing soils subjected to DI water soak: (a) Water content in the mixes (b) Total suction (c) Matrix suction (d) Osmotic suction

Fig. 5-6a clearly demonstrates the occurrence of higher water contents in all sulfate bearing mixes when compared to the control sample. When compared at specific water content, sulfate bearing mixes have a higher suction potential than the control sample (Fig. 5-6b). For mixes RSM and RCM, the higher total suction is contributed by the presence of unreacted salts in the matrix. The osmotic suction component of these mixes, given in Fig. 5-6d, supports this observation. For all mixes, the osmotic suction was found to decrease with increase in water content possibly due to dilution of sulfate concentration by water. However, the decrease in osmotic suction was much smaller when compared to changes in total suction, which is consistent with observations made by Petry and Jiang (2007). The water retention curve, Fig. 5-6c, shows mix RAM to have a higher water retention capacity when compared to all other mixes suggesting a higher composite particle surface area (Petry and Jiang 2007). This is in agreement with evidence that a greater amount of the mineral ettringite was formed in mix RAM as observed in XRD results shown in Fig. 5-5d. The synergy of higher surface area and negative surface charge associated with the mineral ettringite can induce water sorption and also enhance water retention capabilities of the mix (Mehta 1973; Mehta and Wang 1982; Nair and little 2009). Even though similar amounts of sulfate salts were added to all of these mixes, a lower osmotic suction component in mix RAM suggests that most of the soluble salts were transformed into insoluble precipitates. A similar comparison for mixes RSM and RCM reveals a higher osmotic suction in mixes RSM and RCM in comparison to mix RAM, which suggests a relatively lower concentration of ettringite, if any, in these mixes. XRD also verified this observation. Furthermore, observations in Fig. 5-4a show a significantly lower level of swelling in mix RAM where some of the soluble sulfates were converted to ettringite prior to soaking in water. Hence it is reasonable to say that ettringite formation is not the sole (or maybe even primary) causal factor for swelling in mixes RSM and RCM, but instead an increase in water influx caused by a higher salt content caused the mix to swell. Since ettringite grows in these mixtures by consuming components from inside the matrix, the precipitation does not cause appreciable volume change and the ettringite mineral forming after primary swell will be accommodated with in the matrix (Nair and little 2009).

5.6. Conclusions

The following conclusions can be drawn from the study:

1. Volumetric expansion during lime treatment of sulfate bearing soils can occur due to one or a combination of three separate mechanisms - (1) from ettringite precipitation; (2) due to water absorption by the high surface area and high surface potential of ettringite mineral; (3) due to influx of water triggered by a higher osmotic suction created by un reacted salts.
2. The extent of swelling initiated by a higher osmotic suction, due to the presence of sulfate salts within the matrix or due to external sulfate movement, will depend on the timing of the introduction of water, i.e. whether water becomes available immediately after compaction and placement or after the matrix has acquired significant strength due to pozzolanic reactions.
3. In the presence of sulfate salts and available water, stabilized layers may experience heaving with or without significant ettringite formation. Ettringite growth in these layers may be an aftermath of heaving due to geochemically favorable conditions in the distress sections.
4. External sulfate movement, as dissolved ions in water, can trigger immediate swelling in stabilized layers depending on matrix strength and sulfate concentrations in the water. The distress may be amplified if sulfate movement occurs prior to the matrix acquiring significant strength.
5. If the source of sulfates in sulfate laden water is gypsum, then the concentration of dissolved sulfate in water will be low due to limited solubility of gypsum (2.58 g/l)

in water. Observed distress, in this case, will probably not be immediate if sulfate movement occurs during the later stages of stabilization (Fig. 5-1b).

6. CONCLUSIONS, RECOMMENDATIONS AND FUTURE WORK

6.1. Detailed Conclusions and Recommendations

Based on this dissertation the following conclusions are offered:

1. Ettringite precipitation rate and crystal growth in stabilized soils is governed by the synergy of a number of factors.
    a. Sensitivity of soils to ettringite formation was found to be dependent on soil mineralogy.
    b. Soil reactivity closely parallels the available clay content in soils.
    c. No definitive relationship was observed between clay content and weight percent of ettringite formed in soils.
2. The observations validate the empirical evidence from the field that a threshold soluble sulfate level of about 2,000 to 3,000 ppm might differentiate soils with little or no risk from those of notable risk.
3. The time required to form ettringite in treated soils depends upon:
    a. The initial degree of nucleation of ettringite crystals. This further depends on the amount of water used and the ability to uniformly distribute or mix the water with the treated soil.
    b. The relative activities of ions in the aqueous solution and the migration of ions within the aqueous phase. The activities of the key ions are affected, in part, by maintaining a uniformly high pH regime for as long as possible. However, mineralogy strongly impacts activities, and mineralogy may vary widely from

   one soil to another. Besides a uniform pH regime, uniformity in mixing and water content is the best way to support uniform and rapid crystal growth.

   c. The ability to solubilize sufficient reactants into an aqueous phase. Aluminum availability is primarily influenced by the mineralogy of the soil.

4. It is possible to develop conditions in the treated soil that favor more rapid ettringite formation. The kinetics of precipitation can be impacted by:

   a. Using as much water as possible in construction in order to solubilize, initially, as much sulfates as possible. This increases nucleation sites and the probability of a uniform distribution of nucleation sites.

   b. Providing extended mellowing time for low sulfate soils to allow as many ettringite nucleation sites as possible to form before compaction.

   c. Mixing of stabilizers, water and soil as intimately and uniformly as possible to reduce the risk of “hot spots” and non-uniform ion migration and to improve the probability of uniform distribution of nucleation sites.

5. When ettringite is present in soil, influx of water can cause volume change which is caused in part due to crystal growth, i.e., water bonding within the ettringite unit crystal matrix, and in part due to water absorption by ettringite molecules.

6. Timing of the introduction of water determines the extent of expansion in the matrix.

   a. Molar volume calculations prove that water that migrates into the system after mixing and compaction, which cannot be accounted as a part of the initial mixture mass, is responsible for the huge volume changes in the stabilized layer.

Based on calculations presented in Section 2, infusion of this migrating water can result in expansion of up to 137 percent in the stabilized sections.

   b. Ettringite formation using water available in the mixture may not contribute to expansion, but instead, these conditions may actually results in shrinkage of the matrix.
   c. The presence of ettringite in the matrix can cause delayed expansion when water becomes available due to sorption of water within the ettringite matrix with out additional ettringite crystal growth.

7. Volumetric expansion in sulfate bearing soils can occur due to one or a combination of three separate mechanisms - (1) from ettringite precipitation; (2) due to water absorption by the high surface area and high surface potential of ettringite mineral; (3) due to influx of water triggered by a higher osmotic suction created by un reacted salts.
   a. In the presence of sulfate salts and available water, stabilized layers may experience heaving with or without significant ettringite formation. Ettringite growth in these layers may be an aftermath of heaving due to geochemically favorable conditions in the distress sections.
   b. Swelling initiated by a higher osmotic suction, either due to the presence of sulfate salts within the matrix or due to external sulfate movement, will depend on whether water becomes available immediately after compaction and placement or after the matrix has acquired significant strength due to pozzolanic reactions. However, the expansion associated with the influx of sulfate laden

   water may induce a higher level of distress when compared to sulfates already present in the system.

   c. External sulfate movement, as dissolved ions in water, can trigger immediate swelling in stabilized layers depending on matrix strength and sulfate concentrations in the water. The distress may be amplified if sulfate movement occurs prior to the matrix acquiring significant strength. Expansion in this case is partially due to ettringite precipitation using an external source of water, due to the additional crystal growth due to availability of more of the limiting reagent, and due to water movement initiated by the osmotic suction in the matrix.
   d. For soils with gypsum as the major source of sulfates, distress manifestation due to movement of sulfate laden water will probably not be immediate if sulfate movement occurs during the later stages of stabilization.

8. Due to the dominant role of water in causing expansion in sulfate bearing soils, employing good drainage engineering practices from design through construction may reduce the extent of swelling in stabilized layers and may be the most critical factor in many situations regarding damage due to ettringite growth.
9. Whether or not the formation of ettringite causes disruption of the stabilized layer depends, in part, on whether the mineral grows in the voids of the compacted soil or within the dense matrix.
10. Besides the growth of the ettringite crystals themselves, the micro cracks and voids that develop to accommodate crystal growth become part of the expansion mechanism. This contribution requires more sophisticated study and analysis.

6.2. Future Work

The current research makes the case that ettringite formation in soil and the associated swelling to be influenced by the synergy of a number of factors. However, as with any successful research many questions remain unanswered and many arise due to better insight. Also, ideas for future research in this area spring forth. Some of these new ideas areas that can be developed in conjunction with techniques and approaches presented in this dissertation are discussed in the following paragraphs.

6.2.1 Controlling Sulfate Induced Swell in Lime Treated Soils

Researchers have attempted different techniques, including use of additives like fly ash, granulated blast furnace slag and soluble silica to alter the thermodynamic favorability of ettringite precipitation, mellowing the soil with excess water prior to compaction to create more nucleation sites and avoid localized mineral growth, use of non calcium based additives to stabilize soils rich in sulfate content etc. to control ettringite induced swelling in lime stabilized soils. Even though these techniques were found to be effective to a certain extent, the success rate has not been definitive.

This research has shown ettringite formation in lime treated soils to be time dependent and the heaving in stabilized layers to be due to water absorption triggered by sulfate salts and/or the presence of ettringite mineral as well as the growth of ettringite itself. Further more, the swelling due to water absorption, initiated by the osmotic suction potential of sulfate salts, was found to be inversely correlated to the strength of the matrix. Hence, swelling observed in field after months of curing is in part due to precipitation and/or due to swelling of ettringite which may be restricted by creating voids to accommodate the volume changes. A simple, but practical, way of achieving this objective is by creating fractures or micro cracks in the stabilized layer after few days of curing but prior to the achieving significant strength. Even though these voids/cracks may heal due to pozzolanic reactions, the failure planes or pre-existing flaws may remain in soil and can accommodate the stresses generated during ettringite precipitation.

6.2.1.1 Materials and Method

Among the sulfate exposure conditions used in Section 5, the second condition where sulfate sources are directly present in the stabilized soil matrix was investigated during this study. Preparation of cylindrical test samples, curing conditions and swell measurements were done in accordance with details provided in Section 5. The three different sources (5,000 ppm sulfates) listed in section 5 and a control sample (lime treated soil with out sulfates) was used in the study. DI water (without sulfates) was used for capillary soak for the entire duration of swell testing. Changes in test procedure, from Section 5, are listed below.

1. Cylindrical test samples were prepared, in duplicate, at a smaller height to diameter ratio (sample size 1.81-inch x 4.5-inch) to limit excessive deformation during load application.
2. Immediately after the conditioning period, detailed in section 5, the laboratory samples were subjected to unconfined compression testing protocol in accordance with ASTM D 5102 procedure B.

3. Loading was stopped, prior to failure, when visible cracks started to appear on the sample.
4. Samples, with and without cracks, were then subjected to accelerated cure for 7 days at 104 ^{o}F (40 ^{o}C).
5. Volume changes were measured with respect to sample volume after cracking and curing period.

6.2.1.2. Results and Discussion

Fig. 6-1 shows the comparison of measurable swell in 7 day accelerated cured samples, with and without pre-cracking (Fig. 6-1b and 6-1a respectively), when subjected to capillary soak using DI water. All pre-cracked/cured sulfate bearing mixtures showed a lower swelling potential during soaking period. Observations in RAM mixtures, detailed in Section 5, suggest significant ettringite formation within 10 days of mixing and molding. Hence the observed volume change during soaking period in these samples may be attributed in part to water absorption by ettringite mineral and due to additional mineral growth, if any. The observed decrease in swell, approximately 1.2 percent, in pre-cracked RAM mixtures suggests that the swelling induced by ettringite was better accommodated inside the matrix. The effect was more prominent for sodium and calcium sulfate bearing soils (RSM and RCM mixes).

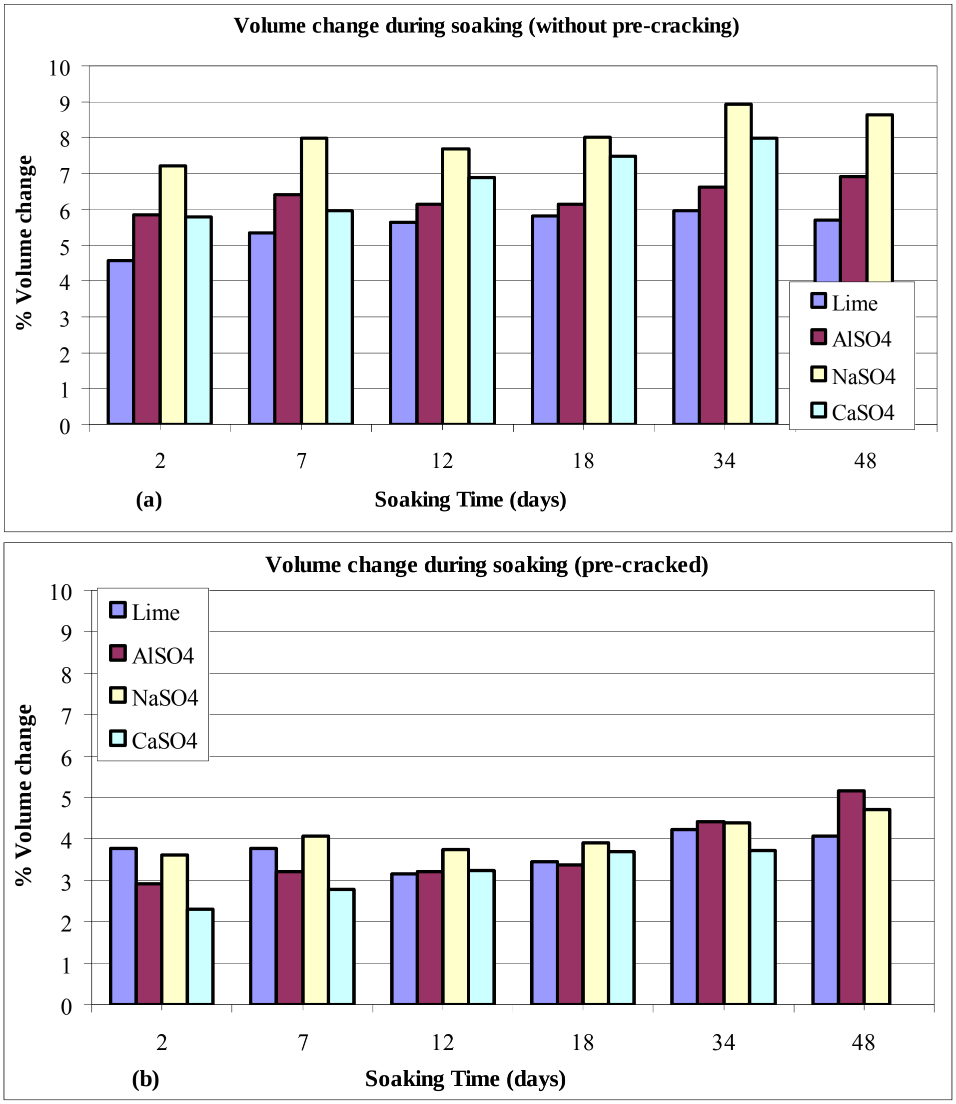


Fig. 6-1. Measured volume changes during capillary soak in lime soil mixtures with 5,000 ppm soluble sulfates (a) 7 day accelerated cure (b) Micro cracked and 7 day accelerated cure

Fig. 6-1b shows the pre-cracked samples to experience significantly lower swelling, when compared to un-cracked samples, upon exposure to water. But, the XRD observations detailed in section 5, suggest that these mixtures form detectable amounts of ettringite only around 28 days of soaking. Hence the possibility of accommodating ettringite crystals may only be considered as a part of the reason for reduced swelling during these early soaking periods. It is possible that any disturbance in the capillary structure of the stabilized layers and/or an increase in capillary pore diameter during pre-cracking may have affected the water flow in to the mixture. Either being the reason for the decreased swell during early hydration periods, research presented earlier in this dissertation support the idea that ettringite growth using internal water may not cause significant expansion in the matrix. Therefore, by limiting the excessive swelling during initial soaking period may significantly reduce the overall expansion in the matrix. Observations in Fig. 6-1 support this hypothesis.

Based on observations in the current research, pre-cracking the samples prior to achievement of significant strength appears to be effective controlling post stabilization sulfate induced swelling in lime treated soils. Micro cracks can easily be created in stabilized layers using vibratory rollers used in soil compaction. Cracks can be created in the stabilized layers after a day or two of placement. Exact time and technique to be used has to be identified in future research. Influence of pre-cracking on engineering properties of stabilized soils also needs to be investigated prior to recommending this approach.

6.2.2 Future Work on Use of Differential Scanning Calorimeter

Further studies on use of differential scanning calorimeter include creating a comprehensive data base for different soil series to identify groups with higher sensitivity to form ettringite. This information can be used to help identify problematic soils along the project alignment. Combining this data base with information’s in soil survey reports can help practitioners delineate areas that require further investigations prior to using calcium based stabilizers.

REFERENCES

Bensted, J. (2000). “Mechanism of thaumasite sulfate attack in cements, mortars and concretes.” *ZKG International*, 53, 704-709.

Bensted, J. (2003). “Thaumasite-direct, woodfordite and other possible formation routes.” *Cement and Concrete Research*, 25, 873-877.

Berger, E., Little, D.N., and Graves, R. (2001). “Technical memorandum: guidelines for stabilization of soils containing sulfates.” Technical Report, *National Lime Association*, Arlington, VA.

Berry, L. G., Mason, B. and Dietrich R. V. (1983). *Mineralogy*, 2nd Ed., Freeman and Company, San Francisco, CA.

Bulut, R., Lytton, R. L., and Wray, W. K. (2001). “Soil suction measurements by filter paper.” Expansive Clay Soils and Vegetative Influence on Shallow Foundations, *Geotechnical Special Publication*, 115, 243-261.

Burkart, B., Goss, G. C., and Kern, J. P. (1999). “The role of gypsum in production of sulfate-induced deformation of lime-stabilized soils.” *Environmental & Engineering Geoscience*, 5(2), 173-187.

Callister, W. D. (2001). *Fundamentals of material science and engineering*. John Wiley & Sons, New York.

Crammond, N. J. (1985). “Thaumasite in failed cement motors and renders from exposed brickwork.” *Cement and Concrete Research*, 15(6), 1039-1050.

Crammond, N. J. (2003). “Thaumasite form of sulfate attack in the UK.” *Cement and Concrete Composites*, 25, 809-818.

Cripps, J. C., Czerewko, M. A., Reid, J. M., and Duffell, C. G. (2003). “Sulfur species in geological materials-sources and quantification.” *Cement & Concrete Composites*, 25, 657-671.

Damidot, D., and Glasser, F. P. (1993). “Thermodynamic investigation of the CaO-Al2O3-CaSO4-H2O system at 250C and the influence of Na2O.” *Cement and Concrete Research*, 23, 221-238.

Deng, M., and Tang, M., (1994). “Formation and expansion of ettringite crystals.” *Cement and Concrete Research*, 24(1), 119-126.

Dermatas, D. (1995). “Ettringite-Induced Swelling in Soils: State-of-the-art.” *Appl. Mech. Rev.*, 48, No. 10, 659-673.

Dermatas, D., Chrysochoou, M., Moon, D. H., Pardali, S., Lazarte, C. A., Briggs, R., French, C., and Kaouris, M. (2005). “Mineralogical characterization of chromite ore processing residue at dundalk marine terminal area 1800.” *Proc., Eighth Int. In Situ and On-Site Bioremediation Symposium*, Baltimore, MD.

Dermatas, D., Chrysochoou, M., Moon, D. H., Grubb, D. G., Wazne, M., and Christodoulatos, C. (2006). “Ettringite – induced heave in chromite ore processing residue (COPR) upon ferrous sulfate treatment.” *Environ. Sci. Technol.*, 40, 5786-5792.

Dermatas D., Bonaparte R., Chrysochoou, M. and Moon, D. H. (2006a). "Chromite ore processing residue (COPR): Hazardous contaminated soil or solid waste?" *Journal of ASTM International,* vol. 3 (7), 145-154.

Fredlund, D. G. and Rahardjo, H. (1993). *Soil mechanics for unsaturated soils*, New York: John Wiley & Sons, Inc.

Hansen, W. C., Offutt, J. S., Roy, D. M., Grutzeck, M. W. and Schatzlein, K. J. (1988). *Gypsum and anhydrite in portland cement. US gypsum*, 3rd Ed., Chicago.

Harris, P., Scullion, T., and Sebesta, S. (2004). "Hydrated lime stabilization of sulfate bearing vertisols in Texas." *Transportation Research Record*, 1868, 31-39.

Harris, P., Scullion, T., Sebesta, S., and Carlos, G. (2003). "Measuring sulfate in subgrade soil-difficulties and triumphs." *Transportation Research Record*, 1837, National Research Council, Washington, DC, 3-11.

Herbert, B and Little, D. (2006). "Identification of potential risks due to sulfate-induced damage in lime-stabilized soils along the sh-130 corridor." *Report Prepared for Chemical Lime Company*, Dallas, TX.

Hoglund, L. O. (1992). "Some notes on ettringite formation in cementitious materials; influence of hydration and thermodynamic constraints for durability." *Cement and Concrete Research*, 22(2-3), 217-228.

Hunter, D. (1988). "Lime induced heave in sulfate-bearing clay soils." *Journal of Geotechnical Engineering*, 114(2), 150-167.

Jallad, K.N., Santhanam, M., and Cohen, M.D. (2003). "Stability and reactivity of thaumasite at different pH levels." *Cement and Concrete Research*, 33(3), 433-437.

Kohler, S., Heinz, D., and Urbonas, L., (2006). “Effect of ettringite on thaumasite formation.” *Cement and Concrete Research*, 36(4), 697-706.

Kota, P. B. V. S., Hazlett, D., and Perrin, L. (1996). “Sulfate-bearing soils: Problems with calcium based stabilizers.” *Transportation Research Record*, 1546, 62-69.

Krahn, J., and Fredlund, D. G. (1972). “On total matric and osmotic suction.” *Soil Science*, 114(5), 339-345.

Langmuir, D. (1997). *Aqueous environmental geochemistry*. Prentice Hall, Upper Saddle River, NJ.

Lerch, W., Ashton, F. W., and R. H. Bogue (1929). “Sulfoaluminates of calcium.” *Journal of Research*, National Bureau of Standards, 2, 715-731.

Lea, F. M., and Desch, C. H. (1940). The chemistry of cement and concrete. E. Arnold & Company, London.

Lee, H., Cody, R. D., Cody, A. M, and Spry, P. G. (2005). “The formation and role of ettringite in Iowa highway concrete deterioration.” *Cement and Concrete Research*, 35, 332-343.

Little, D. N. (1995). *Stabilization of pavement subgrades & base courses with lime,* Kendall/Hunt Publishing Company, Dubuque, IA.

Little, D. N. (2005). “Evaluation of mechanisms of pavement distress on U.S. Highway 287 by-pass, Berthoud, Colorado.” *Report prepared for Colorado Department of Transportation*, Denver, CO.

Little, D. N., and Graves, R. (1995). “Guidelines for using lime in sulfate bearing soils.” *Chemical Lime Company.*

Little, D. N., Herbert, B., and Kunagalli, S. N. (2005). "Ettringite formation in lime-treated soils: Establishing thermodynamic foundations for engineering practice." *Transportation Research Record*, 1936, 51-59.

Little, D., Nair, S., and Herbert, B. (2010). "Addressing sulfate induced heave in lime treated soils", *Journal of Geotechnical and Geoenvironmental Engineering*, ASCE, 136 (1), 110-118.

Little, D. N., and Nair, S. (2007). "Sensitivity of selected Colorado soils to form ettringite/thaumasite when treated with calcium-based stabilizers and when soluble sulfates are available." *Colorado Department of Transportation-Research*, Report No. CDOT-2007-14, Denver, CO.

Mehta, P. K. (1973a). "Mechanism of expansion associated with ettringite formation." *Cement and Concrete Research*, 3(1), 1-6.

Mehta, P. K. (1973b). "Effect of lime on hydration of pastes containing gypsum and calcium aluminates or calcium sulfoaluminate." *Journal of the American Ceramic Society*, 56(6), 315-319.

Mehta, P. K., and Hu, F. (1978). "Further evidence for expansion of ettringite by water adsorption." *Journal of the American Ceramic Society*, 61(3-4), 179-181.

Mehta, P. K., and Wang, S. (1982). "Expansion of ettringite by water absorption." Cement *and Concrete Research*, 12, 121-132.

Mindess, S., Young, H. F., and Darwin, D. (2002). *Concrete*. 2nd Ed., *Prentice Hall Inc.*, Englewood Cliffs, NJ.

Mitchell, J. K. (1986). "Practical problems from surprising soil behavior." *Journal of* Geotechnical *Engineering*, 112(3), 259-289.

Mitchell, J. K., and Dermatas, D. (1992). "Clay soil heave caused by lime-sulfate reactions. Innovations and uses of lime.", *ASTM STP,* 1135, 41-64.

Mohamed, A. M. O., Boily, J. F., Hossein, M., and Hassani, F. P. (1995). "Ettringite formation in lime remediated mine tailings: I. thermodynamic modeling." *CIM Bulletin*, 88(995), 69-75.

Moon, H. M., Dermatas, D., Wazne, M., Sanchez, A. M., Chrysochoou, M., and Grubb, D. G. (2007). "Swelling related to ettringite crystal formation in chromite ore processing residue." *Environmental Geochem Health,* 29, 289-294.

Moore, A. E., and Taylor, H. F. W. (1970). "Crystal structure of ettringite." *Acta Cryst.* B26, 387-393.

Myneni, S. C. B., Traina, S. J., and Logan, T. J. (1997). "Retention of arsenate and chromate by ettringite in alkaline waste environment." Am *Ch. Soc. Div. Environmental Chem. Geol*, 34, 525-527.

Myneni, S. C. B., Traina, S. J., and Logan, T. J. (1998). "Ettringite solubility and geochemistry of the $Ca(OH)_2 - Al_2(SO_4)_3 - H_2O$ system at 1 atm pressure and 298 K." *Chemical Geology*, 148, 1-19.

Nair, S., and Little, D. (2009). "Water: The key to expansion of ettringite in cementitious materials." *Transportation Research Record,* National Research Council, 2104, 55-62.

Odler, I., and Abdul-Maula, S. (1984). “Possibilities of quantitative determination of the AFt-(ettringite) and AFm-(monosulphate) phases in hydrated cement pastes.” *Cement and Concrete Research,* 14(1), 133-141.

Odler, I., and Glasser, M. (1988). “Mechanism of sulfate expansion in hydrated Portland cement.” *Journal of American Ceramic Society*, 71(11), 1015-1020.

Ogawa, K., and Roy, D. M. (1981). “C_4A_3S hydration ettringite formation and its expansion mechanism: I. expansion; Ettringite stability.” *Cement and Concrete Research*, 11 (5-6), 741-750.

Ogawa, K., and Roy, D. M. (1982). “C_4A_3S hydration ettringite formation and its expansion mechanism: II. Microstructural observation of expansion.” *Cement and Concrete Research*, 12, 101-109.

Odler, I., and Subauste, J. (1999). “Investigations on cement expansion associated with ettringite formation.” *Cement and Concrete Research*, 29(5), 731-735.

Ouhadi, V.R., and Yong, R.N. (2008). “Ettringite formation and behavior in clayey soils.” *Applied Clay Science,* 42, 258-265.

Perkins, R.B., and Palmer, C. D. (1999). “Solubility of ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$) at 5-75 degrees C.” *Geochim. Cosmochim. Acta*, 63(13-14), 1969-1980.

Perrin, L. (1992). “Expansion of lime treated clays containing sulfates.” *Proc., 7th International Conference on Expansive Soils*, Dallas, Tx, Vol. 1, 409-414.

Petry, T. M. (1994). “Studies of factors causing and influencing localized heave of lime treated clay soils (Sulfate induced heave).” *Technical Report for U.S. Army Corps of Engineers*, Waterways Experiment Station, Vicksburg, MS.

Petry, T. M. and Jiang, C. P. (2007). “Soil suction and behavior of chemically treated clays.” *Transportation Research Record*, 2026, 30-38.

Petry, T.M., and Little, D.N. (1992). “Update on sulfate-induced heave in treated clays: problematic sulfate levels.” *Journal of Transportation Research Record*, 1362, 51-55.

Puppala, A. J., Chirayus, V., Kruzik, A. P., and Perrin, L. (2002).”Evaluation of modified soluble sulfate determination method for fine grained cohesive soils.” *Geotechnical Testing Journal*, GTJODJ, 25(1), 85-94.

Puppala, A. J., Intharasombat, N., and Vempati, R. K. (2005). “Experimental studies on ettringite-induced heaving in soils.” *Journal of Geotechnical and Geoenvironmental Engineering*, 131(3), 325-337.

Rollings, R. S., Burkes, J. P., and Rollings, M. P. (1999). “Sulfate attack on cement-stabilized sand.” *Journal of Geotechnical and Geoenvironmental Engineering,* ASCE, 125 (5), 364-372.

Sherwood, P. T. (1962). “Effects of sulfates on cement and lime stabilized soils.” *Highway Research Board Bulletin, TRB*, 353, National Research Council, Washington, DC, 20001, 98-107.

Shimada, Y., and Young, J, F. (2001). “Structural changes during thermal dehydration of ettringite.” *Advances in Cement Research*, 13(2), 77-81.

Skalny, J., Marchand, J., and Odler, I. (2002). “Sulfate attack on concrete.” <http://www.netlibrary.com/Details.aspx> (Jan. 20, 2008).

Skoblinskaya, N. N., and Krasilnikov, K. G. (1975). “Changes in crystal structure of ettringite on dehydration 1.” *Cement and Concrete Research*, 5(4), 381-394.

Subauste, J. C and Odler, I. (2002). “Stresses generated in expansive reactions of cementitious systems.” *Cement and Concrete Research*, 32(1), 117-122.

Taylor, H. F. W., Famy, C., and Scrivener, K. L. (2001). “Delayed ettringite formation.” *Cement and Concrete Research*, 31, 683-693.

Tex-Dot manual. (2005). “Tex-145-E Determining sulfate content in soils-colorimetric method.” <http://manuals.dot.state.tx.us/dynaweb> (Sep. 11, 2006).

Warren, C. J., and Reardon, E. J. (1994). “The solubility of ettringite at 25^0C.” *Cement and Concrete Research*, 24(8), 1515-1524.

Wild, S., Tasong, W. A., and Tilley, R. J. D. (1999). “Mechanism by which ground granulated blast furnace slag prevents sulfate attack of lime-stabilized kaolinite.” *Cement Concrete Research*, 29, 975-982.

Zhou,Q., and Glasser, F. P. (2001). “Thermal stability and decomposition mechanism of ettringite at $<120^0$C.” *Cement and Concrete Research*, 31(1333-1339).

APPENDIX A

SYNTHESIS OF PURE ETTRINGITE

The section below details the procedure for synthesis of pure ettringite in the laboratory (Herbert and Little 2006). The process is a modified version of technique used by Perkins and Parmer. The modifications were made the Biogeochemistry research group in Geology and Geophysics Department, Texas A&M University, under the super vision of Professor Bruce Herbert. All chemicals used in the procedure are reagent grade materials.

Reagents and Materials Required:

1. Pipette and pipette tips (5 ml and 10 ml)
2. 50 ml centrifuge tube
3. Filter membranes (Millipore – Isopore membrane filters 1.2μm)
4. Filtration device (vacuum pump, filtering flask, buchner funnel, rubber stopper and tubing)
5. Volumetric flasks (250 ml), Erlenmeyer flask (500 ml and 1000 ml)
6. 500 ml High density polypropylene (HDPP) bottle
7. Nano pure water, plastic containers, beakers, tweezers etc.

Preparing Reagent Solutions:

1. Nano-pure water should be used to dissolve reagents in solution. Water should be purged with ultra high purity (UHP) nitrogen gas for at least 30 minutes and stored in air tight HDPP bottles prior to making reagent solutions. Air space

inside the HDPP bottles should be filled with nitrogen gas before sealing the containers to limit any carbon dioxide contamination.

2. Transfer 500 ml nanopure water in to an HDPP bottle. Dissolve 4.0 g of calcium hydroxide [$Ca(OH)_2$] in 500 ml nitrogen purged nano-pure water to get a saturated calcium hydroxide solution. The solution should be stirred using a magnetic bar for 2 hours to facilitate the dissolution of calcium hydroxide.
3. Centrifuge the solution at 1200 RPM for 5 minutes to separate un-dissolved calcium hydroxide.
4. Dissolve 0.604 g of $Al_2(SO_4)_3 18H_2O$ (Aluminum octa-deca-hydrate) in 250 ml nitrogen purged nano-pure water to get the aluminum sulfate solution.
5. Prepare three liters of one normal NaOH solution.

Mixing of Reagent Solutions:

1. Mixing of solutions and filtration of precipitates should be done inside an air tight glove box.
2. Place all materials including reagents, pipettes, pipette tips, 50 ml centrifuge tubes inside the glove box.
3. Purge the glove box with carbon dioxide free air for 3 hours prior to mixing of solutions. Carbon dioxide is removed by progressively bubbling air through three Erlenmeyer flasks with 1 N NaOH solution. Maintain the purge flow till the mixing process is complete.
4. Pipette out 25 ml of aluminum sulfate solution and place it inside a 50 ml centrifuge tube.

5. Pipette out 20 ml of saturated calcium hydroxide solution and mix with aluminum sulfate solution in the centrifuge tube.
6. Cap the centrifuge tube and mix the contents thoroughly.
7. Sealed centrifuge tubes with the final solutions are left idle for 24 hours.

Filtering the Solutions:

1. Place all materials needed for filtration including filter membranes, filtration device, plastic containers for keeping the filter membranes after filtration, tweezers and 50 ml centrifuge tubes with final solution inside the glove box.
2. Setup the filtration device.
3. Follow step 2 in mixing of solutions to make the glove box carbon dioxide free during filtration of precipitates.
4. Place the filter membrane on top of buchner funnel (shining side up).
5. Mix the solution inside the centrifuge tubes thoroughly and remove the capping.
6. Switch on the vacuum pump and transfer the contents of the centrifuge tube on to the filter membrane. Adjust the speed of transfer to ensure that all of the solution passes through the filter membrane and no precipitate is lost during filtration.
7. Use two filter membrane/centrifuge tube (minimum) to collect the precipitates.
8. Transfer the membranes to plastic containers for storage.
9. Collect the supernatant solution and measure the pH values of solution to ensure that pH is above 10.7.

10. Dry and store the precipitates at room temperature inside a desiccator. A relative humidity of approximately 30 percent and low carbon dioxide level is maintained inside the desiccator using a cup of saturated $CaCl_2$ solution.
11. Perform XRD and SEM analyses to evaluate purity of filtered precipitates.

APPENDIX B

QUANTIFYING ETTRINGITE IN LIME TREATED SOILS USING A DIFFERENTIAL SCANNING CALORIMETER

The section contains detailed procedure to be followed in quantifying ettringite in lime treated soils using a differential scanning calorimeter. A differential scanning calorimeter (Q-2000) manufactured by TA Instruments was used in the study. A QA thermal analysis software also developed by TA Instruments was used in the analyzing the collected data. Sample preparation techniques, curing and testing conditions and analysis techniques are detailed in this section. All lime treated samples should be prepared inside 50 ml centrifuge tubes. A vortex mixture should be used to mix lime-soil-sulfate mixtures to ensure uniformity in mixing process. Water in excess of optimum moisture content may be used while curing the samples to ensure that water availability is not limiting ettringite growth in the samples.

Sample Preparation

Steps involved in preparing natural soil for testing are listed below.

1. Air dry soil samples for 24 hours to a uniform moisture content.
2. Select representative soil samples from field collected natural soil to perform sulfate testing. The testing should be done in accordance with TEX-145E.
3. Pulverize air-dried natural soil to pass 75μ (No. 200) sieve.

4. Select representative soil samples from field collected natural soil by using sampler or by splitting and quartering procedure.

Preparing Control Samples

Control samples, lime treated natural soil without soluble sulfates, are used to identify the response of the soil when known quantities of ettringite are present. Standard curves are generated by adding known amount of synthesized ettringite to these control samples prior to testing in the differential scanning calorimeter. Synthesized ettringite, to be used in this testing, should be prepared in accordance with the procedure listed in Appendix A. Steps involved in preparing control samples are listed below.

1. Prepare triplicate samples for sulfate extraction/sulfate content measurements in accordance with Tex 145-E. The test involves dissolving water soluble sulfates in soil using 1:20 soil to water dilution ratio. Deionized water is typically used in extracting water soluble sulfates.
2. Air dry the residue soil from sulfate testing for 24 hours to uniform water content. All available sulfates in the dried residue soil are removed during sulfate testing and therefore no ettringite forms in control sample during lime treatment.
3. Air dry the residual soil and ground the soil using a mortar and pestle to pass 75μ sieve.
4. Add five percent lime (by weight) and mix thoroughly with water.
5. Keep the samples moist during the curing period.
6. Remove the samples from the centrifuge tube and dry the soil with acetone to remove excess water to stop further hydration.

7. Prepare multiple sub samples (3-5 samples) for DSC testing. Add varying amounts of synthesized ettringite to each sub sample. Ettringite content, starting from 0.5 weight percent, added to each sub sample should be progressively increased in 0.5 percent increments to prepare the standard curve.
8. Preparation of standard curve is detailed in the following sections.

Preparing Soil Samples for Ettringite testing

1. Add increasing concentrations of sulfates (gypsum) to the representative soil samples prepared as discussed earlier. Sulfate contents to be added are 0.2 percent, 0.5 percent and 0.8 percent by weight of the soil used. Replicate samples should be prepared for each soil type and for each sulfate contents.

2. Add five percent lime (by weight) and mix thoroughly with water inside a 50 ml centrifuge tube.

3. Seal the centrifuge tube and cure the samples for different time periods as detailed below.

4. Subject the lime treated soils to accelerated cure at 40 ^{o}C for 7 days, 14 days, 28 days and 56 days. Check the samples intermittently to ensure that the samples are not dried out during curing process. Add excess water, if needed, to keep the sample moist during curing to ensure that water was not a limiting factor in ettringite formation.

5. Remove the lime-soil-sulfate mixtures from the centrifuge tubes at the end of respective curing periods. Dry the samples using acetone to stop further hydration.
6. In case if excess water is present in the lime treated mixtures, a filtration device, as detailed in Appendix A, with a frit sand filter should be used to remove this water prior to drying using acetone.
7. Store the lime soil mixtures inside a desiccator to avoid re-adsorption of water. Conditions detailed in appendix A should be maintained inside the dessicator.
8. Procedure for testing the lime-soil-sulfate mixtures is detailed below.

Testing and Analysis

1. Sub-samples for testing should be randomly selected from the prepared lime-soil mixtures.
2. A slow heating rate of 2.0 ^{o}C/min should be used in all DSC testing.
3. Ultra high purity (UHP) Nitrogen is used as purge gas during testing.
4. Samples should be tested over temperatures ranging of 25 ^{o}C to 175 ^{o}C.
5. Test both control samples with added synthesized ettringite and lime treated natural soil with added sulfates using the DSC.
6. Heat flow signals from the sample at around 110 ^{o}C should be used for analysis.

7. Heat flow from the sample should be integrated over time to determine the energy in Joules. Analysis software with the DSC should be used in analysis of the signals.

8. Determine the normalized heat released by pure ettringite (in the control sample) over the selected temperature range.

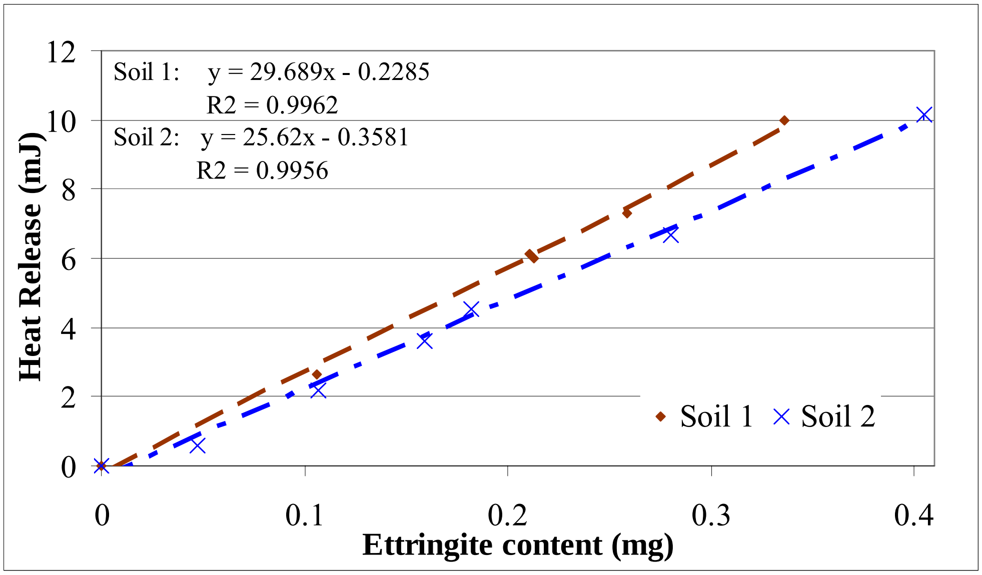


Fig. B-1. Example of standard curve prepared with control sample and known amount of synthesized ettringite for two different soils

9. Compare heat signals from the lime-soil-sulfate mixtures with the standard curve prepared using control sample with known ettringite content to determine the amount of ettringite present in lime-soil-sulfate mixtures. Example standard curve is given in Fig. B-1.

10. The concentrations should then be translated back to percentage fractions in soil (sand, silt and clay combined) based on the law of proportions.
11. Ettringite concentrations are plotted against sulfate content to determine the sensitivity of individual soils to changes in sulfate levels.

APPENDIX C

MODIFIED FRACTIONATION PROCEDURE FOR SEPARATION OF SAND FROM SILT AND CLAY

The section details a simple technique, without the use of strong chemical reagents, which can be used to separate sand fraction in soil from silt and clay. The silt and clay fraction can then be used for ettringite quantification testing by following techniques discussed in Appendix B.

Materials Required:

1. 4.75 mm (No. 4) sieve
2. 50 micron (No. 270) sieve
3. Reagent grade sodium carbonate and sodium chloride
4. 250 ml Centrifuge bottles
5. Large funnel, ring stand and 4 liter beakers
6. Deionized water and conventional heating oven

Preparation of Soil Samples:

1. Air dry natural soil and separate them into two fractions using a 4.75-mm (No. 4) sieve.
2. Remove the obvious rock fragments and visible organic material from the fractions retained on No. 4 sieve.

3. Pulverize the clay lumps retained on No. 4 sieve using a pulverizing apparatus (mortar and pestle) until the fraction is fine enough to pass No. 4 sieve. Pressure applied should not be high enough to crush any rock/sand particles remaining in the soil.
4. Remix the fractions passing No. 4 sieve and select representative soil samples for fractionation by using sampler or by splitting and quartering procedure.

Fractionation Procedure:

1. Prepare a pH 10 sodium carbonate solution by dissolving 2.5 g of Na_2CO_3 in 20 liters of deionized water (0.001M solution). Quantity of solution prepared may be adjusted according to requirement.
2. Place 20 gm of the representative soil sample in a 250 ml centrifuge bottle.
3. Add 20 ml sodium carbonate solution and 180 ml of distilled water to the soil inside the centrifuge bottle.
4. Seal the centrifuge tube and hand mix the solution for few minutes.
5. Leave the centrifuge tube containing the suspension on a shaker for 12 hrs.
6. Place the funnel on the ring stand with the sieve inside the funnel at a slight tilt.
7. Place the 4 liter beaker under the funnel to catch 50 micron fraction in the sample.
8. Remove the centrifuge bottle from the shaker and wait for a minute before pouring the dispersion through the sieve.
9. Proceed slowly with the filtration process so that the sieve is not clogged during the process.

10. Stop intermittently and shake the suspension to allow additional dispersion and repeat steps 8 and 9.
11. Use distilled water from a squirt bottle to wash down the coarser particles remaining inside the centrifuge tube.
12. Wash the sand particles retained on the sieve using distilled water from squirt bottle until the sand fractions appear to be clean.
13. Transfer the sand to a pre-weighed (oven-dry) glass container.
14. Oven-dry the sand fraction (100 °C for a minimum of 12 hrs) to determine the percent sand content in the soil.
15. Transfer the suspension with silt and clay to centrifuge bottles.
16. Use a high speed centrifuge to settle down the suspension. Centrifuge the suspension at 5000 rpm for 10 minutes.
17. Discard the clear supernatant from centrifuge bottles.
18. If the supernatant appears to be turbid, transfer the supernatant, without the settled silt and clay particles, back to the 4 liter beaker. Add one or two teaspoon of sodium chloride to flocculate the suspension.
19. Centrifuge the suspension at 1000 rpm for 5 minutes and perform dialysis of the suspension following procedures outlined by Dixon and White (2003).
20. Dry the silt and clay particles in centrifuge bottles in an oven at 40°C for about 72 hrs or until there is no further water loss from the sample.
21. Determine the dry weight of silt and clay fraction.
22. Pulverize the dried silt and clay particles and store the samples for future use.

VITA

Name: Syam Kumar Kochyil Sasidharan Nair

Address: 601A CE/TTI Building, MS 3135
Texas A&M University
College Station, TX 77843-3135

Email Address: syam.nair@gmail.com

Education: B. Tech, Civil Engineering, College of Engineering, Trivandrum, India, 1997
M. Eng., Civil Engineering, Texas A&M University, College Station, Texas 2006
Ph.D., Civil Engineering, Texas A&M University, College Station, Texas 2010