

Role of Sulfates on Highway Heave in Lake County, Ohio



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<p>Samples from borings in areas of heave on Route 2, Lake County, OH were analyzed for the amount, mineral form, and distribution of sulfates. In addition, samples of non-stabilized (NSS) and cement-stabilized (CSS) soils from three stations along Route 2 were analyzed for mineralogy and sulfate content. Finally, swell tests were run using the NSS samples to evaluate the degree of swelling and the role of ettringite. The sulfate content in the natural subgrade soil samples range from low (<3000 ppm) to unacceptable risk (>10,000 ppm) for heaving based on the TxDOT guidelines, and 36% tested above the moderate risk level (>5000 ppm). Gypsum and/or anhydrite were detected in 64% of the samples. The CSS samples contained white precipitates that were largely calcite, but with measurable amounts of ettringite as well. The NSS did not contain ettringite but had sulfate levels of moderate to high risk (4880 to 6107 ppm). Swelling of up to 8% was observed in the swell test samples; however, the amount of swelling did not correlated with the amount of sulfate present in the soil. Ettringite crystals were found in all of the swell test specimens after the experiment. In some cases the crystals were flat and coated the soil particles while others were long needle-like crystals that radiate out from bundles. This difference in crystal shape is thought to relate to the difference between primary and secondary ettringite growth in the samples.</p>			
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and the U.S. Department of Transportation, Federal Highway Administration

The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Ohio Department of Transportation or the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

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PROBLEM STATEMENT

Significant highway heaving problems have been reported recently in Lake County, Northeast Ohio. The heaving is believed to be due to swelling of sulfate-bearing soils. Many subgrade soils when treated with calcium-based stabilizers such as lime, Portland cement, or type-C fly ash experience deleterious swelling problems due to chemical reactions involving sulfate and/or sulfide minerals. Specifically, the formation of ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$] with its associated 250% volume expansion has been identified as the cause of highway heaving in other locales. These mineral reactions may occur rapidly over hours to days or slowly over months to years.

The goal of this project is to provide sound scientific data regarding the presence of sulfate minerals and the amount of soluble sulfate in the affected soils, and the distribution of sulfates in the soils in order to assist ODOT in determining the most cost effective highway construction method in the area of interest. The guidelines for stabilizing clayey soils containing sulfates indicate it is critical to perform a thorough investigation of any site where sulfate has been identified as differences in mineralogical compositions, hydrological aspects, and the nature of sulfate present will be different for each site.

INTRODUCTION

Reports of problems associated with sulfate in lime or cement stabilized soils dates back to Sherwood (1962) but received little attention until the 1980s when Mitchell (1986) reported the formation of ettringite with its associated 250% volume expansion was the cause of heave in a parking lot in Las Vegas, NV.

All Ca-based stabilizers (lime, cement, flyash-C) develop high pH when mixed with water providing favorable conditions for formation of expansive minerals like ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$]. The Ca comes from the lime/cement stabilizer, Al from dissolution of phyllosilicates (clays, micas), and sulfate comes from dissolution of gypsum either in situ or transported to the site dissolved in water. The chemical component that most likely controls the ettringite formation in most clayey soils is sulfate ions. Hence sulfate availability (either in situ or transportable to the site dissolved in water) is the most important consideration in controlling heave, and sulfate quantification is the key to defining soil reactivity.

Sulfate contents in soils typically exhibit a high degree of spatial heterogeneity often being concentrated along fracture walls, in seams and stratified pockets. This makes selection of appropriate sampling locations for sulfate testing difficult but critical (Little and Nair, 2009).

In 2004-2005, the Texas Transportation Institute issued a series of reports (Harris et al., 2004; 2005a; 2005b) aimed at developing guidelines and procedures for stabilization of sulfate soils in Texas. These reports provide a great deal of useful information regarding stabilization of sulfate-bearing soils including general guidelines for different sulfate levels in the soils. However, one of the most important findings of their studies, as well as more recent studies (*e.g.*, Little et al. 2005, Puppala et al., 2005, and Little et al., 2010), is that each site is different and it is critical to perform a thorough investigation of any site where sulfate has been identified. Specifically, differences in mineralogical composition of the soils, hydrological aspects of the site area, and the size and form of the gypsum in the soils all significantly impact what is an acceptable sulfate content/form in a specific locale. In addition, these studies indicate an

important consideration in evaluating a site is the distribution of sulfate in the soils. In several projects that have experienced swelling the problems were due to seams of high sulfate levels. If the seams can be identified, they can often be dealt with by dispersing the affected soils throughout the site thereby lower the overall sulfate to an acceptable level. It is also important to not only identify the presence of sulfates but also the depth of occurrence. A soil may have an acceptable level of sulfate in the upper few feet making it acceptable for normal surface stabilization, but have an unacceptable level of sulfate deeper down making it a concern in cut and fill areas.

BACKGROUND

Recent History of Route 2 Lake County, OH

In 2010, existing pavement was removed and replaced with an asphalt pavement section. The replacement included adding a third lane in each direction, modifying pavement elevations, adding a center median barrier wall, and widening berms along with removing the grass median. The new pavement consisted of 13.25 inches of asphalt (1.5 inches 12.5 mm surface course, 1.75 inches 19.0 mm intermediate course, and 10 inches asphalt base) underlain by 6 inches of aggregate base on top of 12 inches of cement-stabilized subgrade.

In late winter 2010, longitudinal cracking of the concrete was discovered and documented. In the spring of 2011, evidence of pavement heave of ½ to > 4 inches was observed at the longitudinal joint between the center median barrier wall and shoulder pavement in numerous locations throughout the entire stretch of pavement (Fig. 1). Repetitive cracking in the center median barrier wall was also observed.



Figure 1. Picture showing heave present in the west bound lane of Route 2 at station 560.

Geological Setting

The stretch of Route 2 through Lake County, OH is underlain by the late Devonian-age Ohio Shale. The Ohio Shale is a brownish-black to black shale composed in some locations of nearly

one-third organic matter by volume and containing high concentrations of uranium and heavy metals. In addition, the Ohio Shale is known to contain the iron sulfide minerals pyrite and marcasite providing a potential source of sulfur. The Ohio Shale has been interpreted to have been deposited in a stagnant tropical sea during the rise of the Acadian Mountains. The rise of the Acadian Mountains blocked trade winds and created a rain shadow that greatly decreased stream flow helping to create the stagnant sea environment (Ettensohn and Barron, 1981).

The region is part of the Galion Glaciated Low Plain Till Plain (Brockman and Szabo, 2000). The soil is the Conneaut-Painesville and consists of poorly drained and somewhat poorly drained soils that formed in silty glacial till or loamy material over silty glacial till on the lake plain during the most recent Wisconsinan glaciation (USDA Soil Conservation Service). A detailed description of the glacial geology of Lake County can be found in White (1980, Ohio Div Geol Survey RI 117).

OBJECTIVES

Objective I.

Characterize samples from borings in areas of heave along Route 2 in Lake County, OH provided by ODOT to evaluate the amount, type (i.e., gypsum, anhydrite, etc), and distribution of sulfates. Soil samples to be analyzed for soluble sulfate using the TxDOT Tex-145-E Colorimetric Method and by X-ray diffraction (XRD) to determine mineralogical composition including gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and clays (as a source of Al).

Objective II.

Synthesize pure ettringite in the laboratory to use as a standard for XRD and SEM/EDAX analysis of soils.

Objective III.

Analyze non-stabilized soil samples taken from stations 729+00, 730+00, and 730+80 along Route 2 in Lake County, OH, for soluble sulfate using the TxDOT Tex-145-E Colorimetric Method and by X-ray diffraction (XRD) to determine mineralogical composition including gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as source of sulfate and clays as a source of Al, and using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDAX) to evaluate grain morphologies and soil/mineral grain chemistries.

Analyze the cement-stabilized soils from heaved road sections at stations 729+00, 730+00, and 730+80 using XRD and SEM-EDAX to confirm the presence or absence of ettringite.

Perform swell tests using non-stabilized soil samples taken from stations 729+00, 730+00, and 730+80 along Route 2 in Lake County, OH to evaluate the degree of swelling and the role of ettringite formation.

OBJECTIVE I. CHARACTERIZATION OF BORINGS SAMPLES

Purpose

Twenty eight samples collected from borings sites distributed within sections of Route 2 where heaving occurred, were provided by ODOT for the purpose of determining the amount of soluble sulfate present and to compare with their results. Most (22) of the samples were from the natural subgrade soil with the others sampled at different depths. The samples were also analyzed using X-ray Diffraction (XRD) to determine their mineralogical make-up and specifically to identify the presence of any sulfate minerals.

Materials and Methods

Sulfate Testing

As noted above, sulfate content is typically the most important factor in defining swell hazard in clayey soils. Little and Nair (2009) presented an extensive assessment of different analytical methods that have been employed to measure sulfates, specifically gypsum, in soils. They noted that the TxDOT procedure Tex-145-E Colorimetric Method provided the best results with regard to accuracy and cost. As such, we employed the Tex-145-E method for sulfate analysis of soils at BGSU. Details of the sulfate testing procedures can be found in Appendix I and at the Texas DOT website.

Briefly, 20 grams of each of the soil samples provided by ODOT were first passed through a No. 40 sieve (425 μm). Ten grams of each sample were weighed out and placed into HDPE bottles to which 200 ml of deionized water was added, each sample was then shaken vigorously for one minute. The samples were then allowed to sit undisturbed for a minimum of 24 hours. After the 24-hour period, each sample was shaken gently for one minute and then filtered with 0.45 μm filter paper (Fig. 2). Two drops of concentrated HCl was added to the filtrate followed by a barium chloride packet. Sulfate testing was performed using a Thermo Scientific Orion AQUAfast AQ 3700 Colorimetry Meter following the manufacturer's operating instructions. Three readings were taken and averaged. The first reading was taken immediately upon sample preparation, followed by the second and third readings.

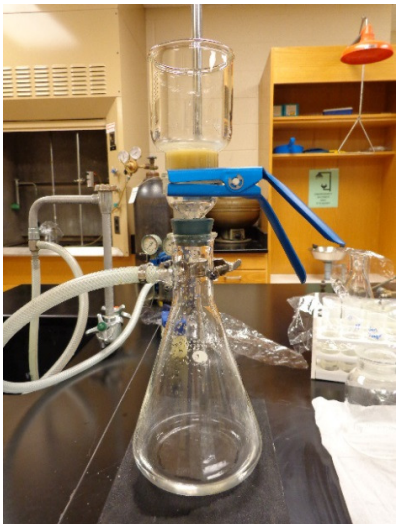


Figure 2. Filtration setup for soil sulfate analysis.

X-ray Diffraction Analysis

The X-ray diffraction analysis followed the guidelines outlined in the USGS Open-File Report 01-041 (Poppe et al., 2001). Powdered samples were prepared for XRD analysis by crushing and grinding using a synthetic sapphire mortar and pestle. The powder was loaded into the well of an Al-planchet or adhered to a glass slide using a Duco cement/acetone solution. The samples were analyzed using a Rigaku Miniflex II X-ray Diffractometer with a Cu K α source operating at 30 kV and 15 mA. Typically, scans were run from 3° to 70° 2 θ at a scan rate of 1.5° 2 θ /minute. When looking for ettringite, scans were run from 3° to 40° 2 θ at a scan rate of to 1.0° 2 θ /minute focusing on the characteristic peaks at 9.14° and 15.86° 2 θ . Mineral identification was done using the PDXL software provided by the manufacturer.

Results

Results of the sulfate analysis of the borings samples are presented in Table 1. The sulfate values in the natural subgrade soils samples range from low risk (<3000 ppm) to unacceptable risk (>10,000 ppm) for heaving of lime/cement stabilized clayey soil based on the TxDOT guidelines (Table 2), and 36% of the natural subgrade samples tested above the moderate risk level (>5000 ppm). The sulfate values measured at BGSU compare well to the values provided by ODOT after the samples were run at BGSU (Fig. 3), the variability observed being due to the heterogeneous distribution of gypsum in the samples and the difficulty of obtaining a truly representative 10 gram aliquot for testing. The samples from bore B5 show a modest increase in sulfate content with depth, but samples from B6 show the opposite trend and the variability may simply reflect the inconsistency in gypsum distribution in the 10 gram sub-samples used for the analysis.

Table 1. Sulfate testing results for borings samples determined at BGSU, associated risk levels, comparison to ODOT results, and presence of gypsum/anhydrite from XRD analysis (Nat Sub = natural subgrade soil, NA = not analyzed, ND = not detected).

Sample	Layer	Sulfate – BGSU (ppm)	Risk Level	Sulfate-ODOT (ppm)	Gypsum/Anhydrite present
B1	Nat Sub	7520	Mod to high	2232	Y
B4	Nat Sub	5600	Mod to high	6687	Y
B5	Top	5600	Mod to high	8000	Y
B5	Top mid	7040	Mod to high	NA	Y
B5	Bot mid	8000	Mod to high	NA	Y
B6	Top	2560	Low	939	Y
B6	Bot mid	1360	Low	NA	Y
B7	Top	5040	Mod to high	4523	Y
B9	Nat Sub	460	Low	1054	ND
B28	Nat Sub	360	Low	354	ND
B30	Nat Sub	10,560	Unacceptable	7564	Y
B31	Nat Sub	5680	Mod to high	5496	Y
B32	Nat Sub	6080	Mod to high	6296	Y
B33	Nat Sub	300	Low	445	ND
B34	Nat Sub	1600	Low	1554	Y
B35	Nat Sub	500	Low	499	ND

B36	Nat Sub	8000	Mod to high	8000	Y
B37	Nat Sub	2800	Low	2132	Y
B38	Nat Sub	5280	Mod to high	3405	Y
B39	Nat Sub	240	Low	261	ND
B40	Nat Sub	240	Low	NA	ND
B42	Nat Sub	6720	Mod to high	7590	Y
B43	Nat Sub	2640	Low	2728	Y
B45	Nat Sub	1840	Low	2026	Y
B46	Nat Sub	1660	Low	1813	Y
B47	Nat Sub	500	Low	451	ND
B49	Nat Sub	2080	Low	4002	Y
B50	Nat Sub	260	Low	NA	ND

Table 2. Risk Levels Associated with Lime Stabilized Sulfate-Bearing Clay Soils.

Risk Involved	Soluble Sulfate Concentrations (ppm)
Low	Below 3000
Moderate	Between 3000 and 5000
Moderate to High	Between 5000 and 8000
High to Unacceptable	Greater than 8000
Unacceptable	Greater than 10,000

(Texas Transportation Institute, after Little and Nair, 2009)

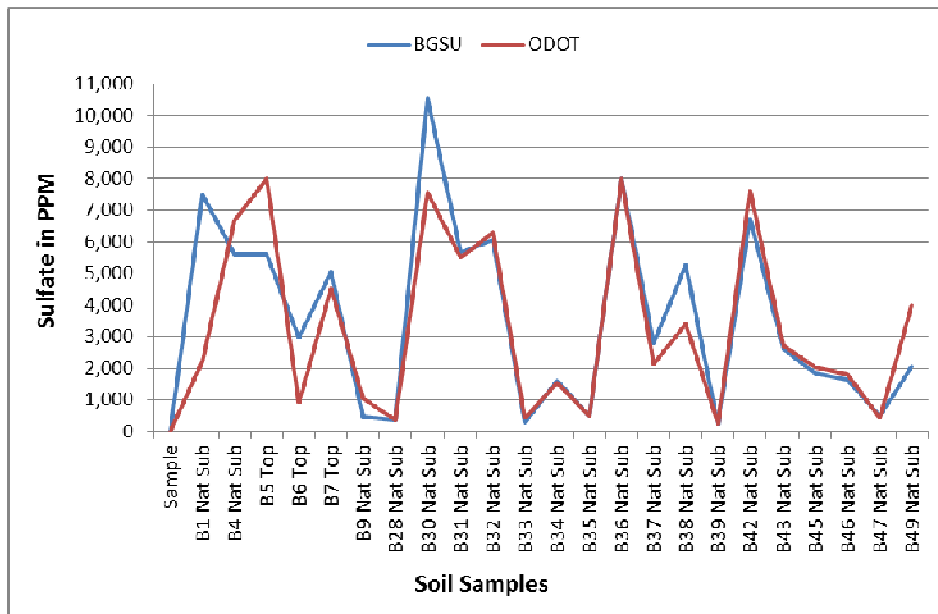


Figure 3. Comparison of sulfate testing results for BGSU and ODOT. Samples run from west to east spatially.

A representative XRD pattern of a borings sample (B7) is presented in Fig. 4. The XRD analysis of the borings samples show the major mineral components are quartz, muscovite/sericite mica, clays (clinochlore, kaolinite, and illite), and hematite (Supplemental data can be obtained from ODOT). Also, the common sulfate minerals gypsum and/or anhydrite were detected in 64% of the natural subgrade samples; all of the samples that had >1000 ppm sulfate. Hence, the primary source of sulfate in these soils is gypsum/anhydrite.

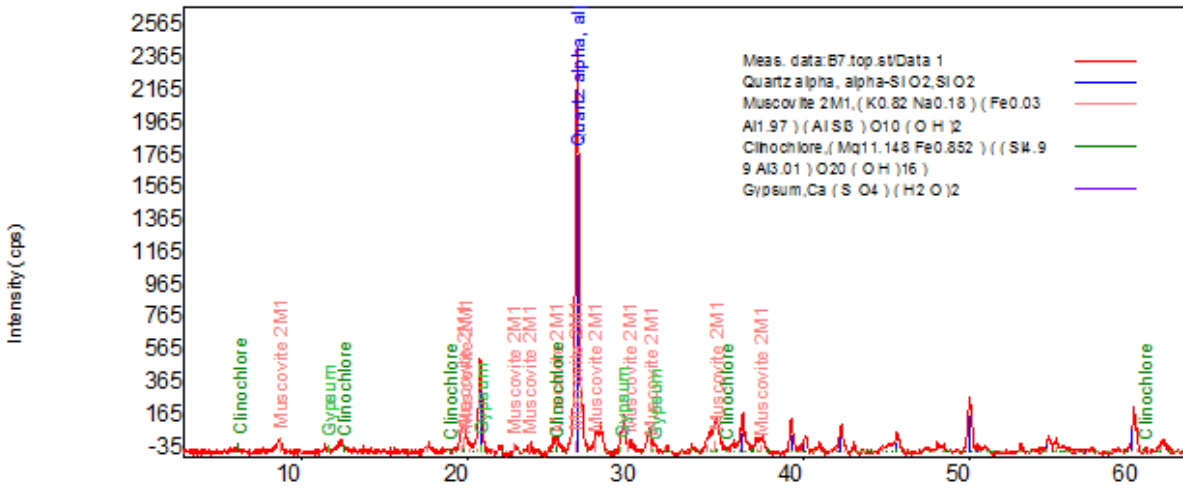


Figure 4. Representative XRD pattern for bore sample (B7).

OBJECTIVE II. SYNTHESIS AND CHARACTERIZATION OF ETTRINGITE

Purpose

To provide a standard for XRD and SEM/EDAX analysis, synthetic ettringite was grown in the laboratory. The synthetic ettringite was then characterized using transmitted light microscopy, XRD, and SEM/EDAX.

Materials and Methods

The method was adopted from Cody et al. (2004). All solutions were made using deionized water and were filtered through Whatman 0.45 micron filter paper before use. A saturated calcium hydroxide solution was produced by adding 2.57 g of CaO to 1 L of deionized water and stirring with a magnetic stir bar for 2 hours. An aluminum sulfate solution was produced by adding 2.61 g of AlSO_4 to 1 L of distilled water. Then, 178 ml of the CaOH solution was placed in an Erlenmeyer flask and dry N_2 gas was bubbled through the solution overnight in order to purge the solution of dissolved CO_2 that could react with the CaOH forming calcite instead of ettringite (Fig. 5A). After bubbling dry N_2 gas through the CaOH solution overnight, 222 ml of the AlSO_4 solution was added to the CaOH solution and again bubbled overnight with dry N_2 gas. A fuzzy, white precipitate formed within an hour of adding the AlSO_4 solution (Fig. 5B). The precipitate was scraped off the sides of the flask, and the solution was filtered through 0.45 micron filter paper (Fig. 5C). The white precipitate was left on the filter paper in a desiccator to air-dry overnight (see Appendix II for details). Note, it is important to NOT dry the ettringite in an oven because at very low humidity it can begin to thermally decompose at $<80^\circ\text{C}$ (Purchez et al., 2006).

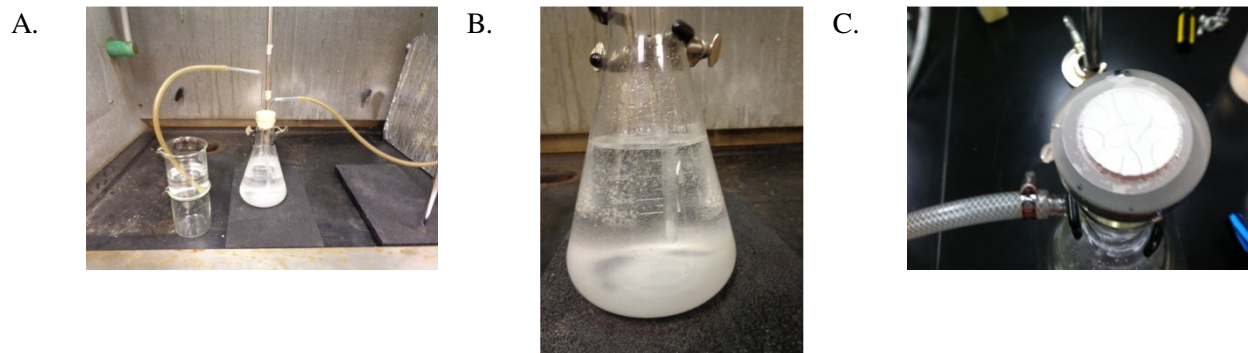


Figure 5. (A) Nitrogen gas bubbler setup. (B) Fuzzy, white precipitate that forms after the addition of the AlSO_4 solution. (C) White precipitate on filter paper after filtration.

Results

The precipitate was identified as ettringite by examining crystals first using a transmitted light (petrographic) microscope, then using XRD and SEM/EDAX. Crystals were viewed with a petrographic microscope by affixing a small sample of the white precipitate to a glass slide using an adhesive (Duco cement in acetone). A few grams of the white precipitate were placed on a 12.7 mm diameter aluminum stub for SEM analysis. The aluminum stub was covered with a carbon adhesive or carbon planchet to prevent erroneously high aluminum EDAX results. The sample was then coated with Au/Pd or C for conductivity.

Under the petrographic microscope, the precipitate crystals appear as long, thin, solitary needles or clusters of needles (Fig. 6A). In the SEM, the crystals also appear elongate and needle-like, and some orientations show the characteristic hexagonal prismatic needle-like morphology (Fig. 6B).

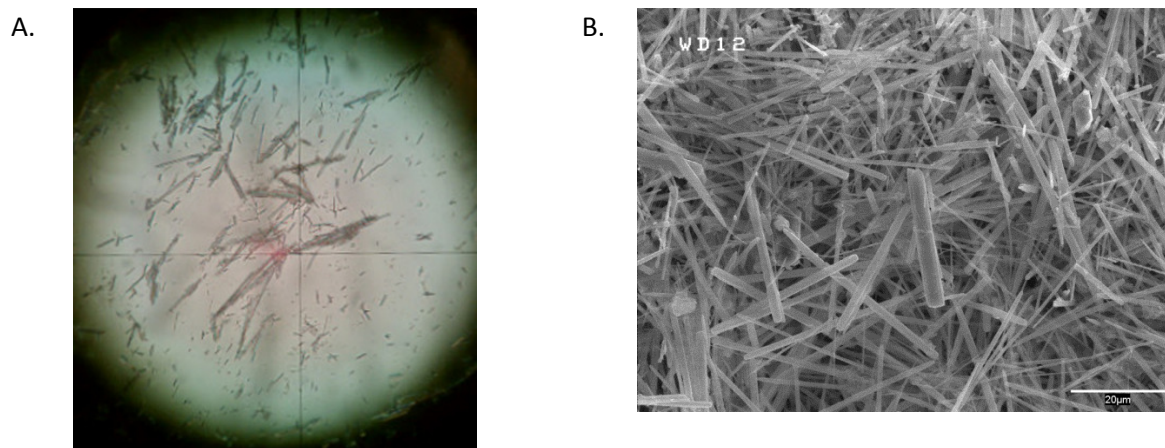


Figure 6. Examples of needle-like morphology of synthetic ettringite crystals. (A) Petrographic microscope (field of view ~1 mm). (B) SEM: 20 kV, Working Distance 12 mm, scale bar = 20 μm.

The EDAX analysis yielded a bulk chemical composition of 46.09 wt% O, 34.61 wt% Ca, 11.91 wt% S, and 7.39 wt% Al, respectively (Fig. 7), and the XRD analysis showed well defined peaks at 9.14 and 15.86° 2θ, characteristic of ettringite (Fig. 8).

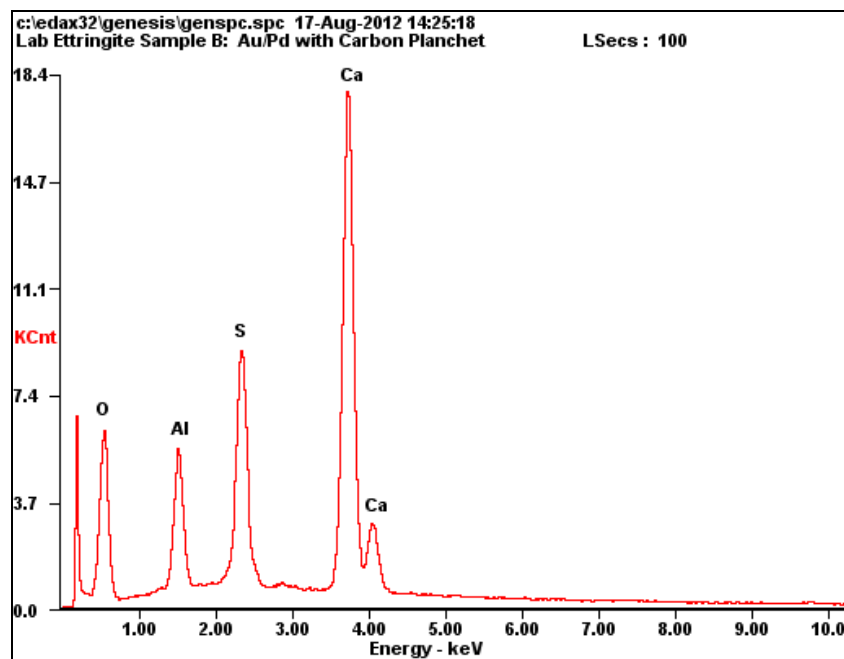


Figure 7. EDAX spectrum of synthetic ettringite.

Qualitative analysis results

ett091112.raw				
Phase name	Formula	Figure of merit	Phase reg. detail	DB card number
Ettringite, syn	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ (H ₂ O) ₂₆	1.052	ICDD (PDF2011)	01-075-7554

Phase data pattern

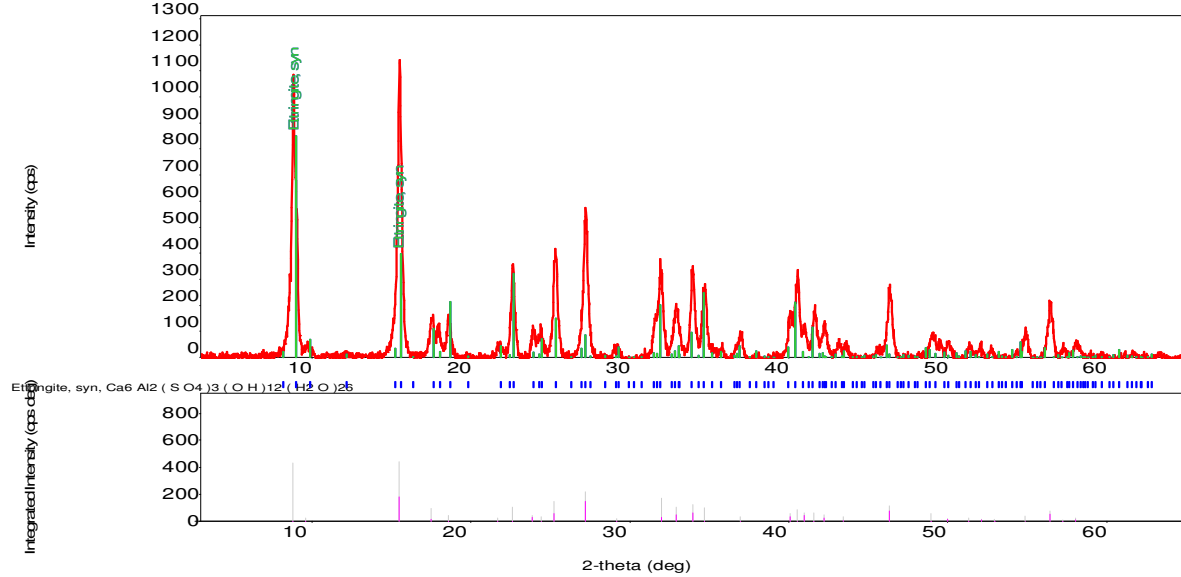


Figure 8. XRD scan of synthetic ettringite.

The XRD and SEM/EDAX analyses confirmed that the white precipitate was ettringite crystals. Literature reviews of similar ettringite studies show the same needle-like morphology and similar elemental weight percents for O, Ca, Al, and S (e.g., Blanco-Varela et al., 2006; Tosun et al., 2009; Tosun-Felekoglu, 2012). These elemental weight percents are consistent with the chemical formula weight percents for ettringite without water [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} + 26 \text{H}_2\text{O}$], which contains 49.57 wt% O, 31.04 wt% Ca, 12.42 wt% S, and 6.97 wt% Al. It is useful to note that when the CaOH and AlSO_4 solutions were reacted without purging the CO_2 from the solutions using dry N_2 gas, the precipitate was calcite (CaCO_3), as confirmed by XRD analysis. Calcite films or overgrowths on ettringite crystals have been reported previously and their presence can hinder its identification/quantification in XRD (e.g., Kota et al., 1996).

OBJECTIVE III. SWELL TESTING

Purpose

The bulk of this research project was focused on determining whether ettringite would form in non-stabilized subgrade soil samples obtained from Lake County, Route 2 sites where heaving was noted. The samples were treated as closely as possible to how they would have been during the road construction and later curing and heaving of the highway. In addition, swell test samples were produced (after Harris et al., 2004, Texas Transportation Institute Report 0-4240-2) and their swelling behavior was monitored for 56 days. All of the soil samples and swell test samples were characterized using SEM/EDAX and XRD.

Soil Samples

Materials and Methods

Samples of both non-stabilized (NSS) and cement-stabilized soils (CSS) from stations 729+00, 730+00, and 730+80 were provided by ODOT. Visual inspections of the samples were made as noted below. The samples of both the NSS and CSS soils were tested for sulfate content following the TxDOT procedure Tex-145-E as outlined above using a 5 minute wait before taking a reading. Three 10-gram sub-samples were randomly taken for each station from both the NSS and CSS samples, for a total of 18 samples. Also, prior to the sulfate analysis, each of the sub-samples was analyzed by XRD to characterize their mineralogical make-up, specifically looking for the presence of sulfates (gypsum/anhydrite) in the NSS and ettringite in the CSS samples.

Both non-stabilized and cement-stabilized soil samples from stations 729+00, 730+00, and 730+80 were also analyzed using a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDAX) to determine the texture/crystal morphologies and chemistry of the soils/mineral grains. The texture/crystal morphologies of some minerals commonly found in the clayey soils are shown in Fig. 9. Clay minerals have characteristic thin pseudo-hexagonal plate morphology (Fig. 9A); gypsum grains are tabular with prominent basal cleavage (Fig. 9B); ettringite are elongated hexagonal needle-like grains (Fig. 9C); and typical soils have platy and rounded to subrounded grains (Fig. 9D).

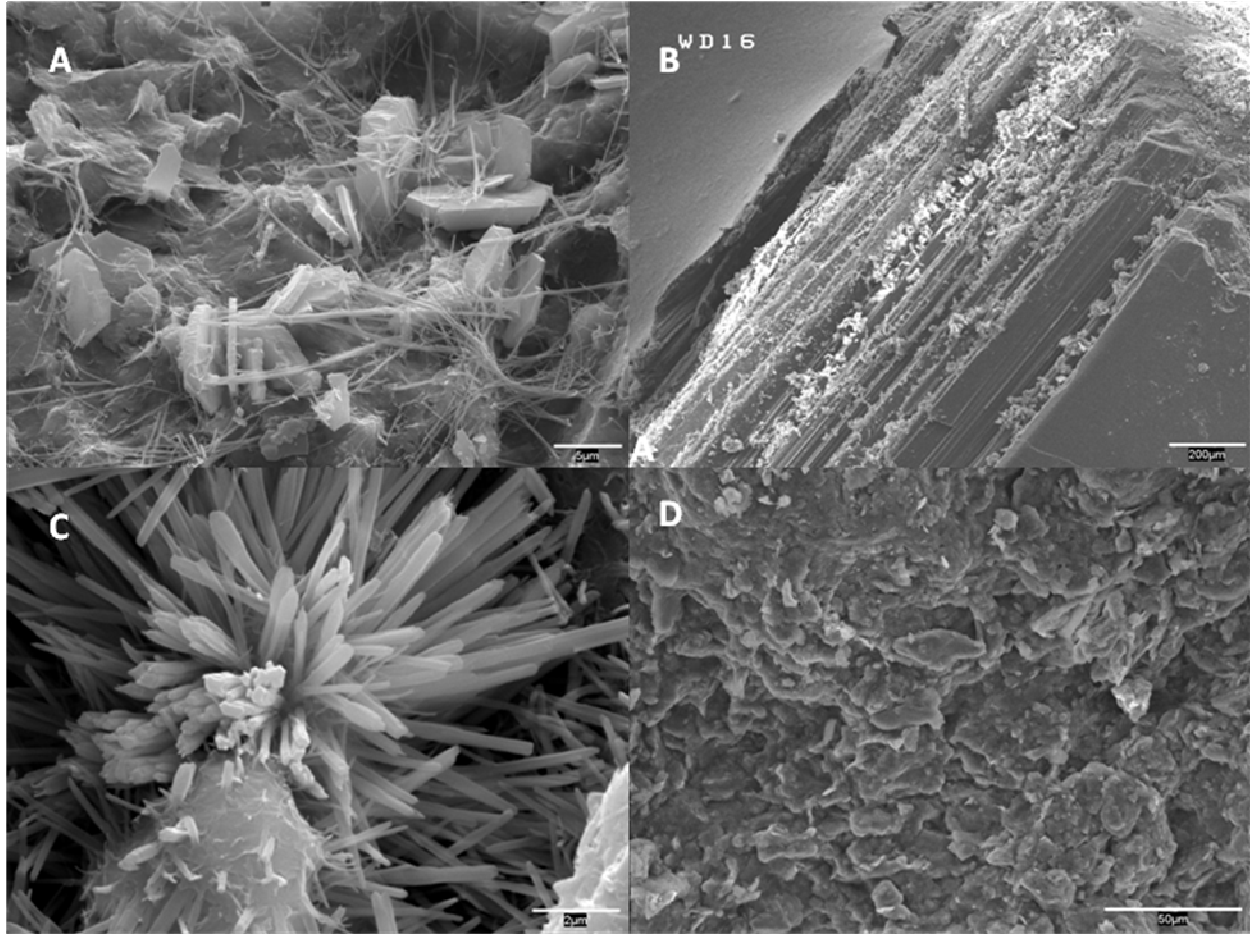


Figure 9. SEM images of common minerals in clayey soils. (A) clays, scale bar = 5 μm . (B) gypsum, scale bar = 200 μm . (C) ettringite, scale bar = 2 μm . (D) typical soil, scale bar = 50 μm .

A total of 18 soil samples were analyzed using SEM/EDAX; 10 were non-stabilized soil samples and 8 were cement-stabilized samples. Each soil sample was air dried for at least three days in a desiccator before sample preparation. Small soil samples were affixed to 12.7 mm aluminum stubs with graphite paint and allowed to air dry for at least two days. Each aluminum stub was covered in either a carbon adhesive or a carbon planchet to ensure that Al readings were from the soil and not the aluminum stub. Samples were sputter coated with Au/Pd for conductivity. A working distance of 12 mm was used for collecting EDAX spectrums.

Results

Visual inspection showed, in general, the soils are brown/gray sandy silts (Soil type A-4a). The non-stabilized samples have abundant clay minerals, and there were gypsum crystals ranging up to 2 cm in diameter as well as clasts 2-3 cm in diameter of the underlying Ohio Shale bedrock. In addition, there was abundant Fe-staining and iron oxides were disseminated throughout the samples (Figs. 10 and 11). The cement-stabilized samples were similar to the NSS samples but also contained several areas covered with a white precipitate (Fig. 12).

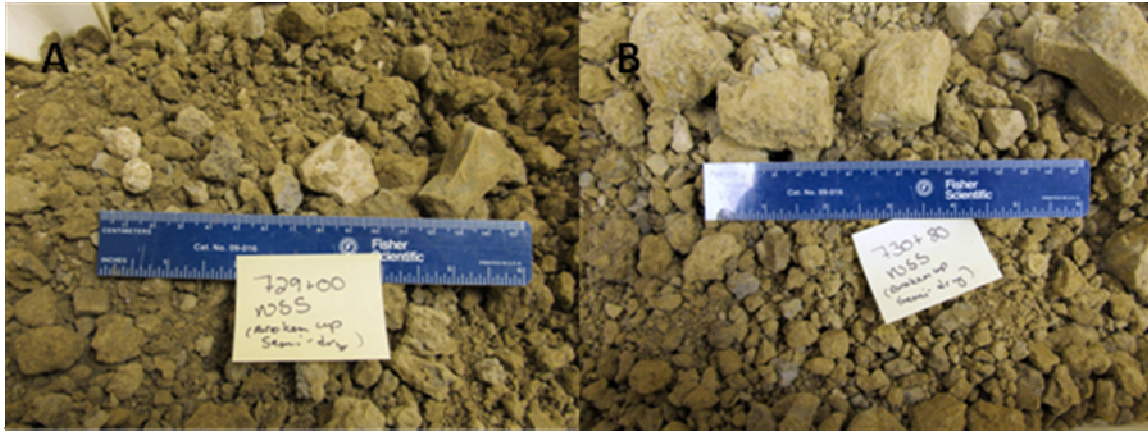


Figure 10. Representative samples of NSS soils. (A) NSS 729+00. (B) NSS 730+80.

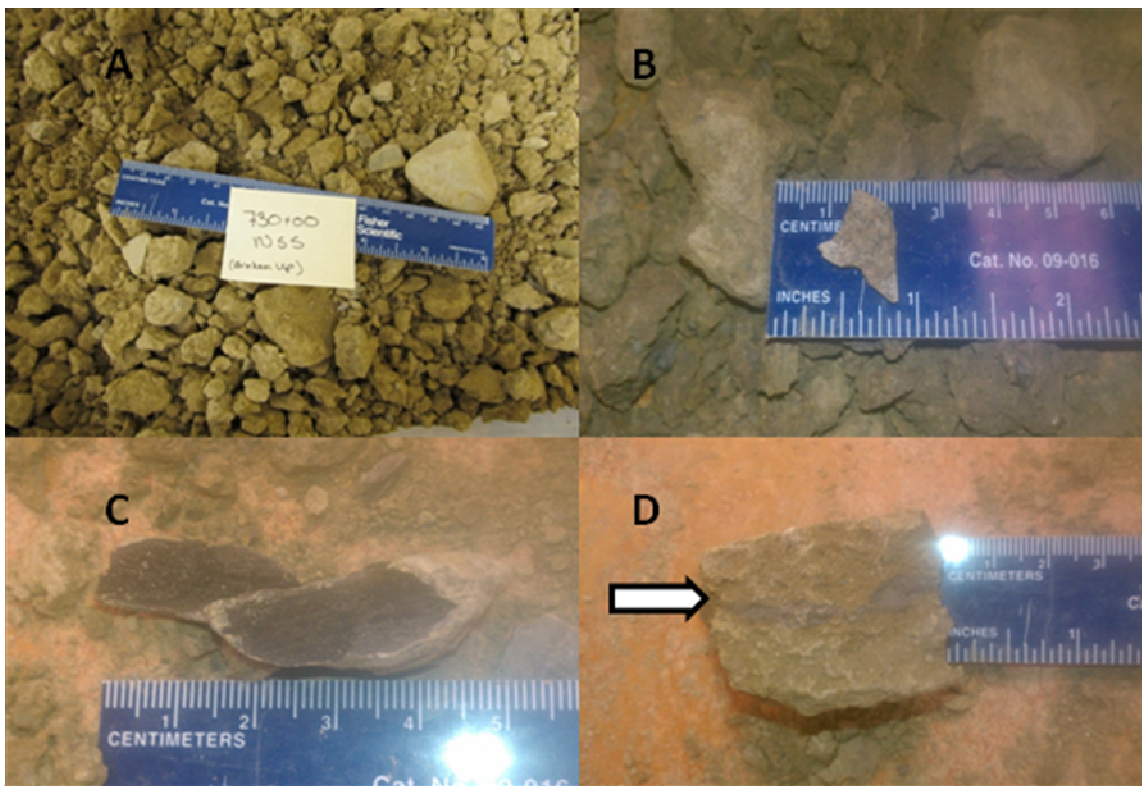


Figure 11. NSS 730+00. (A) Representative soil sample. (B) Large gypsum crystal. (C) Clasts of shale bedrock. (D) Arrow points to clay seam, hematite and iron oxide staining on surface and in the background.

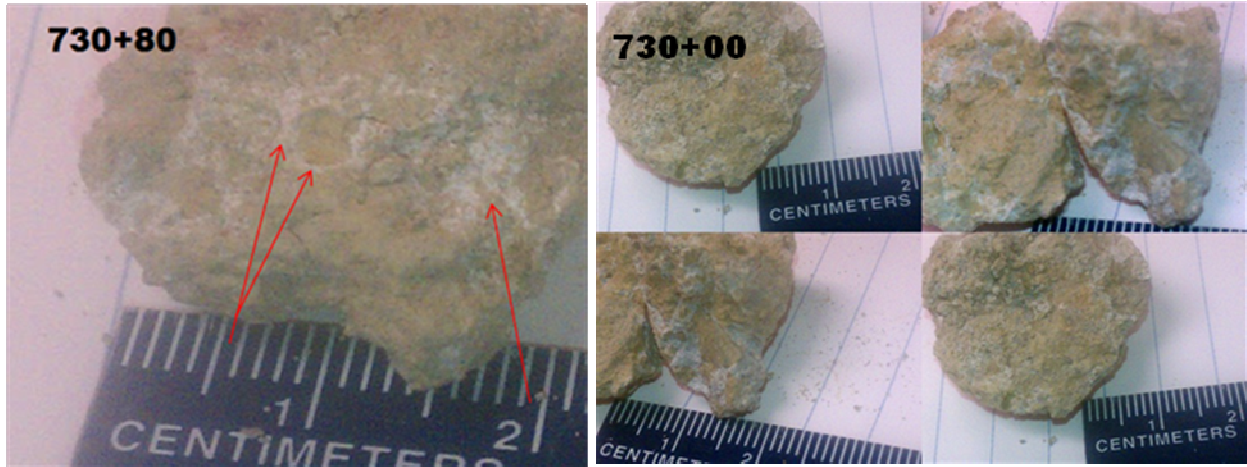


Figure 12. Samples of CSS 730+80 and 730+00 soils. Note the white precipitate.

XRD Results

The XRD analysis confirmed the major mineral components of the NSS and CSS samples are quartz, muscovite/sericite mica, clays (kaolinite, illite, clinochlore), and hematite (Figs. 13 and 14). In addition, gypsum was identified in variable amounts in both the NSS and CSS samples.

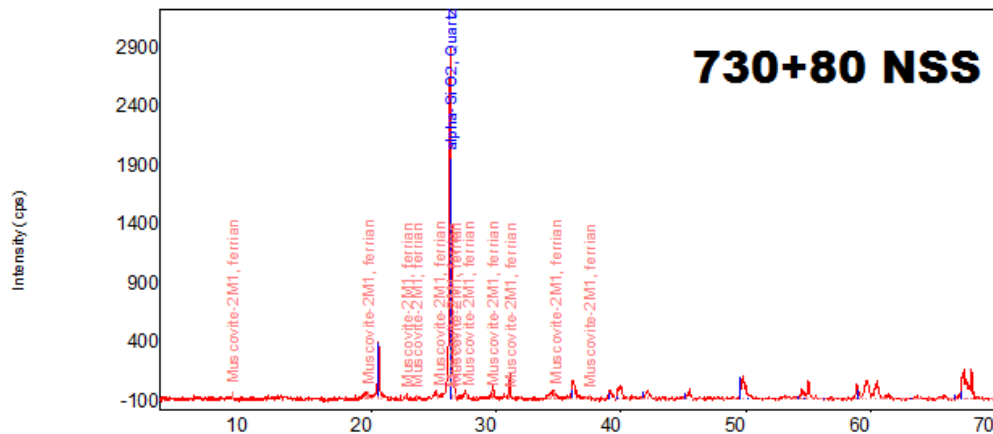


Figure 13. XRD scan of representative sample of NSS 730+80 soil.

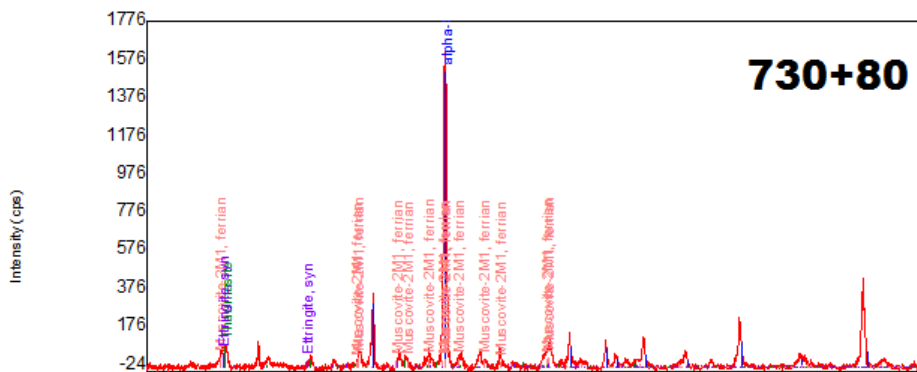


Figure 14. XRD scan of representative sample of CSS 730+80 soil.

The XRD analysis showed that the white precipitate in the CSS samples was largely calcite (Fig. 15) but with measurable amounts of ettringite in some cases (Supplemental data can be obtained from ODOT).

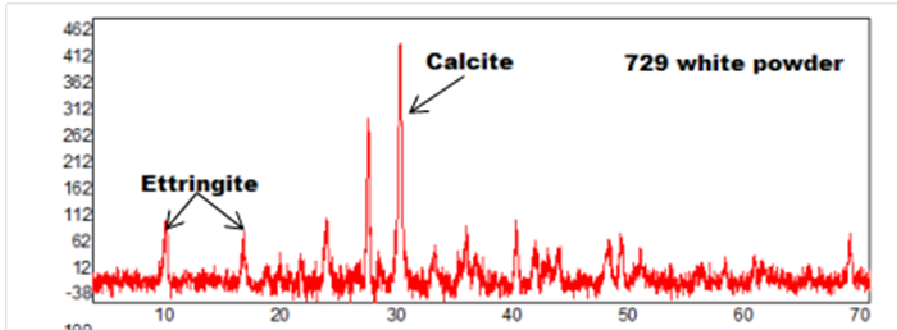


Figure 15. XRD scan of white precipitate from CSS 729+00 soil.

Sulfate Results

Sulfate testing of non-stabilized and cement-stabilized soils from stations 729+00, 730+00, and 730+80 showed a range of 3400 to 6880 ppm (Table 3), putting these soils in the moderate to moderate-to-high sulfate risk categories (Table 2). Even though all samples tested within the moderate to moderate-to-high sulfate risk levels, there was some minor variability among the three different samples taken for each soil station. Given that the same testing procedures were followed, the variability is most likely a reflection of the heterogeneous distribution of gypsum in the soils.

The pH levels were also determined for these soils (Table 3). The NSS soils have typical pH levels for this soil type of 7.4 to 8.8 while the CSS soils all have elevated pH levels of 9.8 to 10.1. Given that the CSS soils were stabilized with 6% cement several years prior to the analysis, the elevated pH levels that persist today clearly indicates that pH values > 10.5 were likely in the soils when the cement was first added which would promote the breakdown of the clays and muscovite mica thereby liberating ample Al for ettringite formation.

Table 3. Sulfate and pH testing results for soils from stations 729+00, 730+00, and 730+80.

Sample	pH	Sulfate (ppm)	Risk	Sample	pH	Sulfate (ppm)	Risk
729+00a NSS		3400	Mod	729+00a CSS		3640	Mod
729+00b NSS	7.93	4400	Mod	729+00b CSS	10.08	6880	Mod to High
729+00c Nss	7.68	5120	Mod to High	729+00c CSS	10.07	6640	Mod to High
Mean/std dev	7.81±0.18	4307±864	Mod	Mean/std dev	10.08±0.01	5720±1805	Mod to High
Sample	pH	Sulfate (ppm)	Risk	Sample	pH	Sulfate (ppm)	Risk
730+00a NSS		3640	Mod	730+00a CSS		4960	Mod
730+00b NSS	7.46	6160	Mod to High	730+00b CSS	9.82	6720	Mod to High
730+00c NSS	7.37	6080	Mod to High	730+00c CSS	9.75	6640	Mod to High
Mean/std dev	7.42±0.06	5293±1432	Mod to High	Mean/std dev	9.79±0.05	6107±994	Mod to High
Sample	pH	Sulfate (ppm)	Risk	Sample	pH	Sulfate (ppm)	Risk
730+80a NSS		6880	Mod to High	730+80a CSS		3200	Mod
730+80b NSS	8.77	5200	Mod to High	730+80b CSS	9.77	6080	Mod to High
730+80c NSS	8.92	6000	Mod to High	730+80c CSS	9.73	5360	Mod to High
Mean/std dev	8.85±0.11	6027±840	Mod to High	Mean/std dev	9.75±0.03	4880±1499	Mod

SEM/EDAX Results

The SEM observations of non-stabilized soil from stations 729+00, 730+00, and 730+80 indicate the substrate has a platy morphology (Fig. 16). The EDAX results show major elemental average abundances in non-stabilized soils were O 39.15 wt%, Si 28.67 wt%, Ca 11.37 wt%, Fe 9.56%, Al 9.54 wt%, K 4.30 wt%, Mg 0.97 wt%, and Ti 0.79 wt%. Minor elements including sulfur, manganese, and sodium were present in the following average weight percent abundances: S 11.53%, Mn 0.58%, and Na 0.53%. Sulfur was classified as a minor element because it was found in only two of the samples.

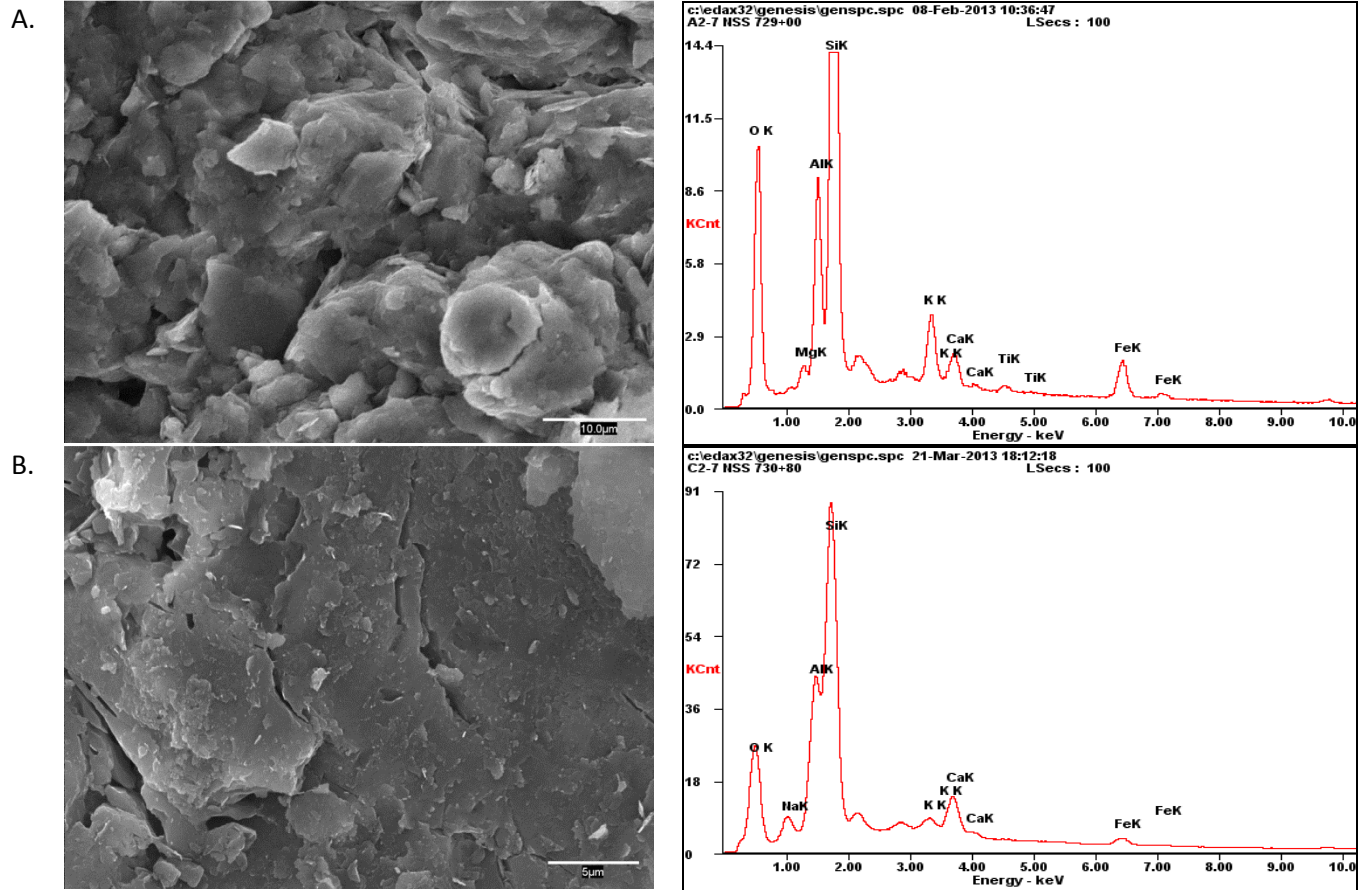


Figure 16. Typical SEM/EDAX results for NSS samples. (A) Sample A2-7 729+00 NSS. Scale bar is 10.0 μm . O 39.86 wt%, Si 35.17 wt%, Al 9.79 wt%, Fe 6.47 wt%, K 4.93 wt%, Ca 2.21 wt%, Mg 1.03, and Ti 0.54 wt%. (B) Sample C2-7 730+80 NSS. Scale bar is 5.0 μm . O 37.15 wt%, Si 34.27 wt%, Al 16.41 wt%, Ca 5.72 wt%, Fe 2.23 wt%, Na 2.23 wt%, and K 2.00 wt%.

The SEM observations for the cement-stabilized soils from stations 729+00, 730+00, and 730+80 indicate a platy substrate morphology as well as numerous areas where the platy soil was covered in long, thin needles (Fig. 17). The EDAX analysis yielded the major elemental average abundances of cement-stabilized soils were O 37.42 wt%, Ca 23.68%, Si 16.01%, S 8.79%, Al 5.13%, Fe 4.77 %, K 2.25%, Mg 0.69%, Ti 0.65%, Na 0.11%, and Cl 0.11%.

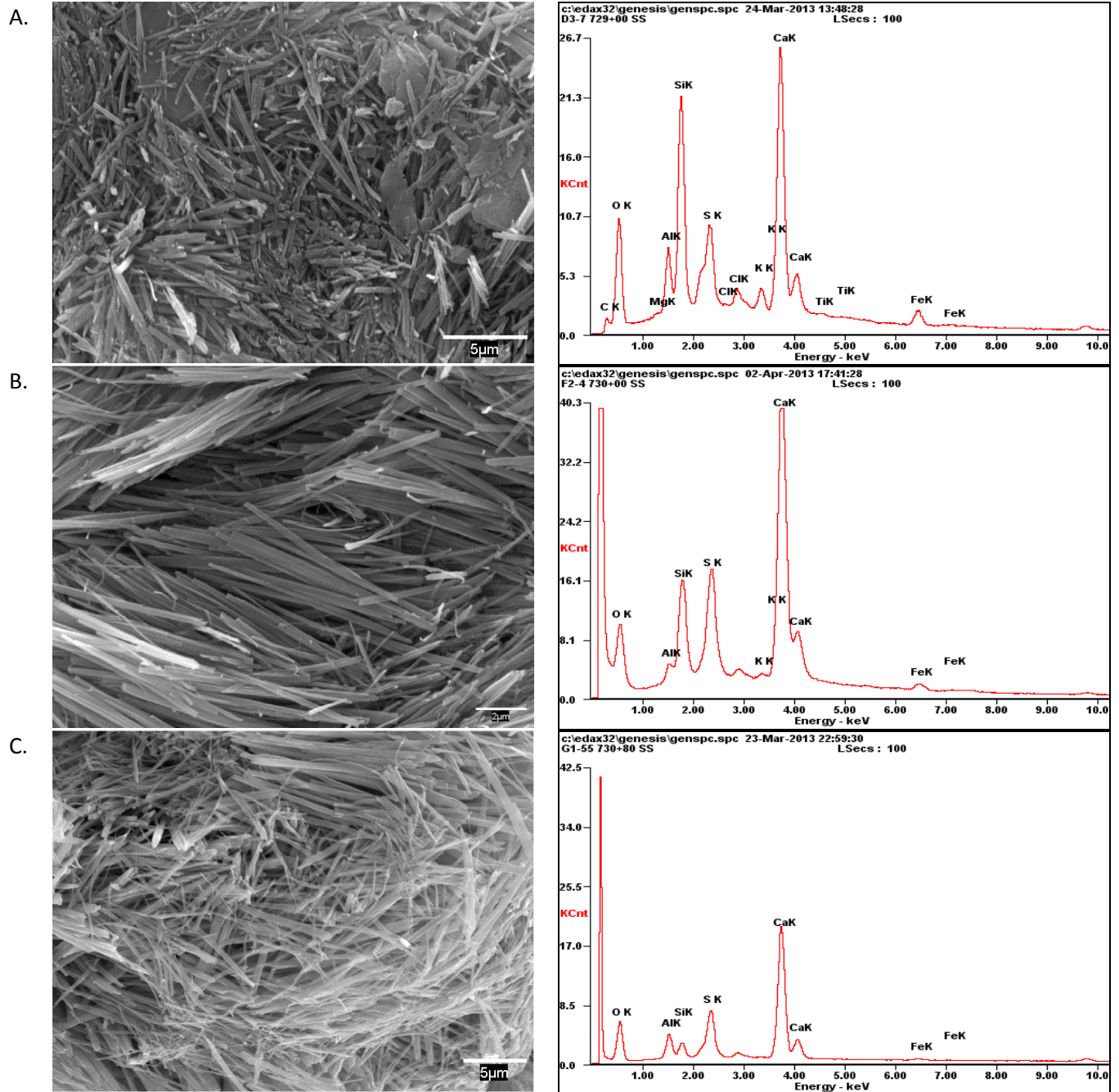


Figure 17. SEM images of regions in CSS samples containing ettringite crystals. (A) Sample D3-7 729+00 CSS. Scale bar is 5 μm . O 37.83 wt%, Ca 24.52 wt%, Si 14.13 wt%, c 7.21 wt%, S 6.03 wt%, Al 4.24 wt%, Fe 3.53 wt%, K 1.80 wt%, Ti 0.42 wt%, Mg 0.17%, and Cl 0.11%. (B) Sample F2-4 730+00 CSS. Scale bar is 2 μm . Ca 39.95 wt%, O 33.66 wt%, S 11.94 wt%, Si 10.22 wt%, Al 2.06 wt%, Fe 1.98 wt%, and K 0.19%. (C) Sample G1-55 730+80 CSS. Scale bar is 5 μm . O 44.82 wt%, Ca 35.71 wt%, S 9.71 wt%, Al 5.34 wt%, Si 3.36 wt%, and Fe 1.05 wt%.

Published SEM images of ettringite show similar needle-like morphologies and similar chemical composition based on EDAX analysis (e.g., Blanco-Varela et al., 2006; Tosun et al., 2009; Tosun-Felekoglu, 2012). All cement-stabilized soil samples tested had ettringite needles present; however, it was noticed that the needles in the 729+00 samples were not as well developed and/or were in much less abundance than in samples from 730+00 and 730+80 soils, indicating a possible limiting factor for ettringite growth in the 729+00 soils. The majority of non-stabilized soil samples had platy substrate morphologies and did not have needles, indicating that ettringite did not form in the non-stabilized soils.

Swell Test Samples

Materials and Methods

The NCHRP web-only document 145 (Little and Nair, 2009) states that the threshold level for swell damage in lime/cement stabilized clay soils should be 2000 to 3000 ppm. In their soil swelling study, Harris et al. (2004) added gypsum crystals (fine, <75 μm , and coarse, 0.425 to 2 mm) to a Vertisol sulfate-deficient soil typically found in Texas. The sulfate testing of the non-stabilized soils from stations 729+00, 730+00, and 730+80 showed a range of 4307 to 6027 ppm, putting these soils in the moderate to moderate-to-high sulfate risk categories, well above the threshold level for potential heave damage. As a result of the high sulfate test results, it was determined that sulfate levels were sufficiently high to produce swelling of soils, and additional gypsum was not added to the swell test specimens. In addition, Harris et al. (2004) treated external water by truck and external groundwater the same. It is reasonable that truck water used on Lake County Route 2 would be locally obtained and thus similar in composition to groundwater. To mimic the very dry conditions found in Texas, Harris et al. (2004) dried their swell test samples for 3 days after compaction. Given the humid conditions that are typical of Northeast Ohio, we ran one set of samples without a 3 day drying period.

Preparing swell test samples

Four swell test samples per station (729+00, 730+00, and 730+80) were made at the ODOT testing facilities for a total of twelve swell test samples. Samples of the 729+00 and 730+00 non-stabilized soils were sieved with a #5 (4 mm) sieve and the 730+80 sample was sieved with a #40 (425 μm) sieve. The samples were compacted using a standard Proctor machine with a 2.5 kg (5.5 lb) rammer and a 305 mm (12 in) drop (Fig. 18). The samples were compacted in a 4 inch diameter by 4.5 inch height mold in three layers which received 25 drops per layer (AASHTO T99 method). All but one of the samples had 1850.0 g of soil, 111.0 g or 6% of cement, and 280.0-400.0 g or 15-22% of distilled water (Appendix III). The type of cement (St Mary's T1) and the amount of cement and water match what was used for the Lake County Route 2 highway, and represents the optimum cement content (6%) and slightly over the optimum moisture content (16%) determined for this soil type (Type A-4a).

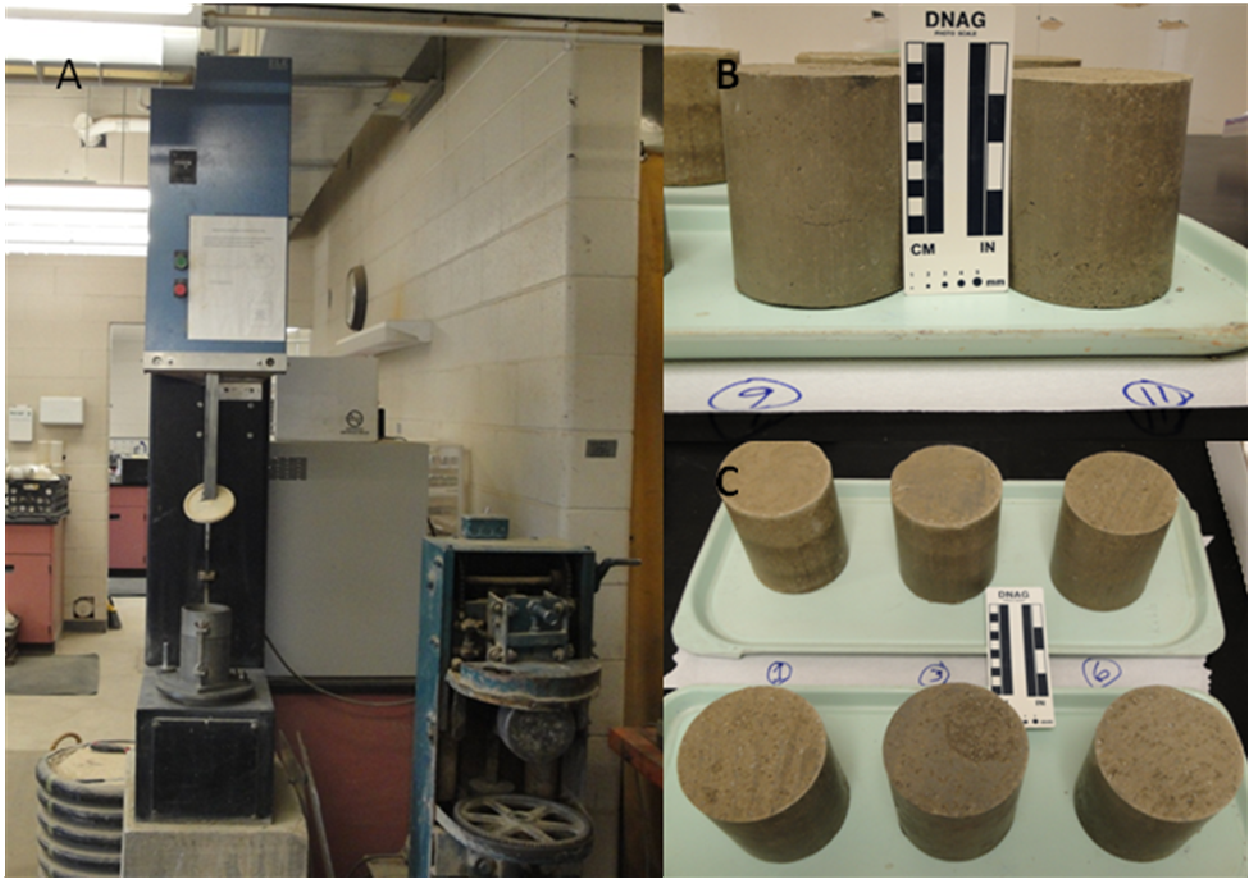


Figure 18. (A) Proctor machine used to produce swell test samples and (B and C) images of resulting swell test sample cylinders.

Samples 1, 2, 3, and 4 were made from soil taken from station 730+80. Samples 5, 6, 7, and 8 were made from soil taken from station 730+00, and samples 9, 10, 11, and 12 were made from soil taken from station 729+00. After being compacted, each of the swell test cylinders was sealed in a plastic bag and left overnight to cure. Samples 1, 3, 6, 8, 9, and 11 were arbitrarily chosen as “dry” (D) samples and 2, 4, 5, 7, 10, and 12 were chosen as “wet” (W) samples. After the overnight cure, the dry samples were removed from the plastic bags, initial measurements of height and circumference taken, and the samples were then left to air-dry for 3 days. The height of each sample was measured at three places 120° apart and the circumference of each of the samples was measured at three heights, bottom, middle and top (Fig. 19). After three days, height and circumference measurements were taken again for the dry samples to determine the amount of shrinkage. A latex sleeve was then slid around each of the dry sample cylinders and porous stones placed on the bottom and top. Measurements of height and circumference were taken again. After three days, the wet samples were removed from the plastic bags, a latex sleeve was placed around each of them and porous stones placed on the bottom and top of each cylinder. The measurements of height and circumference were taken for each of the twelve swell samples each day for a total of 56 days. The average height and average circumference for each sample were calculated each day based on the three measurements taken for each. The average height and circumference were then used to calculate the volume of the specimen. Change in volume for each specimen was calculated by comparison to the initial volumes. Samples 1(D), 2(W), 5(W), 6(D), 9(D) and 10(W) were placed on porous stones sitting on a wire rack in a plastic ice

chest. The chest was filled with deionized water up to the middle of the bottom porous stones. The same setup was used for samples 3(D), 4(W), 7(W), 8(D), 11(D), and 12(W), except that these samples were placed in a 7000 ppm sodium sulfate solution to insure adequate sulfate was available during the experiment and to replicate the conditions employed by Harris et al. (2004).

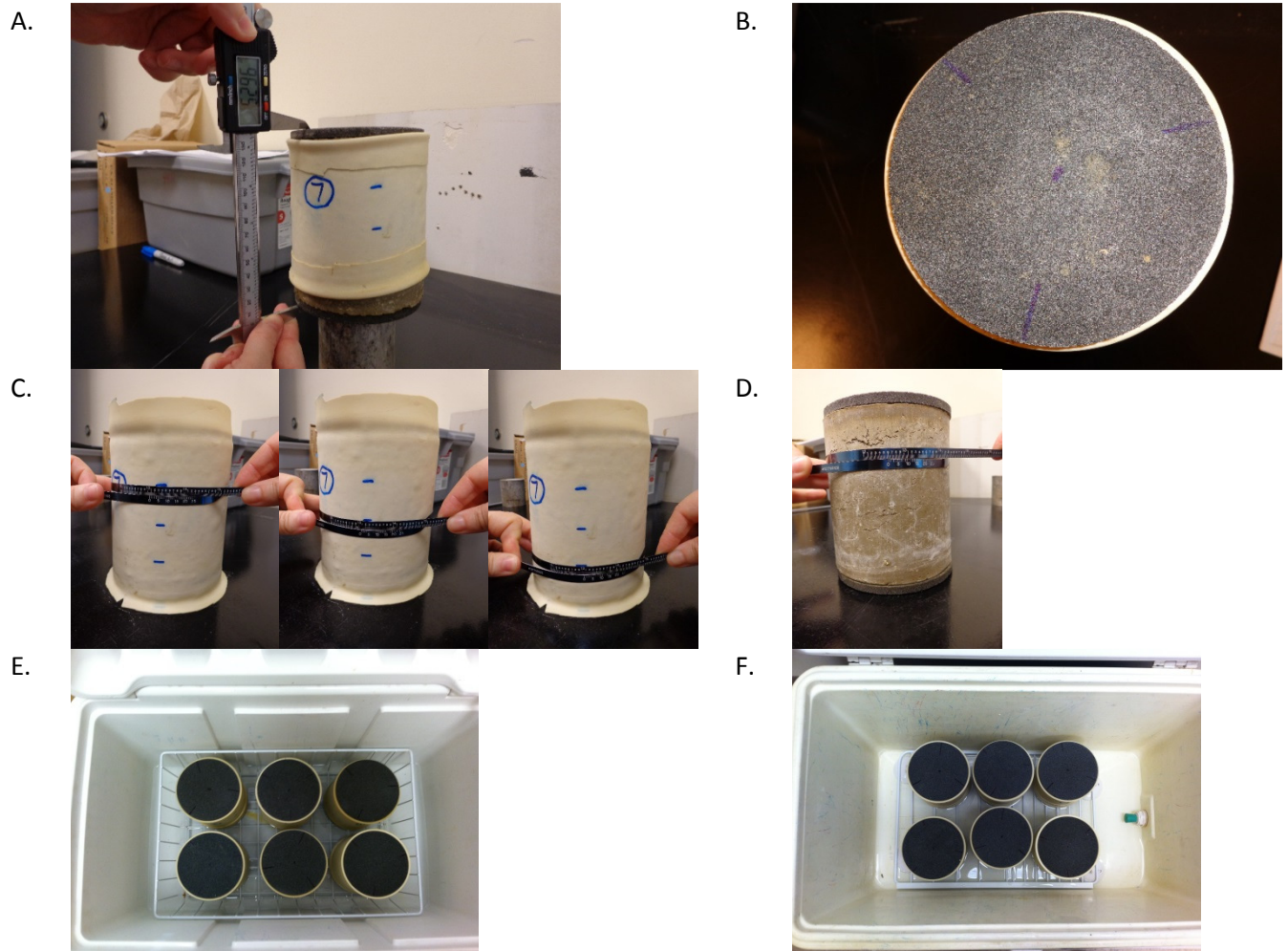


Figure 19. (A) Example of height measurement. (B) Porous stone marked with the three height measurement locations 120° apart. (C) Example of the three circumference measurements: top, middle, and bottom. Note, samples have a latex sleeve. (D) Example of a top circumference measurement without a latex sleeve. (E) Samples 3(D), 4(W), 7(W), 8(D), 11(D), and 12(W) in an ice chest with a 7000 ppm sodium sulfate solution. (F) Samples 1(D), 2(W), 5(W), 6(D), 9(D) and 10(W) in an ice chest with deionized water.

Results

The results of the 56 day swelling test for each sample are plotted in Figure 20. Graph A shows the “wet” samples that were kept in plastic bags for three days before being placed in either deionized water (thick lines) or 7000 ppm sodium sulfate solution (thin lines). Graph B shows the “dry” samples that were air-dried for three days to cause shrinkage before being placed in either deionized water (thick lines) or 7000 ppm sodium sulfate solution (thin lines). Table 4 ranks the samples by highest to lowest amount of swelling.

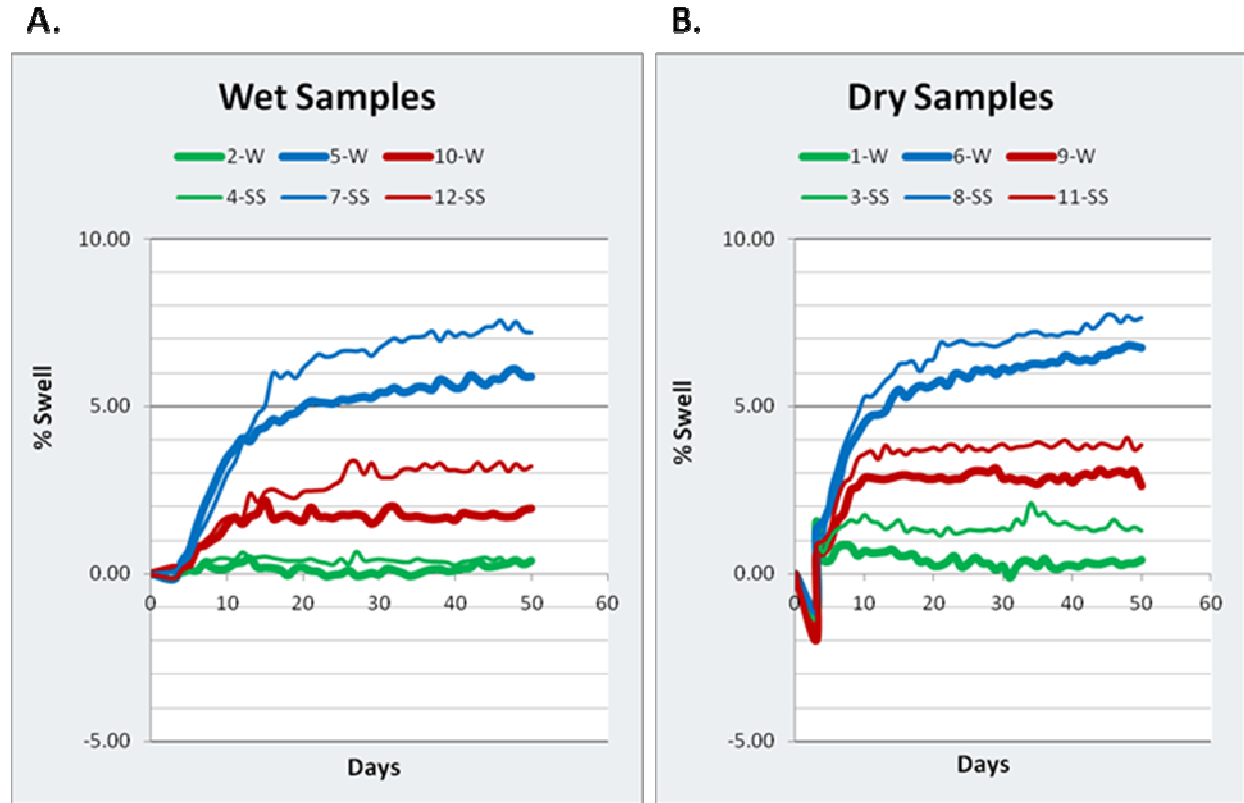


Figure 20. Swelling of test samples over 56 days. (A) Wet swell samples in water (thick lines) or 7000 ppm sodium sulfate solution (thin lines). (B) Dry swell samples in water (thick lines) or 7000 ppm sodium sulfate solution (thin lines).

Table 4: Swell Test Samples Ranked by Maximum Amount of Swelling.

Sample	Station	Max. swell (%)	Deionized water or Na ₂ SO ₄ solution	Dry or Wet	Wet density (PCF)	Weight gain (%)
8	730+00	8	SS	Dry	136	4
7	730+00	8	SS	Wet	136	5
6	730+00	7	DW	Dry	135	4
5	730+00	6	DW	Wet	134	4
11	729+00	4	SS	Dry	137	2
12	729+00	3	SS	Wet	136	3
9	729+00	3	DW	Dry	136	1
10	729+00	2	DW	Wet	137	2
3	730+80	1.5	SS	Dry	132	2
4	730+80	0.5	SS	Wet	131	2
1	730+80	0.5	DW	Dry	130	3
2	738+80	0.5	DW	Wet	130	1

Samples placed in the 7000 ppm sodium sulfate solution swelled slightly more than samples placed in deionized water. In addition, dry samples swelled slightly more than wet samples placed in the sodium sulfate solution. Likewise, dry samples swelled slightly more than wet samples in the deionized water. Soils from station 730+00 swelled the most, followed by soils from station 729+00, and soils from station 730+80 had the least amount of swell. The amount of swelling does not apparently relate to the amount of sulfate initially present as sample 730+80 had the highest and sample 729+00 had the lowest initial sulfate contents (Table 3).

Characterization of samples after the swell test

At the end of the 56-day experiment, the swell test cylinders were removed from the deionized water or sodium sulfate solution baths, and the porous stones and latex sleeves were removed paying particular attention to not disturb the samples. The cylinders were then sawn in half vertically using a diamond tipped saw blade. The split cores were then allowed to air-dry for six weeks. Note, it is important to air-dry the specimens rather than oven-dry them as depending upon the humidity level, ettringite can begin to thermally decompose at temperatures $<80^{\circ}\text{C}$ (Purchez et al., 2006).

Visual inspection of the cylinders after the swell test experiment showed many had fractures that were filled with a white precipitate. In addition, a white precipitate was often found on edges and the top and bottoms of the cylinders (Fig. 21A).

Initially, sample material for SEM/EDAX and XRD analysis was preferentially gathered from the white precipitate areas found on the surface and along fracture fillings. However, the XRD analysis of the white precipitate showed it to be mostly calcite (Fig. 21B), similar to the white precipitate found in the cement-stabilized soils (Figs. 12, 15).

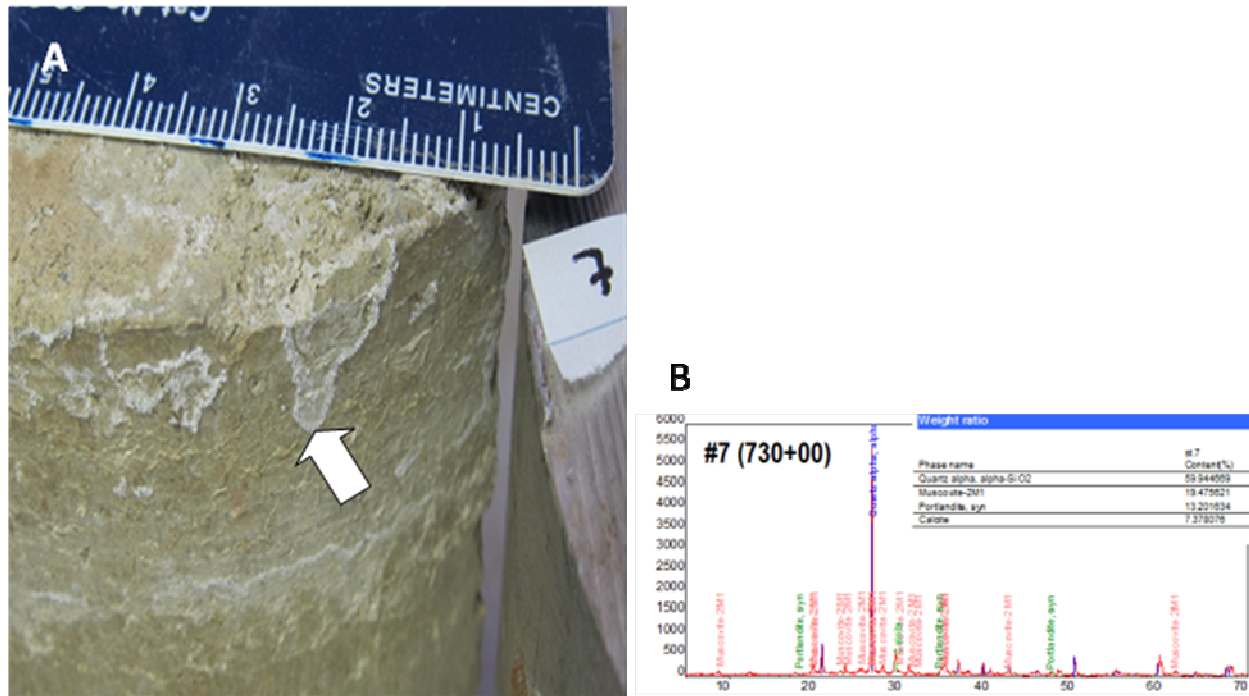


Figure 21. (A) Swell test sample #7 (730+00, SS, Wet) showing white precipitate on surface, and (B) corresponding XRD pattern indicating the white precipitate is mostly calcite (CaCO_3) and portlandite ($\text{Ca}(\text{OH})_2$).

Sampling was then focused on the interior of the split cylinders especially around what appeared to be small vugs or fractures as well as “normal” looking areas. The SEM analysis of these samples showed regions with abundant needle-like bundles of crystals that were confirmed by EDAX analysis and by XRD analysis to be ettringite (Figs. 22, 23).

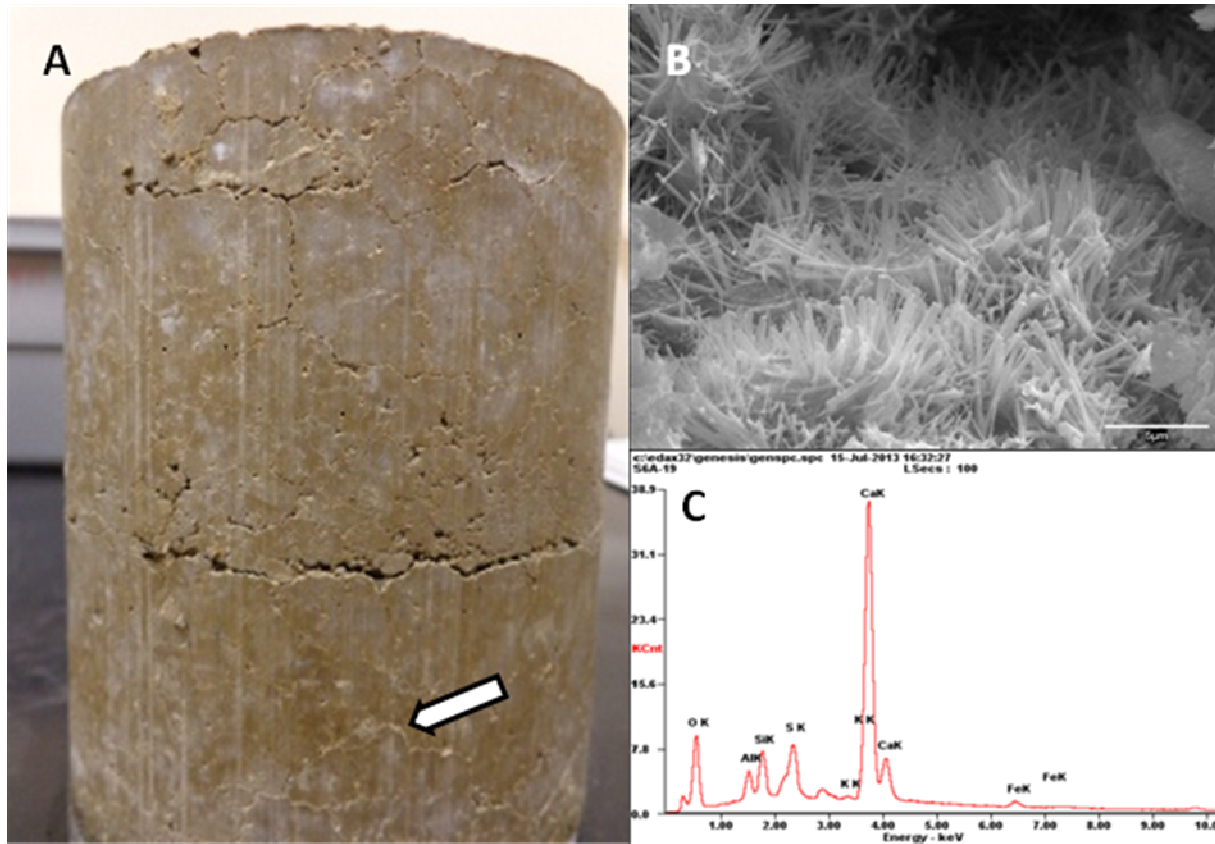


Figure 22. (A) Swell test sample #6 (730+00, DW, Dry) arrow showing location sampled. (B) SEM image of sample material, scale bar = 5 μm. (C) EDAX spectrum for area shown in B indicating the presence of ettringite.

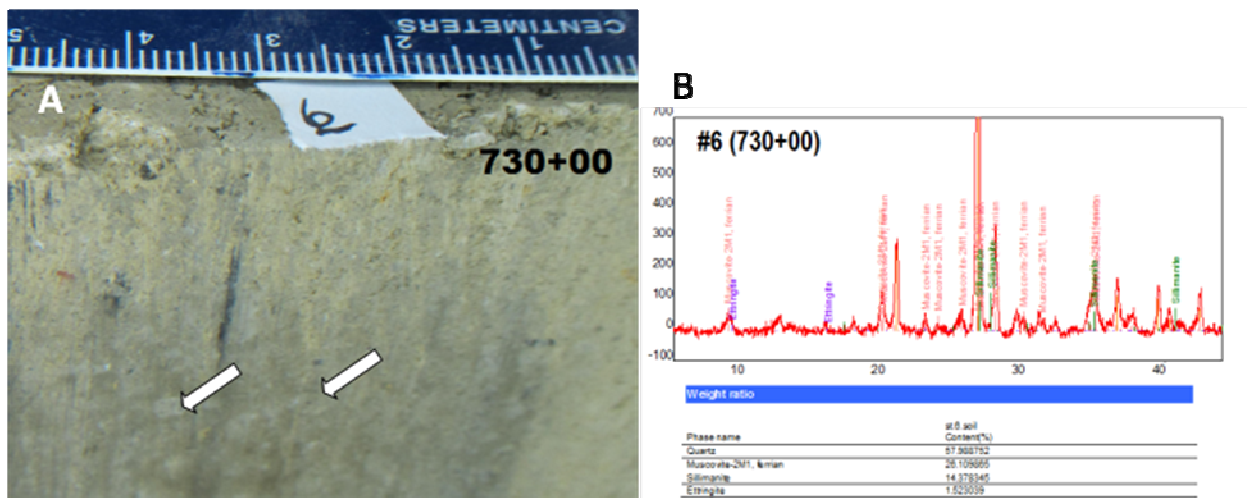


Figure 23. (A) Swell test sample #6 (730+00, DW, Dry) sawn interior surface near top, arrows show locations sampled. (B) XRD pattern of sample confirming the presence of ettringite.

Upon further inspection, ettringite crystals were found throughout all of the test specimens (Fig. 24). Given the heterogeneous nature of its distribution in the swell test samples, it is not possible to quantify the amount of ettringite in each sample, but qualitatively it was more prevalent in the 730+80 samples than in the 729+00 and 730+00 samples even though the 730+80 samples showed the least amount of swelling (Fig. 20, Table 4).

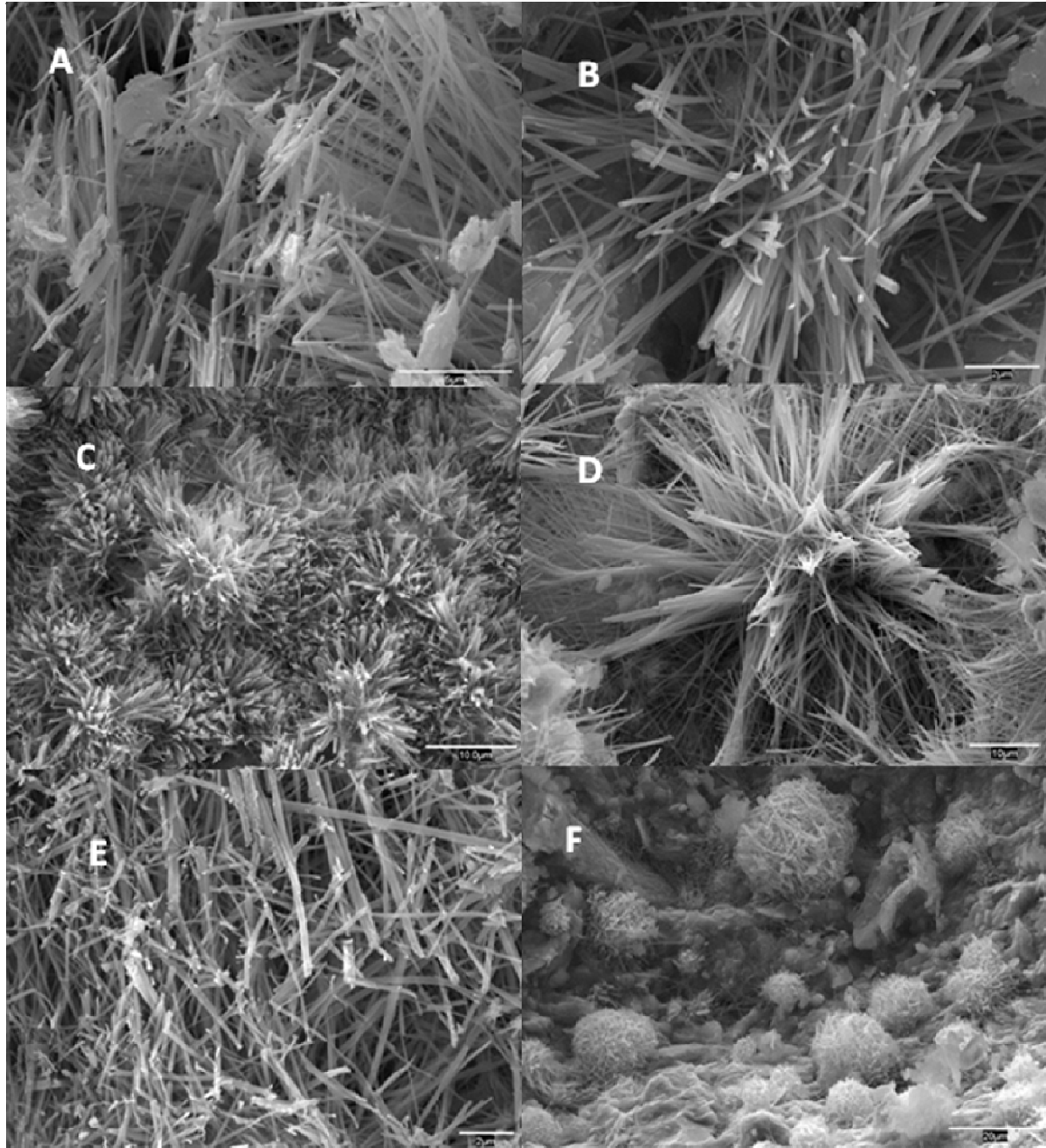


Figure 24. SEM images of ettringite crystals observed in different swell test specimens (A) Sample #1, 730+80, DW, Dry, scale bar = 6 μm . (B) Sample #2, 730+80, DW, Wet, scale bar = 2 μm . (C) Sample #7, 730+00, DW, Dry, scale bar = 10 μm . (D) Sample #9, 729+00, DW, Dry, scale bar = 10 μm . (E) Sample #10, 729+00, DW, Wet, scale bar = 2 μm . (F) Sample #12, 729+00, SS, Wet, scale bar = 20 μm .

DISCUSSION / CONCLUSIONS

There is sufficient sulfate (>4000 ppm), in the form of heterogeneously dispersed gypsum/anhydrite, in natural soils from the Lake County Route 2 site to produce ettringite when stabilized with 6% Portland cement in the presence of water, and to cause significant swelling (up to 8%) that could result in highway heave. As such, our findings are in general agreement with the sulfate risk levels (Table 2) proposed by the Texas Transportation Institute (e.g., Little and Nair, 2009).

The results of the swell test using clayey soils from the Lake County Route 2 area are similar to those reported by Harris et al. (2004) who used a Vertisol sulfate-deficient soil typically found in Texas to which they added gypsum. We found the amount of swelling was slightly greater for samples that were air-dried for 3 days before being placed in contact with water, and also slightly greater for samples in contact with 7000 ppm sulfate solution compared to those in contact with deionized water.

In contrast, the amount of swelling was substantially different between the three different soil samples/stations (Fig. 20). One possible explanation is that the different soils had different initial sulfate contents (Table 3), but the cylinders made using the 730+80 soil which had the highest initial sulfate level yielded the least amount of swelling (Fig. 20). The lack of a correlation between sulfate content and swelling has been noted by others (e.g., Little and Nair, 2009 and references therein). Interestingly, ettringite crystals were found throughout the samples of the 730+80 soils which showed little (<1.5%) swelling, although it has also been reported that in some systems ettringite formation is not associated with expansion (e.g., Hime and Mather, 1999; Odler and Colan-Subauste, 1999).

RECOMMENDATIONS

The amount of swelling observed in our swell test samples is significant (up to 8% in 56 days) and alternative construction practices should be considered as outlined by Harris et al. (2004). It is important to note that the formation of ettringite is not necessarily detrimental and there is not a simple proportionality between the amount of ettringite formed and the amount of expansion (Odler and Colan-Subauste, 1999). Ettringite formed early in the cement hydration process contributes to the strength of concrete (Kosmaka, 1988). In contrast, it is the secondary or delayed ettringite, formed after the cement matrix has developed that is deleterious (e.g., Mehta, 1973). The expansion is believed to be due to topotactic formation of ettringite and to its anisotropic crystal growth (e.g., Ogawa et al., 1981; Odler and Yan, 1994). As such, one alternative construction technique that has been suggested for high sulfate soils (e.g., Berger et al., 2001; Harris et al., 2004) is the process of mellowing where lime/cement stabilized soil is allowed to remain in a soft, loamy state for a period of 1 to 7 days for chemical reactions to occur before compacting to final density. In addition, elevating the moisture contents 3 to 5% above optimum can enhance the chemical reaction rates. Likewise, Harris et al. (2004) have shown that adding smaller grain size (i.e., greater surface area available for reaction) gypsum can increase the rate of the initial chemical reactions and primary ettringite formation.

It is noteworthy that sample 730+80 was ground to pass through a #40 sieve (<425 μm) while samples 729+00 and 730+00 were passed through a much coarser #5 sieve (< 4 mm). Hence, the observation that ettringite was more prevalent in the 730+80 samples after the swell test, and that the 730+80 soil had the highest initial sulfate content, yet the 730+80 cylinders

yielded the least amount of swelling may reflect significant, rapid primary ettringite formation; whereas, the coarser samples had more secondary or delayed ettringite formation.

The SEM analysis of the cement stabilized soils and our swell test samples showed that sometimes the ettringite crystals were flat and more of a coating on the soil particles (Fig. 25 A, B) while at other times the ettringite appears as long needles in loose bundles with radiating flower-like structures (Fig. 25 C, D). The flat crystals coating the soil particles are likely primary ettringite whereas the radiating bundles are secondary. A time-series swell test wherein some samples are mixed but left to cure uncompactd for a day or two, and wherein some swell tests are stopped after a few days rather than running the entire 56 days of this study, then analyzed for the presence and the texture/morphology of the ettringite could refine the role of primary versus secondary ettringite formation and swelling.

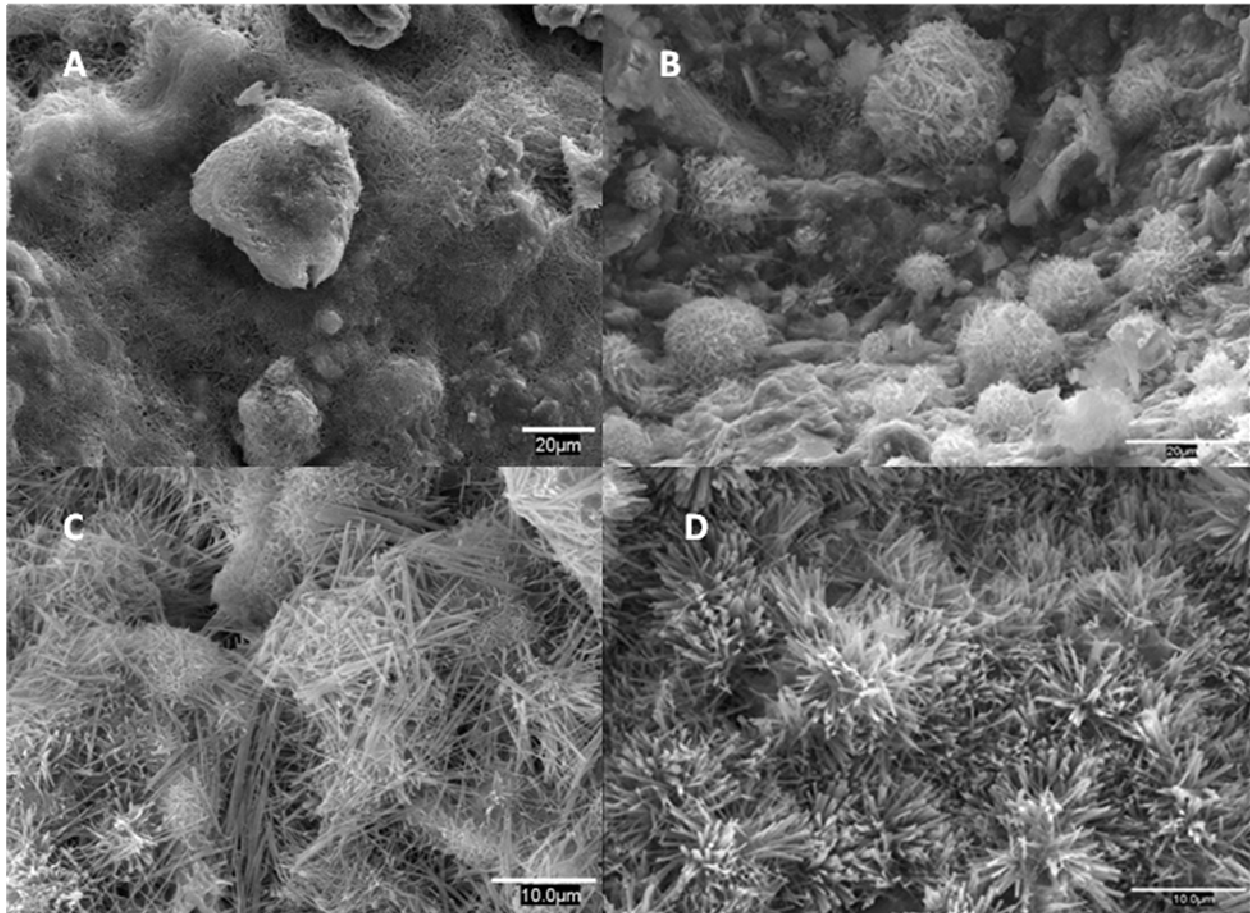


Figure 25. SEM images of ettringite crystals observed in different specimens. (A) 730+80 CSS, primary, scale bar = 20 μm . (B) 730+00, swell, SS, Wet, primary going into secondary, scale bar = 20 μm . (C) 730+80, CSS, secondary, scale bar = 10 μm . (D) Sample #9, 729+00, swell, SS, Wet, secondary, scale bar = 10 μm .

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APPENDIX I. SULFATE TESTING PROCEDURES

- Refer to TxDOT Tex-145-E (determining sulfate content in soils – colorimetric method) procedures.
- Used a Thermo Scientific Orion AQUAfast AQ 3700 Colorimetry meter.
- Pass soil samples through a No. 40 (425 μm) sieve.
- Measure out 10.0 g of soil and place in a HDPE bottle.
- Add 200 ml of deionized water to the soil in the HDPE bottle for a 1:20 ratio and shake the sample vigorously by hand for one minute.
- Let the sample sit for a minimum of 24 hours.
- After 24 hours, gently shake the sample again for one minute.
- Filter the soil solution with a 0.45 μm filter paper.
- Using a pipette and a graduated cylinder, measure out 10 ml of filtrated solution into a beaker (filtrate should be clear; if it is not then filter again).
- Add two drops of concentrated HCl to the beaker and stir.
- Add a barium chloride packet to the beaker containing the filtrated solution with HCl and stir, making sure that all barium chloride crystals dissolve.
- Using a small funnel, pour solution into a colorimeter test vial.
- Wipe the outside of the vial with a Kimwipe to remove any dirt and fingerprints.
- Use either program 355 (sulfate with tablet) or program 360 (sulfate with powder pack) on the colorimeter. Program 360 provides an automatic 5 minute countdown before a reading. The readings for program 355 must be taken manually. Five minutes was determined to be the optimal wait time before taking a reading when barium chloride packets are used.
- Prepare a 10 ml vial of deionized water for zero test calibration. Perform a zero test calibration periodically throughout testing.
- After the addition of the barium chloride packet, wait five minutes and then immediately place sample in the colorimeter for sulfate testing.
- BGSU colorimeter reads concentrations from 5-100 mg, and therefore if results are over range, the solutions must be diluted.
- Solutions should be prepared and sulfate levels should be determined as follows:
 - 1:20 ratio – 10 ml of filtrate
 - If result is “below the measuring range,” report as < 100 ppm.
 - If result is “overrange,” then proceed to 1:40 ratio.
 - If reading is given, convert mg reading to ppm by multiplying mg by 20.
 - 1:40 ratio – 5 ml of filtrate and 5 ml of deionized water
 - If result is “overrange,” then proceed to 1:80 ratio.
 - If reading is given, convert mg reading to ppm by multiplying mg by 40.
 - 1:80 ratio – 5 ml of filtrate and 15 ml of deionized water. Make solution, stir, and then measure out 10 ml of solution with a pipette. Add HCL and barium chloride to the 10 ml of solution.
 - If result is “overrange,” then proceed to 1:160 ratio.
 - If reading is given, convert mg reading to ppm by multiplying mg by 80.

- 1:160 ratio – 5 ml of filtrate and 35 ml of deionized water. Make solution, stir, and then measure out 10 ml of solution with a pipette. Add HCL and barium chloride to the 10 ml of solution.
 - If result is “overrange,” then report results > 8000 ppm.
 - If reading is given, convert mg reading to ppm by multiplying mg by 160.
- Wash all glassware and rinse three times with deionized water between sample preparations.

APPENDIX II. PROCEDURES FOR SYNTHESIZING ETTRINGITE

- Add 2.57 g of calcium oxide (CaO) to a 1000 ml beaker and fill to the 1 L (1000 ml) line. Stir solution with a magnetic stir bar for 2 hours.
- Add 2.61 g of aluminum sulfate (AlSO₄) to a 1000 ml beaker and fill to the 1 L (1000 ml) line. Filter solution through a Whatman 0.45 micron filter paper and store solution in a 1000 ml flask.
- After two hours, filter the calcium hydroxide solution twice with a Whatman 0.45 micron filter paper and store solution in a 1000 ml flask.
- Using a graduated cylinder, measure out 178 ml of CaOH solution and add to a 500 ml flask. Setup a nitrogen gas bubbler and attach to the 500 ml flask. The nitrogen gas prevents CO₂ from reacting with CaOH to form calcite instead of ettringite. Bubble the CaOH solution for at least two hours, but overnight provides better results.
- Add 222 ml of AlSO₄ to the 500 ml flask containing the bubbled CaOH solution and bubble the mixed solution overnight. A fuzzy, white precipitate should form within an hour of mixing the solutions.
- Scrape the precipitate from the sides of the flask and filter the white precipitate in flask with a Whatman 0.45 micron filter paper.
- Leave the precipitate on the filter paper and place in a dessicator overnight to dry.
- NOTE, do not place ettringite crystals in a drying oven as the ettringite can begin to thermally decompose at <80°C.
- Verify with a petrographic microscope, XRD, and SEM/EDS to determine that ettringite and not calcite was formed.

APPENDIX III. SWELL TEST SAMPLE DATA

Sample	Station	Soil (g)	Cement (g)	Water (g)	Weight mold (g)	Water (%)	Density wet (PCF)	Density dry (PCF)
1	738+80	2254	136	380	1933	16	130	110
2	738+80	1850	111	400	1931	20	130	104
3	738+80	1850	111	350	1966	18	1320	109
4	738+80	1850	111	350	1945	18	131	108
5	730+00	1850	111	350	1988	18	134	110
6	730+00	1850	111	320	2008	16	135	113
7	730+00	1850	111	300	2023	15	136	116
8	730+00	1850	111	300	2014	15	136	115
9	729+00	1850	111	300	2024	15	136	116
10	729+00	1850	111	280	2036	14	137	118
11	729+00	1850	111	280	2028	14	137	117
12	729+00	1850	111	280	2028	14	137	117