Calcium-Based Stabilizer Induced Heave in Oklahoma Sulfate-Bearing Soils

FINAL REPORT – FHWA-OK-11-03
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by

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16. ABSTRACT

The addition of lime stabilizers can create problems in soils containing sulfates. In most cases, lime is mixed with expansive soils rendering them non-expansive; however, when a certain amount of sulfate is present naturally in expansive soils, the lime reacts with gypsum to create an expansive mineral ettringite and causes the soil to become more expansive.

The goal of this study was to provide a more accurate sulfate determination method and determine the physical, chemical, and mineralogical characteristics of Oklahoma soils that may predict vulnerability to adverse reactions from calcium-based stabilizers and attempt to relate these characteristics to free swell. Through this project, it was found that the current method of testing soil sulfate, Oklahoma Highway Department's (OHD) L-49, resulted in substantial sulfate solubility issues and did not in all cases accurately determine sulfate concentrations in soils. Several bench studies were performed to understand the solubility problems and modifications were proposed.

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(Modern Metric) Conversion Factors

APPROXIMATE CONVERSIONS TO SI UNITS				
SYMBOL	**WHEN YOU KNOW**	**MULTIPLY BY**	**TO FIND**	**SYMBOL**
LENGTH				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
AREA				
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
VOLUME				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: volumes greater than 1000 L shall be shown in m^3				
MASS				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
TEMPERATURE (exact degrees)				
^{o}F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	^{o}C
ILLUMINATION				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
FORCE and PRESSURE or STRESS				
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS				
SYMBOL	**WHEN YOU KNOW**	**MULTIPLY BY**	**TO FIND**	**SYMBOL**
LENGTH				
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
AREA				
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
VOLUME				
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
MASS				
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
TEMPERATURE (exact degrees)				
^{o}C	Celsius	1.8C+32	Fahrenheit	^{o}F
ILLUMINATION				
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
FORCE and PRESSURE or STRESS				
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.(Revised March 2003)

Disclaimer

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List of Symbols

ENGLISH

e_0 = Initial Void Ratio (unitless)
w_c = Water Content (%)
CR = Compression ratio (unitless)
SR = Swelling ratio (unitless)
C^*_c = Intrinsic compression index (unitless)
C_s = Swell index (unitless)

GREEK

γ_T = Total Unit Weight (kg/m^3)

Executive Summary

The addition of lime stabilizers can create problems in soils containing sulfates. In most cases, lime is mixed with expansive soils rendering them non-expansive; however, when a certain amount of sulfate is present naturally in expansive soils, the lime reacts with gypsum to create an expansive mineral ettringite and causes the soil to become more expansive.

The goal of this study was to provide a more accurate sulfate determination method and determine the physical, chemical, and mineralogical characteristics of Oklahoma soils that may predict vulnerability to adverse reactions from calcium-based stabilizers and attempt to relate these characteristics to free swell.

Through this project, it was found that the current method of testing soil sulfate, Oklahoma Highway Department's (OHD) L-49, resulted in substantial sulfate solubility issues and did not in all cases accurately determine sulfate concentrations in soils. Several bench studies were performed to understand the solubility problems and modifications were proposed. The solubility of gypsum and methods to test soil sulfate became a major focus of this research. Several testing methods were used from various sources as well as some modified and devised methods to find a more accurate method. The most accurate method proved to be centrifuging the samples with the addition of $NaCO_3$. Understanding soil sulfate solubility and determining a more precise method of testing for soil sulfate will significantly help with planning the use of stabilizers in many engineering projects.

Laboratory experiments have addressed threshold determinations for the sulfate concentration above which, lime stabilization causes sulfate-induced heave. Previous results found in the literature have placed the threshold in natural soils between 700 and 8000 parts per million, which is a large range. Since locating natural soils with incremental differences in sulfate proved to be difficult, this research program focused on manufacturing soils with controlled amounts of sulfate to more closely pinpoint a threshold level where the sulfate-induced heave began. These soils were mixed in varying percentages along with reagent grade gypsum and 5% lime by weight to determine the sulfate threshold above which using lime for soil stabilization is no longer viable. 1-D free swell tests were performed with different mixtures of Kaolinite and Bentonite with varying amounts of sulfate to determine a threshold for sulfate-induced heave.

1 Introduction

1.1 General

Lime and other calcium-based stabilizers are added to soils in order to reduce their plasticity, increase their shear strength, reduce their compressibility, and reduce their tendency to undergo volume change when subjected to variations in water content. In simple terms, additives like lime render highly plastic expansive soils non-plastic and non-expansive. However, when a soil stabilizer such as lime is added to soil containing soluble sulfate the resulting reactions can have the opposite effect and actually make the volume change tendencies much more devastating.

Soils and shales containing gypsum are common in Oklahoma; gypsum is a primary source of soluble sulfate. Generally, when soils/shales containing soluble sulfates are mixed with lime and given access to water, there is the potential for significant increases in soil volume (swelling) due to the formation of calcium-aluminum-sulfate-hydrate minerals such as ettringite. Based on a review of the literature (Austin White Lime 2000; Harris et al. 2004; Hunter 1988; Kota et al. 1996; Mitchell 1986; Perrin 1992; Petry and Little 1992), it appears that soluble sulfates may be problematic at sulfate contents as low as 0.3% (3000 ppm); however, if any soluble sulfate is detected, prudence warrants that appropriate design and mix procedures should be followed.

When soluble sulfates are present and stabilization is required, measures must be taken to counter the adverse effects of adding a calcium-based stabilizer. Such measures typically aim at promoting and accelerating the adverse reactions in the soil prior to compaction. For example, this might include using a prolonged mellowing period (typically 3 to 7 days) after mixing and prior to final compaction, providing plenty of water to promote the reactions during mixing (typically 3 to 5 percentage points above optimum), and providing additional water during mellowing and curing (Austin White Lime 2000). Finally, stabilization with a calcium based stabilizer may be ruled out as a viable option should the potential for sulfate-induced heave be too great.

While significant research has been performed in some areas of the country, such as at the Texas Transportation Institute (e.g. Bredenkamp and Lytton 1994; Harris et al. 2002; Harris et al. 2004; Hunter 1988; Kota et al. 1996), there is a need to study sulfate induced heave in Oklahoma soils and develop a local database of soils susceptible to this problem. This is especially true given that the geochemistry of soils can vary widely within and across geographic regions; the geochemistry is critically important in the resulting chemical reactions. Of particular need is to develop indicators that correlate strongly with the potential for sulfate-induced heave. Some have suggested threshold levels of soluble sulfate, above which the adverse reactions occur; however, there is lack of data and lack of agreement in the literature as to what this threshold might be (Hunter 1988; Kota et al. 1996; Mitchell 1986). In Texas (Harris et al. 2004), the threshold appears to be about 3000 ppm; however, some data suggests problems may occur for concentrations as low as 700 ppm (Hunter 1988) in Las Vegas. Whether a threshold of 3000 ppm, similar to Texas, is reasonable for Oklahoma soils is questionable (personal communication with Dr. James Nevels, PE of ODOT, Sept. 2005). It is reasonable to assume given the complexity of clay behavior and the tremendous variations in clay-pore fluid chemistry that exist in nature, that no single threshold level of soluble sulfate will suffice in all situations. A primary goal of this research was to study the mineralogical and chemical characteristics of sulfate bearing Oklahoma soils to assess parameters that reveal susceptibility to sulfate-induced heave. In addition, the mechanical response of these soils to lime treatment and saturation with water was examined using the oedometer. A similar approach was successfully used by researchers in Texas (Bredenkamp and Lytton 1994). In this way the link between chemical and/or physical indicators and heave susceptibility can be identified. Soils with varying amounts of added sulfate (reagent grade gypsum) were also tested to supplement the natural clay database and help establish sulfate "thresholds."

1.2 Objectives

The overriding goal of this research was to reveal the physical, mineralogical, electrical, and chemical characteristics of Oklahoma soils that are vulnerable to adverse sulfate reactions due to calcium-based stabilizers. In achieving this goal, ODOT's current method of soil-sulfate testing was critically assessed to determine the most accurate and repeatable soil sulfate test methodology possible. The research objectives were met through a detailed study of clay mineralogy/chemistry and physical characteristics of several natural sulfate-bearing clay soils from Oklahoma. In addition, the mechanical response of these soils to calcium-based stabilizer treatment and saturation with water were examined using the oedometer. In this way, the link between chemical and/or physical indicators and heave susceptibility were identified. Specific research objectives and associated tasks for the proposed research were as follows.

Objective A: *Determine an accurate, repeatable and economical soil sulfate test methodology.*
Task A.1: Formulate and validate an improved soil sulfate test methodology to be used by ODOT.

Objective B: *Collect and characterize selected sulfate bearing soils in Oklahoma.*
Task B.1: Through consultation with ODOT personnel, identify soils containing sulfates and obtain sufficient samples to add to the testing program and soil database and collect available information on the geology and soil properties of test site locations.
Task B.2: Conduct basic index property and physical property tests on test soils.
Task B.3: Conduct laboratory tests to determine the electrical and chemical properties of test soils.
Task B.4: Conduct free swell tests on selected compacted test soils in an oedometer apparatus with and without calcium-based stabilizer additive.
Task B.5: Conduct free swell tests on carefully prepared and controlled manufactured single mineral and mixed mineral compacted soils in an oedometer apparatus, with and without sulfate and with and without lime to try and isolate ettringite formation from other soil parameter heave influences.

Objective C: *Identify soil properties that are indicators of severity of sulfate induced heave caused by calcium-based stabilizers by the end of the second year.*
Task C.1: Use the centralized sulfate-soil database for a multivariable parameter (ANOVA) analysis and statistically examine the relationship between *individual* soil properties and *combinations* of soil properties and volume change behavior measured in the laboratory in both the natural and manufactured soils.
Task C.2: Validate the statistically determined relationships with additional test soils.

1.3 Report Layout

This report is organized into seven chapters. Chapter 2 reviews published studies on sulfate induced heave in lime stabilized soils across the country. Chapter 3 provides detailed descriptions of the test procedures. Chapter 4 presents the results of the index testing and XRD analysis. Chapter 5 presents the soil sulfate testing results. Chapter 6 discusses the oedometer results for both the natural and pure clays. Finally, Chapter 7 presents a summary and conclusions of the present work and recommendations for future work.

2 Literature Review

2.1 General

The problems caused by sulfate-induced heave have been studied for over twenty years (Harris 2003). Sulfate-induced heave causes millions of dollars worth of damage every year in the United States (Puppala et al. 2002). It is a problem that occurs when lime, a typical soil stabilizer, is added to soil containing gypsum or other sulfate bearing minerals. Currently, one of the most economical and accepted means to stabilize expansive soils is to add lime to the soils before compaction. Lime stabilization started as an aid in roadway maintenance and now covers all highway construction (Eades 1966). This method reduces the soil's plasticity and its ability to undergo volume change when wetted or dried. Lime improves the plasticity, workability, and strength properties of a soil (Thompson 1966). Lime stabilization increases the soil's bearing strength and permeability, while reducing potential volume changes (Hunter 1988), therefore rendering a stronger soil mixture that will react less, or not at all, to changing moisture conditions. Adding lime converts the soil to a rigid or granular mass where the particles are strongly bound by pozzolanic cementitious compounds that are formed by reactions with soil silica and lime in the presence of water (Sivapullaiah 2006). Three reasons for stabilizing natural soils beneath pavements include providing a working table for construction equipment during wet weather, reducing roughness due to expansive clay subgrades, and to provide a permanent layer in the pavement structure that is stiffer than the natural soil (Rajendran 1997). However, treating soils that contain natural sulfate with lime or other cementitious material may lead to a problem that is as bad as or worse than leaving the soil untreated in its natural state (Burkart 1999).

Sulfate induced heave has become a problem because more and more departments of transportation are using calcium based chemical stabilization on their roadway subgrades to increase the strength of the soil beneath the pavement. Lime stabilization is a common technique used to reduce the shrink-swell potential in plastic clays. The addition of lime also increases the strength of the soil, increases the permeability, and reduces the dry density (Hunter 1988; Petry and Das 2001). The stabilization occurs by cation exchange, flocculation of the clay particles, carbonation reactions, and pozzolanic reactions (Hunter 1988). Cation exchange and flocculation make the soil more workable, and the carbonation and flocculation reactions cement the soil particles increasing the strength (Hunter 1988). When sulfate is present in lime-treated soil, it can interfere with the long-term pozzolanic reactions (cementation process) between the lime and silica or alumina in the clay particles (Mitchell 1986; Hunter 1988). Interference with the pozzolanic reactions reduces the long-term strength gain in the soil, but cation exchange, flocculation, and carbonation are not affected. Thus, there might not be an initial sign that the soil is going to have problems with heaving.

Volume change resulting from ettringite formation is a problem seen more often in clay rich soils than in sandy soils (Puppala et al. 2005) because clay-sized particles have a high surface area, making them highly reactive. The addition of lime to clay increases the pH of the soil to about 12.3, which helps dissolve the clay minerals alumina and amorphous silica (Mitchell 1986; Hunter 1988; Petry and Das 2001). Aluminum from the soil combined with the calcium from lime or other stabilizers, soluble sulfate in the soil, and water react to form ettringite. The chemical reaction for ettringite formation is as follows:

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

Equation 1

Once ettringite starts to form, it can grow in its mostly pure form until the temperature drops below 15°C (Hunter 1988), or until the reactants present in the soil are used up in the chemical reaction (Puppala et al. 2005). In addition to the chemical elements necessary for ettringite formation, the mineralogy of the soil, activity of aqueous ions, and reaction kinetics all effect ettringite formation (Little et al. 2010). Ettringite formation affects clay properties such as consistency, compaction characteristics, and the cation exchange process (Rajasekaran and Rao 2004). Ettringite can be extremely detrimental because it has the potential to swell up to 250 percent of its original volume (Puppala and Cerato 2009).

There are two theories on the expansion of ettringite. Some believe the crystallization pressure, crystal interlocking, and oriented crystal growth cause the expansion in the matrix, but other researchers believe water absorption by the ettringite molecule is the reason it expands (Nair and Little 2009). In all likelihood, the expansion is a combination of the two, but either way, water is crucial to ettringite expansion (Nair and Little 2009). Initial water used in mixing and compaction of stabilized soils is too low to dissolve all sulfates available into solution for ettringite formation (Little et al. 2010). Water from an external source, such as heavy rainfall, is able to dissolve more of the soluble sulfate than the mix water, making the ions more available for ettringite formation and expansion later on.

Common forms of sulfate found in soil include gypsum, anhydrite, barite, and jarosite (Little et al. 2010). The dominant sulfate form in soil is gypsum, a common rock-forming mineral, classified as an evaporite, that has precipitated from lakes and sea water (Puppala and Cerato 2009; Herrero et al. 2009). The solubility of gypsum is approximately 2.58 grams per liter of water (Little et al. 2010), but depends on the pH. Gypsum has a high solubility at a low pH and the solubility decreases as the pH increases (Petry and Das 2001).

Natural soil sulfate is most often present as gypsum. Gypsum crystals can be visible to the naked eye, but can also be so small that you must use a microscope or scanning electron microscope to see them (Jafarzadeh 1992). Gypsum is often found below the water table, but if it is above the water table, it commonly precipitates interstitially within the host sediment or as huge lenses (Livneh 1998). When a certain amount of sulfate is present naturally in the expansive soil, lime (CaO) mixes with gypsum ($CaSO_4 \cdot 2H_2O$) in a basic environment (pH between 11 and 13) to create an expansive sulfate mineral, known as ettringite and causes the soil to become more expansive. The drop in pH with this reaction and the formation of the high swelling compounds like ettringite and thaumasite due to lime-sulfate reactions cause several adverse effects on the engineering behavior of a soil (Rajasekaran 1997). Removal of sulfate enriched material by excavation increases “waste disposal costs,” so studies of ettringite and its long-term stability are needed (Rajasekaran 2005). This mineral will continue to form as long as there are sufficient amounts of reactants present in the soil (Puppala 2005). The combination of sulfates in the soil, calcium in the stabilizer, aluminum in the clay structure, and water create calcium-aluminate-sulfate-hydrate minerals, such as ettringite. The chemical formula for ettringite is $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, which holds large amounts of water in its structure, and has the potential to swell 250% (TxDOT 2000).

The fact that ettringite holds so much water within its structure, explains why swelling is much more significant when this reaction occurs in the soil. Ettringite has a larger volume than its original constituents, which results in massive swelling and cracking when it forms in sufficient amount (Rao 2005). The heave due to the ettringite formation can sometimes be higher than one foot (Chen 2005). The kinetics of the ettringite precipitation-dissolution reaction are fast and come to steady state in about 150 hours at a pH of 11.5 (Little 2005). A picture of the ettringite crystal can be seen in Figure 2-1.

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Figure 2-1: Ettringite crystal from http://www.mindat.org/min-1414.html

The ettringite formation process was given by Harris (2004) as:

$Ca(OH)_2 \rightarrow Ca^{2+} + 2(OH)^-$

(Ionization of lime; pH rises to 12.3)

$Al_4Si_4O_{10}(OH)_8 + 4(OH)^- + 10H_2O \rightarrow 4Al(OH)^{4-} + 4H_4SiO_4$

(Dissolution of kaolinite at pH > 10.5)

$CaSO_4\cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$

(Dissolution of gypsum)

$6Ca^{2+} + 2Al(OH)^{4-} + 4(OH)^- + 3(SO_4)^{2-} + 26H_2O \rightarrow Ca_6[Al(OH)_6]_2\cdot(SO_4)^3\cdot 26H_2O$

(Formation of ettringite)

Lime ionizes as well as the naturally present gypsum when it comes in contact with water. The gypsum dissolves into ions of calcium and sulfate. The kaolinite mineral also dissolves partially into its ions to give the aluminum for the reaction. All of these ions come together under the right conditions to form ettringite as seen in the final reaction. This reaction with lime is most likely to occur when the soil has a large clay fraction and when the moisture content of the soil is likely to increase above the level at which it was compacted (Sherwood 1962). Two mechanisms thought to lead to ettringite formation are the topotactical mechanism, which has to do with internal displacements within the molecule, and the through-solution mechanism, which is where ions from the reactants enter the solution (Havlica 1992).

Gypsum is a common rock forming mineral composed of calcium sulfate dehydrate that is a primary source of sulfate in soils. It is one of the most commonly occurring sulfate minerals and occurs as geologic deposits and constituents of soils (Eswaran 1991). It is classified as an evaporite and forms as a precipitate from lakes and sea water. Western Oklahoma has a tremendous amount of natural sulfate in the form of gypsum ($CaSO_4 \cdot 2H_2O$) present in the soils and shale, which makes these soils susceptible to sulfate induced heave if lime stabilization is used. These visible gypsum crystals in Western Oklahoma are likely to have formed under Le Chatelier's advancement of the general theory that when a system of anhydrous constituents that are unstable in water reacted, they produced a solution that was supersaturated with respect to the stable system of hydrated products (Lea 1949).

Figure 2-2 shows a typical gypsum outcrop as seen in Western Oklahoma.

Figure 2-2: Outcrop containing gypsum in Western Oklahoma

Fine-grained soils in the desert southwest of the United States contrast with other soils in different areas because they often contain large amounts of sulfates and carbonates (Mitchell 1986). The United States is not the only area that has these gypsum-containing soils. Eastern Saudi Arabia has expansive soils that contain gypsum and anhydrite (Azam 1998). British soils contain naturally occurring sulfates usually in the form of calcium sulfate but also magnesium and sodium sulfate (Sherwood 1958). Soils with gypsum are common across the United States. Figure 2-3 shows the locations of soil with gypsum across the U.S.

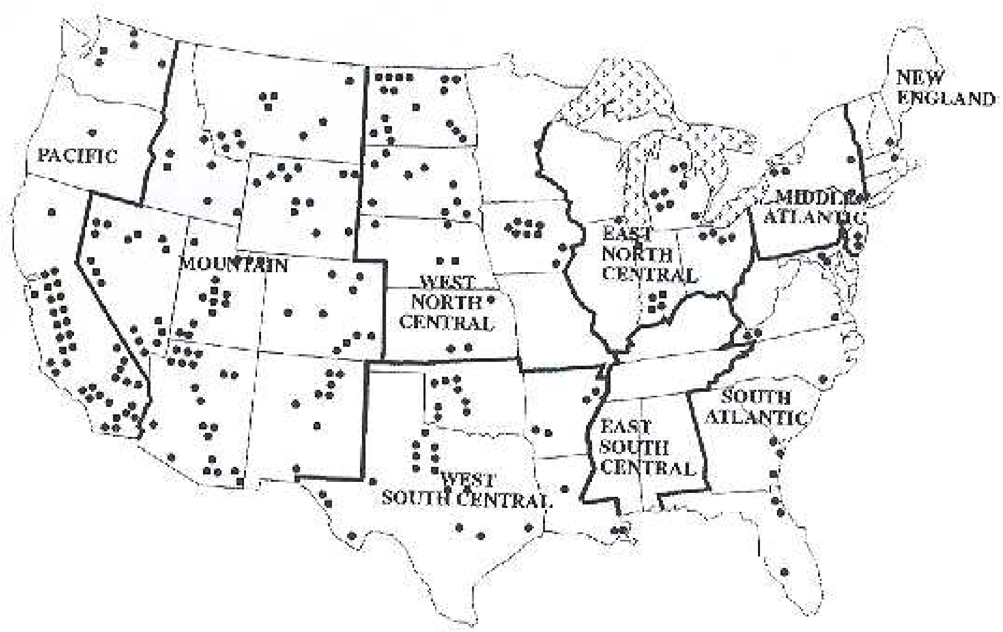


Figure 2-3: Soils containing gypsum in the U.S. (Kota 1996)

2.2 Case Studies

The large majority of sulfate-induced heave problems are in Texas, Nevada, Louisiana, Kansas, Oklahoma, and Colorado because lime and cement are frequently used to stabilize soil subgrades that are rich in natural sulfates (Puppala 2004). An example of sulfate induced heave damage is explained in Chen’s (2005) paper, which discusses an 8.8 mile section of road on U.S. 82 in Texas that was treated with lime stabilization and heaved due to expansion causing $12.7 million dollars in damage (Chen et. al. 2005). This example also illustrates how important it is to test many different locations in a construction area because; in this particular case study, the west side of the project did not experience heave and had different soil mineralogy.

An example of sulfate heave damage can be seen in Figure 2-4. Notice that this stretch of U.S. 67 would no longer be drivable due to differences in elevation from one section of the road to the next. Thus, from examples like Figure 2-4, it is important to know whether or not clay soils contain sulfate, and in what quantities, before adding calcium-based stabilizers.

Figure 2-4. Sulfate Heave on U.S. 67 in Waxahachie, TX from Harris et al. 2003

A particular highway failure case occurred on Stewart Avenue in Las Vegas, Nevada where heave in some parts of the pavement exceeded 30.48 cm. Often the adjacent pavement had also been heaved so that the maximum uplift was hard to gauge (Hunter 1988). Other cases involving sulfate induced heave in lime stabilized soils have been noted in Texas, Kansas, and Utah. Another case that involved sulfate attack on cement-stabilized sand was on Bush Road in Chatham County, Georgia near Savannah. Unexplained bumps formed in the roadway, and it was later found that they were due to the formation of ettringite. The well water that they used to mix with the cement and sand contained sulfates (Rollings 1999). Several miles of park roads and auxiliary airfield in Texas had severe pavement distress due to vertical and lateral heave of the lime-stabilized clay subgrade. In some places the buckling and shearing was as much as 12 inches (Perrin 1992). While significant research has been performed in Texas, research of Oklahoma soils is needed due to the significant differences that can exist in soils across geographic regions.

In 2004, several miles of Oklahoma State Highway 412 failed due to sulfate induced heave. This failure cost the State of Oklahoma millions of dollars to repair. A picture of the damage to the roadway on this Oklahoma highway is shown in Figure 2-5. This particular area of western Oklahoma is believed to have once been under the ancient Western Interior Sea during the Cretaceous period. This possible oceanic condition would be ideal for the formation of gypsum deposits. An example of gypsum formation from sea water occurred in Southwestern Texas. The gypsum precipitates from highly saline sea water which periodically moves in wind-blown sheets across the surface of the mudflats and sinks into underlying sediments (Masson 1955).

Figure 2-5 shows a cross-section view of Highway 412 after the sulfate-induced heave damage occurred. As one can see, the subbase soil swelled after it was mixed with lime. Because the subbase soil used came from a borrow source that contained large amounts of gypsum, the ettringite reaction occurred and ruined this section of roadway.

Figure 2-5: Cross-section of Highway 412 in Woodward, OK from Dr. Jim Nevels

2.3 Methods for Determining Sulfate Content

It is difficult to determine the actual amount of sulfate in the soils, but it is critical since this is the main mineral that causes the ettringite to form (Harris et. al. 2002). The structures affected by this geotechnical problem include embankments, airfields, highway pavements, and building structures (foundations) (Puppala et. al. 2002). There are different methods that have been used to try to determine sulfate content. TxDOT uses a gravimetric technique which takes 3 days to perform, and the results vary greatly. The ion chromatography (IC) method is faster to perform and produces more accurate results than gravimetric analysis at lower concentrations (Harris 2003). However, IC requires expensive equipment and experimental technicians. One method for determining gypsum content in soils is based on loss of crystal water of gypsum when it is heated to 105°C (Nelson 1978). There are two methods described in a paper by Lagerwerff (1965). One method involves determining the gypsum unsaturation by taking electrical conductivity measurements before and after saturating the extract with reagent grade gypsum. The second method is performed by precipitating the gypsum in the dilute soil extract with acetone (Lagerwerff 1965). Another method converted soil gypsum into $CaCO_3$ (s) and Na_2SO_4 by ultrasonic dispersion of the samples twice with 25 mL increments of 0.5M Na_2CO_3 so that the sulfates were now in a completely soluble compound (Berigari 1989). Some of the methods mentioned in Puppala (2002) are the Texas Department of Transportation Method in Tex-620-J, the U.S. Army and Air Force Method in TM 5-822-14/AFJMAN 32-1019, and the University of Texas at Arlington or UTA Method (1994 and 2000) (Puppala et. al. 2002). The United Kingdom has problems with sulfates in the soil attacking and degrading concrete. They use a total sulfur method for determining sulfate content, and it is described in a TRL report (Reid 2001). Their method uses combustion techniques which involve the rapid heating of the sample using an induction furnace in an oxidizing atmosphere at high temperature with the assistance of a combustion catalyst and the determination of the evolved sulfur dioxide gas (Reid 2001). These tests and their similarities and differences with the ODOT OHD-L49 and TRL methods are summarized in Table 2-1

Table 2-1: Test methods from Puppala 2002 compared with ODOT and TRL methods

Method	Similarities & differences
Tex-620-J	• 1:10 dilution ratio • No centrifuging • Heat near boiling for 24 hours • No acid added • Barium sulfate precipitation
US Army & Airforce	• 1:30 dilution ratio • No centrifuging • Heat solution to boiling point • HCL added • Barium sulfate precipitation
UT Arlington (1994)	• 1:10 dilution ratio • Centrifuge at 4500 rpm for 15 minutes • Heat solution to boiling point • No acid added • Barium sulfate precipitation
UT Arlington (2000)	• 1:10 dilution ratio • Centrifuge at 14000 rpm for 30 minutes • Heat solution to boiling point • No acid added • Barium sulfate precipitation
ODOT OHD-L49	• 1:40 dilution ratio • Gravimetric filtration • Barium sulfate precipitation • No Centrifuging or heating • No acid added
TRL Water-soluble sulfur (WSS) (2001)	• 2:1 water to sample ratio • Gravimetric filtration • Barium sulfate precipitation • No heating or acid added
TRL Acid-soluble sulfur (ASS) and monosulfide (MS) (2001)	• MS driven off as hydrogen sulfide • Dilute hydrochloric, hydroiodic, or phosphoric acid digestion • Gravimetric filtration • Barium sulfate precipitation • No heating
TRL Total reduced sulfur (TRS) (2001)	• Determination of copper by acidified copper (II) reduction • Evaluation of reduced sulfur from entrapped hydrogen sulfide gas within copper nitrate using iodometric titration
TRL Total Sulfur Method (TS) (2001)	• Heating in induction furnace to high temperatures • Uses a catalyst • Measures sulfur dioxide gas that comes off in the reaction

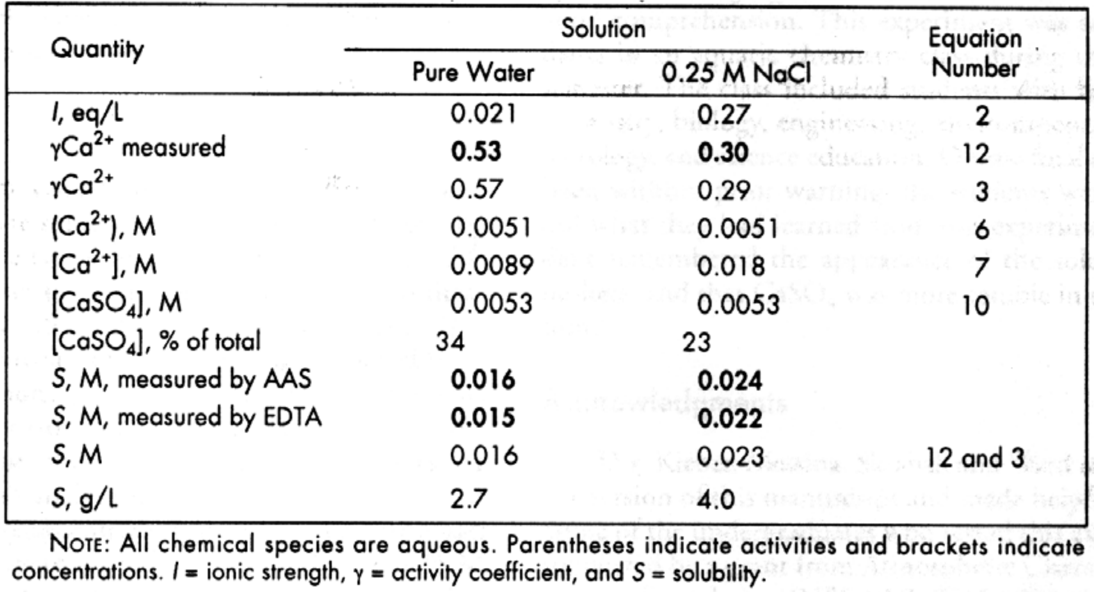
2.4 Solubility of Gypsum

Sulfate heave problems have led to the development of dissolution techniques and test methods to determine the sulfate concentration in soils. Before the sulfate concentration can be found, the sulfate must be extracted or dissolved. The dissolution rate of minerals vary with crystal structure and particle size, and extraction depends on their association with other soil constituents in the soil matrix such as mineral surface coating, complexes with organic matter, or interlayers (Shang and Zelazny 2008). Other factors that affect the extraction of sulfate include sample preparation, soil extractant ratio, and shaking time (Tabatabai 1996).

Remembering solubility rules from basic chemistry, most sulfate salt compounds are soluble with the exception of Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Ag^{+}, and Hg^{2+}. Mercury, calcium, and silver sulfate are considered to be slightly soluble (Horsthemke 2007). This tells us that gypsum (calcium sulfate) is only slightly soluble in water. Knowing these solubility rules made it necessary to not only study the calcium sulfate compound, but also to study the behavior of a completely soluble sulfate compound like sodium sulfate. The ionic strength of a solution has an effect on the solubility of an electrolyte. In particular, gypsum is generally considered insoluble in water although it is slightly soluble in reality. Soluble sulfate in soils can be extracted with water or salt solutions containing NaCl, LiCl, or $CaCl_2$; salt solutions are often preferred because they help with dispersion (Tabatabai 1996). If sodium chloride is added to a solution of gypsum and deionized water, it will increase the solubility of the gypsum allowing for the dissolution of more solid gypsum (Willey 2004). A table from Willey (2004) is shown below as

Table 2-2. It shows the increase in solubility, S, with the addition of 0.25M NaCl.

Table 2-2: Solubility with NaCl from Willey 2004



Quantity	Solution		Equation Number
	Pure Water	0.25 M NaCl	
I, eq/L	0.021	0.27	2
γCa^{2+} measured	**0.53**	**0.30**	12
γCa^{2+}	0.57	0.29	3
(Ca^{2+}), M	0.0051	0.0051	6
$[Ca^{2+}]$, M	0.0089	0.018	7
$[CaSO_4]$, M	0.0053	0.0053	10
$[CaSO_4]$, % of total	34	23	
S, M, measured by AAS	**0.016**	**0.024**	
S, M, measured by EDTA	**0.015**	**0.022**	
S, M	0.016	0.023	12 and 3
S, g/L	2.7	4.0	

NOTE: All chemical species are aqueous. Parentheses indicate activities and brackets indicate concentrations. I = ionic strength, γ = activity coefficient, and S = solubility.

The addition of more NaCl should be considered to possibly increase the solubility further as well as imitate the salinity of the Cretaceous Western Interior Sea. Chloride is also shown to influence the solubility of ettringite and inhibit the precipitation of expansive sulphoaluminates, and chloride in high concentrations may therefore decrease the stability of ettringite (Höglund 1992). Alkaline solutions such as $NaHCO_3$ and $CaCO_3$ can also be effective but these reagents can also extract part of the organic Sulfur (Tabatabai 1996). Total sulfates can be extracted using acid dissolution. Acid dissolution yields the maximum possible sulfate in the soil because it releases most sulfate components (Little and Nair 2009). However, this is an overestimation for the sulfate that might react to cause heave problems because the pH in lime-treated soils is high, and some of the sulfate species might not be soluble at these pH levels (Little and Nair 2009). Water soluble sulfates are of most concern for sulfate induced heave because in the field the dissolution method is more likely to be water.

In the lab there are several techniques to more easily dissolve the soluble sulfate. Shang and Zelazny (2008) suggest a sodium carbonate dissolution method for gypsum (most predominant form of sulfate in soil), which dissolves sulfate more accurately than sodium chloride (NaCl) solutions. In this method, an air-dried soil sample of 2 grams is washed with an ethanol solution to remove any soluble salts. Then the sample is washed with the sodium carbonate (Na_2CO_3) solution multiple times until a test with $BaCl_2$ comes out negative (no longer produces $BaSO_4$). The sulfate content is then found using colorimetry, gravimetry, chromatography, or spectroscopy.

The sodium carbonate dissolution technique was used in this thesis research, and since it was not mentioned in any of the other geotechnical engineering literature, nor has it been used for soil sulfate extraction, the results will be of benefit. In addition, the particle size effect on dissolution was studied, for this thesis, by sieving the soil past different sieves before using the Na_2CO_3 wash method. This has not been studied either, and the only mention of particle size in a study was in Harris et al. (2004); they introduced the sulfate to the samples in fine-grained (past #200 sieve) or coarse-grained (past #10) form and found that the fine-grained sulfate test sample swelled more and reached equilibrium more quickly than the coarse-grained sulfate sample. The thought was that the dissolution of sulfate would increase as the particle size decreased because the surface area for reaction is larger for smaller particles.

The most common sulfate dissolution and detection methods are gravimetric techniques, colorimetry, x-ray diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP), ion chromatography (IC), and several less popular methods. Little and Nair summarized the various sulfate determination methods used by different agencies in their NCHRP Web Only Document 145 in 2009. This is a good resource and comparison tool.

There are various gravimetric methods used by different agencies such as Texas Department of Transportation (TxDOT), American Association of State Highway and Transportation Officials (AASHTO), and the U.S. Army and Air Force. Gravimetric methods involve a weight comparison of soil and precipitated barium sulfate, which forms when barium chloride is added to sulfate (Little and Nair 2009). All the gravimetric methods, summarized by Little and Nair 2009, involve sieving the soil, mixing it with deionized water, boiling the mixture, adding hydrochloric acid (HCl), filtering the sample, adding barium chloride ($BaCl_2$), and heating again until precipitation ceases. The solution is then filtered again and the precipitated barium sulfate ($BaSO_4$) is washed and weighed. The different methods vary slightly in the sieve size specified (#10 or #40), dissolution ratio (1:10 or 1:30), heating time (24 hours or 1.5 hours), and final weight determination (wet or ignited weight). From many studies, the general consensus is that gravimetric tests are highly variable, with low repeatability and accuracy (Puppala et al. 2002; Harris et al. 2003; Little and Nair, 2009). This variability can be seen in Figure 2-6 from tests performed by Harris et al. (2003). The gravimetric samples have a much larger deviation from the perfect fit line, which would be the point where the test results produce the known sulfate content in the sample. Thus gravimetric analysis was not used to determine the sulfate content in this thesis research.

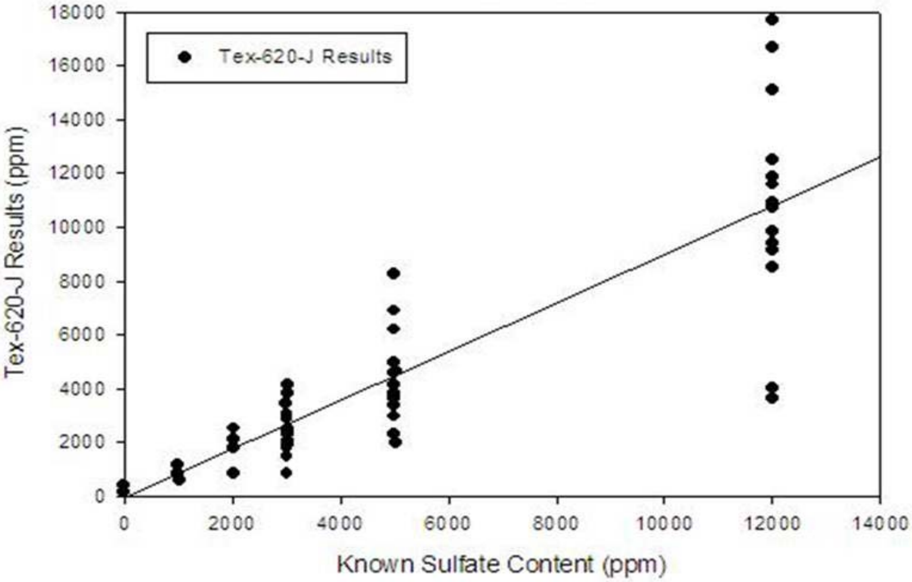


Figure 2-6. Comparison of Colorimetric and Gravimetric Techniques after Harris et al. 2003

Colorimetry tests measure the concentration of ions based on the absorption of radiation at a certain wavelength, and correlates the absorption to a concentration of sulfate (Little and Nair 2009). Little and Nair (2009) summarized the Colorado Department of Transportation (CDOT), TxDOT, and AASHTO methods. Each method specifies mixing sieved soil with deionized water, shaking the solution vigorously, and allowing the mixture to sit for 12 or more hours. After letting the solution rest, it is filtered, a vial of the filtrate is collected, and the colorimeter is calibrated for the initial sulfate level. A barium chloride ($BaCl_2$) tablet is then added to the vial and, once it is completely dissolved, the colorimeter is used to measure the turbidity. The colorimeter reading is the ion concentration, but this must be adjusted by the dilution factor. The test methods vary by sieve specification, time for the solution to rest, and temperature conditions. Colorimetry is more accurate at lower concentrations of sulfate and has fairly good repeatability when performed under exact standards (Puppala et al. 2002; Harris et al. 2003; Little and Nair 2009). In Figure 2-6, the colorimetric points are much closer to the perfect fit line than the gravimetric points. This shows higher accuracy and repeatability. Colorimetry is the preferred method of sulfate detection in the literature for low sulfate concentrations, so this technique was used in this thesis research for comparison purposes. However, the Oklahoma Department of Transportation (ODOT) has had accuracy problems with colorimetry, especially for high sulfate concentrations, so other sulfate determination methods were also explored in this research.

X-ray diffraction (XRD) is the process used to pass x-ray beams through a sample producing a diffraction pattern whose peaks can be compared to those of known minerals. XRD is reliable for samples with less than 50% gypsum (Herrero et al. 2008). XRD data is only semi-quantitative, so this method is probably not the best tool for quantitative analysis.

Ion chromatography (IC) samples are prepared by dissolving sulfate compounds and introducing small amounts of the aliquot into the IC machine. The sample is then passed through ion exchange columns using inert compounds, and different ions attract to resins in the columns and are released at different times by the conductivity detectors (Little and Nair 2009). To quantify the concentration of sulfate ions, the conductivity of the solution is compared with standard solutions. It is a fairly good technique for measuring sulfate at low concentrations (Tabatabai 1996; Harris et al. 2003; Little and Nair, 2009). Figure 2-7 shows results from IC tests performed by Harris et al. (2003). The data points are fairly close to the perfect fit line for the sulfate content below 6,000 ppm, but the test becomes inaccurate at 12,000 ppm sulfate. Again, this test is acceptable for low sulfate concentrations.

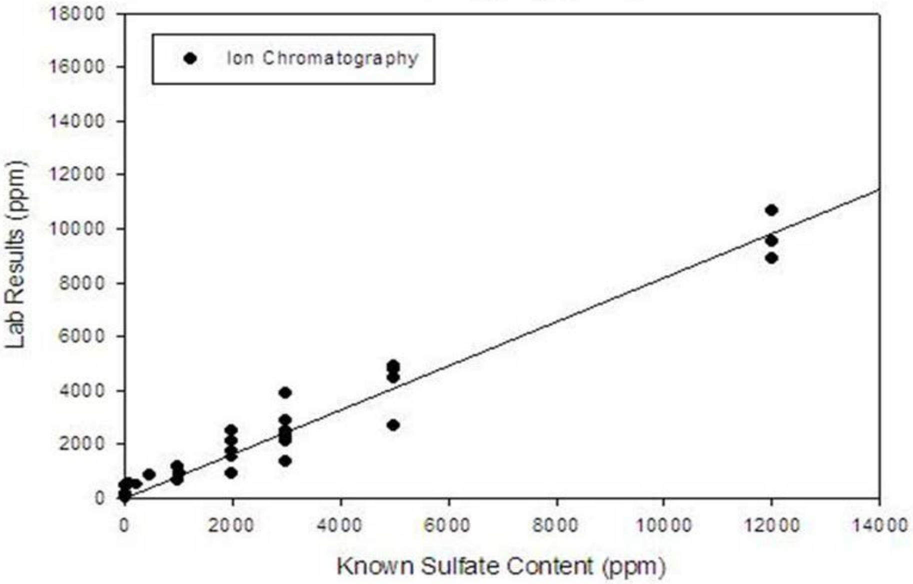


Figure 2-7. IC Technique vs. Known Sulfate from Harris et al. 2003

Inductive coupled argon plasma (ICP) atomic emission spectroscopy involves dissociation of soil samples in an argon plasma stream, which produces element-specific spectral lines by excited atoms (Little and Nair 2009). The recorded spectra are compared with calibration lines and intensities are converted to concentrations. This method is accurate and precise at low detection limits (Little and Nair 2009).

Many of these detection methods are only accurate for low concentrations of sulfate (up to 10,000 ppm) because as the dilution ratio is increased for higher concentrations, the error increases. Part of the problem with high concentrations of sulfate is the dissolution process. If the dissolution of sulfate can be increased, maybe the detection methods will show higher, more accurate results for sulfate concentration. From the previous literature, it is clear that the best methods for increasing sulfate dissolution are to try different salt solutions and/or decrease the pH of the solution.

This thesis will add to the current literature on sulfate detection and dissolution because researchers have not tried particle size analysis for colorimetry tests, or sodium carbonate washes. There is practically no literature on the dissolution of sulfate using sodium carbonate washings, so the results from these tests will show whether or not this method is effective in dissolving more sulfate than DI water. In addition, the research presented here will more clearly define the swelling trend for soils with varying amounts of sulfate and the influence of intrinsic soil properties on swelling. This will directly affect the construction practices for structures on sulfate-rich soils by providing a guideline for soil properties and sulfate levels which indicate the potential for heaving.

2.5 Threshold Concentration of Sulfate

Sulfate induced heave is directly affected by the amount of sulfates in the soil as well as other soil parameters. Little et al. (2010) suggest from field evidence that expansive minerals are not likely to form if soluble sulfate levels are below 2000 ppm or 0.2 percent. However, from many case studies, the sulfate content needed, or present, to produce heave varied from 300 mg/kg (ppm) to 43,500 ppm, and the time for appearance of heave varied from several days to 18 months (Puppala et al. 2005). In other studies, after short periods of time, soils containing sulfate which are stabilized with calcium-based stabilizers show strength improvement, but after long periods of time show the formation of ettringite and heaving (Sivapullaiah et al. 2006). The variations in sulfate content and time for heave to occur depend on soil properties and environmental conditions including temperature and humidity (Puppala et al. 2005). Many factors affect ettringite formation and heaving in lime-stabilized soils, but the sulfate content is a major factor in determining what reactions will occur.

Problems with heave were reported at a sulfate level of 700 ppm in the Stewart Avenue report (Las Vegas) (Hunter 1988), and a level of 2000 ppm was suggested in a Texas report (Chen 2005), while a Texas Technical Memorandum identifies sulfate levels under 3000 ppm as “too low to be of concern” (TxDOT 2000). These discrepancies are most likely due to the differences in physicochemical properties of the soil deposits and possibly the solubility of the sulfate in a particular chemical environment. “Based on experiences in Southern California, Mitchell suggested that lime should not be used as a stabilizer if there are more than 5000-ppm native sulfate in the soil” (Rao 2005). Many papers have different threshold values for this reaction. “Based on several investigations of sulfate attack of lime-stabilized soils in Texas, Petry suggested that soils containing sulfate contents of 2000 ppm have the potential to cause swelling, and levels of 10,000 ppm have the potential to cause serious damage on lime addition” (Rao 2005). The level of soluble sulfates that can cause harm is as low as 2000 ppm but also depends on the percentage of clay in the soil. Chen’s paper (2005) suggests the level of sulfate that can cause harm can be as low as 200 ppm. Soils that have relatively high amounts of sulfate but low clay content might not be problematic (Little 1992). Also, soils that contain large amounts of 1:1 clay minerals absorb more sulfate than soils containing predominantly 2:1 clay minerals (Kamprath 1955). It is difficult to find a single threshold value. It is a complex problem related to soil composition, construction methods, availability of water, ion migration, and the ability of the void structure to accommodate the expansive mineral growth (Little 2005).

The Texas Department of Transportation has performed many studies relating to sulfate-induced heave. One study involved two different sulfate compounds that were added to the soil: sodium sulfate (Na_2SO_4) and gypsum ($CaSO_4 \cdot 2H_2O$). Samples containing sulfate concentrations of 0, 1000, 2000, 3000, 5000, 7000, and 12,000 parts per million (ppm) were subjected to a three-dimensional swell test for a minimum of 45 days. They found that soils with up to 3000 ppm of sulfate can be treated with the traditional lime stabilization method. They used a system of mellowing out the lime for higher concentrations, but this was only effective to concentrations up to 7000 ppm (Harris 2004).

2.6 Ettringite Formation and its Influence on Swell

Several studies have been conducted to try to understand the behavior of soils experiencing sulfate-induced heave. One of the first comprehensive studies was performed by James K. Mitchell and Dimitris Dermatas in 1992. They tested artificial samples composed of 30% kaolinite or montmorillonite and 70% quartz with varying parameters such as composition, curing, and soaking conditions, as seen in Table 2-3.

Mitchell and Dermatas (1992) performed unconfined compression tests (UCT), swell tests, x-ray diffraction (XRD) analysis, and scanning electron microscope (SEM) analysis on their samples. XRD results showed the presence of ettringite in all samples for both clay types except those without lime and sulfate, or those cured for only one day. The SEM results showed large crystals identified as ettringite in the kaolinite-sand samples, but it was difficult to identify ettringite crystals in the montmorrillonite-sand samples because the crystals were so small. For kaolinite samples tested for swelling, the 30-day cured samples showed softening and volume increase from 2-5% when soaked in water or the sulfate solution. The kaolinite samples cured for 6-months showed a volume increase from 18-19% when soaked in water. The untreated montmorillonite samples swelled up to 100%, but the treated material cured for one day swelled around 4%, and no swelling was seen for samples cured for 30 days or 6 months.

From their results, Mitchell and Dermatas (1992) found that ettringite will form whenever sulfates and alumina are present in lime-treated soil. However, significant swelling was not seen in the early stages after lime treatment, which Mitchell and Dermatas explain could be due to the ettringite swelling into void space. At later stages, the stabilized soil has a more rigid structure with less pore space, so swelling pressures are larger than the cohesion in the soil and swelling results (Mitchell and Dermatas 1992). Mitchell and Dermatas (1992) explain that the reason for the difference in swelling in the montmorillonite and kaolinite has to do with the quantity and rate of release of alumina; the rate and amount is higher for kaolinite than for montmorillonite. Also, the source of sulfate affects the heave. Sources of sulfate such as Na_2SO_4, K_2SO_4, and $MgSO_4$ have a higher dissolution rate than gypsum ($CaSO_4{\cdot}2H_2O$). The slower rate of dissolution for gypsum provides a continuous source of sulfate to the system, allowing more time for the formation of ettringite (Mitchell and Dermatas 1992). From these experiments, Mitchell and Dermatas (1992) showed that the clay type and amount, amount of alumina present, the surface area, and form of soluble sulfates determine the strength, swelling potential, and influence of sulfate in lime-stabilized soils. It was not in the scope of their study to determine the threshold of sulfate required for ettringite formation.

Table 2-3. Test Conditions for Kaolinite-Sand and Montmorillonite-Sand Mixtures from Mitchell and Dermatas (1992)

Composition						Curing			Soaking		
#	% Lime	% Calcium Carbonate	% Sodium Sulfate	% Gypsum	% SO_4	1 Day	30 to 36 Days	6 Months	Temp. °C	Water	Na_2SO_4 Solution
1	0	10	1	10	5.9		x		20	x	
2	5	10	1	10	5.9		x		20	x	
3	5	0	1	10	5.9		x		20	x	
4	5	10	1	0	0.3		x		20	x	
5	5	10	0.5	10	5.75		x		20	x	
6	5	10	2	10	6.2		x		20	x	
7	5	0	1	10	0.3		x		20	x	
8	5	0	0	10	5.6		x		20	x	
9	5	10	0	10	5.6		x		20	x	
10	5	10	0	0	0		x		20	x	
11	5	0	0	0	0		x		20	x	
12	5	10	1	10	5.9		x		20		x
13	5	10	1	10	5.9		x		10	x	
14	5	10	1	10	5.9		x		10		x
15	5	10	1	10	5.9	x			20	x	
16	5	10	1	10	5.9			x	20	x	
17	3	10	1	10	5.9		x		20	x	
18	7	10	1	10	5.9		x		20	x	
19	5	10	1	10	5.9	x			20		x
20	5	10	1	10	5.9	x			10		x
21	5	10	1	10	5.9		x			No Soak	
22	5	10	1	10	5.9		x		40	x	
23	5	10	1	10	5.9		x		60	x	
24	5	10	1	10	5.9		x		80	x	
25	5	10	1	10	5.9		x		90	x	
26	5	0	1	0	0.3		x		90	x	

In other research, Harris et al. (2004) tested Vertisol soil from the Texas Coastal Plain region containing smectite clay minerals because this soil has a high shrink-swell potential, is typical of lime-stabilized soils in Texas, and has sulfate levels less than 100 ppm. In these tests, sodium sulfate (Na_2SO_4) and gypsum ($CaSO_4{\cdot}2H_2O$) were added to samples in concentrations of 0; 1,000; 2,000; 3,000; 4,000; 5,000; 7,000; and 12,000 ppm. The Na_2SO_4 was added to the mix water of some samples and the water bath of other samples, and the gypsum was added to the soil having passed a #200 sieve or #10 sieve. Some samples were tested immediately and other samples were allowed to mellow for 1-3 days. Harris et al. explain mellowing as adding lime to the soil and allowing the soil-lime mixture to sit in a sealed bag for 1-3 days before compaction. They also used single applications of lime (all 6% of lime added at once) or double applications of lime (3% lime was added and the soil was allowed to mellow, then the other 3% was added right before compaction). All samples were mixed to a water content of 2% above optimum. Three-dimensional free swell tests were performed on all samples, and XRD and SEM analyses were performed on one untreated and one lime-treated sample.

Harris et al. (2004) found that lime treatment without sulfate reduced the swell compared to the soil with no stabilization. XRD and SEM confirmed the formation of ettringite in the lime-treated sample. For the coarse-grained sulfate (#10 sieve), increasing amounts of sulfate resulted in more swelling. The fine-grained sulfate (#200 sieve) also caused swelling with increasing sulfate, but reached equilibrium much more quickly than the coarse-grained sulfate. The samples with the sulfate introduced through the molding water had the highest swell. Less swelling was exhibited for a single application of lime than for a double application of lime. Also, samples mellowed for two days had the lowest volume increase.

From these three-dimensional swell tests, Harris et al. (2004) determined coarse-grained sulfates require a longer time to form harmful reaction products than fine-grained sulfates. They also found that the use of mellowing for up to 3 days, after lime application, reduces swell for sulfate concentrations up to 7,000 ppm. Above 10,000 ppm sulfate, mellowing was not effective in reducing swell. Single application of lime reduced swelling better than double applications of lime. The authors believe using moisture contents 2% above optimum produces lower swell because the lower density results in more voids for the ettringite to swell into and removes sulfates for reaction more quickly (Harris et al. 2004). From their tests and other literature, Harris et al. (2004) recommend the sulfate cutoff for lime stabilization be 3,000 ppm.

Figure 2-8, from Harris et al. (2004), shows the comparison of different sulfate contents with 6% lime to a blank sample and a sample with 6% lime but no sulfate. The apparent compression before the swelling is probably an error in the plot or the data itself. Notice they never compared the swelling trend (larger swelling with increasing sulfate content) to samples containing different amounts of sulfate without lime, which is another important comparison. Also, Harris et al. (2004) used a naturally sulfate-deficient soil from Texas, instead of a standard inert soil like pure kaolinite, so their results are only applicable to the soil they tested.

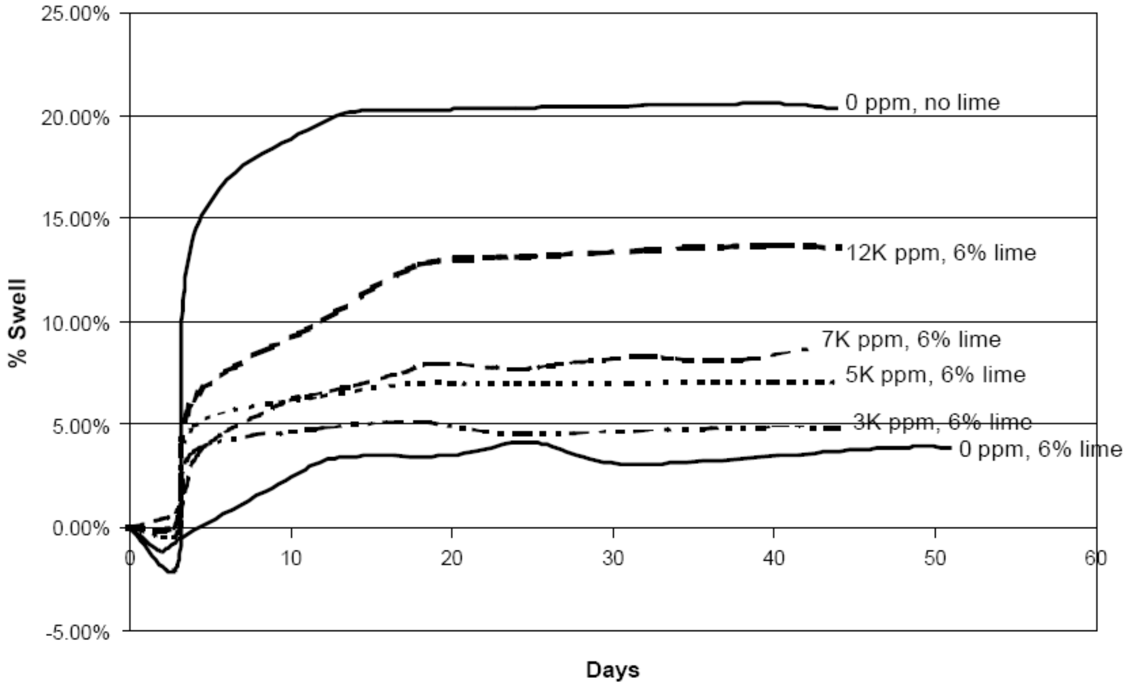


Figure 2-8. 3-D Swell with Different Concentrations of Coarse-Grained Gypsum from Harris et al. 2004

In order to add to the existing literature, the tests in this research were performed in triplicate and pure kaolinite was used, so more general observations could be made. Also in this research, samples with sulfate and lime were compared to samples with sulfate and no lime.

Puppala et al. (2005) performed research to better understand ettringite formation and heave mechanisms in lime-treated soils by conducting one-dimensional free swell tests, XRD, SEM, and EDAX analyses. Their test specimens were made up of kaolinite clay with 0; 1,000; 2,500; 5,000; or 10,000 ppm sulfate. Mixed soil (30% kaolinite clay and 70% sand) was tested with 0; 5,000; and 10,000 ppm sulfate and pure sand was tested with 0 and 10,000 ppm sulfate. All samples were tested with 0, 4, or 8% quick lime (CaO). Some samples were soaked in an aqueous solution of 4.46 mmol of sodium sulfate (Na_2SO_4) and 4.46 mmol of sodium aluminum oxide ($Al_2O_3Na_2O$), which provided soluble sulfates and reactive alumina. Also, some natural samples were mixed with synthesized ettringite, made by mixing quick lime, sodium sulfate, and sodium alumina oxide in water for 10 min at room temperature, to see if swelling was still observed.

From these tests Puppala et al. (2005) found that under natural conditions kaolinite clay exhibited higher swelling than the sandy soil specimens, and soluble sulfates in untreated samples had no noticeable effect on swell behavior. Both the mixed and clayey soils were more susceptible to sulfate-induced heave than the sandy soil. Lime-treated samples showed an initial decrease in swell, compared to the control samples with no sulfate, and then the swell increased as the sulfate dosage increased. At higher soluble sulfate levels the samples treated with 8% lime showed more heave than the samples with only 4% lime, as seen in Figure 2-9, because there was more calcium to react with the alumina ions. It seems unusual that the sample with no lime swelled 25% because pure kaolinite has a low swelling potential. No explanation for this was provided in Puppala et al. (2005). Mixing synthesized ettringite into compacted samples did not result in ettringite-induced heave in the samples (Puppala et al. 2005).

Puppala et al. (2005) found that ettringite can be synthesized in the laboratory and mixing synthesized ettringite with compacted soils will not result in ettringite induced heave. This is most likely due to the strengthening reactions of the ettringite in the soils and low moisture absorption capacities of the ettringite minerals (Puppala et al. 2005). The synthesized ettringite has already had time to reach equilibrium with the water, and thus cannot take up any more water into its structure. Ettringite-induced heave in the tested soils was caused by crystal growth and when the pore space could not accommodate the growth, swelling was seen.

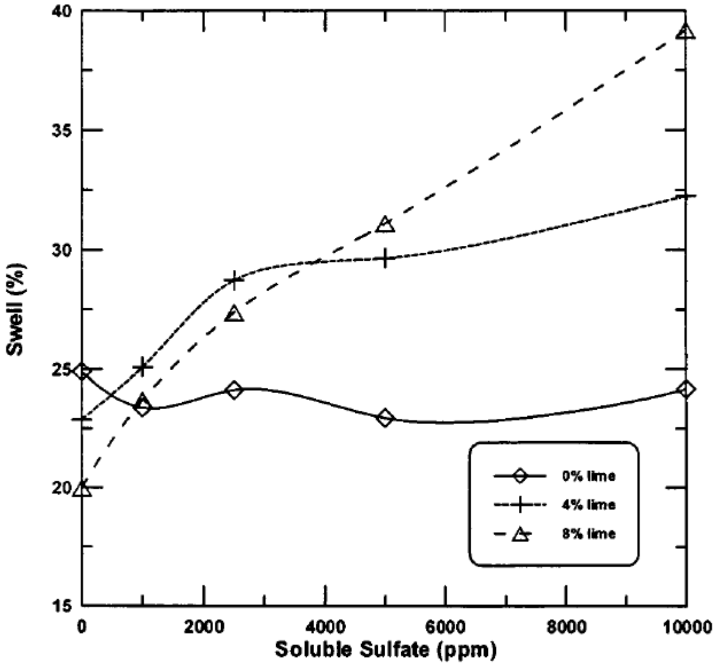


Figure 2-9. Kaolinite Clay with Varying Sulfate Contents and Lime Percentages from Puppala et al. 2005

Thus, the lower the void space, the higher the sulfate heaving in the soils. At sulfate levels below 2,500 ppm, the stabilized soils experienced small amounts of heaving, maybe due to the lime treatment reactions dominating (Puppala et al. 2005). At higher sulfate levels, greater than 2,500 ppm, increasing lime stabilization produced higher amounts of heave due to higher ettringite formation (Puppala et al. 2005). XRD and SEM studies show the presence of ettringite, and Puppala et al. recommend these two analysis methods should be used together for better results (2005).

Puppala et al. (2005) used quick lime (CaO) in their studies as the source of calcium in the ettringite formation reaction. Another common form of lime for soil stabilization is hydrated lime ($Ca(OH)_2$), so to add to Puppala et al.'s work and better represent field practices in Oklahoma, the swell test specimens presented in this thesis were made with hydrated lime. Also, there is a gap in Puppala et al.'s data between 5,000 and 10,000 ppm sulfate, so in this research, an additional data point was added at a sulfate concentration of 8,000 ppm.

The three studies discussed previously, along with others, gave insight into the process of ettringite formation and sulfate-induced heave. They showed what variables are needed for ettringite to form and also what affects the amount of swelling if ettringite does form. More research is needed to try to define a threshold sulfate content causing detrimental swelling in soils, which is one goal of the research presented herein. This will add significantly to the literature. However, the previous research has at least given a range of sulfate contents to keep in mind when designing stabilization procedures for soils containing sulfate. In order to help prevent detrimental stabilization designs, there must be an accurate way to detect and quantify sulfate in soils.

3 Methodology

3.1 Introduction

A detailed description of the test soils, sample preparation and test procedures is presented.

3.2 Test Soils

Eight natural soils from western Oklahoma were collected and two pure clays, including Hickory Glaze Kaolinite and Bentonite were used in the manufactured free swell 1-D consolidation tests. The locations of the natural soils are shown in Figure 3-1.

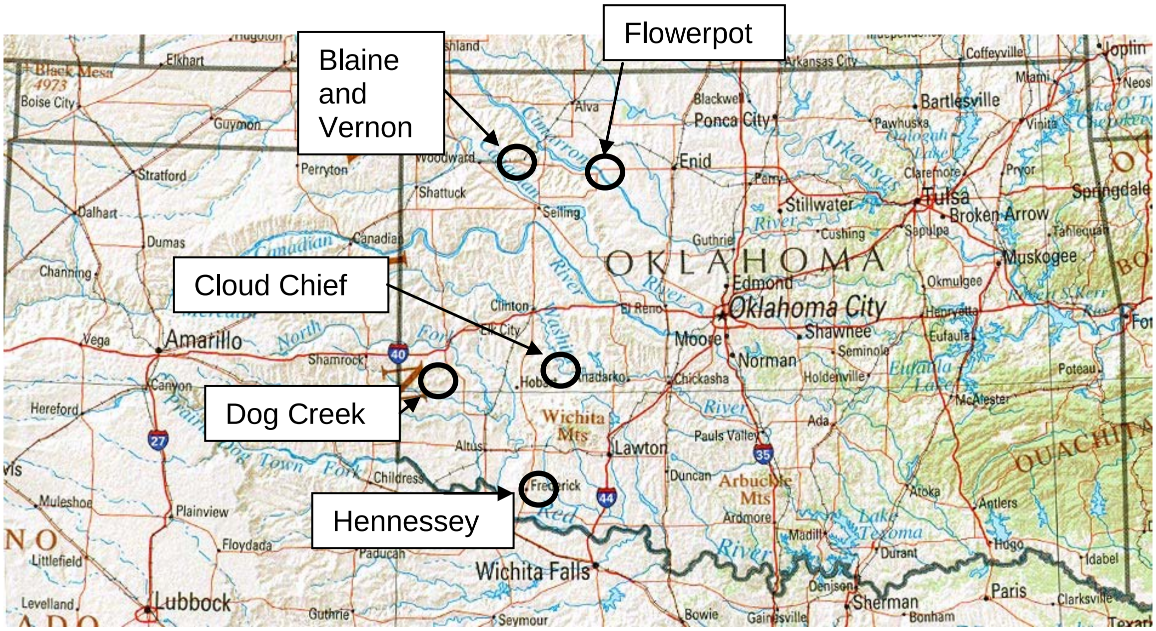


Figure 3-1 Locations of Natural Test Soils

Hickory Glaze #1 from the Old Hickory Clay Company is a high kaolin clay conventionally used for ceramic glazes. The other soil that was used in this project was Bentonite, bought from Fisher Scientific. The two clays were chosen for their widely different clay mineralogy. Hickory Glaze #1 is a kaolinite, which has a 1:1 structure of aluminum and silicon. It is a non-swelling clay in its natural form with a small diffuse double layer (water and ion film around each clay particle), which produces a tendency to form a flocculated structure (particles stack end to face). It has larger particles than the Bentonite, which is sodium montmorillonitic clay. The Bentonite has a 2:1 structure with two aluminums to one silicon particle. Bentonite is an expansive clay that has a much larger diffuse double layer, relative to the particle size, which produces a tendency to form a dispersed structure (particles lay flat in sheets). The two different types of

Sulfate used in the experiments were gypsum (calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$) from Fisher Scientific and Sodium Sulfate Anhydrous (Na_2SO_4).

3.3 Test Procedures

3.3.1 Atterberg Limits

The Atterberg Limits Determination was performed in general accordance with American Society for Testing and Materials (ASTM) D 4318-95a Standard Test Method for *Liquid Limit, Plastic Limit, and Plasticity Index of Soils* (ASTM 1998).

Shrinkage tests were also conducted following the American Society for Testing and Materials (ASTM) D 427-04 Standard Test Method for *Shrinkage Factors of Soils by the Mercury Method* (ASTM 2005).

3.3.2 Grain-Size Analysis

The grain-size distribution was determined using the hydrometer analysis performed in general accordance with American Society for Testing and Materials (ASTM) D 422-63 Standard Test Method for *Particle-Size Analysis of Soils* (ASTM 1998).

3.3.3 Standard Proctor Tests

Following ASTM Standard D 698 -91, Proctor compaction tests were conducted to determine the compacted moisture-density relationships of the test soils. The bracketed water contents were based on an analysis of the plastic limit, estimating the optimum water content at 2% below the plastic limit. Five specimens were used to give a five-point curve. These Proctor tests were then performed on the soil with 5% lime added, with the estimated optimum water content at 6% above that of the soil-only Proctor.

3.3.4 Specific Gravity

The Specific Gravity of selected samples was measured in general accordance with American Society for Testing and Materials (ASTM) D 854-92 Standard Test Method for *Specific Gravity of Soils* (ASTM 1998). Specific Gravity tests were performed to determine the void ratio of the soils that were tested as remolded oedometer specimens.

3.3.5 Linear Shrinkage

The Linear Shrinkage Test appears to have been first introduced by the Texas Highway Department in 1932 (Heidema 1957) and is currently described as a standard test procedure in British Standard BS 1377:1990, Test 5. The bar linear shrinkage test was found to be the most reliable calcrete soil constant in road construction (Netterberg 1978) and most significant indicator of plasticity/cohesion for a gravel wearing course material (Paige-Green 1989). Haupt (1980) and Emery (1985) performed studies to determine subgrade moisture prediction models and indicated that the inclusion of the bar linear shrinkage produced as good, if not better, prediction models than the inclusion of any of the other Atterberg Limit results. Paige-Green and Ventura (1999) conclude from their evaluations of various bar linear shrinkage tests performed that the bar linear shrinkage test is a more effective test to indicate material performance than the more traditional Atterberg limits.

The Linear Shrinkage Limit test was performed with one hundred and fifty grams of soil mixed with tap water until reaching a consistency of 15 blows in the Casagrande cup. A third of the soil was placed in a greased brass mold approximately 140 mm long and 25 mm in diameter. The soil was placed in the mold in three layers and tapped against a flat surface in between the layering to remove air bubbles from the soil. The sample was allowed to air dry for four hours. Then the soil sample was placed in an oven at 105˚C for 18 hours.

After the soil was dry, the mold was removed from the oven and allowed to cool. The length of the soil sample was measured three times with digital calipers and the average was used to calculate linear shrinkage using the equation:

$$LS = \left(1 - \frac{L_{avg}}{L_o}\right) \times 100$$

Equation 2

where:

LS = Linear Shrinkage (%)
L_{avg} = Average Length (mm)
L_o = Original Length of Brass mold (mm)

The Linear Shrinkage test potentially has a number of advantages over other tests, including:

1. The test is simple to perform
2. The test is essentially independent of operator and therefore may be subject to less variability.
3. The equipment is simple and inexpensive.
4. The test does not require use of toxic materials.
5. The test can be used for soils of low plasticity, such as silts, as well as for clays.
6. The test directly measures the desired behavior; i.e., shrinkage.

To calculate the volumetric shrinkage from a linear shrinkage test, uniform 3-D shrinkage is assumed and the volumetric shrinkage is calculated as:

$$VS = 1 - \frac{V_f}{V_o} \times 100\% .$$

Equation 3

where:

VS = Volumetric Shrinkage (%)

$V_f = 0.5 L_f \pi r_f^2$ = final measured volume (in^3)

Equation 4

L_f = final measured length (in)
π = constant = 3.14
r_f = final calculated radius assuming constant 3D shrinkage (in)

$V_o = 0.5 L_o \pi r_o^2$ = initial volume (in^3)

Equation 5

L_0 = original measured inside length of mold (in)
r_0 = initial measured inside radius of mold (in).

This volumetric shrinkage calculation may be related to the shrinkage index, I_s, which is the difference between LL and SL.

3.3.6 pH Tests

The pH of the samples was determined using an Orion pH/ISE meter model 710A with an epoxy Orion Thermo Ross Sure-Flow pH probe. The meter was calibrated using the machine's automatic two-point calibration method. The probe was inserted into the first standard with a pH of 4.01. The machine was allowed to stabilize. The probe was then washed in deionized water and inserted into the second standard with a pH of 10.01 and allowed to stabilize to this value. Once the machince stabilized to this value, the calibration was complete and the "Measure" button was pressed to exit calibration. The pH probe was washed with deionized water and placed in the sample bottle with the 40:1 soil, water, and gypsum mixture. The pH probe sat in the sample until it stabilized to a constant value and beeped to indicate the value was reached. The probe was washed with deionized water and placed in the next sample. This process, with the exception of calibrating the machine, was repeated for each sample.

3.3.7 Conductivity

Conductivity of the samples was taken in much the same way as the pH. An Orion 3Star Benchtop conductivity meter. The calibration was done in the same way as the pH meter. The two standards used were 1413 µS/cm and 12.9 mS/cm. Once the machine was calibrated, the probe was washed with deionized water, placed in a sample, and allowed to stabilize to a constant value. This process was repeated for each sample, washing the probe with deionized water between each sample.

3.3.8 Specific Surface Area and Cation Exchange Capacity Tests

Two general approaches have been used to determine specific surface area of clays; (1) the measurement of total surface area by the adsorption of polar liquids as a means of describing the behavior of expanding clay minerals, whose inner surfaces are inaccessible to nitrogen; and (2) the measurement of external surface areas by the adsorption of simple molecules, such as nitrogen at low temperatures, with surface areas being derived from adsorption isotherm data and the application of BET theory (Brunauer et al. 1938). The measurement of total surface area was conducted using the polar liquid Ethylene Glycol Monoethyl Ether (EGME) Method and the measurement of external surface area was performed using the BET method.

3.3.8.1 Ethylene Glycol Monoethyl Ether (EGME) Method

The test procedure described follows the general methodology presented by the Soil Science Society of America *Methods of Soil Analysis, Physical and Mineralogical Methods*, Standard Test Method for Ethylene Glycol Monoethyl Ether Method (EGME) for Determination of Specific Surface Area given by Carter et al. (1986). Since the present applications of SSA being considered are related to the field of soil mechanics, rather than agronomy, a number of variations in this test procedure were evaluated in order to determine the reliability of the measurements.

3.3.8.2 Apparatus

Specific Surface Area tests were conducted in four vacuum desiccators: two having a 210 mm inside diameter and two with a 250 mm inside diameter measurement. Four aluminum tares were used in the smaller dessicators and six aluminum tares were used in the two larger desiccators. Aluminum tares were used since the mass remains constant during the evacuation and handling while weighing. A shallow tare was used since it is essential that the soil be spread thinly in the bottom of the tare to ensure that there is complete coverage of the EGME over all soil particles. Aluminum tares with dimensions of 76 mm in diameter by 25 mm in height were used. This size tare allowed the soil to be spread adequately over the bottom and efficiently fit into the desiccators.

A Calcium Chloride and EGME desiccant was mixed and placed in a glass dish at the bottom of the desiccators. Approximately 110 grams of 40-Mesh Anhydrous Calcium Chloride is placed in an oven for one hour. The Calcium Chloride was then taken out of the oven and 100 grams is poured into a beaker. 20 mL of EGME was added to the beaker and mixed thoroughly. The desiccant was then spread evenly into a glass dish and placed in the bottom of the desiccator. The desiccant should always be stored in a sealed dessicator when not in use.

Plexiglass lids were placed on top of each aluminum tare to prevent the soil from being pulled out of the tare during the evacuation process. Lids were fabricated from 1 mm thick plexiglass and a 2 mm gap was created between the tare and the plexiglass lid using a thin piece of plexiglass. A vacuum pump was attached to the top of the desiccator. Figure 3.2 shows a schematic of the test equipment and Figure 3.3 shows the actual equipment in use.

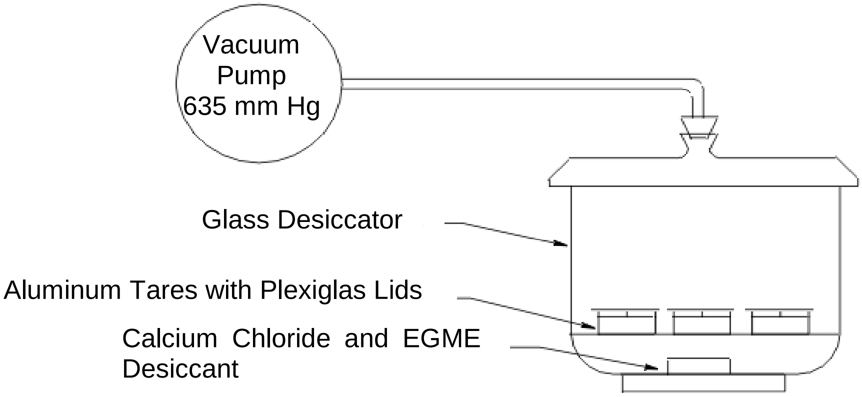


Figure 3-2 Schematic of EGME Method Test Equipment.

Figure 3-3 Laboratory Testing Set-up at the University of Oklahoma.

3.3.8.3 Test procedure

The procedure used to determine SSA was conducted on oven-dried soil. All soil samples were first air-dried and pulverized using a rubber tipped pestle to pass a #40 sieve. A small amount of this sample was then placed in the oven overnight to remove water at 105°C. After oven drying, approximately one gram of soil was spread into the bottom of the aluminum tare. The mass of the soil was determined using an electronic analytical balance with 0.001 gm accuracy. Approximately 3 mL of laboratory grade EGME was added to the soil with a pipette and gently mixed by hand with a swirling motion to create a slurry. The tare was then placed inside of a standard laboratory glass sealed vacuum dessicator and was allowed to equilibrate for twenty minutes. The desiccators were evacuated using a vacuum pump providing a vacuum of 762 mm Hg (30 in). A perfect vacuum never occurred and therefore 635 mm Hg was adequate in evacuating the sample within 24 hours.

Initially, the tares were removed from the desiccators and weighed every 6 to 8 hours using an analytical balance. However, it was soon discovered that the samples equilibrated after a period of between 18 and 24 hours, and therefore one measurement was taken 12 to 16 hours after the initial evacuation and again after a period of 24 hours. This method was considered sufficiently accurate since the mass did not vary more than 0.001 grams.

If the mass of the sample varied by more than 0.001 grams, it was placed back in the desiccator and evacuated again for an additional 2 hours. This process was continued until the sample mass did not vary by more than 0.001 grams. Weighing the samples twice instead of every 6 hours reduced the amount of molecular displacement that could occur between H_2O molecules in the atmosphere and EGME. A routine procedure of weighing the samples between 12 and 16 hours and again at a final time of

24 hours was adopted and found adequate for samples with the highest SSA. The SSA is calculated as

Equation 6

where:

SSA = Specific Surface Area in m^2/g
W_a = weight of ethylene glycol monoethyl ether (EGME) retained by the sample in grams (final slurry weight – W_s)
W_s = oven dry weight of soil (g)
0.000286 = weight of EGME required to form a monomolecular layer on a square meter of surface (g/m^2)

3.3.8.4 BET Method

The BET Method of determining surface area is based on the work by Brunauer et al. (1938). The adsorption of nitrogen and the application to the isotherms of the BET equation is widely recognized method for calculating the “external” surface area of soil particles. Weakly adsorbed nitrogen does not penetrate the interlayer surfaces so that the measurement obtained is only for external surfaces, whereas polar molecules such as ethylene glycol monoethyl ether are strongly adsorbed and penetrate into the interlayer surfaces producing total surface area measurements. Although “total area” of soils containing swelling clay minerals cannot be determined, the method remains a useful means of comparing two different soils.

The BET method works by measuring the quantity of adsorbate gas adsorbed on a solid surface by sensing the change in thermal conductivity of a flowing mixture of adsorbate and an inert carrier gas. Usually the adsorbate is nitrogen and the inert carrier gas is helium (Figure 3.4). The Quantachrome Corporation’s MONOSORB®, a direct-reading dynamic flow surface area analyzer, was used for these tests.

A small soil sample was placed in a sample tube and inserted into the cell holder. A Dewar Flask was filled with liquid nitrogen and raised until the liquid nitrogen was 0.5 inches from the top of the cell. The flow of gas began and nitrogen was adsorbed. The liquid nitrogen was removed and the desorption of the gas from the soil began. When desorption was completed, the integrator displayed a number which was the sample surface area in square meters. Dividing by the sample mass gave the external specific surface area of the sample.

3.3.9 Cation Exchange Capacity

The cation exchange capacity was determined by Harris Laboratory, Inc., Lincoln, Nebraska using a 1 N ammonium acetate extraction method (Rhoades 1982).

3.3.10 X-Ray Diffraction

X-Ray Diffraction (XRD) has been used to determine the crystalline structure of clay minerals since the early 1900's. An experiment performed with X-rays established the three prevailing concepts of X-ray diffraction: 1. that atomic particles within crystals are arranged in orderly, three-dimensional, repeating pattern; 2. that these regular arrangements have spacings of approximately the same dimensions as the wavelength of X-rays and therefore, because diffraction does take place, that 3. X-rays are wavelike in nature (Moore and Reynolds 1997). Around the same time, W.L. Bragg discovered the Bragg equation in 1912 (Moore and Reynolds 1997). This equation relates the angle of diffraction with the wavelength and d-spacing or particle width and is stated as

$$2d \sin\phi = n\lambda$$

Equation 7

where:

d = spacing between rows of atoms
ϕ = angle of incidence between glass slide and x-ray beam
n = integral number relating to wavelengths
L = wavelength.

Figure 3-4 Quantachrome MONOSORB® Apparatus for performing BET Analysis.

In this study, Copper-K Alpha radiation was used, where copper has a wavelength, λ, of 1.54049. These major breakthroughs were the beginning of a century of the study of clay minerals through the use of X-rays. Over the years, the theories and practices of X-ray diffraction have produced numerous diffractograms generated from many naturally occurring clay minerals. In addition to creating diffractograms on real samples, "ideal" diffractograms were created using numerical modeling programs and are now used to identify minerals in natural samples.

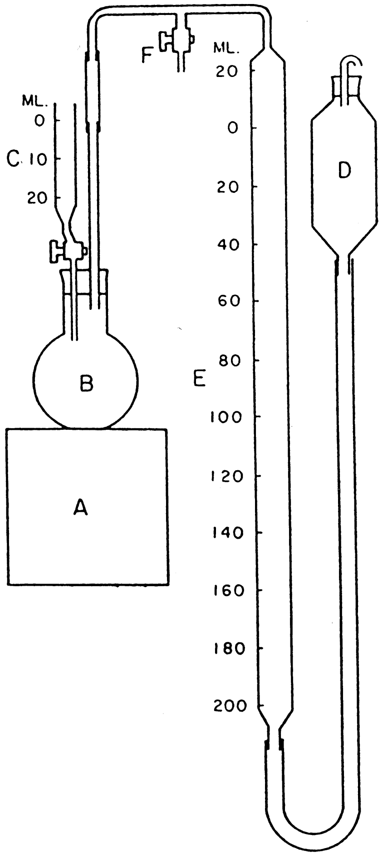
For the XRD analyses, samples were finely ground, mixed with water and dried as a smear on a glass slide. A Rigaku automated wide-angle x-ray diffractometer (4 to 70 degrees 2-theta) with copper anode tube (40kV/30mV) generated Copper-K Alpha (Cu-K-alpha) radiation with a graphite monochrometer before the detector was used. Data were analyzed with Jade version 3.1 software and the ICDD-PDF (International Center for Powder Diffraction Data-Powder Diffraction File) database.

3.3.11 Carbonate Content

The carbonate content determination test was determined using the Chittick Apparatus and the procedure presented by Dreimanis (1962). The Chittick Apparatus measures the amount of carbonates in the soil by measuring the amount of carbon dioxide that evolves from carbonates reacting with dilute hydrochloric acid. All soil samples were passed through the number 40 sieve and placed in the oven overnight. 1.70 grams of oven-dried soil were placed in a 250-ml Erlenmeyer flask along with a plastic coated stirring magnet and fit onto the apparatus (Figure 4.1). The pipette was filled with 20-mL of a 6 N hydrochloric acid solution, which is made by mixing 109.4 mL of hydrochloric acid in 1000 mL of distilled water. The reservoir was raised until the level in the annulus and the reservoir was even at the top. Once this beginning value was noted, the reservoir was lowered to keep a slight vacuum in the system. The clock was started and the acid pipette valve was opened so that 20 mL of acid flowed into the erlenmeyer flask over a period of approximately 45 seconds. When one minute was reached, the reservoir was brought up even with the level of the annulus and a reading was taken, R_1. The temperature in the beaker and the barometric pressure were recorded. When twenty minutes was reached, the reservoir was again brought up and leveled with the annulus and a second reading, R_2, was recorded.

The temperature and barometric pressure were recorded again. Using these measurements and a table of correction factors, the calcite and dolomite contents were determined using the calculation procedure described by Dremanis (1962). The test is able to distinguish between calcite, which is digested in about 30 seconds, and dolomite, which takes about 20 minutes to digest. The total carbonate content was taken as the sum of the calcite and dolomite contents.

If the carbonate content of a soil is high, it may be necessary to reduce the amount of soil placed in the flask. Initially, reduce the amount of soil by 50%. If the carbon dioxide gas still displaces all of the annulus fluid, the amount of soil is reduced to 25 % of the original soil mass. This allows the test enough room in the annulus to accommodate the carbon dioxide from the hydrochloric acid reacting with the carbonate. Once the measurements are taken, the amounts of gas evolved must be multiplied by the fraction of the measured amount and 1.7 grams. This calculation will ensure that the proper carbonate content is recorded for the particular specimen.



A. Magnetic stirrer
B. Decomposition flask
C. Pipette
D. Leveling bulb
E. Measuring burette
F. Leveling stopcock

Figure 3-5 Schematic of the Chittick Apparatus (from Jordan 1995).

3.3.12 Organic Content

The organic content of the soil was measured in general accordance with American Society for Testing and Materials (ASTM) D 2974-95 Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils (ASTM 1998). Test Method C, ash content, was used in this study. The soil was first oven-dried at 105 ^{o}C and a mass of solids was obtained. Then the oven-dried soil was placed in a muffle furnace, which was brought to a temperature of 440 °C and left for 24 hours. The sample was removed, cooled and weighed. The test was complete when the sample was completely ashed (no additional loss in mass with repeated heating and weighing cycles). The organic content was then determined as

$$\text{Organic Matter (\%)} = 100 - \text{Ash Content (\%)}$$

Equation 8

where :

Ash Content (%) = ————————

Equation 9

3.3.13 Sulfate Testing

3.3.13.1 Colorimetry

The sulfate test was performed according to the Oklahoma Highway Department (OHD) L-49 Method of Test for Determining Soluble Sulfate Content in Soil with some minor changes. This exact procedure is located in Appendix G. Calculated amounts of gypsum powder (ppm = mg/kg) were added to 10 grams of soil to make known sulfate concentrations in the different samples. One change was the dilution ratio. A 20:1 dilution was used in this experiment so that 10 grams of soil/sulfate could be used per 250 mL HPDE bottle, whereas the dilution in the original OHD L-49 method was 40:1 and only 5 grams of soil/sulfate per bottle were used. This was to allow for a higher amount of sulfate proportionally to make weighing the minute amounts of gypsum easier.

Several different batches were made for the sulfate testing. The first was a non-volumetric 20:1 dilution of gypsum, meaning the samples were not mixed in volumetric flasks, but rather crude beakers without adequate precision. The next was a volumetric (using volumetric flasks for measuring the water) 20:1 dilution of gypsum. Another volumetric dilution was done by first adding the water to the dry gypsum powder in a 250 mL beaker and heating the mixture to 70ºC before mixing it with the soil in the HPDE bottles.

A repeatability experiment was done by taking 50 grams of a fine-grained sand and mixing it with 250 ppm sulfate and dividing it into 5 HPDE bottles, each with 10 grams. This was also done with sand for 10000 ppm of sulfate. Another volumetric batch of Hickory Glaze samples were made with sodium sulfate to test the solubility constraints of the gypsum. Several other different methods were tried to determine a more accurate method of determining the total sulfate content.

Sulfate levels were also measured using Ion Chromatography to compare both measurements. Manufactured solutions were used to test the solubility of gypsum ($CaSO_4$), as well as the ability of the colorimetry and IC testing methods to measure sulfate concentration accurately.

3.3.13.1.1 pH

The pH was considered for solubility of gypsum. First, the pH was lowered using hydrochloric acid. A 10000 ppm sample was made with lab grade gypsum and deionized water in a beaker. The sample was placed on a magnetic stirrer, and the pH was monitored using a pH meter. The hydrochloric acid was added with a pipette by drop to the sample until the pH was approximately 1. The same test was run with sodium hydroxide in the same manner, and it was added to the sample until the pH reached a constant value of 12.

3.3.13.1.2 Centrifuge and NaCl

The centrifuge test is meant to possibly replace the gravitational filtration method. A Beckman TJ-6 centrifuge was used, and 250 mL polycarbonate centrifuge bottles were ordered to fit the machine. The samples were prepared in the same manner as the gravitational filtration method using a 40:1 dilution of 5 grams of soil to 200 mL of deionized water. The samples were placed on a shaker table for 5 minutes before being centrifuged. The samples were placed four at a time into the centrifuge and were run for 30 minutes at the maximum speed of the machine. The samples were removed from the centrifuge and 10 mL of the liquid was filtered into the colorimeter testing vials using a 0.20 micron syringe filter. The sample was tested and if it was too turbid for the colorimeter, 10 more mL of the sample was syringe filtered into a beaker and mixed with 100 mL of deionized water to make a new dilution of 400:1 and 10 mL of the new solution was tested in the colorimeter. The remaining liquid in the centrifuge bottle sample was carefully poured off and a new wash of 200 mL of deionized water was added. The process was repeated for multiple washes until a constant concentration was reached in the colorimeter for each sample.

Lab grade sodium chloride was added to some of the samples. Seven grams was added to the 40:1 dilution sample to create a concentration of 35000 ppm of NaCl. This was to approximate the average salinity of ocean water. Sodium chloride was added to only the first wash on some of the samples, while it was added to every wash on others. The sodium chloride was known to have a very slight amount (0.004%) of sulfate, so blank samples of water with 7 grams of NaCl were made and this colorimeter reading was subtracted from the centrifuge samples. A blank was also made of deionized water to test its influence to the colorimeter reading as well.

3.3.13.1.3 Na_2CO_3 Wash Method

Test samples included blank gypsum, a mixture of 1:1 sand to hickory clay with 10,000 ppm sulfate, and three of the natural soils (Blaine, Vernon, and Flower Pot). The sodium carbonate (Na_2CO_3) wash method, described by Shang and Zelazny 2008, was used to remove the soluble sulfate in the soil, so that the sulfate content could then be determined. In this test, 2 g of an air-dried soil sample was weighed and placed into a centrifuge-safe bottle. 25 mL of a 50% ethanol solution was added to the bottle, the mixture was shaken for 1 hour, and centrifuged at 1000 g for 10 minutes. The supernatant (liquid) was filtered and set aside. To the remaining sediment, 25 mL of a 0.5 M Na_2CO_3 solution was added, the sediment was re-suspended by sonification for 30 seconds, centrifuged for 10 minutes at 1000 g, and the supernatant was filtered and collected. A small amount of the supernatant was mixed in a 1:1 ratio with 6 M HCl until no more bubbles surfaced, and was tested for sulfate turbidity with barium chloride ($BaCl_2$); $BaCl_2$ reacts with sulfate to form a white precipitate $BaSO_4$ thus producing turbidity. This addition of HCl was not mentioned in the method described by Shang and Zelazny 2008, but was necessary to prevent the formation of barium carbonate ($BaCO_3$), another white precipitate. The Na_2CO_3 washes were repeated until the turbidity test came out negative. The total volume of the solution, from all the Na_2CO_3 washes, was measured and colorimetry was performed using the OHD L-49 method described previously. The concentration from colorimetry and the volume of the solution were used to calculate the concentration of sulfate in the soil. The calculations are as follows:

Equation 10

where
s = sulfate content in grams (g)
D_f = dilution factor
CR = colorimetry reading in parts per million (ppm)
V_T = total volume of wash solution in milliliters (mL)

$$C = \frac{s}{w}$$

Equation 11

where
C = concentration of sulfate present in the soil (ppm)
s = sulfate content in milligrams (mg)
w = weight of initial soil sample in kilograms (kg)

3.3.13.1.3.1 Number of Washes Comparison

Blank gypsum was tested using the Na_2CO_3 wash method with varying numbers of washes. The purpose of this exercise was to determine whether or not the sulfate content increased by increasing the number of washes after the first negative test for $BaSO_4$ turbidity. Samples were washed 8, 10, 12, or 14 times and the results were compared.

3.3.13.1.3.2 Grain-Size Comparison

For both the Na_2CO_3 wash method and colorimetry, the effect of the particle size was compared. Blank gypsum was sieved past a #10, #60, #100, #200, #400, or #500 sieves and then used in the two test methods to determine if the solubility increased or decreased with decreasing grain size. The natural soils were also tested at various particle sizes.

3.3.13.2 Ion Chromatography (IC)

The filtrates were taken from the filtered samples and sent to the OU Environmental Engineering Laboratory to perform IC sulfate content testing according to the ASTM standard, E2469-06: Standard Test Method for Chloride in Monoethylene Glycol by Ion Chromatography.

3.3.13.3 Sulfate Burn Test

Soil test samples included gypsum, sand, hickory clay, and a mixture of the three. The sulfate burn test was based on ASTM D 2974 “Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils,” and D 2492 “Standard Test for Forms of Sulfur in Coal.” D 2974 is used to measure the moisture content, ash content, and organic matter in peat or other organic soils. D 2492 is used to determine the sulfate sulfur and pyritic sulfur in coal. Both methods were combined and used to determine the sulfate content in clay soils by first burning off any organic matter present, and then burning off sulfate sulfur in the muffle furnace.

The initial weight of a porcelain tare was recorded, a soil sample of about 20 grams was added to the tare, and the total weight was recorded to the nearest 0.01 gram. Then the sample was placed in the oven at 110° C for at least 16 hours or until there was no change in mass of the sample. The free water was removed in this step, and the water content was calculated. Next, the soil sample was placed in the muffle furnace at 440° C until there was no change in mass of the sample after a further period of heating, and the mass was recorded. This step should have burned off any organic matter in the soil. Finally, the sample was placed in the muffle furnace at 800° C until there was no change in mass of the sample after a further period of heating, and this mass was recorded. This last step should have burned off the sulfate in the soil, so the sulfate content could be calculated.

The sulfate content was calculated as follows:

1) weight of organics = (wt. tare and oven dry soil 110°C) – (wt. tare and soil after 440°C burn)
2) weight of sulfate = (wt. tare and soil after 440°C burn) – (wt. tare and soil after 800°C burn)
3) concentration sulfate = wt. sulfate (mg)/ wt. oven dry soil (kg) (ppm)

3.3.13.3.1 Hydrochloric Acid Wash

Soil test samples were the same as for the burn test. The hydrochloric acid wash test was based on ASTM D 2492 “Standard Test for Forms of Sulfur in Coal” part 6.3.1. This method was used to dissolve/extract sulfate from the soil sample, so that it could be burned off in the muffle furnace. The procedure for this test was the same as the sulfate burn, until the organic content was taken at 440° C. At that point, the sample was mixed with 50 mL of 12 M (molar) hydrochloric acid (HCl). The mixture was boiled on the hotplate for half an hour, filtered through filter paper, and washed with deionized water to ensure the transfer all the HCl to the beaker. The soil and filter were placed in a crucible and the muffle furnace at 800° C. The sulfate content was calculated in the same manner as for the sulfate burn test.

3.3.14 Oedometer Tests

Oedometer free swell tests were conducted to analyze the volume change behavior of the soils, following ASTM Standard D4546 – 96 – Method A. The free swell tests were also conducted on the soil mixed with 5% lime.

<u>Oedometer mixes:</u>

One dimensional free swell tests were run on mixtures of the two manufactured soils. Mixtures of 95% kaolinite with 5% bentonite, 90% kaolinite with 10% bentonite, 85% kaolinite with 15% bentonite, 75% kaolinite with 25% bentonite, and 50% kaolinite with 50% bentonite were mixed. Blank samples of these mixtures were run as well as with a known concentration of sulfate and 5% lime added. Blank samples of 100% kaolinite and 100% bentonite were run as well. On each mixture, an Atterberg limits tests was run before the oedometer samples were made to determine the plastic limit. The oedometer samples were all mixed to the plastic limit of that particular mixture and allowed to sit overnight. The next day, 5% lime was added for the samples tested with lime, and the samples sat for one hour before being placed in the oedometer cell ring and on the frame. The samples were compacted in three layers based on the height of the ring. Since the samples were reasonably soft, there was no need to use a compaction hammer. Either a small weight or fingers were used to press the sample into the ring. The same method for free swell that was used on the other oedometers was used on these tests.

4 Index, Chemical and Physical Testing Results

4.1 Soil Classification

4.1.1 Natural Soils

The eight natural soil samples were tested using several index tests and the results are shown in Table 4-1, Table 4-2, Table 4-3, Table 4-4 and Table 4-5. Seven of the soils classify as lean clay, CL, while one classifies as silt, ML, using the USCS classification. The classifications using AASHTO classification are A-4, A-6 and A-7-6. The range of sulfate concentration, which was the focus of this report, was very wide from 120-84,000 ppm. These varying sulfate concentrations were used to study soil behavior with the addition of lime. The pH of all the soils was slightly basic with a range of 8-9.1 and the amount of organic content in all soils was low. The specific surface areas ranged from 47-127 m^2/g, which indicates kaolinitic/illitic mixed clays, and supports the XRD results.

4.1.2 Pure Clays

When the Hickory Glaze results are compared with the Hickory Glaze with lime results, one can see that the index parameters are increased with lime except for the total surface area. The total surface area of the Hickory without lime was over double that of the Hickory with lime which was expected, but the PI increased with lime, which was opposite of what should have occurred. This behavior may explain why the Hickory (kaolinite) did not swell at all in the saturated, remolded free swell testing. When the Bentonite and Bentonite with lime are compared, the lime drastically decreased the liquid limit and decreased all other index parameters with the exception of the plastic limit, which is expected with the addition of lime. The results for the index testing were close to what was expected for the Bentonite. The cation exchange capacity, shown in Table 4-6, was low for the Hickory Glaze and higher for the Bentonite. The cation exchange results are from samples sent to Harris Labs. The cation exchange for Bentonite was not quite as high as one would expect for a montmorillonite clay, but it was still much higher in comparison with the Hickory Glaze. A typical range of CEC values for kaolinite is 3-15 meq/100g, illite is 10-40 meq/100g, and montmorillonite is 80-150 meq/100g. A typical range of values for SSA of kaolinte is 10-20 m^2/g, illite is 65-100 m^2/g, and montmorillonite is 600-870 m^2/g (Mitchell 1993). Various mixtures of hickory clay and bentonite clay were made to test the effect of the amounts of the different clay minerals to the swell potential.

Table 4-1 Soil Classification of the Natural Soils.

	Soil Name	D_{30} mm	D_{50} mm	D_{60} mm	Gravel %	Sand %	Fines %	Silt %	Clay Size %	USCS Classification	AASHTO Classification
Soil #1	Blaine Shale	-	0.023	0.280	0.2	48.4	51.4	11	40.5	CL-sandy lean clay	A-7-6(8) Clayey soils
Soil #2	Vernon Soil	-	0.001	0.003	0.3	7.5	92.2	35	57.4	CL-lean clay	A-7-6(18) Clayey soils
Soil #3	Dog Creek Top	-	0.017	0.047	0	24.6	75.4	38	37.0	CL-lean clay with sand	A-6(10) Clayey soils
Soil #4	Dog Creek Bottom	-	0.050	0.016	0	14.0	86.0	43	43.4	CL-lean clay	A-6(15) Clayey soils
Soil #5	Hennessey Top	-	0.009	0.036	0	24.0	76.0	38	38.1	CL-lean clay with sand	A-6(11) Clayey soils
Soil #6	Hennessey Bottom	-	0.004	0.045	0.2	39.5	60.2	15	45.5	CL-sandy lean clay	A-7-6(8) Clayey soils
Soil #7	Cloud Chief	0.014	0.041	0.049	3.3	7.2	89.5	76	13.9	ML-silt	A-4 (0) Silty Soils
Soil #8	Flower Pot	-	-	0.002	0	7.6	92.4	30	62.1	CL-lean clay	A-6(18) Clayey soils

Table 4-2 Index Properties of the Natural Soils.

	Soil Name	*Colorimetry* Sulfate ppm	*IC* Sulfate ppm	pH	Conductivity mS	Moisture Content (%)	Organic Content (%)	G
Soil #1	Blaine Shale	84000	80979	7.9	1870	16.2	2.0	2.95
Soil #2	Vernon Soil	8533	9186	8.1	2035	10.9	2.4	2.77
Soil #3	Dog Creek Top	200	194	8.1	118	7.6	2.9	2.77
Soil #4	Dog Creek Bottom	200	135	8.0	391	11.6	2.7	2.75
Soil #5	Hennessey Top	240	498	8.4	479	8.0	2.5	2.67
Soil #6	Hennessey Bottom	493	344	8.7	756	7.4	2.8	2.78
Soil #7	Cloud Chief	120	40	9.1	54	2.1	1.4	2.7
Soil #8	Flower Pot	4133	3928	8.3	546	8.8	2.8	2.8

Table 4-3 Index Properties of the Natural Soils (cont)

	Soil Name	LL %	PL %	PI %	LS %	SL %	SSA m^2/g	Ext. SSA m^2/g	Int. SSA m^2/g	CEC (meq/100g)	Calcite %	Dolomite %	Carbonate %
Soil #1	Blaine Shale	49.2	27.2	22.0	11.6	19.0	101	46	55	126.1	1.7	1.85	3.6
Soil #2	Vernon Soil	44.6	28.1	16.5	13.2	15.3	127	72	55	36.6	2.2	0.76	2.9
Soil #3	Dog Creek Top	36.0	22.0	14.0	8.7	4.9	61	41	20	23.9	11.9	3.28	15.2
Soil #4	Dog Creek Bottom	39.0	22.0	17.0	11.3	6.9	50	44	6	22.9	2.0	2.57	4.6
Soil #5	Hennessey Top	36.3	20.2	16.1	10.4	12.1	63	38	26	28.9	26.4	3.02	29.4
Soil #6	Hennessey Bottom	42.8	27.7	15.1	14.0	10.1	118	65	53	30.7	4.8	2.47	7.2
Soil #7	Cloud Chief	NP	NP	NP			47	16	31	15.8	6.3	9.9	16.2
Soil #8	Flower Pot	36.7	17.3	19.4			120	60	60	35.3	4.3	2.3	6.6

Table 4-4 Standard Proctor Tests With and Without Lime for the Natural Soils.

		Without Lime		With Lime	
		OMC	γ_{dmax}	OMC	γ_{dmax}
	Soil Name	%	pcf		pcf
Soil #1	Blaine Shale	27.2	97.9	30.3	91.6
Soil #2	Vernon Soil	27.4	95.4	30.1	89.0
Soil #3	Dog Creek Top	19.9	104.9	24.9	96.7
Soil #4	Dog Creek Bottom	20.0	106.2	21.0	102.4
Soil #5	Hennessey Top	17.0	113.2	20.5	103.0
Soil #6	Hennessey Bottom	18.2	96.7	18.9	97.9
Soil #7	Cloud Chief	16.5	109.4	18.0	103.0
Soil #8	Flower Pot	20.0	106.8	23.0	98.6

Table 4-5 Comparison of Soil Properties with and without Lime for the Natural Soils.

		Without Lime				With Lime			
		SSA	Ext. SSA	Int. SSA	CEC	SSA	Ext. SSA	Int. SSA	CEC
	Soil Name	m^2/g	m^2/g	m^2/g	(meq/100g)	m^2/g	m^2/g	m^2/g	(meq/100g)
Soil #1	Blaine Shale	101	46	55	126.1	89	42	47	125.4
Soil #2	Vernon Soil	127	72	55	36.6	82	43	39	60.4
Soil #3	Dog Creek Top	61	41	20	23.9	56	22	34	124.8
Soil #4	Dog Creek Bottom	50	44	6	22.9	55	26	29	78.9
Soil #5	Hennessey Top	63	38	26	28.9	68	22	46	60.7
Soil #6	Hennessey Bottom	118	65	53	30.7	59	41	18	39.1
Soil #7	Cloud Chief	47	16	31	15.8				
Soil #8	Flower Pot	120	60	60	35.3				

Table 4-6: Combined index test results of pure clays.

	LL (%)	PL (%)	CF (% <2μm)	Total SSA (m^2/g)	External SSA (m^2/g)	LS (%)	Carbonate (%)	CEC (meq/100g)
Hickory Glaze	71.3	32.4	63.6	42	18	13.4	1.33	2.3
Hickory Glaze w/lime	91.5	42.2	n/a	17	22	15.7	n/a	n/a
Bentonite	625.9	60.1	75.1	554	23	49	1.94	39.6
Bentonite w/lime	276.8	76.4	n/a	409	17	44.2	n/a	n/a

4.1.3 XRD

The results of the X-Ray Diffraction tests performed on each sample are shown in diffractograms below. The most common clay mineral present in these eight samples are chlorite and illite with a mixed mineral type of smectite. Most samples contain sulfate and some non-clay components including feldspars and quartz.

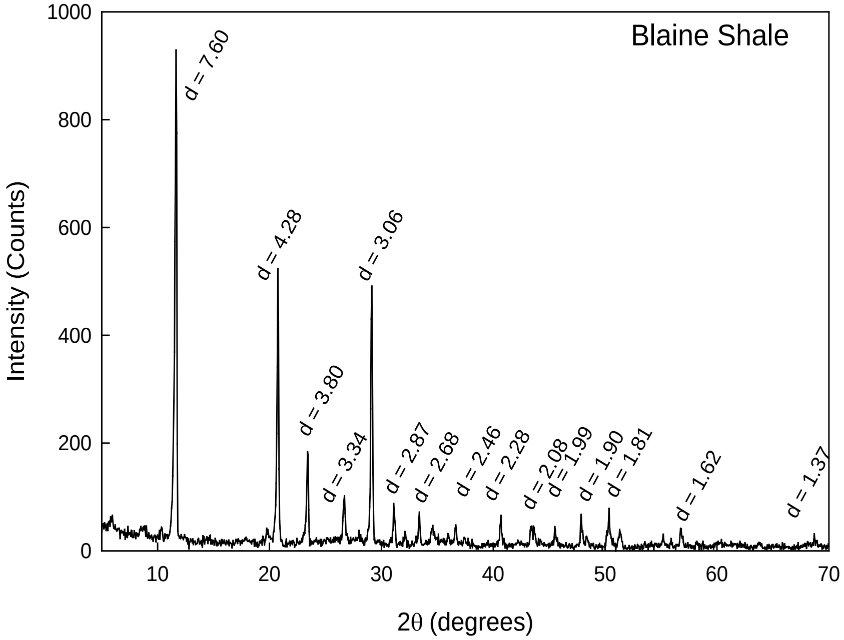


Figure 4-7 Soil #1, Blaine Shale Diffractogram.

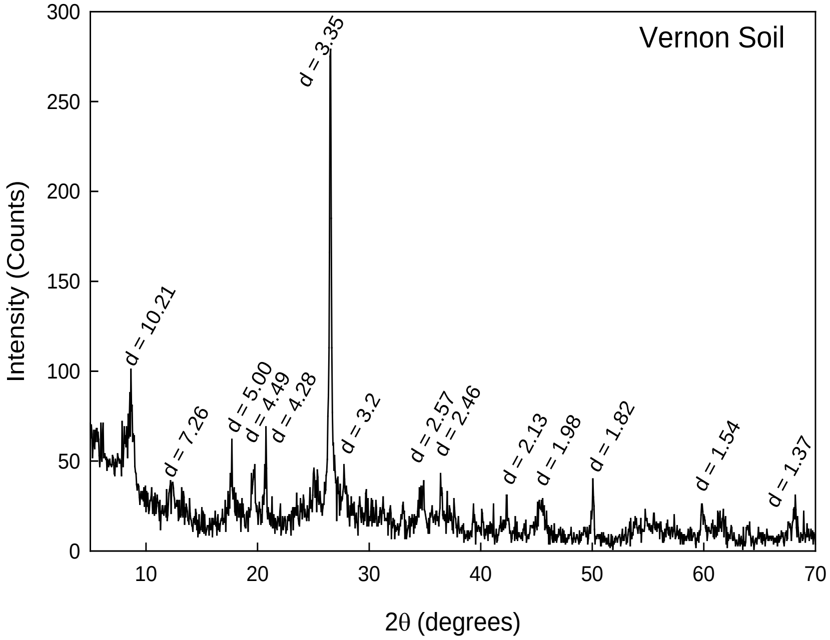


Figure 4-8 Soil #2, Vernon Soil Diffractogram

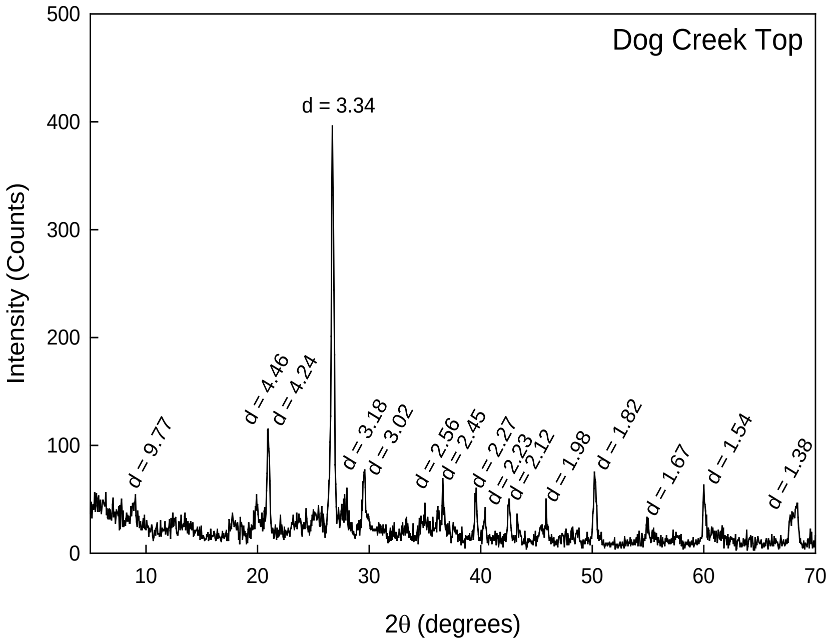


Figure 4-9 Soil #3, Dog Creek Top Diffractogram

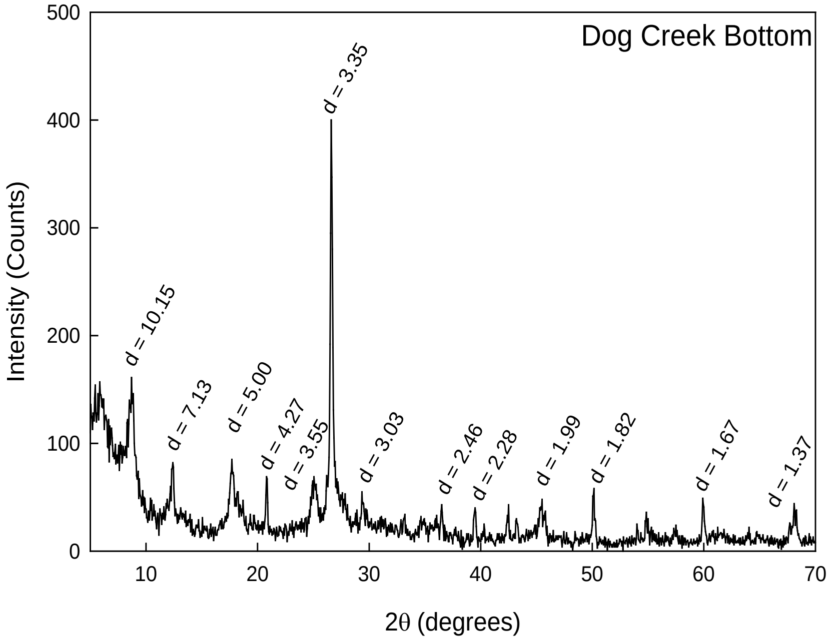


Figure 4-10 Soil #4, Dog Creek Bottom Diffractogram

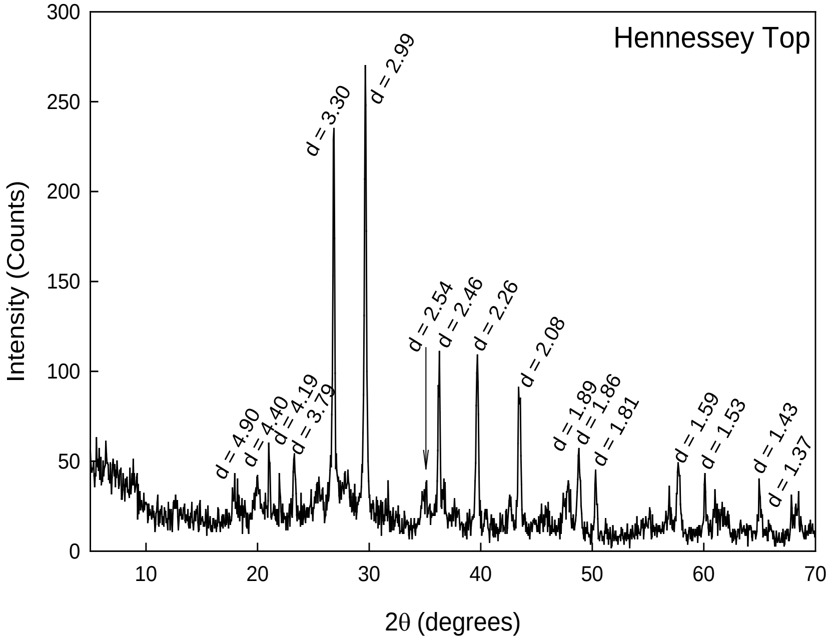


Figure 4-11 Soil #5, Hennessey Top Diffractogram

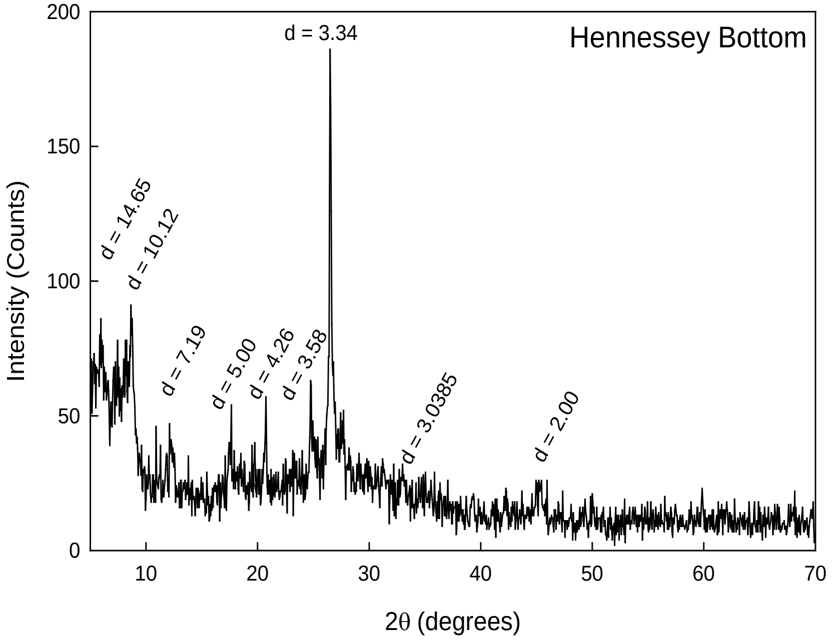


Figure 4-12 Soil #6, Hennessey Bottom Diffractogram

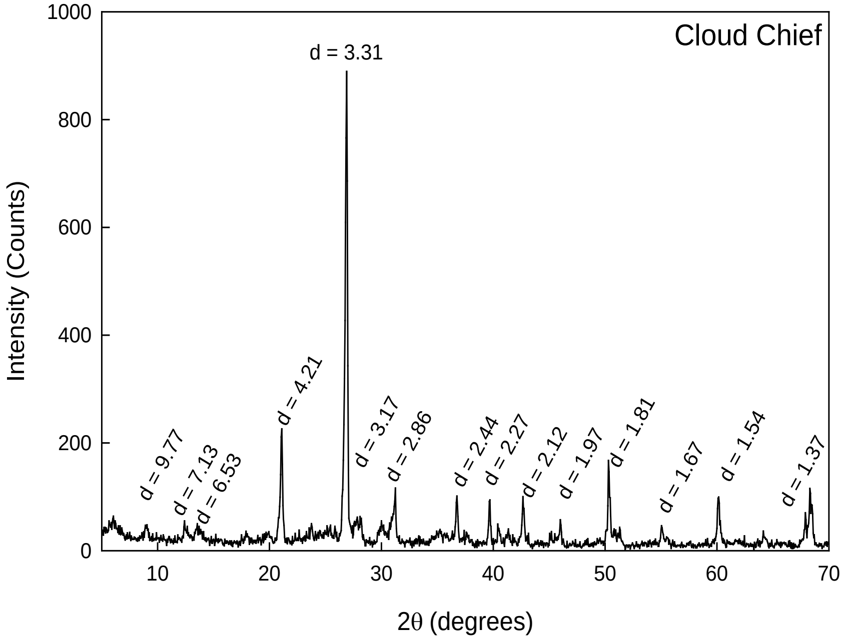


Figure 4-13 Soil #7, Cloud Chief Diffractogram

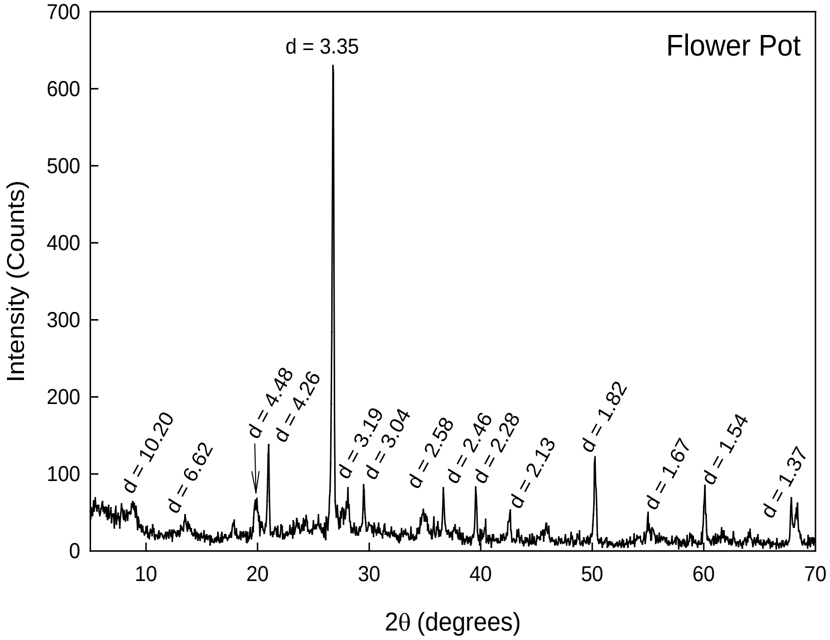


Figure 4-14 Soil #8 Flower Pot Diffractogram

Table 4-7 shows the mineral compositions of these soils, which were found through identifying standard peaks on the XRD diffractograms using JADE software. It was not possible to extract quantitative or semi-quantitative data from these figures because the samples contained other particles than clay. Thus only qualitative information was available. Most of the soils contain at least one clay mineral (illite, montmorillonite, or kaolinite) and two contain multiple clay minerals. All the soils contained quartz.

Table 4-7. Mineral Components of Eight Natural Soils

	Minerals						
Soil	Quartz	Gypsum	Anorthite	Illite	Montmorillonite	Calcite	Halloysite
Blaine Shale	**x**	**x**		**x**	**x**		
Vernon	**x**			**x**			
Flower Pot	**x**		**x**	**x**		**x**	
Dog Creek Top	**x**					**x**	
Dog Creek Bottom	**x**			**x**		**x**	**x**
Hennessey Top	**x**			**x**		**x**	
Hennessey Bottom	**x**						
Cloud Chief	**x**	**x**		**x**			

Perhaps the amount of swelling seen in natural samples depends on not only the sulfate content and lime but also the mineralogical make-up of the soil. The presence of certain minerals in the same soil could indicate a greater potential for swelling. Blaine Shale, Vernon, Flower Pot, and Hennessey Bottom all experienced swelling with the addition of lime. Montmorillonite has the highest swelling potential of all the clay minerals, so it likely contributes to the swelling. Quartz is mostly inert, so should not affect swelling properties of the soils. It is difficult to identify which minerals contribute most to the swelling potential since the data are only qualitative. Also, the swelling potential cannot be solely based on mineral presence because some of the natural soils which did not swell contained some of the same minerals as the swelling soils.

More research is necessary to identify mineral combinations along with certain sulfate contents which indicate a higher possibility for ettringite formation and swelling. It would be useful to compare quantitative or semi-quantitative data for the mineral composition of the soils with the free swell and sulfate content to see if any correlations exist.

5 Sulfate Testing Results

5.1 Introduction

The current soil sulfate test performed by the Oklahoma Highway Department, is (OHD) L-49 Method of Test for Determining Soluble Sulfate Content in Soil. As mentioned above, this is a gravitational filtration method that calls for a natural soil sample to be passed through a #10 sieve, and then placed into a jar and filled with water, creating a slurry of dilution ratio 40:1. This slurry is then shaken for 15 minutes and left to sit for 16 hours before being poured into a filter paper cone. The filtrate is then used in the colorimeter with Barium Chloride tablets to measure the turbidity of the sample. While outside of our original scope of work, an investigation was conducted to determine whether the method accurately measured the total amount of available sulfates in the soil. Subsequently, we formulated questions with the current soil sulfate testing method, and therefore, spent considerable time determining an appropriate methodology to use.

5.2 Colorimetry Validation with Repeatability Studies

Our first step was to use a manufactured solution of laboratory grade gypsum ($CaSO_4$) and water to ensure that the colorimeter readings were measuring actual gypsum concentrations. In addition, we had those same concentrations tested using the IC method to double check the colorimetry results.

Repeatability studies were performed on manufactured concentrations of 250 ppm and 10000 ppm sulfate. Because of the large scale difference they are shown on two different graphs (Figure 5-1 and Figure 5-2). For the lower concentration (250 ppm), the colorimeter read five results with a range of 187-347 ppm, an average of 252 ppm and a standard error of 30.7 ppm. At this low concentration, the colorimeter accurately measured the manufactured concentration, however, there still was some variability in the measurements.

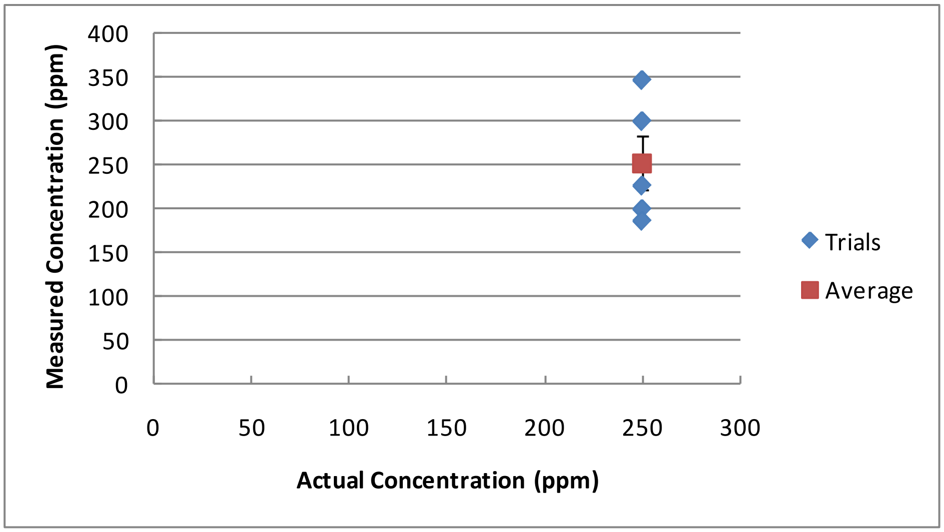


Figure 5-1 Repeatability Study with 250 ppm in the Colorimeter.

The repeatability study with 10000 ppm sulfate showed a range of 4200 to 7200 ppm, which not only had significant variability, but underpredicted the actual sulfate concentration. The colorimeter can read 0-200 ppm, ± 10 ppm, therefore, any concentrations above this have to be diluted to a higher dilution ratio. The higher dilution ratio, the more the error can propagate (i.e., a reading of 30 ppm on the colorimeter at a dilution ratio of 40 would be 1200 ppm ± 400 ppm). This becomes especially troublesome at concentrations as high was 10,000 ppm because this particular solution had to be diluted by 200:1, therefore, the error would actually be ±2000 ppm according to the manufacturers specifications. This repeatability study brought to light some of the problems with the colorimetry method as well as some solubility issues at high sulfate concentrations.

Once it was discovered that high concentrations of sulfate were not being measured correctly by the colorimeter, an ion chromatography test was added to check the results of the colorimeter. Figure 5-3 shows the results of sulfate testing using both the colorimetry and IC methods. As can be seen, both the colorimetry and IC tests underestimated the concentrations of sulfate above 3000 ppm, which was now being preliminarily concluded to be a function of the solubility of gypsum.

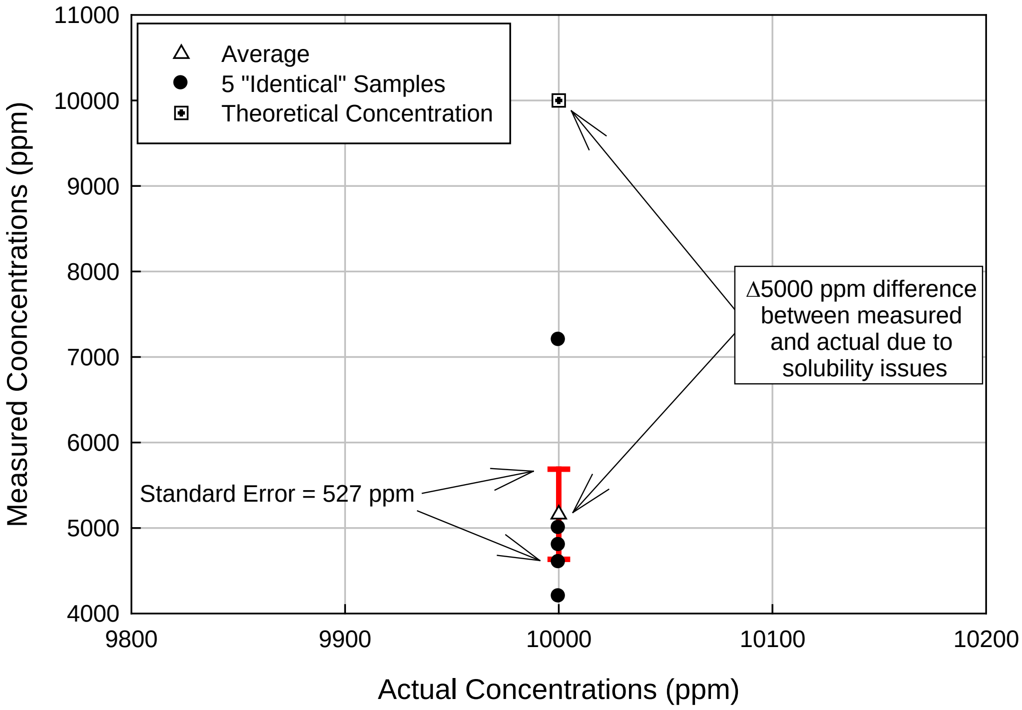


Figure 5-2 Repeatability Study with 10,000 ppm in the Colorimeter

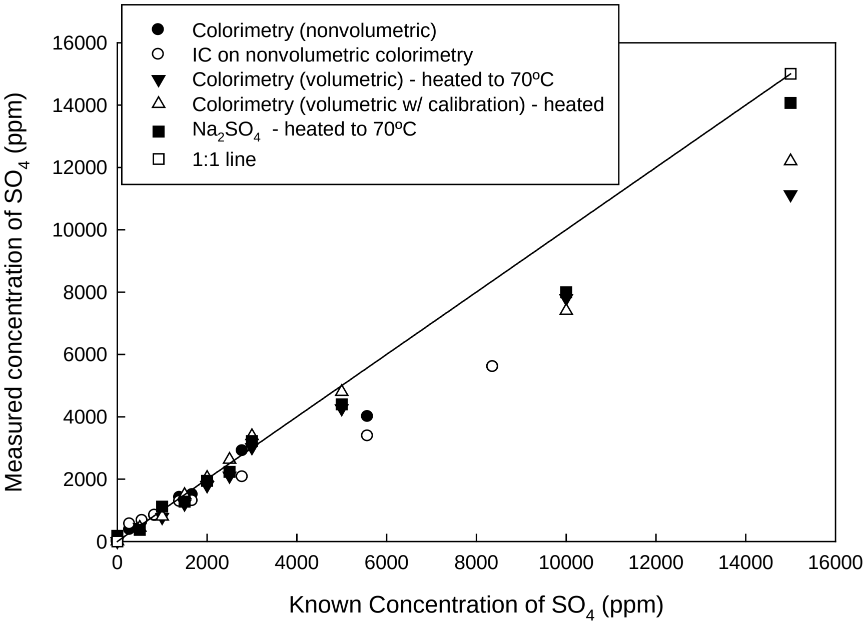


Figure 5-3: Colorimetry and IC results compared with 100% solubility recovery (from Adams 2008).

As a quality control check on the methods used in the lab, an additional study two years after the original data were gathered was performed. As can be seen in Figure 5-4, the same solubility issues above 3000 ppm exist.

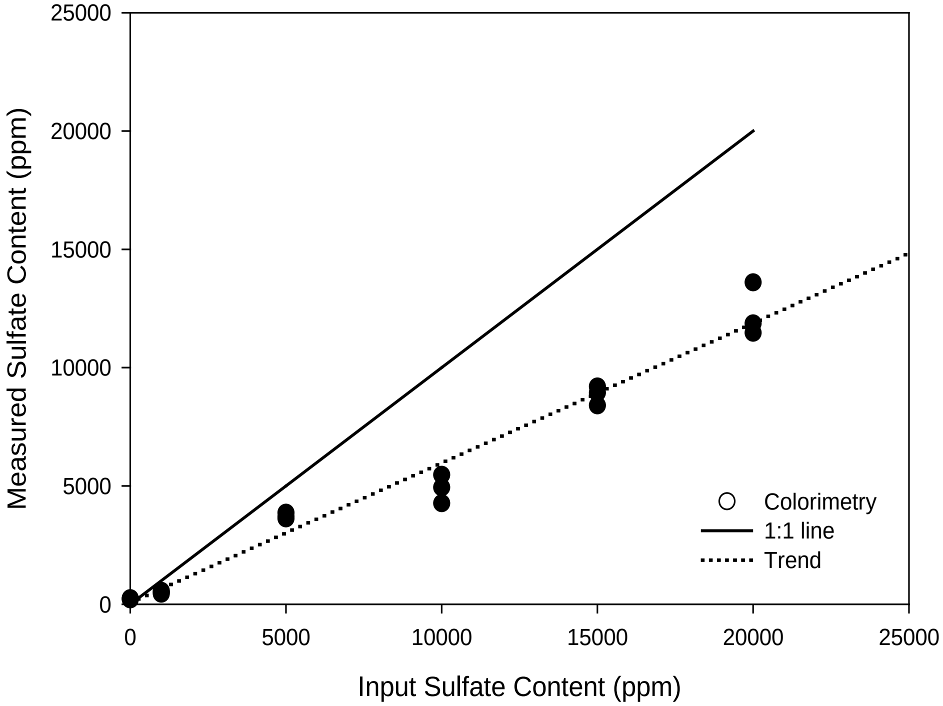


Figure 5-4. Known Sulfate Content versus Colorimetry Values for Manufactured Soil (from Campbell 2010).

Since colorimetry does not accurately measure sulfate contents above 3,000 ppm, other methods were tried.

5.3 Testing the Solubility of Sulfate

Since both the colorimeter and the IC methods under predicted actual $CaSO_4$ concentrations above 3000 ppm, we chose to check both methods using another type of sulfate; sodium sulfate (Na_2SO_4) is known to be completely soluble in water.

Several Na_2SO_4 test samples were made to show the accuracy of the colorimetry and IC tests. The sodium sulfate proved that the colorimetry test and the IC test was testing the sulfate levels fairly close to the true values at lower concentrations of sulfate, as seen in Figure 5-3 above, but the sodium sulfate still did not give a 1-1 correlation between theoretical and measured sulfate at higher sulfate concentrations. It is still not completely understood why the sodium sulfate content was underestimated at higher concentrations. A possible reason is that the $CaSO_4$ and Na_2SO_4 reach a saturation level at a certain point that no amount of dilution can reverse.

Once it was determined that the sulfate testing machines were working and validating each other, we had to determine why not all the sulfate was being measured after following the OHD L-49 sample preparation method. It appeared that simply shaking the gypsum in water and gravitationally filtering it was not dissolving all the sulfate, and therefore, several additional methods were attempted. The first method was heating the samples to 70 °C. This did not significantly increase the solubility of the manufactured solutions.

The next method entailed adjusting the pH by adding both hydrochloric acid (HCl) and sodium hydroxide (NaOH) to see if it resulted in increased solubility. The manufactured sulfate concentration was 10,000 ppm with an original pH of 7.2. The pH was lowered to 1 using HCl and raised to above 12 using NaOH, while taking sulfate samples at each pH step. As can be seen in Figure 5-5, bringing the pH down from ~ 7.5 to ~1 with the HCl test had limited affect on the sulfate concentration. The colorimetry sulfate testing method measured 6400 ppm at a pH of 7.2 and 6400 ppm at a pH of 1.2. At a final pH of about 1, the sulfate concentration did not change. As can be seen, the colorimetry results showed a concentration hovering around ~6,400 ppm, severely underreporting the true concentration. The pH appears to have little to no affect on sulfate solubility.

The discrepancy at a pH of ~7 between two 'identical' samples mixed to 10,000 ppm, may possibly be contributed to variable partial solubility. This means that when two samples are mixed with identical amounts of gypsum, and left for 16 hours to soak, as the current OHD L-49 method recommends, different amounts of sulfate can dissolve in the time allotted, giving two different concentrations. In this case, the difference was 2000 ppm. This difference is not only a function of partial solubility, but of inherent colorimetry machine error, which is ± 10 ppm. At a dilution of 1:400, this error could be as much as ± 4000 ppm, which encompasses the 2000 ppm difference between the two 'identical' samples. The combination of partial solubility and colorimeter error margins needs to be addressed in order to accurately measure sulfate concentrations.

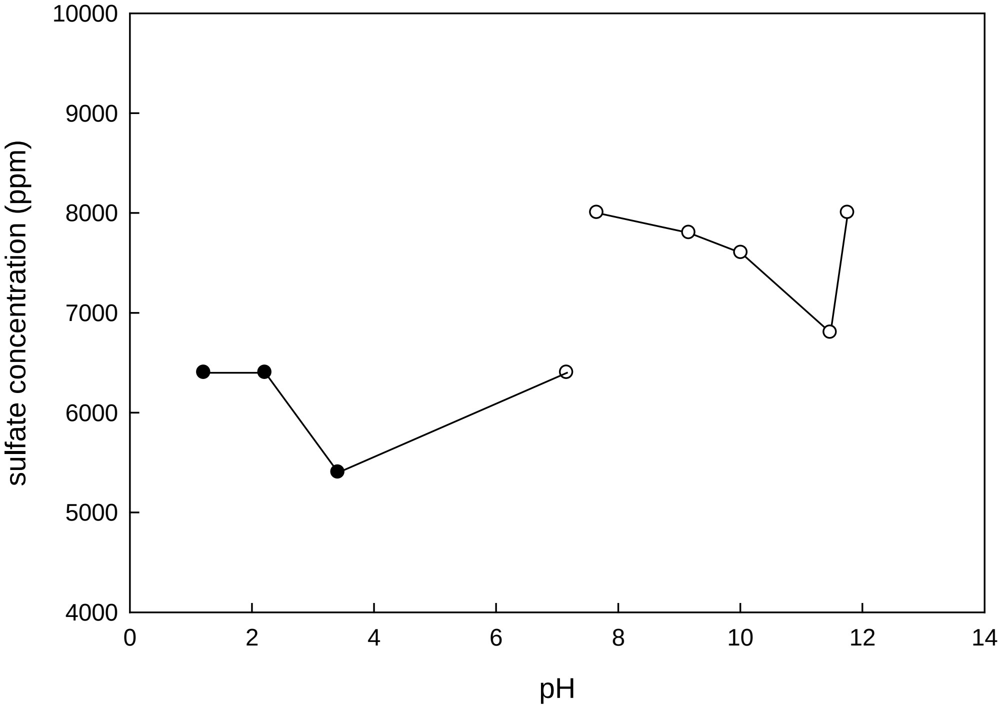


Figure 5-5: HCl test

The next step was to determine if solubility of our samples at a dilution of 1:20-1:100 was indeed reaching a saturation point. As was previously mentioned, the colorimeter and the IC were measuring lower concentrations than were actually present. We needed to understand why this was occurring and therefore chose to use multiple washes to determine if the original dilution was reaching saturation. If it was, then at what point would the sulfate all be accounted for? In the field, theoretically, the groundwater would never reach a saturation point because it is constantly recharging and moving, and therefore, if a rainfall event occurred several years after road way construction, there was a chance that the road base would still be reactive.

However, in order to test the saturation point of the solubility of gypsum, we had to use a different method to separate the soil from the water, other than gravity filtration, as it sometimes took 1 full day to filter the soil sample. Several methods were attempted, including water aspiration and glass sintered funnels, along with vacuum filtration, but the filters clogged and ripped and repeated washes were impossible to conduct because of lost sample. Therefore, a centrifuge was obtained and samples were centrifuged for a certain amount of time in order for the solution to be clear and all the soil to be packed on the bottom of the bottle. The solution was then pipetted into a colorimeter and IC sample bottle. The sample was tested, and then the remaining water was poured off and a new wash with the original dilution ratio, was introduced. This process was repeated until a stable concentration was noted.

Figure 5-6 shows the results of a multiple-wash test performed using a centrifuge. One can see that at known concentrations of 1000, 5000 and 12000 ppm sulfate, the first wash showed much less than the known concentration. With multiple washes, the 1000 ppm sample improved only slightly (~20% recovery after 4th wash), where the 5000 ppm sample increased from 1500 ppm on the first wash to 2200 ppm on the 4th wash and stabilized (~40% recovery after 4th wash). The 12000 ppm sample showed the most marked increase with increasing washes from 3000 ppm to 8000 ppm (~65% recovery after the fourth wash). Even though the sulfate concentration increased with additional washes, the concentrations never reached the theoretical concentration.

Therefore, the test was repeated with new samples using sodium chloride in the water to simulate ocean water conditions. As can be seen, after the first wash, much more sulfate dissolved out of solution; over 80% of the theoretical in all three cases and the second wash didn't improve these values at all, and so the test was stopped after 2 washes. Figure 5-7 shows the same test results for the experiment in Figure 5-6, but it shows only the concentration of sulfate after the last wash for the NaCl and without NaCl tests, versus the theoretical values.

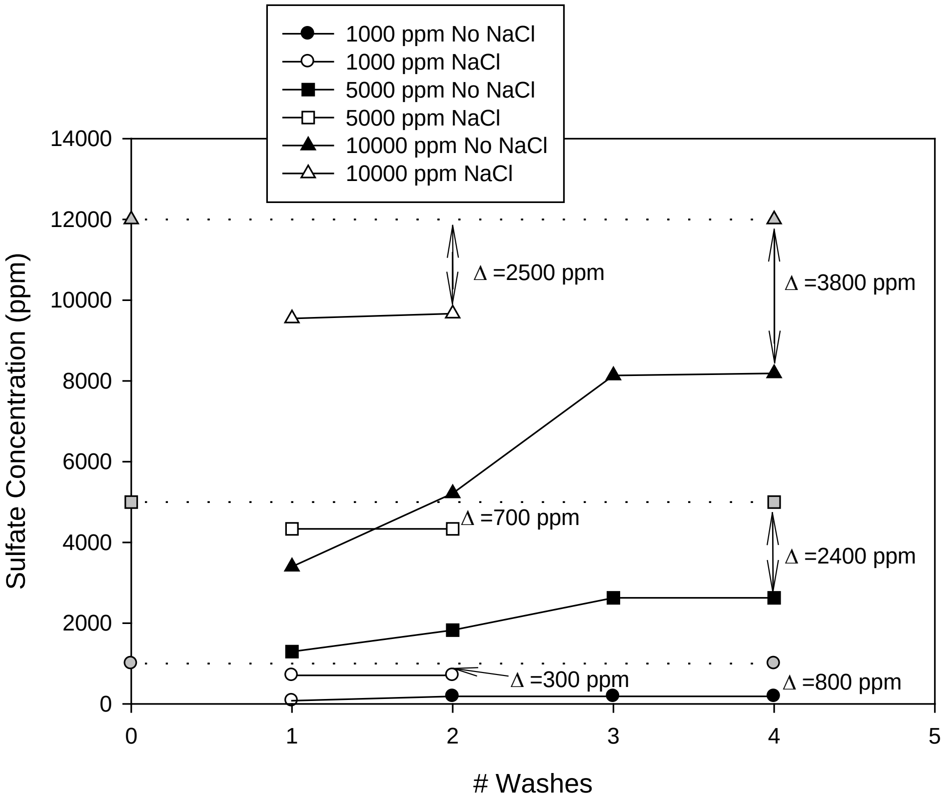


Figure 5-6: NaCl Centrifuge Results – Additional Washes

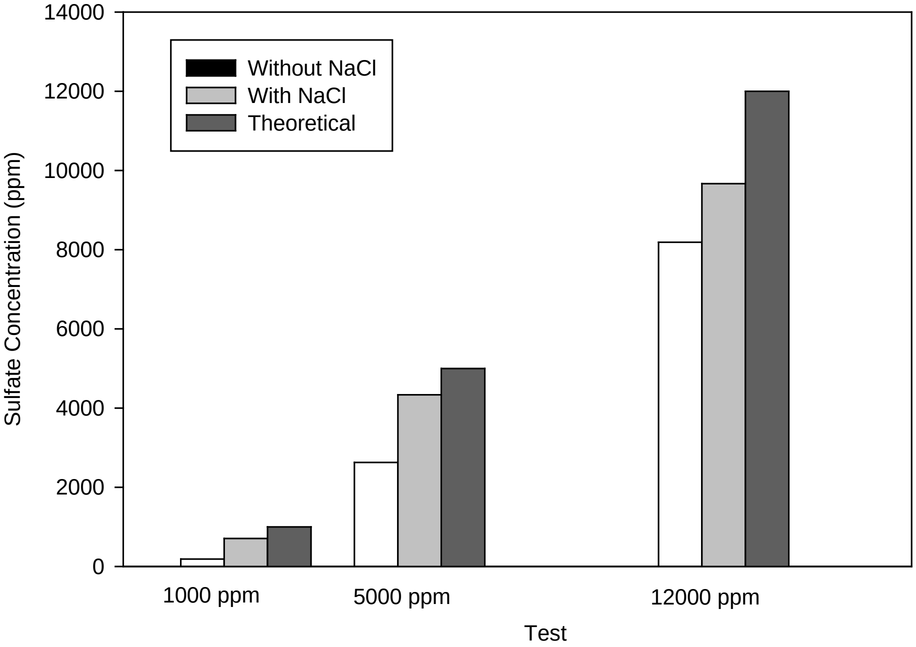


Figure 5-7: NaCl Centrifuge Results – With and Without NaCl

5.3.1 Sulfate Burn Test

The sulfate burn test was performed on kaolinite clay (Hickory Clay), sand, and gypsum ($CaSO_4 \cdot 2H_2O$). The samples were individually tested to determine whether or not sulfate would be the only substance to burn off at 800°C. The Hickory Clay and sand contain no sulfate. Figure 5-8 shows the weight of material burned at 800°C versus the sulfate in the sample.

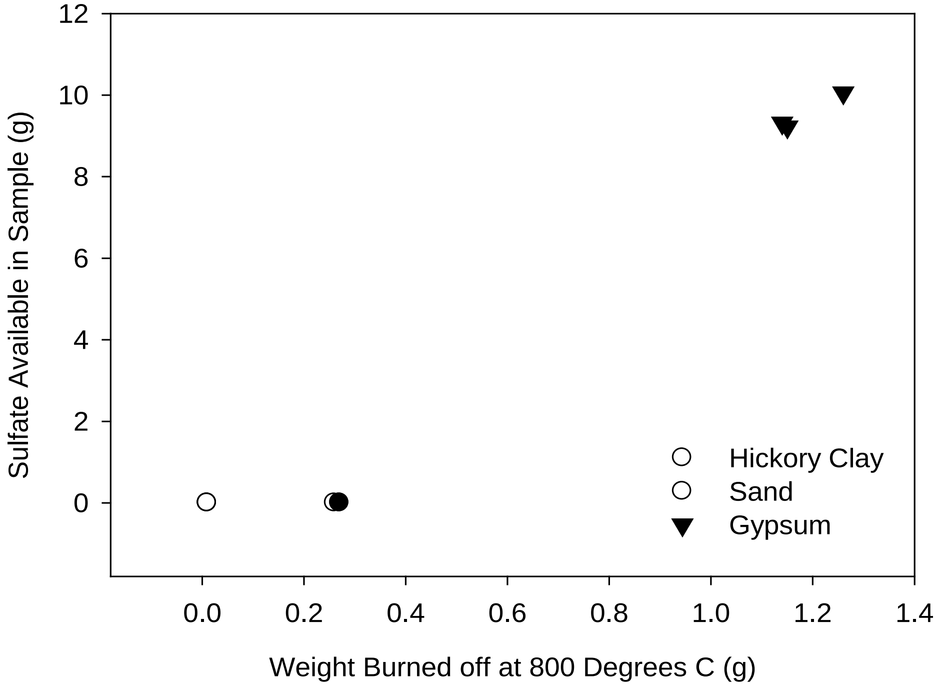


Figure 5-8. Available Sulfate Compared with Burned Weight

The figure shows that kaolinite lost mass at 800°C, but this mass must be something other than sulfate, since kaolinite does not contain any sulfate as seen in its chemical formula, $Al_2Si_2O_5(OH)_4$. The only other possibilities would be that aluminum, silicon, or water burned off the kaolinite. Aluminum burns at 3826.85°C and silicon melts at 1414°C and boils at 2900°C, so the burn temperature of silicon has to be higher than the melting or boiling point. Thus neither aluminum nor silicon burned off at 800°C. According to Wittberg and Wang's (1999) study, kaolinite dehydrates (loses structurally bound water) somewhere between 650-770°C. The sample was heated to 800°C, so the kaolinite must have lost water from its structure when the temperature rose above 650°C.

The gypsum also lost mass during the burn test. For the gypsum, the substance that burned off is most likely sulfate because above 250° C gypsum turns into anhydrite ($CaSO_4$) leaving no more water in the structure. Also, calcium burns off at temperatures higher than its boiling point of 1484°C. Sulfate ignites at 800°C, but only part of the sulfate burned off, approximately 12%, so there was still a significant amount of sulfate left in the sample. This could be due to the structure of the gypsum or 800°C not being high enough to ignite all the sulfate. Since gypsum is a common form of sulfate in natural soil, these results indicate that tests on natural soils would probably only partially remove the sulfate. The sulfate burn method, therefore, seems to be an inaccurate method for determining sulfate content in soils because not all the sulfate is removed and there is no way to account for structurally bound water in clays which might be removed.

5.3.2 Na_2CO_3 Wash Method

In previous water chemistry studies, it was shown that a Na_2CO_3 solution could be used, instead of water, to dissolve gypsum because it removes more of the soluble sulfate than water. Therefore, this method was used to determine if more sulfate could be extracted from the manufactured soil samples. Figure 5-9 shows a calibration curve for the Na_2CO_3 wash method with known input sulfate concentrations. Two samples were tested at 1,000; 3,000; and 5,000 ppm sulfate and four samples were tested at 10,000 ppm sulfate. The measured sulfate content falls below the 1:1 line, indicating that this method does not detect 100% of the sulfate in the sample. However, it will still be compared to colorimetry to see whether or not it is more accurate than that test.

Within the Na_2CO_3 wash method, two separate studies were performed including testing the number of washes and particle size to see if either affected the amount of sulfate measured.

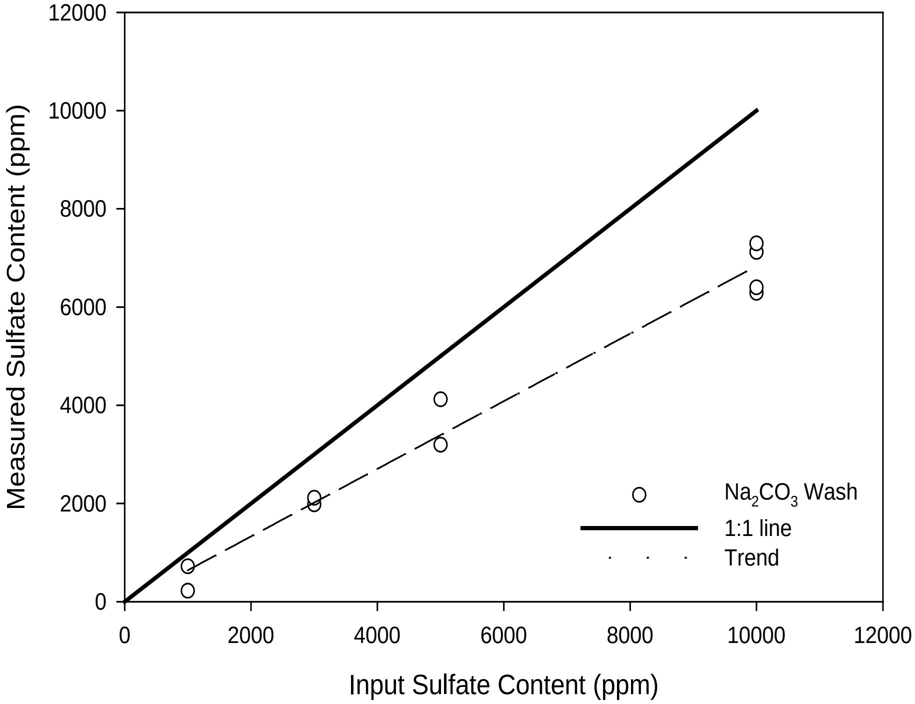


Figure 5-9. Known Sulfate Content versus Na_2CO_3 Wash Values for Manufactured Soil

5.3.2.1 Number of Washes Comparison

Soil samples were again manufactured using 1g kaolinite clay, 1g sand, and 10,000 ppm sulfate in the form of gypsum. The samples were tested using the Na_2CO_3 wash method, and a negative test for $BaSO_4$ occurred after 8 washes. In order to determine if additional washings with Na_2CO_3, after a negative test for $BaSO_4$, would dissolve more sulfate, samples were then washed 10, 12, or 14 times. Figure 5-10 shows the number of Na_2CO_3 washes versus the sulfate concentration. From this figure it is clear that further washings after a negative test for $BaSO_4$ did not result in significantly more sulfate being dissolved. Thus it is not worth the extra time or effort to continue to perform washes after a negative test for $BaSO_4$ occurs. However, at no time did the measured sulfate content equal the sulfate amount used to prepare the samples. While this method seems to measure about 75% of the initial sulfate content in manufactured soils, there is still 25% sulfate left in the sample. It is unclear if simply extending the wash cycle out would eventually remove all of the sulfate, making this test unmanageable in terms of time and effort, or if the bound gypsum would never be recovered because it is held so tightly to the Ca.

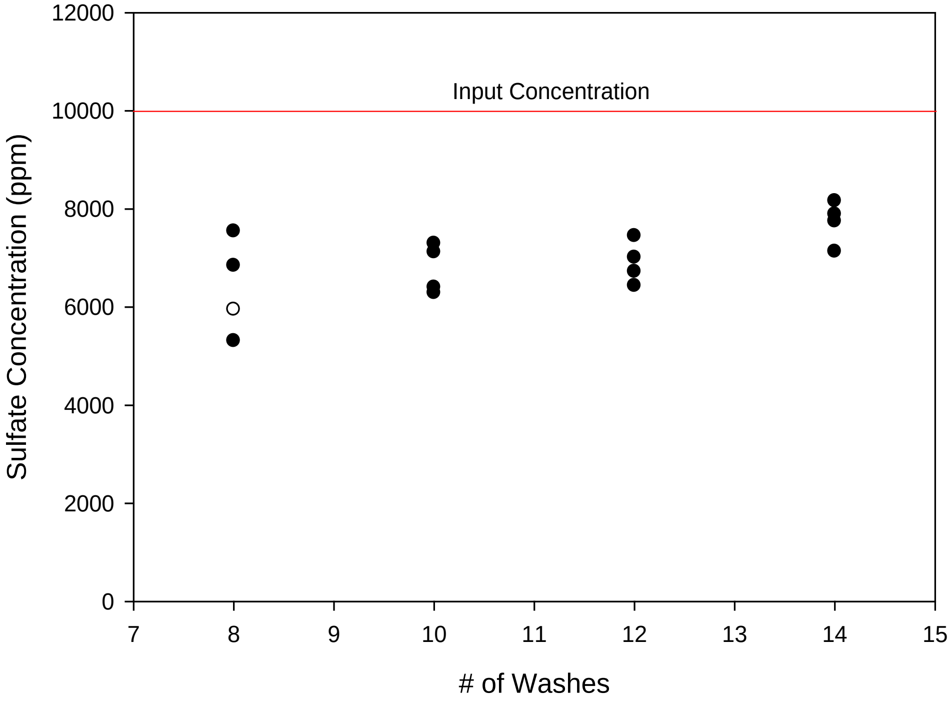


Figure 5-10. Number of Washes versus Sulfate Concentration for Na_2CO_3 Wash Method

5.3.2.2 Particle Size Analysis

Manufactured soil samples composed of 1g kaolinite clay, 1g sand, and 10,000 ppm sulfate in the form of gypsum were tested using the Na_2CO_3 wash method. The gypsum was sieved past a #60, #100, #200, #400, or #500 sieve before being added to the rest of the soil sample. Figure 5-11 shows the results from the particle size analysis. It is clear that the samples sieved past a #200 sieve showed the highest sulfate concentration. Even so, none of the samples showed an output sulfate concentration equal to the input concentration of 10,000 ppm.

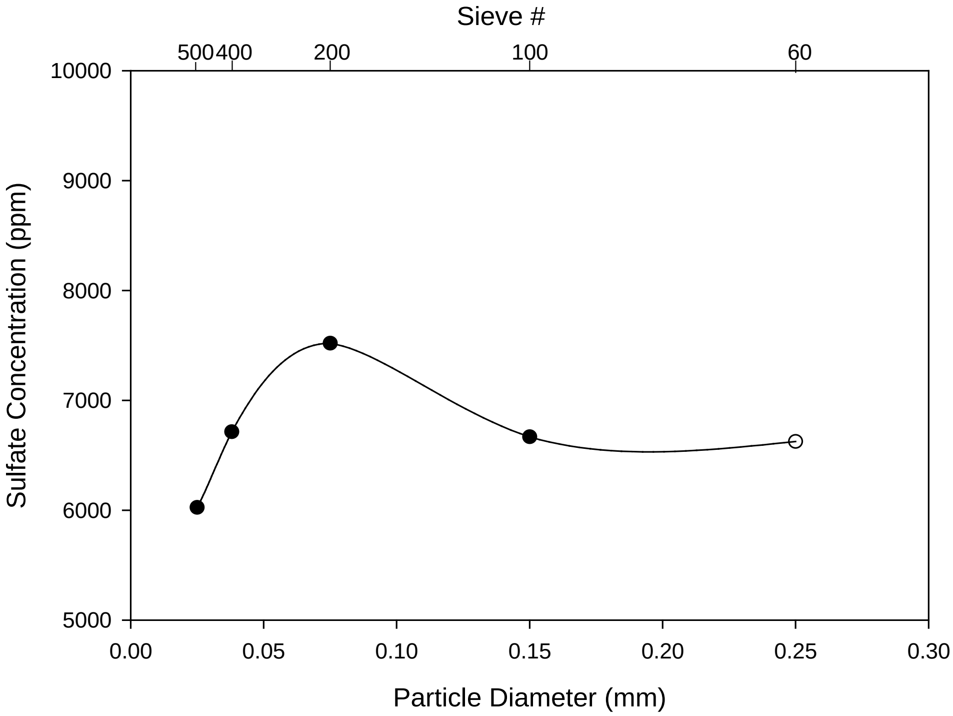


Figure 5-11. Particle Size analysis for the Na_2CO_3 Wash Method

From the literature, it was found that particle size affects the dissolution and swelling. Generally the smaller the particle size, the faster the dissolution and the greater the swelling in a sample. The smallest particle size discussed in the literature was the #200 sieve (0.075 mm), so this study extended the particle size range to include the #400 and #500 sieves.

As the particle size decreased, the sulfate concentration able to be measured increased at the #200 sieve. This makes sense because the smaller the particle, the larger the surface area for reactions or dissolutions to occur. However, as the particle size was decreased to the #400 and #500 sieves, the measured sulfate concentration decreased. At first this seemed illogical, but after further consideration, it is likely the particles started sticking together again after passing through the sieve because the particles were so small, or the gypsum was not being crushed small enough to pass these sieves, and therefore, more soil than gypsum was being sieved resulting in a smaller measured sulfate concentration. Thus the #200 sieve was considered the optimum sieve size for dissolving the largest amount of sulfate.

5.3.3 Method Comparison

When colorimetry was compared to the Na_2CO_3 wash method, the wash method showed higher sulfate contents for the manufactured soil samples. Figure 5-12 compares soil sieved past a #10 and a #200 sieve for the Na_2CO_3 wash method and colorimetry method for a known input sulfate concentration of 10,000 ppm. From this figure, it is clear the Na_2CO_3 wash method produces the highest measured sulfate concentration for soil sieved past the #10 sieve. The point for the #200 sieved Na_2CO_3 wash method is partially behind the point for the #200 sieved colorimetry method, so only shows a slightly higher sulfate concentration. Overall, for both tests, the samples sieved past the #200 sieve show higher measured sulfate concentrations than those sieved past a #10 sieve.

4 samples were tested for the #10 sieve of each method and 3 samples were tested for the #200 sieve for each method. The quality of the repeatability will be defined by the coefficient of variation, COV, which is equal to the mean divided by the standard deviation. If COV ≤ 5, then the samples exhibit good repeatability, if 5 < COV ≤ 10 the samples exhibit satisfactory repeatability, and if COV > 10 the samples exhibit poor repeatability. The COV for the #10 sieve Na_2CO_3 wash method was 6.2, so satisfactory repeatability, and the COV was 19 for the #10 sieve colorimetry method, so poor repeatability. The #200 sieve samples for both methods have a COV value less than 5, so show good repeatability.

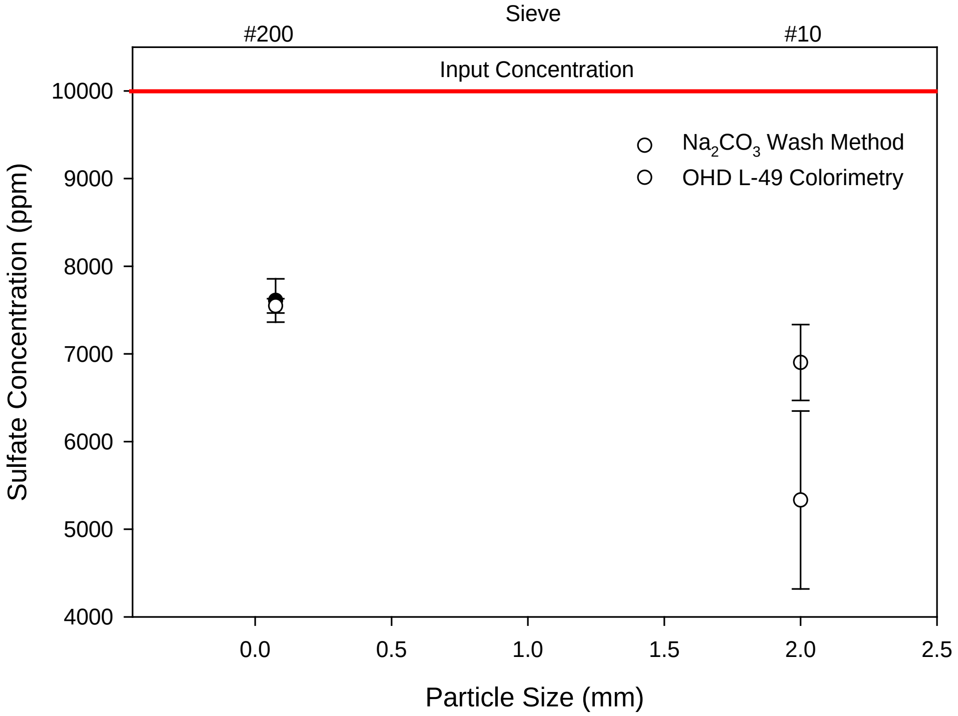


Figure 5-12. Comparison of the Two Test Methods for Manufactured Soil

It was also important to look at the two test methods for varying sulfate contents, specifically 3,000 ppm to 10,000 ppm sulfate where colorimetry is known to be inaccurate. Figure 5-13 shows the calibration curves for the Na_2CO_3 wash method and colorimetry. It appears that the Na_2CO_3 wash method detects slightly more sulfate than colorimetry starting at 3,000 ppm sulfate. Even though the Na_2CO_3 wash method seems to be more accurate than colorimetry for higher sulfate concentrations, it does not detect 100% of the sulfate as shown by the 1:1 line in the figure. Using the equations for the trend lines of the Na_2CO_3 method and colorimetry, it would be possible to input the measured sulfate values and calculate the true sulfate content.

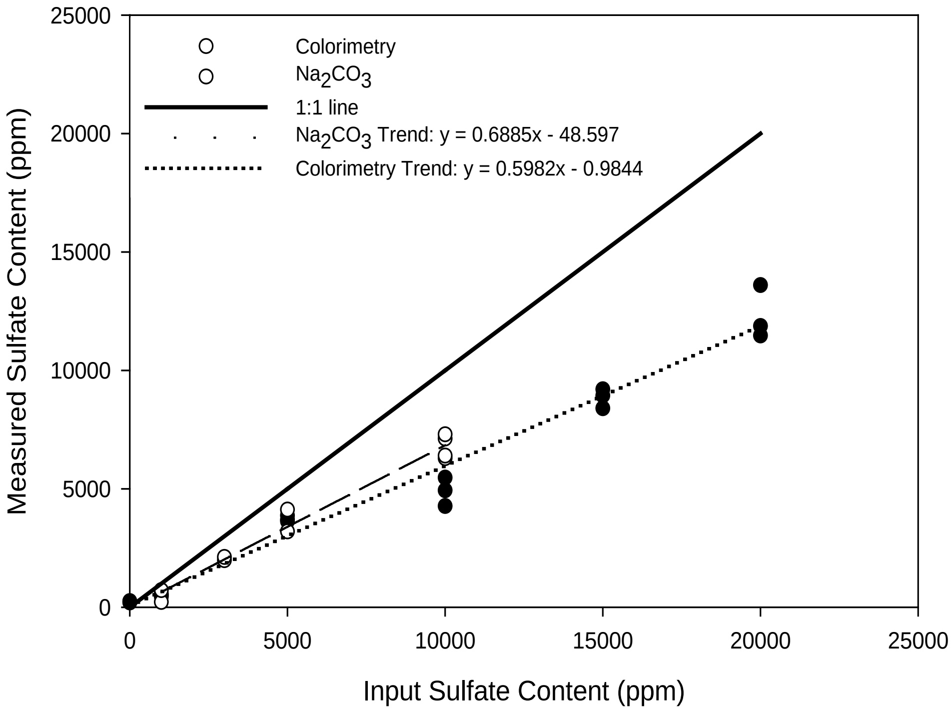


Figure 5-13. Calibration Curve Comparison for Na_2CO_3 Wash and Colorimetry

More research needs to be performed on testing soil sulfate and understanding the solubility issues. The current testing method does not accurately measure available sulfate that will react with lime and water inundated with repeated slugs of fresh water, as can be seen by the results of the study above. Currently, only a portion of the sulfate is being captured in the gravitational filter method. If excess water from rain or a flood were to inundate a stabilized road base, it could trigger an additional ettringite formation and therefore, expansion. Also, if NaCl were placed on roads as a deicer and then infiltrated into the sub-base, it would solubilize the remaining sulfate and reinitiate the heave.

5.4 Natural Soil Results

5.4.1 Flower Pot

Flower Pot soil was sieved past a #10 sieve to mimic the current colorimetry test standard and a #200 sieve because the results found in the study with the manufactured soils showed that the maximum amount of sulfate was removed from the soil at this particle size. The sulfate content for Flower Pot soil was found using colorimetry and the Na_2CO_3 wash method. For the wash method, the soil was washed 10 times with Na_2CO_3 solution during testing because it took 8 washes to get a negative test for $BaSO_4$ and 2 more washes were performed to make sure the sulfate was removed. Figure 5-14 shows the results from the colorimetry and Na_2CO_3 wash test methods for Flower Pot. Notice the sulfate content is significantly higher for the soil sieved past the #10 sieve (2 mm opening) than for the soil sieved past the #200 sieve (0.075 mm opening), which is opposite of what was found in the manufactured soils. Also, the sulfate content is higher for the OHD L-49 colorimetry test than for the Na_2CO_3 wash method for both particle sizes. Note the error bar for the #200 sieve wash method extends past the error bar for the #200 colorimetry method.

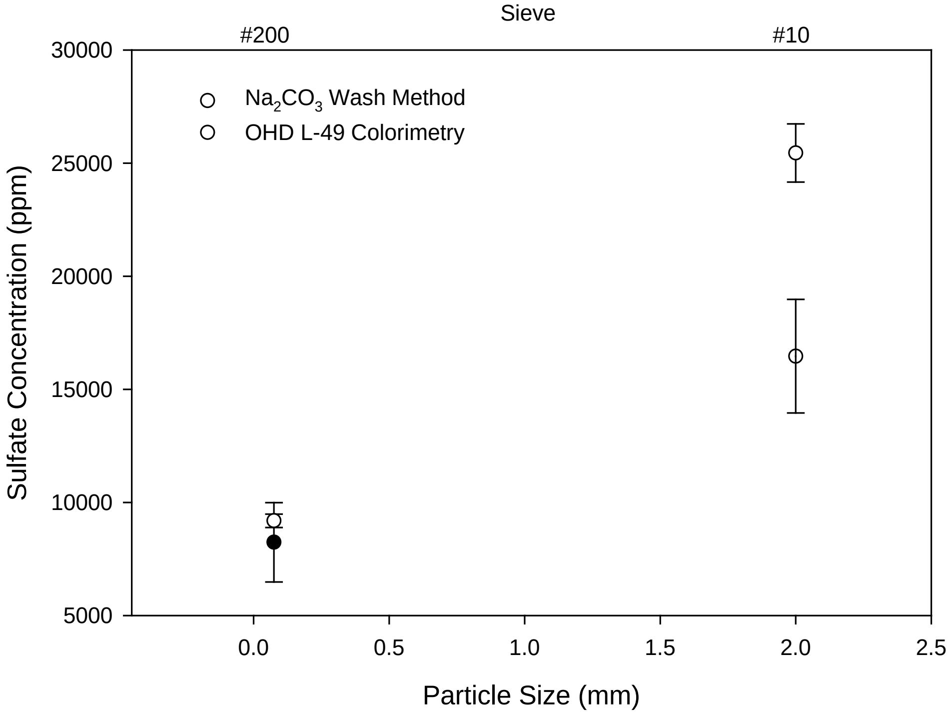


Figure 5-14. Particle Size versus Sulfate Content from Colorimetry and Na_2CO_3 Wash Method on Flower Pot Soil

The Na_2CO_3 wash test produced higher measured sulfate contents for the manufactured soil, but the Flower Pot results show a higher measured sulfate content with the colorimetry method. This is most likely due to the sulfate being bound within the natural soil structure or strongly bonded to the soil preventing more sulfate from dissolving. Whereas in the manufactured soil samples, about 75% of the gypsum is unbound, so dissolves more easily. The difference in natural soil compared to manufactured soil could also be a sample bias due to the gypsum not crushing at the same rate as the soil, resulting in more soil passing through the sieve than the gypsum.

As defined previously, if COV ≤ 5, then the samples exhibit good repeatability, if 5 < COV ≤ 10 the samples exhibit satisfactory repeatability, and if COV > 10 the samples exhibit poor repeatability. From colorimetry tests, the three samples sieved past the #10 sieve had a COV =5, so good repeatability and the three samples sieved past the #200 sieve had a COV =3, so also good repeatability. For the Na_2CO_3 wash method, the five samples sieved past the #10 sieve had a COV= 15, so poor repeatability, and the six samples sieved past the #200 sieve had a COV=21, so they also exhibited poor repeatability. The poor repeatability for several of the tests was most likely caused by the sample quality. The sample size (2 grams) specified was probably too small to accurately represent the soil from one test to another.

5.4.2 Vernon

Vernon soil was sieved past both a #10 and a #200 sieve before sulfate tests were performed, so the effect of particle size could be observed. The sulfate content was found using colorimetry and the Na_2CO_3 wash test. For the wash method, the soil was washed 8 times with Na_2CO_3 solution during testing because it took 6 washes to get a negative test for $BaSO_4$ and 2 more washes were performed to make sure the sulfate was removed. Figure 5-15 shows the colorimetry and Na_2CO_3 wash method results for Vernon soil. These results clearly show a higher sulfate content for the samples sieved past the #10 than the soil sieved past the #200 sieve for both methods. Again the colorimetry method shows higher sulfate concentrations than the Na_2CO_3 wash method, which is opposite the manufactured samples. Vernon is a clay, like Flower Pot, so the sulfate is most likely embedded in the soil structure and does not dissolve as easily as the unbound gypsum in the manufactured samples. Again, the difference in natural soil compared to manufactured soil could also be attributed to the soil having varying properties.

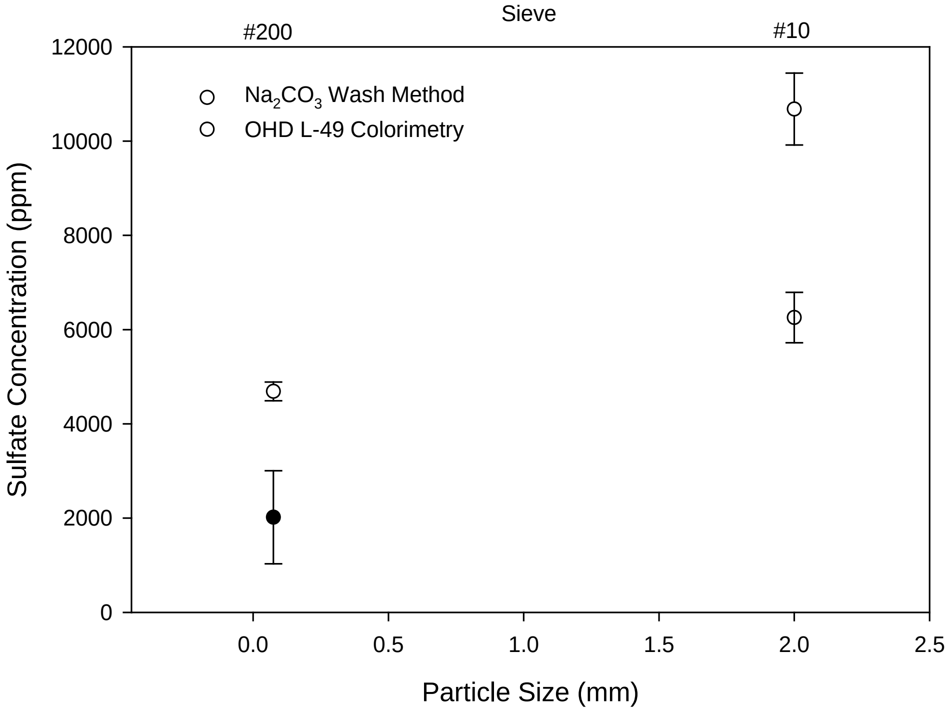


Figure 5-15. Particle Size versus Sulfate Content from Colorimetry and Na_2CO_3 Wash Method on Vernon

The three #10 sieved samples for colorimetry have a COV=8, so satisfactory repeatability, and the four #200 sieved samples have a COV=4, so good repeatability. The five #10 sieved samples from the Na_2CO_3 wash method have a COV=8.5, so satisfactory repeatability, and the four #200 sieved samples have a COV=49 so poor repeatability. The variation in repeatability between sieve opening sizes and test methods must have to do with the soil sample again being too small to fully represent the soil properties.

5.4.3 Blaine Shale

Blaine shale was sieved past both a #10 and a #200 sieve before sulfate tests were performed, so the effect of particle size could be observed. The sulfate content was found using colorimetry and Na_2CO_3 wash tests. For the wash method, the soil was washed 22 times with Na_2CO_3 solution during testing because it took 20 washes to get a negative test for $BaSO_4$ and 2 more washes were performed to make sure the sulfate was removed. The high wash number is indicative of how high the sulfate content is in this particular soil, compared with the other natural soils. Figure 5-16 shows the results from colorimetry and the Na_2CO_3 wash method on Blaine Shale. The Na_2CO_3 wash method resulted in a higher sulfate content than colorimetry for the soil sieved past the #200 sieve. Also, unlike the previous soils, the Na_2CO_3 wash method showed a higher sulfate content for the #200 sieve than for the #10 sieve. Blaine Shale more closely followed the same trend as the manufactured soil. Colorimetry results on Blaine Shale show a lower sulfate concentration for the #200 sieve, which is the same trend as the other natural soils. The difference in results between Blaine Shale and the other natural soils was due to intrinsic mineralogical and chemical properties of the soils.

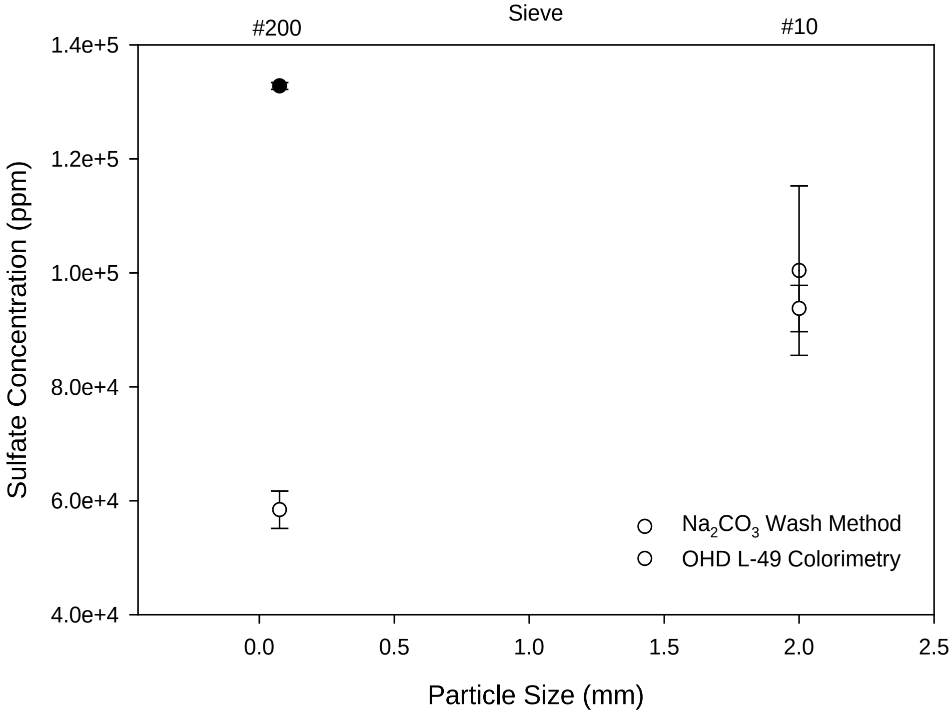


Figure 5-16. Particle Size versus Sulfate Content from Colorimetry and Na_2CO_3 Wash Method on Blaine Shale

The three #10 sieved samples for colorimetry have a COV=4, so good repeatability, and the three #200 sieved samples also had a COV=5.6, so satisfactory repeatability. The three #10 sieved samples from the Na_2CO_3 wash method have a COV=15, so poor repeatability. This poor repeatability could be due to a higher dilution ratio for one of the samples (6 as opposed to 3), which would increase the error. The three #200 sieved samples have a COV=0.5, so good repeatability. The differences in repeatability occurred because the soil had such a large quantity of sulfate in it, which increased sampling and testing errors significantly between samples.

From the manufactured soil tests, it appears the Na_2CO_3 wash method has the potential to extract more sulfate than the current OHD L-49 colorimetry method used by ODOT. However, from the natural soil tests, there is no definite trend in the data to verify this. When performing these tests, it is very important to take a representative sample of soil and make sure to crush and sieve all the soil past the specified sieve. These tests may want to be revised to include a larger soil sample for each test. A soil sample of 2 grams is specified for the Na_2CO_3 wash method and a sample size of 5 grams is required for the colorimetry tests. These samples requirements are small and it is unlikely that characteristics and properties can be accurately obtained from such a small soil sample. Thus an increase in sample size could increase the repeatability in testing and more clearly show the relationship between the two test methods.

5.4.4 Outside Chemical Analysis

Samples of all the natural soils were sent to an independent commercial lab for chemical analysis to find the total sulfur and sulfate sulfur in each soil. The total sulfur analysis was performed using a Leco sulfur analyzer. The samples were heated to 1350°C in an induction furnace while oxygen was passed over the samples. Any sulfur dioxide released was measured with an IR detection system. The sulfate sulfur analysis was performed using a carbonate leach method, which is basically a gravimetric method. The samples were sieved passed #10, #80, and #200 sieves to try to observe a grain size effect.

Table 5-1 shows the sulfur and sulfate contents for each of the soils and sieve numbers. The total sulfur content is very close to the sulfate content, indicating that the majority of the sulfur in the samples was in the form of sulfate. The repeatability between each soil type is generally good as well. It is clear the chemical analysis did not detect as much sulfate as colorimetry or the Na_2CO_3 wash method. This test is supposedly a “Total Sulfate/Sulfur” test, but apparently it does not measure total, but available. It is uncertain at this time why the results from this test method provide smaller sulfate values than the turbidimetric methods. This could be due to the fact that the sulfate testing method used by the lab was a gravimetric method, which was shown previously to be inaccurate at sulfate contents higher than 5,000 ppm. There still seems to be valid questions surrounding the ability to capture all sulfate in a sample. While thermodynamically, sulfate is shown to be completely soluble and therefore, available, all the literature and this study point to the fact that we cannot measure all existing sulfate and we do not know if this sulfate will continue to be available in the long-term to be a source for ettringite formation.

For the Flower Pot and Blaine Shale, the sulfate content seemed to increase with increasing sieve numbers (or decreasing particle size). This was the trend found previously with the manufactured samples. More soil sulfate testing using this method should be attempted in order to garner a larger database with which to analyze.

Table 5-1. Sulfur and Sulfate Contents from Outside Chemical Analysis

Soil and Sieve #	Sample Weight (kg)	Sulfur Content (%)	Sulfur Content (ppm)	Sulfate Content (%)	Sulfate Content (ppm)
Flower Pot #10	0.11	0.24	2400	0.22	2200
Flower Pot #80	0.07	0.89	8900	0.87	8700
Flower Pot #200	0.06	0.82	8200	0.83	8300
Blaine Shale #10	0.11	3.74	37400	3.75	37500
Blaine Shale #80	0.06	4.34	43400	4.14	41400
Blaine Shale #200	0.06	4.17	41700	4.24	42400
Vernon #10	0.1	0.43	4300	0.4	4000
Vernon #80	0.06	0.38	3800	0.37	3700
Vernon #200	0.04	0.38	3800	0.36	3600

6 Oedometer Testing Results

6.1 Introduction

One-dimensional free swell tests were conducted on samples with and without lime to assess the heave induced by adverse sulfate-lime-soil reactions. Lime dosing was determined using standard procedures for lime stabilization established by ODOT. Samples were compacted via moist tamping in two layers in oedometer rings to densities and moisture contents simulating field placement, subjected to a nominal vertical pressure simulating stress conditions in a shallow pavement subbase, and then inundated with water. Vertical deformations were recorded with time. Samples were then incrementally loaded until at least the sample height returned to the original height before inundation. Eight test soils were collected from the field and several additional manufactured test soils were created by adding reagent grade sulfate.

6.2 Natural Soils

The natural soils were collected with the ODOT Materials Division help to show the variability in sulfate concentrations across the state where lime stabilization has often been used. Blaine Shale was sampled alongside Route 412 near Woodward, OK, and using the standard OHD L-49 soil sulfate method, was found to have 84,000 ppm sulfate. As can be seen in Figure 6-1, the addition of 5% lime caused the soil to swell more than it did in its natural state. This is an indication of ettringite formation. Both the sample with the lime and the sample without the lime were compacted to the optimum moisture content and 95% of maximum dry density, as determined from the two Standard Proctor tests performed. This was to simulate field conditions as closely as possible.

On the other hand, the second soil, Vernon Soil, also sampled alongside Route 412 near Woodward, was found to have 8,400 ppm of sulfate, but swelled even more than the Blaine Shale (Figure 6-2). In each case the amount of swelling that occurred with the lime is significant. The comparison of these two soils indicates that additional parameter(s) are controlling the swell potential in the sample. It could be the difference in clay fraction, specific surface area or cation exchange capacity (CEC), or a combination of these plus others. Of particular interest in this case is the significantly larger CEC of the Blaine Shale. A multiparameter analysis to assess the influence of the various soil parameters on swelling behavior with addition of lime deserves further study.

Dog Creek was sampled from Route 283 in southwestern Oklahoma, just south of I-40. Two samples were gathered from here, including a ‘top’ and ‘bottom’ deposit. Dog Creek top and bottom samples were found to have 200 ppm of sulfate. As can be seen in Figure 6-3 and Figure 6-4, the addition of lime arrested the swell. Therefore, 200 ppm availability of sulfate in these soils was apparently insufficient to form ettringite and cause swelling under laboratory conditions.

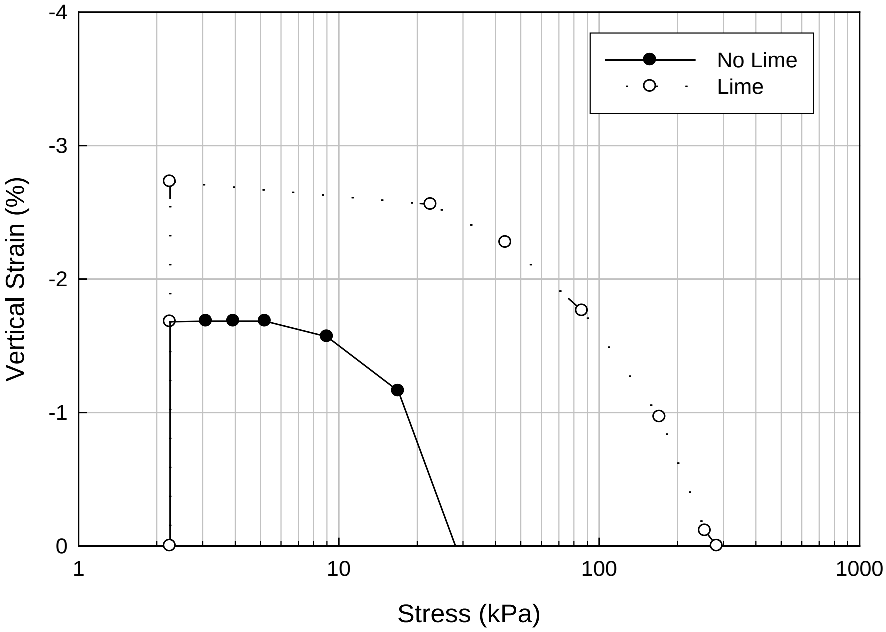


Figure 6-1 Blaine Shale

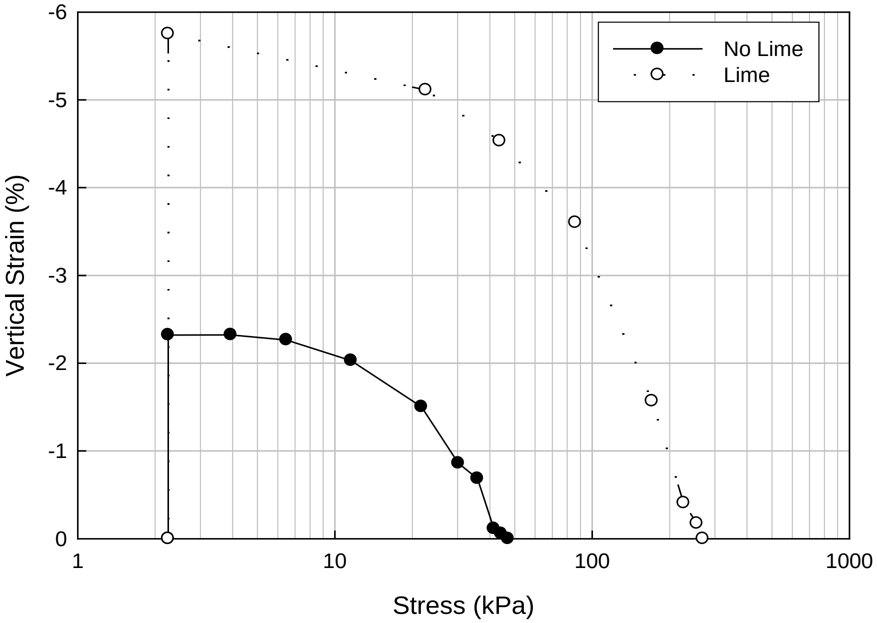


Figure 6-2 Vernon Soil

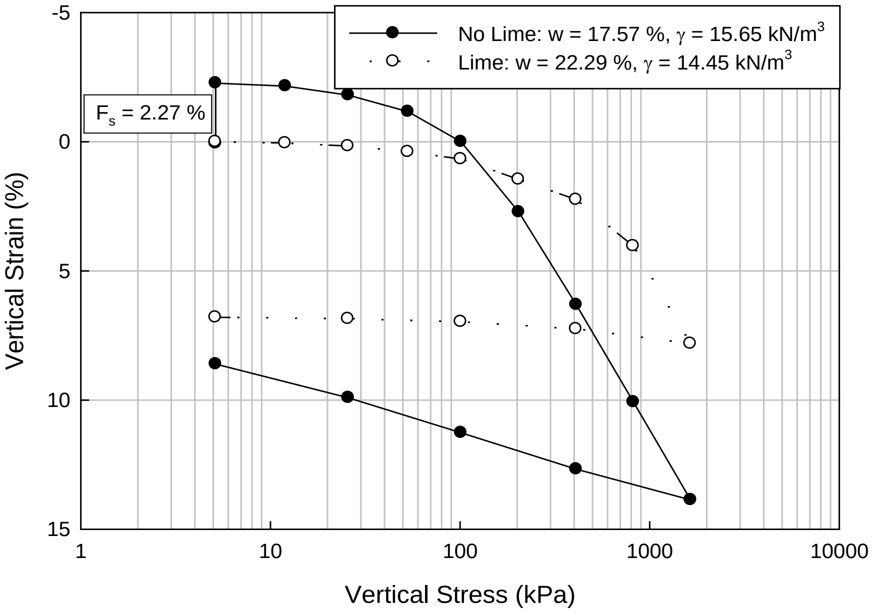


Figure 6-3 Dog Creek Top

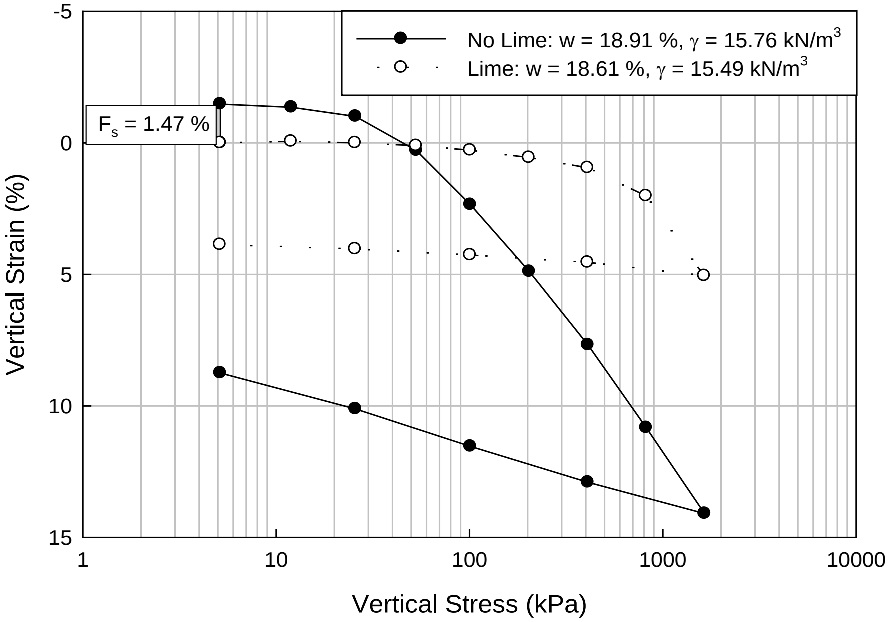


Figure 6-4 Dog Creek Bottom

The Hennessey soils were sampled along State Route 183 in southwestern Oklahoma and were also sampled as a 'top' and 'bottom.' Both Hennessey samples showed about 500 ppm of sulfates, depending on which method the results are taken from. As can be seen in Figure 6-5 and Figure 6-6, these samples had a relatively high natural free swell without lime. But when 5% lime was added, it arrested the swell;

100% arrested in Hennessey Top, and 86% arrested in Hennessey Bottom. Therefore, it may be concluded that 500 ppm sulfates in this particular soil was not enough to form ettringite and see additional swell with the addition of lime.

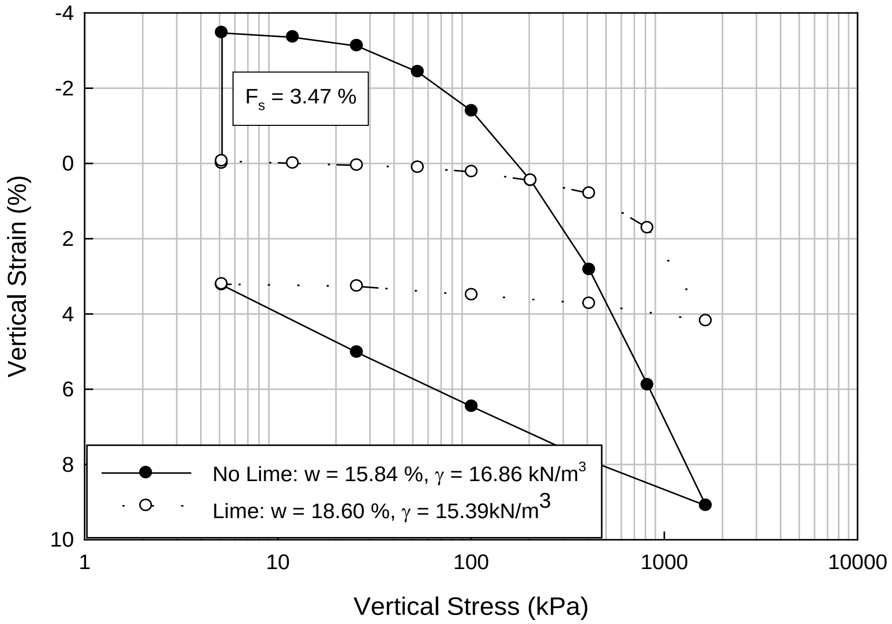


Figure 6-5 Hennessey Top

Cloud Chief was sampled outside of Anadarko, in Southwestern OK. It classified as an ML soil, and therefore, showed no swell in its natural state as well as with the addition of 5% lime (Figure 6-7). When tested, it showed extremely low sulfate levels of 40-120 ppm depending on soil sulfate testing methodology.

Flower Pot was sampled near the Cimmaron River, south of Route 64 in Northwestern Oklahoma. It classified as lean clay (A-6), and was found to have about 4000 ppm of sulfate present. It had a small amount of free swell initially, however, when 5% lime was added, there was no free swell under 5kPa stress. However, after the first loads were put on, the soil seemed to swell slightly and remained at this level until almost 400 kPa. There was very little deformation in this sample, and repeatability tests are currently being performed on this sample. It is possible that 4000 ppm is nearing a threshold, and initially there was no reaction, but with time, the ettringite started forming.

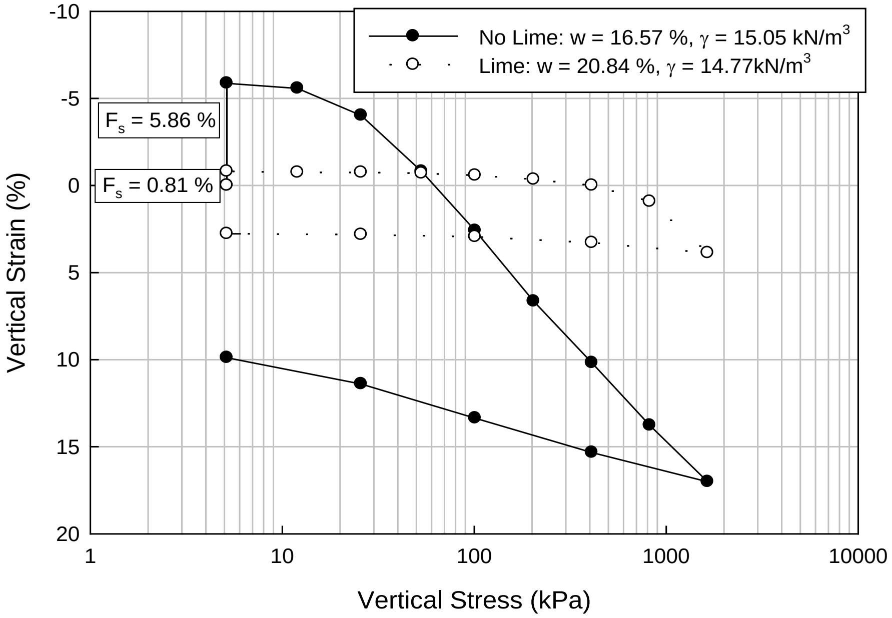


Figure 6-6 Hennessey Bottom

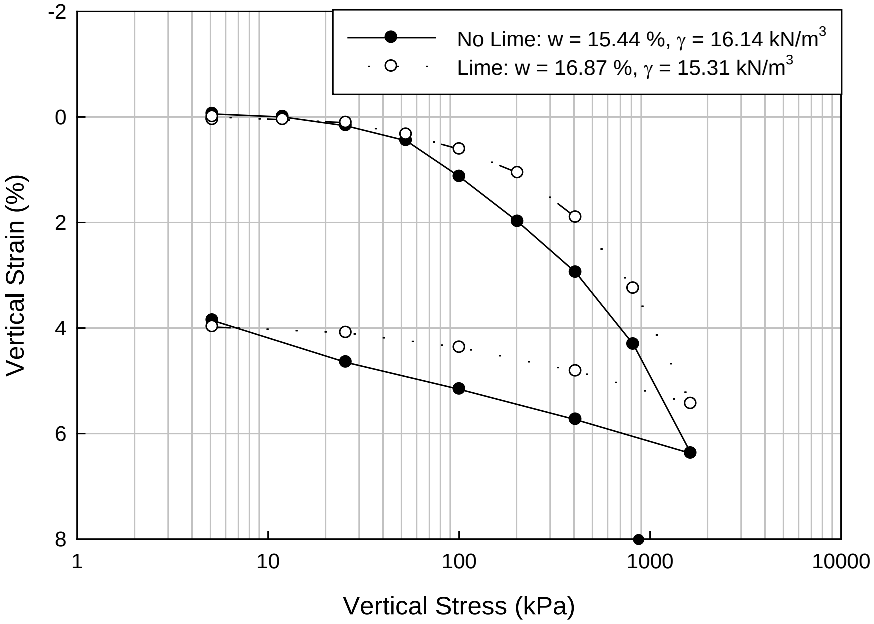


Figure 6-7 Cloud Chief

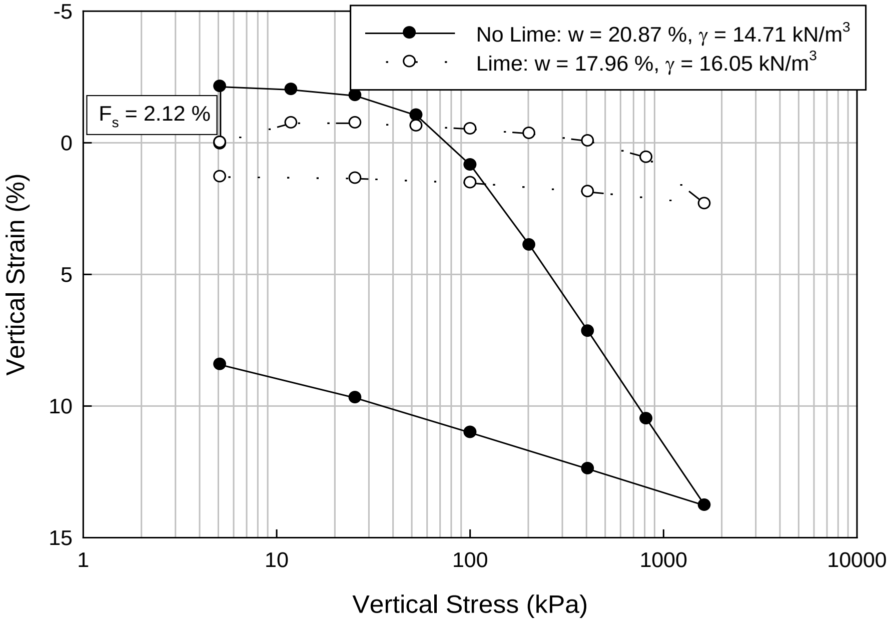


Figure 6-8 Flower Pot

These natural soils have had many index, mineralogical and free-swell oedometer tests performed in order to fully characterize the soil to understand behavior. Since there was a wide variety of sulfate contents in the sampled soils (40 ppm – 84,000 ppm), it was clear that lime reacted with the higher sulfate concentrations but did not react with the very low sulfate contents. We were unable to identify, however, an exact threshold level where the lime started to react with the sulfate. In addition to the threshold level, there seemed to be other parameters, besides the sulfate content, that was contributing to the swell (i.e., 8,400 ppm Vernon soil swelled more than the 84,000 ppm Blaine shale). This phenomenon was investigated further with a multi-parameter analysis to determine what soil parameters control swell in a sulfate bearing soil, as discussed in Section 6.4.

6.3 Manufactured Soils

Both Hickory Glaze (Kaolinite) and Bentonite were used for the manufactured soil oedometer tests. These soils were tested individually remolded and compacted to near the Plastic Limit (PL) and mixed in different percentages compacted to the PL.

6.3.1 Hickory Glaze compacted 1-D Swell/Compression Tests

Free swell oedometer tests were performed in order to determine a swelling trend based on the change in sulfate content of the soil. To accomplish this, samples included blank hickory clay, hickory clay with 1,000; 3,000; 5,000; 8,000; or 10,000 ppm sulfate, hickory clay with 5% lime, and hickory clay with 5% lime and 1,000; 3,000; 5,000; 8,000; or 10,000 ppm sulfate. Each test was performed in triplicate to show repeatability. Efforts were made to mix all samples to the same water content of 35% and compact them to a unit weight of 17.6 kN/m^3. The soil and gypsum were mixed to a water content of about 35% based on the OMC and plastic limit of Hickory Clay. This unit weight was chosen because it was easy to reach consistently.

The Hickory Clay was mixed with the gypsum and water and placed in the humid room until it was time to compact the samples in the oedometer ring. If the samples contained lime, it was added just before the sample was compacted into the ring, to ensure the sample did not start swelling before being placed in the frame. There was no delay between compaction and placement in the oedometer frame for testing.

Figure 6-9 shows the results of the free swell oedometer tests on blank Hickory Clay. These were the control samples, showing the behavior of just the Hickory Clay kaolinite with water. It is clear that the blank samples did not exhibit swelling when they were inundated with the water. These two tests show good repeatability since they have very close water contents and unit weights, and the curves lie almost directly on top of each other.

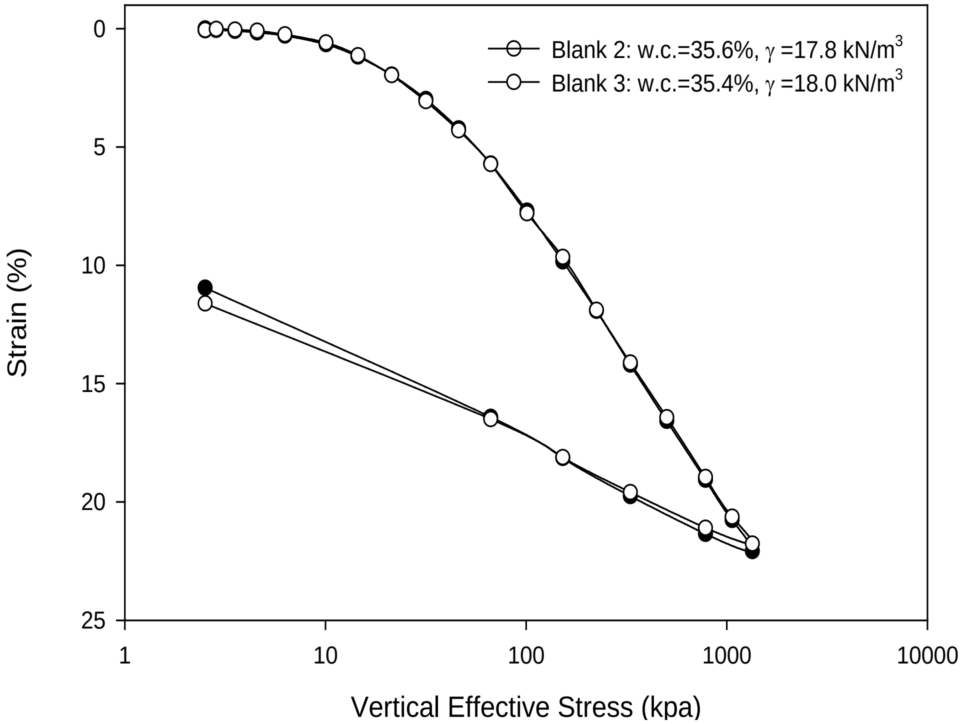


Figure 6-9. Free Swell Oedometer Tests on Blank Hickory Clay

In Figure 6-10, the free swell oedometer results on blank Hickory Clay with 5% lime can be seen. No swelling is seen. The test 1 and 2 curves start the same but then test 2 becomes offset which can be explained by sample variability. Even though efforts were made to produce identical samples for each test, there is always slight variability because the samples were mixed separately. These tests show no swelling, and the repeatability is satisfactory when considering sample variability.

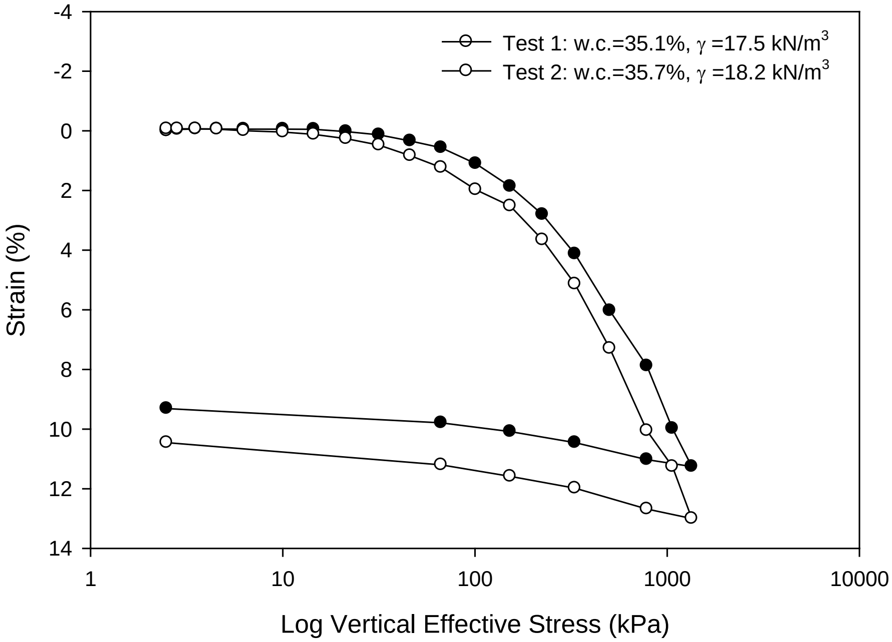


Figure 6-10. Free Swell Oedometer Tests on Blank Hickory Clay with 5% Lime

Figure 6-11 shows the average of the blank Hickory Clay tests and the blank Hickory Clay with 5% lime. Again, it is clear that no swelling occurred for either set of tests. The main difference between the samples with lime and without is that the samples with lime show a decrease in the overall strain. This is due to the strengthening reactions from the addition of lime. These two tests are the control tests for comparison with the samples containing sulfate and those containing sulfate and lime

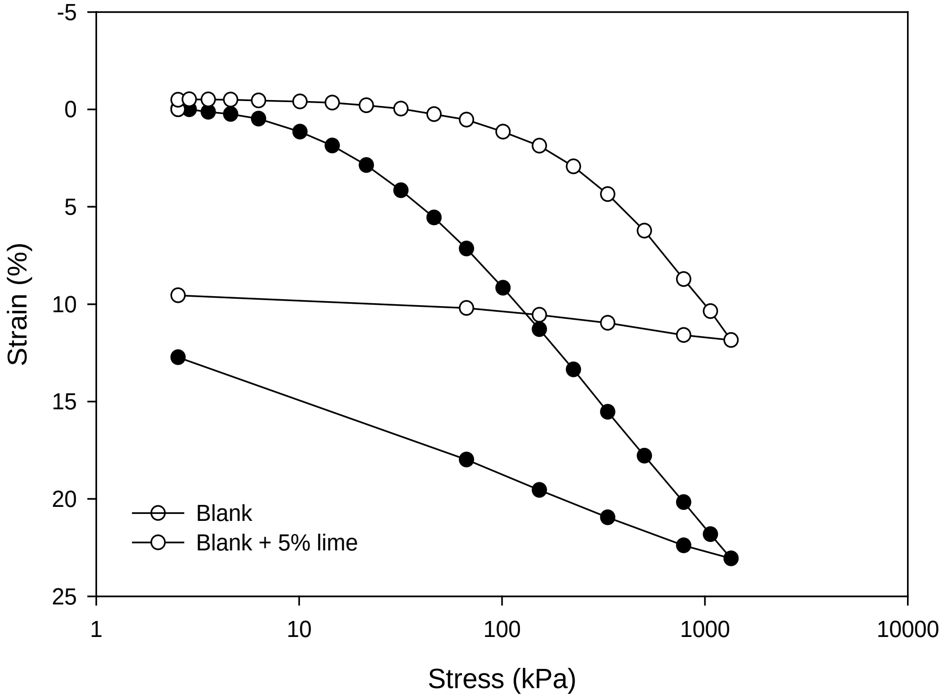


Figure 6-11. Average Free Swell Oedometer Results for Blank Hickory Clay and Hickory Clay with 5% Lime

Figure 6-12 shows the results from the free swell oedometer tests on Hickory Clay with 1,000 ppm sulfate. This figure shows that no swelling occurred in any of the three samples.

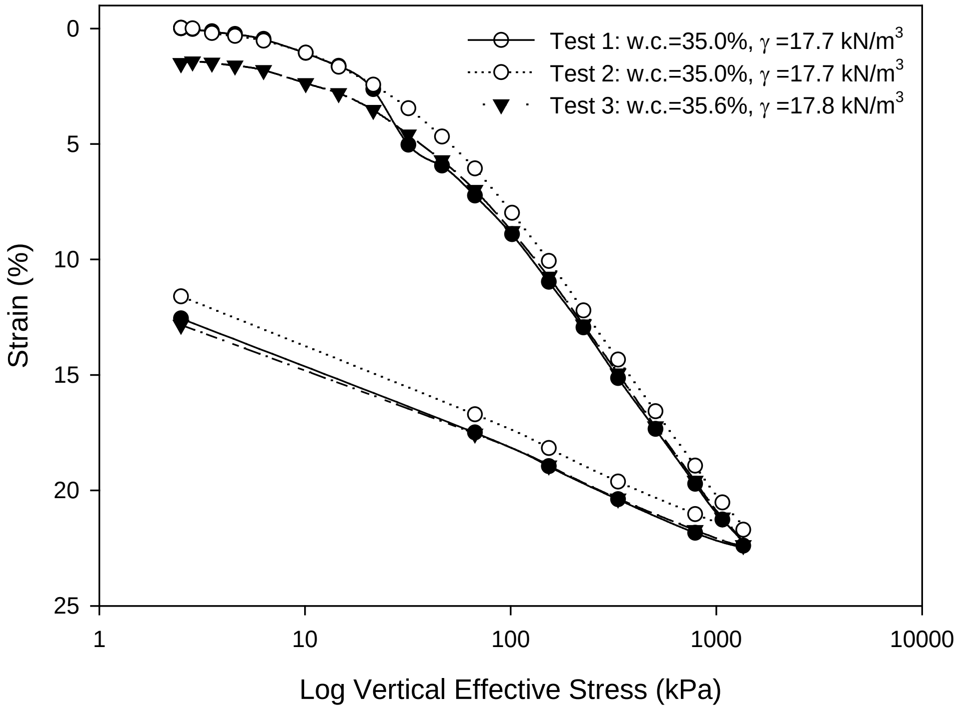


Figure 6-12. Oedometer Results for Hickory Clay with 1,000 ppm Sulfate

In Figure 6-13, the results for free swell oedometer tests on Hickory Clay with 1,000 ppm sulfate and 5% lime can be seen. Swelling occurred in both samples likely due to the formation of ettringite from the aluminum in kaolinite, calcium in lime, sulfate in gypsum, and water present.

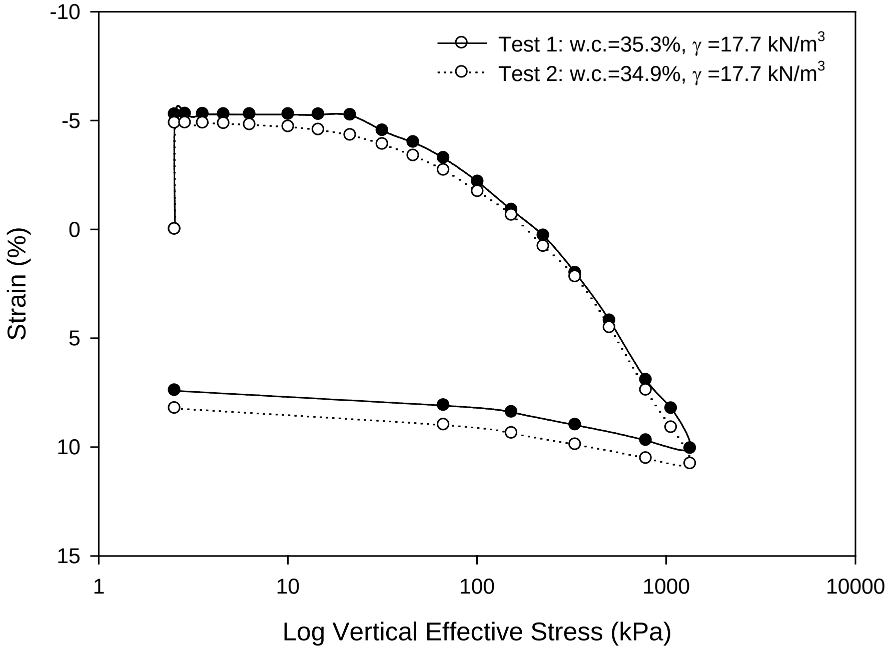


Figure 6-13. Oedometer Results for Hickory Clay with 1,000 ppm Sulfate and 5% Lime

The average free swell oedometer results for Hickory clay with 1,000 ppm sulfate, Hickory Clay with 1,000 ppm sulfate and 5% lime, and blank Hickory Clay are shown in Figure 6-14. It is clear from this figure that the samples with lime and sulfate swelled about 5% of their original height whereas the blank samples or samples with only sulfate showed no swelling. The average blank samples and average samples with 1,000 ppm sulfate show the same trend, indicating the sulfate had no effect on the samples. Thus in order to induce ettringite formation and swelling, lime must be present in the sample in addition to sulfate.

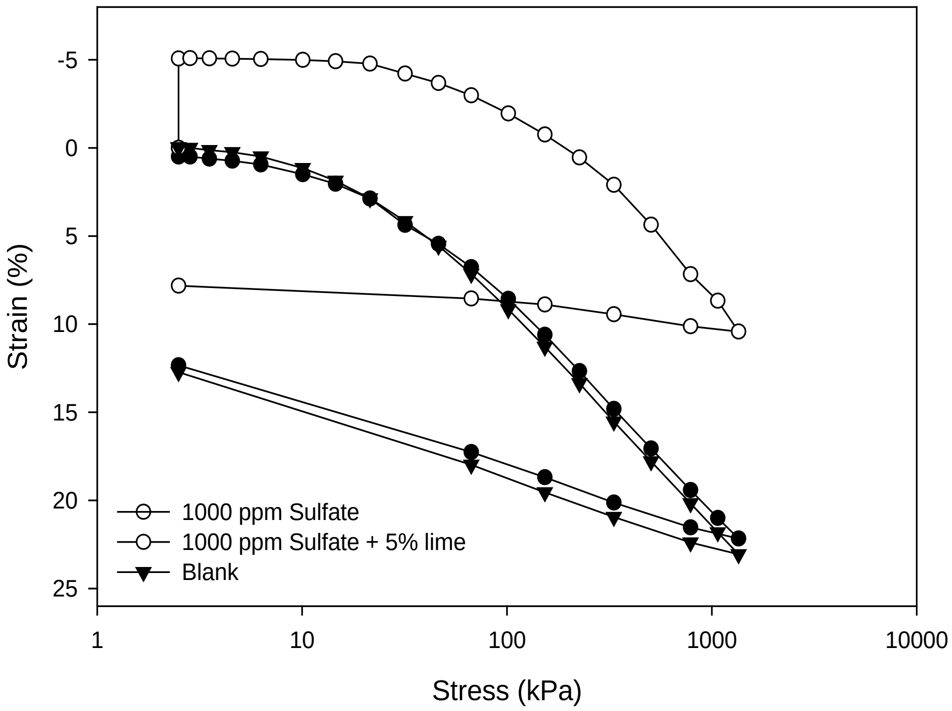


Figure 6-14. Avg. Hickory Clay with 1,000 ppm Sulfate, Avg. Hickory Clay with 1,000 ppm Sulfate and 5% Lime, and Avg. Blank Hickory Clay

The results from free swell oedometer tests on Hickory Clay with 3,000 ppm sulfate can be seen in Figure 6-15. Again, no swelling was seen in these samples because lime was not present to form ettringite.

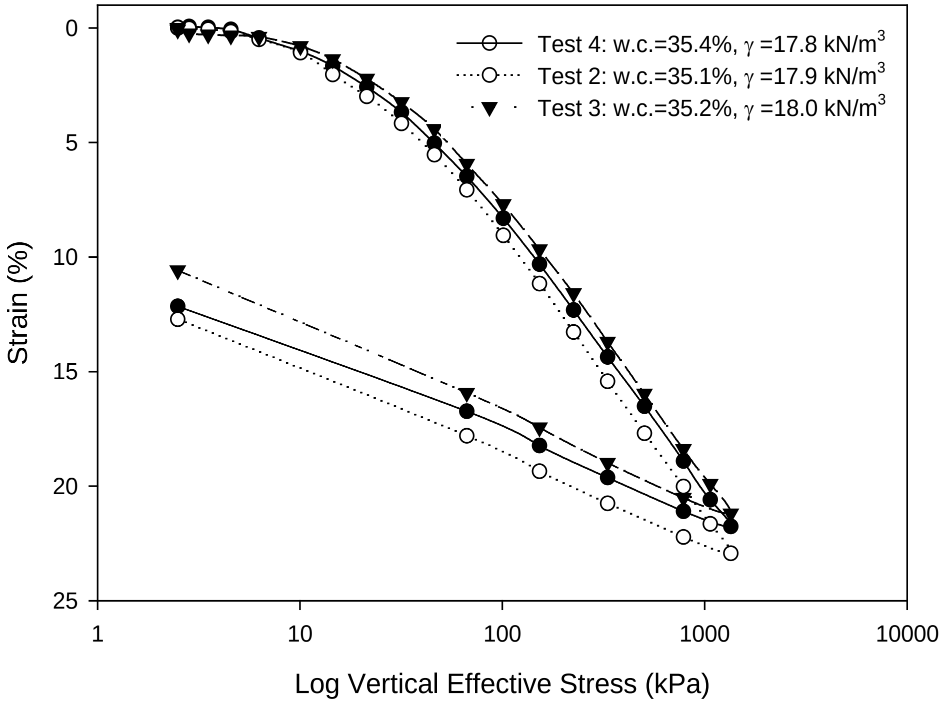


Figure 6-15. Oedometer Results for Hickory Clay with 3,000 ppm Sulfate

Figure 6-16 shows the results from free swell oedometer tests on Hickory Clay with 3,000 ppm sulfate and 5% lime.

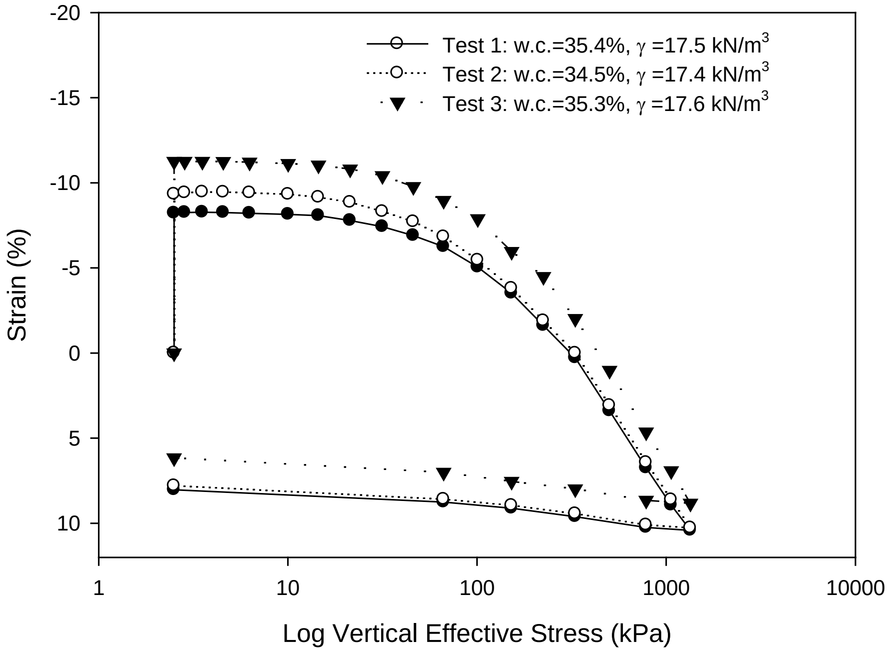


Figure 6-16. Oedometer Results for Hickory Clay with 3,000 ppm Sulfate and 5% Lime

The average of the free swell oedometer tests for Hickory Clay with 3,000 ppm sulfate, 3,000 ppm sulfate and 5% lime, and blank Hickory Clay are shown in Figure 6-17. This figure shows that the samples with lime swelled an average of about 10% from the original height of the sample. The average blank samples and samples with 3,000 ppm sulfate show a very similar trend, indicating the sulfate had no effect on the Hickory Clay. Again the swelling in the samples with lime occurred due to the formation of ettringite.

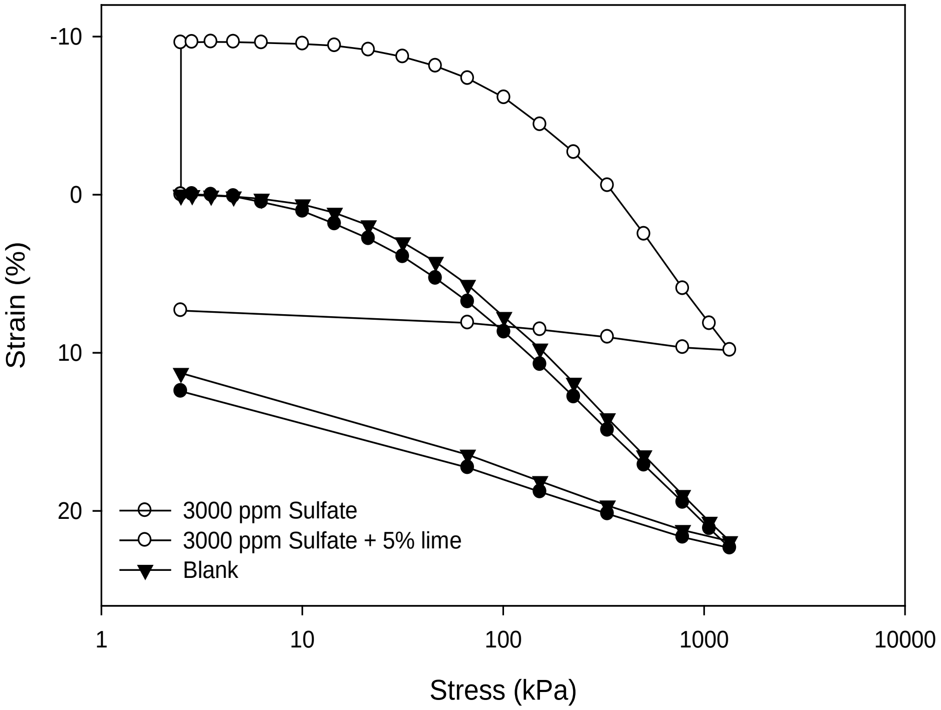


Figure 6-17. Avg. Hickory Clay with 3,000 ppm Sulfate, Avg. Hickory Clay with 3,000 ppm Sulfate and 5% Lime, and Avg. Blank Hickory Clay

Figure 6-18 shows the stress versus strain plots from free swell oedometer tests on Hickory Clay with 5,000 ppm sulfate. It is clear from this figure that no swelling was seen in these samples.

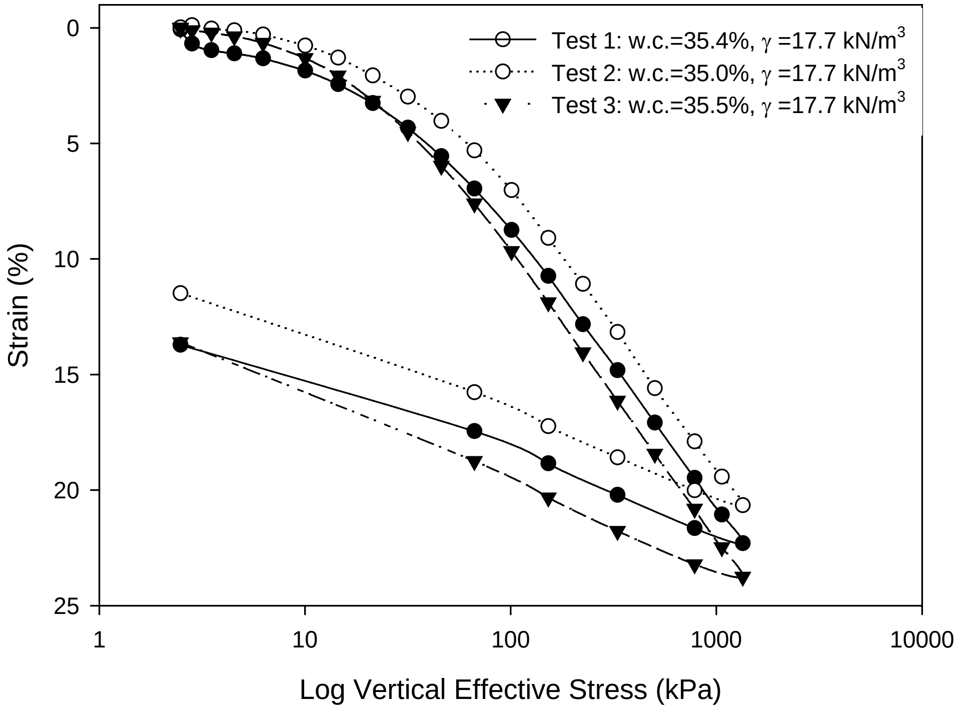


Figure 6-18. Free Swell Oedometer Results for Hickory Clay with 5,000 ppm Sulfate

The results from free swell oedometer tests on Hickory Clay with 5,000 ppm sulfate and 5% lime are shown in Figure 6-19. Significant swelling occurred in these samples.

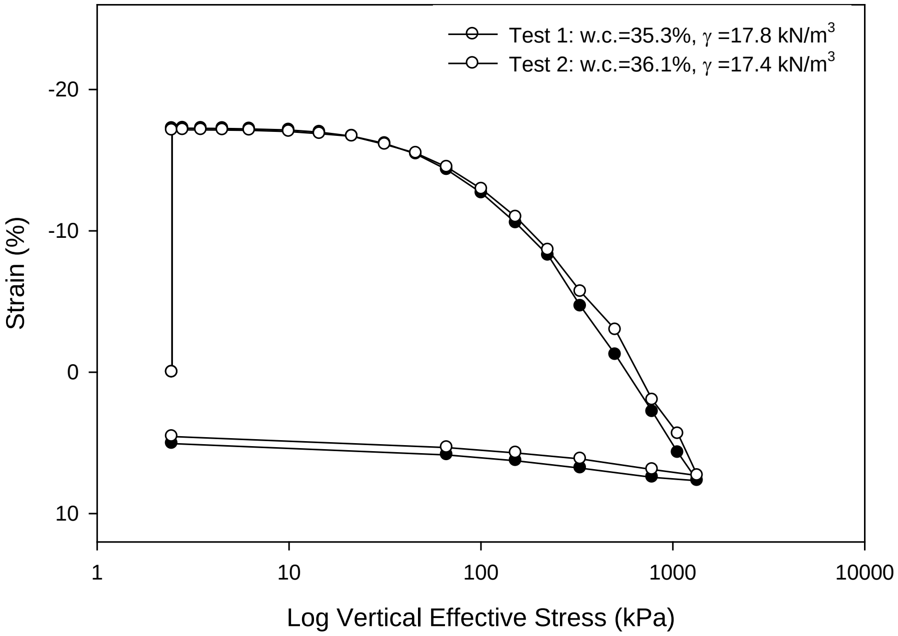


Figure 6-19. Free Swell Results for Hickory Clay with 5,000 ppm Sulfate and 5% Lime

Figure 6-20 shows the average of the samples with 5,000 ppm sulfate, 5,000 ppm sulfate and 5% lime, and blank Hickory Clay. The swelling of the sample with 5% lime is more pronounced when shown with the sample with no lime. The average blank samples and samples with 5,000 ppm sulfate show the same trend again, indicating the sulfate did not affect the hickory clay. The samples with lime swelled an average of about 16% from their original height. Again, the swelling occurred because lime was introduced and ettringite formed in the samples.

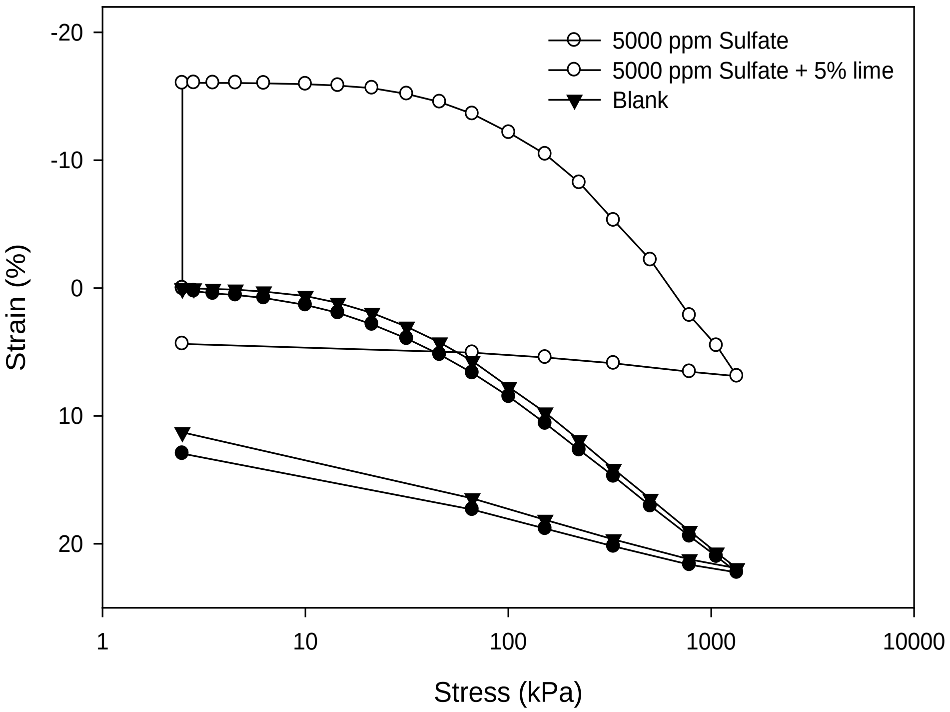


Figure 6-20. Avg. Free Swell Oedometer Results for Hickory Clay with 5,000 ppm Sulfate, Hickory Clay with 5,000 ppm Sulfate and 5% Lime, and Blank Hickory Clay

Figure 6-21 shows the results from the free swell oedometer tests on Hickory Clay with 8,000 ppm sulfate. No swelling was exhibited in any of the tests. The slight jog in the data on the rebound curve was due to removal of a different load than what was specified. It was repeated on all three samples to stay consistent.

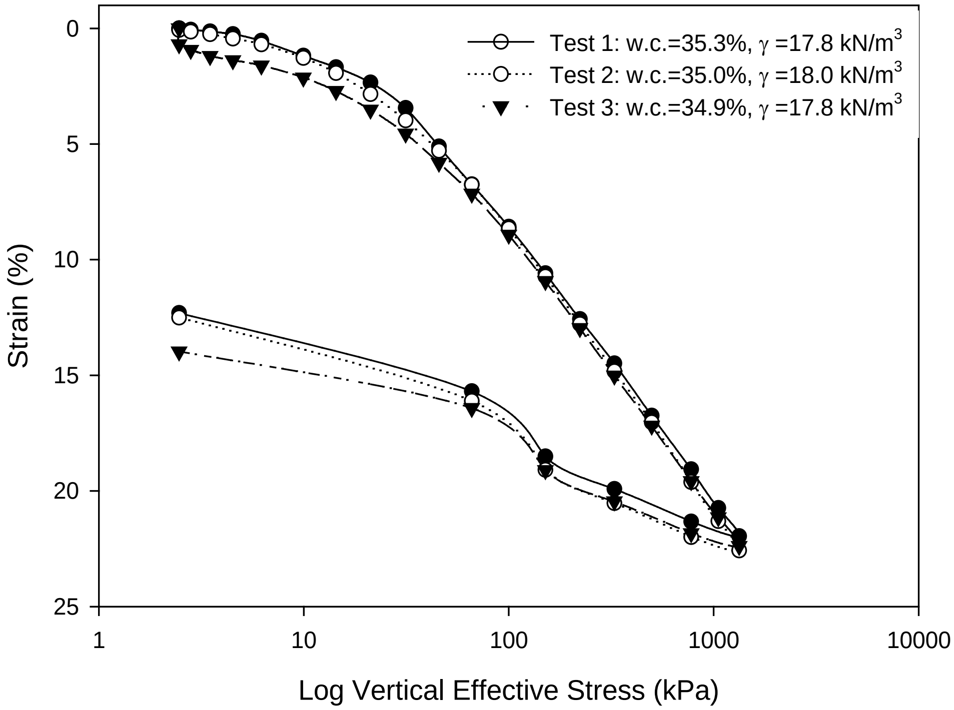


Figure 6-21. Free Swell Oedometer Results for Hickory Clay with 8,000 ppm Sulfate

In Figure 6-22, the results from the free swell oedometer tests on Hickory Clay with 8,000 ppm sulfate and 5% lime are shown. The swelling was most likely caused by the formation of ettringite in the soil samples.

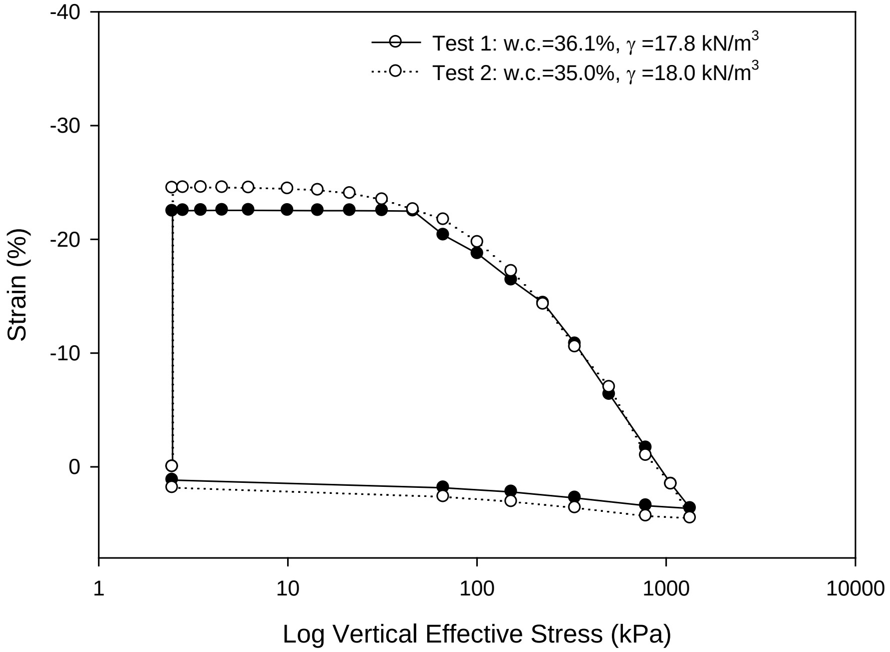


Figure 6-22. Free Swell Oedometer Results for Hickory Clay with 8,000 ppm Sulfate and 5% Lime

The average results for the Hickory Clay samples with 8,000 ppm sulfate, 8,000 ppm sulfate and 5% lime, and blank Hickory Clay can be seen in Figure 6-23. The blank samples and samples with 8,000 ppm sulfate show the same trend, indicating the sulfate had no effect on the soil. The tests with 8,000 ppm sulfate and 5% lime show an average swelling of about 23%. Again the swelling likely occurred due to the formation of ettringite in the samples with lime and sulfate.

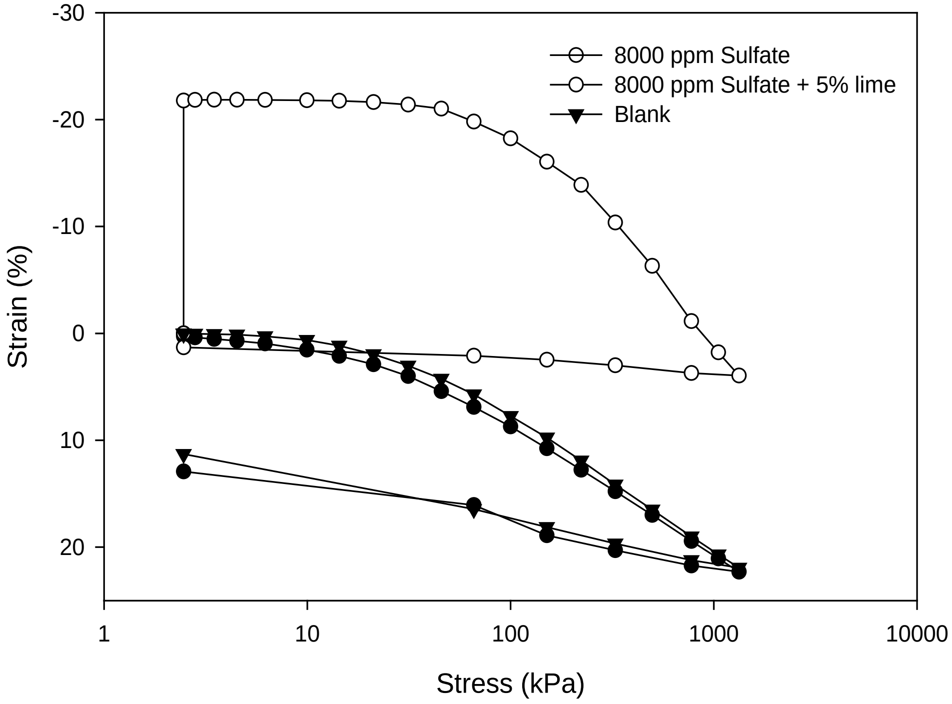


Figure 6-23. Average Free Swell Oedometer Results for Hickory Clay with 8,000 ppm Sulfate, Hickory Clay with 8,000 ppm Sulfate and 5% Lime, and Blank Hickory Clay

Figure 6-24 shows the results from free swell oedometer tests on Hickory Clay with 10,000 ppm sulfate. None of the three samples experienced swelling, as expected.

Figure 6-25 shows the free swell oedometer tests on Hickory Clay with 10,000 ppm sulfate and 5% lime.

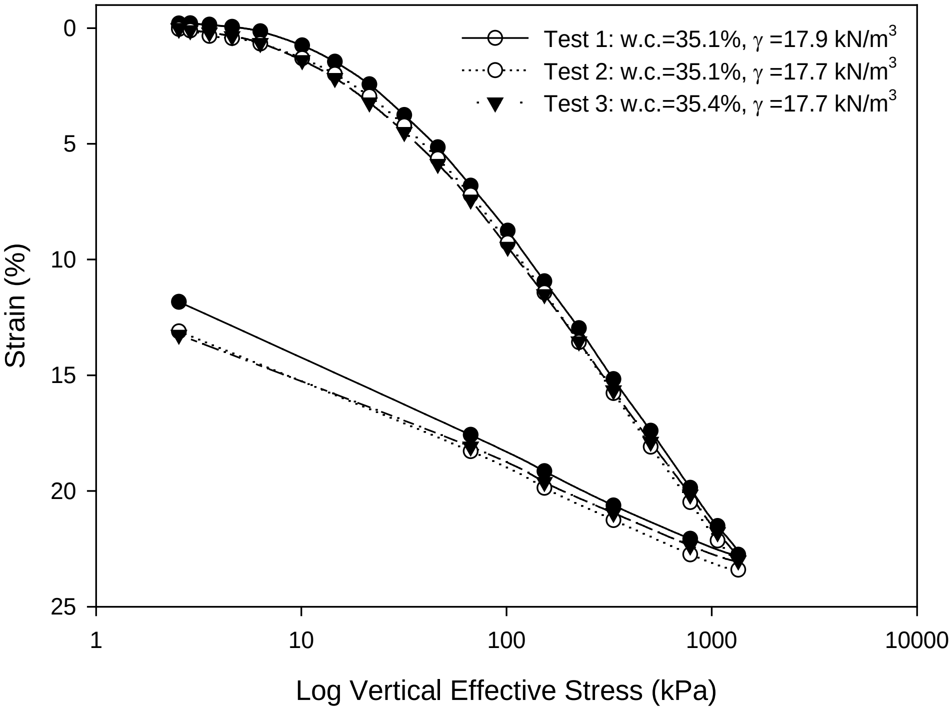


Figure 6-24. Free Swell Oedometer Results for Hickory Clay with 10,000 ppm Sulfate

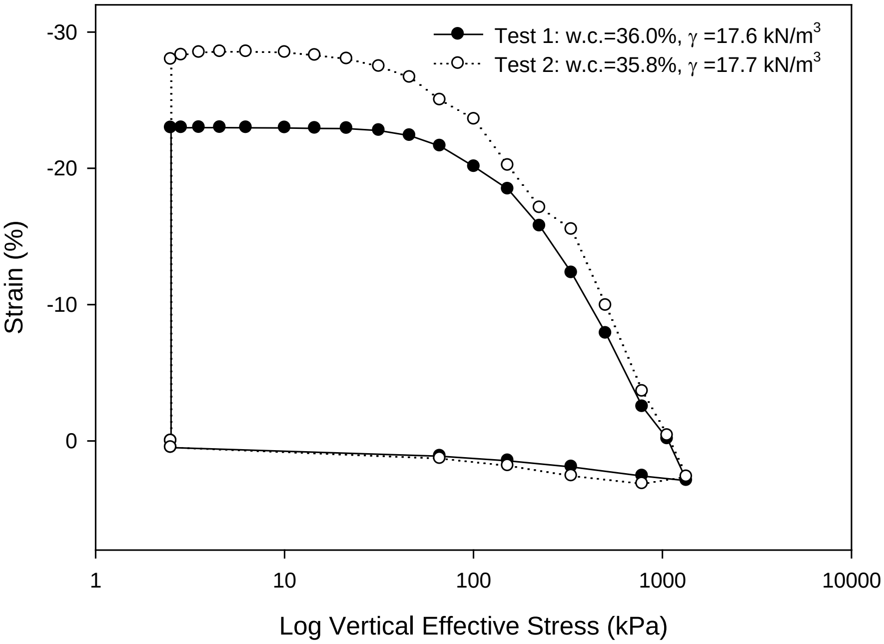


Figure 6-25. Free Swell Oedometer Results for Hickory Clay with 10,000 ppm Sulfate and 5% Lime

The average results for the Hickory Clay samples with 10,000 ppm sulfate, 10,000 ppm sulfate and 5% lime, and blank Hickory Clay can be seen in Figure 6-26. The blank samples and samples with 10,000 ppm sulfate show the same trend, indicating the sulfate had no effect on the soil. The tests with 10,000 ppm sulfate and 5% lime show an average swelling of about 22%. Again the swelling likely occurred due to the formation of ettringite in the samples with lime and sulfate.

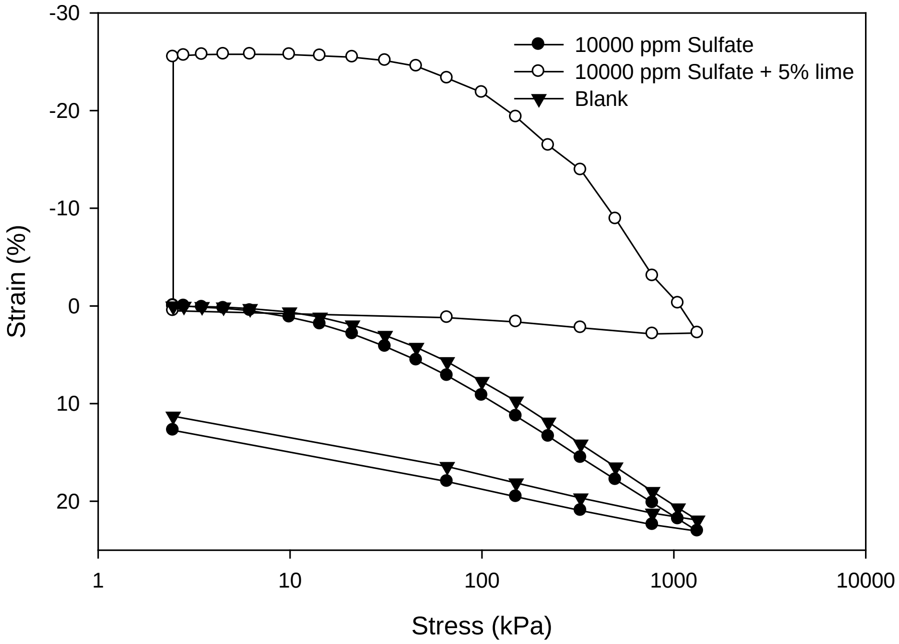


Figure 6-26. Average Free Swell Oedometer Results for Hickory Clay with 10,000 ppm Sulfate, Hickory Clay with 10,000 ppm Sulfate and 5% Lime, and Blank Hickory Clay

From all the free swell oedometer results of the samples with sulfate and lime, shown in Figure 6-27, a trend in swelling can be seen. The bars show the average free swell with range bars from each sulfate increment. As the sulfate content increased, the free swell increased because the higher sulfate content allowed for the formation of more ettringite. There was enough lime present in the samples to continue to form ettringite as the sulfate content was increased. The percentage of swelling seen is directly related to the amount of sulfate in the sample, since the percentage of lime was held constant at 5% for all samples.

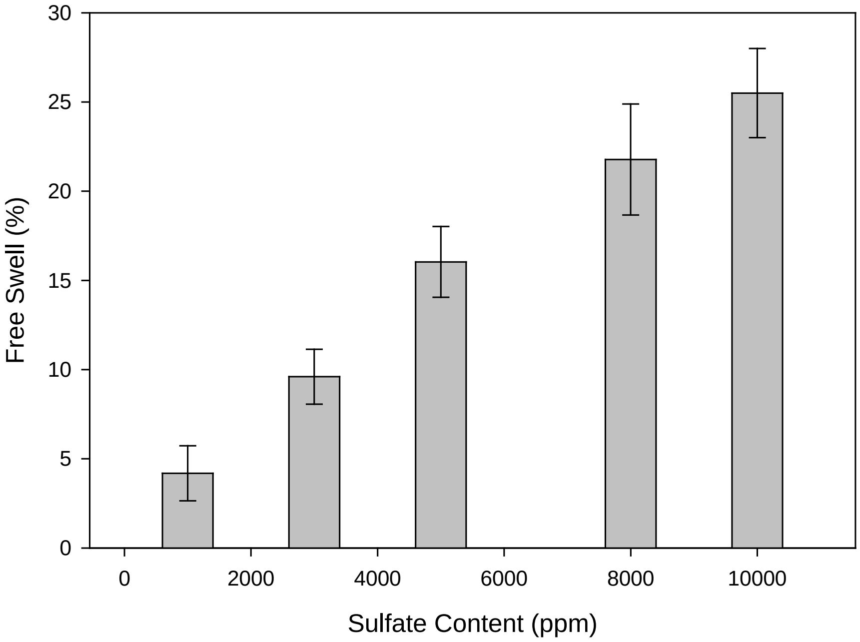


Figure 6-27. Sulfate Content versus Free Swell for Samples with Sulfate and Lime

Another interesting trend is the time versus swelling for the different sulfate contents. Figure 6-28 shows the time for swelling versus the average strain or free swell from three samples at each sulfate content. It is clear that as the free swell increases, the time for swelling increases. The samples with higher sulfate contents take longer to reach equilibrium, or swell because the ettringite reaction continues until one or more of the components are used up.

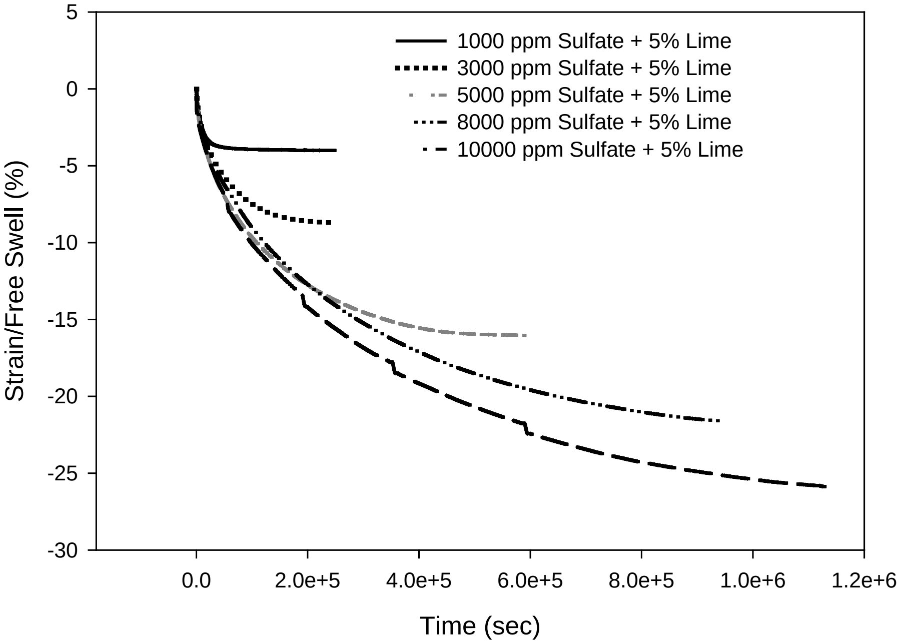


Figure 6-28. Time versus Average Strain for Samples with Sulfate and 5% Lime

The overall trend can possibly be seen more clearly in Figure 6-29. This figure shows the average total free swell with time. Again with increasing free swell the time for swelling increases. Also, the higher the sulfate content the longer the samples swelled before reaching equilibrium.

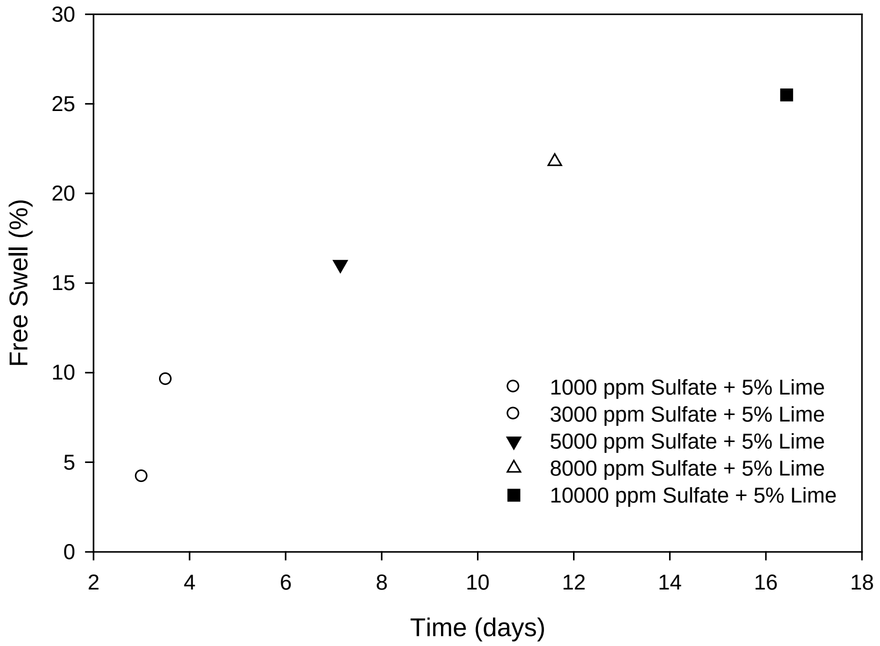


Figure 6-29. Total Average Free Swell versus Time for Sulfate and 5% Lime

The blank samples of Hickory Clay, blank samples with 5% lime, and samples containing only sulfate experienced no swelling. This occurred because of the low shrink-swell potential of kaolinite clay with fluctuation in water content and the lack of all the chemicals needed to form ettringite. For ettringite to form, calcium (from lime in this case), sulfate, alumina, and water must be present. The addition of lime in the blank sample containing only lime stiffened the clay, but did not cause swelling because the sample contained no sulfate. The samples containing both sulfate and 5% lime swelled apparently due to the formation of ettringite. It is clear that, based on the chemical formulas and properties of kaolinite, gypsum, and lime, the only possible explanation for swelling could be the formation of the expansive mineral ettringite.

6.4 Swelling Characteristics Compared with Physical, Chemical, and Mineralogical Properties

Cerato et al. 2007 determined many physical, mineralogical and chemical soil properties for eight different Oklahoma soils. They performed free swell oedometer tests on these soils, and the free swell values will be compared to these properties. Data from all these tests were shown in Table 4-1 through Table 4-3. More parameters were found for these soils, but only the most relevant ones were included. A comparison of natural soil parameters may identify a trend in mineralogy and swelling better than trying to relate the manufactured soils to the natural soils.

It is hard to see a trend just by studying the swelling data compared to the physical, chemical, and mineralogical soil properties. None of the soils follow an exact trend for one specific parameter. For example, it seems that, in general, the lower the SSA, the lower the swelling. However, the Blaine Shale has a lower SSA than

Hennessey Bottom, but swelled more. This shows that perhaps the properties cannot be used individually to find swelling trends, but several properties must be combined to find a correlation. Blaine Shale has the highest specific gravity and shrinkage limit (SL). Hickory Clay has the highest clay fraction (CF). These physical parameters do not seem to indicate a trend as far as sulfate content is concerned. Blaine Shale has the highest cation exchange capacity (CEC) and the highest sulfate content. Perhaps the high CEC for Blaine Shale has something to do with the Na_2CO_3 wash method producing a higher amount of sulfate than colorimetry for this soil. The Na_2CO_3 solution provides more ions for the sulfate to bond with than water, and the higher CEC value for Blaine Shale indicates a greater capacity to exchange cations. The negative carbonate ions can bond with the positive cations available in the soil while the positive sodium ions can bond with the negative sulfate ions. Thus, more sulfate is extracted from the soil with the Na_2CO_3 solution. Maybe the CEC is an important parameter in sulfate dissolution and sulfate content determination.

The clay fraction for Blaine Shale is lower than that of Flower Pot or Vernon. Perhaps the lower clay content for Blaine indicates that the sulfate is less tightly bound than in the other two soils. Blaine has fewer clay particles for the sulfate to be imbedded in, so maybe this is one reason why the sulfate can be dissolved more easily. It might be more important to look at chemical or mineralogical properties for sulfate dissolution and determination.

Studies are still ongoing as to what the specific method to determine sulfate should be, however, research advanced to look for soil parameters that are indicators of sulfate. As can be seen from Figure 6-39, as sulfate concentration increases, pH increases. Samples were made of pure lab grade gypsum and water at different concentrations. The samples were heated to 70°C and then tested for pH.

Figure 6-40 shows an increase in conductivity as the concentration of sulfate increased as well. Samples of pure gypsum and water at different concentrations were heated to 70°C and tested for conductivity. As a comparison for solubility, similar samples were made at the same concentrations using sodium sulfate rather than gypsum.

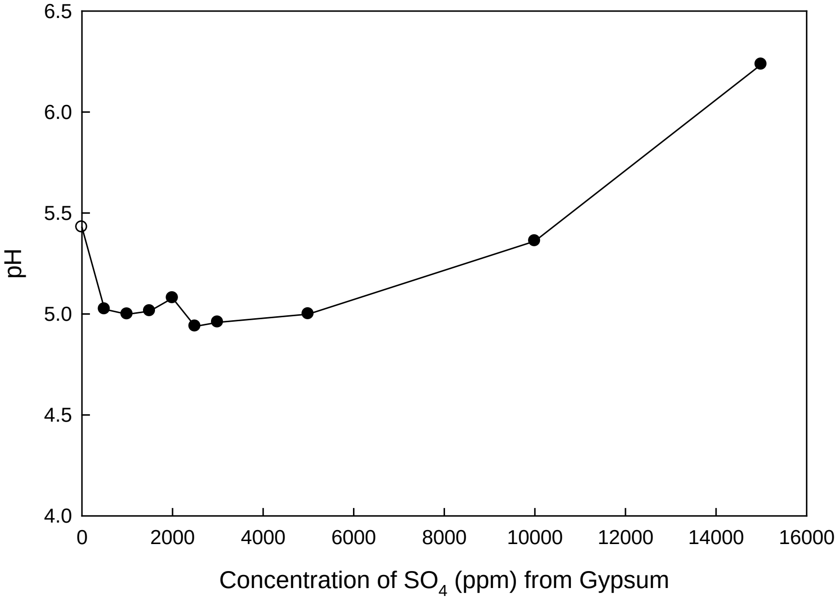


Figure 6-30: pH of Heated Gypsum

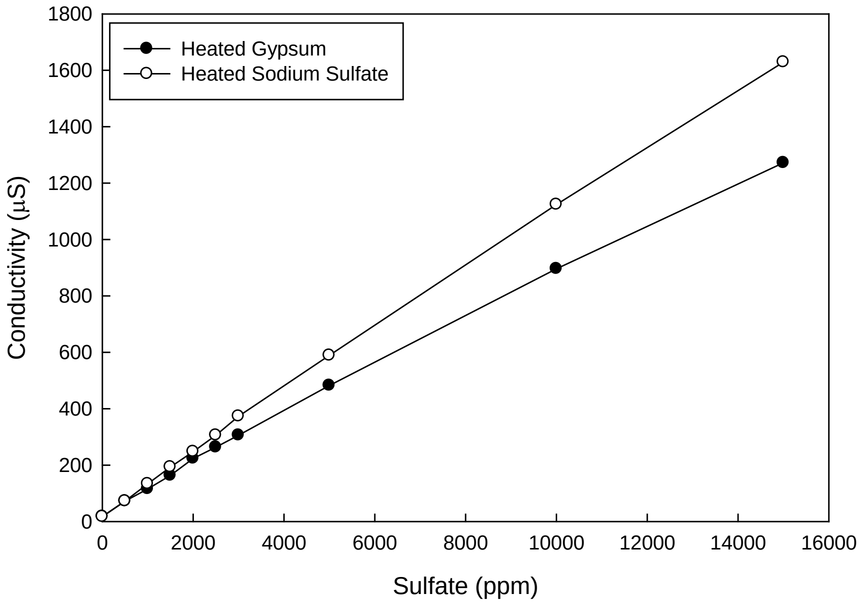


Figure 6-31: Conductivity

This conductivity increase was even more prominent in the sodium sulfate data because Na_2SO_4 is completely soluble in water, so higher sulfate concentrations were measured. The sodium sulfate was completely ionized in water whereas the gypsum was only slightly ionized. A fair amount of visible gypsum stayed in solid precipitate form and this amount increased with higher concentrations of the gypsum. This may have been because the gypsum reached its saturation point at this dilution. Further research should be performed on the saturation level of gypsum at different dilutions.

In natural soils there are many other factors that will influence the pH and conductivity measurements, other than sulfate. However, pH and conductivity measurements may along with other soil parameters may be useful in estimating the presence of sulfate in a soil. They may also be useful on a site specific basis when calibrated against data from sulfate measurement tests.

One possible way to find a correlation between free swell and multiple soil properties would be to run a multi-variable linear regression analysis. A linear analysis would be the simplest way to relate the parameters, and the equation would be easier to use later.

Thus a multi-variable linear regression analysis was performed using the SPSS software. The free swell with lime was the dependent variable and all the other soil properties were the independent variables. When choosing the independent variables, it is important to choose two variables that are truly independent. For example, if the LL and PL are input, then the plasticity index (PI) should not be used because the PI is the LL minus the PL. The program produces coefficients for each of the independent variables input and the greater they are, the more weight they have in the correlation equation. In other words, the higher the coefficients are, the more they affect the free swell. Also, the program excludes parameters from the equation that it finds to be poorly correlated to the free swell. These would be parameters that have a coefficient much less than 1. An R^2 value is also given, which shows the accuracy of the model, and the closer to 1, the more accurate.

The variables included by the program in the regression were sulfate, pH, conductivity, linear shrinkage (LS), shrinkage limit (SL), total specific surface area (SSA), and carbonate. However, the only parameter with a coefficient greater than 1 was pH, but it was only 1.6, so it still does not strongly influence the free swell. The variables the program excluded were LL, PL, clay fraction, CEC, calcite, and dolomite. Interestingly, the sulfate concentration had a coefficient of 3×10^{-5}, which means it has practically no correlation with the free swell in this particular dataset. This could be partially due to only 75% (or less) of the sulfate in the soil being detected by the colorimetry and Na_2CO_3 wash tests; an assumption made from the results of the tests performed on the manufactured soils. Perhaps the correlation between sulfate and free swell would be stronger if 100% of the sulfate in the soil could be measured and input into the regression analysis.

The results from this linear regression analysis show a poor correlation between the free swell and the chosen physical, chemical, or mineralogical parameters. One possible reason for this could be that only eight natural soils were used in the analysis. Another reason could be the inability to measure the entire sulfate concentration present in the soil at this time. Adding more soils would increase the likelihood for a stronger correlation because additional data points usually produce a more apparent trend. Further testing is needed to increase the database of soils which might then produce a stronger correlation between soil properties and free swell, as well as determining a more accurate sulfate testing method.

7 Conclusions and Recommendations

7.1 Conclusions

Several new methods for sulfate detection and quantification were performed in this study. The sulfate burn method turned out to be inaccurate due to loss of structural water at testing temperatures, and the sulfate not entirely burning off. Thus this method is not recommended as a reliable sulfate methodology.

The Na_2CO_3 wash method was performed in order to determine if more sulfate could be dissolved and therefore, measured, in soil samples, which would improve upon the OHD L-49 colorimetry method. The number of washes depends on the soil and is determined by the occurrence of a negative test for $BaSO_4$. From preliminary tests on manufactured soil with a known sulfate concentration, the Na_2CO_3 wash method was more accurate and repeatable when combined with the existing OHD L-49 colorimetric method. Also, within this method, the particle size of the sample affected the amount of sulfate extracted. The maximum sulfate was extracted at the particle size of 0.075 mm (#200 sieve), which was found to be the optimum particle size.

It appears that the Na_2CO_3 wash method has the potential to be more accurate and repeatable than the current OHD L-49 colorimetry method based on the manufactured soil and Blaine Shale results. Even so, the Na_2CO_3 wash method only removed about 75% of the sulfate in the manufactured soil after a certain gypsum concentration. The dissolution trend with increasing sulfate content was found to be linear, with good repeatability. Thus it may be possible to estimate the actual sulfate content of a natural soil by using the correlation:

$$y = 1.60x$$

Where x = measured sulfate concentration and y = actual sulfate concentration. This correlation is only applicable at measured concentrations above 3000 ppm. Below 3000 ppm, the colorimeter accurately measures sulfate content. The results of this study confirm those found in the literature that show that gypsum is not 100% soluble in water or a Na_2CO_3 solution; and therefore, this correlation between actual sulfate content and the amount of sulfate able to be measured with the dissolution methods found in this research may be the most accurate sulfate determination method available at this time. It is recommended that the soil be processed past a #200 sieve, and that the Na_2CO_3 wash method be utilized to increase the accuracy and repeatability of the current OHD L-49 colorimetry method. It is also recommended that the correlation given above be used to estimate the actual sulfate content of a natural soil, if needed.

Free swell oedometer tests were conducted on kaolinite with varying concentrations of sulfate and with sulfate and 5% lime to examine the mechanical response of the soil with the addition of lime. From these tests, it was found that the blank samples and samples with only sulfate did not experience swelling. The samples containing both sulfate and lime all experienced swelling, apparently due to the formation of ettringite in the samples. As the sulfate content increased, the free swell increased because there was more sulfate present to react and form ettringite. In addition, as the free swell increased, the time to reach equilibrium increased. The higher sulfate contents allowed for the formation of more ettringite, which takes longer to use up reaction products. While it is not expected that these tests alone can show an absolute threshold of sulfate, above which, destructive swelling occurs, it does show the effect of sulfate content on ettringite formation in soils. It is very likely that the amount of swelling occurring in sulfate bearing soils with the addition of lime is directly linked to not only the amount of sulfate, but the mineralogy, as well as chemistry, present. Any presence of sulfate in the natural soil, therefore, could produce ettringite if calcium based stabilizers are used.

7.2 Recommendations for Further Study

Based on the results from these studies, there is still a significant amount to learn about sulfate detection, ettringite formation from lime stabilization, and mineralogical properties affecting free swell when ettringite forms. The following items are recommended to further understand the topic of sulfate induced heave and its implications in practice.

1. After dissolving pure gypsum in water, if there is any remaining solid, perform XRD or SEM to determine its content to understand the solubility mechanisms.
2. Sample additional sulfate bearing natural soils to add to the database to increase the chances of finding correlations between physical, chemical, mineralogical, and electrical characteristics and sulfate induced free swell.
3. Determine a quantitative way to describe the qualitative XRD mineralogical data and add it to the database in order to compare the mineralogical characteristics of natural soils and find a correlation between mineralogy and free swell.

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